X-Ray Diffraction Study of Aged Copper Beryllium Alloys

by

Chang-Hong Wu

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Approved:

C. R. Houska, Chairman

T. K. Lee

G. V. Gibbs

W. T. Reynolds, Jr.

R. Kuzel

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Committee Chairman: C. R. Houska
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(ABSTRACT)

X-ray polycrystalline diffraction techniques are used to determine the defect structure in a commercial Cu-11.55 at.%Be-0.23 at.%Co alloy during low temperature aging. The analysis of the X-ray diffraction patterns is aided by the computer modeling of the defects inside the crystals using an elastic model. The research is to provide more detailed understanding of the precipitate structures in the process of aging and the age hardening mechanism of the alloy.

The diffraction profiles from samples aged for different times at 315°C are collected using a position sensitive proportional counter with Cu $K_{\alpha}$ radiation. The hardness values of the samples are also measured. An elastic model for the coherent precipitates in anisotropic matrix is developed according to Eshelby's treatment of transformed regions in an elastic continuum. The displacement fields generated by the precipitates in the surrounding matrix, obtained through the elastic model, are used to explain the (110) streaks near the Bragg reflection, and to calculate the powder diffraction patterns from the aged alloys. For the latter purpose, a general X-ray diffraction theory is developed, combining the work of Krivoglaz and Dederichs. The X-ray diffraction patterns are compared with existing TEM observations in the literature.

The analysis of the diffraction patterns suggests that the precipitates in the early stages of aging (GP zones) can be the matrix constrained version of $\gamma$, the equilibrium phase, similar to an observation by Khatchaturyan and Laughlin on $\gamma''$ and $\gamma'$. The quantitative calculation based on this model shows excellent agreement with experimental data for samples aged at 315°C. The averaged inter-precipitate spacing in the crystals for the optimally aged sample at 315°C is determined to be 200–300Å.

A simplified method of evaluating the thermal diffuse scattering and a method for calculating the diffuse scattering from polycrystalline materials with textures are also presented.
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Chapter 1

Introduction

1.1 Properties of the Copper Beryllium Alloy

Copper is an important material because its high electric and thermal conductivity, non-magnetic characteristics and corrosion resistance. However, it is often too soft to be used in conditions or environments that require mechanical strength. One popular method of increasing the mechanical strength of a metal is through alloying.

Of all copper-base alloys, copper beryllium alloy has the highest strength attainable. After high temperature solution treatment and optimal low temperature aging, the hardness of the alloy can reach a level four times as high as the alloy in the as-quenched condition and almost ten times higher than that of pure copper. Its aged hardening property also enable the parts made of this material to be formed in the soft as-quenched condition and hardened by simple low temperature aging treatment. As a consequence of the high strength, copper beryllium alloys also offer excellent wear resistance and spark resistance properties.

There are two kinds of copper beryllium alloys widely used in commercial environments. One usually contains less than 0.8 weight percent of beryllium. This kind of alloys retain the high electric and thermal conductivity of pure copper and is of moderate strength. They are often used under circumstances that electric and thermal conductivity is important. Another kind copper beryllium alloys have 1.6 to 2.0 weight percent of beryllium. This type of alloys reach maximum mechanical strength after heat treatment and have moderate electric and thermal conductivity. These alloys are suitable for strength sensitive applications. The alloy used in this research belongs to the latter category. The
composition of the alloy as given by the manufacturer is listed in Table 1.1.

The purpose of this research project is to study the structure property relations of the high strength copper beryllium alloys during the aging process. The structure and the phase evolution of the system in the precipitation hardening process is studied through X-ray diffraction in connection with the mechanical properties.

1.2 Metastable Phase Diagram and Precipitation Sequence

The phase diagram of copper beryllium alloys is shown in Figure 1.1. Our primary interest is on the copper-rich side of the spectrum. Following the usual practice of heat treatment for high strength Cu-Be alloys, the material is first homogenized by solution treatment at high temperatures (700–850°C). Then it is quenched rapidly to room temperature to form a supersaturated solid solution. By subjecting the material to intermediate temperatures (150–550°C), the extra Be atoms in the solution will precipitate out in the form of small clusters. The clusters grow as aging continues.

The precipitation sequence and the morphology of the precipitates have been studied by numerous researchers for several decades [2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19]. Until very recently, the decomposition process is thought to pass through several intermediate metastable phases prior to the equilibrium. It can be represented as [15, 17]:

\[ \alpha_s \rightarrow \alpha + \text{GP zone} \rightarrow \alpha + \gamma'' \rightarrow \alpha + \gamma' \rightarrow \alpha + \gamma, \]

where \( \alpha_s \) is the supersaturated solid solution.

The GP zones are thin, disk shaped particles on \{100\} planes of the matrix phase. The interface between them and the matrix is believed to be coherent. The GP zones exhibit long \langle 100 \rangle \) diffraction streaks in X-ray or TEM diffraction patterns. At the same time, strong but shorter scattering streaks are also observed near the Bragg reflections, along \langle 110 \rangle \) directions (see Figures 1.2 and 1.3). These latter streaks are present even before the \langle 100 \rangle \) streaks can be resolved. It is also reported [15] that equi-axed clusters exist before the plate-like GP zones are formed.

As aging continues, GP zones are thickened into the \( \gamma'' \). In diffraction patterns, the formation of \( \gamma'' \) is indicated by the "bunching up" of streak intensities near \((4/3,0,0)\) [13, 15].
Table 1.1: Composition of the alloy supplied by the manufacturer

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight Percent</th>
<th>Atomic Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>1.84</td>
<td>11.55</td>
</tr>
<tr>
<td>Co</td>
<td>0.23</td>
<td>0.23</td>
</tr>
<tr>
<td>Ni</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Fe</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>Si</td>
<td>0.11</td>
<td>0.22</td>
</tr>
<tr>
<td>Al</td>
<td>0.06</td>
<td>0.13</td>
</tr>
<tr>
<td>Sn</td>
<td>$\sim 0.005$</td>
<td>$\sim 0.002$</td>
</tr>
<tr>
<td>Zn</td>
<td>$\sim 0.01$</td>
<td>$\sim 0.009$</td>
</tr>
<tr>
<td>Cr</td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>Pb</td>
<td>$\sim 0.003$</td>
<td>$\sim 0.001$</td>
</tr>
<tr>
<td>Cu</td>
<td>Balance</td>
<td>87.74</td>
</tr>
</tbody>
</table>
Figure 1.1: Phase diagram of binary Cu-Be alloy [1].
Figure 1.2: Schematic diffuse scattering pattern on (001) reciprocal space plane passing through the origin [9, 6, 19].

Figure 1.3: Schematic diffuse scattering pattern on (011) reciprocal space plane passing through the origin [9, 6, 13].
The precipitates still have \{100\} habit and the interface is still coherent. The measurement of the lattice parameters showed that \(\gamma''\) has an apparent tetragonal crystal structure with \(a = 2.53\text{Å} \) and \(c = 2.9\text{Å}\) [20]. The latter value is somewhat approximate because of the broadened diffraction peaks.

Further aging of Cu-Be transforms \(\gamma''\) into \(\gamma'\). The diffraction patterns begin to change into an arrowhead shape and then to form separated dots about the original positions [13, 15]. This is illustrated in Figure 1.4 [21]. This was interpreted as a change of the habit plane of the precipitates from \{100\} of the matrix phase into \{112\} or \{113\} of matrix phase. The lattice parameters are \(a = 2.70\text{Å} \) and \(c = 2.56\text{Å}\) [15].

The equilibrium \(\gamma\) phase was determined to be of B2 (ordered BCC) structure with a lattice parameter of \(2.70\text{Å}\) [14, 15]. The unit cell is like that of CsCl, with Be atoms at the corners and Cu atoms at the center. The equilibrium structure is observed only in very high temperature aging. At lower temperatures, the transformation are too slow to be completed in reasonable amount of time. The \(\gamma\) phase is reported to have a habit plane of \{112\} or \{113\} of matrix phase.

Prior to the formation of \(\gamma'\), the TEM images of the Cu-Be alloys show regular “tweed”-like structures along the traces of \{110\} planes [6, 13, 15, 22]. It was proposed that this is caused by regularly arranged precipitates along the (110) directions in the alloys [8, 23, 24, 17, 19]. But the evidence of the existence of such regularity in the alloys has not been conclusive.

The metastable phase diagram has been measured experimentally [1]. It is reproduced as Figure 1.5.

Recently, Khachaturyan and Laughlin [21] proposed that \(\gamma''\) and \(\gamma'\) are actually matrix constrained \(\gamma\) phase. The variation of lattice parameters of these “metastable” phases is due to the difference in elastic matrix accommodation for precipitates of different habit planes. With an elastic model of infinitesimally thin ellipsoidal clusters, the theoretically predicted lattice parameters agree with the experimental values to a certain degree. The theory also predicted the habit plane orientations of the \(\gamma'\) precipitates in the later stage of aging, using hypothetical elastic constants for the precipitates. According to their theory, the decomposition involves three steps:

1. Be atoms clustered to form GP zones of FCC structure.
Figure 1.4: Schematic sections from a [110]$_a$ diffraction pattern showing: (a) (001)$_\gamma$ reflection of a coherent $\gamma$ phase precipitate with the (hhl)$_\alpha$ habit; (b) superposition of the (001)$_\gamma$ reflection from the $\gamma$ phase precipitates with different habits ranging from (001)$_\alpha$ to (112)$_\alpha$; (c) the (112)$_\alpha$ variant of the coherent $\gamma$ phase attributed to the $\gamma'$ phase. Figure and caption are from [21].
Figure 1.5: Metastable phase diagram of binary Cu-Be alloy [1].
2. The FCC structure suffered a Bain-like distortion and formed BCC unit cells.

3. Ordering occurred in the precipitates.

Of the three, 2 and 3 can progress simultaneously. The change in habit planes of the precipitates in the later stage of aging was due to the demand for minimizing the elastic energy caused by the precipitates.

The main problem of this theory lies with the assumption that the precipitates are infinitesimally thin [25]. By the time that the precipitates are observed to change their habit planes, they already have a significant thickness as shown by X-ray diffraction patterns. One conclusion from this theory that one of the lattice parameters is constant is in clear contradiction with experimental results, since measurements indicate that lattice parameters change with different aging states.

1.3  Growth of Precipitates and Mechanical Effects

1.3.1  Precipitate Growth Mechanism [26]

The precipitation transformation involves change of composition when precipitates are formed. The precipitates have a higher content of beryllium than the matrix; so the long range transportation of beryllium atoms through the matrix to the precipitates has to occur for the precipitates to grow in size. Therefore, the diffusion of beryllium in copper plays an important role in the growth of the precipitates.

At the interface of the precipitates and the matrix, there can be two possible extreme situations. In the first situation, the beryllium atoms may cross the interface very easily into the precipitate. The growth of the precipitate is therefore only limited by the rate of diffusion of the beryllium atoms through the matrix. In this case the transformation is called diffusion controlled. Since there is a state of local thermodynamic equilibrium at the interface, the composition of the matrix at the interface is not the same with the matrix far away from the interface. In other circumstances, there can be another extreme that the beryllium atoms are very difficult to become attached to the surface of the precipitate. In this case, the growth of the precipitates will depend solely on the rate of the atoms crossing the interface. The diffusion of beryllium atoms through the matrix causes extra
Figure 1.6: The composition profiles under different growth control mechanisms. $C_p$, $C_0$, and $C_e$ are the compositions of the precipitate, in the matrix far away from any precipitates, and dictated by local equilibrium at the interface, respectively.

beryllium atoms to be piled up at the interface until the matrix composition becomes uniformly distributed. This latter transformation is termed interface controlled. In real systems, the situation is always between the two extremes. The composition of the matrix at the interface is larger than the thermodynamic equilibrium value and smaller than the composition far away from the interface. The control mechanism for growth is now called mixed. The composition profiles of these transformations are illustrated in Fig. 1.6.

While the composition of the matrix at the interface is determined by the diffusion
Figure 1.7: Concentration profile in a typical crystal undergoing precipitation. The concentration spikes are supposed to be precipitates. The slopes of the profiles depend on many factors.
coefficients and the speed of particles crossing the interface, the slope of the concentration profiles in a real solid (see Figure 1.7) depend on a few more factors such as inter-particle spacing and the stage of growth. In general, small ratio of precipitate size to inter-precipitate spacing, small diffusion coefficients, and early stage of growth favor large slopes. On the other hand, transformations with larger ratio of size to spacing, large diffusion coefficients, and in the later stage will be have smaller slopes. Because the diffusion coefficients increase rapidly with rising temperature, the temperature of aging will play important roles in determining the slopes of the concentration profiles in the aged Cu-Be alloys.

1.3.2 Deformation of Crystals Containing a Second Phase

Unlike in the case of solid solutions, in which the hardening is accomplished by creating an atmosphere around the dislocations, the rigid second phase particles in the crystal can serve as obstacles to the movement of the dislocations. The deformation of the crystal is then limited to one of the following two ways:

1. cutting through the particles;

2. bowing around the particles.

The relative importance of the two depends on many factors. In general, cutting is more difficult with larger particles, ordered second phase, stiffer elastic behavior in precipitates, and bigger difference in lattices between precipitates and matrix. On the other hand, bowing is easier with smaller lattice strain due to the precipitates and larger spacing between them.

The hardening mechanism of the aged-hardenable alloys is like the following. In the initial stage, the cutting mechanism dominates. As the precipitates grow in size, the movement of the dislocations become increasingly difficult. This causes the increase of hardness. But with the growing size of the precipitates, the spacing between the precipitates also increases. There will be a point when it becomes easier for the dislocations to bow around the precipitates. At this point, the hardness of the material starts to decrease. And the alloy is said to be overaged. It is one of the goals of this research to determine the critical precipitate size or spacing.
1.4 Extracting Information from X-ray Scattering from Crystals Containing Defects

When defects are introduced into a crystal, the diffraction from the crystal is changed in two ways. Because the defect atoms usually have different scattering power compared with the original ones, the spatial distribution of the defect atoms will alter the long range order of the original crystal and change the diffraction pattern. Furthermore, these defect atoms are often different in size from the matrix atoms. Therefore, they can cause lattice disturbance in the matrix surrounding them. This will introduce special diffraction effects. The distribution and disturbance aspects are always related to each other. This makes extracting structure information from X-ray diffraction patterns for crystals containing defects a very complicated problem.

Simple systems or complex systems with simplifying assumptions can be described in simple theories. For truly random binary systems with no size difference, the scattering is described as Laue monotonic, which depends on the difference in the scattering power of the two kinds of atoms. For systems that local atomic arrangement exhibit preferred neighbors, a set of short range order parameters can be introduced to determined the atomic arrangements and diffraction effects. "Size effect" coefficients are used to account for atomic size difference of the nearest neighbors. All of these scattering effects are not concentrated and are distributed all over the reciprocal space.

For more complicated systems, there are in general two kinds of methods to extract the information from the diffraction patterns. One is to phenomenologically separate the contributions from the distribution and disturbance effects of the defects directly from the X-ray diffraction patterns. From these parameters the atomic arrangements in the crystal are deduced. The other method is to use some kind of model for the defects; and from the model X-ray scattering results are interpreted.

1.4.1 Phenomenological Methods

Cohen et. al. has developed a method to determine the short range order and local atomic arrangements in disorder binary alloys. This method was used on a number of alloy systems [27, 28, 29, 30], including the recent application on Cu-10.9 at. %Be during early stages of aging [17, 18, 19].
The main point of this analysis is to expand the scattering intensity expression in the reciprocal space into a power series of atomic displacements from their equilibrium positions (excluding thermal diffuse scattering):

\[ I = I_{\text{SRO}} + \text{First order terms} + \text{Second order terms} + \cdots, \tag{1.1} \]

where \( I_{\text{SRO}} \) is a Fourier series of the Warren-Cowley short range order parameters and does not depend on atomic displacements. First order terms are Fourier series of averaged displacements. Second order terms include Fourier series that depend on the pair correlation of the displacements. And so on. Typically, up to second order terms are used in real applications [17].

When conducting experiments, a set of points in the reciprocal space is carefully selected according to symmetry relationship so that each term in the above expression have same magnitude and different sign at these point. The values of the terms in reciprocal space are obtained by least squared principles. The short range order parameters, averaged displacements, averaged correlations are determined from their Fourier series. Special attentions are then placed on the short range order parameters. A computer simulation program is used to try to determined the local atomic arrangements of the defects from them.

There are several problems associated with this analysis. The first is that the convergence of the expansion has to be justified, especially for systems like Cu-Be where the size difference between the two kinds of atoms is large. Table 1.2 shows the breakdown of the magnitude of the terms as percentage of total intensity in when this method is applied to as-quenched and aged Cu-Be alloy [17]. From the data listed it is not convincing that the series expansion is convergent. Even without the convergence problem, when higher order terms of comparable magnitude are added, the values of the lower order terms and hence the short range order parameters will be altered very significantly.

Secondly, the short range order parameters do not specify completely the atomic configuration of a severely clustered system. A highly heterogeneous system can have large short range order coefficients in one region and small ones in another. The averaged short range order parameters will not reflect this important information.

Finally, this analysis treats the distribution of the defect atoms (short range order) and
Table 1.2: Various intensity contributions to total intensity for as-quenched and aged Cu-Be samples (in percent) [17].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>$i_{SRO}$</th>
<th>First order terms</th>
<th>Second order terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>as quenched</td>
<td>(1.9,1.1,0.0)</td>
<td>12.6</td>
<td>13.2</td>
<td>14.1</td>
</tr>
<tr>
<td>as quenched</td>
<td>(2.1,0.1,0.0)</td>
<td>35.2</td>
<td>21.8</td>
<td>32.5</td>
</tr>
<tr>
<td>Early GP</td>
<td>(2.3,0.0,0.0)</td>
<td>20.2</td>
<td>36.4</td>
<td>35.8</td>
</tr>
<tr>
<td>Late GP</td>
<td>(2.3,0.0,0.0)</td>
<td>17.6</td>
<td>43.2</td>
<td>39.4</td>
</tr>
<tr>
<td>$\gamma''$</td>
<td>(2.3,0.0,0.0)</td>
<td>28.2</td>
<td>37.3</td>
<td>33.7</td>
</tr>
</tbody>
</table>
the influences in the matrix (displacements) as separate quantities. In reality, these two aspects are interrelated because the lattice disturbance around the precipitates are caused by the exact same segregation of the defect atoms. This relationship is not considered and the compatibility of the two components of the same physical origin are not guaranteed in the analysis. To alleviate this problem, one needs to resort to modeling method to extract information from X-ray diffraction patterns.

1.4.2 Modeling Methods

In modeling methods, one usually assumes the structure and configuration of the defects. The mechanism of the influence on the surrounding matrix also needs to be established. The elasticity theory is popular for modeling the long range influence of the defects on the lattice. Potential theory and discrete lattice dynamics are also used for disturbance very close to the defects. The combined system of defects and their surrounding is used to interpret experimental scattering results. Some parameters of the models are sometimes left to be determined from the comparison.

Point defects and their clusters of low concentration (small distortion)

The scattering from crystals containing randomly arranged defects that induce displacements was first studied by Eckstein [31] and Huang [32]. The theory is later extended by several authors [33, 34, 35, 36] and summarized in a paper by Dederichs [37].

In this theory, the defects are modeled by a set of forces (Kanzaki forces) on atoms. The displacement field \( u(R^n) \) of the atom at \( R^n \) is determined though lattice statics by [38]

\[
u_i(R^n) = \sum_m \sum_{j=1}^3 G_{ij}(R^n - R^m)F_j(R^m), \quad (1.2)\]

where \( G_{ij} \) is the lattice Green function of the ideal lattice, and \( F(R_m) \) is the Kanzaki force on atom \( m \). For distance \( R \) far away from the defect, continuum theory can be used. The defects are characterized by a dipole tensor

\[
P_{ji} = \sum_m F_j(R^m)R_i^m. \quad (1.3)
\]
And the asymptotic displacement field is calculated by [38]

\[ u_i(R) = -\sum_{i,j=1}^{3} \frac{\partial G_{ij}(R)}{\partial R_i} P_{ji}, \]  

(1.4)

where \( G_{ij} \) is now the elastic Green function.

When displacements caused by the defects are present in the lattice, they have two effects on the X-ray scattering. The first is that the Bragg peaks are shifted and attenuated. The second is that diffuse scattering appears in between Bragg reflections in reciprocal space.

For randomly arranged defects with concentration \( c \) and dipole tensor \( P_{ij} \), the Bragg reflections are shifted in the reciprocal space by [37]

\[ \Delta H_i = -\frac{c}{V_c} \sum_{k,l,j=1}^{3} S_{ijkl} P_{kl} H_i^0, \]  

(1.5)

where \( V_c \) is the unit cell volume, \( S_{ijkl} \) is the elastic compliance tensor and \( H_i^0 \) is the original Bragg peak position. And the intensities of the peaks are reduced by a factor of \( e^{-2M} \), where the Debye-Waller factor \( M \) is given by [39, 37]

\[ M = c \sum_{m}(1 - \cos 2\pi H \cdot u(R^m)) \]  

(1.6)

for \( c \ll 1 \).

When the concentration of defects in the crystal is small and the distortion caused by these defects is not large \( (2M \ll 1) \), the diffuse scattering is given as [37]

\[ I_1 = cN \left| f^D + f \sum_n e^{2\pi i H \cdot R^n} \left[ e^{2\pi i H \cdot u^n} - 1 \right] \right|^2, \]  

(1.7)

where \( N \) is the total number of atoms in the crystal, \( f^D \) is the difference between the scattering powers of the original lattice atoms and the defect atoms, and, \( f \) is the scattering powder of the original lattice atoms.

In regions very close to the Bragg reflections, the scattering is in the form of Huang scattering, which varies as \( 1/q^2 \) with \( q \) being the distance from the nearest reciprocal lattice.
point. The Huang scattering depends upon the displacement fields far away from the defect. The symmetry of the defects can be obtained from the symmetry of the Huang diffuse scattering [35].

In addition to the Huang scattering, there is also a term which varies at $1/q$ near the Bragg reflections. This term is asymmetric about the Bragg reflection and contains information on the type of defects. If more intensity is on the low Bragg angle side, the defects are of vacancy type. And if the intensity is distributed the other way, the defects will be of interstitial type. The origin of this term is from the interference of the scattering from regions far away from the defect and regions close to the defect [37].

For scattering far away from the Bragg reflections, it depends sensitively on the displacements close to the defects. The intensity in general varies with $1/q^4$.

**Defect clusters that induce large displacements**

Krivoglaz and co-workers [40, 41, 39, 42, 43, 44] also studied the X-ray scattering from crystals containing defects extensively. He classified defects into two classes according to their behavior in causing long range displacements in the parent lattice.

If the displacements they create in the lattice far away from the defect fall off as $1/r^2$, where $r$ is the distance, the defects are Class I. Point-like defects belong to this class. The X-ray diffraction from crystal containing this class of defects in general should have both the Bragg peaks and diffuse scattering, because the Debye-Waller factor $2M$ is finite in these cases.

When the defects in the crystal produce displacement fields that fall off more slowly than $1/r^{3/2}$, the situation is different. Under these circumstances, the Debye-Waller factor is infinite and the original Bragg peaks vanish completely. The diffuse scattering appears in place of the original Bragg peaks. These kinds of defects are classified as Class II. A dislocation extended through out the crystal generates displacement field which approaches infinity as $1/r$. Thus it belongs to the second class of defects.

Even with defects of the first class, when the strength of the defects is large enough, there is interesting phenomenon in the diffraction patterns. Krivoglaz treated a system of randomly arranged point defects in an elastically isotropic crystal. The displacement field
produced by one defect is given by

\[ u_{ts} = C \frac{r_{ts}}{r_{ts}^3} \quad \text{for} \quad r_{ts} > r_0, \]  

(1.8)

where \( r_{ts} \) is the vector drawn from the defect (at position \( t \)) to the point under consideration (point \( s \)). The constant \( C \) is the strength of the defect and is independent of direction. The displacements in the lattice are superposition of all displacements from all defects. From small concentration of defects, \( c \), the diffuse scattering equals [41, 39]

\[ I = j^2 \sum_s \sum_{t'} e^{i(qt-R_s-R_{s'})} e^{-T}, \]  

(1.9)

where

\[ T = c \sum_t \{1 - \exp(iq_1 \cdot (u_{ts} - u_{ts'}))\}, \]  

(1.10)

and \( u_{ts} \) is given in Eq. (1.8). In the equations, \( q_1 \) is the diffraction vector, \( q = q_1 - 2\pi K_n \) (\( K_n \) is the reciprocal lattice vector nearest to the end of vector \( q_1/2\pi \), and, \( R_s \) is the position of atom \( s \) in the lattice expanded by the image force only.

When the strength of the defects \( C \) is extremely large, the Debye-Waller factor becomes much greater than 1 and the intensity of the Bragg peaks, attenuated by \( e^{-2M} \), will be very small. At the same time, the diffuse scattering is sharpened to a bell-shape distribution with their maxima lying at the reciprocal lattice points corresponding to the lattice expanded by the image forces only. The width of this peak, referred to as "quasi-line", is comparable to the that of the Bragg peaks in an ordinary cold-worked metal. The appearance of the quasi-line was later demonstrated by Dederichs using a slightly different approach [45].

Research has been done to extend the above theory to powder diffraction from isotropic crystals with point defects in the intermediate 2\( M \) range [46]; and the effect of anisotropy on the above theory [47]. But they are at most performed on a semi-quantitative bases and are not in a form useful enough to be applied to real physical systems.
1.5 Organization of this Dissertation

This dissertation deals with the extraction of structural information of the defects in a commercial copper beryllium alloy from X-ray diffraction experiments during the course of the age-hardening process. The information obtained is used to show the phase evolution and structure property relation of the alloy.

The experimental details are described in Chapter 2. Polycrystalline X-ray diffraction and hardness measurements are performed on as-quenched and aged samples at every condition. Texture analysis is done on the as-quenched samples.

Chapter 3 presents the elastic model of the defects to be used to interpret diffraction data. The precipitates are modeled as transformed regions in an anisotropic elastic continuum.

Quantitative analysis of diffuse scattering from polycrystalline materials with textures is almost non-existence in the literature. Chapter 4 attempts to give a general theory on the calculation of diffuse scattering from this kind of materials. A sample thermal diffuse scattering calculation for the textured alloys used in this research is done with a simplified procedure in obtaining thermal diffuse scattering (TDS).

During the very early stages of aging, the clusters are small and the distortion caused by them is not severe. In Chapter 5, we use Dederichs' theory on Huang diffuse scattering to obtain information on the symmetry of the defects, based on the elastic model presented above and the experimental evidence in the literature. The discussion in this Chapter is the primary basis for the selection of parameters for the computer simulation.

As aging time increases, quasielines become more important in the diffraction near the Bragg reflections. Krivoglaz's theory is extended to be applicable to the alloy system being studied. This appears as Chapter 6.

In Chapter 7, the theory is applied to simulate the experimental data in the middle stage of aging and determine the critical parameters of the precipitates. Data from later stage of aging are also discussed.

Finally, conclusions are drawn in Chapter 8 about the diffraction results, phase transformation and their relation to the hardness of the material.
Chapter 2

Experimental Procedures and Results

2.1 Samples and Apparatus

2.1.1 Sample Preparations

The samples used in this research are the commercial Brush Alloy 25 Beryllium Copper polycrystalline alloy from Brush Wellman, Inc. The compositions of the alloy supplied by the manufacturer is given in Table 1.1. The alloy is mainly consisted of copper and 11.55% of beryllium, with 0.23% of cobalt and others. The composition of this alloy is similar to the Telcon 250 alloy (11.50% Be, 0.30% Co) used in [13]. It was described in [13] that the presence of small amount of cobalt does not change significantly the precipitation sequence. It is added to control the grain sizes in the forming processes. It acts to slow down the precipitation transformation. The alloy was drawn and hard tempered to rod shape with a diameter of 0.875 inch by the manufacturer. Samples for diffraction experiments are cut from these rods to a thickness of about 0.1 inch. They are mechanically polished to improve the surface smoothness. The samples are then solution treated in an Ar protected furnace for 15 minutes at 780°C. The solution treatment is to relax the stresses in the samples introduced in the manufacturing, cutting and grinding processes. The time of the treatment is limited by the grain size in the samples. The grain size must be small enough to ensure that there are reasonable amount of grains participating in the diffraction process at every moment so that every orientation of the grains are equally represented in the powder diffraction profiles.

The samples are quenched into salt water at room temperature after solution treatment.
Diffraction experiments are performed on these samples to obtain the composition and texture information. They are subsequently aged to different times at 315°C in a salt bath. At every aging condition, microhardness and diffraction measurements are done for the samples. The samples are stored in a freezer of −4°C when not in use. They are exposed to room temperature only when experiments are performed.

2.1.2 Diffraction Apparatus

Diffraction experiments are conducted on a Siemens D500 diffractometer mounted horizontally with a copper target. A quartz monochromater is installed on the incident beam so that only $K_{\alpha_1}$ radiation of copper (1.5405Å) is used. Most of the work is done with a Position Sensitive Proportional Counter (PSPC) from MBraun. A conventional proportional counter is also used for calibration.

The setup is illustrated schematically in Figure 2.1. The detector has a wide open window. A curved wire which spans for over 12° is used to detect X-ray photons. Once a pulse is generated on the wire by an X-ray photon, the analyzer determines the position of the incident photon by the difference in propagation time for the pulse to reach the two ends of the wire. The counts are tallied separately according to the positions of the incident photons. In this way, the detector is able to measure the intensity distribution for over 10° at a time, thus speeding up the experiments by a factor of 10–100.

A similar setup is also used to measure low angle scattering of the samples. A regular proportional counter is used in those experiments; and chromium is the target instead of copper. The wavelength of chromium $K_{\alpha_1}$ is 2.289Å.

2.2 Mechanical Property of Aged Alloys

To determine the progress of the aging process, microhardness is measured for the as-quenched samples and samples at all aging conditions. The measurements were done on a hardness tester with a diamond indenter. The load is kept at 1000 grams for 10 seconds. The functional dependency of the hardness on aging time at 315°C is tabulated in Table 2.1 and shown in Figure 2.2. Also plotted on Figure 2.2 is the yield tensile strength of the samples aged at 600°F (316°C) extracted from [50]. It can be seen that the hardness
Figure 2.1: Schematic diagram of X-ray diffraction setup.

Table 2.1: Microhardness of the samples at different aging times at 315°C

<table>
<thead>
<tr>
<th>Aging Time (minutes)</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>105.3</td>
</tr>
<tr>
<td>5</td>
<td>120.7</td>
</tr>
<tr>
<td>15</td>
<td>200.5</td>
</tr>
<tr>
<td>30</td>
<td>302.4</td>
</tr>
<tr>
<td>180</td>
<td>378.2</td>
</tr>
<tr>
<td>1440</td>
<td>369.9</td>
</tr>
<tr>
<td>10080</td>
<td>334.7</td>
</tr>
</tbody>
</table>
Figure 2.2: Function of Hardness and Yield Strength on Aging Time
increases from 105.3 at the as-quenched state to about 400 around 5 hours aging. Then it starts to decrease as the samples become overaged.

2.3 Results from As-Quenched Samples

Metallographic microscopy was performed on one of the as-quenched samples. The sample is first polished mechanically. Then it is etched with a solution mixed with 3 parts of distill water, 5 parts of NH₄OH and three parts of H₂O₂. The photograph, shown in Figure 2.3, is taken with a magnification of 1000. From this, the grain size of the metal is measured to be 16μm.

Four samples in the as-quenched condition were examined by X-ray diffraction. The Bragg peak positions and integrated intensity under the Bragg peaks for (111), (200), (220), (311), (222), and (400) for all samples were measured. The average lattice parameter from these measurements is 3.579±0.002 Å. If the composition is assumed to be binary (Be-Cu), the concentration of Be obtained from the average lattice parameter is 11.16±0.60, based upon the volume size factor and atomic volume given in [51].

An analysis of the integrated intensity data reveals that the samples have a preferred orientation. Because the samples are spun about the normal of the surfaces when collecting X-ray diffraction data, the texture involved in our calculation can be treated as a fiber texture with the fiber axis coincided with the normal of the surface. For our purpose, it is sufficient to know the relative intensity ratio of the (hkl) peaks between the present samples and the ideal random powder. This ratio is equal to the g_{hkl}(χ = 0) in texture analysis. The integrated intensity and the corresponding g factors are listed in Table 2.2.

The experimental integrated intensities are first divided by the theoretical value for a random powder. Then the normalized g factors are obtained through relation

\[ 0.076g_{200} + 0.169g_{111} + 0.484g_{311} + 0.271g_{110} = 1. \]  

(2.1)

The integrated intensities of the (111) and (200) peaks for all as-quenched sample are lower

*Use of this equation implies that a fourth order Lagendre polynomial is used to represent the orientation distribution function [52]. It presents no problem here because we are only interested in the relative values of the texture factors.
Figure 2.3: Photograph of as-quenched Cu-Be-Co (x1000).
Table 2.2: Integrated intensities and $g$ factors

<table>
<thead>
<tr>
<th>$hkl$</th>
<th>111*</th>
<th>200*</th>
<th>220</th>
<th>311</th>
<th>222</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samples</td>
<td>ideal powder</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A1</td>
<td>Integrated intensity</td>
<td>182.018</td>
<td>61.3116</td>
<td>5.6718</td>
<td>19.8988</td>
<td>18.6769</td>
</tr>
<tr>
<td></td>
<td>Real/Ideal powder</td>
<td>0.01052</td>
<td>0.00772</td>
<td>0.00134</td>
<td>0.00417</td>
<td>0.01329</td>
</tr>
<tr>
<td></td>
<td>$g_{hkl}$</td>
<td>1.990</td>
<td>1.459</td>
<td>0.254</td>
<td>0.789</td>
<td>2.513</td>
</tr>
<tr>
<td>C9</td>
<td>Integrated intensity</td>
<td>152.697</td>
<td>51.658</td>
<td>4.93</td>
<td>18.3327</td>
<td>14.5338</td>
</tr>
<tr>
<td></td>
<td>Real/Ideal powder</td>
<td>0.00883</td>
<td>0.0065</td>
<td>0.00117</td>
<td>0.00384</td>
<td>0.01034</td>
</tr>
<tr>
<td></td>
<td>$g_{hkl}$</td>
<td>1.965</td>
<td>1.447</td>
<td>0.260</td>
<td>0.855</td>
<td>2.303</td>
</tr>
<tr>
<td>M2</td>
<td>Integrated intensity</td>
<td>149.837</td>
<td>47.3892</td>
<td>3.7758</td>
<td>15.778</td>
<td>14.7298</td>
</tr>
<tr>
<td></td>
<td>Real/Ideal powder</td>
<td>0.00866</td>
<td>0.00596</td>
<td>0.00089</td>
<td>0.00331</td>
<td>0.01048</td>
</tr>
<tr>
<td></td>
<td>$g_{hkl}$</td>
<td>2.114</td>
<td>1.456</td>
<td>0.218</td>
<td>0.807</td>
<td>2.558</td>
</tr>
<tr>
<td>L4</td>
<td>Integrated intensity</td>
<td>167.335</td>
<td>56.8425</td>
<td>5.9759</td>
<td>19.4121</td>
<td>17.6019</td>
</tr>
<tr>
<td></td>
<td>Real/Ideal powder</td>
<td>0.00967</td>
<td>0.00715</td>
<td>0.00141</td>
<td>0.00407</td>
<td>0.01252</td>
</tr>
<tr>
<td></td>
<td>$g_{hkl}$</td>
<td>1.903</td>
<td>1.408</td>
<td>0.278</td>
<td>0.800</td>
<td>2.465</td>
</tr>
<tr>
<td>Average $g_{hkl}$</td>
<td>1.993</td>
<td>1.442</td>
<td>0.252</td>
<td>0.813</td>
<td>2.460</td>
<td>1.613</td>
</tr>
<tr>
<td>Error</td>
<td>0.060</td>
<td>0.017</td>
<td>0.017</td>
<td>0.021</td>
<td>0.079</td>
<td>0.041</td>
</tr>
<tr>
<td>Percentage Error</td>
<td>3.03</td>
<td>1.21</td>
<td>6.82</td>
<td>2.61</td>
<td>3.19</td>
<td>2.56</td>
</tr>
</tbody>
</table>

* The experimental intensities of (111) and (200) peaks are reduced due to extinction and are not used to determine $g_{hkl}$. 
than expected because of the extinction effect. These data are not used to determine the \( g \) factors.

Apart from the Bragg scattering, there are some small scattering peaks around regions that the precipitate scattering is about to appear. Detailed analysis of them is given in Section 2.5. These peaks are stable in both position and intensity throughout the aging process. It is not clear whether they are the residue precipitates not dissolved by the solution treatment or they are formed during the quench.

### 2.4 Scattering Near Bragg Peaks of the Matrix

The diffraction near the Bragg peaks of the matrix goes through dramatic changes in the course of aging. Figures 2.4, 2.5, 2.6, 2.7, 2.8 and 2.9 are scattering near \((111)\), \((200)\), \((220)\), \((311)\), \((222)\) and \((400)\) peaks, respectively. In each figure, the diffraction patterns for the as-quenched, 15 minute aged, 30 minute aged, 3 hour aged, 24 hour aged, and 168 hour aged samples are shown. The vertical dash lines in the figures are the positions of the Bragg peaks of pure copper.

Little changes are observed for the 5 minute aged sample when compared with the as-quenched one. The peak heights and integrated intensities actually increase for the lower few order peaks. This is because the segregation of very small precipitate particles distorted the perfect crystals and lessened the extinction effects. For the 15 minute aged sample, the Bragg peaks are attenuated, more so on the high order ones. And diffuse scattering appears on the low angle side of the Bragg peaks. The positions of the Bragg peaks, however, remain unchanged.

After 30 minutes in the aging treatment, the scattering near \((111)\) becomes very broad and asymmetric. The position of the intensity maximum is at an angle slightly higher than the original Bragg peak. For scattering near all other Bragg positions, the distribution are very broad and shifted towards the pure copper positions (indicated by the dash lines in the figures), which are at lower angle side of the original diffraction peaks. The broadening and the shifting towards pure copper positions continue (or initiated for \((111)\)) for the scattering from the sample aged for 3 hours. The sample is now very close to the hardness maximum (see Figure 2.2).
Figure 2.4: (111) matrix scattering
Figure 2.5: (200) matrix scattering
Figure 2.6: (220) matrix scattering
Figure 2.7: (311) matrix scattering
Figure 2.8: (222) matrix scattering
Figure 2.9: (400) matrix scattering
Further aging treatments on the samples decrease the hardness of the material. In this overaged stage, the diffraction intensities near the Bragg peaks start to sharpen again. And the positions of the intensity maxima move slightly back to high angles.

2.5 Precipitate Scattering

After 30 minute of aging at 315°C, very complex diffraction patterns develops around the small scattering peaks (later identified as beryllides) presented at the as-quenched state. According to their positions and the existing literature, these intensities may be indexed according to the B2 crystal structure and have a lattice parameter about 2.7Å. The diffraction patterns of the (100) precipitate peak for an as-quenched sample and samples aged for 30 minutes, 3 hours, 24 hours and 168 hours are shown in Figure 2.10. The patterns for (111) precipitate peak are given in Figure 2.11. As much as four peaks can be resolved from some diffraction patterns. A non-linear least square procedure is established to fit each peak with a Pearson-VII function.

The parameters of the separated peaks are given in Tables 2.3–2.5. The particle dimensions listed in the tables are estimated using the measured FWHM of the peaks and Scherrer’s equation: [53]

\[
\text{FWHM}(2\theta) = \frac{0.9\lambda}{L \cos \theta}
\]

2.6 Low Angle Scattering

Low angle diffraction experiments are performed for a series of sample aged at 250°C. The data are measured on a conventional θ–2θ diffractometer by reflection. The purpose of the low angle scattering is to examine whether regularity exists for the arrangement of precipitates in the aged crystals. It may also be possible to obtain the “radius of gyration” for the precipitates using the theory developed by Guinier [54].

The data is shown in Figure 2.12. The data is plotted with the natural log of the intensity as the y-axis and \((2\theta)^2\) as the x-axis. According to Guinier’s formula, the slopes of the curves are proportional the radius of gyration of the particles inside the crystal that cause the diffractions.

Because the experiments are done with the reflection method, the irradiated surface
Figure 2.10: (100) Precipitate scattering
Figure 2.11: (111) Precipitate scattering
Table 2.3: Diffraction peaks of beryllides

<table>
<thead>
<tr>
<th>Aging Time at 315°C</th>
<th>As quenched</th>
<th>30 minutes</th>
<th>3 hours</th>
<th>24 hours</th>
<th>168 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>2θ</td>
<td>33.76</td>
<td>33.74</td>
<td>33.73</td>
<td>33.75</td>
</tr>
<tr>
<td></td>
<td>FWHM</td>
<td>0.18</td>
<td>0.16</td>
<td>0.18</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>Area</td>
<td>0.40</td>
<td>0.22</td>
<td>0.40</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>Lattice Parameter (Å)</td>
<td>2.652</td>
<td>2.654</td>
<td>2.655</td>
<td>2.654</td>
</tr>
<tr>
<td></td>
<td>Particle Size (Å)</td>
<td>588</td>
<td>685</td>
<td>574</td>
<td>640</td>
</tr>
<tr>
<td>111</td>
<td>2θ</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>FWHM</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Area</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lattice Parameter (Å)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Particle Size (Å)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.4: Diffraction peaks of discontinuous precipitates

<table>
<thead>
<tr>
<th>Aging Time at 315°C</th>
<th>30 minutes</th>
<th>3 hours</th>
<th>24 hours</th>
<th>168 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>2θ</td>
<td>33.16</td>
<td>33.17</td>
<td>33.18</td>
</tr>
<tr>
<td></td>
<td>FWHM</td>
<td>0.32</td>
<td>0.32</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>Area</td>
<td>0.063</td>
<td>0.51</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>Lattice Parameter (Å)</td>
<td>2.700</td>
<td>2.698</td>
<td>2.698</td>
</tr>
<tr>
<td></td>
<td>Particle Size (Å)</td>
<td>284</td>
<td>286</td>
<td>431</td>
</tr>
<tr>
<td>111</td>
<td>2θ</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>FWHM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Area</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lattice Parameter (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Particle Size (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2.5: Diffraction peaks of continuous precipitates

<table>
<thead>
<tr>
<th>Aging Time at 315°C</th>
<th>30 minutes</th>
<th>3 hours</th>
<th>24 hours</th>
<th>168 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 Sharp</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2\theta$</td>
<td>34.79</td>
<td>34.41</td>
<td>33.69</td>
<td></td>
</tr>
<tr>
<td>FWHM</td>
<td>1.49</td>
<td>0.96</td>
<td>1.34</td>
<td>Can</td>
</tr>
<tr>
<td>Area</td>
<td>0.96</td>
<td>1.11</td>
<td>0.72</td>
<td>not be</td>
</tr>
<tr>
<td>Lattice Parameter (Å)</td>
<td>2.577</td>
<td>2.604</td>
<td>2.658</td>
<td>separated</td>
</tr>
<tr>
<td>Particle Dimension (Å)</td>
<td>58.7</td>
<td>90.9</td>
<td>64.8</td>
<td></td>
</tr>
<tr>
<td>100 Broad</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2\theta$</td>
<td></td>
<td>31.99</td>
<td>32.68</td>
<td>33.35</td>
</tr>
<tr>
<td>FWHM</td>
<td>&gt;5</td>
<td>3.93</td>
<td>1.88</td>
<td>0.98</td>
</tr>
<tr>
<td>Area</td>
<td>2.88</td>
<td>2.56</td>
<td>5.04</td>
<td></td>
</tr>
<tr>
<td>Lattice Parameter (Å)</td>
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<td>2.737</td>
<td>2.684</td>
<td></td>
</tr>
<tr>
<td>Particle Dimension (Å)</td>
<td>&lt;16.6</td>
<td>22.0</td>
<td>46.1</td>
<td>89.2</td>
</tr>
<tr>
<td>111</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2\theta$</td>
<td></td>
<td>59.77</td>
<td>59.48</td>
<td>59.48</td>
</tr>
<tr>
<td>FWHM</td>
<td>Not Observed</td>
<td>3.01</td>
<td>1.54</td>
<td>0.93</td>
</tr>
<tr>
<td>Area</td>
<td>0.56</td>
<td>0.44</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>Lattice Parameter (Å)</td>
<td>2.677</td>
<td>2.689</td>
<td>2.689</td>
<td></td>
</tr>
<tr>
<td>Particle Dimension (Å)</td>
<td>31.8</td>
<td>62.0</td>
<td>102.8</td>
<td></td>
</tr>
</tbody>
</table>
Figure 2.12: Low angle scattering for sample aged at 250°C. Horizontal axis is in units of degree squared.
of the sample gets larger and larger as the diffraction angle decreases. With the smallest entrance slit (\(\frac{1}{4}^\circ\)) and our sample size, part of the beam is expected to get off the sample surface at an incident angle of 0.7\(^\circ\). This means that the relative intensities for \(2\theta < 1.4^\circ\) is not quantitatively reliable.

In low angle reflective scattering, the intensities scattered from the air and into the detector are not negligible. In our setup, a special edge aperture is used to block the air scattering. The aperture is mounted directly in front of the center of the sample, and its edge is located as close to the sample surface as possible without blocking the main X-ray beam. This adjustment is done at angle \(2\theta = 0^\circ\). If the aperture does not block the beam at this angle, the X-ray beam will not hit it at any other angles.

At such small angles, the X-ray beam almost comes in parallel to the surface of the samples. The surface roughness of the samples thus profoundly influences the diffraction intensity. The samples used for low angle scattering are all electro-polished in a solution of 1 part of nitric acid and 2 parts of methanol. Experiments show that the low angle diffraction intensity for a polished sample can be 10 times higher than that for an unpolished one. Even with a well-polished sample, the diffraction intensity still decreases by as much as 50\% in several hours' time during X-ray diffraction measurement as the sample surface gets oxidized.

The surface condition issue may cause the measurements of the radius of gyration giving unreasonable results. The calculation shows that the radius of gyration for the precipitates in as-quenched samples is roughly the same as that of the precipitates in a sample near hardness maximum. This result is unacceptable and must be due to some effects beyond our control.

Useful results can still be obtained from these low angle diffraction experiments. The diffracted intensities of all samples show no peaks or modulations at angles \(2\theta > 1.4^\circ\). This means that no structures in the crystal have strong periodicity with periods less than 94Å. The small "peak" at about \(2\theta = 3^\circ\) for one sample was related to a diffraction peak from the aluminum holder. The holder without a sample gives a peak in the same positions; and this peak does not appear in the diffraction patterns of other samples.

The experimental results obtained in this Chapter will be analyzed in Chapter 7 using the theory developed in subsequent chapters.
Chapter 3

Elastic Model of the Precipitates

3.1 Precipitates as Transformed Regions in Matrix

The phase transformation involving structure and/or composition change has the characteristics that inside the regions of the second phase the lattice is distorted with respect to the original matrix. This will create a lattice and volume mismatch at the interfaces between the two. It is the interaction of the atoms at the interfaces that causes distortion on both sides.

The distortion caused by a transformed region can be evaluated using Eshelby's method. The analysis divide the transformation and interaction into several steps:

1. Cut the region to be transformed out of the embedded matrix.

2. Let the cut out region transform without the constraint imposed by the matrix. The strain with respect to the original matrix, obtained under this condition, is called the stress-free transformation strain. This strain represents the inherent property of the transformation.

3. Apply surface forces to the transformed region to restored its original form.

4. Put the region with the force applied back to the matrix.

5. Assert another set of surface forces that are equal and opposite the forces applied in item 3 and let the system (matrix and transformed region) deformed under the latter applied forces according to the theory of elasticity and their own constitutive laws.
Because the two external applied surface forces cancel each other, there is no net external force added to the system. The deformation obtained from the above procedure is the actual distortion caused by the transformation of the precipitates, and is relatable to the measured parameters of the crystal.

The steps are illustrated in Figure 3.1. The filled circles in the figure are just for showing the change in positions of the points inside the material caused by the transformed region. They are not necessarily "atoms" since a continuum model is being considered. The property of the continuum is described by the elastic constants of the material.

3.2 Displacement Fields Generated by a Transformed Ellipsoid

3.2.1 Notations

In the chapter, the notations follow the conventions used in most texts for continuum mechanics.

Vectors (first order tensors) is represented by boldface letters, like \( \mathbf{u} \). The elements of the vector \( \mathbf{u} \) are given as \( u_i \), where \( i \) can take on the values of 1, 2, and 3. An italic alphabet, for example \( u \), represents the length of the vector, \( \mathbf{u} \). The unit vector corresponding to a vector \( \mathbf{u} \) is denoted by \( \hat{u} \). Multiple order tensors are generally represented in their component forms only. All un-constrained indices varies from 1 to 3. Repeated indices in a term imply summations over all possible values of the indices unless indicated otherwise.

Functions of real space positions are written normally, as \( f(\mathbf{r}) \). The Fourier transform of the function \( f(\mathbf{r}) \) is represented as \( \tilde{f}(k) \). The notation \( d^3r \) means a three dimensional differential element in the \( r \)-space.

3.2.2 Assumptions of Linear Elasticity

In the following analysis, the crystal is to be treated as a linear elastic continuum. Because the size of the precipitates is generally much larger than the lattice parameter, the continuum assumption can be a good approximation in most of the crystal. In addition, the elasticity theory requires small deformations which should be satisfied except in the immediate vicinity of the precipitates.
Figure 3.1: Eshelby's method of treating a transformed region in a matrix. 
Step 1: Region is cut out of the matrix. Step 2: Region transforms without the constraint of matrix. Step 3: Surface forces are applied to restore the original size and shape. Step 4: Put it back inside the matrix. Step 5: Assert opposite forces and restore the net force to zero. This final condition satisfies the requirements of a mechanical equilibrium.
In the continuum theory of elasticity, the displacement field \( u(r) \) is defined at every point \( r \) in the material. It represents the movement of the atoms in the material from their normal positions. The deformation of the continuum can be specified by the strain tensor, \( \epsilon_{ij} \), which is defined as

\[
\epsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i} \right). \tag{3.1}
\]

The surface force on the continuum is the stress, \( \sigma_{ij} \), defined as the force per unit area. The material is called linear elastic when the strain is proportional to the applied stress, i.e.,

\[
\sigma_{ij} = c_{ijkl} \epsilon_{kl}. \tag{3.2}
\]

The proportional constant, \( c_{ijkl} \), is called elastic modulus of the material. It is a material constant which can be determined from bulk experimental results. Most materials are linear when the deformation is not large.

When the displacement fields are calculated in this chapter, the crystal is also assumed to be infinitely large. The effect of the stress-free surfaces will be considered in the theory of diffraction.

### 3.2.3 Same Elastic Moduli in Ellipsoid and Matrix

**Equation of equilibrium [55]**

In this section, we consider an ellipsoidal inclusion in an infinite matrix. Both the inclusion and matrix have the same elastic constant \( c_{ijkl} \). The ellipsoidal inclusion suffered a stress-free transformation strain \( \epsilon_{ij}^T \). The elastic energy density at an arbitrary point in the medium can be represented as

\[
w(r) = w_0 + \sigma_{ij}^0 \epsilon_{ij} + \frac{1}{2} c_{ijkl} \epsilon_{ij} \epsilon_{kl}, \tag{3.3}
\]

where \( \epsilon_{ij} \) is the strain at the point, \( w_0 \) and \( \sigma_{ij}^0 \) are constants. The stress field is then

\[
\sigma_{ij} = \frac{\partial w}{\partial \epsilon_{ij}} + c_{ijkl} \epsilon_{ij}, \tag{3.4}
\]
or,
\[ \sigma_{ij} = \sigma_{ij}^0 + c_{ijkl} \epsilon_{ij}. \]  
(3.5)

By the definition of the stress-free transformation strain, if the strain is \( \epsilon_{ij}^T \) inside the inclusion and 0 outside of it, the stress field is zero. That is, if
\[ \epsilon_{ij} = \epsilon_{ij}^T \theta(\mathbf{r}), \]  
(3.6)

where \( \theta(\mathbf{r}) \) is defined as
\[ \theta(\mathbf{r}) = \begin{cases} 
1, & \text{if } \mathbf{r} \text{ is inside the inclusion;} \\
0, & \text{if } \mathbf{r} \text{ is outside of the inclusion;} 
\end{cases} \]  
(3.7)

it should have
\[ \sigma_{ij} = \sigma_{ij}^0 + c_{ijkl} \epsilon_{ij}^T \theta(\mathbf{r}) = 0. \]  
(3.8)

This leads to
\[ \sigma_{ij}^0 = -c_{ijkl} \epsilon_{ij}^T \theta(\mathbf{r}). \]  
(3.9)

Substituting this result back to Eq. (3.5), the equilibrium condition \( \frac{\partial \sigma_{ij}}{\partial r_j} = 0 \) gives
\[ -c_{ijkl} \epsilon_{kl} \frac{\partial \theta(\mathbf{r})}{\partial r_j} + c_{ijkl} \frac{\partial \epsilon_{kl}}{\partial r_j} = 0, \]  
(3.10)

or,
\[ c_{ijkl} \frac{\partial^2 u_l(\mathbf{r})}{\partial r_j \partial r_k} = c_{ijkl} \epsilon_{kl} \frac{\partial \theta(\mathbf{r})}{\partial r_j}. \]  
(3.11)

Comparing this with the usual equilibrium equation [56]
\[ c_{ijkl} \frac{\partial \epsilon_{kl}}{\partial r_j} + f_i = 0, \]  
(3.12)

the deformation is equivalent to those caused by force density
\[ f_i(\mathbf{r}) = -c_{ijkl} \epsilon_{kl} \frac{\partial \theta(\mathbf{r})}{\partial r_j}. \]  
(3.13)

This force exists only on the surface of the inclusion due to the behavior of the step function \( \theta(\mathbf{r}) \) at the interface. It corresponds to the surface forces that are applied to relax the system.
in the Eshelby consideration presented in the previous section.

Displacement field in Fourier space

Using Fourier transform

$$f(r) = \int \tilde{f}(k) e^{2\pi i k \cdot r} d^3 k,$$

and

$$\tilde{f}(k) = \int f(r) e^{-2\pi i k \cdot r} d^3 r,$$

Eq. (3.11) can be expressed in the form of Fourier transforms:

$$-4\pi^2 c_{ijkl} k_i k_j \tilde{u}_l(k) = 2\pi i c_{ijkl} \epsilon^{ik}_{jl} k_j \tilde{\theta}(k),$$

where $\tilde{u}_l(k)$ and $\tilde{\theta}(k)$ are Fourier transforms of $u_l(r)$ and $\theta(r)$, respectively, and,

$$\tilde{\theta}(k) = \int \theta(r) e^{-2\pi i k \cdot r} d^3 r = \int e^{-2\pi i k \cdot r} d^3 r,$$

where $V$ stands for the inside of the inclusion. If the vector $k$ is represented as a product of its length and unit vector, i.e.,

$$k = k \hat{k},$$

Eq. (3.16) can be written in the form of

$$\tilde{T}_{il}(k) \tilde{u}_l(k) = -\frac{i}{2\pi} c_{ijmn} T_{mn}^{T_{imn}}(k) \frac{k_j}{k} \tilde{\theta}(k),$$

where

$$\tilde{T}_{il}(k) = c_{ijkl} \hat{k}_j \hat{k}_k.$$  

Therefore, the solution for the Fourier transform of $u_l(r)$, $\tilde{u}_l(k)$, is

$$\tilde{u}_l(k) = -\frac{i}{2\pi} c_{ijmn} T_{mn}^{T_{imn}}(k) \frac{k_j}{k} \tilde{\theta}(k),$$

*Use substitutions $f(r) \rightarrow \tilde{f}(k), \partial/\partial r \rightarrow 2\pi i k.$
where $\tilde{G}_{il}(\hat{k})$ is defined as

$$G_{il}(\hat{k}) = \frac{1}{T_{il}^{-1}(\hat{k})}, \quad (3.22)$$

The function $\tilde{G}_{il}(\hat{k})$ is sometimes called the Green function (in Fourier space). In a cubic crystal, it can be written in close form [57, 37]:

$$G_{ij}(\hat{k}) = \frac{\delta_{ij}}{c_{44} + d \hat{k}_i^2} - \frac{\hat{k}_i \hat{k}_j}{(c_{44} + d \hat{k}_i^2)(c_{44} + d \hat{k}_j^2) \left[ 1 + \sum_{l=1}^{3} (c_{44} + c_{12}) / (c_{44} + d \hat{k}_l^2) \hat{k}_l^2 \right]}, \quad (3.23)$$

where

$$d = c_{11} - c_{12} - 2c_{44}. \quad (3.24)$$

For an ellipsoidal inclusion with semi-axes $a_1$, $a_2$ and $a_3$,

$$\tilde{\theta}(k) = \frac{4\pi}{3} a_1 a_2 a_3 \frac{3(\sin 2\pi R - 2\pi R \cos 2\pi R)}{(2\pi R)^3}, \quad (3.25)$$

in which

$$R = \sqrt{k_1^2 a_1^2 + k_2^2 a_2^2 + k_3^2 a_3^2}, \quad (3.26)$$

with $k_1$, $k_2$ and $k_3$ representing the components of $k$ in the directions of the three semi-axes, respectively.

**Displacement field in real space**

From its Fourier transform,

$$u_i(r) = \int \frac{i}{2\pi} c_{ijmn} \epsilon_{mn}^T \tilde{G}_{il}(\hat{k}) \frac{\hat{k}_i}{k} \tilde{\theta}(k) e^{2\pi i k \cdot r} d^3 k$$

$$= -\frac{1}{4\pi^2} c_{ijmn} \epsilon_{mn}^T \int \tilde{G}_{il}(k) \frac{1}{k^2} \tilde{\theta}(k) \frac{\partial}{\partial r_j} e^{2\pi i k \cdot r} d^3 k$$

$$= -\frac{1}{4\pi^2} c_{ijmn} \epsilon_{mn}^T \int \left\{ \tilde{G}_{il}(\hat{k}) \frac{\partial}{\partial r_j} \left[ \int_0^{\infty} \tilde{\theta}(k) e^{2\pi i k \cdot r} dk \right] \right\} d\Omega_k, \quad (3.27)$$

where $d\Omega_k$ is the differential solid angle in $k$-space, and

$$d^3 k = k^2 dk d\Omega_k. \quad (3.28)$$
The integral inside the square bracket, denoted by \( I(r) \), is

\[
I(r) = \int_{0}^{\infty} \hat{\theta}(k) e^{2\pi i k \cdot r} dk.
\]

\[
= \int_{0}^{\infty} dk \int_{V} e^{-2\pi i k \cdot (r' - r)} d^3 r'.
\]

(3.29)

using Eq. (3.17). Because the displacement is a real function, only the real part on the right hand side in Eq. (3.27) needs to be considered. Exchanging the order of integration in Eq. (3.29) gives

\[
Re[I(r)] = \frac{1}{2} \int_{V} \delta(\hat{k} \cdot r' - \hat{k} \cdot r) d^3 r'.
\]

(3.30)

For an ellipsoidal inclusion with semiaxes \( a_1, a_2 \) and \( a_3 \), the surface of the ellipsoid is defined by

\[
\frac{r_1^2}{a_1^2} + \frac{r_2^2}{a_2^2} + \frac{r_3^2}{a_3^2} = 1,
\]

(3.31)

if the coordinate axes are chosen to be coincided with the three principle axes of the ellipsoid. Use variable substitutions [58]

\[
t_i = \frac{r_i}{a_i}, \quad t_i' = \frac{r_i'}{a_i},
\]

(3.32)

and

\[
s_i = \frac{\hat{k}_i a_i}{\mu},
\]

(3.33)

where

\[
\mu = \sqrt{\hat{k}_1^2 a_1^2 + \hat{k}_2^2 a_2^2 + \hat{k}_3^2 a_3^2},
\]

(3.34)

Equation (3.30) will become

\[
Re[I(t)] = \frac{a_1 a_2 a_3}{2\mu} \int_{\text{unit sphere}} \delta(s \cdot t' - s \cdot t) d^3 t'.
\]

(3.35)

For a particular \( t \), the integration is equal to the area of the portion of the plane \( s \cdot t' - s \cdot t = 0 \) that is inside the surface of the unit sphere in \( t' \)-space. The distance from the origin \( (t' = 0) \) to this plane is \( |s \cdot t| \). When \( |s \cdot t| < 1 \), the area is \( \pi[1 - (s \cdot t)^2] \). When \( |s \cdot t| > 1 \), no intersection of the plane with the sphere is possible; therefore, the integration should be
zero. So
\[
Re[I(t)] = \frac{a_1 a_2 a_3}{2\mu} \pi [1 - (s \cdot t)^2] \Theta[1 - (s \cdot t)^2],
\] (3.36)
where \(\Theta(x)\) is defined by
\[
\Theta(x) = \begin{cases} 
1 & \text{if } x > 0, \\
0 & \text{if } x < 0.
\end{cases}
\] (3.37)
With this result, Eq. (3.27) can be written as
\[
u_i(r) = -\frac{a_1 a_2 a_3}{8\pi} c_{ijmn} \epsilon_{mn} \int \limits_{all \text{ angles}} \tilde{G}_{ii}(\tilde{k}) \frac{1}{\mu} \frac{\partial}{\partial r_j} \left\{ [1 - (s \cdot t)^2] \Theta[1 - (s \cdot t)^2] \right\} d\Omega_k,
\] (3.38)
or, using Eqs. (3.32)–(3.34),
\[
u_i(r) = \frac{a_1 a_2 a_3}{4\pi} c_{ijmn} \epsilon_{mn} \int \limits_{all \text{ angles}} \tilde{G}_{ii}(\tilde{k}) \frac{\tilde{k} \cdot r}{\mu^2} \frac{\partial}{\partial \tilde{k}_j} \Theta \left[ 1 - \left( \frac{\tilde{k} \cdot r}{\mu} \right)^2 \right] d\Omega_k.
\] (3.39)
The final result can be viewed as a two-dimensional surface integration over the surface of a unit sphere in \(k\)-space. Only those regions satisfying the relation
\[
\left| \frac{\tilde{k} \cdot r}{\mu} \right| < 1
\] (3.40)
contribute to the integration. If a Cartesian coordinate system with its three axes coincided with the three axes of the ellipsoid is chosen, and the spherical angles \(\phi\) and \(\theta\) are defined in their common sense, then
\[
\hat{k}_1 = \sin \phi \cos \theta,
\]
\[
\hat{k}_2 = \sin \phi \sin \theta,
\]
\[
\hat{k}_3 = \cos \phi,
\] (3.41)
and
\[
d\Omega_k = \sin \theta d\theta d\phi,
\] (3.42)
and \( \mu \) is given by Eq. (3.34). The result represented in Eq. (3.39) can be further written as

\[
    u_i(r) = \frac{a_1 a_2 a_3}{4\pi} c_{ijmn} T_{mn}^{T} \int_{0}^{2\pi} \left[ \int_{\Theta_i} \hat{G}_{ij}(\hat{k}) \frac{\hat{k}_j \cdot r}{\mu^3} \hat{k}_j \hat{k}_j \hat{k}_j \hat{k}_j \hat{k}_j \hat{k}_j d\hat{k} \right] d\Theta,
\]

(3.43)

where \( \Theta_1 \) and \( \Theta_2 \) are determined by the limits defined by the inequality in Eq. (3.40). The computer code for calculating the displacement is given in Appendix A.1.

**Final strain inside the ellipsoid and dipole tensor**

From Eq. (3.39), the strain inside the ellipsoid at equilibrium can be deduced. When \( r \) is inside of the ellipsoid, \( \left| \frac{\hat{k} \cdot r}{\mu} \right| < 1 \) is always true; so \( \Theta \left[ 1 - \left( \frac{\hat{k} \cdot r}{\mu} \right)^2 \right] = 1 \). The displacement is a linear function of \( r \). Therefore, the final strain inside the ellipsoid is

\[
    \epsilon_{ia} = \frac{a_1 a_2 a_3}{8\pi} c_{ijmn} T_{mn}^{T} \int_{\Theta_i} \hat{G}_{ij}(\hat{k}) \hat{k}_j \hat{k}_j \hat{k}_j \hat{k}_j \hat{k}_j \hat{k}_j d\Omega_k,
\]

(3.44)

a constant of position. This strain defines the equilibrium state of the transformed region. For a precipitate inside a matrix, the apparent (or measured) structure of the precipitate inside the matrix is determined by subjecting the original atomic positions to this final strain, \( \epsilon_{ia} \). From the definition of the stress-free transformation strain \( \epsilon_{ij}^T \), the structure of the precipitate would have been determined by \( \epsilon_{ij}^T \) should there be no restriction imposed by the surrounding matrix. From this analysis, the elastic interaction between the precipitate and the matrix can alter the apparent crystal structure of the precipitate.

The dipole tensor of the ellipsoidal inclusion can also be obtained from the Kanzaki force expression Eq. (3.13). The dipole tensor

\[
    p_{ij} = \int r_i f_j(r) d^3r = c_{ijkl} \epsilon_{kl}^T V_e,
\]

(3.45)

where \( V_e \) is the volume of the ellipsoid. Equation (3.45) actually holds for any shape of inclusions, not just for ellipsoids. The dipole tensor determines the far field behavior of the displacement field caused by the defect.
3.2.4 Different Elastic Moduli in Ellipsoid and Matrix

The analysis used in the last section cannot be directly applied to the situation when the elastic moduli are different in the ellipsoid and the matrix, since the equilibrium equation, Eq. (3.11), will have to be changed and the Fourier method can no longer be used. But, because the final strain inside an ellipsoidal cluster is constant, the solution can be found based upon the uniqueness theorem of elasticity.

Suppose that the elastic modulus is $c'_{ijkl}$ inside the ellipsoidal inclusion and $c_{ijkl}$ inside the matrix. The stress-free transformation strain for the ellipsoid is $\epsilon^T_{ij}$. If a fictitious inclusion with elastic modulus $c_{ijkl}$ and equivalent stress-free transformation strain $\epsilon^T_{ij}$ can be found that produces the stress and strain fields that satisfy the constitutive law of the new problem and the theory of elasticity, the field generated by the fictitious inclusion is the solution in the real situation.

The constitutive relation outside of the ellipsoid is automatically satisfied since the elastic modulus is still $c_{ijkl}$. Inside the inclusion, if the final strain with respect to the matrix is

$$\epsilon^C_{kl} = S_{klmn}\epsilon^T_{mn},$$

(3.46)

where, according to Eq. (3.44),

$$S_{klmn} = \frac{a_1a_2a_3}{8\pi}c_{ijmn}\int_{\text{all angles}} \frac{\tilde{G}_i(k)\tilde{k}_k + \tilde{G}_j(k)\tilde{k}_k k_j}{\mu^3}d\Omega_k,$$

(3.47)

the strain with respect to their equilibrium positions is $\epsilon^C_{kl} - \epsilon^T_{kl}$ for the real problem ($c'_{ijkl}$), and $\epsilon^C_{kl} - \epsilon^T_{kl}$ for the fictitious ellipsoid ($c_{ijkl}$). If the stress induced in these two cases are equal, the requirements outlined in the last paragraph are satisfied. The stress relation can be written as [59]

$$c'_{ijkl}(\epsilon^C_{kl} - \epsilon^T_{kl}) = c_{ijkl}(\epsilon^C_{kl} - \epsilon^T_{kl}),$$

(3.48)

or in a slightly different form,

$$[(c'_{ijkl} - c_{ijkl})S_{klmn} + c_{ijkl}\delta_{km}\delta_{ln}]\epsilon^T_{mn} = c'_{ijkl}\epsilon^T_{kl},$$

(3.49)
There are six independent variables and six independent equations\(^1\) in Eq. (3.49).

Therefore, with a problem of an ellipsoidal inclusion with different elastic modulus from the matrix, the displacement field is found by first obtaining an equivalent stress-free transformation strain \(e_{ij}^T\) from Eq. (3.49); then using it to calculate the field with the method presented in the previous section. Equation (3.49) indicates that the solution will satisfy the constitutive law and the uniqueness theorem of the theory of elasticity guarantees that it is the proper solution.

There is always an equivalent stress-free transformation strain that corresponds to any true transformation strain in a precipitate. The equivalent transformation strain also gives more directly information on the displacement field generated in the matrix, since the calculations from true transformation strains always involve an extra step. For these reasons, in the chapters that follow, we will be primarily using the equivalent transformation strain in our discussions. The equivalent transformation strain is sometimes called directly the transformation strain, without the word "equivalent." The true transformation strain, \(e_{ij}^T\), is always used with the word "true."

3.3 Displacement Field Generated by a Transformed Disk

If the shape of the transformed region in the continuum is a circular disk, often begin referred to in Cu-Be region, most of the derivation in the last section can not be applied. The reason is that the variables defined in Eqs. (3.32) and (3.33) do not lead to any simplifications as in the case of an ellipsoid. The Fourier method for solving for the displacement fields around a transformed disk is therefore inefficient since the Fourier transforms with infinite limits can not be handled numerically in an efficient way.

A better approach is to sum up the effects of the force density, given in Eq. (3.13), in real space. In this case, the displacement field at position \(\mathbf{R}\) caused by a transformed disk is given by [38]

\[
\mathbf{u}_i(\mathbf{R}) = \int G_{ij}(\mathbf{R} - \mathbf{r}) f_j(\mathbf{r}) d^3\mathbf{r}
\]

\(^1\)Because of the symmetry of \(e_{ij}^T\) and \(c_{ijkl}\).
\[ = \int_S G_{ij}(\mathbf{R} - \mathbf{r})c_{mnkl}T_{ij}^Tn_j(\mathbf{r})dS, \tag{3.50} \]

where \( S \) is the surface of the disk, and \( n_j(\mathbf{r}) \) is the outward normal of the surface at position \( \mathbf{r} \) on the surface. The function \( G_{ij}(\mathbf{R}) \) is the elastic Green's function (in real space), which should satisfy the equation [38]

\[
c_{ijkl}\frac{\partial^2 G_{km}(\mathbf{R})}{\partial R_j \partial R_l} + \delta_{im}\delta(R_j) = 0. \tag{3.51} \]

The Green's function can be calculated in a number of ways. A popular method is to perform the following integration over the solid angles in k-space [38]:

\[
G_{ij}(\mathbf{R}) = \frac{1}{8\pi^2 R} \int G_{ij}(k)\delta(k \cdot \hat{R})d\Omega_k, \tag{3.52} \]

where \( R \) and \( \hat{R} \) are the length and unit vector of vector \( \mathbf{R} \), respectively, and \( G_{ij}(k) \) is given in Eq. (3.22).

In performing the integration over the surface of the disk in Eq. (3.50), the surface of the disk is divided into pieces and the integration is approximated by the summation of the effect from all pieces. Because of this, the displacement fields calculated are more accurate for the points far from the disk and less accurate close in, since the granularity is seen more clearly closed in.

The final strain inside the circular disk is not a constant even if the transformation strain for the transformation is. This differs from the cases of ellipsoids, for which the final strain inside the ellipsoid is always constant, provided that the stress-free transformation strain is a constant. This can have significant implication in the diffraction from the precipitates (precipitate peak broadening due to the non-uniform strain), depending on whether the precipitates are in the shape of ellipsoids or disks.

### 3.4 Sample Displacement Fields around Inclusions

In the section, sample displacement fields are calculated and plotted. The effects of the shape, stress-free transformation strain on the displacement fields in a matrix with cubic symmetry both close to and far away from the ellipsoidal and disk inclusions are
Figure 3.2: Equi-displacement contours on (010) plane for an ellipsoidal defect with $a = b = 35\text{Å}$ and $c = 6\text{Å}$, $\epsilon_{11}^T = \epsilon_{22}^T = 0.112$ and $\epsilon_{33}^T = -0.334$. The flat face of the ellipsoid is lying on the (001) plane. All numbers in the figure have a unit of Å.

Figure 3.2 shows the equi-displacement contours of the field generated by an ellipsoid with its face lying on the (001) plane of the crystal. The plane plotted is the (010) plane. The ellipsoid has the parameters of $a = b = 35\text{Å}$, $c = 6\text{Å}$, $\epsilon_{11}^T = \epsilon_{22}^T = 0.112$, $\epsilon_{33}^T = -0.334$, and $\epsilon_{12}^T = \epsilon_{13}^T = \epsilon_{23}^T = 0$. The elastic constants of the matrix are $c_{11} = 1.76$, $c_{12} = 1.34$, and $c_{44} = 0.76$. The labels of the axes and on the contours are all in units of Å.
The displacement field contours far away from the ellipsoid are very similar to those presented in [60], where the displacement field is generated by point defects. This should come with no surprise because when observing from a distance, the ellipsoid becomes equivalently a point defect. The difference in the fields is in the region close to the defects.

Figure 3.3 has the equi-displacement contours generated by the same ellipsoidal defect but on a different plane. This illustrates the elastic anisotropy of the matrix. If the matrix were to be elastically anisotropic \((c_{11} - c_{12} = 2c_{44})\), Figures 3.2 and 3.3 would be identical.
Figure 3.4: Directions of the displacement fields. The arrows show the direction of the displacements on the 0.6Å and 0.15Å equi-displacement contours.
Figure 3.5: Equi-displacement contours on (010) plane for a circular disk
defect with 35Å radius and 8Å thickness, and, $\varepsilon_{11}^T = \varepsilon_{22}^T = 0.112$
and $\varepsilon_{33}^T = -0.334$. The flat disk is lying on the (001) plane.

The directions of the displacement fields on the contours, 0.6Å and 0.15Å as in Figure
3.2, are shown by the arrows in Figure 3.4. The fields far away from the ellipsoid
change directions from contraction to expansion as the angle from the z-axis increases
from 0 to 90°. The fields closer in have very strong [001] components.

Figure 3.5 is the displacement contours for a circular disk with 35Å radius and 8Å
thickness, i.e., it has the same volume as the ellipsoid considered. All other parameters are
Figure 3.6: Equi-displacement contours on (010) plane for an ellipsoidal defect with $a = b = 20\text{Å}$ and $c = 18.375\text{Å}$. Other conditions are the same as those in Figure 3.2.

The contours far away show no difference with those in Figure 3.2. The fields closer in do not get up to as large as those generated by an ellipsoid. This means that the fields generated by a disk with the same lateral dimension as an ellipsoid vary more slowly than the fields generated by the ellipsoidal counterpart. This is easily understandable considering the electrostatic analogy of the field generations.

The effects of changing parameters of the ellipsoidal inclusion on the fields are illus-
Figure 3.7: Equi-displacement contours on (010) plane for an ellipsoidal defect \( \varepsilon_{11}^T = \varepsilon_{22}^T = 0.05 \) and \( \varepsilon_{33}^T = -0.21 \). Other conditions are the same as those in Figure 3.2.
Figure 3.8: Equi-displacement contours on (010) plane for an ellipsoidal defect with $a = b = 45\text{Å}$ and $c = 1.9\text{Å}$, $\epsilon_{11}^T = \epsilon_{22}^T = 0.112$ and $\epsilon_{33}^T = -0.334$. The flat face of the ellipsoid is lying on the (001) plane. All numbers in the figure have a unit of Å.

trated in Figures 3.6 and 3.7. Figure 3.6 shows the effect of a more spherical inclusion. The fields close to the surface of the inclusion are changed significantly; but the far fields almost exhibit no changes. However, the change of the tetragonality of the stress-free transformation strain causes significant changes in the displacement fields both close and far away from the defect, as shown in Figure 3.7.

The figures described above are all for illustration purpose. Figure 3.8 shows the real
fields generated by an ellipsoid whose parameters are used to simulate the diffraction patterns from the sample aged for 15 minutes at 315°C (see Chapter 7).
Chapter 4

Diffuse Scattering from Materials with Textures

X-ray diffuse scattering is an important technique for investigating local atomic arrangements and defects in crystals. Previous quantitative analyses are all based upon single crystals or ideally random powder samples. In reality, most polycrystalline materials have a certain degree of texture or preferred orientation due to sample preparation. Therefore, it is still necessary to develop a quantitative theory to access the importance of texture on the diffuse scattering from these materials. One important kind of diffuse scattering that exists in all materials is the thermal diffuse scattering (TDS). In short range order studies, TDS must be subtracted, as a correction, from the total diffuse scattering before other forms of scattering can be analyzed. Traditionally, TDS is calculated from the eigenvalues and eigenvectors of the equations of lattice dynamics [61], which are cumbersome to compute. In this paper, a simplified method of calculating the TDS is described, based on interatomic force constants and the lattice Green’s function. This procedure recognizes the properties of the lattice Green’s function and eliminates the need of solving the many equations of lattice dynamics. It can be applied to single crystals at or above the Debye characteristic temperature with only one kind of atom. It can also be used approximately for a random mixture of different kinds of atoms using average parameters. As in Debye’s theory, the material is treated as a pure element with average parameters such as an average mass distributed at each lattice point. A calculation of the TDS in a polycrystalline copper beryllium solution having a fiber texture is given using these procedures. Our approach is compared with a random powder calculation using additional simplifying
assumptions [62]. A more general treatment for other kinds of diffuse scattering, using the inverse pole density function [63], is also discussed.

4.1 TDS from Lattice Green’s Function

Based upon the harmonic approximation, the motion of atoms in a crystal is described by a set of normal modes of vibration. The thermal motion of atoms influences the X-ray diffraction pattern in two ways: (i) Bragg reflections are attenuated; and (ii) this loss of intensity produces diffuse scattering that strongly depends upon the position of the diffraction vector relative to the Bragg positions.

In Born-von Karman theory, the interatomic force acting on an atom is given by

$$ F^i = \sum_m \sum_{j=1}^{3} D^{ij}(r_m)u^j, $$

where $D^{ij}(r_m)$ is the interatomic force constant, representing the force component in the direction $i$ ($= 1, 2, 3$) on this atom caused by a unit motion in the $j$ direction of another atom that is $r_m$ away. The summation over $m$ goes over all possible atomic positions in the crystal. Force constants are typically obtained experimentally from neutron scattering. The eigen-frequency $\omega_{gj}$ and eigenvectors $e_{gj}$ for a normal mode designated by wave vector $g$ and polarization $j$ ($j = 1, 2, 3$) can be obtained from the following eigenequations:

$$ \sum_{v=1}^{3} \tilde{D}^{uv}(g)e^u_{gj} = m_a \omega_{gj}^2 e^u_{gj}, \quad u = 1, 2, 3, $$

where $\tilde{D}^{uv}(g)$ is defined by

$$ \tilde{D}^{uv}(g) = -\sum_m D^{uv}(r_m) \cos 2\pi g \cdot r_m, \quad u, v = 1, 2, 3, $$

and $m_a$ is the mass of the atoms. The allowed values of "$g" depend on the boundary conditions of the crystal and are confined to the first Brillouin zone. An explicit form of $\tilde{D}^{uv}(g)$ can be found, for example, in the book by Warren [61] for a FCC crystal using force constants up to the third nearest neighbors.

The diffracted intensity for a crystal, in electron units, with thermal motion having
only one kind of atom at or above the Debye characteristic temperature is given by [61]

\[ I = N f^2 \sum_m \sum_n e^{2\pi i S_\lambda \cdot (r_m - r_n)} \exp \left\{ -\frac{4\pi^2 kT}{Nm a} \sum_g \sum_{j=1}^{3} \frac{\langle S_\lambda : e_{gj} \rangle^2}{\omega_{gj}^2} [1 - \cos 2\pi g \cdot (r_m - r_n)] \right\}, \]

(4.4)

where the summations extend over all possible wave vectors and all atomic positions \( m \) and \( n \). The quantity \( k \) is Boltzman's constant, \( T \) is the absolute temperature, \( N \) is the total number of atoms in the crystal, \( f \) is the atomic scattering factor, \( S_\lambda \) is the diffraction vector given by

\[ S_\lambda = \frac{s - s_0}{\lambda}, \]

(4.5)

where \( s \) and \( s_0 \) are unit vectors in the directions of the diffracted and incident beams, respectively, and \( \lambda \) is the wavelength of the radiation.

Traditionally, the TDS is calculated from Eq. (4.4) by solving Eq. (4.2) to obtain the eigen-frequencies, \( \omega_{gj} \), and eigenvectors, \( e_{gj} \). Because this approach requires considerable computing resources, a simplified procedure is presented utilizing the properties of the lattice Green's function and thereby eliminates the need of solving the eigen-equations. It can be shown that \( 1/m_a \omega_{gj}^2 \) is the eigenvalue of \( \tilde{G}^{uv}(g) \), the inverse matrix of \( \tilde{D}^{uv}(g) \), with the same eigen-vectors, i.e.,

\[ \sum_{u=1}^{3} \tilde{G}^{uv}(g) e_{gj}^u = \frac{1}{m_a \omega_{gj}^2} e_{gj}^u, \quad u = 1, 2, 3. \]

(4.6)

And furthermore, the three polarization vectors \( e_{g1}, e_{g2}, \) and \( e_{g3} \) form an orthonormal set of vectors for every \( g \). Because

\[
\begin{pmatrix}
e_{g1}^1 & e_{g1}^2 & e_{g1}^3 \\
e_{g2}^1 & e_{g2}^2 & e_{g2}^3 \\
e_{g3}^1 & e_{g3}^2 & e_{g3}^3
\end{pmatrix}
\]

is a coordinate transformation matrix from an orthonormal set of vectors to another, and for every \( g \), it must satisfy [56]

\[
\begin{pmatrix}
e_{g1}^1 & e_{g1}^2 & e_{g1}^3 \\
e_{g2}^1 & e_{g2}^2 & e_{g2}^3 \\
e_{g3}^1 & e_{g3}^2 & e_{g3}^3
\end{pmatrix} \begin{pmatrix}
e_{g1}^1 & e_{g1}^2 & e_{g1}^3 \\
e_{g2}^1 & e_{g2}^2 & e_{g2}^3 \\
e_{g3}^1 & e_{g3}^2 & e_{g3}^3
\end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix},
\]

(4.7)
or simply
\[ \sum_{j=1}^{3} e_{g_j}^ue_{g_j}^v = \delta^{uv}, \quad u, v = 1, 2, 3. \] (4.8)

where \( \delta^{uv} \) is 1 when \( u = v \) and 0 when \( u \neq v \). The function \( \tilde{G}^{uv}(g) \) is called the lattice Green's function in Fourier space and is defined by
\[ \sum_{u=1}^{3} \tilde{G}^{uv}(g) \tilde{D}^{uw}(g) = \delta^{uw}, \quad u, w = 1, 2, 3. \] (4.9)

From the properties of the Green's function and its eigen-vectors, the summation over \( j \) in Eq. (4.4) can be evaluated as follows:
\[
\sum_{j=1}^{3} \frac{(S_\lambda \cdot e_{g_j})^2}{m_\alpha \omega_{g_j}^2} = \sum_{j=1}^{3} \sum_{u=1}^{3} \sum_{v=1}^{3} \frac{S_\lambda^u e_{g_j}^u e_{g_j}^v}{m_\alpha \omega_{g_j}^2} = \sum_{j=1}^{3} \sum_{u=1}^{3} \sum_{v=1}^{3} S_\lambda^u \tilde{G}^{uk}(g)e_{g_j}^k S_\lambda^v e_{g_j}^v = \sum_{u=1}^{3} \sum_{v=1}^{3} S_\lambda^u \tilde{G}^{uv}(g)S_\lambda^v,
\]
giving
\[ I = N f^2 \sum_{m} \sum_{n} e^{2\pi i S_\lambda \cdot (r_m - r_n)} \exp\left\{ -\frac{4\pi^2 kT}{N} \sum_{g} \sum_{u=1}^{3} \sum_{v=1}^{3} S_\lambda^u \tilde{G}^{uv}(g)S_\lambda^v [1 - \cos 2\pi g \cdot (r_m - r_n)] \right\}. \] (4.10)

The Green's function in real space is related to \( \tilde{G}^{uv} \) through
\[ G^{uv}(r) = \frac{1}{N} \sum_{g} \tilde{G}^{uv}(g) \cos 2\pi g \cdot r, \quad u, v = 1, 2, 3, \] (4.11)

Substituting Eq. (4.11) into Eq. (4.10) gives
\[ I = N f^2 \sum_{m} \sum_{n} e^{2\pi i S_\lambda \cdot (r_m - r_n)} \exp\left\{ -4\pi^2 kT \sum_{u=1}^{3} \sum_{v=1}^{3} S_\lambda^u S_\lambda^v [G^{uv}(0) - G^{uv}(r_m - r_n)] \right\}. \] (4.12)

Letting
\[ 2M = 4\pi^2 kT \sum_{u=1}^{3} \sum_{v=1}^{3} S_\lambda^u S_\lambda^v G^{uv}(0), \] (4.13)
Eq. (4.12) can be rewritten as

$$I = N f^2 e^{-2M} \sum_m \sum_n e^{2\pi i S_\lambda \cdot (r_m - r_n)} \exp[4\pi^2 kT \sum_{u=1}^{3} \sum_{v=1}^{3} S^u_\lambda S^v_\lambda G^{uv}(r_m - r_n)]. \quad (4.14)$$

The last exponential function is commonly expanded into a power series with the first term giving the Bragg peak attenuated by $e^{-2M}$, while the second term yields the first order TDS,

$$I_1 = N f^2 e^{-2M} 4\pi^2 kT \sum_{u=1}^{3} \sum_{v=1}^{3} S^u_\lambda S^v_\lambda G^{uv}(S_\lambda). \quad (4.15)$$

Subsequent terms of this series give second, third, ..., order TDS, and involve multiple convolutions by summation of $\tilde{G}^{uv}(g)$. Normally their contribution to the total TDS is significantly smaller than that from the first order TDS. The Green's function is found to peak sharply at the Bragg points in reciprocal space so that it can be approximated by a Dirac $\delta$-function at the zone center beyond the first order. This is equivalent to the method suggested by Warren [61] to take into account higher order TDS. This effectively assumes that the shape of the higher order TDS has the same shape as the first order which is a good approximation if $2M$ is small. With this approximation, the total TDS for a single crystal is given by

$$I_{\text{TDS}}(S_\lambda) = N f^2 (1 - e^{-2M}) 4\pi^2 kT \sum_{u=1}^{3} \sum_{v=1}^{3} S^u_\lambda S^v_\lambda \tilde{G}^{uv}(S_\lambda), \quad (4.16)$$

which requires the Green's function and not the eigenvalues and eigenvectors of it. This expression, strictly speaking, can be applied to materials with only one kind of atom. If the material under investigation is a random solid solution of more than one kind of atom, and the interatomic force constants are obtained by fitting a model of "average" atoms, with this set of force constants and an average atomic scattering factor.

### 4.2 TDS for Polycrystalline Materials with Texture

In an actual diffraction experiment with polycrystalline materials, the diffraction vector determined by the instrument, $S_w$, is localized to a small volume in reciprocal space for each diffraction angle, and the reciprocal lattices of the crystallites in the sample take on
all possible orientations. Each crystallite has a set of reciprocal axes \((b_1, b_2 \text{ and } b_3)\) with position in reciprocal space given by

\[
S'_{\lambda} = h_1 b_1 + h_2 b_2 + h_3 b_3. \tag{4.17}
\]

The rotation of each crystallite and therefore its reciprocal axes is relatable to the texture found in the sample. This causes the same \(S_{\lambda}\) to be decomposed into different \((h_1, h_2, h_3)\), all located on the surface of a sphere, for each crystallite. For brevity, \(S'_{\lambda}\) is used in the following discussions. The measured TDS from such a polycrystalline sample is therefore the average of \(I_{TDS}(S'_{\lambda})\) over all orientations weighted by the volume fraction of the sample that scattered at a position in reciprocal space located by the condition \(S_{\lambda} = S'_{\lambda}\). Thus \(S'_{\lambda}\) takes on all orientations while keeping the magnitude constant.

In the case of an ideally random polycrystalline sample, all the reciprocal lattice directions oriented in the direction of \(S_{\lambda}\) have the same probability. The TDS for such a sample is just the integral of \(I_{TDS}(S'_{\lambda})\) over the surface of a sphere, divided by the total solid angle \(4\pi\). However, in a polycrystalline material with a texture, the relative volume fractions of crystallites that have their reciprocal space direction \(S'_{\lambda}\) oriented in a particular sample direction (defined by \(S_{\lambda}\)) is given by the inverse pole density function (or inverse pole figure), \(R(S'_{\lambda})\), of that sample direction [63]. This can deviate greatly from the random case. The measured TDS from a polycrystalline material with a texture can be expressed as

\[
I_{TDS}^{P}(S_{\lambda}) = N f^2 (1 - e^{-2M}) 4\pi^2 kT \int_{\text{orientations}} \frac{1}{4\pi} R(S'_{\lambda}) \sum_{u=1}^{3} \sum_{v=1}^{3} S'^{*}_{\lambda} S^{'*}_{\lambda} u v G^{uv}(S'_{\lambda}) d\Omega_{S'_{\lambda}}, \tag{4.18}
\]

in electron units, where \(d\Omega_{S'_{\lambda}}\) is the differential solid angle of \(S'_{\lambda}\).

Experimentally, the inverse pole density function has been traditionally derived from the measurement of several complete pole figures which are used to obtain the orientation distribution function. This in turn is integrated to obtain the inverse pole density function [63]. He, Rao, and Houska [64] recently developed a simplified method to obtain the orientation distribution function for a polycrystalline material with a true fiber texture or a fiber texture artificially produced by spinning a sample having a more complex texture.
This simplified method applied to a cubic system can be more generally applied to obtain the inverse pole density function for any texture in any crystal system. For the special case of a fiber texture, the inverse pole density function for the fiber axis is equal to the orientation distribution function [63]. In this method, each crystallographic direction, $S'_\lambda$, is characterized by a set of spherical polar angles, $(\Omega, \psi)$. The inverse pole density function is expanded in terms of spherical harmonics according to

$$R(\Omega, \psi) = \sum_{n=0}^{\infty} A_{n0} P_n^0(\cos \Omega) + 2 \sum_{n=1}^{\infty} \sum_{m=0}^{n} \left[ A_{nm} P_n^m(\cos \Omega) \cos m\psi + B_{nm} P_n^m(\cos \Omega) \sin m\psi \right],$$

(4.19)

where $P_n^m(\cos \Omega)$ is the normalized associated Legendre polynomial [65]. If the series is truncated to a finite number of terms related to the finite sharpness of the texture distribution, the coefficients $A_{nm}$ and $B_{nm}$ can be determined from the values of $R(\Omega, \psi)$ at a finite number of reciprocal space points corresponding to the Bragg reflections, with the direction of the diffraction vector, $S_\lambda$, coinciding with the direction for which the inverse pole density function is being constructed. The value of $R(\Omega, \psi)$ at these points can be calculated from the ratio of the experimental to the theoretical integrated intensities for an ideal powder [64]. After the coefficients are determined, the values of the inverse pole density function for all other orientations of $S'_\lambda$ can be evaluated from Eq. (4.19). If the texture is not too severe, Eq. (4.19) may be truncated to a small number of terms and only a few number of Bragg peaks are required.

Figure 4.1 shows the calculated total TDS [normalized by $N f^2(1-e^{-2M})16\pi^2 kT(\sin \theta/\lambda)^2$] for a fiber texture obtained from a copper 11.6 atomic percent beryllium alloy. The sample was water quenched after annealing at 780°C for 15 minutes. The direction of the instrumental diffraction vector coincides with the fiber axis of the texture so the orientation distribution function given by He et al [64] may be used in place of the inverse pole density function. Interatomic force constants were determined from neutron scattering experiments by Koo et al [18]. Only the coefficients up to the third nearest neighbors are used. TDS for an ideally random polycrystalline material but with all other conditions identical is also computed and plotted in Fig. 4.1 for a comparison. The latter curve is essentially the same as the result obtained by Warren [62] who used an approximate method that assumed a linear dispersion relation between $\omega$ and $|g|$. An examination of the maxima
Figure 4.1: TDS from polycrystalline materials with and without texture. The plotted normalized intensity $I'$ is defined as $I_{\text{TDS}} / N \int f^2 (1 - e^{-2M}) 16\pi^2 k T (\sin \theta / \lambda)^2$. The attenuation factor $2M$ is evaluated to be $0.00523T(\sin \theta / \lambda)^2$, where $T$ is in K and $\lambda$ is in Å.
Figure 4.2: Orientation distribution function of the texture used to calculate TDS [64]. The base plane shows the two dimensional contours of the function. A plane at $\omega = 1$ would represent an ideal random powder.
and minima in Fig. 4.2 shows a preferred orientation in the (111) and (100) directions and is non-preferred in the (110) direction. As a result, the TDS for the sample with texture has higher values near the (111) and (200) Bragg reflections and smaller values near the (220) reflection when compared with the scattering from an ideal powder sample.

4.3 Other Diffuse Scattering from Polycrystalline Materials with Texture

The discussion at the beginning of the last section applies not only to the TDS, but also to other forms of diffuse scattering such as short range order scattering. In general, if the diffuse scattering for a single crystal is \( I^S(S'_\lambda) \), the diffuse scattering from the same material in polycrystalline form with a texture is given by

\[
I^P(S_\lambda) = \int_{all\,\text{orientations}} \frac{1}{4\pi} R(S'_\lambda) I^S(S'_\lambda) d\Omega_{S'_\lambda},
\]

(4.20)

where \( R(S'_\lambda) \) is the inverse pole density function, of the texture, for the sample direction that coincides with the diffraction vector, \( S_\lambda \). If the single crystal diffuse scattering depends strongly on the direction of the diffraction vector with a fixed magnitude, like the TDS which peaks sharply in the region close to the Bragg reflections, the intensity from the polycrystalline sample with a texture will differ considerably from an ideally random powder. This is shown in Fig. 4.1 in regions close to the Bragg reflections. On the contrary, if the diffuse scattering is not a strong function of scattering direction like short range order scattering, the resulting intensity from materials with a texture will be similar to that from an ideal powder. Of course, this must be treated with some caution. If the texture of the material is very strong, even a small variation of the scattering with respect to the diffraction direction can lead to a very different diffraction pattern compared with the ideally random one. The example can be considered as having an intermediate texture.
4.4 Discussions

In this chapter, a simplified method for calculating the TDS from single crystals using interatomic force constants is described. This method is based upon the lattice Green's function and does not require the extensive computing required to solve the eigen-equations from lattice dynamics. Only the expressions of the lattice dynamics matrix and its inverse, the Green's function, are needed. The treatment should only be applied with sample temperatures that are comparable or higher than the Debye characteristic temperature so that equipartition of the thermal energy for the individual normal modes is applicable.

The diffuse scattering from polycrystalline materials with a texture can be calculated from the diffuse intensities from single crystals and the inverse pole density function. A TDS calculation for a copper beryllium solid solution with an intermediate fiber texture has shown a significant difference when compared with that from an ideal powder. In general, the difference between the diffuse scattering from a textured sample and those from an ideal powder depends upon both the severeness of the texture and the directional dependency of the diffuse scattering. The discrepancy will normally become more evident when the texture is strong and when the directional dependency of the scattering is high.
Chapter 5

HDS Analysis on Scattering from Cu-Be Alloys during Very Early Stage of Aging

Low temperature aging of supersaturated Cu-Be (with 1–2 wt.% of Be) solid solutions produces Be-rich precipitates in the Be-depleted matrix. During the early stage of aging, it is observed, from the diffraction patterns, that the precipitates are disk shaped GP zones with habit plane being \{100\} planes of the matrix. The interface between the zones and the matrix is believed to be coherent. Due to the small sizes of the precipitates in the early stage, the direct scattering from these precipitates themselves are very diffuse and extremely difficult to be resolved from the background. But because of the large size difference between Cu and Be atoms and the coherent interface, the existence of the precipitates produces large atomic displacements in the surrounding matrix. The distortion leads to special diffuse scattering patterns near Bragg reflections, as observed experimentally in X-ray oscillation photographs [9], electron diffractions [6], and X-ray diffraction from single crystals [19]. The origin of these diffraction effects and their implication on the structure of the GP zones has been the subject of several investigations [9, 6, 66, 67, 22]. But none of these can explain all observed experimental facts satisfactorily. The special diffuse scattering patterns were attributed to the elastic anisotropy of the copper matrix and the disk like shape of the GP zones [6]. But it has been reported that these effects are observable before the disk shaped GP zones are formed [68, 22]. There are theories that proposed that tetragonal distortions in the matrix could generate these special diffuse
scattering patterns [66, 22, 69, 70]. But the ability to observe the effect under the disk shaped GP zones was questioned [66, 22].

In this chapter, we first briefly review the experimental observation and existing theories of the diffuse scattering near Bragg reflection from aged Cu-Be alloys. The shortcomings of the theories are discussed. We then use the theory of Dederichs [37] on Huang diffuse scattering and show that the existence of a tetragonal transformation strain in the precipitates, rather than the anisotropy of the matrix, is the necessary condition for the special diffuse scattering effects. We will also show through a simulation of the scattering intensity that the effect is observable under the conditions of disk shaped precipitates. The implication of the existence of the tetragonal crystal structure of the precipitates at the early stage of aging is discussed concerning the phase separation sequence of the Cu-Be alloys.

5.1 Summary of Experimental Evidence and Existing Theories

During early stage of aging, the diffuse scattering from Cu-Be alloys concentrates in certain directions around Bragg reflections. Apart from the long and weak streaks in <100> directions due to the disk-like shape of the precipitates, there are intense but short scattering stubs being referred to as <110> streaks. The diffuse intensities show different shapes near different reflections. The scattering near <111> is concentrated on the reciprocal lattice plane that passes through the <111> spot and is perpendicular to [111] direction. There is almost no scattering in the [111] direction. Around the <220> spot, diffuse streak is found only in the [110] direction and not the [110]. Whereas near <200> reflection, both [110] and [110] streaks are observed. The streaks intensified with aging in the early stages. Figures 1.2 and 1.3 summarize schematically the observed and absent diffuse streaks near the Bragg reflections on (100) and (011) reciprocal space planes, respectively.

Tyapkin [9] first noted the existence of <110> diffuse streaks from X-ray oscillation photographs from a Cu-Be alloy. He suggested that these streaks could be caused by monoclinic {110}(110) shear strains in the matrix. But the origin of the shear strains was not clearly identified. Tanner [6] reproduced these streaks using electron diffraction and proposed that the shear strains were due to the presence of the disk shaped precipitates (GP zones) in a highly elastically anisotropic copper matrix. The {100} precipitates are
approximated by prismatic dislocation loops with Burger’s vectors in the \( \langle 100 \rangle \) directions. Because of the elastic anisotropy of the copper matrix, it is energetically more favorable for each loop to dissociate into two dislocation loops with Burger’s vector \( \frac{2}{3} \langle 110 \rangle \). Based upon the directions of the Burger’s vectors and the diffraction vectors, the missing streaks near several Bragg reflections were explained. In this theory the high elastic anisotropy was essential. Contrast was made with similar GP zones in Al-4% Cu alloy. The lack of \( \langle 110 \rangle \) streaks in these alloys was attributed to the nearly elastic isotropy of the aluminum matrix. This explanation is subjected to challenge in at least two aspects: (1) the equivalency of GP zones and dislocation loops is not well understood; and (2) the diffraction effect of the dissociated dislocation loops should depend on the fields they created rather than the directions of their Burger’s vectors. It was shown that the directions of the displacement fields can be very different from the direction of the Burger’s vector of the dislocation loop [57]. Also, \( \langle 110 \rangle \) streaks are reported to be observed before the \( \langle 100 \rangle \) streaks can be seen [68, 22]. This suggests that the disk-like shape of the GP zones is not the main cause of the \( \langle 110 \rangle \) streaks.

More recently, it is pointed out by several authors that tetragonal distortions could lead to \( \langle 110 \rangle \) streaks near selected Bragg reflections [66, 67, 22], using the analysis of Huang scattering due to long range elastic distortion from the defects. But for Cu-Be alloys this is not widely accepted. The authors argued that because of the disk like shape of the GP zones, the Huang scattering generated by the distortion of the GP zones would be confined to the \( \langle 100 \rangle \) directions and could not be the cause of the \( \langle 110 \rangle \) streaks observed. Instead, some other sources like some domain structures were proposed to account for the latter streaks. But so far no experimental evidence has indicated the existence of such alternate sources.

An detailed analysis of the Huang scattering near major Bragg reflections based upon an elastic model of the precipitates is presented next. It shows that a tetragonal transformation strain in the precipitates is necessary and sufficient for the observed \( \langle 110 \rangle \) streaks.

5.2 Huang Scattering Analysis from Matrix Containing Precipitates

In this analysis, the elastic model presented in Chapter 3 is used for the precipitates. For a precipitate that suffered a stress-free transformation strain \( \epsilon^T_{ij} \), the Fourier transformation
of the displacement field is given by Eq. (3.21) with \( \tilde{\theta}(k) \) defined in Eq. (3.17).

### 5.2.1 HDS Evaluated from Equivalent Point Defects

The diffuse scattering near the Bragg reflections from crystals containing small concentration of defects has been studied extensively by Krivoglaz [39], Dederichs [45, 37], Trinkaus [35]. The formalism presented in [37] is used in the following analysis. In regions very close to the Bragg reflections, Huang diffuse scattering accounts for most of the diffuse intensity. For a crystal with small defect concentration \( c \), and all the defects are identical and randomly arranged, the Huang intensity at a reciprocal space point \( \mathbf{H} \) that is very close to a reciprocal lattice vector \( \mathbf{H}^0 \) is given by [37]

\[
S_{\text{Huang}}(\mathbf{H}) = 4\pi^2 cN |f|^2 |\mathbf{H}^0 \cdot \mathbf{u}(k)|^2,
\]

where \( N \) is the total number of atoms in the crystal, \( f \) is the atomic scattering factor, \( k \) is the vector from the nearest reciprocal lattice point to \( \mathbf{H} \), i.e., \( \mathbf{H} = \mathbf{H}^0 + \mathbf{k} \), and \( \mathbf{u}(k) \) is the Fourier transform of the displacement field produced by a defect. Substituting the result of Eq. (3.21), the Huang intensity becomes

\[
S_{\text{Huang}}(\mathbf{H}) = cN |f|^2 |\mathbf{H}^0_i c_{ijmn} \varepsilon_{mn}^T \tilde{\mathbf{G}}_{ii}(\mathbf{k}) \frac{k^i}{k} \tilde{\theta}(k)|^2.
\]

Notice that the only term in Eq. (5.2) that depends on the shape and size of the defects is \( \tilde{\theta}(k) \). The HDS intensity for a crystal containing certain shape of defects is equal to the HDS intensity for a crystal containing infinitesimally small point defects with the same strength [37] modulated by the shape factor \( |\tilde{\theta}(k)|^2 \). In this section, for the sake of using an analytical form, we neglect the shape factor of the defects, i.e., the Huang intensities are calculated from random distribution of point defects with the same strength with the precipitates. In next subsection, the shape factor of the GP zones will be taken into account. It will be shown through a computer simulation that the shape factor will not change the characteristics of the HDS so the conclusion obtained in the section still holds.

In a crystal with cubic symmetry, precipitates have equal opportunities orienting in three equivalent cubic directions. Averaging these equivalent orientations and neglecting
\( \theta(r) \) in Eq. (5.2), Huang scattering due to the defects is [37]

\[
S_{\text{Huang}}(H) = cN|f|^2 \left( \frac{H_0}{k} \right)^2 \left( \gamma^{(1)}(\hat{k})\Pi^{(1)} + \gamma^{(2)}(\hat{k})\Pi^{(2)} + \gamma^{(3)}(\hat{k})\Pi^{(3)} \right),
\]

(5.3)

where \( \hat{k} \) is the unit vector in the direction of \( k \), \( k \) is the magnitude of \( k \), and the coefficients \( \gamma^{(i)} \)'s are related to the elastic property of the crystal and the location in reciprocal space through [37]

\[
\gamma^{(1)}(\hat{k}) = \frac{1}{3} \left( T_{11} + T_{22} + T_{33} \right)^2,
\]

\[
\gamma^{(2)}(\hat{k}) = \frac{1}{3} \left\{ \left( T_{11} - T_{22} \right)^2 + \left( T_{22} - T_{33} \right)^2 + \left( T_{33} - T_{11} \right)^2 \right\},
\]

\[
\gamma^{(3)}(\hat{k}) = \frac{1}{2} \left\{ \left( T_{12} + T_{21} \right)^2 + \left( T_{23} + T_{32} \right)^2 + \left( T_{13} + T_{31} \right)^2 \right\},
\]

(5.4)

with

\[
T_{ij} = \hat{H}_{i}^0 \hat{G}_{ii}(\hat{k}) \hat{k}_{j},
\]

(5.5)

where \( \hat{G}_{ii}(\hat{k}) \) is the Green's function in Fourier space as defined in Chapter 3. The parameters \( \Pi^{(i)} \) in Eq. (5.3) are related to the components of the transformation strain by

\[
\Pi^{(1)} = \frac{1}{3} \left( \sigma_{11}^T + \sigma_{22}^T + \sigma_{33}^T \right)^2,
\]

\[
\Pi^{(2)} = \frac{1}{6} \left\{ \left( \sigma_{11}^T - \sigma_{22}^T \right)^2 + \left( \sigma_{22}^T - \sigma_{33}^T \right)^2 + \left( \sigma_{33}^T - \sigma_{11}^T \right)^2 \right\},
\]

\[
\Pi^{(3)} = \frac{2}{3} \left( \sigma_{12}^T \sigma_{23}^T \sigma_{31}^T \right).
\]

(5.6)

where \( \sigma_{ij}^T \) is defined as

\[
\sigma_{ij}^T = c_{ijkl} \epsilon_{kl}^T.
\]

(5.7)

For \( c_{ijkl} \) with cubic symmetry, it is immediately apparent that \( \Pi^{(1)} \) is related to the sum of the diagonal components of the transformation strain (i.e., the volume change), \( \Pi^{(2)} \) is a measure of the tetragonality of the transformation strain, and \( \Pi^{(3)} \) is determined by the shear components of it.

Table 5.1 gives the calculated \( \gamma^{(i)} \)'s for a pure copper matrix as well as whether diffuse streak is observed experimentally in aged Cu-Be alloys in that particular direction near
Table 5.1: $\gamma^{(i)}$ coefficients for pure copper matrix for selected directions near (111), (200) and (220) reciprocal lattice points. Parameters used are $c_{11} = 1.70 \times 10^{11} \text{N/m}^2$, $c_{12} = 1.225 \times 10^{11} \text{N/m}^2$. $c_{44} = 0.758 \times 10^{11} \text{N/m}^2$. The $\gamma^{(i)}$s are in the unit of $10^{-22} \text{m}^4/\text{N}^2$.

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Table 5.2: $\gamma^{(1)}$ coefficients for aluminum matrix: $c_{11} = 1.056 \times 10^{11} N/m^2$,
$c_{12} = 0.639 \times 10^{11} N/m^2$, $c_{44} = 0.285 \times 10^{11} N/m^2$. The coefficients
are again in the unit of $10^{-22} m^4/N^2$.

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<td>4.104</td>
</tr>
<tr>
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<td>0.087</td>
<td>2.312</td>
</tr>
<tr>
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<td>1 0 0</td>
<td>0.000</td>
<td>7.668</td>
<td>2.052</td>
</tr>
<tr>
<td>1 1 1</td>
<td>1 0 0</td>
<td>0.000</td>
<td>7.668</td>
<td>2.052</td>
</tr>
<tr>
<td>1 1 1</td>
<td>0 1 1</td>
<td>0.000</td>
<td>7.668</td>
<td>2.052</td>
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<td>1 1 1</td>
<td>0.249</td>
<td>0.000</td>
<td>0.497</td>
</tr>
</tbody>
</table>

that particular Bragg reflection. It can be seen that for all the directions that have strong
streaking, the coefficients $\gamma^{(2)}$ are large compared with those for other directions, while
$\gamma^{(1)}$ and $\gamma^{(3)}$ do not exhibit this property. Therefore, the strong anisotropy of scattering
distributions has to be caused by the term $\gamma^{(2)}\Pi^{(2)}$ in Eq. (5.3). The existence of tetragonality
in the transformation strain is essential for the streaking effects observed. One other
important information that can be derived from Table 5.1 is that due to the lack of intensity
in [010] direction compared with [100] direction near (200) reflection, the shear components
of the transformation must be very small or vanished.

But are the large $\gamma^{(2)}$ coefficients due to the anisotropy of the copper matrix? The answer
is no when the $\gamma^{(i)}$ coefficients for the aluminum matrix listed in Table 5.2 are examined. Aluminum is nearly elastically isotropic. The $\gamma^{(2)}$ coefficients for the directions in which the streaks are observed are still much larger than those of the rest of the directions. The HDS intensities would still be concentrated in these (110) directions should there be a large enough tetragonality in the dipole tensor associated with the precipitates in Al matrix. It is clear, therefore, from these values of the $\gamma^{(i)}$ coefficients that the strong streaking in selected (110) directions in the alloys should be attributed to the existence of tetragonal distortions exerted by the defects in these alloys. The elastic anisotropy is not necessary for the streaks to occur. The anisotropy, however, does increase the ratio between the coefficients of the directions with and without streaks, as can be seen by comparing Table 5.1 and 5.2. The implication of this as well as other factors that influence the observability of the (110) streaks will be considered in more detail in Section 5.3.

5.2.2 Simulation of HDS with the Shape Factor of GP Zones

In this section, a computer simulation taking into account the disk-like shape of GP zones will show that tetragonally transformed GP zones can produce observable Huang intensity streaks in the directions where streaks are observed experimentally.

The GP zones in aged Cu-Be alloys are taken to be of the shape of squashed ellipsoids of revolution with semi-axes $a_1$, $a_2 (=a_1)$ and $a_3$. These ellipsoids are lying in the (100) planes of the matrix because of minimum elastic energy requirements. The function $\theta(k)$ defined in Eq. (3.17) in this case is given in Eq. (3.25). The HDS produced by a crystal containing $cN$ number of this kind of defects can be obtained by substituting Eq. (3.25) into Eq. (5.2). If the ellipsoids are assumed to have equal probability to be on one of the three equivalent (100) planes, the total HDS intensity will be the arithmetic average of the three cases.

Figures 5.1, 5.2, and 5.3 are computer generated images of HDS intensity near Bragg reflections (111), (200), and (220), respectively. The parameters used to calculated these images are the size of the GP zones: $a_1 = a_2 = 25 \AA$, $a_3 = 1.725 \AA$; the transformation strain: $\epsilon_{T1}^E = \epsilon_{T2}^E = 0.12$, $\epsilon_{T3}^E = -0.373$, $\epsilon_{T2}^F = \epsilon_{T3}^F = c_{T3}^F = 0$; the elastic constants of the matrix of pure copper as given in the caption of Table 5.1. In the pictures, the brightness is made directly proportional to the calculated HDS intensities. Figures 5.1(a), 5.2(a), and 5.3(a) are
Figure 5.1: Simulated Huang scattering near (111) Bragg reflection on (1\bar{1}0) reciprocal space plane passing through the origin.
Figure 5.2: Simulated Huang scattering near (200) Bragg reflection on (001) reciprocal space plane passing through the origin.
Figure 5.3: Simulated Huang scattering near (220) Bragg reflection on (001) reciprocal space plane passing through the origin.
to emulate a high contrast and low intensity condition. Figures 5.1(b), 5.2(b), and 5.3(b) are produced under high intensity conditions and the regions in the center of the images are over exposed. The latter figures are also 2:1 zoomed-out versions of the former, with the directions unchanged. Figure 5.1 shows the HDS intensities on the (110) plane around (111) spot in the reciprocal space. Directions are marked on the figure. It is clear that the diffuse intensities are mostly perpendicular to the diffraction vector [111], as reveal in Ref. [6]. Higher intensity in Figure 5.1(b) reveals the long diffuse streaks observed in Selected Area Diffraction Patterns (SADP) on this plane as observed in Ref. [13]. Figures 5.2 and 5.3 show diffuse intensities on (001) reciprocal lattice plane, around (200) and (220) spots, respectively. Both [110] and [110] streaks are obtained near (200) spot, and only [110] streak is shown near (220), which is exactly what is observed experimentally [9, 6, 19]. The high intensity images show (100) streaks that are observed in all TEM SADP observations. The missing [010] streak near (200) spot is not clear in most of the SADP’s because most of the time the long streak from (220) goes into the (200) spot. But this is shown clearly in single crystal X-ray diffraction pattern [19]. The visible (110) streaks in these pictures extend to 1/10–2/10 of the reciprocal spacing and correspond approximately to available experimental pictures (see, for example, Ref. [6]).

5.3 Discussions

In last section, it is shown that in a crystal containing disk shaped GP zones, the tetragonal transformation strain in the precipitates is a necessary and sufficient condition to account for the observed ⟨110⟩ streaks in the diffraction patterns of aged Cu-Be alloys during the early stage of aging. Quantitatively, from Eq. (5.2), the HDS is proportional to the concentration of the defects and to the square of the volume of a defect, since $\tilde{\theta}(k)$ is directly proportional to the volume of a defect (see Eq. (3.25)). In the cases for which no solute atoms are coming in from the matrix and the large precipitates are growing at the expense of the small ones, the product of the concentration and the volume of one defect is the total volume fraction of the defect atoms in the crystal, which is a constant. The net result is that the HDS is proportional to the volume of one individual defect. During the early stages, solute atoms still come in to the precipitates from the matrix, the HDS
is expected to increase faster than the volume of a defect. Because the volume of the precipitate increases with aging, this explains the fact that the diffuse streaks intensify as the aging process goes on, observed by every diffraction experiments [6, 13]. This trend continues until the HDS is no longer important in the total diffraction intensities (See Chapter 6).

As to the observation of (110) diffuse streaks before the formation of (100) disk shaped GP zones during very early stage of aging at very low temperatures, they could be caused by the equi-axial precipitates observed in Ref. [15] under similar conditions. As long as the spherical zones have a tetragonal transformation strain, they can produce tetragonal distortion in the matrix regardless of their shapes. The Huang diffuse scattering effect from these long range strain in the matrix will result in the observed (110) streaks.

The existence of the tetragonal transformation strain in precipitates indicates that the structure of the precipitates is different from that of the matrix. This contradicts the common belief that the transformation at the early stage is isostructural [21]. However, the claim of isostructural transformation does not have substantial experimental support. Because of the small size of the precipitates, the lattice parameters of the precipitates can not be measured from usual Bragg reflection techniques. Even if the lattice parameters are measured for these precipitates, the parameters do not necessary represent the true crystal structure of them, since the coherent elastic interaction between the precipitate and the matrix can distorted the atomic spacing in the precipitate.

The origin of this proposed tetragonally transformed crystal structure for the precipitates during the early stage of aging can be traced into the equilibrium phase of the phase separation. From the equilibrium phase diagram of the Cu-Be alloys, the decomposition of the supersaturated solid solution should lead to two equilibrium phases, a Cu-rich α phase of fcc structure, and a γ phase of B2 (ordered bcc) structure. While the fcc structure can be viewed as a bct, it is necessary to have a tetragonal distortion to the unit cell to make it into a B2 unit cell, similar to that of Bain distortion (See Figure 5.4). If the precipitates observed in the early stage of aging are a “metastable” phase en route to the equilibrium γ phase, it is reasonable for them to have a tetragonal transformation strain with respect to the fcc Cu-rich matrix. It was recently reported by Khachaturyan and Lauglin [21] that γ" and γ' could be identified as matrix constrained γ. Our result, combined with this
Figure 5.4: Illustration of transformation from fcc to B2 (or bcc) structures. The upper figure shows two adjacent fcc unit cells, from which a body center tetragonal cell can be realized. A tetragonal distortion in the vertical direction is necessary to transform this bct cell to B2 (when ordered) or bcc (when disordered) structures.
theory, suggests that the "metastable" phases in the entire phase separation processes are actually matrix constrained \( \gamma \) phase. The elastic distortion from the interaction between precipitates and the matrix made them appeared as different phases.

Based on the same reasoning, the similar \{100\} Cu-rich zones in Al-4\% Cu should possess a tetragonal transformation strain. Yet \{110\} diffuse streaks are not observed in the diffraction patterns from these alloys [6]. This can be explained from a quantitative point of view. As can be seen from the analysis above, the intensity of the Huang diffuse scattering (relative to the Bragg intensity) is proportional to the volume fraction of the defect atoms in the crystal if the volume of individual defects are approximately the same. The volume fraction of Be atoms in the Cu-Be alloys from which the \{110\} streaks are observed is ranged from 12–20\%, while the Al-4 wt. \%Cu alloy have only about 4\% of defects. The small figure for the Al-Cu alloy can cause the diffuse scattering near the Bragg reflections to be unobservable with the strong Bragg intensity nearby. The elastic isotropy of the aluminum matrix further reduces the directional contrast of the diffuse scattering, as shown in Table 5.2.

In summary, the analysis of the Huang diffuse scattering near the Bragg reflections from tetragonally transformed precipitates satisfactorily explains the directional streaking effects in the experimentally observed diffraction patterns. It must be noted that when calculating the diffuse scattering, this paper takes into account only the Huang scattering contribution. Other scattering components, such as Stokes-Wilson scattering, quasilines, and also the Bragg peak intensities are not included. Therefore, quantitative agreement between experimental data and the analysis presented in this chapter should not be expected.
Chapter 6

X-ray Diffraction from Severely Distorted Lattices

As aging proceeds, the precipitates continue to grow. At certain stage, the matrix surrounding the precipitates will become very distorted and the assumptions used in arriving at the theory presented in Chapter 5 are no longer valid [45, 40, 39, 41, 48]. When the distortion in the lattice becomes extremely large, the diffraction pattern near the Bragg reflections changes significantly compared with the situations when the distortion is small. The Bragg peaks become practically vanished. The diffuse scattering forms a broad peak, referred to in the literature as the “quasiline,” with the maximum shifted from the original Bragg position [39, 45]. However, the previous developments have been dealing only with very restricted assumptions, like extreme distortions, isotropic crystals, point defects, etc. In this chapter, the theory is extended to more general situations and quantitatively apply the theory to Cu-Be alloys in the intermediate stage of aging.

6.1 X-ray Diffraction Theory

In this section, a general theory on the x-ray diffraction from crystals containing precipitates is developed. The precipitates have different scattering power from the matrix atoms and produce distortion in the surrounding lattices. Our theory essentially follows that of Krivoglaz [39], except that we take the free surface effect (image field) explicitly into account, using the idea of Dederichs [45]. The difference between our theory and Dederichs’ is that the scattering of precipitates is included in the discussion.

Supposed the atoms in an ideal crystal (no defects) are at positions $R_m$, where $m$
identifies the individual atoms. When defects are introduced into the crystal, the atom at position \( m \) is displaced from its original position by \( r_m \) and the scattering factor of the atom is now \( f_m \), which may or may not be the same with original one. The diffraction intensity from such a crystal is then

\[
I_T(\mathbf{H}) = \sum_{m,n} f_m f_n e^{2\pi i \mathbf{H} \cdot (\mathbf{R}_m - \mathbf{R}_n)} e^{2\pi i \mathbf{H} \cdot (\mathbf{r}_m - \mathbf{r}_n)},
\]

where \( \mathbf{H} \) is the reciprocal space vector and the summations for \( m \) and \( n \) go over all atoms in the crystal.

The displacement at position \( m \) can be evaluated as the sum of the displacements caused by all defects. If the defect configuration in the crystal is represented by a set of coefficients \( c_t \), which takes on the value of 1 if a defect is present at position \( t \) and is 0 when no defect is at \( t \), the total displacement at position \( m \) is

\[
r_m = \sum_t c_t u_{t,m},
\]

where \( u_{t,m} \) is the displacement at position \( m \) caused by a defect at position \( t \). It in general contains two contributions. One is the "real" displacement field generated by the defect as if it were in an infinite medium. The other is the so-called "image" field that is caused by the free surface of the crystal. Physically, the free surface of the crystal is supposed to be stress free. The "real" field itself will violate this boundary condition. The image field has to be introduced to cancel out the "real" field at the surface. The "real" field at distance far away from the defect is \( \sim \Delta V / R^2 \), where \( \Delta V \) is the volume difference between the defect and the original atom, and \( R \) is the distance from the defect. So the magnitude of the image field is about \( \sim \Delta V / R_{\text{cryst}}^2 \), where \( R_{\text{cryst}} \) is the dimension of the crystal [45]. The "real" displacement field depends only on the relative positions of the defect and the point of interest. But the "image" field is a function of the absolute positions of both in the crystal. The image field is in general a slow varying function.

The scattering factor \( f_m \) can also be expressed as a function of \( c_t \). If a function \( \Delta f_{t,m} \) is defined as

\[
\Delta f_{t,m} = \begin{cases} 
  f_p - f, & \text{if } \mathbf{R}_m - \mathbf{R}_t \text{ is in the precipitate,} \\
  0, & \text{otherwise;}
\end{cases}
\]

90
where $f_p$ is the scattering factor of the atoms in precipitates and $f$ is the scattering factor for the original atoms, the scattering factor of an atom at an arbitrary position is

$$f_m = f + \sum_t c_t \Delta f_{t,m}.$$  \hspace{1cm} (6.4)

The function $\Delta f_{t,m}$ is only a function of relative positions of $t$ and $m$.

The total intensity can be conveniently separated into two parts, Bragg diffraction

$$I_B = \sum_{m,n} e^{i2\pi H \cdot (R_m - R_n)} \left\langle f_m e^{i2\pi H \cdot r_m} \right\rangle \left\langle f_n e^{-i2\pi H \cdot r_n} \right\rangle,$$  \hspace{1cm} (6.5)

and diffuse scattering

$$I_D = \sum_{m,n} e^{i2\pi H \cdot (R_m - R_n)} \left[ \left\langle f_m f_n e^{i2\pi H \cdot (r_m - r_n)} \right\rangle - \left\langle f_m e^{i2\pi H \cdot r_m} \right\rangle \left\langle f_n e^{-i2\pi H \cdot r_n} \right\rangle \right],$$  \hspace{1cm} (6.6)

where the symbol $\langle \cdots \rangle$ stands for the average over all possible defect configurations. The Bragg diffraction deals with the uncorrelated displacements and will become $\delta$-functions if the crystal is infinitely large. The diffuse scattering does not contain $\delta$-like peaks.

### 6.1.1 Bragg Diffraction

Let's first examine the Bragg diffraction and the term $\left\langle f_m e^{i2\pi H \cdot r_m} \right\rangle$ in Eq. (6.5). By substituting Eqs. (6.2) and (6.4) into the expression, it becomes

$$\left\langle f_m e^{i2\pi H \cdot r_m} \right\rangle = \left\langle \left( f + \sum_t c_t \Delta f_{t,m} \right) e^{i2\pi H \cdot \sum s \Delta c_{s,t} u_s r_m} \right\rangle$$

$$= \left\langle f \prod_t e^{i2\pi c_t H \cdot u_t r_m} + \sum_t c_t \Delta f_{t,m} \prod_s e^{i2\pi c_s H \cdot u_s r_m} \right\rangle,$$  \hspace{1cm} (6.7)

where $\sum_t$ stands for summation over all possible defect positions, and $\prod_t$ means multiplication over all possible defect positions. Assuming that the defects are randomly and independently distributed in the lattice and have a concentration $c$, every $c_t$ has a probability $c$ of being 1 and a probability of $(1 - c)$ of being 0. The average of an arbitrary function
\( f_1(c_i)f_2(c_j) \), where \( i \neq j \), is

\[
\langle f_1(c_i)f_2(c_j) \rangle = \langle f_1(c_i) \rangle \langle f_2(c_j) \rangle \\
= (c f_1^{(d)} + 1 - c f_1^{(0)})(c f_2^{(d)} + 1 - c f_2^{(0)}),
\]  

(6.8)

where, for \( l = 1,2 \), \( f_i^{(d)} \) is the value of the function \( f_i \) with a defect present at position \( t \), whereas \( f_i^{(0)} \) is the value of the function with no defect at position \( t \). Because on this formula, the expression on the right hand side of Eq. (6.7) becomes

\[
f \prod_t (ce^{i2\pi H \cdot u_{t,m}} + 1 - c) + \sum_t \left[ (c \Delta f_{t,m} e^{i2\pi H \cdot u_{t,m}}) \prod_{s \neq t} (ce^{i2\pi H \cdot u_{s,m}} + 1 - c) \right].
\]  

(6.9)

Following the derivation of Krivoglaz [39], the following product in Eq. (6.9) can be written as

\[
\prod_t (ce^{i2\pi H \cdot u_{t,m}} + 1 - c) = e^{\sum_t \ln \left[ 1 + c \left( e^{i2\pi H \cdot u_{t,m}} - 1 \right) \right]},
\]

\[
\simeq e^{c \sum_t \left( e^{i2\pi H \cdot u_{t,m}} - 1 \right)},
\]

(6.10)

when \( c \ll 1 \), since

\[
\ln(1 + x) \approx x, \quad \text{when} \quad x \ll 1.
\]

Substitute Eq. (6.10) back into Eq. (6.9) and keep only to \( c \)'s first power, we have

\[
\langle f_m e^{i2\pi H \cdot x_m} \rangle = \left( f + c \sum_s \Delta f_{s,m} e^{i2\pi H \cdot u_{s,m}} \right) e^{c \sum_t \left( e^{i2\pi H \cdot u_{t,m}} - 1 \right)}.
\]

(6.11)

At the beginning of this section, it is mentioned that the displacement field contains both the real and image fields:

\[
u_{t,m} = u_{t,-m}^r + u_{t,m}^i;
\]

(6.12)

and the image field has the magnitude in the order of \( \Delta V/R_{\text{vert}}^2 \). The image field can not be neglected from the exponent of the last exponential terms in Eq. (6.11). If it were
neglected, it would introduce an error (considering the exponent only)

\[
c \sum_t \left( e^{i2\pi \mathbf{H} \cdot (\mathbf{u}^t_{t-m} + \mathbf{u}^i_{t,m})} - 1 \right) - c \sum_t \left( e^{i2\pi \mathbf{H} \cdot \mathbf{u}^i_{t,m}} - 1 \right) = c \sum_t \left( e^{i2\pi \mathbf{H} \cdot \mathbf{u}^i_{t,m}} - 1 \right) e^{i2\pi \mathbf{H} \cdot \mathbf{u}^t_{t-m}} \\
\approx c \sum_t i2\pi \mathbf{H} \cdot \mathbf{u}^i_{t,m} e^{i2\pi \mathbf{H} \cdot \mathbf{u}^t_{t-m}} \\
\sim O(cR_{crys}/a) \gg 1,
\]  

(6.13)

where \( a \) is the lattice parameter and \( O(\ldots) \) stands for "in the same order of magnitude of \( \ldots \)". However, we can use the following trick, as suggested by Dederichs [45]. We write, by adding and subtracting the same term,

\[
e^{c \sum_t \left( e^{i2\pi \mathbf{H} \cdot \mathbf{u}^i_{t,m}} - 1 \right)} = \exp \left[ i2\pi c \mathbf{H} \cdot \sum_t (\mathbf{u}^t_{t-m} + \mathbf{u}^i_{t,m}) \right] \\
\times \exp \left\{ c \sum_t \left[ e^{i2\pi \mathbf{H} \cdot (\mathbf{u}^t_{t-m} + \mathbf{u}^i_{t,m})} - 1 - i2\pi \mathbf{H} \cdot (\mathbf{u}^t_{t-m} + \mathbf{u}^i_{t,m}) \right] \right\}.
\]

(6.14)

The image field can be neglected in the second exponential term since the error is in the order of [comparing with Eq. (6.13)]

\[
\sum_t \left( e^{i2\pi \mathbf{H} \cdot \mathbf{u}^t_{t-m}} - 1 \right) 2\pi \mathbf{H} \cdot \mathbf{u}^i_{t,m} \sim \sum_t (\mathbf{H} \cdot \mathbf{u}^t_{t-m}) (\mathbf{H} \cdot \mathbf{u}^i_{t,m}) \sim O((\Delta V/V_c)^2 a/R_{crys}) \ll 1,
\]

(6.15)

where \( V_c \) is the unit cell volume. Therefore, by neglecting the image field from the second exponent in Eq. (6.14), we have

\[
\langle f_m e^{i2\pi \mathbf{H} \cdot \mathbf{r}_m} \rangle \simeq \exp \left[ i2\pi c \mathbf{H} \cdot \sum_t (\mathbf{u}^t_{t-m} + \mathbf{u}^i_{t,m}) \right] \left( f + c \sum_s \Delta f_{s,m} e^{i2\pi \mathbf{H} \cdot \mathbf{u}^t_{t-m}} \right) \\
\times \exp \left( c \sum_t \left( e^{i2\pi \mathbf{H} \cdot \mathbf{u}^t_{t-m}} - 1 - i2\pi \mathbf{H} \cdot \mathbf{u}^i_{t,m} \right) \right).
\]

(6.16)

Here we also neglected \( u^i_{s,m} \) from the term containing \( \Delta f_{s,m} \). We can do this because \( \Delta f_{s,m} \) is non-zero only in a finite region in space so the situation pertaining to Eq. (6.13) does not
apply. By defining an *averaged* scattering factor for the crystal with defects

\[ \overline{f} = f + c \sum_t \Delta f_{t,m}, \quad (6.17) \]

the following term in Eq. (6.16) can be approximated:

\[ f + c \sum_s \Delta f_{s,m} e^{i2\pi \mathbf{H} \cdot \mathbf{u}_{s,m}^r} \simeq \overline{f} \exp \left[ c \sum_t \frac{\Delta f_{t,m}}{\overline{f}} \left( e^{i2\pi \mathbf{H} \cdot \mathbf{u}_{t,m}^r} - 1 \right) \right], \quad (6.18) \]

since \( c \ll 1 \). Putting this equation back to Eq. (6.13), we have

\[
\langle f_m e^{i2\pi \mathbf{H} \cdot \mathbf{r}_m} \rangle = \overline{f} \exp \left[ i2\pi c \mathbf{H} \cdot \sum_t (\mathbf{u}_{t,m}^r + \mathbf{u}_{t,m}^i) \right] \\
\times \exp \left\{ c \sum_t \left[ e^{i2\pi \mathbf{H} \cdot \mathbf{u}_{t,m}^r} - 1 - i2\pi \mathbf{H} \cdot \mathbf{u}_{t,m}^r + \frac{\Delta f_{t,m}}{\overline{f}} \left( e^{i2\pi \mathbf{H} \cdot \mathbf{u}_{t,m}^r} - 1 \right) \right] \right\},
\]

(6.19)

Substituting this result back into Eq. (6.5), we have the Bragg scattering

\[
I_B = \overline{f}^2 \sum_{m,n} e^{i2\pi \mathbf{H} \cdot \langle (\mathbf{R}_m) - (\mathbf{R}_n) \rangle} \\
\times \exp \left\{ c \sum_t \left[ e^{i2\pi \mathbf{H} \cdot \mathbf{u}_{t,m}^r} - 1 - i2\pi \mathbf{H} \cdot \mathbf{u}_{t,m}^r + \frac{\Delta f_{t,m}}{\overline{f}} \left( e^{i2\pi \mathbf{H} \cdot \mathbf{u}_{t,m}^r} - 1 \right) \right] \right\} \\
\times \exp \left\{ c \sum_s \left[ e^{i2\pi \mathbf{H} \cdot \mathbf{u}_{s,n}^r} - 1 + i2\pi \mathbf{H} \cdot \mathbf{u}_{s,n}^r + \frac{\Delta f_{s,n}}{\overline{f}} \left( e^{-i2\pi \mathbf{H} \cdot \mathbf{u}_{s,n}^r} - 1 \right) \right] \right\},
\]

(6.20)

where

\[
\langle \mathbf{R}_m \rangle = \mathbf{R}_m + c \sum_t (\mathbf{u}_{t,m}^r + \mathbf{u}_{t,m}^i)
\]

(6.21)

is the average position of the atom \( m \) in the lattice distorted by the defects. The last two exponents in Eq. (6.20) are actually independent of \( m \) and are complex conjugate of each other. Therefore, the Bragg diffraction from the distorted lattice is shifted to a new position,
defined by the average position \( \langle R_m \rangle \), and is attenuated by a factor of \( e^{-2M} \), with

\[
M = -c \sum_t \text{Re} \left[ e^{i2\pi \mathbf{H} \cdot \mathbf{u}_{t-m}^*} - 1 - i2\pi \mathbf{H} \cdot \mathbf{u}_{t-m}^* + \frac{\Delta f_{t,m}}{f} \left( e^{i2\pi \mathbf{H} \cdot \mathbf{u}_{t-m}^*} - 1 \right) \right], \tag{6.22}
\]

or, in the continuum approximation

\[
M = -\frac{c}{V_c} \int \text{Re} \left[ e^{i2\pi \mathbf{H} \cdot \mathbf{u}(r)} - 1 - i2\pi \mathbf{H} \cdot \mathbf{u}(r) + \frac{\Delta f(r)}{f} \left( e^{i2\pi \mathbf{H} \cdot \mathbf{u}(r)} - 1 \right) \right] d^3r
= \frac{c}{V_c} \int \left[ 1 - \cos 2\pi \mathbf{H} \cdot \mathbf{u}(r) \right] \left[ 1 + \frac{\Delta f(r)}{f} \right] d^3r, \tag{6.23}
\]

where \( V_c \) is the volume of the unit cell, and \( d^3r \) symbolizes a three dimensional differential element in \( r \)-space.

### 6.1.2 Diffuse Scattering

The diffuse scattering, Eq. (6.6), can be treated in a similar way. Following the same procedure, we have

\[
\langle f_m f_n e^{i2\pi \mathbf{H} \cdot \langle \mathbf{r}_m - \mathbf{r}_n \rangle} \rangle = e^{i2\pi \mathbf{H} \cdot \left[ c \sum_t (\mathbf{u}_{t-m}^* + \mathbf{u}_{t,m}^* - \mathbf{u}_{t-n}^* - \mathbf{u}_{t,n}^*) \right]}
\times \left[ \frac{1}{\langle \mathbf{f}^2 \rangle} + c \sum_t \Delta f_{t,m} \Delta f_{t,n} e^{i2\pi \mathbf{H} \cdot \langle \mathbf{u}_{t-m}^* - \mathbf{u}_{t-n}^* \rangle} \right]
\times \exp \left\{ c \sum_s \left[ e^{i2\pi \mathbf{H} \cdot (\mathbf{u}_{s-m}^* - \mathbf{u}_{s-n}^*)} - 1 - 2\pi \mathbf{H} \cdot (\mathbf{u}_{s-m}^* - \mathbf{u}_{s-n}^*) \right]
+ \frac{\Delta f_{s,m} + \Delta f_{s,n}}{f} \left( e^{i2\pi \mathbf{H} \cdot (\mathbf{u}_{s-m}^* - \mathbf{u}_{s-n}^*)} - 1 \right) \right\}. \tag{6.24}
\]

Put this back into Eq. (6.6), the diffuse scattering can be written in the form of

\[
I_D = \sum_{m,n} e^{i2\pi \mathbf{H} \cdot (\langle \mathbf{r}_m \rangle - \langle \mathbf{r}_n \rangle)} e^{-2M \frac{1}{f}} \left[ (1 + P_{mn}) e^{\Phi_{mn}} - 1 \right], \tag{6.25}
\]

where \( M \) is given in Eq. (6.22), and

\[
P_{mn} = c \sum_t \frac{\Delta f_{t,m} + \Delta f_{t,n}}{f^2} e^{i2\pi \mathbf{H} \cdot (\mathbf{u}_{t-m}^* - \mathbf{u}_{t-n}^*)}. \tag{6.26}
\]
also,

\[
\Phi_{mn} = c \sum_f \left\{ e^{i2\pi H \cdot (u_{\text{r},m} - u_{\text{r},n})} + 1 - e^{i2\pi H \cdot u_{\text{r},m}} - e^{-i2\pi H \cdot u_{\text{r},n}} 
+ \frac{1}{f} \left[ (\Delta f_{t,m} + \Delta f_{t,n}) e^{i2\pi H \cdot (u_{\text{r},m} - u_{\text{r},n})} - \Delta f_{t,m} e^{i2\pi H \cdot u_{\text{r},m}} - \Delta f_{t,n} e^{-i2\pi H \cdot u_{\text{r},n}} \right] \right\}. \tag{6.27}
\]

Since the image field appears only in the averaged lattice positions \( \langle R_m \rangle \) in Eqs. (6.25–6.27), there will be no confusion even if we omit the superscript \( r \) for the real field in the equations. This is the convention we will adapt from now on. Using the continuum approximation and converting the summations into integrals, we have

\[
P(R) = \frac{c}{V_c} \int \frac{\Delta f(r + R) \Delta f(r)}{\bar{f}} e^{i2\pi H \cdot (u(r+R) - u(r))} \, d^3 r, \tag{6.28}
\]

and

\[
\Phi(R) = \frac{c}{V_c} \int \left\{ e^{i2\pi H \cdot (u(r+R) - u(r))} + 1 - e^{i2\pi H \cdot u(r+R)} - e^{-i2\pi H \cdot u(r)} 
+ \frac{1}{f} \left[ (\Delta f(r + R) + \Delta f(r)) e^{i2\pi H \cdot (u(r+R) - u(r))} - \Delta f(r + R) e^{i2\pi H \cdot u(r+R)} - \Delta f(r) e^{-i2\pi H \cdot u(r)} \right] \right\} \, d^3 r. \tag{6.29}
\]

And the intensity expressions become

\[
I_B = \frac{N}{V_c} \int e^{i2\pi \Delta H \cdot R} e^{-2M \tau^2} \, d^3 R, \tag{6.30}
\]

and

\[
I_D = \frac{N}{V_c} \int e^{i2\pi \Delta H \cdot R} e^{-2M \tau^2} \left[ (1 + P(R)) e^{\Phi(R)} - 1 \right] \, d^3 R, \tag{6.31}
\]

where \( N \) is the total number of atoms in the crystal, and \( \Delta H \) is the vector from the nearest reciprocal lattice point, defined by the average lattice positions \( \langle R_n \rangle \), to the end point of the vector \( H \), i.e.,

\[
H = H_0 + \Delta H, \tag{6.32}
\]

where \( H_0 \) is the nearest reciprocal lattice point defined the average lattice positions \( \langle R_n \rangle \).
The function \( P(R) \) is non-zero only if \( \Delta f(r) \) is non-zero; so it is related to the scattering from the precipitates themselves. The function \( \Phi(R) \) depends for the most part upon the distortion induced by the defects. It takes on the value of \( 2M \) when \( R = 0 \) and \( 0 \) when \( R \to \infty \). These two functions, defined in Eqs. (6.28) and (6.29), can both be written conveniently in the forms of auto-convolutions:

\[
P(R) &= \frac{c}{V_c} \int \left[ \frac{\Delta f(r + R)}{f} e^{i2\pi H u(r+R)} \right] \times \left[ \frac{\Delta f(r)}{f} e^{-i2\pi H u(r)} \right] d^3r, \\
&= \frac{c}{V_c} \int A_2(r + R)A_2^*(r)d^3r, \quad (6.33)
\]

and,

\[
\Phi(R) &= \frac{c}{V_c} \int \left\{ \left[ e^{i2\pi H u(r+R)} - 1 + \frac{\Delta f(r + R)}{f} e^{i2\pi H u(r+R)} \right] \times \left[ e^{-i2\pi H u(r)} - 1 + \frac{\Delta f(r)}{f} e^{-i2\pi H u(r)} \right] \\
&\quad \times \left[ \frac{\Delta f(r + R)}{f} e^{i2\pi H u(r+R)} \right] \times \left[ \frac{\Delta f(r)}{f} e^{-i2\pi H u(r)} \right] \right\} d^3r \\
&= \frac{c}{V_c} \int \{ [A_1(r + R) + A_2(r + R)] [A_1^*(r) + A_2^*(r)] - A_2(r + R)A_2^*(r) \} d^3r, \quad (6.34)
\]

where the functions \( A_1(r) \) and \( A_2(r) \) are defined by

\[
A_1(r) = e^{i2\pi H u(r)} - 1, \quad (6.35)
A_2(r) = e^{i2\pi H u(r)} \frac{\Delta f(r)}{f}. \quad (6.36)
\]

and \( A_2^*(r) \) stands for the complex conjugate of \( A_2(r) \). Using the properties of the Fourier transform on convolution integrals, the Fourier transforms of \( P(R) \) and \( \Phi(R) \) are

\[
\tilde{\Phi}(q) = \frac{c}{V_c} \left( |\tilde{A}_1(q) + \tilde{A}_2(q)|^2 - |\tilde{A}_2(q)|^2 \right), \quad (6.37)
\]

and

\[
\tilde{P}(q) = \frac{c}{V_c} |\tilde{A}_2(q)|^2, \quad (6.38)
\]

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in which \( \tilde{A}_1(q) \) and \( \tilde{A}_2(q) \) are the Fourier transforms of \( A_1(r) \) and \( A_2(r) \), respectively, i.e.,

\[
\tilde{A}_1(q) = \int \left( e^{i2\pi \mathbf{H} \cdot \mathbf{u}(r)} - 1 \right) e^{i2\pi q \cdot \mathbf{r}} d^3r,
\]

(6.39)

and

\[
\tilde{A}_2(q) = \int e^{i2\pi \mathbf{H} \cdot \mathbf{u}(r)} \frac{\Delta f(r)}{\mathbf{f}} e^{i2\pi q \cdot \mathbf{r}} d^3r.
\]

(6.40)

The Fourier transforms of the functions \( P(R) \) and \( \Phi(R) \), defined in Eqs. (6.37) and (6.38), should be easier to handle than their definitions, Eqs. (6.28) and (6.29), despite the two extra Fourier transformations involved [from \( u(r) \) to \( \tilde{A}_i(q) \) and from \( \tilde{\Phi}(q) \) to \( \Phi(R) \)]. This is because the displacement field \( u(r) \) is difficult to calculate, and it converges reasonable fast when \( r \) approaching infinity [which makes Eq. (6.39) easier to calculate].

6.1.3 Special Cases

Small distortion

When the distortion in the lattice is small, i.e., \( 2M \ll 1 \), we have \( \Phi(R) \ll 1 \) as well. The approximation

\[
e^{\Phi(R)} \approx 1 + \Phi(R)
\]

(6.41)

can be used. If the attention is confined to reciprocal space regions near the Bragg reflections, the reciprocal space vector \( \mathbf{H} \) can be written as the sum of the nearest reciprocal lattice vector and the vector from that lattice point, as in Eq. (6.32), and \( \Delta \mathbf{H} \) is a very small quantity. We then approximate the vector \( \mathbf{H} \) in the expressions of \( \Phi(R) \) and \( P(R) \) by \( H_0 \).

With this change and under the assumption of small distortions, we have

\[
I_D(\Delta \mathbf{H}) \approx \frac{N}{V_c} \frac{e^{-2\pi i \Delta \mathbf{H} \cdot \mathbf{R}} [\Phi(\mathbf{R}) + P(\mathbf{R})]}{\mathbf{f}} d^3R
\]

\[
= \frac{e^{-2\pi i \Delta \mathbf{H} \cdot \mathbf{R}}}{V_c} \left| \tilde{A}_1(\Delta \mathbf{H}) + \tilde{A}_2(\Delta \mathbf{H}) \right|^2,
\]

(6.42)

where \( A_1(\Delta \mathbf{H}) \) and \( A_2(\Delta \mathbf{H}) \) are given by

\[
\tilde{A}_1(\Delta \mathbf{H}) = \int \left( e^{2\pi H_0 \cdot \mathbf{u}(r)} - 1 \right) e^{2\pi i \Delta \mathbf{H} \cdot \mathbf{r}} d^3r,
\]

(6.43)
and

\[ \tilde{A}_2(\Delta H) = \int e^{i2\pi H_0 \cdot u(r)} \frac{\Delta f(r)}{f} e^{i2\pi \Delta H \cdot r} d^2 r. \]  

(6.44)

The quantity represented in Eq. (6.42) is the part of diffuse scattering that is frequently considered in the literature. In regions very close to Bragg reflections, \( \tilde{A}_1(\Delta H) \) accounts for most of the intensities, and can be further categorized into Huang, asymmetric and Stokes-Wilson scattering [37]. It is clear from the derivation that this is only valid when the distortion is small, or \( 2M \ll 1 \).

**Small angle scattering**

For small angle scattering, the approximation represented in Eq. (6.41) is always valid. So the diffuse intensity expression, Eq. (6.42), holds. This result is similar to the one obtained in [45] (Eq. (14) in the paper). But in [45] the direct scattering from the defects is added in a phenomenological way. It is obtained here in a natural manner. It should be noted that the small angle scattering contains two parts. One of them is the direct scattering from the precipitates. The other is the scattering from the "density change" in the lattice.

**6.1.4 Powder Diffraction**

If the scattering is sufficiently concentrated around the Bragg reflections, the powder pattern near the Bragg peak can be approximated by an integration of the diffraction intensities from a single crystal over a slab that is perpendicular to the reciprocal lattice vector \( H_0 \) [61]. According to the powder diffraction theorem [61], the powder diffuse scattering intensity received by a diffractometer equipped with a monochromater as a function of \( 2\theta \) is given by

\[ I_D(2\theta) = K \int e^{2\pi \Delta H \cdot R} e^{-2M \cdot f^2} \left[ (1 + P(R))e^{\Phi(R)} \right] d^3 R d\Delta H_1 d\Delta H_2 \]

\[ = K \int e^{2\pi \Delta H_3 R_3} e^{-2M \cdot f^2} \left[ (1 + P(R_3))e^{\Phi(R_3)} \right] dR_3, \]  

(6.45)
where $R_3$ is the component of $\bf{R}$ in the direction of $H_0$, $\Delta H_1$ and $\Delta H_2$ are components of $\Delta H$ perpendicular to $H_0$, $\Delta H_3$ is the component of $\Delta H$ in the direction of $H_0$, and

$$
\Phi(R_3) = \Phi(R_1 = R_2 = 0; R_3) = \frac{c}{V} \int \left( |\tilde{A}_1(\Delta H) + \tilde{A}_2(\Delta H)|^2 - |\tilde{A}_2(\Delta H)|^2 \right) e^{-i2\pi\Delta H_3 R_3} d^3 \Delta H, \quad (6.46)
$$

and

$$
P(R_3) = P(R_1 = R_2 = 0; R_3) = \frac{c}{V} \int |\tilde{A}_2(\Delta H)|^2 e^{-i2\pi\Delta H_3 R_3} d^3 \Delta H. \quad (6.47)
$$

The value of $M$ is still given by Eq. (6.23). The scaling factor $K$ can be decomposed into [71]

$$
K = K' \frac{1 + P \cos^2 2\theta}{(1 + P) \sin^2 \theta} \rho_{hkl} g_{hkl} e^{-2M_T}, \quad (6.48)
$$

where $K'$ is another constant that does not change if the setup of the diffractometer and the material under investigation are not changed, $P$ is the polarization factor which is 1 if no monochromator is used, $\rho_{hkl}$ is the multiplicity of the $\{hkl\}$ peak, $g_{hkl}$ is the orientation correction factor for plane $\{hkl\}$ if the sample has a texture (see Chapter 2), and $e^{-2M_T}$ is the thermal attenuation factor for the matrix. The constant $K'$ can be determined experimentally by the integrated intensities of the Bragg peaks, which should be given by [71]

$$
I_{hkl} = K' \lambda \frac{1 + P \cos^2 2\theta_{hkl}}{(1 + P) \sin^2 \theta_{hkl} \cos \theta_{hkl}} \rho_{hkl} g_{hkl} e^{-2M_T f^2}, \quad (6.49)
$$

where $\lambda$ is the wavelength of the radiation used, and $2\theta_{hkl}$ is the diffraction angle for the Bragg peak $\{hkl\}$.

Back to Equation (6.45). Near the Bragg reflections, the scattering from the precipitates is in general much smaller than that resulting from the displacements [45]. So we will, for clarity, neglect the effect due to $P(R_3)$ in the following discussions. Just as its single crystal counterpart, the function $\Phi(R_3)$ takes on limiting values of $2M$ when $R_3 = 0$ and 0 when $R_3 \to \infty$. The diffuse scattering for powder can be divided into two parts. The first part, which is a good approximation of the total diffuse scattering when the distortion is small ($2M \ll 1$ or $\Phi(R_3) \ll 1$), is obtained by expanding $e^{\Phi(R_3)}$ to the linear term. We call this
part the Static Diffuse scattering:

\[ I_{SD} = K \int e^{i2\pi \Delta H_3 R_3} e^{-2M \Phi(R_3)} dR_3. \quad (6.50) \]

The rest of the diffuse scattering is termed the Quasiline:

\[ I_Q = K \int e^{i2\pi \Delta H_3 R_3} e^{-2M (e^{\Phi(R_3)} - 1 - \Phi(R_3))} dR_3. \quad (6.51) \]

And, for completeness, the intensity from the Bragg scattering is

\[ I_B = K \int e^{i2\pi \Delta H_3 R_3} e^{-2M} dR_3. \quad (6.52) \]

In this way, the total scattering from a crystal containing defects are divided into three parts: Bragg diffraction (\(I_B\)), static diffuse scattering (\(I_{SD}\)) and quasi-line (\(I_Q\)). Because Eqs. (6.50–6.52) are all in the form of Fourier integrals, the integrated intensities of the scattering components are equal to the values of the integrands at \(R_3 = 0\) in these equations, respectively. Therefore, the relative integrated intensities of the three parts are \(e^{-2M}, 2Me^{-2M}\) and \((1 - e^{-2M} - 2Me^{-2M})\), respectively. Figure 6.1 shows the relative integrated intensities for the three parts of scattering as a function of \(2M\). It is easy to see from this figure that, only when \(2M\) is very small, the static diffuse scattering can be a good approximation of the total diffuse scattering. When \(2M\) gets very large, both the Bragg peak and static diffuse scattering become negligible and the quasi-line accounts for most of the intensity.

More insight into the problem can be obtained by examining the Fourier coefficients of the three parts of the scattering. According to Eqs. (6.50–6.52), the Fourier coefficients as a function of \(R_3\), apart from a common constant factor, are

\[
\begin{align*}
\text{Bragg peak} : & \quad e^{-2M}, \\
\text{Static Diffuse} : & \quad e^{-2M} \Phi(R_3), \\
\text{Quasiline} : & \quad e^{-2M} (e^{\Phi(R_3)} - 1 - \Phi(R_3)).
\end{align*}
\quad (6.53)
\]

When \(2M \ll 1\), the breakdown of the total magnitudes of the Fourier coefficients into the three parts is shown schematically as a function of \(R_3\) in Figure 6.2. The values of the
Figure 6.1: Relative integrated intensities of three scattering components as a function of $2M$.

Figure 6.2: Schematic diagram of Fourier coefficients of the three components when $2M \ll 1$. 
functions at $R_3 = 0$ are proportional to their integrated intensities. The total magnitude starts out at the value of 1 at $R_3 = 0$ and approaches $e^{-2M}$ as $R_3 \to \infty$. This is the expected behavior from the properties of $\Phi(R_3)$. It can be seen that the quasi-line contributes little to the total scattering, and the Fourier components with large $R_3$ values play important roles in the diffuse scattering.

In the case when $2M \gg 1$, the situation is different. Because $e^{-2M} \ll 1$, static diffuse and Bragg diffraction are exponentially small. Almost all the intensities are coming from the quasi-line. The Fourier coefficient breakdown are given schematically in Figure 6.3. The total magnitude starts out at 1 and quickly converges to almost 0 in a limited range of $R_3$ values. The diffraction profile is determined primarily by the small $R_3$ components. The phase angles of the Fourier coefficients, or, the imaginary part of $\Phi(R_3)$, have to start out from 0 at $R_3 = 0$, increase to a certain finite value and back to 0 again as $R_3 \to \infty$, since $\Phi(R_3)$ is real at both limits. Therefore, when $2M$ is large, the maximum position of the scattering, quasi-line, is determined by the slope of the imaginary part of $\Phi(R_3)$ at small values of $R_3$. This position is measured as a shift from the Bragg peak position.

In the intermediate $2M$ range, the problem is much more complicated. All three parts
of the scattering can be present and are of comparable magnitudes. If the Bragg peaks are broadened by instrumental and other effects, all three can be blended together to form a complex profile. This is the situation in the intermediate stage of aging for the Cu-Be-Co alloy. We will use precise numerical technique to solve this problem based upon the elastic model of the precipitates as presented in Chapter 3.

6.2 Diffraction Model of Aged Cu-Be-Co Alloy

6.2.1 Diffraction Formula for Multiple kinds of Defects

We are primarily interested in the aging stages before or at the time of the appearance of the direct precipitate scattering. If the scattering from precipitates is present, the information of the precipitates is more easily and accurately obtained from the direct scattering. Only in the earlier stage we have to use the diffuse scattering to get information on precipitates. In this stage, the precipitates in the alloy are observed to be plate-like particles with \{100\} habit planes.

There are three equivalent \{100\} planes in crystals with cubic symmetry, like copper. Experimental evidences from TEM and X-ray single crystal diffractions indicate that all three variants of the precipitates exist. When observing from the [001] zone axis, the diffraction patterns show long streaks coming out of Bragg reflection spots in both the [100] and [010] directions. They are caused by the precipitates with habit planes (100) and (010), respectively [6]. There are also very faint diffraction spots at the positions \{110\}, where the Bragg scattering from the fcc matrix is prohibited [5, 6, 15]. It was pointed out by Price and Kelly [5] that these spots are due to the intersections of the diffraction plane and the long [001] streaks coming out of the \{111\} Bragg reflections (see Figure 6.4). The [001] streaks can only be caused by precipitates with (001) habit planes. These streaks and spots are most clearly shown in various TEM observations [6, 15]. The recent X-ray single crystal diffraction study also demonstrated this effect [17].

The theory presented in the last section, which deals only with one kind of defect, needs to be extended to handle this situation. The modification goes back to as early as the transition from Eq. (6.7) to Eq. (6.9), which deals with the Bragg peak. If the three kinds of defects have concentrations of \(c^{(1)}\), \(c^{(2)}\), and \(c^{(3)}\), respectively, for every \(i\) in Eq. (6.7), there
Figure 6.4: Reciprocal lattice of a face centered cubic crystal with streaks running through all reciprocal lattice points in (100) directions (After [5]). It illustrates the formation of the faint (110) spots in diffraction patterns.
is a probability \(c^{(1)}\) of it being occupied by defect 1, \(c^{(2)}\) of it being occupied by defect 2, \(c^{(3)}\) of it being occupied by defect 3, and \((1 - c^{(1)} - c^{(2)} - c^{(3)})\) of it not being occupied by any defect. For a function \(f_1(c_i)f_2(c_j)\), where \(i \neq j\), since the defect distribution is assumed to be independent, we have

\[
\langle f_1(c_i)f_2(c_j) \rangle = \langle f_1(c_i) \rangle \langle f_2(c_j) \rangle
\]

\[
= \left[ c^{(1)}f_1^{(1)} + c^{(2)}f_1^{(2)} + c^{(3)}f_1^{(3)} + (1 - c^{(1)} - c^{(2)} - c^{(3)})f_1^{(0)} \right]
\times \left[ c^{(2)}f_2^{(2)} + c^{(3)}f_2^{(3)} + (1 - c^{(1)} - c^{(2)} - c^{(3)})f_2^{(0)} \right],
\]

(6.54)

where, for \(l = 1, 2, 3\), \(f_1^{(l)}\) and \(f_2^{(l)}\) are the values of the function \(f_1\) and \(f_2\), respectively, when defect \(l\) is present at the lattice point, and \(f_1^{(0)}\) and \(f_2^{(0)}\) are the values of the functions when no defect is present. Therefore, the equation that corresponds to Eq. (6.9) for the case of multiple kinds of defects is

\[
f \prod \left( c^{(1)}e^{i2\pi H \cdot u^{(1)}_{i,m}} + c^{(2)}e^{i2\pi H \cdot u^{(2)}_{i,m}} + c^{(3)}e^{i2\pi H \cdot u^{(3)}_{i,m}} + (1 - c^{(1)} - c^{(2)} - c^{(3)}) \right)
\]

\[
+ \sum \left[ \left( c^{(1)}\Delta f^{(1)}_{i,m} + c^{(2)}\Delta f^{(2)}_{i,m} + c^{(3)}\Delta f^{(3)}_{i,m} \right) e^{i2\pi H \cdot u^{(1)}_{i,m}} \right]
\times \prod \left( c^{(2)}e^{i2\pi H \cdot u^{(2)}_{i,m}} + c^{(3)}e^{i2\pi H \cdot u^{(3)}_{i,m}} + (1 - c^{(1)} - c^{(2)} - c^{(3)}) \right),
\]

(6.55)

where the superscripts \(^{(l)}\) indicate the properties of that particular kind of defects. Carrying out this change through the whole procedure and keeping only to the linear term of the concentrations, we arrive at the following replacement formulae for \(P(R)\) and \(\Phi(R)\):

\[
P(R) = P^{(1)}(R) + P^{(2)}(R) + P^{(3)}(R),
\]

(6.56)

\[
\Phi(R) = \Phi^{(1)}(R) + \Phi^{(2)}(R) + \Phi^{(3)}(R),
\]

(6.57)

with, for \(i = 1, 2, 3\),

\[
P^{(i)}(R) = \frac{c^{(i)}}{V_c} \int \frac{\Delta f^{(1)}(r + R) \Delta f^{(1)}(r)}{\tilde{f}} e^{i2\pi H \cdot (u^{(i)}(r + R) - u^{(i)}(r))} d^3r,
\]

(6.58)
\[
\Phi^{(i)}(R) = \frac{e^{(i)}}{V_c} \int \left\{ e^{i2\pi \mathbf{H} \cdot (u^{(i)}(r+R) - u^{(i)}(r))} + 1 - e^{i2\pi \mathbf{H} \cdot u^{(i)}(r+R)} - e^{-i2\pi \mathbf{H} \cdot u^{(i)}(r)} \\
+ \frac{1}{f} \left[ (\Delta f^{(i)}(r + R) + \Delta f^{(i)}(r)) e^{i2\pi \mathbf{H} \cdot (u^{(i)}(r+R) - u^{(i)}(r))} \\
- \Delta f^{(i)}(r + R) e^{i2\pi \mathbf{H} \cdot u^{(i)}(r+R) - \Delta f^{(i)}(r) e^{-i2\pi \mathbf{H} \cdot u^{(i)}(r)} \right] \right\} d^3r. \tag{6.59}
\]

The Bragg and diffuse scattering intensities are still given by Eqs. (6.30) and (6.31), respectively, when the functions \( P(R) \) and \( \Phi(R) \) are given by Eqs. (6.58) and (6.59), and the following relationship for \( 2M \) still holds

\[
2M = \Phi(R = 0). \tag{6.60}
\]

The powder diffraction equations are derived in the same way as before.

It is not difficult to notice that Eqs. (6.58) and (6.59) are of the same form as Eqs. (6.28) and (6.29), which apply to cases with only one kind of defect. Therefore, we can summarize the following rules for calculating the diffraction from a single crystal containing more than one kind of defect: first, calculate the functions \( P(R) \) and \( \Phi(R) \) for each kind of defects as if they were the only kind of defect in the crystal; then, sum up all the individual \( P(R) \) and \( \Phi(R) \)'s as the total for all defects; finally, use the resultant functions to Eqs. (6.30) and (6.31) and obtain the diffraction pattern. These rules apply to the calculations of powder diffraction profiles as well.

### 6.2.2 Model Parameters

With the theoretical foundation laid down, we can turn and concentrate on what parameters to use for the precipitates. In Chapter 5, we concluded that the precipitates need to have a tetragonal stress-free transformation strain and went on to relate the origin of this strain to the equilibrium structure \( \gamma \). If we adopt this model, the precipitates will have an ordered B2 structure and contain \( \sim50\% \) Be. The size and the aspect ratio of the ellipsoidal precipitates are functions of aging time. They are the important parameters to be determined from the calculation. The only restriction placed on them is that the thickness of the precipitates should not be smaller than one atomic layer.
The concentration of Be in the matrix is also a variable because we can not determine how far along the transformation has proceeded. Any value between the solvus line of the metastable phase and the equilibrium concentration is treated as acceptable value.

The real stress-free transformation strain of the precipitates, $\epsilon'_{ki}$, can be estimated from the lattice parameter information of $\gamma$ and the matrix. If the measured bulk lattice parameters for $\gamma$ and the matrix are $a_\gamma$ and $a_\alpha$, respectively, because the two lattices are rotated by $45^\circ$ about the z-axis (see Fig. 5.4), the real stress-free transformation strain for the phase transformation is

$$
\epsilon'_{11} = \epsilon'_{22} = \frac{a_\gamma - a_\alpha}{a_\alpha\sqrt{2}},
$$

$$
\epsilon'_{33} = \frac{a_\gamma - a_\alpha}{a_\alpha},
$$

$$
\epsilon'_{12} = \epsilon'_{13} = \epsilon'_{23} = 0,
$$

With these estimated true stress-free transformation strain and the elastic constants of both the precipitate and the matrix, the lattice disturbance generated by the precipitates can be calculated from the theory presented in Chapter 3. Unfortunately, the elastic constants $c'_{ijkl}$ of the precipitates are unknown quantities. In the simulations, we will propose some reasonable elastic constants for the precipitates, and assume that they are not changed during the aging process. From the assumed elastic constants and the real stress-free transformation strain, the equivalent transformation strain and the displacement field are calculated using Eq. (3.49) and other equations in Chapter 3.

The requirement for the assumed elastic constants for the precipitates is that they should not lead to any conclusions which are in clear conflict with available experimental results. The precipitate $\gamma$ has a cubic structure, so three independent elastic constants, $c'_{11}$, $c'_{12}$, and $c'_{44}$, should completely specify the elastic behavior of it. Because the alloy gets strengthened with the introduction of the precipitates, the precipitates probably should have higher elastic strength than that of copper matrix.

The proposed elastic constants for the precipitates which are used in all of our simulations are assumed to be

$$
c'_{11} = 2.70 \times 10^{11} \text{ N/m}^2,
$$

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\[ c_{12}' = 1.55 \times 10^{11} \text{N/m}^2, \]
\[ c_{44}' = 1.50 \times 10^{11} \text{N/m}^2. \]

These numbers, along with the experimental lattice parameters \( a_a = 3.615 \text{Å} \) and \( a_r = 2.698 \text{Å} \), which gives a true stress-free transformation strain

\[
\varepsilon_{ij}' = T \begin{pmatrix} 0.0554 & 0 & 0 \\ 0 & 0.0554 & 0 \\ 0 & 0 & -0.2537 \end{pmatrix}, \tag{6.62}
\]

predicts exactly the same habit plane orientation for the precipitates in later stage of aging as by Khachaturyan and Laughlin [21], using the same theoretical framework outlined in their paper. The predicted habit plane has a normal of \((0.349, 0.349, 0.869)\), right between the experimental observed habit planes of (112) and (113).

When an ellipsoidal precipitate with \( a = b = 40 \text{Å} \) and \( c = 1.75 \text{Å} \) and of the above properties are placed in a copper matrix (\( c_{11} = 1.70 \times 10^{11} \text{N/m}^2, c_{12} = 1.225 \times 10^{11} \text{N/m}^2, c_{44} = 0.758 \times 10^{11} \text{N/m}^2 \)), the equivalent stress-free transformation strain obtained from solving Eq. (3.49) is

\[
\varepsilon_{ij}' = T \begin{pmatrix} 0.1124 & 0 & 0 \\ 0 & 0.1124 & 0 \\ 0 & 0 & -0.3518 \end{pmatrix}. \tag{6.63}
\]

An interesting fact from the equivalent transformation strain is that the sum of the diagonal elements is \(-0.127\). This means that, to the matrix, every atom in the precipitates introduces a \(-12.7\%\) volume change. Because the precipitates are assumed to be of 50\% Be, every Be atom in the precipitates effectively has a volume change of \(-25.4\%\) compared with pure copper atoms. The number \(-25.4\%\) comes very close to the volume size factor of a Be atom in a dilute Cu-Be solid solution, \(-26.45\%\) [51]. Therefore, the Be atoms in the precipitates introduce roughly the same volume effect as the atoms in the solid solution, which explains the constant positions of the Bragg peaks in the early stage of aging observed in previous experiments [52].

With these parameters, we are now ready for numerical calculation of the diffraction profiles.
6.3 Numerical Calculation of Powder Diffraction Profiles

6.3.1 Numerical Considerations

To calculate the powder diffraction profile, we start from Eqs. (6.46) and (6.47). It can be shown that,

\[
P(R_3) = \frac{c}{V_c} \int \left( e^{-i2\pi q_3 R_3} \int |A_p|^2 \, dr_1 \, dr_2 \right) \, dq_3, \tag{6.64}\]

\[
\Phi(R_3) + P(R_3) = \frac{c}{V_c} \int e^{-i2\pi q_3 R_3} \times \left\{ \int \left[ |A_{sw} + A_p|^2 + 2Re ((A_{sw} + A_p)A_H^\ast) \right] \, dr_1 \, dr_2 + I_H \right\} \, dq_3, \tag{6.65}\]

where

\[
A_p = \int e^{i2\pi q_3 r_3} e^{i2\pi \mathbf{H} \cdot \mathbf{u}(r_1, r_2, r_3)} \frac{\Delta f(r_1, r_2, r_3)}{f} \, dr_3, \tag{6.66}\]

\[
A_{sw} = \int e^{i2\pi q_3 r_3} \left[ e^{i2\pi \mathbf{H} \cdot \mathbf{u}(r_1, r_2, r_3)} - 1 - i2\pi \mathbf{H} \cdot \mathbf{u}(r_1, r_2, r_3) \right] \, dr_3, \tag{6.67}\]

\[
A_H = \int e^{-i2\pi (q_1 r_1 + q_2 r_2)} i2\pi \mathbf{H} \cdot \tilde{u}(q_1, q_2, q_3) \, dq_1 \, dq_2, \tag{6.68}\]

\[
I_H = \int |2\pi \mathbf{H} \cdot \tilde{u}(q_1, q_2, q_3)|^2 \, dq_1 \, dq_2. \tag{6.69}\]

In these equations, the integrations over \(r_1\) and \(r_2\) represent summations of quantities for all columns parallel to the diffraction vector \(\mathbf{H}_0\). The grid of \(r_1\) and \(r_2\), on the plane perpendicular to \(\mathbf{H}_0\), is taken to be of polar type in the calculation. Therefore, the calculation of profiles turns into the numerical evaluation of \(A_p\), \(A_{sw}\), and \(A_H\) for each individual column, in addition to the integration that gives the quantity \(I_H\).

Out of the four quantities, \(A_p\) is the easiest to handle because the integration region covers only the inside of the precipitate and the displacement inside the precipitate is a linear function of positions (see Chapter 3). The function can be evaluated analytically; and the result is

\[
A_p = \frac{\Delta f}{f} e^{i2\pi \mathbf{H}_0 \cdot \mathbf{e}_1 (q_1 + \mathbf{e}_2 r_2)} e^{i\pi (q_3 + H_3 \mathbf{e}_3^\ast)(t + b)} \sin \pi \left( q_3 + H_3 \mathbf{e}_3^\ast \right) \frac{\sin \pi (q_3 + H_3 \mathbf{e}_3^\ast)(t - b)}{\pi (q_3 + H_3 \mathbf{e}_3^\ast)}, \tag{6.70}\]
where $\epsilon_{ij}$ is the strain inside the precipitate in the coordinate system with its Z-axis oriented along the direction of $H_0$; and $t$ and $b$ is the $z$ coordinates of the intersections with the surface of the ellipsoidal precipitate of the column that passes through $(r_1, r_2)$ which is also parallel to $H_0$. The center of the coordinate system is taken to be at the center of the precipitate.

The integrand of the Stokes-Wilson amplitude, $A_{sw}$, converges rapidly as the distance from the center of the ellipsoidal precipitate increases. This is because the zeroth and first order terms of the expanded integrand ($e^{2\pi H_i \mathbf{u}(r_1, r_2, r_3)}$) has been subtracted. The integration, therefore, can be performed efficiently with a small region close to the precipitate. An integration region of $7a_0$, where $a_0$ is the length of the long semiaxis of the precipitate, provides very accurate evaluation of the integral. The displacement fields for the calculation of the integral are evaluated using Eq. (3.39).

The same method cannot be used to evaluate the integration that gives the Huang intensity, $I_H$. The reason is that the integrand does not converge to zero as fast when the distance from the origin in the reciprocal space increases. Convergence of integrand also changes for different $q_3$ values. Fortunately, the integrand is available as an analytical function in Eq. (3.21). We used a modified QUADPACK routine that deals with infinite integration limits. The algorithm is globally adaptive according to the properties of the integrand. It subdivides the integration regions that have the largest errors on every pass until the predefined convergence condition is satisfied.

The final integration which gives $A_H$ is the most difficult one. It involves a two dimensional Fourier transform; and the integrand converges quite slowly approaching infinity. There are algorithms that deal specifically for this kind of integration, but they are simply too slow to be used. The method employed in our calculation is to use the final divisions and integration grids defined when calculating the integral for $I_H$. As expected, the results are excellent for small $r_1$, $r_2$, and $q_3$ values. The deviation of the results using this method from those computed using the more accurate algorithm gets larger with increasing values of these quantities. A comparison between the two methods indicates that the deviations are within $\sim 10\%$ for most of the data points we considered.

These four integrations, along with the two dimensional integrations over $r_1$ and $r_2$ in Eqs. (6.64) and (6.65), are performed by the program whose source is listed in Appendix A.2. The inverse Fourier transforms and the calculation of the intensity distributions of the three
diffraction components, Bragg peaks, static diffuse scattering and the quasilines, are done by the program which is listed in Appendix A.3.

Therefore, with a certain configuration of precipitates, for each of the diffraction peaks, the following procedure needs to be performed:

1. For each non-equivalent diffraction directions relative to the defects, calculate \( H_0 \cdot u(r_1, r_2, r_3) \) on a set of grid points in the coordinate system that has the z-axis pointing in the direction of \( H_0 \). There is, for example, only one equivalent (111) direction for an ellipsoid defect lying in the \( \{001\} \) plane; whereas, the directions [100] and [001] are not equivalent to each other.

2. For each non-equivalent diffraction directions, calculate \( P(R_3) \) and \( \Phi(R_3) + P(R_3) \) using Eqs. (6.64–6.69) and the displacement fields from the last step.

3. With the \( P(R_3) \) and \( \Phi(R_3) \) values for each non-equivalent directions, evaluate the total \( P(R_3) \) and \( \Phi(R_3) \) according to Eqs. (6.56) and (6.57) and the multiplicity of the directions. The Bragg peaks and diffuse scattering intensities are then obtained through Eqs. (6.30) and (6.31). The \( 2M \) value is also produced at this stage.

In the actual implementation, the Fourier transforms that give \( P(R_3) \) and \( \Phi(R_3) + P(R_3) \) are put into Stage 3. The order of evaluation is not important since the sum of the Fourier transforms is equal to the Fourier transform of the sum.

### 6.3.2 Scaling and Background Corrections for Simulated Results

The calculation presented above does not take the factors like texture and polarization, etc., into account. In fact, the programs listed in the Appendix do not even include the scattering factor. The results are just the values of the integrations in Eqs. (6.50–6.52). In order to compare the simulation results with the experimental data, the proportional factors and backgrounds need to be accounted for.

Table 6.1 listed the factors and backgrounds. All symbols and formulae in the table correspond to those shown in Eqs. (6.48) and (6.49). The thermal factor, \( e^{-2MT} \), is calculated by the formula on Page 191 of [61] for pure copper. The texture factors \( g_{hkl} \) are those obtained experimentally in Chapter 2. The value of \( P \) is taken to be \( \cos^2 2\theta' \), where \( 2\theta' = 26.8^\circ \) is the diffraction angle of the monochromater. The row labeled \( K' \) is determined from
Table 6.1: Proportional factors and additive backgrounds to transform the simulation results for comparison with experimental data.

<table>
<thead>
<tr>
<th>Items</th>
<th>Near Bragg peak index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>111</td>
</tr>
<tr>
<td>Multiplicity ($p_{hkl}$)</td>
<td>8</td>
</tr>
<tr>
<td>$e^{-2M_T}$</td>
<td>0.936</td>
</tr>
<tr>
<td>$f^2$</td>
<td>386.078</td>
</tr>
<tr>
<td>Texture ($g_{hkl}$)</td>
<td>2.460</td>
</tr>
<tr>
<td>$\frac{1+P \cos^2 2\delta}{(1+P) \sin^2 \delta}$</td>
<td>5.553</td>
</tr>
<tr>
<td>$K_f^2 / K'$</td>
<td>39488</td>
</tr>
<tr>
<td>$K'$</td>
<td>4.23 x 10^{-6}</td>
</tr>
<tr>
<td>Scaling ($K_f^2$)</td>
<td>0.167</td>
</tr>
<tr>
<td>Background</td>
<td>0.0</td>
</tr>
</tbody>
</table>
the average of the ratios between the experimental and calculated integrated intensities of the diffraction [see Eq. (6.49)]. The row labeled “Scaling” contains the scaling factors to be multiplied onto the calculated profiles to match them with experimental ones. The background values are obtained by inspecting the data. They should be added to the converted calculated profiles.

The background values listed in Table 6.1 are applicable to calculations for 315°C aged samples only. Because there is peak overlapping for the diffraction from samples aged at 200°C, the background correction for these peaks are listed separately in the next chapter when the calculation is discussed.
Chapter 7

Diffraction Data Analysis with Computer Simulation

In this chapter, the diffraction data presented in Chapter 2 are analyzed using the elastic and diffraction model outlined in the previous few chapters. As noted in Chapter 1, the success of a modeling approach depends heavily on the prior knowledge on the system being investigated. The parameters in the model are determined both from experimental results in the literature and from the comparison of the simulation and our experimental results.

The emphasis of the analysis are placed on the diffraction data from a series of samples aged for different times at 315°C. The sample aged for only 5 minutes at this temperature shows little effect comparing with the as-quenched ones, so the data from this sample is not analyzed in detail. Computer simulations of the diffraction near the Bragg reflections are performed on models corresponding to aging times 15 and 30 minutes. Analyses on the precipitate scattering are done for samples with aging times greater than 30 minutes.

Diffraction data from several samples aged at 200°C are also analyzed. The collection of these data is described in [52].

7.1 Aging At 315°C

7.1.1 Aged for 15 Minutes—GP Zone Stage

According to the TEM observations on similar samples aged at 315°C [13], the precipitates would not turn into γ" until aged for 30 minutes or more. Therefore, the precipitates are still in the form of GP zones, which are disk-like thin plates with {100} habit planes
and have a coherent interface with the matrix. From the metastable phase diagram of binary Cu-Be alloys [1], the solvus line of the GP zones is at about 9 at.% Be at this temperature. This value represents the composition of the matrix when GP zones start to form. Depending on the stage of the aging process, the Be concentration in the matrix can be less than this value in the GP zone stage. The Be concentration in the matrix in the following simulation (15 minutes aging) is chosen to be 8 at.%, because it is already halfway in aging time in the GP zone stage.

The elastic constants for the precipitates throughout the simulations have been selected as \( c'_{11} = 2.70 \), \( c'_{12} = 1.55 \), and \( c'_{44} = 1.50 \), since, according to the reasoning presented in Chapter 6, they give results in good agreement with known properties of the alloy. With an ellipsoid size of \( a = b = 45 \text{Å} \) and \( c = 1.9 \text{Å} \), the equivalent stress-free transformation strain is evaluated, using Eq. (3.49), to be \( \epsilon_{11}^T = \epsilon_{22}^T = 0.112 \), \( \epsilon_{33}^T = -0.334 \), and \( \epsilon_{12}^T = \epsilon_{13}^T = \epsilon_{23}^T = 0 \). The Bragg peaks are modeled as the Gaussian function with widths 0.07, 0.15, 0.24, 0.20, 0.15, 0.40 for peaks 111, 002, 220, 113, 222, 004, respectively. These values are adjusted so that the total calculated profiles (including Bragg and diffuse scattering) fit best with the experimental curves.

Based on these parameters, the diffraction patterns from a polycrystalline sample containing precipitates with these properties can be calculated using the method outlined in Chapter 6. The displacement fields are first obtained by using Eq. (3.39). The functions \( P(R) \) and \( \Phi(R) \) are then calculated using Eqs. (6.64–6.70) for each non-equivalent diffraction plane. Finally, the contributions are summed up by Eqs. (6.56) and (6.57), and the diffraction profiles are calculated using Eqs. (6.50–6.52). The scaling factor in these equations and the additional background corrections are discussed in detail in Section 6.3.2. The resulting calculated profiles near the matrix Bragg reflections are plotted in Figures 7.1–7.6, along with the corresponding experimental intensity distributions. The partitioning of the total calculated profiles into the three components, Bragg reflections, static diffuse scattering and quaselines, is also shown in the figures.

Considering the wide variety in shapes and intensities of the diffraction patterns for different peaks, the theoretical calculations are in very good agreement with the experimental work. There are slight discrepancies on the low angle side of the \{111\} and \{002\} peaks. This is because the Bragg peaks at low angles are asymmetric due to the axial
Figure 7.1: Simulated \( \{111\} \) diffraction profile: aged for 15 minutes at 315°C.
Figure 7.2: Simulated \{002\} diffraction profile: aged for 15 minutes at 315°C.
Figure 7.3: Simulated \{220\} diffraction profile: aged for 15 minutes at 315°C.
Figure 7.4: Simulated \{113\} diffraction profile: aged for 15 minutes at 315°C.
Figure 7.5: Simulated \{222\} diffraction profile: aged for 15 minutes at 315°C.
Figure 7.6: Simulated \{004\} diffraction profile: aged for 15 minutes at 315°C.
Table 7.1: Calculated $2M$ values for samples aged for 15 minutes at $315^\circ$C.

<table>
<thead>
<tr>
<th>Peaks</th>
<th>$2M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>0.463</td>
</tr>
<tr>
<td>002</td>
<td>0.605</td>
</tr>
<tr>
<td>220</td>
<td>1.224</td>
</tr>
<tr>
<td>113</td>
<td>1.650</td>
</tr>
<tr>
<td>222</td>
<td>1.817</td>
</tr>
<tr>
<td>004</td>
<td>2.270</td>
</tr>
</tbody>
</table>

Figure 7.7: $2M$ values as a function of $(h^2 + k^2 + l^2)$: aged 15 minutes at $315^\circ$C.

divergence of the X-ray beam. The asymmetry is also observed for the {111} and {002} peaks from the as-quenched samples, and, therefore, is not an effect of aging.

The calculated $2M$ values of all peaks are listed in Table 7.1. The values are also plotted as a function as $(h^2 + k^2 + l^2)$ in Figure 7.7. It can be seen that the values fall on a straight line passing through the origin, signifying a proportional relationship between $2M$ and
the square of the distance from the origin of the reciprocal space. This relation agrees with Krivoglaz's conclusion in cases of small distortion [39].

It is interesting to note that this relation can not be easily obtained from the experimental diffraction profiles directly. By inspecting the diffraction profiles only, there is an apparent "anisotropy." For example, the \{113\} and \{222\} peaks are closed to each other in terms of the distance from the center of the reciprocal space. The diffraction patterns, however, are very different. Moreover, the \{113\} peak appears to have more diffuse scattering than the \{222\} peak because the latter peak is sharper and less asymmetric. If the usual peak separation technique is employed to separate the scattering of the Bragg peak and the diffuse scattering, the diffuse scattering will have more area, or intensity, near the \{113\} peak than near the \{222\} peak, a contradiction to Krivoglaz's prediction.

However, the simulation profiles and the corresponding $2M$ values show a different reason for this apparent "anisotropy." The results indicate that intensities of the diffuse scattering increase steadily with increasing distance out in the reciprocal space. It is the different distributions of the diffuse scattering near different Bragg peaks that cause the total diffraction profiles to be "anisotropic." For example, near the \{113\} peak, the diffuse scattering is broad and shifted away the position of the Bragg peak; so the diffuse scattering is easily recognizable. Near the \{222\} peak, however, the diffuse scattering is quite sharp and not shifted from the position of the Bragg scattering; most of the intensity of the diffuse scattering can be erroneously regarded as part of the Bragg scattering by using the usual peak separation techniques.

The distributions of the diffraction intensities are more clearly shown by the Fourier coefficients of the profiles plotted in Figures 7.8–7.13. In each of the figures, subfigure (a) contains the magnitudes of the scattering components, Bragg peak, static diffuse scattering, and quasiline, stacked up one above another. The horizontal axis $R$ is the variable $R_3$ in Eq. (6.53) and Figs. 6.2 and 6.3, in units of Angstroms. Under the lowest curve is the contribution from the Bragg scattering. Because the broadening of the Bragg peaks is not modeled, the magnitude of the Fourier coefficient is a constant. The middle is the effect of

*It must be emphasized that Krivoglaz's theory is based upon isotropic defects in an elastically isotropic crystal. Therefore, it is not entirely unreasonable for the diffraction effects in an anisotropic crystal to be different from what his theory predicts. The interesting point is that our theory shows that Krivoglaz's prediction still holds (see the $2M$ values in Fig. 7.7).
Figure 7.8: Fourier coefficients of calculated \{111\} diffraction profile: aged for 15 minutes at 315°C. (a) Magnitudes. (b) Phase angles.
Figure 7.9: Fourier coefficients of calculated \{002\} diffraction profile: aged for 15 minutes at 315\textdegree C. (a) Magnitudes. (b) Phase angles.
Figure 7.10: Fourier coefficients of calculated \{220\} diffraction profile: aged for 15 minutes at 315°C. (a) Magnitudes. (b) Phase angles.
Figure 7.11: Fourier coefficients of calculated \{113\} diffraction profile: aged for 15 minutes at 315°C. (a) Magnitudes. (b) Phase angles.
Figure 7.12: Fourier coefficients of calculated \{222\} diffraction profile: aged for 15 minutes at 315°C. (a) Magnitudes. (b) Phase angles.
Figure 7.13: Fourier coefficients of calculated \{004\} diffraction profile: aged for 15 minutes at 315°C. (a) Magnitudes. (b) Phase angles.
the static diffuse scattering. The top portion belongs to the quasiline. The interceptions of
the curves with the vertical-axis represent the integrated intensities of the components. The
top curve is the sum of the magnitudes of the Fourier coefficients, which is approximately
equal to the magnitude of the total Fourier coefficients of the profile since the imaginary
part is quite small. The correspondence is exact at \( R = 0 \) and \( R = \infty \), where the imaginary
part of the Fourier coefficients vanishes. In subfigure (b), the phase angles in radians of
the static diffuse scattering and the quasiline are plotted as a function of \( R \). The origin
of \( \Delta H_3 \) [in Eqs. (6.50–6.52)] is chosen to be the position of the Bragg peak. Therefore, the
Fourier coefficients of the Bragg peak have no imaginary part, and the phase angle of the
Bragg peak is at the horizontal axis.

From the magnitudes of the Fourier coefficients, it can be seen that the coefficients of
the diffuse scattering for \{222\} converge more slowly to zero than those of the diffuse
scattering for \{113\}. Therefore, the diffuse scattering for \{222\} is sharper in reciprocal
space than that for \{113\}. The fact that the coefficients converge more slowly also makes
the components that have high \( R \) values more important to the diffuse scattering profile.
The phase angles of the high \( R \) components are smaller than those of the intermediate
range. This results in less shift in the profile from the origin, i.e., the position of the Bragg
peak. The sheer magnitudes of the phase angles contribute to greater shift for the \{113\}
diffuse scattering as well.

Comparing all the different diffraction directions, the magnitudes of the Fourier coeffi-
cients for the \{002\} and \{004\} diffuse scattering converge the fastest.\(^\dagger\) This makes their
diffuse scattering profiles the broadest. The Fourier coefficients for the \{111\} and \{222\}
converge very slowly. Therefore, the diffuse scattering for them is quite sharp and close to
the Bragg reflections. For the same direction but different orders, like \{002\} and \{004\}, or
\{111\} and \{222\}, the higher order diffraction has a larger \( 2M \), and the Fourier coefficients
also converge faster.

Physically, the "anisotropy" of the positions of the diffuse scattering near different
diffraction directions is due more to the act of powder diffraction technique than to the

\(^\dagger\) Actually, most of the magnitudes in the Fourier coefficients for the \{002\} and \{004\} peaks come from one
variant of the defect which has the habit plane normal parallel to the diffraction vector. This is because a flat
ellipsoid with tetragonal distortion induces most of the displacement fields in the direction of its habit plane
normal.
real distribution of the diffraction intensity in the three dimensional reciprocal space. As indicated in Chapter 5, the diffuse scattering near \( \{111\} \) is concentrated on the plane that is perpendicular to the diffraction vector. When performing powder diffraction, the observed intensity is the integration of the diffraction intensities on the diffraction sphere. Near the Bragg reflection, the integration is done almost perpendicular to the diffraction vector. This integration, in effect, collects all the diffuse intensity perpendicular to the diffraction vector to a sharp peak under the Bragg reflection. This special spatial distribution of diffuse scattering is also present near the \( \{220\} \), but does not appear near the \( \{002\} \), \( \{113\} \), and \( \{004\} \) reflections. Therefore, the powder diffuse scattering near these peaks will appear to be larger than those near \( \{111\} \), \( \{220\} \), and \( \{222\} \) peaks.

### 7.1.2 Aged for 30 Minutes—Start of \( \gamma'' \) Stage

According to the TEM studies [13], aging for 30 minutes at 315°C is the start of the \( \gamma'' \) stage. At the time, the “bunched up” intensity from the precipitates is first observed at the \( (4/3,0,0) \) position. The habit planes of the precipitates are still \( \{100\} \).

The diffraction patterns near the Bragg reflections changed dramatically when the sample is aged from 15 minutes to 30 minutes at 315°C. The maximum intensities for all matrix peaks are reduced, and the widths of the peaks are increased by large amounts. The maxima of the scattering are shifted to the low angles away from the original Bragg peak positions, except for the \( \{111\} \) peak, whose maximum shifts slightly upward.

When defects of smaller dimension than the lattice atoms are introduced into the lattice, they tend to create an elastic distortion around them that leads to a larger average spacing in the matrix in the immediate vicinity of the defects. The diffuse scattering caused by this part of the matrix should therefore be located on the low angle side of the whole matrix scattering. The upward shift of the maximum of the \( \{111\} \) scattering is highly unusual and must be due to some other effects.

Considering the spatial distribution of the scattering intensity near \( \{111\} \) reflection, the upward shift can be explained by an optical effect of powder scattering. The process is illustrated in Figure 7.14. As mentioned before, the diffuse scattering near \( \{111\} \) reflection is concentrated on the plane perpendicular to the diffraction vector. This intensity distribution is represented as a slab in the figure. The position of the Bragg scattering is
Figure 7.14: Illustration of peak shift due to powder scattering effect.
located at point $X$ in the reciprocal space. The intensities of the powder scattering is determined by the total intensities that the diffraction spheres pick up. When there is no diffuse scattering, the maximum intensity of the powder scattering is of course corresponding to sphere $A$ that passes through point $X$. However, when there are strong diffuse intensities distributed perpendicular to the diffraction vector, sphere $B$, which is a little further away from the center of reciprocal space than sphere $A$, may pick up more total intensities than sphere $A$ because it intercepts with more volume of the diffuse scattering cloud. In powder diffraction patterns, this appears as a shift in the intensity maximum.

This shifting effect was also observed for the scattering near $\{111\}$, $\{220\}$, and $\{222\}$ reflections from samples aged at 200°C [52]. According to the analysis in Chapter 5, these are the peaks for which the diffuse scattering distribution is concentrated on the plane that perpendicular to the diffraction vectors. The magnitudes of the shifts were not as great because in those cases the Bragg peaks are still quite strong. For the case being studied here, the Bragg peak is weakened by the attenuation factor, so the shifting effect is more prominent.

The parameters used to simulate the scattering are selected as follows. The concentration of Be in the matrix is 5 at.% according to the $\gamma^\prime$ solvus line in the meta-stable phase diagram [1]. The precipitates are modeled as ellipsoids with $a = b = 100\,\AA$, and $c = 5\,\AA$. The elastic constants of the precipitates and the widths of the Bragg peaks are not changed from the previous simulation. The simulated and experimental profiles are given in Figures 7.15–7.20. The calculated profiles near $\{111\}$ reflection are adjusted upwards by 0.06°2θ to account for the shift discussed above.

The correspondences between the simulated and experimental profiles are only of modest success. The calculated profile for $\{111\}$ is too asymmetric, and that of $\{002\}$ is broader than the experimental one. No change in parameters can provide better fit for all peaks. A tighter fit on a diffraction peak usually causes misfits in one and more other peaks.

The $2M$ values of the scattering are listed in Table 7.2. It can be seen that the $2M$ values are all much greater than 1. Therefore, the Bragg diffraction and static diffuse components are severely attenuated, and the quasilines are the dominant components of the scattering. This is evident in the figures showing the calculated profiles.
Figure 7.15: Simulated \{111\} diffraction profile: aged for 30 minutes at 315°C.

Table 7.2: Calculated $2M$ values for samples aged for 30 minutes at 315°C.

<table>
<thead>
<tr>
<th>Peaks</th>
<th>$2M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>5.509</td>
</tr>
<tr>
<td>002</td>
<td>6.647</td>
</tr>
<tr>
<td>220</td>
<td>13.46</td>
</tr>
<tr>
<td>113</td>
<td>16.76</td>
</tr>
<tr>
<td>222</td>
<td>19.63</td>
</tr>
<tr>
<td>004</td>
<td>24.13</td>
</tr>
</tbody>
</table>
Figure 7.16: Simulated \{002\} diffraction profile: aged for 30 minutes at 315°C.
Figure 7.17: Simulated \{220\} diffraction profile: aged for 30 minutes at 315°C.
Figure 7.18: Simulated \{113\} diffraction profile: aged for 30 minutes at 315°C.
Figure 7.19: Simulated \{222\} diffraction profile: aged for 30 minutes at 315°C.
Figure 7.20: Simulated {004} diffraction profile: aged for 30 minutes at 315°C.
While the $2M$ values still increase with increasing $2\theta$, they do not fall on a straight line as in the case of the diffraction from the sample aged for 15 minutes. Comparing the $2M$ values between \{111\} and \{222\}, or between \{002\} and \{004\}, the ratios are between the small distortion limit of $(h^2 + k^2 + l^2)$ and the large distortion limit of $(h^2 + k^2 + l^2)^{3/4}$.

The magnitudes and phase angles of the Fourier coefficients of the calculated profiles are given in Figures 7.21–7.26. For all peaks, the contributions from Bragg scattering and static diffuse scattering are very small. The coefficients converge to zero faster than those presented in the last subsection, thus lead to broader diffraction profiles.

The length of the long semi-axis of the ellipsoids, used in the matrix calculations, is greater than the Characteristic Size of the precipitates estimated using Scherrer’s equation with the directly scattering of the precipitates, as listed in Table 2.5. There are several reasons for this: first, the size predicted by Scherrer’s equation is the “mean” size of the particle, but the length of the semi-axis is the maximum dimension of the particle; second, the value listed in Table 2.5 does not take into account the extra broadening introduced by the lattice distortion on the diffraction of the precipitates, as indicated in Eq. (6.45); third, the shape of the precipitates may not be of an exact ellipsoid, and if it is a disk, there will be non-uniform strains inside the precipitates (see Section 3.3) and broader diffraction profiles than the case of an ellipsoid with uniform strain; fourth, some smaller size precipitates may exist which produce broader peaks. If all this extra broadening is taken to be due to size, a smaller than actual particle size will be obtained.

Because the diffraction due to the matrix is small and slowly varies in the vicinity of the diffraction peaks of the precipitates, the powder diffraction profiles from the precipitates are given by the term containing $P(R_3)$ in Eq. (6.45), i.e.,

$$I_P(2\theta) \propto \int e^{2\pi i H_3 R_3} e^{-2M} P(R_3) e^{i\Phi(R_3)} dR_3,$$

(7.1)

where

$$P(R_3) = \frac{c}{V_c} \int \int e^{2\pi i H_3 R_3} \frac{\Delta f(r)}{f} e^{2\pi i H \cdot r} d^3 r e^{-2\pi i H_3 R_3} d^3 \Delta H.$$  

(7.2)

Recognizing the fact that the function $\Delta f(r)$ is a constant inside the precipitates and zero outside, plus inside an ellipsoidal precipitate, the displacement field is a linear function of the position $r$, the function $P(R_3)$ can be evaluated in a way similar to Eqs. (6.64) and
Figure 7.21: Fourier coefficients of calculated \{111\} diffraction profile: aged for 30 minutes at 315°C. (a) Magnitudes. (b) Phase angles.
Figure 7.22: Fourier coefficients of calculated (002) diffraction profile: aged for 30 minutes at 315°C. (a) Magnitudes. (b) Phase angles.
Figure 7.23: Fourier coefficients of calculated \{220\} diffraction profile: aged for 30 minutes at 315°C. (a) Magnitudes. (b) Phase angles.
Figure 7.24: Fourier coefficients of calculated \{113\} diffraction profile: aged for 30 minutes at 315°C. (a) Magnitudes. (b) Phase angles.
Figure 7.25: Fourier coefficients of calculated \{222\} diffraction profile: aged for 30 minutes at 315°C. (a) Magnitudes. (b) Phase angles.
Figure 7.26: Fourier coefficients of calculated \{004\} diffraction profile: aged for 30 minutes at 315°C. (a) Magnitudes. (b) Phase angles.
Figure 7.27: Precipitate scattering profiles with and without the factor $e^{-2M \Phi(R_3)}$ as well as instrumental broadening.

(6.70). In fact, the only difference between Eq. (7.1) and the ordinary precipitate scattering is the existence of the factor $e^{-2M \Phi(R_3)}$ inside the integrand. This factor reduces the Fourier coefficients for large $R_3$ values that are due only to the precipitate size, $P(R_3)$, and therefore, introduces additional broadening to the diffraction peaks from the precipitates. This effect becomes more important when the size of the precipitates is large. If the size of the precipitates is small, the values of $P(R_3)$ are non-zero only for small $R_3$ values. For these small $R_3$, the factor $e^{-2M \Phi(R_3)}$ is very close to 1, since $\Phi(R_3) \to 0$ when $R_3 \to 0$. Therefore, the extra factor has no effect in these cases.

The results obtained from Eq. (7.1), however, does not take into account the extra broadening caused by the instrumental effect. The actual observed diffraction pattern is the convolution of the results from Eq. (7.1) and a function representing the instrumental broadening. Figure 7.27 shows the \{100\} precipitate diffraction profiles [Eq. (7.1)] of ellipsoidal precipitates of size 100\AA, 100\AA, 5\AA with the factor $e^{-2M \Phi(R_3)}$ and with the
instrumental effect, with the factor $e^{-2M e^{\Phi(R_3)}}$ and without the instrumental effect, and, without the factor $e^{-2M e^{\Phi(R_3)}}$ and without the instrumental effect. The function representing instrumental broadening is taken to be the shape of the beryllide diffraction peak at the as-quenched condition (see Chapter 2)

$$f(2\theta) = \frac{1.6014}{1 + \left( \frac{(2\theta - 2\theta_0)}{0.6994} \right)^2}^{1.2567},$$  \hspace{1cm} (7.3)

normalized to unit area. Without the factor $e^{-2M e^{\Phi(R_3)}}$ and instrumental broadening, the FWHM of the peak is about 0.7° 2θ. Considering the distortion factor $e^{-2M e^{\Phi(R_3)}}$ and without the instrumental broadening gives a peak width of about 1.0° 2θ. Considering both effects yields a FWHM of about 1.1–1.2° 2θ. While this number is still smaller than the measured value of FWHM determined by Pearson VII peak separation (1.49°, see Table 2.5 under the column of 30 minute aging), the discrepancy is not large even without taking into account the third and fourth possibilities stated above. With a 3% change in the lattice parameters in the precipitates, the center of the diffraction peak is shifted by about 1.5° 2θ. Therefore, it is very possible that the remaining discrepancy in the peak width is caused by non-uniform strain inside the precipitates.

### 7.1.3 Aged for Longer Times—Late γ'' and γ' Stages

As aging continues, the precipitate scattering is detected by X-ray diffraction. From the results presented in Figures 2.10 and 2.11, the diffraction patterns near the precipitate peaks are very complex. As many as four different peaks can be separated from one profile for near the {001} precipitate scattering. Near {111} precipitate scattering, three peaks are usually enough to described the composite profiles.

According to the TEM observations on similar samples aged under similar conditions [13], the precipitate scattering is also observed in selected area diffraction patterns. The patterns go through substantial changes as aging proceeds. At 30 minutes aging, elongated diffraction spots barely appear around positions (4/3,0,0). Starting from 3 hours of aging, the spots turn into an arrowhead shape, signifying a change in the habit plane of the precipitates. Further aging sees the arrowheads sharpened into two distinct points.
The positions of the spots change slightly in the process. For the powder diffraction experiments we are performing, the change of habit planes can not be observed; but the change in the sharpness of the peaks, related mainly to the size of the precipitates, and the peak positions, related mainly to the lattice spacing inside the precipitates, are reflected in the powder diffraction patterns. The effects are in agreement with the TEM observations.

For the diffraction pattern near $2\theta = 33.5^\circ$, four peaks can be separated from each of the profiles, as shown in Figure 2.10. It is believed that four peaks also exist in the case of 30 minutes aging. The broadest peak is too broad to be distinguish from the background but can be observed for aging time greater than 3 hours. For the diffraction near $2\theta = 60^\circ$ (see Fig. 2.11), three peaks are separated from each profile.

One of the peaks [for both (100) and (111)] is stable in both position and intensity throughout the aging process. These peaks are identified as the scattering from beryllides in the grain boundaries. They are present in the as-quenched samples. The measured average lattice parameter, 2.654 Å, is between the lattice parameters of equilibrium Cu-Be (2.7 Å) and Co-Be (2.6 Å), both of B2 structure. It is expected that the beryllides have a B2 structure with Be at the corners and random distribution of Cu and Co at the centers.

Another sharp peak barely appears after 30 minute aging [for (100), not resolved for (111)] and grows in both intensity and size with increasing aging time at the underaged stage. This growth is stopped or slowed in the overaged stage. The positions of the peaks are very stable despite the intensity changes. This implies that there is little or no interaction with the matrix. These intensities seem to be correlated with the discontinuous precipitates observed in [14]. These precipitates are grown from the grain boundaries and have an incoherent interface with the matrix. Therefore, no lattice parameter changes can be observed. The structure of the discontinuous precipitates should be of B2, with Be atoms at the corners and Cu atoms at the centers. The measured average lattice parameter, 2.698 Å, agrees reasonable well with 2.70 Å, the lattice parameters of $\gamma'$ and $\gamma$ reported in the literature.

The appearance of the extra intensity at high angle side of beryllide (100) peak after 30 minute aging coincides with the TEM observation of "bunched" up of [100] intensity streaks to point (4/3, 0, 0) in [13]. The latter signifies the formation of $\gamma''$ (called $\gamma'$ in [13]). The lattice parameter measured from the X-ray diffraction peak, 2.577 Å (see Table 2.5),
agrees well with one of the lattice parameters, 2.53 Å, reported for the "tetragonal" structure of γ" in the literature [20]. The peak that corresponds to the other lattice parameter, 2.9 Å, is believed to be on the low angle side of the beryllide peak, and is too broad to be resolved from the background at this time.

For (100) scattering, after 3 hours of aging, the extra intensity can indeed be separated into two peaks, one sharp and one broad. When aging progresses to 24 hours, both of the integrated intensities increase and the peaks sharpen. In the mean time, both of the peaks are shifted towards the position of the discontinuous precipitates. After 168 hours of aging, these two peaks are so sharp and close to each other that only one large peak can be resolved from the fitting procedure. The ranges of the lattice parameters, 2.604–2.658 Å for the sharp peak, and 2.684–2.795 Å for the broad peak, correspond roughly to the lattice parameters reported for γ'(2.56 Å and 2.70 Å [15]). The minor discrepancy should not cause concern because there is a wide range of lattice parameters reported in the literature depending on the exact aging states at which the measurements are taken. Errors can also be introduced when the peak separation procedure is applied to separate peaks that are close to each other and of similar width, as in the cases of 24 hours and 168 hours aging.

During the same period of time, in TEM observation, the "bunched" up intensity at the (4/3,0,0) position changes to an arrowhead shape and later sharpens to two separated spots [13] after 168 hours of aging. This phenomenon was interpreted as the change of habit planes for the continuous precipitates from {100} to {112} or {113}. X-ray powder scattering is not sensitive to habit plane changes without a change in the lattice parameter; so this effect is not seen in our observations. The changes in lattice parameters and sharpness of the scattering are observed in X-ray diffraction, and are consistent with the TEM results in these aspects. The sharpening of the dots in TEM and peaks in X-ray diffraction is an indication of the growing sizes of the precipitates.

As suggested by Khatchaturyan and Laughlin [21] and continuously advocated in the previous chapters of this dissertation, the precipitates, whether GP zones, γ", or γ', are matrix constrained version of the equilibrium phase γ. Therefore, their intrinsic structure should be cubic. The reason that the precipitates are recorded as tetragonal or monoclinic in X-ray and TEM experiments is that the interaction between the precipitates and the matrix forces changes in lattice spacing inside the precipitates. As indicated in Section 6.2.2 and
Table 7.3: Relative amount of precipitate phases as a function of aging time

<table>
<thead>
<tr>
<th>Phase</th>
<th>30 minutes</th>
<th>3 hours</th>
<th>24 hours</th>
<th>168 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discontinuous</td>
<td>area</td>
<td>0.063</td>
<td>0.51</td>
<td>0.66</td>
</tr>
<tr>
<td>Precipitate</td>
<td>fraction</td>
<td>6%</td>
<td>11%</td>
<td>17%</td>
</tr>
<tr>
<td>Continuous</td>
<td>area</td>
<td>0.96</td>
<td>3.99</td>
<td>3.32</td>
</tr>
<tr>
<td>Precipitate</td>
<td>fraction</td>
<td>94%</td>
<td>89%</td>
<td>83%</td>
</tr>
</tbody>
</table>

Fig. 5.4, the disk like precipitates need to contract in the thin dimension and to expand in the base plane to transform itself from the FCC structure to B2 structure. The elastic interaction causes the lattice spacing in the thin dimension and in the base plane of the precipitate to be greater and less than its equilibrium value, respectively. In X-ray diffraction patterns from the precipitates, this produces a sharper peak (corresponding to the longer sides of the precipitate) on the high angle side of the equilibrium peak position, and a broader peak (corresponding to the thin dimension) on the low angle side. This is exactly what the patterns in Figure 2.10 show. In TEM observations, for a precipitate with habit plane (001), the “bunched” up intensity near (0,0,4/3) corresponds to the broad peak in X-ray diffraction. Because on the habit plane the unit cell axes of the precipitate make 45° angle with the unit cell axes of the matrix, the scattering related to the sharper peak appears at position (\(\frac{4}{3}\sqrt{2}, \frac{4}{3}\sqrt{2}, 0\)) in the reciprocal space. The intensity at this position is of needle shape with the elongated direction perpendicular to the (001) reciprocal lattice plane. In TEM experiments, this will appear as a dot very close to the (110) spot where there was intensity due to the [001] streaks from (111); so it is not easily recognizable. The positions of the diffraction spots (or relrods) in the reciprocal space and their implications on powder X-ray diffraction pattern are illustrated in Figure 7.28.

For (111) scattering, the broad intensity distribution can be accounted for by only one diffraction peak. This is because that there is only one kind of (111) dimension for a plate or a ellipsoid, in contrast to directions (100), where a thick and a thin dimensions exist. The maxima of the lone broad peaks are changing with aging. They are shifted toward the position of the discontinuous precipitates, similar to the observation with the (100) scattering.

The lattice parameters, estimated dimensions, and peak areas of the various precipitates...
Figure 7.28: Illustration of the diffraction patterns in the reciprocal lattice of a face centered cubic crystal with plate like precipitates with (001) habit. The black dots are the Bragg reflections from the matrix. The thin long lines are the streaks due to the precipitates as discussed in Chapter 5. The short stubs are the direct (100) diffraction from the precipitates.
phases obtained from both (100) and (111) scattering are given in Tables 2.3–2.5. As seen from the changes in peak areas as a function of aging time, the relative amount of different phases in the crystals should change with aging time. Because the beryllide peaks appear to be stable and exist even in the as-quenched state, the beryllium atoms precipitated out of the matrix go to the discontinuous and continuous precipitates only. Table 7.3 gives the relative amount of the two precipitate phases at a range of aging time from 30 minutes to 168 hours. Both phases are not detected at the as-quenched and 15 minute aged conditions. The fraction of a particular phase is determined from the (100) peak area of the phase as a fraction of the total area (discontinuous plus continuous). It can be seen from the table that the discontinuous precipitates contribute to only a small fraction of the total precipitates, especially in the early stage. This justifies the choices of parameters in the calculation of the profiles, for which all beryllium atoms precipitates out of the matrix are assumed to go into the continuous precipitates. It should be noted that, because the peak separation procedure applied to several peaks that are very close to each other, there are large errors involved in the area parameters. Therefore, these numbers should only be used in a qualitative or semi-quantitative sense.

7.1.4 Precipitate Spacing in the Crystals

With the size, shape, and matrix concentration parameters obtained through the above analyses, the spacing between precipitates in the crystals can be estimated. The particle spacing is believed to be an important parameter related to the mechanical property of the material, according to the theory described in Chapter 1.

Assuming that each precipitate has a volume of $V_p$, and the concentration of Be in the original matrix, inside the precipitates, and remaining in the matrix are $C$, $C_p$, and $C_0$, respectively, from the principle of conservation of Be atoms, the average distance between precipitates should be

$$d = 3 \sqrt[3]{\frac{V_p C_p}{C - C_0}}. \quad (7.4)$$

The values of $d$ for different aging times are given in Table 7.4. The concentration of Be atoms in the precipitates is taken to be 50% for all cases. The size of the precipitates and matrix concentration for 15 and 30 minute aged are those determined by computer
Table 7.4: Average distance between precipitates in the crystal.

<table>
<thead>
<tr>
<th>Aging Time</th>
<th>Shape</th>
<th>Size</th>
<th>$C_0$</th>
<th>$d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15m</td>
<td>Ellipsoid</td>
<td>$a = b = 45\text{Å}, c = 1.9\text{Å}$</td>
<td>8%</td>
<td>63.4Å</td>
</tr>
<tr>
<td>30m</td>
<td>Ellipsoid</td>
<td>$a = b = 100\text{Å}, c = 5\text{Å}$</td>
<td>5%</td>
<td>119Å</td>
</tr>
<tr>
<td>3h</td>
<td>Parallelepiped</td>
<td>$L_1 = L_2 = 90.0\text{Å}, L_3 = 22\text{Å}$</td>
<td>2%</td>
<td>99.7Å</td>
</tr>
<tr>
<td>24h</td>
<td>Parallelepiped</td>
<td>$L_1 = L_2 = 129.6\text{Å}, L_3 = 46.1\text{Å}$</td>
<td>0.5%</td>
<td>154Å</td>
</tr>
<tr>
<td>168h</td>
<td>Parallelepiped</td>
<td>$L_1 = L_2 = 200\text{Å}, L_3 = 89.2\text{Å}$</td>
<td>0%</td>
<td>252Å</td>
</tr>
</tbody>
</table>

Simulation. The shape of the precipitates is ellipsoidal, same as what is used in the simulations. In the cases of longer aging times, the sizes of the precipitates for most are taken to be the values obtained by peak width analysis, as listed in Table 2.5. Because peaks are too close to each other in the diffraction profiles, the widths of the sharp peaks are very questionable. The long dimensions of the precipitates in samples aged for 24 hours and 168 hours are estimated values only. The precipitates are assumed to be of the shape of parallelepipeds because the values are evaluated with Scherrer's equation. The concentration of the Be atoms remaining in the matrix is estimated based on the trends.

The average distances between precipitates are also plotted as a function of $\ln(\text{Aging Time})$ in Figure 7.29. It can be noticed that there is an obvious problem with the values of $d$. The values shown decrease when the sample aged from 30 minutes to 3 hours. This is an unreasonable result. It is due to the inaccuracy of the determination of the size of the precipitates, either because of the inability to unscramble the overlapped diffraction peaks, or from one or more of the peak broadening effects discussed in Section 7.1.2.

In spite of the problems, the critical distance between the precipitates when the alloy achieves the hardness maximum can still be estimated from Figure 7.29. From Chapters 1 and 2, the hardness maximum is obtained when the alloy is aged for about 5 hours, i.e., 300 minutes. Following the straight line in the Figure, the average separation at 300 minutes is about 200Å. If we follow the trend of the first two aging times, for which the sizes are determined by computer simulations, a corresponding value of 300Å is obtained. Therefore, it can be concluded the critical distance between precipitates when the hardness maximum is reached is 200–300Å.
Figure 7.29: Distances between precipitates as a function of aging time.
Table 7.5: Calculated $2\theta$ values for samples aged for 960 minutes at 200°C.

<table>
<thead>
<tr>
<th>Peaks</th>
<th>2\theta</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>0.682</td>
</tr>
<tr>
<td>002</td>
<td>0.891</td>
</tr>
<tr>
<td>220</td>
<td>1.802</td>
</tr>
<tr>
<td>113</td>
<td>2.441</td>
</tr>
<tr>
<td>222</td>
<td>2.691</td>
</tr>
<tr>
<td>004</td>
<td>3.365</td>
</tr>
</tbody>
</table>

7.2 Aging At 200°C

In this section, the diffraction patterns from several Cu-Be samples aged at 200°C are examined with computer simulations. These data are collected with a similar setup as described in Chapter 2 [52]. Because the aging temperature for these samples is much lower than the temperature considered above, the progress of the precipitation process is much slower. This is reflected on the diffraction patterns. Even with 64 hours of aging at 200°C, the amount of diffuse scattering in the diffraction patterns near the Bragg reflections is not nearly as much as those present in the diffraction patterns from the sample aged for 30 minutes at 315°C. For this reason, it is believed that the precipitates are all in the “GP zone” stage for aging at 200°C.

7.2.1 Simulated Diffraction Profiles

The same model is used to calculate the diffraction patterns for this aging temperature. Only the parameters are changed. The concentration of Be in the matrix is taken to be 6%, according to the value of the GP zone solvus line at 200°C in the meta-stable diagram. For the sample aged for 960 minutes (16 hours), the semiaxes of the ellipsoidal clusters are $a = b = 40\AA$ and $c = 1.7\AA$. The elastic constants in the precipitates stated in the previous section are used without change.

The simulation results, along with the corresponding experimental data, are shown in Figures 7.30–7.35. Linear background correction is used for all peaks. The background values, determined from the two points (for each peak) listed in Table 7.6, are added to
Figure 7.30: Simulated \{111\} diffraction profile: aged for 960 minutes at 200°C.

Table 7.6: Background corrections for all peaks from the sample aged for 960 minutes at 200°C

<table>
<thead>
<tr>
<th>Peak</th>
<th>At 2θ</th>
<th>Background</th>
<th>At 2θ</th>
<th>Background</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>—</td>
<td>0.0</td>
<td>—</td>
<td>0.0</td>
</tr>
<tr>
<td>002</td>
<td>46.778</td>
<td>3.0605</td>
<td>55.262</td>
<td>0.9395</td>
</tr>
<tr>
<td>220</td>
<td>—</td>
<td>1.2</td>
<td>—</td>
<td>1.2</td>
</tr>
<tr>
<td>113</td>
<td>85.7072</td>
<td>1.60129</td>
<td>96.5928</td>
<td>2.79871</td>
</tr>
<tr>
<td>222</td>
<td>90.8471</td>
<td>2.82832</td>
<td>102.273</td>
<td>0.771678</td>
</tr>
<tr>
<td>004</td>
<td>—</td>
<td>1.0</td>
<td>—</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Figure 7.31: Simulated \{002\} diffraction profile: aged for 960 minutes at 200°C.
Figure 7.32: Simulated \{220\} diffraction profile: aged for 960 minutes at 200°C.
Figure 7.33: Simulated \{113\} diffraction profile: aged for 960 minutes at 200°C.
Figure 7.34: Simulated \{222\} diffraction profile: aged for 960 minutes at 200°C.
Figure 7.35: Simulated \{004\} diffraction profile: aged for 960 minutes at 200°C.
Figure 7.36: $2M$ values as a function of $(h^2 + k^2 + l^2)$: aged 960 minutes at 200°C.
the scaled calculated profiles. The $2M$ values are listed in Table 7.5 and are plotted in Figure 7.36. It shows that the values of $2M$ are proportional to $(h^2 + k^2 + l^2)$, regardless of directions of the diffraction vectors.

For a sample aged for 3840 minutes (64 hours) at 200°C, precipitates of ellipsoidal shape with $a = b = 40\AA$ and $c = 2.5\AA$ are assumed. The Be concentration in the matrix is taken as 5%.

The calculated and experimental diffraction profiles for this sample are plotted in Figures 7.37–7.42. Linear background correction is again used for all peaks. The background values, determined from the two points (for each peak) listed in Table 7.8, are added to the scaled calculated profiles. The $2M$ values are in Table 7.7 and Figure 7.43. Again, the values of $2M$ are roughly proportional to $(h^2 + k^2 + l^2)$. However, the proportionality is not as good as that shown by the values for the 960 minutes aged sample. This may correspond to the change of the proportional property of $2M$ values on the distances out
Figure 7.38: Simulated \{002\} diffraction profile: aged for 3840 minutes at 200°C.

Table 7.7: Calculated $2\theta$ values for samples aged for 3840 minutes at 200°C.

<table>
<thead>
<tr>
<th>Peaks</th>
<th>$2\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>1.141</td>
</tr>
<tr>
<td>002</td>
<td>1.460</td>
</tr>
<tr>
<td>220</td>
<td>2.982</td>
</tr>
<tr>
<td>113</td>
<td>3.979</td>
</tr>
<tr>
<td>222</td>
<td>4.429</td>
</tr>
<tr>
<td>004</td>
<td>5.214</td>
</tr>
</tbody>
</table>
Figure 7.39: Simulated \{220\} diffraction profile: aged for 3840 minutes at 200°C.

Table 7.8: Background corrections for all peaks from the sample aged for 3840 minutes at 200°C

<table>
<thead>
<tr>
<th>Peak</th>
<th>At 2θ</th>
<th>Background</th>
<th>At 2θ</th>
<th>Background</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>—</td>
<td>0.0</td>
<td>—</td>
<td>0.0</td>
</tr>
<tr>
<td>002</td>
<td>46.778</td>
<td>3.2726</td>
<td>55.262</td>
<td>0.7274</td>
</tr>
<tr>
<td>220</td>
<td>—</td>
<td>1.38</td>
<td>—</td>
<td>1.38</td>
</tr>
<tr>
<td>113</td>
<td>85.7072</td>
<td>1.78358</td>
<td>96.5928</td>
<td>3.41642</td>
</tr>
<tr>
<td>222</td>
<td>90.8471</td>
<td>2.82832</td>
<td>102.273</td>
<td>0.771678</td>
</tr>
<tr>
<td>004</td>
<td>—</td>
<td>1.06</td>
<td>—</td>
<td>1.06</td>
</tr>
</tbody>
</table>
Figure 7.40: Simulated \{113\} diffraction profile: aged for 3840 minutes at 200°C.
Figure 7.41: Simulated \{222\} diffraction profile: aged for 3840 minutes at 200°C.
Figure 7.42: Simulated (004) diffraction profile: aged for 3640 minutes at 200°C.
Figure 7.43: $2M$ values as a function of $(h^2 + k^2 + l^2)$: aged 3840 minutes at 200°C.
Figure 7.44: Simulated {002} diffraction profile with the quasiline shifted by $-0.35^\circ 2\theta$: aged for 960 minutes at 200°C.

in the reciprocal space, as mentioned in Section 7.1.2.

7.2.2 Other Factors Contributing to Diffraction Profiles

The calculated diffraction profiles do not agree well with the experimental ones for 200°C aging samples, especially for the diffraction peaks that have large components in the {001} directions, the direction of the flat face of the ellipsoidal precipitates. The slight mismatch in positions for the {111}, {220}, and {222} peaks are believed to be due to the “powder diffraction effect” discussed in Section 7.1.2. According to Chapter 5, the diffuse scattering near these reflections has strong intensity in the plane perpendicular to the diffraction vectors. The peak shifts also get more severe with increasing aging time. This is consistent with the explanation because longer aging time causes more intensity to be redistributed from the Bragg peaks to the diffuse scattering thus enhancing the effect.

The peaks which have the most serious mismatching problem are {002}, {113}, and
Figure 7.45: Simulated \{113\} diffraction profile with the quasiline shifted by $-0.4^\circ 2\theta$: aged for 960 minutes at 200°C.
Figure 7.46: Simulated \{004\} diffraction profile with the quasiline shifted by $-1.0^\circ 2\theta$: aged for 960 minutes at 200°C.
Figure 7.47: Simulated \{002\} diffraction profile with the quasiline shifted by $-0.35^\circ 2\theta$: aged for 3840 minutes at 200°C.
Figure 7.48: Simulated \{113\} diffraction profile with the quasiline shifted by \(-0.4^\circ 2\theta\): aged for 3840 minutes at 200°C.
Figure 7.49: Simulated {004} diffraction profile with the quasiline shifted by $-1.0^\circ 2\theta$: aged for 3840 minutes at 200°C.
{004}. For these peaks, the diffuse scattering needs to shift a bit more to the lower angle side in order to match to experimental results. The amount of the diffuse scattering relative to the Bragg peaks appears to be in accord with those associated with the observed profiles. In fact, as shown in Figures 7.44–7.49, the agreement between experimental and calculated profiles is greatly improved if the quasiline in the profiles are shifted to the low angle side by the amount indicated in the figure captions. The mismatching problem can not be cured by changing the parameters of the elastic model. It is believed that they are caused by some other factors not considered in the model.

The diffuse scattering produced by the Be rich clusters in the Cu matrix is at the lower side of the Bragg diffraction. This is because the precipitates' elastic effect expands the matrix surrounding them. The expansion in the average lattice parameter causes the diffuse scattering to be located in a smaller diffraction angle. The above simulation results indicate that more expansion of the matrix around the precipitates are necessary to explain the experimental profiles.

One possible source of this extra expansion can be provided by the diffusion concentration gradients around the precipitates as described in Chapter 1. If the growth mechanism of the precipitates is diffusion controlled or mixed controlled, the Be concentration near the precipitate surface is smaller than that in the matrix far away from the precipitates. The smaller Be concentration leads to a greater average lattice parameter since Be is a smaller atom than Cu. This effect will give an extra lattice expansion not considered in the elastic model.

By comparing the calculated and experimental diffraction profiles for samples aged at 200°C and 315°C, it is clear that, whatever the cause for this expansion effect is, the mechanism should exist only at 200°C and not at 315°C, because the mismatch problem is only observed for samples aged at the lower temperature. If the diffusion effect is the cause, it must satisfy this criterion as well.

As discussed briefly in Chapter 1, large inter-particle spacing, small diffusion coefficient, and early stage of reaction tend to encourage the formation of a concentration gradients around the surface of the precipitates. More concisely, for a diffusion process with diffusion coefficient $D$ and at a time $t$ after the start of the process, if the "diffusion distance," $\sqrt{2Dt}$, is smaller than or close to the inter-precipitate spacing $d$, there should be
a concentration gradient. On the other hand, if $\sqrt{2Di} \ll d$, the diffusion progresses much further than the inter-precipitate spacing, the concentration profile in the matrix should be almost flat.

There is no accurate diffusion coefficient study of Be in Cu in the literature. However, a rough estimate of the diffusion coefficient can be obtained from diffusion coefficients for other elements in copper. Experimental studies have been done on the diffusion of isotopes of hydrogen, H, D, and T, in copper single crystals [72]. In the form of

$$D = D_0 e^{-\Delta H/RT},$$

(7.5)

the results were,

<table>
<thead>
<tr>
<th>$H$</th>
<th>$D$</th>
<th>$T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_0 (10^{-3} \text{cm}^2/\text{sec})$</td>
<td>11.31 ± 0.40</td>
<td>7.30 ± 1.05</td>
</tr>
<tr>
<td>$\Delta H (\text{cal})$</td>
<td>9286 ± 65</td>
<td>8794 ± 244</td>
</tr>
</tbody>
</table>

Following the trend of the mass dependency in these three elements, it is reasonable to assume that for Be atoms, which have a atomic weight of 9.023, should approximately have [72]

$$D_0 = 3.7 \times 10^{-3} \text{cm}^2/\text{sec},$$

$$\Delta H = 8600 \text{ cal}.$$

The ratio of $D_0$ for Be to $D_0$ for H is approximately equal to the square root of their mass ratio, agreeing with the principle of the authors of the paper tried to demonstrate. The $\Delta H$ for Be in Cu in the above equation is only the portion of the activation energy that deals with the movement of the Be atoms. Because Be diffuses in Cu substitutionally, the total activation energy should include the formation energy of a vacancy in Cu as well. According to [73] (Page 39), the vacancy formation enthalpy for a vacancy in Cu is 1.03 eV. This translates to an energy of 23746 cal per mole. Therefore, the total activation energy of diffusion for Be in Cu is 32346 cal. With these values, the diffusion coefficient of Be in Cu
can be evaluated using Eq. (7.5). The results are,

\[ D = 5.23 \times 10^{-18}\text{cm}^2/\text{sec}, \quad \text{for } T = 200^\circ\text{C}, \]
\[ D = 4.20 \times 10^{-15}\text{cm}^2/\text{sec}, \quad \text{for } T = 315^\circ\text{C}. \]

Using these numbers, for \( t = 960 \) minutes at 200\(^\circ\)C,

\[ \sqrt{2Dt} = 7.76 \times 10^{-7}\text{cm} = 77.6\text{Å}, \]

and, for \( t = 15 \) minutes at 315\(^\circ\)C,

\[ \sqrt{2Dt} = 2.75 \times 10^{-6}\text{cm} = 275\text{Å}. \]

At both times, the inter-precipitate spacing is approximately 100Å. Therefore, it is possible to have a concentration gradient around the precipitates when aged at 200\(^\circ\)C, and the gradient should not be present when aged even for just 15 minutes at 315\(^\circ\)C.

Quantitative evaluation of the effect of the concentration profiles on the diffraction patterns requires the accurate modeling of the diffusion concentration profiles around the ellipsoidal precipitates and the elastic implications of the profiles on the matrix both near and far away from the surface of the precipitates. Ham [74] studied the diffusion-controlled growth of precipitates and the concentration profiles around them. But the theory was limited in cases when the precipitates were very small and had large inter-particle spacing. Krivoglaz investigated the diffraction effects of several shapes of concentration profiles around a spherical precipitates in an isotropic continuum.

We attempted to estimate the elastic effect of some fictitious concentration profiles around an ellipsoidal precipitate with simple scaling of the field according to a rule derived from Krivoglaz's work [75]. The result was unsuccessful in matching the positions of the experiment curves. More accurate modeling of both the concentration profiles and the elastic effect of them are needed. The concentration profile around an ellipsoid should be significantly different from that around a sphere because of the large nearly flat surface of a flat ellipsoid like the ones we considered. Therefore, it is possible that the concentration profile affects mostly the displacement components in the flat direction of the ellipsoid.
Table 7.9: Parameters used to calculate diffraction profiles.

<table>
<thead>
<tr>
<th>Sample Condition</th>
<th>Transformation Strain</th>
<th>Matrix Composition</th>
<th>Site Probability</th>
<th>Defect Dimension</th>
<th>Elastic Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aged for 15 minutes at 315°C</td>
<td>$\epsilon_{11} = 0.112$</td>
<td>$\epsilon_{33} = -0.334$</td>
<td>$8%$</td>
<td>$4.49 \times 10^{-5}$</td>
<td>$a = 45\AA$</td>
</tr>
<tr>
<td></td>
<td>$\epsilon_{22} = 0.112$</td>
<td></td>
<td></td>
<td></td>
<td>$b = 45\AA$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$c = 1.9\AA$</td>
</tr>
<tr>
<td>Aged for 30 minutes at 315°C</td>
<td>$\epsilon_{11} = 0.128$</td>
<td>$\epsilon_{22} = 0.128$</td>
<td>$5%$</td>
<td>$6.74 \times 10^{-6}$</td>
<td>$a = 100\AA$</td>
</tr>
<tr>
<td></td>
<td>$\epsilon_{33} = -0.368$</td>
<td></td>
<td></td>
<td></td>
<td>$b = 100\AA$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$c = 5\AA$</td>
</tr>
<tr>
<td>Aged for 960 minutes at 200°C</td>
<td>$\epsilon_{11} = 0.114$</td>
<td>$\epsilon_{22} = 0.114$</td>
<td>$6%$</td>
<td>$1.01 \times 10^{-4}$</td>
<td>$a = 40\AA$</td>
</tr>
<tr>
<td></td>
<td>$\epsilon_{33} = -0.338$</td>
<td></td>
<td></td>
<td></td>
<td>$b = 40\AA$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$c = 1.7\AA$</td>
</tr>
<tr>
<td>Aged for 3840 minutes at 200°C</td>
<td>$\epsilon_{11} = 0.125$</td>
<td>$\epsilon_{22} = 0.125$</td>
<td>$5%$</td>
<td>$8.43 \times 10^{-5}$</td>
<td>$a = 40\AA$</td>
</tr>
<tr>
<td></td>
<td>$\epsilon_{33} = -0.360$</td>
<td></td>
<td></td>
<td></td>
<td>$b = 40\AA$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$c = 2.5\AA$</td>
</tr>
</tbody>
</table>

thus creating an “anisotropic” shifting of the diffuse scattering, i.e., the peaks that have a large components are shifted the most while the other peaks are nearly unaffected. With the introduction of the concentration profiles, the parameters of the size and shape of the precipitates are expected to change since the elastic influence in the region far away from the precipitates and the number of precipitates are function of the profiles. The parameters obtained in the above simulations need to be re-examined with a more exact model.

Table 7.9 lists the parameters used to calculate the diffraction profiles for the four samples in this Chapter.

7.3 Discussions

7.3.1 X-ray Scattering from Aged Alloys

In our classification scheme, the diffraction from any material is divided into two parts, the Bragg diffraction and the diffuse scattering. The relative intensity between the two is controlled by the attenuation factor $2M$, which is in turn determined by the distortion in the lattice through Eq. (6.22) or (6.23). In one chooses, the diffuse scattering can be further
divided into two components, the static diffuse scattering and the quasiline. The former is important when the distortion is small, and the latter dominates when the distortion is large.

In the extremely early stage of aging, the sizes of the precipitates are small. Consequently, the elastic distortion is small, thus the value of $2M$ is small. Therefore, most of the diffracted intensities belong to the Bragg peak. The diffuse scattering is mostly the static diffuse scattering component, which is sharp and located near the Bragg reflections.

With the precipitate growing as aging progresses, elastic distortion created by the precipitates in the matrix gets more prominent. The value of $2M$ increases, causing more intensity to be re-distributed from the Bragg peaks to the diffuse scattering, and the quasiline becomes a larger and larger portion of the diffuse intensities at the expense of the static diffuse component. Because of this, the total diffuse scattering gets broader and shifts its maximum further away from the Bragg diffraction positions. With atoms with smaller dimension forming clusters, the shift is to the low angle side of the Bragg peaks. The effects of this intermediate stage of aging are illustrated by the computer simulations presented in this Chapter.

When the precipitates grow to very large sizes, the matrix gets severely distorted by the elastic fields generated by the precipitates. As a result, the value of $2M$ becomes so large that the integrated intensity of the Bragg peak, proportional to $e^{-2M}$, is practically zero. All scattered intensity goes to the diffuse scattering (or the quasiline), which is very broad and shifted even further away from the Bragg peak positions. This stage corresponds to from 30 minutes to 3 hours of aging at 315°C for the Cu-Be alloy used.

In the above situations, the interface between the precipitates and the matrix is assumed to be coherent. Therefore, the distortion increases with increasing precipitate size. At one point, however, it may be energetically more favorable for the interface between precipitates and the matrix to become incoherent or semi-coherent. From this time on, the strain in the matrix caused by the elastic influence of the precipitates is relaxed. This results in sharper diffraction lines from the matrix. The experimental profiles from 24 hours and 168 hours aged sample at 315°C confirm this conclusion. The decline of the hardness values for these samples also implies that the incoherency starts around 5 hours of aging at this temperature.
Without a detailed model of how the incoherency starts and proceeds, it is impossible to analyze quantitatively the diffraction profiles after the incoherency occurs. The elastic model presented in Chapter 3 can deal only with coherent interfaces. The following discussions are concerned with this situation only.

Although it is the general trend that the diffuse scattering gets broadened and is shifted further away from the Bragg peak positions with increasing 2M values, and the values of 2M increases with increasing sizes of the precipitates, there are a few other factors which influence the diffraction profile properties as well.

The first is that the value of 2M increases also with the length of the diffraction vector. The diffraction vector comes into Eq. (6.23) as \( \mathbf{H} \cdot \mathbf{u} \). The physical reason behind this is that the lattice parameter for a higher order peak is smaller than that of a lower order peak. The same lattice distortion is therefore "felt" much more severely by the higher order peaks, thus leading to a greater 2M value.

The second factor is that the diffraction patterns for diffraction vectors that have different directions can not be compared by their 2M only. As discussed in Section 7.1.2, because the special spatial distribution around Bragg reflections caused by the tetragonal distortion, the diffuse scattering for \{222\} is sharper and closer to the its Bragg peak than its counterpart for \{113\}, although \{222\} peak has a greater 2M.

The third factor is an interesting one. An increase in the long semi-axes of the ellipsoidal precipitates makes the diffuse scattering (quasiline) sharper although it also increases the resultant 2M. This is probably because the increase of the diameter of ellipsoid creates a more uniformly spaced matrix volume above the flat surface of the ellipsoid. Uniform spacing leads to sharp diffraction peaks.

Finally, because of the special effect of the transformation strain on the intensity distributions around the Bragg peaks, the increase of the tetragonality of the transformation strain \( |(\epsilon_{11}^T - \epsilon_{33}^T)|/\frac{1}{3}(2\epsilon_{11}^T + \epsilon_{33}^T) \) should sharpen the \{111\}, \{220\}, and \{222\} diffuse scattering and in the mean time broaden the \{002\}, \{113\}, and \{004\} diffuse scattering. However, the increase of the tetragonality also increases the value of 2M in a significant way, which broadens all peaks. The two effects can not be separated cleanly.

All changes of other factors, like the length of the short semi-axis, the amount of Be that goes into the precipitates, give expected results, i.e., at the same time when the 2M is
increases, the diffuse scattering is also broadened and shifted away.

As to the determination of precipitate parameters using computer simulations, the method is more effective for samples in the intermediate stage, where the values of 2M is not too large. In these cases, the Bragg peaks are still sharp and clearly recognizable. The partition of intensities between the Bragg peaks and the diffuse scattering puts strict conditions on the the value of 2M and parameters of the precipitates. A parameter change which causes a 10% change in 2M produces huge effects on the higher order peaks. Therefore, relatively little degree of freedom exists for the precipitate parameters thus allowing more accurate estimation of them. In the cases for which 2M is very large, all intensities are lumped into the quaselines. No partitioning of intensities between the Bragg scattering and the diffuse scattering can be used as references in determining 2M. There can be a large range of 2M's that still match the experimental profiles. The parameters of the precipitates can not be determined accurately. Furthermore, when the distortion becomes so large, the diffraction profiles will be very sensitively to the fields in the vicinity of the precipitates. The exact shape of the precipitates, i.e., whether they are ellipsoids or disks, becomes very important. Therefore, the calculated parameters for the precipitates may not correspond well to the actual situations when the 2M is too large.

7.3.2 Phase Transformation Sequence and Mechanical Property

It was concluded in Chapter 5 that there is a tetragonal stress-free transformation strain associated with the precipitates in the very early stage of aging. It was also speculated that the possible cause of the transformation strain is the transformation from the fcc unit cell in as-quenched Cu-Be alloy to the B2 unit cell in the equilibrium γ. The precipitates were then assumed to be of the structure of γ throughout the precipitate sequence. This assumption was carry over to the elastic and diffraction model used in Chapter 6 and this chapter. The computer simulation using this model successfully calculated the diffraction profiles from samples aged at 315°C.

The assumption that the "GP zones" are also a matrix constrained version of γ is a natural extension of the recent theory by Khachatryan and Laughlin [21], who demonstrated that γ″ and γ′ can be matrix constrained γ. In their theory, the GP zones were assumed to have a volume change only strain relative to the matrix, which, according to Chapter 5,
can not explain the (110) streaking effect observed.

The precipitation sequence of an alloy is controlled by the relative importance of various types of energies at different stages of precipitation. There are two types of energies that are always present in any phase transformations. These are the interface free energy and the bulk free energy. The interface free energy tends to decrease the total surface area of the precipitates and the bulk free energy tries to increase the total volume of the precipitates. In Cu-Be alloys, because of the large size difference between the Cu and Be atoms, strain energy produced by the precipitates plays a very important role in the precipitate process. The strain energy depends not only on the volume of the precipitates, but also the shape (aspect ratio), habit plane orientation, and coherency between the surface of the precipitates and the matrix.

At the initial stage of the precipitation, the size of the precipitates is small. The effect of the surface free energy dominates, and the shape of the precipitates is roughly spherical. As the precipitate grows, the strain energy increases. It becomes energetically more favorable for the precipitates to have a flat shape lying on (100) planes in matrix such as Cu [21]. At this stage, the effect of the surface free energy still functions: the (100) habit plane has the best lattice matching capability between the precipitate lattice and the matrix. As the aging continues further, the need to reduce the strain energy overcomes the tendency of staying in a "good" habit plane by changing the precipitate habit plane to (113) to (112), on which the precipitates can have lower strain energy, as shown in [21]. After that, the coherency on the surface of the precipitates breaks down. The increase of surface free energy due to an incoherent surface is offset by the reduction in the strain energy, which is dominant at this moment. The bulk free energy is the driving force behind the precipitate growth.

Under this scheme, the GP zones, \( \gamma'' \), and \( \gamma' \) precipitates are just difference instances of \( \gamma \) under different conditions. Because the severe elastic distortion the matrix asserts on them, the precipitates can appear to be tetragonal, monoclinic, etc., in different stage of aging. Furthermore, since the precipitates have different strain energy associated with them, the matrix can also have varying Be concentrations, as illustrated in Figure 7.50. In the "GP zone" stage, for example, the precipitates have more strain energy per atom, and the free energy curve appears higher up. The common tangent intersects with the free energy curve of the matrix at a greater concentration of Be compared with the cases of \( \gamma'' \),
Figure 7.50: Free energy diagram of matrix and precipitates. Note that different precipitates have different "equilibrium" matrix concentration.
As the precipitates grow and change appearance, the hardness of the alloy increases initially, reaches a maximum and slowly decreases. From the experimental data presented in Chapter 2, the alloy reaches maximum hardness after about 5 hours of aging at 315°C. At this time, the average precipitate separation in the crystal is 200–300Å. According to the theory briefly described in Chapter 1, this critical separation signifies that the dislocation movement in the crystal starts bowing around the precipitate obstacles. Before this time, the dislocation moves mainly be cutting through hard precipitates. From the X-ray diffraction patterns, 5 hours of aging also correspond to the time when the interface between the precipitates and the matrix starts to become incoherent. This relaxes part of the strain in the matrix caused by the elastic interaction. The coincidence of time between the decrease of hardness values and the loss of interface coherency indicates that the coherency strain before this time may have contributed to the nice age-hardening property of the Cu-Be alloy.
Chapter 8

Summary

In the research presented in this dissertation, X-ray polycrystalline diffraction techniques are used to determine the defect structures in a commercial Cu-Be-Co alloy in the process of low temperature aging. The analysis of the X-ray diffraction patterns is aided by the computer modeling of the defects using an elastic model. It was hoped that this would provide more detailed understanding of the precipitate structures in the process of aging and more insight into the age hardening mechanism of the alloy.

The diffraction profiles from a series of samples aged for different times at 315°C are collected using a position sensitive proportional counter with Cu $K_{\alpha_1}$ radiation. The hardness values for the samples are also measured. Several samples aged at 250°C are examined with low angle scattering. It is concluded that, since no low angle peaks were observed, no regular periodicity with period smaller than 94Å exists in the samples.

An elastic model for coherent precipitates in anisotropic matrix is developed using Eshelby's method of evaluating transformed regions in an elastic continuum. The displacement fields generated from a transformed ellipsoid in the matrix are calculated, provided that the elastic constants of the precipitates are the same as the matrix. It is shown that a constant stress-free transformation strain results in constant final strain inside any ellipsoidal inclusions. Based on this fact, ellipsoidal precipitates with different elastic constants can also be handled by the theory. An equivalent stress-free transformation strain can always be obtained and substituted into the formulae that deal with same elastic constants. The displacement fields generated by a transformed flat disk are also
calculated, but only cases with same elastic constants inside and outside of the disk can be handled.

The elastic model, along with the Huang diffuse scattering (HDS) theory by Ded-erichs [37], is used to explain the strong ⟨110⟩ diffraction streaks near certain Bragg reflections reported in the literature. It is concluded from the analysis that a tetragonal stress-free transformation strain associated with the precipitates is necessary for these streaks to occur. With a computer simulation of the HDS from matrix containing disk-like ellipsoidal precipitates, it shows that these streaks can indeed be observed under these conditions.

The HDS analysis forms the basis for parameter selection in the later computer calculation of powder diffraction profiles. The existence of the tetragonal stress-free transformation strain at the very early stage of precipitation leads to the assumption that GP zones are also matrix constrained version of γ, just like γ″ and γ′ as suggested by Khachaturyan and Laughlin [21].

A general X-ray diffraction theory describing the scattering from crystals containing random identical defects is developed, combining the work of Krivoglaz [39] and Ded-erichs [45]. The theory is also extended to the case of powder scattering and multiple kinds of defects. An algorithm is designed to calculate the diffraction profiles accurately and efficiently.

The algorithm is implemented and applied the several Cu-Be samples aged for different times at 315°C and 200°C, using the elastic model developed as the model for the precipitates. The calculated diffraction profiles compare very well with the experimental ones for samples aged at 315°C, not as favorably for samples aged at 200°C. It is proposed that the discrepancy at the lower aging temperature may be due to concentration gradient of Be near the surface of the precipitates due to diffusion limited growth.

It is the result of the theory and the computer calculation that the diffraction from materials containing defects can be divided into two parts, the Bragg diffraction and the diffuse scattering. If one chooses, the diffuse scattering can be further categorized into static diffuse scattering and quasi-line. The partitioning of the total diffraction intensities is controlled by a factor $2M$. The intensity of the Bragg peak is proportional to $e^{-2M}$, and the intensity of the total diffuse scattering is proportional to $(1 - e^{-2M})$, with the static diffuse scattering and the quasi-line getting $2M e^{-2M}$ and $(1 - e^{-2M} - 2Me^{-2M})$, respectively. The
values of $2M$ increase with the growth of the precipitates and the elastic distortion in the lattice. As the result, the intensity under the Bragg peak becomes smaller and smaller because of the attenuation factor, and the diffuse scattering gets more and more shares of the total intensity. In the mean time, the maxima of the diffuse scattering are shifted away from the original Bragg peak positions and broadened as the quasiline portion of the diffuse scattering becomes more important.

The values of $2M$ are proportional to the square of the distances from the center of the reciprocal space when the distortion is not too large. With greater distortions, the trend of increment still holds but not as rapid. The relative intensity between the Bragg peak and the diffuse scattering always follows the values of $2M$. The shape and position of the diffuse scattering, however, depend on a few more factors. The tetragonal stress-free transformation strain in the precipitates makes the powder diffraction very sharp and close to the Bragg peaks for diffraction vectors in the $\{111\}$ direction, i.e., the $\{111\}$ and $\{222\}$ peaks. This effect is the reason why the $\{222\}$ peaks always appear to have less diffuse scattering than the $\{113\}$ peaks, although the former is further out in the reciprocal space. The sharpness of the diffuse scattering creates the illusion that it is part of the Bragg peak. The special spatial distribution of the diffuse scattering near certain Bragg reflections is also the reason for the slight peak maxima upward shifts for the $\{111\}$, $\{220\}$, and $\{222\}$ peaks. Another interesting factor for the shape of the diffuse scattering is that an increase of the diameter of the precipitates decreases the width of the diffuse scattering (quasiline) although it makes to value of $2M$ greater.

At the later stages of aging, the diffraction profiles from the matrix get sharper. From the TEM observations during the same period of aging time, the precipitates change habit planes and become incoherent as they grow. The relax of the elastic strain in the lattice causes the diffraction peaks to sharpen. The X-ray scattering from the precipitates, although does not show the habit plane changes, confirms the growth of the precipitates and the drift of the precipitate lattice parameters as observed by TEM experiments [13, 14].

From the X-ray diffraction results and the computer simulation, the inter-particle spacing when the hardness of the material reaches maximum is 200–300Å. The time, 5 hours of aging at 315°C, also coincides with the approximate time range when the interface between the precipitates and the matrix loses its coherency. It is possible that the coherency strain
contributed to the age hardening property of the Cu-Be alloys.

Due to the success of the computer simulation of the diffraction profiles with the $\gamma$ like GP zones in the intermediate stage of aging, the assumption that the GP zones are also the matrix constrained version of $\gamma$ gets re-affirmed. The new precipitation sequence of the Cu-Be alloys can be explained with the competition of the different types of free energies: the bulk free energy, the interface energy, and the strain energy.

In this dissertation, a new and simple way of calculating the thermal diffuse scattering (TDS) using the lattice Green function. This method is used to illustrate the principles of evaluating the diffuse scattering in a polycrystalline material with a texture. It is useful for the quantitative evaluation of diffuse scattering in such important kind of materials.
Bibliography


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Appendix A

Programs Listings

A.1 Elastic Fields around an Ellipsoid

A.1.1 Programs

```fortran
implicit double precision (a-h,o-z)
dimension eps(3,3),d(3,3),sigma(3,3),u(3,3),g(3,3),sum(3,3,3)
dimension xx(3),x(3),a(3),c(3,3,3),z(80),w(80)
dimension sigm2(3,3),dil2(3,3),u3(3),dip(3,3),eps2(3,3)
dimension dc(3,3),x(3),eps3(3,3),eps4(3,3),u3(3),u4(3)
dimension dil3(3,3),dil4(3,3),sigm3(3,3),sigm4(3,3),dil7(3,3)
dimension dil5(3,3),dil6(3,3),sigm5(3,3),sigm6(3,3),u5(3),u6(3)
dimension eps5(3,3),eps6(3,3),eps7(3,3),sigm7(3,3),u7(3)
pi=dacos(-1.0)
    c
    do 86328 i=1,3
     read(5,*)dc(i,j),j=1,3
     dcll=dsqrt(dci(1,1)**2+dc(i,2)**2+dc(i,3)**2)
     do 86328 j=1,3
86328 dc(i,j)=dcll(dci,j)/dcll
    c
    read(5,*)a
    read(5,*)cl1,cl2,c44
    read(5,*)(( eps(1,j),j=1,3),i=1,3)
    read(5,*)(( eps2(1,j),j=1,3),i=1,3)
    read(5,*)nl,m1
    c
    call zw(ml,z,w)
    if (ml.eq.0) goto 74896
    call cijkl(c,cl1,cl2,c44)
    do 820 i=1,3
    do 820 j=1,3
    sigma1,j=0.d0
    do 830 li=1,3
    do 830 jj=1,3
    sigma1,j=sigma1,j+c(li,jj)*epst(li,jj)
830 continue
820 continue
    c
    do 1005 jjj=0,300,10
    do 111 kkk=0,10
```

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if (jjjj.eq.0.and.kkkk.ne.0) goto 105
  x(1)=jjjj*dcos(kkkk*pi/5.)
x(2)=jjjj*dsin(kkkk*pi/5.)
do 111 lii=0,500,5
  x(3)=iiii
  do 222 lii=1,3
  r(lii)=dd0
  do 333 jjj=1,3
  r(lii)=r(lii)+dc(jjj,lii)*x(jjj)
  333 continue
  continue
  do 105 lii=1,3
  t(iii)=sqrt(r(iii)/a(iii))
  105 continue
  iiii=0
  if ((t(2).ge.t(3)).and.(t(2).ge.t(1))) then
    iiii=2
    call rotate(r(1),r(2),r(3))
    call rotate(a(1),a(2),a(3))
    do 706 lii=1,3
    call rotate(sigma(1,1),sigma(1,2),sigma(1,3))
    706 continue
    do 705 lii=1,3
    call rotate(sigma(1,i),sigma(2,i),sigma(3,i))
    705 continue
  elseif ((t(1).ge.t(2)).and.(t(1).ge.t(3))) then
    iiii=1
    call rotate(r(1),r(2),r(3))
    call rotate(r(1),r(2),r(3))
    call rotate(a(1),a(2),a(3))
    call rotate(a(1),a(2),a(3))
    do 406 lii=1,3
    call rotate(sigma(1,1),sigma(1,2),sigma(1,3))
    call rotate(sigma(1,1),sigma(1,2),sigma(1,3))
    406 continue
    do 407 lii=1,3
    call rotate(sigma(1,i),sigma(2,i),sigma(3,i))
    call rotate(sigma(1,i),sigma(2,i),sigma(3,i))
    407 continue
  end if
  do 100 lii=1,3
  do 100 jji=1,3
  do 100 lii=1,3
  sum(i,j,1)=0.d0
  h=pi/n1
  do 712 lii=0,n1
    mult=2
    if ((ii.eq.0).or.(ii.eq.n1)) mult=1
    phi=ii*h
    call limit(phi,r,a,x11,x12,x13,x14)
    cosphi = dcos(phi)
    sinphi = dsqrt(1.d0-cosphi*cosphi)
    c1=(x12-x11)*0.5d0
    d1=(x12+x11)*0.5d0
    do 200 jji=1,m1
      theta=ci. z(jji)+d1
      costheta = dcos(theta)
      sintheta = dsqrt(1.d0 - costheta*costheta)
      xk(1)=cosphi*sintheta
      xk(2)=sinphi*sintheta
      xk(3)=costheta
      r*xr=r(1)*xk(1)+r(2)*xk(2)+r(3)*xk(3)
      200 continue
axk=a(1)*a(1)*xk(1)*xk(1)+a(2)*a(2)*xk(2)*
    xk(2)+a(3)*a(3)*xk(3)*xk(3)
call greencu(c1l,c12,c44,xk,g)
xmid=xk*sintheta* w(jj)*0.5d5*h*mult*c1/dsqrt(axk**3)
do 300 j=1,3
do 300 i=1,3
do 300 l=1,1
   sum(i,j)=sum(i,1,j)*g(i,1,l)*xk(j)*xmid
300 continue
200 continue
   if (x13.gt.1d-8) then
      x11=x13
      x12=x14
      x13=0.0d0
      x14=0.0d0
      goto 10
   end if
712 continue
do 310 j=1,3
   sum(1,2,j)=sum(2,1,j)
   sum(1,3,j)=sum(3,1,j)
310 sum(2,3,j)=sum(3,2,j)
do 8 i=1,3
   u(i)=0.0d0
   do 9 jj=1,3
      u(j)=u(jj)+sum(i,i,jj)*sigma(i,jj)
9 continue
   u(i)=u(i)*a(1)*a(2)*a(3)/(2.0d0*pi)
8 continue
do 905 l=1,iii
   call rotate(r(i),r(2),r(3))
   call rotate(u(i),u(2),u(3))
   call rotate(a(i),a(2),a(3))
do 903 j=1,3
      call rotate(sigma(1,j),sigma(2,j),sigma(3,j))
903 continue
do 904 jj=1,3
      call rotate(sigma(j,1),sigma(j,2),sigma(j,3))
904 continue
905 continue
   varvr=(u(1)*dc(3,1)+u(2)*dc(3,2)+u(3)*dc(3,3))*1d-5
   write(6,20)varvr
20 format(7e11.5)

1005 continue
74896 end
C subroutine rotate(a,b,c)
double precision x,a,b,c
x=c
x=b
b=a
a=x
return
end subroutine limit(phi,r,a,x11,x12,x13,x14)
implicit double precision (a-h,o-z)
dimension r(3),a(3)
pi=dcos(-1.0d0)
b=r(1)*dcos(phi)+r(2)*dsin(phi)
d=a(1)*a(1)*dcos(phi)**2+a(2)*a(2)*dsin(phi)**2
deltas=(3)*a(3)*b*b*(r(3)*r(3)-a(3)^2)*d
if(delta.le.0.0) then
  x1=0.0d0
  x2=pi
  x3=0.0d0
  x4=0.0d0
else if(dabs(r(3)*r(3)-a(3)^2).gt.1d-8 ) then
  theta=atan2((r(3)*r(3)-a(3)^2),(-r(3)*b+dsqrt(delta)))
  if(theta1.lt.0.) theta1=theta1+pi
  theta2=atan2((r(3)*r(3)-a(3)^2),(-r(3)*b-dsqrt(delta)))
  if (theta21 gt theta2) theta2=theta2+pi
  theta3=theta1
  theta1=theta2
  theta2=theta3
end if
else if((r(3)*r(3)-a(3)^2).lt.1d-8 ) then
  x1=theta1
  x2=theta2
  x3=0.0d0
  x4=0.0d0
else
  x1=0.0d0
  x2=theta1
  x3=theta2
  x4=pi
end if
else if (dabs(r(3)*b).lt.1d-8 ) then
  x1=0.0d0
  x2=pi
  x3=0.0d0
  x4=0.0d0
else if((r(3)*b).gt.1d-8 ) then
  theta=atan2(2.*r(3)*b,(d-b*b))
  if (theta1.lt.0.) theta1=theta1+pi
  x1=theta1
  x2=pi
  x3=0.0d0
  x4=0.0d0
else
  theta=atan2(2.*r(3)*b,(d-b*b))
  if (theta11 lt theta1) theta1=theta1+pi
  x1=0.0d0
  x2=theta1
  x3=0.0d0
  x4=0.0d0
end if
return
end

subroutine greenu(c11,c12,c44,xk,g)
implicit double precision (a-h,o-z)
dimension xk(3),d(3),g(3,3)
dd=c11-c12-2.0d0*c44
d(1)=c44+dd*xk(1)*xk(1)
d(2)=c44+dd*xk(2)*xk(2)
d(3)=c44+dd*xk(3)*xk(3)
d1=1.0d0
do 2 i=1,3
  d1=d1+(c12+c44)*xk(i)*xk(i)/d(i)
2 continue
do 3 i=1,3

do 3 j=1,1
   g(1,j)=-(c12+c44)*xk(i)*xk(j)/|d(i)*d(j)|
   if (i.eq.j) g(1,j)=g(1,j)+1./d(i)
 3 continue

! main program
 g(1,2)=g(2,1)
g(1,3)=g(3,1)
g(2,3)=g(3,2)
return
end

! subroutine cijkl(c,i1,i2,i3,i4)
 implicit double precision (a-h,o-z)
 dimension c(3,3,3,3)
 do 1 i=1,3
 do 1 j=1,3
 do 1 k=1,3
 do 1 l=1,3
1 c(i,j,k,l)=0.d0
c(i,i,i,i)=c11
c(i,i,i,2)=c11
c(i,i,2,2)=c11
c(i,2,2,2)=c11
c(1,1,1,1)=c11
c(1,1,1,2)=c11
c(1,1,2,1)=c11
c(1,1,2,2)=c11
c(1,2,1,1)=c11
c(1,2,1,2)=c11
c(1,2,2,1)=c11
c(1,2,2,2)=c11
c(2,2,1,1)=c11
c(2,2,1,2)=c11
c(2,2,2,1)=c11
c(2,2,2,2)=c11
c(1,1,1,1)=c11
c(1,1,1,2)=c11
c(1,1,2,1)=c11
c(1,1,2,2)=c11
c(1,2,1,1)=c11
c(1,2,1,2)=c11
c(1,2,2,1)=c11
c(1,2,2,2)=c11
c(2,2,1,1)=c11
c(2,2,1,2)=c11
c(2,2,2,1)=c11
c(2,2,2,2)=c11
c(i,i,i,i)=c11
c(i,i,i,2)=c11
c(i,i,2,2)=c11
c(i,2,2,2)=c11
c(2,2,2,2)=c11
return
end

! subroutine zw(ml,zw)
 implicit double precision (a-h,o-z)
 dimension z(80),w(80),zw(6)
 do 1 i=1,6
1 zw(i)=0.d0
 data zw/0.238619186083197d0,0.661209386466265d0,
1 0.932469514203152d0,0.d0,0.d0,0.d0/

! data w(1:6)
1 data w/0.467913934572691d0,0.360761573048139d0,
1 0.171324492379170d0,0.d0,0.d0,0.d0/
2 data z15/0.d0,0.201194093997435d0,0.394151347077563d0,
1 0.570972172608539d0,0.72447731360170d0,
2 0.848206583410427d0,0.937273392400706d0,
3 0.987992518020485d0,0.d0,0.d0,0.d0,0.d0,0.d0/
4 data w15/0.202578241925561d0,0.198431485327111d0,
1 0.186161000115562d0,0.166269205816994d0,
2 0.139570677926154d0,0.107159220467172d0,
3 0.070366047488108d0,0.030753241996117d0,
4 0.d0,0.d0,0.d0,0.d0,0.d0,0.d0/

! if (ml.eq.6) then

! c
do 1000 i=4,6
   z6(i)=z6(i-3)
   w6(i)=w6(i-3)
1000  continue
   do 9364 i=1,ml
      z(i)=z6(i)
      w(i)=w6(i)
9364  continue
   else (ml.eq.15) then
   do 2000 i=9,15
      z15(i)=z15(i-7)
      w15(i)=w15(i-7)
2000  continue
   else (ml.eq.40) then
      z(1)= .99823770971055920d0
      z(2)= .99072623069945701d0
      z(3)= .9725994996377426d0
      z(4)= .95791681921379165d0
      z(5)= .93281280827867653d0
      z(6)= .90209880696887429d0
      z(7)= .8659595032122595d0
      z(8)= .8246122308333116d0
      z(9)= .77830565142651939d0
      z(10)= .72731825518927110d0
      z(11)= .67195668461417954d0
      z(12)= .6125538896798023d0
      z(13)= .5494671259512920d0
      z(14)= .48307580168617871d0
      z(15)= .41377920437160500d0
      z(16)= .3419409082575847d0
      z(17)= .26815218500725368d0
      z(18)= .1926975070137110d0
      z(19)= .11608407067525521d0
      z(20)= .10772417506060822d-1
      w(1)= .45212770985331912d-2
      w(2)= .10498284531152814d-1
      w(3)= .16421058381907887d-1
      w(4)= .22245849194166957d-1
      w(5)= .27937006980023401d-1
      w(6)= .33460195282547847d-1
      w(7)= .38782167974477201d-1
      w(8)= .43870908185673272d-1
      w(9)= .48695807635072232d-1
      w(10)= .53227846983936824d-1
      w(11)= .5743976099391551d-1
      w(12)= .61306242492928939d-1
      w(13)= .64804013456601038d-1
      w(14)= .67912045815233394d-1
      w(15)= .70511647919286780d-1
      w(16)= .72886582395804059d-1
      w(17)= .74723169057968264d-1
      w(18)= .7611036190626242d-1
      w(19)= .77039818164247964d-1
      w(20)= .77505947978424811d-1
A.1.2 Sample Inputs to the Programs

-1.000000  1.000000  0.000000
-1.000000 -1.000000  2.000000
1.000000  1.000000  1.000000
40.000000 40.000000  1.750000
1.757798  1.340138  0.760752
0.0757343  0.0  0.0
0.0  0.0757343  0.0
0.0  0.0  -0.270511
50
40

The meaning of the parameters are

\[ a_{11} \quad a_{12} \quad a_{13} \quad \text{Vector } \perp \text{ to diffraction vector} \]
\[ a_{21} \quad a_{22} \quad a_{23} \quad \text{Vector } \perp \text{ to diffraction vector and the last one} \]
\[ a_{31} \quad a_{32} \quad a_{33} \quad \text{Diffraction vector} \]
\[ a \quad b \quad c \quad \text{Semi-axes of the ellipsoid} \]
\[ c_{11} \quad c_{12} \quad c_{13} \quad \text{Elastic moduli of the matrix} \]
\[ c_{21} \quad c_{22} \quad c_{23} \]
\[ c_{31} \quad c_{32} \quad c_{33} \quad \text{Stress-free transformation strain} \]
\[ n_1 \quad n_2 \quad n_3 \quad \text{Integration parameters} \]
\[ m_1 \quad \text{Please do not change} \]

The program produces an output file containing the displacement field projected onto the direction of the diffraction vector. It will be used as the input of the program described in the next section. The program accepts input from the standard input and outputs to the standard output. The program needs to be run \( n \) times for \( n \) non-equivalent directions (see Chapter 6).

A.2 Diffraction

A.2.1 Programs

IMPLICIT none
double precision DP(3,3),QQQ(3),K(3),rstep,rpstep,rastep
double precision qastep,ep1,ep2,ep3
double precision Q(302),TV(3,3),u,tur(61,15,151),tui(61,15,151)
double precision GPUN(3,3),boun,rbound,klen
double precision EPSI(3,3),CFAC(302),expon,excos,exsin,termr
double precision termri,termir,termil,swpr(101,15),swpi(101,15)
double precision swnt(101,15), swni(101,15)
double precision LAC, c11, c12, c44, can, a, b, c, rfin, rpfni, dfpf22
double precision pi, tvlength, vols, conc, voir, recd, recfi, cfl
double precision recf, recs, xint, xerr, angle, a1, a2, abserr, r1302;
double precision resabs, resasc, result, huang, work(1000)
double precision rangle(31), omega(302, 15), ramp(302, 15)
double precision sum(302, 15), sum2(302, 15), lamb(302, 15)
double precision aa, bb, cc, ends, endd, endf, endg, deita, deltsar
double precision sincf, pprf(101, 15), prpi(101, 15), sinc1, sinc2

double precision prn(101, 15), prni(101, 15), rv1, rv2

double precision hiamp(201), phiamp(201), phipr(201)
double precision prpiint(201), prnint(201), crstmp(201), crstmn(201)
double precision tmp1, tmp2, tmp3, tmp4, tmpf1, tmpf22

double precision dsin, dcos, dsqrt, dfloat, dacos, dabs

double precision i, j, kterm, nqr, nqr1, nqa, nr, nra, ntp, jj, index

double precision x41, last, ier, iwork(200), il, limit, il1

double precision *auxfile, field, outfile

common /trnsn, dp

common /posis/q, k, a1, a2, index

common /elast/c11, c12, c44, can, a, b, c

external huang

limit=20

read('"', '(a)') auxfile
read('"', '(a)') field
read('"', '(a)') outfile

open(7, file='auxfile', status='old')
open(8, file='field', status='old')
open(9, file='outfile', status='unknown')

READ(7, *) C11, C12, C44, LAC, NQR, NQR1, NQA, NR, NRA, NRP
READ(7, *) A, B, C, CF, CF, K(1), K(2), K(3), RFIN, RPFNI
READ(7, *) ITERM, DPPF22

CAN=C11-C12-2.*C44

PI=DACOS(-1.0D0)

DO 999 I=1,3

READ(7, *) (TV(I,J), J=1,3)

TVLENGTH=DSQRT(TV(I,1)**2+TV(I,2)**2+TV(I,3)**2)

DO 3548 J=1,3

TV(I,J)=TV(I,J)/TVLENGTH

3548 CONTINUE

READ(7, *) (EPSI(I,J), J=1,3)

K(I)=K(I)**2.*PI/LAC

999 continue

kien = dsqrt(k(1)**2+k(2)**2+k(3)**2)

C............Projected strain in diffraction coordinates in ellipsoids....

EP1=(EPSI(1,1)*TV(1,1)+EPSI(1,2)*TV(1,2)+EPSI(1,3)*TV(1,3))**K(1)+
1 K(2)*EPSI(2,1)*TV(2,1)+EPSI(2,2)*TV(2,2)+EPSI(2,3)*TV(2,3))**K(2)+
2 K(3)*EPSI(3,1)*TV(3,1)+EPSI(3,2)*TV(3,2)+EPSI(3,3)*TV(3,3))**K(3)+

EP2=K(1)**EPSI(1,1)*TV(1,1)+EPSI(1,2)*TV(1,2)+EPSI(1,3)*TV(1,3))**K(1)+
1 K(2)*EPSI(2,1)*TV(2,1)+EPSI(2,2)*TV(2,2)+EPSI(2,3)*TV(2,3))**K(2)+
2 K(3)*EPSI(3,1)*TV(3,1)+EPSI(3,2)*TV(3,2)+EPSI(3,3)*TV(3,3))**K(3)+

EP3=K(1)**EPSI(1,1)*TV(1,1)+EPSI(1,2)*TV(1,2)+EPSI(1,3)*TV(1,3))**K(1)+
1 K(2)*EPSI(2,1)*TV(2,1)+EPSI(2,2)*TV(2,2)+EPSI(2,3)*TV(2,3))**K(2)+
2 K(3)*EPSI(3,1)*TV(3,1)+EPSI(3,2)*TV(3,2)+EPSI(3,3)*TV(3,3))**K(3)
VOLS=(LAC**3/4.)**2

VOLR=DGRT(1./VOLS)*(2.*PI)**3
RECD=(VOLR**3./PI)**(1D0/3D0)/2.

DO 6112 J=1,3
   READ(7,*) (DP(J,J),JJ=1,3)
   c......read in displacement fields......
   c       do 913 i=1,nrp
   c         read(8,*)u
   c       u = klen*u
   c       tur(1,1,i) = dcos(u)-1.0d+00
   c       tui(1,1,i) = dsin(u)-u
   c
   913 continue
   c       do 914 i=2,2*nra-1
   c         do 914 j=1,nrp
   c         tur(1,i,j) = tur(1,1,j)
   c         tui(1,i,j) = tui(1,1,j)
   c
   914 continue
   c       do 915 i=2,nr
   c         do 915 j=1,2*nra-1
   c         do 915 ii=1,nrp
   c         read(8,*)u
   c         u = klen*u
   c         tur(1,j,ii) = dcos(u)-1.0d+00
   c         tui(1,j,ii) = dsin(u)-u
   c
   915 continue
   c
   c........Various grid steps for integration........
   c
   c         rpstep = rfin/dfloat(nrp-1)
   c         rastep = pi/dfloat(nra-1)
   c         rstep = rfin/dfloat(nr-1)
   c         qastep = 2.0d+00*pi/dfloat(nqa-1)
   c
   c         RECI=0.0005
   c         RECF=RECF*CF
   c         RECS=(RECF-RECI)/(NQR-1.)
   c
   c         Q(1)=RECI
   c         DO 6253 I=1,NQR-1
   c         Q(I+1)=Q(I)+RECS
   c
   6253 CONTINUE
   c
   c       do 786 ii=1,nr
   c         rl(ii) = rstep*dfloat(ii-1)
   c
   786 continue
   c       do 787 jj=1,nra*2-1
   c         rangle(jj) = rstep*dfloat(jj-1)
   c
   787 continue
   c
   c       do 9113 i=1,nqr
   c
   9113 cfac(i) = 1D0
   c
   9114 cfac(i) = 0.125D0
   c         do 9114 i=2,11
   c
   9114 cfac(i) = 0.25D0
   c         do 9115 i=12,63
   c
   9115 cfac(i) = 0.5D0
   c
   c         rbound = recd*cf1*0.5d+00
   c
   c
   c
   205
.........Huang intensity and Huang amplitude for powder.......
do 201 ii=1,nr
    termr = 0.3d+00
    termr = 0.0d+00
    termi = 0.0d+00
    idx = .false.
do 202 jj=1,nrp
    exp = g(index)*rstep*dfloat(j-1)
    excos = dcos(exp)
    exsin = dsin(exp)
    termr = termr+excos*trui(ii,jj,jj)
    termr = termr+excos*tui(ii,jj,jj)
    termi = termi+exsin*trui(ii,jj,jj)
    termi = termi+exsin*tui(ii,jj,jj)
    202 continue
    swpr(ii,jj) = termr-termi
    swpi(ii,jj) = termi+termr
    swnr(ij,jj) = termr+termi
    swni(ii,jj) = termi-termi
    201 continue

do 203 ii=1,nr
    do 203 jj=1,nra-1
        swpr(iii,jj) = (swpr(ii,jj)+swpr(iii,jj+nra-1))*rstep
        swpi(iii,jj) = (swpi(ii,jj)-swpi(iii,jj+nra-1))*rstep
        swnr(iii,jj) = (swnr(ii,jj)+swnr(iii,jj+nra-1))*rstep
        swni(iii,jj) = (swni(ii,jj)-swni(iii,jj+nra-1))*rstep
        swpr(ii,jj+nra-1) = swpr(ii,jj)
        swpi(ii,jj+nra-1) = -swpi(ii,jj)
        swnr(ii,jj+nra-1) = swnr(ii,jj)
        swni(ii,jj+nra-1) = -swni(ii,jj)
    203 continue

c.................Precipitate Scattering Amplitude.................
c
AA=(TV(1,1)/A)**2+(TV(1,2)/B)**2+(TV(1,3)/C)**2
DO 510 II=1,NR
DO 510 III=1,NRA+NRA-2
rv1 = r(iii)*dcos(rangle(iii))
rv2 = r(iii)*dsin(rangle(iii))
BB=TV(1,1)*(TV(2,1)*RV1+TV(3,1)*RV2)/A**2+
  TV(1,2)*(TV(2,2)*RV1+TV(3,2)*RV2)/B**2+
  TV(1,3)*(TV(2,3)*RV1+TV(3,3)*RV2)/C**2
CC=((TV(2,1)*RV1+TV(3,1)*RV2)/A)**2+
  (TV(2,2)*RV1+TV(3,2)*RV2)/B**2+
  (TV(2,3)*RV1+TV(3,3)*RV2)/C**2-1.0
delta = BB**2-AA**2
IF (delta.gt.0.000) then
don = SQRT(delta)
END1 = (-BB+delta)/aa
END2 = (-BB-delta)/aa
END5 = (END1+END2)/2.
END6 = DABS(END1-END2)*0.5d+00
tmp = Q(I)*ENDS
tmp2 = RV1*EP2+RV2*EP3
sinc1 = sincf((pi1+epi2)*endd)*endd*2.0d+00
prpr(iii,iii) = dcos(tmp1+tmp2)*sinc1*(-dfpf22)
prpi(iii,iii) = dsin(tmp1+tmp2)*sinc1*(-dfpf22)
sin2 = sincf((-pi1+epi2)*endd)*endd*2.0d+00
pvr(i,i,ii) = dcos(-tmp1+tmp2)*sinc2*(-dfpf22)
pri(i,i,ii) = dsin(-tmp1+tmp2)*sinc2*(-dfpf22)
else
    pvr(i,i,ii) = 0.0d+00
    pri(i,i,ii) = 0.0d+00
    prnr(i,i,ii) = 0.0d+00
    prnr(i,i,ii) = 0.0d+00
end
510 CONTINUE
C
C...........Summing up contributions from all columns........
C
phi(pri) = 0.0d+00
crtemp(i) = 0.0d+00
phi(pri) = 0.0d+00
crtemp(i) = 0.0d+00
prrint(i) = 0.0d+00
prnrnt(i) = 0.0d+00

620 iel=1,nr
    tmp1 = 0.0d+00
tmp11 = 0.0d+00
tmp2 = 0.0d+00
tmp22 = 0.0d+00
tmp3 = 0.0d+00
tmp4 = 0.0d+00
rangle(2*nra-1) = rangle(1)
so the integration goes from 1 to nra*2-2
do 610 jj=1,nra*2-2
    tmp1 = tmp1+(swpr(i,ii,jj)+prr(i,ii,jj))**2
    tmp11 = tmp11+2.0d+00*((swpr(i,ii,jj)
                   +prr(i,ii,jj))*ramp(ii,ii, jj)
                   +(swpr(i,ii,jj)+prr(i,ii, jj))*iamp(ii,ii, jj))
    tmp2 = tmp2+(swpr(i,ii,jj)+prnr(i,ii, jj))**2
    tmp22 = tmp22+2.0d+00*((swpr(i,ii, jj)
                   +prnr(i,ii, jj))*(-ramp(ii,ii, jj))
                   +(swpr(i,ii, jj)+prnr(i,ii, jj))*iamp(ii,ii, jj))
    tmp3 = tmp3+(prr(i,ii, jj))**2+prpr(i,ii, jj)**2
    tmp4 = tmp4+(prnr(i,ii, jj))**2+prpr(i,ii, jj)**2
710 continue
if (i.eq.1.or.i.eq.nr) then
    tmp1 = tmp1*0.5d+00
    tmp11 = tmp11*0.5d+00
    tmp2 = tmp2*0.5d+00
    tmp22 = tmp22*0.5d+00
    tmp3 = tmp3*0.5d+00
    tmp4 = tmp4*0.5d+00
endif
phi(pri) = phi(pri)+tmp1*rl(i, ii)
crtemp(i) = crtemp(i)+tmp1*rl(i, ii)
phi(pri) = phi(pri)+tmp2*rl(i, ii)
crtemp(i) = crtemp(i)+tmp2*rl(i, ii)
prrint(i) = prrint(i)+tmp3*rl(i, ii)
prnrnt(i) = prnrnt(i)+tmp4*rl(i, ii)
620 continue
phi(pri) = phi(pri)*rastep*retep
c...........All done...........
c
278 continue
c
..............Output..............
c
        format is q3, phi(r3), p(r3)
c
        write(9,'(1x,6e15.6)')(-q(i), phi(r3), p(r3))
1 +hint(i), prnt(i), hint(i). phi(r3),
2 crstmn(i). lsnqr, l-1
write(9,'(1x,6e15.6)') (q(i), phipr(i), crstmp(i), prmpint(i))
1 +hint(i), prtpint(i), hint(i). phipr(i),
2 crstmp(i), lsl=1, nqr
END
c
double precision function hamp(qr)
IMPLICIT none
double precision qr, qsums, sum, rsts, rstl, fac1
double precision dp(3,3), qqq(3)
double precision GFUN(3,3), q(302)
double precision g, tv(3,3), q1, a1, a2, gq, q2
double precision cl1, c12, c44, can, a, b, c, k(3)
integer kk, jj, jjl, index
common /trans/tv, dp
common /posis/q, k, a1, a2, index
common /elasc/c11, c12, c44, can, a, b, c
C q1 = qr * a1
gq = qr * a2
gq = q(index)
qqq(1) = (q3**2 + q1**2 + q2**2)
qqq(1) = (q3**2 + q1**2 + q2**2)
qqq(2) = (q3**2 + q1**2 + q2**2)
qqq(3) = (q3**2 + q1**2 + q2**2)
C
SUM=1.000
DO 6413 KK=1,3
6413 SUM=SUM+(C44+C12)/(C44+CAN*QQQ(KK)**2)*QQQ(KK)**2

DO 6412 JJ=1,3
6412 DO 6413 JJ=1,3
6413 SUM=SUM+(C44+C12)/(C44+CAN*QQQ(JJ)**2)*QQQ(JJ)**2

DO 6412 JJ=1,3
6412 IF(JJJ.EQ.JJ)G=0.1.000/(C44+CAN**QQQ(JJ)**2)
6412 GFUN(JJJ,JJ)=G/qqsums**2
C
HAMP=0.
DO 6313 JJJ=1,3
6313 DO 6313 JJJ=1,3
6313 HAMP=HAMP-K(JJJ) *GFUN(JJJ,JJ) *DP(JJJ, JJ)*QQQ(KK)
RSTS=(QQQ(1)**2+QQQ(1)**B)**2+QQQ(3)**C**2
RSTS=DSQRT(RSTS)
FAC1=qqsums*RSTS
HAMP=HAMP-1.0*DSQRT(FAC1) /FAC1**3*3.*qqsums
END
double precision function huang(qr)
    implicit none
    double precision qr, hamp
    huang = hamp(qr)**2*qr
    return
end

double precision function rhamp(rp)
    implicit none
    double precision rp, hamp
    rhamp = hamp(rp)**rp
    return
end

double precision function sincf(x)
    implicit none
    double precision x, dsin, dabs
    if (dabs(x).le.1.5d-10) then
        sincf = 1.0d+00
    else
        sincf = dsin(x)/x
    endif
    return
end

subroutine relay(last, limit, work, omega, nr, nra, sum1, sum2)
    implicit none
    double precision work(1000), rham, omega(302,15)
    double precision a, b, sum1(302,15), sum2(302,15)
    double precision res1(302,15), res2(302,15)
    integer last, l, limit, j, m, nr, nra
    external rham

    do 30 j=1,302
        do 30 m=1,15
            sum1(j,m) = 0.0d+00
        sum2(j,m) = 0.0d+06
    30 continue
    do 10 i=1,last
        a = work(i)
        b = work(limit+i)
        call dgm61s(rham, omega, nr, nra, a, b, res1, res2)
        do 20 j=1,302
            do 20 m=1,15
                sum1(j,m) = sum1(j,m) + res1(j,m)
                sum2(j,m) = sum2(j,m) + res2(j,m)
    20 continue
    10 continue
    return
end

subroutine relay1(last, limit, work, omega, nr, nra, boun, sum1, sum2)
    implicit none
    double precision work(1000), rham, omega(302,15)
    double precision a, b, sum1(302,15), sum2(302,15)
    double precision res1(302,15), res2(302,15), boun
    integer last, l, limit, j, m, nr, nra
    external rham

    do 30 j=1,302
        do 30 m=1,15

210
sum1(j,m) = 0.0d+00
sum2(j,m) = 0.0d+00
30 continue
do 10 i=1,last
   a = work(i)
b = work(limit+i)
call dqk61i(f,ramp,omega,nr,nra,boun,a,b,res1,res2)
do 20 j=1,502
do 20 m=1,15
   sum1(j,m) = sum1(j,m)+res1(j,m)
   sum2(j,m) = sum2(j,m)+res2(j,m)
20 continue
do 10 continue
return
end

subroutine dqk61i(f,boun,inf,a,b,result,abserr,rsabs,rsasc)
implicit none
***begin prologue  dqk61i
***date  920229
***keywords  61-point transform gauss-kronrod rules
***author  hacked by -chh- from two routines in QUADPACK (dqk51) and
          dqk61) to form a 61 point quadrature for the
          infinite integrals. This should provide the
          same functionality of dqk51, only to use a 61 point
          rule. QUADPACK was created by Robert Piessens and
          Elise de Doncker.
***purpose  the original (infinite integration range is mapped
          onto the interval (0,1) and (a,b) is a part of (0,1).
          It is the purpose to compute
          \[ I = \text{integral of transformed integrand over } (a,b), \]
          \[ J = \text{integral of abs(transformed integrand) over } (a,b). \]
***description
  integration rule
  standard fortran subroutine
  double precision version
parameters
on entry
  f - double precision
     function subprogram defining the integrand
     function f(x), the actual name for f needs to be
     declared external in the calling program.
  boun - double precision
     finite bound of original integration
     range (set to zero if inf = +2)
  inf - integer
     if inf = -1, the original interval is
     \( (-\infty, \text{bound}), \)
     if inf = +1, the original interval is
     \( (\text{bound}, +\infty), \)
     if inf = +2, the original interval is
     \( (-\infty, +\infty) \) and
     the integral is computed as the sum of two
     integrals, one over \( (-\infty, 0) \) and one over
     \( (0, +\infty). \)
  a - double precision
     lower limit for integration over subrange
     of \( (0, 1) \)
b - double precision
upper limit for integration over subrange
of (0,1)
on return
result - double precision
approximation to the integral i
result is computed by applying the 61-point
kronrod rule(resk) obtained by optimal addition
of abscissae to the 30-point gauss rule(resg).
abserr - double precision
estimate of the modulus of the absolute error,
which should equal or exceed abs(i-result)
resabs - double precision
approximation to the integral j
resasc - double precision
approximation to the integral of
abs((transformed integrand)-i/(b-a)) over (a,b)

***references (none)
***routines called dlmach
***end prologue dqk611

double precision a,dabsc,abserr,b,centr,dabs,dhlgth,dmaxi,dmini,
* dimach,epmach,f,fc,fsnum,fval1,fval2,fvl1,fv2,hlgth,rsabs,rsasc,
* resg,rsrk,rsrkh,result,uflow,wgk,xgk,abscl,
* absc2,boun,tabscl,tabscl2,fac
integer j,jtw,jtwi,inf,dinf
external f

dimension fvi(30),fv2(30),xgk(31),wgk(31),wg(15)

the abscissae and weights are given for the
interval (-1,1), because of symmetry only the positive
abscissae and their corresponding weights are given.
xgk - abscissae of the 61-point kronrod rule
xgk(2), xgk(4) ... abscissae of the 30-point
gauss rule
xgk(1), xgk(3) ... optimally added abscissae
to the 30-point gauss rule
wgk - weights of the 61-point kronrod rule
wg - weights of the 30-point gauss rule

gauss quadrature weights and kronron quadrature abscissae and weights
c as evaluated with 80 decimal digit arithmctic by l. w. fullerton,
c bell labs, nov. 1981.
data wg ( 1) / 0.0079681924 9616660561 5465882474 674 d0 /
data wg ( 2) / 0.0184664681 1109095914 2302131912 047 d0 /
data wg ( 3) / 0.0287847078 8332336934 9719179611 292 d0 /
data wg ( 4) / 0.0387991295 6962704959 5801936446 348 d0 /
data wg ( 5) / 0.0484026728 3059405290 2938140422 808 d0 /
data wg ( 6) / 0.0574931562 1761906648 1721689402 056 d0 /
data wg ( 7) / 0.0659742298 8218049512 8128515115 962 d0 /
data wgk ( 22) / 0.0460592382 710069881 6271735559 374 d0 /
data wgk ( 23) / 0.0471855465 6929915394 5261478181 099 d0 /
data wgk ( 24) / 0.0481858617 5708712914 0779492296 105 d0 /
data wgk ( 25) / 0.0490564145 5502977888 7528165367 218 d0 /
data wgk ( 26) / 0.0497356834 2707420635 7811569379 942 d0 /
data wgk ( 27) / 0.0504019214 0278234684 0893085653 585 d0 /
data wgk ( 28) / 0.0508817958 9874960649 2297473049 805 d0 /
data wgk ( 29) / 0.0512215478 4925877217 0656282604 944 d0 /
data wgk ( 30) / 0.0514261128 3745902593 3862879215 781 d0 /
data wgk ( 31) / 0.0514947294 2945156755 8340433647 099 d0 /

list of major variables
---------------------
centr - mid point of the interval
h1ght - half-length of the interval
dabs - abscissa
fv1* - function value
resg - result of the 30-point gaussian rule
resk - result of the 61-point Kronrod rule
reskh - approximation to the mean value of f
over (a,b), i.e. to i/(b-a)

c** first executable statement dqnsi1

epmach = dimach(4)
uflow = dimach(1)
dinf = min(0,1,inf)

centr = 0.5d+00*(b+a)
h1ght = 0.5d+00*(b-a)
dh1ght = dabs(h1ght)

compute the 61-point Kronrod approximation to the integral, and estimate the absolute error.

tabscl = boun+dinf*(1d0-centr)/centr
fvall = f(tabscl)
if(linf.eq.2) fval1 = fval1+f(-tabscl)
resg = 0.0d+00
fc = fval1/centr/centr
resk = wgk(31)*fc
resabs = dabs(resk)
do 10 j=1,15
jtwp = j**2

dabs = h1ght*xgk(jtwp)
dabs = cntrt-dabs

tabscl = boun+dinf*(1d0-abscl)/abscl
tabscl = boun+dinf*(1d0-abscl)/abscl
fv1* = f(tabscl)
fv1 = f1(tabscl)
if(linf.eq.2) fval1 = fval1+f(-tabscl)
if(linf.eq.2) fval2 = fval2+f(-tabscl)
fvall = fval1(abscl/abscl
fvall = fval1(abscl/abscl
fvall = fval1/abscl/abscl
fvall = fval1/abscl/abscl
fvall = fval1/abscl/abscl
fv1(jtwp) = fval1
fv2(jtwp) = fval2
fsum = fval1+fval2
resg = resg+wgk(j)*fsum
resk = resk+wgk(jtwp)*fsum
resabs = resabs+wgk(jtwp)*dabs(fval1)+dabs(fval2))
10 continue
do 15 j=1,15
  jtwml = j**2-1
  dabsc = higch*xgk(jtwml)
  absc1 = centr-dabsc
  absc2 = centr+dabsc
  tabscl = boun+dfn*(1.0-absc1)/absc1
  tabsc2 = boun+dfn*(1.0-absc2)/absc2
  fval1 = f(tabscl)
  fval2 = f(tabsc2)
  if (inf.eq.2) fval1 = fval1+f(-tabscl)
  if (inf.eq.2) fval2 = fval2+f(-tabsc2)
  fval1 = fval1/absc1/absc1
  fval2 = fval2/absc2/absc2
  fvl(jtwml) = fval1
  fvl(jtwml) = fval2
  fsum = fval1+fval2
  resk = resk+wgk(jtwml)*fsum
  resab = resab+wgk(jtwml)*(dabs(fval1)+dabs(fval2))
  if (fsum < 0.5d0) continue
  if (j .eq. 1) continue
  if (j .eq. 30) continue
  resk = resk*0.5d0
  resab = resab*0.5d0
  resk = resk+0.5d0
  resab = resab+0.5d0
  fsum = fsum+fsum
  resk = resk+fsum
  resab = resab+fsum
  if (resk .ne. 0.0d0 .and. resab .ne. 0.0d0)
    return
end

subroutine dgm6is(f,omega,nr,nra,boun,a,b,result1,result2)
  implicit none
  double precision a,dabsc,b,centr,dabsc1,dabsc2,cos1,cos2,sin1,
    * f,fc,fval1,fval2,higch,omi,om2,omc,sin2,
    * wgk,xgk,tabscl,tabsc2,boun
  double precision omega(302,15),result1(302,15),result2(302,15)
  double precision resk(302,15),reskl(302,15)
  integer j,i,m,nr,nra
  external f

  dimension xgk(31),wgk(31)

  the abscissae and weights are given for the
  interval (-1,1). because of symmetry only the positive
  abscissae and their corresponding weights are given.

  xgk  - abscissae of the 61-point kronrod rule
    xgk(2), xgk(4) ... abscissae of the 30-point
    gauss rule
    xgk(1), xgk(3) ... optimally added abscissae
    to the 30-point gauss rule

  wgk  - weights of the 61-point kronrod rule

  gauss quadrature weights and kronron quadrature abscissae and weights
  as evaluated with 80 decimal digit arithmetic by l. w. fullerton,
  bell labs, nov. 1981.
data wkg (31) / 0.0514261285 3745902593 3862879215 781 d0 /
data wkg (31) / 0.0514947294 2945156755 8340433647 099 d0 /

list of major variables

----------
centr - mid point of the interval
hlght - half-length of the interval
dabsc - abscissa
fval* - function value
resk - result of the 61-point kronrod rule

centr = 0.5d+00*(b+a)
hlght = 0.5d+00*(b-a)

c compute the 61-point kronrod approximation to the
t integrals f(x)*cos(omega*x) and f(x)*sin(omega*x)
tabscl = boun+(0.1d+01-centr)/centr
fval1 = f(tabscl)
fval = fval1/centr/centr*wkg(31)
do 99 i=1,nr
do 99 m=1,nra
omc = omega(i,m)*tabscl
reskl1(i,m) = f*dcos(omc)
resk2(i,m) = f*dslin(omc)
98 continue
do 10 j=1,30

dabsc = hlgth*xgk(j)
dabsc1 = centr-dabsc

dabsc2 = centr+dabsc
tabscl = boun+(0.1d+01-dabsc1)/dabsc1
tabscl2 = boun+(0.1d+01-dabsc2)/dabsc2
fval2 = f(tabscl1)
fval12 = f(tabscl2)
fval1 = fval1/dabsc1/dabsc1
fval2 = fval2/dabsc2/dabsc2
do 99 i=1,nr
do 99 m=1,nra
om1 = omega(i,m)*tabscl1
om2 = omega(i,m)*tabscl2
cos1 = dcos(om1)
sin1 = dslin(om1)
cos2 = dcos(om2)
sin2 = dslin(om2)
reskl1(i,m) = reskl1(i,m)+wkg(j)*(fval1*cos1+fval12*cos2)
resk2(i,m) = resk2(i,m)+wkg(j)*(fval1*sin1+fval12*sin2)
99 continue
10 continue
do 101 i=1,nr
do 101 m=1,nra
result1(i,m) = reskl1(i,m)*hlght
result2(i,m) = resk2(i,m)*hlght
101 continue
return
end

The following files are extracted from QUADPACK, LTNPACK, and the CNU library:

 subroutine dqagf(a,b,epsabs,epsrel,key,result,abserr,neval,ier,
" limit,lenw,last,iwork,work)
c***begin prologue  dqag
  c***date written  000101  (yymmd)
  c***revision date  030518  (yymmd)
  c***category no.  h2al0d
  c***keywords  automatic integrator, general-purpose,
              integrand examiner, globally adaptive,
              gauss-kronrod
  c***author  piessens,robert,appl. math. & progr. div - k.u.leuven
              de doncker,elise,appl. math. & progr. div - k.u.leuven
  c***purpose  the routine calculates an approximation result to a given
              definite integral \( \int_{a}^{b} f(x) \) over \([a,b]\),
              hopefully satisfying following claim for accuracy
              \( |r - \text{result}| \leq \max(\epsilon_{sabs}, \epsilon_{srel} |r|) \).
  c***description
  c  .
  c    computation of a definite integral
  c    standard fortran subroutine
  c    double precision version
  c    
  c    \( f \) - double precision
  c    function subprogram defining the integrand
  c    function \( f(x) \).  the actual name for \( f \) needs to be
  c    declared external in the driver program.
  c    
  c    \( a \) - double precision
  c    lower limit of integration
  c    
  c    \( b \) - double precision
  c    upper limit of integration
  c    
  c    \( \epsilon_{sabs} \) - double precision
  c    absolute accuracy requested
  c    
  c    \( \epsilon_{srel} \) - double precision
  c    relative accuracy requested
  c    if \( \epsilon_{sabs} \leq 0 \)
  c    and \( \epsilon_{srel} \lt \max(50*\text{rel.mach.acc.}, 0.5d-28) \),
  c    the routine will end with \( ier = 6 \).
  c    
  c    \( \text{key} \) - integer
  c    key for choice of local integration rule
  c    a gauss-kronrod pair is used with
  c    7 - 15 points if \( \text{key} \leq 2 \),
  c    10 - 21 points if \( \text{key} = 2 \),
  c    15 - 31 points if \( \text{key} = 3 \),
  c    20 - 41 points if \( \text{key} = 4 \),
  c    25 - 51 points if \( \text{key} = 5 \),
  c    30 - 61 points if \( \text{key} > 5 \).
  c    
  c    on return
  c    \( \text{result} \) - double precision
  c    approximation to the integral
  c    
  c    \( \text{abserr} \) - double precision
  c    estimate of the modulus of the absolute error,
  c    which should equal or exceed \( |r - \text{result}| \)
  c    
  c    \( \text{neval} \) - integer
  c    number of integrand evaluations
  c    
  c    \( ier \) - integer
  c    \( ier \neq 0 \) normal and reliable termination of the
  c    routine.  it is assumed that the requested
accuracy has been achieved.

ier.gt.0 abnormal termination of the routine
the estimates for result and error are
less reliable. It is assumed that the
requested accuracy has not been achieved.

error messages
ier = 1 maximum number of subdivisions allowed
has been achieved. One can allow more
subdivisions by increasing the value of
limit (and taking the according dimension
adjustments into account). However, if
this yield no improvement it is advised
to analyze the integrand in order to
determine the integration difficulties.
if the position of a local difficulty can
be determined (i.e., singularity,
discontinuity within the interval) one
will probably gain from splitting up the
interval at this point and calling the
integrator on the subranges. If possible,
an appropriate special-purpose integrator
should be used which is designed for
handling the type of difficulty involved.

= 2 the occurrence of roundoff error is
detected, which prevents the requested
tolerance from being achieved.

= 3 extremely bad integrand behaviour occurs
at some points of the integration
interval.

= 6 the input is invalid, because
(epsabs.le.0 and
epsrel.lt.max(50*rel.mach.acc., 0.5d-28))
or limit.lt.1 or lenw.lt.limit*4.
result, abserr, neval, last are set
to zero.
except when lenw is invalid, iwork(1),
work(limit*2+1) and work(limit*3+1) are
set to zero, work(1) is set to a and
work(limit+1) to b.

dimensioning parameters

limit - integer

dimensioning parameter for iwork
limit determines the maximum number of subintervals
in the partition of the given integration interval
(a,b), limit.ge.1.
if limit.lt.1, the routine will end with ier = 6.

lenw - integer
dimensioning parameter for work
lenw must be at least limit*4.
if lenw.lt.limit*4, the routine will end with
ier = 6.

last - integer
on return, last equals the number of subintervals
produced in the subdivision process, which
determines the number of significant elements
actually in the work arrays.

work arrays
iwork - integer
c vector of dimension at least limit, the first k
elements of which contain pointers to the error
estimates over the subintervals, such that
work(limit*3+iwork(1)), ..., work(limit*3+iwork(k))
form a decreasing sequence with k = last if
last.le.(limit/2+1), and k = limit-1-last otherwise

c work - double precision
type of dimension at least lenw
on return
work(1), ..., work(last) contain the left end
points of the subintervals in the partition of
[a,b],
work(limit+1), ..., work(limit+last) contain the
right end points,
work(limit+2+1), ..., work(limit+2+last) contain
the integral approximations over the subintervals,
work(limit+3+1), ..., work(limit+3+last) contain
the error estimates.

*c**references (none)
c**routines called dqage,xerror
c**end prologue dqag

double precision a,abserr,b,epsabs,epsrel, f,result,work
integer ier,iwork,key,last,lenw,limit,lvl,11,12,13,neval

c dimension iwork(limit),work:lenw

c external f

c check validity of lenw.

c**first executable statement dqag

ier = 6
neval = 0
last = 0
result = 0.0d+00
abserr = 0.0d+00
if(limit.lt.1.or.lenw.lt.limit*4) go to 10

prepare call for dqage.

11 = limit+1
12 = limit+11
13 = limit+12

call dqage(f,a,b,epsabs,epsrel,key,limit,result,abserr,neval,
+ ier,work(1),work(11),work(12),work(13),iwork,last)

call errhandler if necessary.

c lvl = 0
10 if(ier.eq.6) lvl = 1
  if(ier.ne.0) call xerror(26,abnormal return from dqag,26,ier,lvl)
if(ier.ne.0) write(*,'("abnormal return from dqag\"')
return

end

subroutine dqagi(f,bound,inf,epsabs,epsrel,result,abserr,neval,
+ ier,limit,lenw,last,iwork,work)
c**begin prologue dqagi

c**date written 800101 (ymmdd)
c**revision date 830518 (ymmdd)
c***category no. h2a3a1,h2a4a1

***keywords automatic integrator, infinite intervals,
  general-purpose, transformation, extrapolation,
  globally adaptive

***author piessens,robert, appl. math. & progr. div. - k.u. leuven
  de doncker, elise, appl. math. & progr. div. - k.u. leuven

***purpose the routine calculates an approximation result to a given
  integral \( \int = \text{integral of } f \text{ over } (\text{bound},+\infty) \)
  or \( \int = \text{integral of } f \text{ over } (-\infty,\text{bound}) \)
  or \( \int = \text{integral of } f \text{ over } (-\infty,+\infty) \)
  hopefully satisfying following claim for accuracy
  \( \text{abs}(1-\text{result}) \leq \text{max(epsabs,epsrel*abs(1))}. \)

***description

integration over infinite intervals
standard fortran subroutine

parameters
on entry
  f - double precision
    function subprogram defining the integrand
  bound - double precision
    finite bound of integration range
    (has no meaning if interval is doubly-infinite)
  inf - integer
    indicating the kind of integration range involved
    inf = 1 corresponds to (bound, +\infty),
    inf = -1 to (-\infty, bound),
    inf = 2 to (-\infty, +\infty).
  epsabs - double precision
    absolute accuracy requested
  epsrel - double precision
    relative accuracy requested
    if epsabs.le.0
    and epsrel.lt.max(50*rel.mach.acc., 0.5d-28),
    the routine will end with ier = 6.

on return
  result - double precision
    approximation to the integral
  abserr - double precision
    estimate of the modulus of the absolute error,
    which should equal or exceed abs(1-result)
  neval - integer
    number of integrand evaluations
  ier - integer
    ier = 0 normal and reliable termination of the
    routine. it is assumed that the requested
    accuracy has been achieved.
    - ier.gt.0 abnormal termination of the routine. the
      estimates for result and error are less
      reliable. it is assumed that the requested
      accuracy has not been achieved.
error messages

ier = 1 maximum number of subdivisions allowed
has been achieved. one can allow more
subdivisions by increasing the value of
limit (and taking the according dimension
adjustments into account). however, if
this yields no improvement it is advised
to analyze the integrand in order to
determine the integration difficulties. if
the position of a local difficulty can be
determined (e.g. singularity,
discontinuity within the interval) one
will probably gain from splitting up the
interval at this point and calling the
integrator on the subranges. if possible,
an appropriate special-purpose integrator
should be used, which is designed for
handling the type of difficulty involved.

ier = 2 the occurrence of roundoff error is
detected, which prevents the requested
tolerance from being achieved.
The error may be underestimated.

ier = 3 extremely bad integrand behaviour occurs
at some points of the integration
interval.

ier = 4 the algorithm does not converge.
Roundoff error is detected in the
extrapolation table.
It is assumed that the requested tolerance
cannot be achieved, and that the returned
result is the best which can be obtained.

ier = 5 the integral is probably divergent, or
slowly convergent. it must be noted that
divergence can occur with any other value
of ier.

ier = 6 the input is invalid, because
(epsabs.le.0 and
epsrel.lt.max(50*rel.mach.acc., 0.5d-20))
or limit.lt.1 or leniw.lt.limit*4.
result, abserr, rinfo, last are set to
zero. except when limit or leniw is
invalid, iwork(1), work(limit*2+1) and
work(limit*3+1) are set to zero, work(1)
is set to a and work(limit+1) to b.

dimensioning parameters

limit - integer
dimensioning parameter for iwork
limit determines the maximum number of subintervals
in the partition of the given integration interval
(a,b), limit.ge.1.
if limit.lt.1, the routine will end with ier = 6.

lenw - integer
dimensioning parameter for work
lenw must be at least limit*4.
if lenw.lt.limit*4, the routine will end
with ier = 6.

last - integer
on return, last equals the number of subintervals
produced in the subdivision process, which
determines the number of significant elements actually in the work arrays.

work arrays

iwork - integer
vector of dimension at least limit, the first
K elements of which contain pointers
to the error estimates over the subintervals,
such that work(limit*3+iwork(1)), ... ,
work(limit*3+iwork(K)) form a decreasing
sequence, with k = last if last .le. (limit/2+2), and
k = limit+1-last otherwise

work - double precision
vector of dimension at least lenw
on return
work(1), ..., work(last) contain the left
end points of the subintervals in the
partition of (a,b),
work(limit+1), ..., work(limit+last) contain
the right end points,
work(limit*2+1), ..., work(limit*2+last) contain the
integral approximations over the subintervals,
work(limit*3+1), ..., work(limit*3)
contain the error estimates.

***references (none)
***routines called dqagie,xerror
***end prologue dqagi

double precision abserr, bound, epsabs, epsrel, f, result, work
integer ier, inf, iwork, last, lenw, limit, lvi, li, l2, l3, neval

dimension iwork(limit), work(lenw)

eexternal f

c check validity of limit and lenw.

***first executable statement dqagi
ier = 6
neval = 0
last = 0
result = 0.0d+00
abserr = 0.0d+00
if(limit.lt.1.or.lenw.lt.limit*4) go to 10

c prepare call for dqagie.

l1 = limit+1
l2 = limit+11
l3 = limit+12

call dqagie(f, bound, inf, epsabs, epsrel, limit, result, abserr,
* neval, ier, work(1), work(11), work(12), work(13), iwork, last)

call error handler if necessary.

lvi = 0
if(ier.eq.6) lvi = 1
if(ier.ne.0) call xerror(26,abnormal return from dqagi,26,ier,lvi)
if(ier.ne.0) write(***,*)ier
return
end

subroutine dgm61sf, omega, nr, a, b, result1, result2
implicit none
double precision a, dabsc, b, centr, dabsc1, dabsc2, cos1, cos2, sin1,
  f, fc, fval1, fval2, hlght, resk1(302,15), resk2(302,15),
  om1, om2, omc, sin2,
  result1(302,15), wgk, xgk, result2(302,15), omega(302,15)
integer j, l, m, nr, nra
external f

dimension xgk(31), wgk(31)

the abscissae and weights are given for the
interval (-1,1), because of symmetry only the positive
abscissae and their corresponding weights are given.

xgk - abscissae of the 61-point kronrod rule
xgk(2), xgk(4) ... abscissae of the 30-point
gauss rule
xgk(1), xgk(3) ... optimally added abscissae
to the 30-point gauss rule

wgk - weights of the 61-point kronrod rule

gauss quadrature weights and kronrod quadrature abscissae and weights
as evaluated with 80 decimal digit arithmetic by l. w. fullerton,
bell labs, nov. 1981.

data xgk ( 1 ) / 0.9994844100 5043903757 1325895705 811 40 /
data xgk ( 2 ) / 0.968931840 7464554027 1630050918 695 40 /
data xgk ( 3 ) / 0.9163099680 7040459485 8628366109 486 40 /
data xgk ( 4 ) / 0.9036681232 7974720997 9032581605 663 40 /
data xgk ( 5 ) / 0.9731163225 0112626837 4693984237 707 40 /
data xgk ( 6 ) / 0.9600218649 6830751221 6871025581 798 40 /
data xgk ( 7 ) / 0.9443744447 4855997941 5831324037 439 40 /
data xgk ( 8 ) / 0.9262000000 9847352587 9324277908 474 40 /
data xgk ( 9 ) / 0.9055733076 9990779894 6522559925 958 40 /
data xgk (10) / 0.8825605357 9205268154 3116462530 226 40 /
data xgk (11) / 0.8572052335 4601659895 8658510558 944 40 /
data xgk (12) / 0.8296557623 8276839744 2898119732 502 40 /
data xgk (13) / 0.7997278358 2183908301 3668942322 683 40 /
data xgk (14) / 0.7677774321 048261689e 7977340794 503 40 /
data xgk (15) / 0.7337900624 5322680472 6171131369 528 40 /
data xgk (16) / 0.6978504947 9331579693 2292388802 460 40 /
data xgk (17) / 0.6600610641 2662696137 0053668149 271 40 /
data xgk (18) / 0.6205261829 8924268114 0477556431 189 40 /
data xgk (19) / 0.5793452558 2636169175 6024933172 540 40 /
data xgk (20) / 0.5364241481 4220899226 4169793111 073 40 /
data xgk (21) / 0.4924804678 6177857499 3693061207 709 40 /
data xgk (22) / 0.4470337595 3808917678 0609900322 954 40 /
data xgk (23) / 0.4004012548 3039439253 5476211542 661 40 /
data xgk (24) / 0.3527047255 5087811347 1037207089 374 40 /
data xgk (25) / 0.3040732022 7362507737 2677107199 257 40 /
data xgk (26) / 0.2546369261 6789884643 9805129817 805 40 /
data xgk (27) / 0.2045251156 8230909143 8957671002 025 40 /
data xgk (28) / 0.1538699136 0858354696 3794672743 256 40 /
data xgk (29) / 0.1028306979 6757393128 7096751138 001 40 /
data xgk (30) / 0.0514718425 5551769643 9302531136 723 40 /
data xgk (31) / 0.0000000000 0000000000 0000000000 000 40 /
data wgk ( 1 ) / 0.0013890136 9867700762 4551591225 760 40 /
data wgk ( 2) / 0.003804611 2709984055 1267201844 516 do / 
data wgk ( 3) / 0.0066307039 1593129217 3319826369 750 do / 
data wgk ( 4) / 0.0092732796 5951776342 8441146802 924 do / 
data wgk ( 5) / 0.0118230152 5349634174 2232289885 251 do / 
data wgk ( 6) / 0.0143697295 9704580481 2451435443 580 do / 
data wgk ( 7) / 0.0169208891 9605327262 7572289420 322 do / 
data wgk ( 8) / 0.0194144141 9394238217 3408951050 128 do / 
data wgk ( 9) / 0.0218280358 2169192229 7167485738 339 do / 
data wgk (10) / 0.0241911620 7808060136 5686370725 232 do / 
data wgk (11) / 0.0265995548 8233312161 0601709335 075 do / 
data wgk (12) / 0.0287540487 6504143928 3978785354 374 do / 
data wgk (13) / 0.0309072575 6238767697 2884252943 92 do / 
data wgk (14) / 0.0329814470 5748397260 3233191061 954 do / 
data wgk (15) / 0.0349793380 2806002413 7499670731 468 do / 
data wgk (16) / 0.0368823646 5182122922 3911005617 336 do / 
data wgk (17) / 0.0386789456 2472759295 0346651532 281 do / 
data wgk (18) / 0.0403745389 515595911 1995279752 468 do / 
data wgk (19) / 0.0419698102 1516424614 7147541285 970 do / 
data wgk (20) / 0.0434525397 0135601931 6831728117 073 do / 
data wgk (21) / 0.0448148001 3316266319 2355551616 723 do / 
data wgk (22) / 0.0460592382 7106698811 6271735559 174 do / 
data wgk (23) / 0.0471855465 6929915394 5261478181 09 do / 
data wgk (24) / 0.0481858617 5708712914 0779492298 105 do / 
data wgk (25) / 0.0490554345 5502977888 7528165367 338 do / 
data wgk (26) / 0.0497956834 2707420635 7811569379 942 do / 
data wgk (27) / 0.0504059214 0278234684 0593055653 585 do / 
data wgk (28) / 0.0508679758 9874960649 2297470049 806 do / 
data wgk (29) / 0.0512215478 4925877217 0656282604 944 do / 
data wgk (30) / 0.0514261285 3745902593 3862879215 781 do / 
data wgk (31) / 0.0514947294 2945156755 8340433647 099 do / 

list of major variables
-----------------------

centr  - mid point of the interval 
hlght  - half-length of the interval
dabsc  - abs(cissa) 
fcval  - function value 
resk   - result of the 61-point kronrod rule

centr = 0.5d+00*(b-a) 
hlght = 0.5d+00*(b-a)

c compute the 61-point kronrod approximation to the
integrals f(x)*cos(omega*x) and f(x)*sin(omega*x)

cfc = f(centr)*wgk(31) 
do 97 i=1,nr 
do 97 m=1,nra 
  omc = omega(1,m)*centr 
  resk1(i,m) = fc*cos(omc) 
  resk2(i,m) = fc*sin(omc) 
continue 
do 10 j=1,30 
dabsc = hlgth*wglk(j) 
dabsc1 = centr-dabsc 
dabsc2 = centr+dabsc 
fval1 = f(dabsc1) 
fval2 = f(dabsc2) 
do 98 i=1,nr 
do 98 m=1,nra

```
\[ \text{om1} = \Omega(i,m) \times \text{dabs} + 1 \]
\[ \text{om2} = \Omega(i,m) \times \text{dabs} + 2 \]
\[ \text{cos1} = \cos(\text{om1}) \]
\[ \text{sin1} = \sin(\text{om1}) \]
\[ \text{cos2} = \cos(\text{om2}) \]
\[ \text{sin2} = \sin(\text{om2}) \]
\[ \text{reskl}(i,m) = \text{reskl}(i,m) + \text{wgk}(j) \times ( \text{fval1} \times \text{cos1} + \text{fval2} \times \text{cos2} ) \]
\[ \text{resk2}(i,m) = \text{resk2}(i,m) + \text{wgk}(j) \times ( \text{fval1} \times \text{sin1} + \text{fval2} \times \text{sin2} ) \]

98 continue
10 continue
   do 99 i=1,nr
     do 99 m=1,nra
       \[ \text{result1}(i,m) = \text{reskl}(i,m) \times \text{hig} \text{th} \]
       \[ \text{result2}(i,m) = \text{resk2}(i,m) \times \text{hig} \text{th} \]
99 continue
   return
end

subroutine dqage(f,a,b,epsabs,epsrel,key,limit, result, abserr, 
   * neval,ier,alist,blist,clist,elast,iord,last)

***begin prologue dqage
***date written 800101  (yymmdd)
***revision date 890518  (yymmdd)
***category no.  h2a1a1
***keywords automatic integrator, general-purpose,
   * integrand evaluator, globally adaptive,
   * gauss-kronrod
***author piessens,robert,appl. math. & progr. div. - k. u. leuven
   * de doncker.elise,appl. math. & progr. div. - k. u. leuven
***purpose the routine calculates an approximation result to a given
   * definite integral \( \int_a^b f(x) \, dx \),
   * hopefully satisfying following claim for accuracy
   * \( |\text{abs}(\text{result} - \text{result})| \leq \max(\text{epsabs}, \text{epsrel} \times |\text{result}|) \).
***description
   * computation of a definite integral
   * standard fortran subroutine
   * double precision version

parameters on entry
   * f - double precision
     * function subroutine defining the integrand
   * a - double precision
     * lower limit of integration
   * b - double precision
     * upper limit of integration
   * epsabs - double precision
     * absolute accuracy requested
   * epsrel - double precision
     * relative accuracy requested
     * if epsabs.le.0
     * and epsrel.lt.max(50*rel.mach.acc.,0.5d-28),
     * the routine will end with ier = 6.
   * key - integer
     * key for choice of local integration rule
     * a gauss-kronrod pair is used with

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limit - integer
  gives an upper bound on the number of subintervals
  in the partition of (a,b), limit >= 1.

on return
  result - double precision
  approximation to the integral

  abserr - double precision
  estimate of the modulus of the absolute error,
  which should equal or exceed abs(i-result)

  neval - integer
  number of integrand evaluations

  ier - integer
  0 normal and reliable termination of the
  routine. it is assumed that the requested
  accuracy has been achieved.
  ier.gt.0 abnormal termination of the routine
  the estimates for result and error are
  less reliable. it is assumed that the
  requested accuracy has not been achieved.

error messages
  ier = 1 maximum number of subdivisions allowed
  has been achieved. one can allow more
  subdivisions by increasing the value
  of limit.
  however, if this yields no improvement it
  is rather advised to analyze the integrand
  in order to determine the integration
  difficulties. if the position of a local
difficulty can be determined(e.g. singularity, discontinuity within the
interval) one will probably gain from
splitting up the interval at this point
and calling the integrator on the
subranges. if possible, an appropriate
special-purpose integrator should be used
which is designed for handling the type of
difficulty involved.

  2 the occurrence of roundoff error is
  detected, which prevents the requested
tolerance from being achieved.
  3 extremely bad integrand behaviour occurs
  at some points of the integration
  interval.
  6 the input is invalid, because
  epsabs.le.0 and
  epsrel.lt.max(50*rel.mach.acc.,0.5d-28),
  result, abserr, neval, last, rlist(1),
  elist(1) and iord(1) are set to zero.
  alist(1) and blist(1) are set to a and b
  respectively.
alist - double precision
   vector of dimension at least limit, the first
   last elements of which are the left
   end points of the subintervals in the partition
   of the given integration range (a, b)

blist - double precision
   vector of dimension at least limit, the first
   last elements of which are the right
   end points of the subintervals in the partition
   of the given integration range (a, b)

rlist - double precision
   vector of dimension at least limit, the first
   last elements of which are the
   integral approximations on the subintervals

elist - double precision
   vector of dimension at least limit, the first
   last elements of which are the moduli of the
   absolute error estimates on the subintervals

iord - integer
   vector of dimension at least limit, the first k
   elements of which are pointers to the
   error estimates over the subintervals,
   such that elist(iord(1)), ..., elist(iord(k)) form a decreasing sequence,
   with k = last if last.le.(limit/2+2), and
   k = limit+1-last otherwise

last - integer
   number of subintervals actually produced in the
   subdivision process

***references (none)
***routines called dlmach, dqk15, dqk21, dqk31,
   dqk41, dqk51, dqk61, dqpk1t
***end prologue dqag

double precision a, abserr, alist, area, area1, area2, area2, a1, a2, b,
   blist, b1, b2, dabs, defabs, defab1, defab2, dmax1, dimach, elist, epmach,
   epsabs, epsrel, errbd, errmax, error1, error2, errof1, errof2, errsa,f,
   resabs, result, rlist, uflow
integer ier, iord, iroff1, iroff2, k, key, keyf, last, limit, maxerr, neval,
   nmax

dimension alist(limit), blist(limit), elist(limit), iord(limit),
   rlist(limit)

external f

list of major variables
------------------------

alist - list of left end points of all subintervals
considered up to now
blist - list of right end points of all subintervals
considered up to now
rlist(i) - approximation to the integral over
   (alist(i), blist(i))
elist(i) - error estimate applying to rlist(i)
maxerr - pointer to the interval with largest error estimate
errmax - elist(maxerr)
area - sum of the integrals over the subintervals
errsum - sum of the errors over the subintervals
errord - requested accuracy max(epsabs,epsrel*abs(result))

*****l - variable for the left subinterval
*****2 - variable for the right subinterval
last - index for subdivision

machine dependent constants
------------------------

epmach is the largest relative spacing.
uflow is the smallest positive magnitude.

**first executable statement dqge
epmach = dimach(4)
uflow = dimach(1)

test on validity of parameters
-----------------------------

ier = 0
neval = 0
last = 0
result = 0.0d+00
abstol = 0.0d+00
dlist(l) = a
blist(l) = b
rlist(l) = 0.0d+00
eelst(l) = 0.0d+00
iord(l) = 0
if(epsabs .le. 0.0d+00 .and.
* epsrel .lt. dmax1(0.5d+02*epmach,0.5d-28)) ier = 6
if(ier .eq. 6) go to 999

first approximation to the integral
----------------------------------

keyf = key
if(key .le. 0) keyf = 1
if(key .ge. 7) keyf = 6
neval = 0
if(keyf .eq. 1) call dqk15(f,a,b,result,abstol,defabs,resabs)
if(keyf .eq. 2) call dqk21(f,a,b,result,abstol,defabs,defabs,defabs)
if(keyf .eq. 3) call dqk31(f,a,b,result,abstol,defabs,defabs,defabs)
if(keyf .eq. 4) call dqk41(f,a,b,result,abstol,defabs,defabs,defabs)
if(keyf .eq. 5) call dqk51(f,a,b,result,abstol,defabs,defabs,defabs)
if(keyf .eq. 6) call dqk61(f,a,b,result,abstol,defabs,defabs,defabs)
last = 1
rlist(l) = result
eelst(l) = abstol
iord(l) = 1

test on accuracy.

errord = dmax1*epsabs,epsrel*abs(result))
if(abstol .le. 0.5d+02*epmach*defabs .and. abstol .gt. errord) ier = 2
if(limit .eq. i) ier = 1
if(ier.ne.0.or.(abserr.ie.errbnd.and.abserr.ne.resabs)
  .or.abserr.eq.0.0d+00) go to 60

        initialization

        -----------------

        errmax = abserr
        maxerr = 1
        area = result
        errsum = abserr
        nmax = 1
        iroff1 = 0
        iroff2 = 0

        main do-loop

        ------------

        do 30 last = 2,limit

    bisect the subinterval with the largest error estimate.

        a1 = aild(maxerr)
        b1 = 0.5d+00*(aild(maxerr)+blist(maxerr))
        a2 = b1
        b2 = blist(maxerr)
        if(keyf.eq.1) call dqk15(f,a1,b1,area1,erreur1,resabs,defab1)
        if(keyf.eq.2) call dqk21(f,a1,b1,area1,erreur1,resabs,defab1)
        if(keyf.eq.3) call dqk31(f,a1,b1,area1,erreur1,resabs,defab1)
        if(keyf.eq.4) call dqk41(f,a1,b1,area1,erreur1,resabs,defab1)
        if(keyf.eq.5) call dqk51(f,a1,b1,area1,erreur1,resabs,defab1)
        if(keyf.eq.6) call dqk61(f,a1,b1,area1,erreur1,resabs,defab1)
        if(keyf.eq.1) call dqk15(f,a2,b2,area2,erreur2,resabs,defab2)
        if(keyf.eq.2) call dqk21(f,a2,b2,area2,erreur2,resabs,defab2)
        if(keyf.eq.3) call dqk31(f,a2,b2,area2,erreur2,resabs,defab2)
        if(keyf.eq.4) call dqk41(f,a2,b2,area2,erreur2,resabs,defab2)
        if(keyf.eq.5) call dqk51(f,a2,b2,area2,erreur2,resabs,defab2)
        if(keyf.eq.6) call dqk61(f,a2,b2,area2,erreur2,resabs,defab2)

        improve previous approximations to integral
        and error and test for accuracy.

        neval = neval+1
        area12 = area+area2
       erreur2 = erreur1+erreur2
        errsum = errsum+erreur2-errmax
        area = area+area12-rlist(maxerr)
        if(defab1.eq.erreur1.or.defab2.eq.erreur2) go to 5
        if(dabs(rlist(maxerr)-area12).le.0.1d-04*dabs(area12)
    * .and.erreur2.ge.0.99d+00*errmax) iroff1 = iroff1+1
        if(last.gt.10.and.erreur2.gt.errmax) iroff2 = iroff2+1
        rlist(maxerr) = area1
        rlist(last) = area2
        errbnd = xmax(epsabs,epsrel*dabs(area))
        if(errsum.le.errbnd) go to 8

        test for roundoff error and eventually set error flag.

        if(iroff1.ge.6.or.iroff2.ge.20) ier = 2

        set error flag in the case that the number of subintervals
        equals limit.
if(last.eq.limit) ier = 1
set error flag in the case of bad integrand behaviour
at a point of the integration range.
if(dmax1(dabs(a1),dabs(b2)).le.(0.1d+01+0.1d+03*
  * epmach)*(dabs(a2)+0.1d+04*uflow)) ier = 3
append the newly-created intervals to the list.
8 if(error2.gt.error1) go to 10
alist(last) = a2
blist(maxerr) = b1
blist(last) = b2
eclist(maxerr) = eror1
eclist(last) = error2
go to 20
10 alist(maxerr) = a2
alist(last) = a1
blist(last) = b1
rclist(maxerr) = area2
rclist(last) = area1
eclist(maxerr) = error2
elist(last) = error1
call subroutine dqagse to maintain the descending ordering
c in the list of error estimates and select the subinterval.
c with the largest error estimate (to be bisected next).
c
20 call dqagse(limit,last,maxerr,eromax,elist,iord,eromax)
***jump out of do-loop
if(ier.ne.0.or.errsum.le.errbnd) go to 40
continue
40 result = 0.0d+00
do 50 k=1,last
   result = result+rclist(k)
50 continue
abserr = errsum
60 if(keyf.ne.1) neval = (10*keyf+1)*(2*neval+1)
   if(keyf.eq.1) neval = 30*neval+15
999 return
end

subroutine dqagse(f,bound,inf,epsabs,epsrel,limit,result,aberr,
  * neval,ierr,alist,blist,rlist,elist,iord,last)
c**begin prologue  dqagse
c***date written  800101 (ymmd)
c***Revision date  830518 (ymmd)
c***category no.  h2a3a1,h2a4a1
c***keywords  automatic integrator, infinite intervals,
c general-purpose, transformation, extrapolation,
c globally adaptive
c***author  piessens,robert,appl. math & progr. div - k.u.leuven
c de doncker,elise,appl. math & progr. div - k.u.leuven
c***purpose  the routine calculates an approximation result to a given
c integral i = integral of f over (bound, infinity)
c or i = integral of f over (-infinity,bound)
c or i = integral of f over (-infinity, infinity),

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hoefully satisfying following claim for accuracy
abs(i-result).le.max(epsabs,epsrel*abs(i))

***description

integration over infinite intervals
standard fortran subroutine

f - double precision
function subprogram defining the integrand
function f(x). the actual name for f needs to be
declared external in the driver program.

bound - double precision
finite bound of integration range
(has no meaning if interval is doubly-infinite)

inf - double precision
indicating the kind of integration range involved
inf = 1 corresponds to (bound, +infinity),
inf = -1 to (-infinity, bound),
inf = 2 to (-infinity, +infinity).

epsabs - double precision
absolute accuracy requested

epsrel - double precision
relative accuracy requested
if epsabs.le.0
and epsrel.lt.max(50*rel.mach.acc.,0.5d-28),
the routine will end with ier = 6.

limit - integer
gives an upper bound on the number of subintervals
in the partition of (a,b), limit.ge.1

on return
result - double precision
approximation to the integral

abserr - double precision
estimate of the modulus of the absolute error,
which should equal or exceed abs(i-result)

neval - integer
number of integrand evaluations

ier - integer
- ier = 0 normal and reliable termination of the
routine. it is assumed that the requested
accuracy has been achieved.
- ier.gt.0 abnormal termination of the routine. the
estimates for result and error are less
reliable. it is assumed that the requested
accuracy has not been achieved.

error messages
- ier = 1 maximum number of subdivisions allowed
has been achieved. one can allow more
subdivisions by increasing the value of
limit (and taking the according dimension
adjustments into account). however, if
this yields no improvement it is advised
to analyze the integrand in order to
determine the integration difficulties.
if the position of a local difficulty can
be determined (e.g. singularity,
discontinuity within the interval) one
will probably gain from splitting up the
interval at this point and calling the
integrator on the subranges. If possible,
an appropriate special-purpose integrator
should be used which is designed for
handling the type of difficulty involved.

= 2 the occurrence of roundoff error is
detected, which prevents the requested
tolerance from being achieved.
the error may be under-estimated.
= 3 extremely bad integrand behaviour occurs
at some points of the integration
interval.
= 4 the algorithm does not converge.
roundoff error is detected in the
extrapolation table.
it is assumed that the requested tolerance
cannot be achieved, and that the returned
result is the best which can be obtained.
= 5 the integral is probably divergent, or
closely convergent. It must be noted that
divergence can occur with any other value
of ier.
= 6 the input is invalid, because
{epsabs ≤ 0 and
epsrel.lt.max(50*rel.mach.acc., 0.5d-28),
result, abserr, neval, last, rlist(1),
elist(1) and iord(1) are set to zero.
ellelist(1) and blist(1) are set to 0
and 1 respectively.

alist  - double precision
vector of dimension at least limit, the first
last elements of which are the left
end points of the subintervals in the partition
of the transformed integration range (0,1).

blist  - double precision
vector of dimension at least limit, the first
last elements of which are the right
end points of the subintervals in the partition
of the transformed integration range (0,1).

rlist  - double precision
vector of dimension at least limit, the first
last elements of which are the integral
approximations on the subintervals

elist  - double precision
vector of dimension at least limit, the first
last elements of which are the moduli of the
absolute error estimates on the subintervals

iord   - integer
vector of dimension limit, the first k
elements of which are pointers to the
error estimates over the subintervals,
such that elist(iord(1)), ..., elist(iord(k))
form a decreasing sequence, with k = last
if last <= (limit/2+2), and k = limit-1-last
otherwise

last - integer
number of subintervals actually produced
in the subdivision process

**references (none)**

**routines called dimach, dqelg,dqk611,dqpsrt**

**end prologue dqaglb**

double precision abscts, abserr, al ist, area, area1, area2, al,
* a2, blist, boun, bound, bl1, bl2, correc, dabs, defabs, defab1, defab2,
* dmaxl, dres, dimach, elist, epsmach, epsabs, epsrel, erladv, erlast,
* errbd, errmax, error1, error2, erro1, erro2, error3, erlast, f, oflow, resabs,
* respts, result, resla, rlist, rlist2, small, uflow
integer id, ker, ierro, inf, iord, iroff1, iroff2, iroff3, junbd, k, ksgn,
* ktmn, last, limit, maxerr, neval, nres, nrmax, numr12
logical extrapol

**dimension al ist(limit), blist(limit), elist(limit), iord(limit),
* resla(3), rlist(limit), rlist2(52)**

**external**

the dimension of rlist2 is determined by the value of
limexp in subroutine dqelg.

**list of major variables**

--------------------------

alist - list of left end points of all subintervals
considered up to now

blist - list of right end points of all subintervals
considered up to now

rlist(i) - approximation to the integral over
(alist(i),blist(i))

rlist2 - array of dimension at least (limexp+2),
containing the part of the epsilon table
which is still needed for further computations

eclist - error estimate applying to rlist(i)

maxerr - pointer to the interval with largest error

estimate

errmax - elist(maxerr)

erlast - error on the interval currently subdivided
(before that subdivision has taken place)

area - sum of the integrals over the subintervals

errsum - sum of the errors over the subintervals

errbd - requested accuracy max(epsabs, epsrel*
abs(result))

***1 - variable for the left subinterval

***2 - variable for the right subinterval

last - index for subdivision

nres - number of calls to the extrapolation routine

numr12 - number of elements currently in rlist2. if an
appropriate approximation to the compounded
integral has been obtained, it is put in
rlist2(numr12) after numr12 has been increased
by one.

small - length of the smallest interval considered up
to now, multiplied by 1.5

erladv - sum of the errors over the intervals larger
extrap - logical variable denoting that the routine is attempting to perform extrapolation, i.e. before subdividing the smallest interval we try to decrease the value of eriarg.

noext - logical variable denoting that extrapolation is no longer allowed (true-value)

machine dependent constants

epmach is the largest relative spacing.
uflow is the smallest positive magnitude.
oflow is the largest positive magnitude.

*** first executable statement dqagie

epmach = dimach(4)
test on validity of parameters

ier = 0
neval = 0
last = 0
result = 0.0d+00
abserr = 0.0d+00
alist(1) = 0.0d+00
blist(1) = 0.1d+01
rlist(1) = 0.0d+00
ealist(1) = 0.0d+00
lord(1) = 0
if(epmach.le.0.0d+00.and.epsrel.lt.dmax1(0.5d+02*epmach,0.5d-28))
  ier = 6
  if(ier.eq.6) go to 999

first approximation to the integral

determine the interval to be mapped onto (0,1).
if inf = 2 the integral is computed as i = i1+i2, where
i1 = integral of f over (-infinity,0),
i2 = integral of f over (0, +infinity).

boun = bound
if(inf.eq.2) boun = 0.0d+60
call dqg61lf(f,boun.inf,0.0d+00,0.1d+91,result,abserr,
  * dfabs,resabs)
test on accuracy

last = 1
rlist(1) = result
ealist(1) = abserr
lord(1) = 1
dres = dabs(result)
errbnd = dmax1(epsabs,epsrel*dres)
if(abserr.le.1.0d-02*epmach*fabs.abserr.gt.errbnd) ier = 2
if(1limt.eq.1) ier = 1
if(ier.ne.0.or.(abserr.le.errbnd.and.abserr.ne.resabs).or.
  * abserr.eq.0.0d+00) go to 120
. initialization

----------

uflow = dimach(1)
oflow = dimach(2)
nlist2(1) = result
errmax = abserr
maxerr = 1
area = result
e rsum = abserr
abserr = oflow
nmax = 1
nres = 0
kmin = 0
numrl = 2
extrap = .false.
noext = .false.
iero = 0
irowf = 0
irowf2 = 0
irowf3 = 0
ksg = -1

if(dres.ge.(0.1d+01-0.5d+02*epmach)*de(abs)) ksg = 1

main do-loop

----------

do 90 last = 2,limit

   bisect the subinterval with nmax-th largest error estimate.

   a1 = a list(maxerr)
   b1 = 0.5d+00*(alist(maxerr)+blist(maxerr))
   a2 = b1
   b2 = bl ist(maxerr)
   erlast = errmax
   call dqx61i(f, boun, inf, a1, b1, area1, error1, resabs, defab1)
   call dqx61i(f, boun, inf, a2, b2, area2, error2, resabs, defab2)

   improve previous approximations to integral
   and error and test for accuracy.

   area2 = area1-area2
   errol2 = erro1+error2
   errsum = errsum+errol2-errmax
   area = area+area2-rlist(maxerr)
   if(defab1.eq.error1.or.defab2.eq.error2) go to 15
   if(dabs(rlist(maxerr)-area2).gt.0.1d-04*dabs(area2))
      .or.errol2.lt.0.99d+00*errmax) go to 10
   if(extrap) irowf2 = irowf2+1
   if(.not.extrap) irowf1 = irowf1+1
   10 if(last.gt.10.and.errol2.gt.errmax) irowf3 = irowf3+1
      rlist(maxerr) = area1
      rlist(last) = area2
      errbd = dmaxl(efabs, epsrel*dabs(area))
   15 test for roundoff error and eventually set error flag.

      if(irowf1+irowf2.ge.10.or.irowf3.ge.20) ier = 2
      if(irowf2.ge.5) ierro = 3

   set error flag in the case that the number of
subintervals.equals limit.
if(last.eq.limit) ier = 1

set error flag in the case of bad integrand behaviour
at some points of the integration range.
if(dmax1(dabs(a1),dabs(b2)).le.(0.1d+01+0.1d+03*epmach)*
   (dabs(a2)+0.1d+04*uflow)) ier = 4

append the newly-created intervals to the list.
if(error2.gt.error1) go to 20
alist(last) = a2
blist(maxerr) = b1
alist(last) = b2
eclist(maxerr) = error1
eclist(last) = error2
go to 30
20 alist(maxerr) = a2
alist(last) = a1
blist(last) = b1
celist(maxerr) = area2
delist(last) = area1
eclist(maxerr) = error2
eclist(last) = error1

call subroutine dqpsrt to maintain the descending ordering
in the list of error estimates and select the subinterval
with nmax-th largest error estimate (to be bisected next).
30 call dqpsrt(limit,last,maxerr,errmax,elist,ilord,nrmax)
   if(errsum.1e.errbnd) go to 115
   if(ier.ne.0) go to 100
   if((last.eq.2) go to 80
   if(noext) go to 90
erlarg = erlarg-erlast
   if(dabs(b1-al()).gt.small) erlarg = erlarg+error2
   if(extrap) go to 40
c
test whether the interval to be bisected next is the
smallest interval.
if(dabs(blist(maxerr)-alist(maxerr)).gt.small) go to 90
extrap = .true.
nrmax = 2
40 if(ierro.eq.3.or.erlarg.1e.ertest) go to 60
c
the smallest interval has the largest error.
before bisecting decrease the sum of the errors over the
larger intervals (erlarg) and perform extrapolation.
c
id = nrmax
jupbd = last
if(last.gt.(2*limit/2)) jupbd = limit+3-last
do 50 k = id,jupbd
   maxerr = ilord(nrmax)
   errmax = elist(maxerr)
   if(dabs(blist(maxerr)-alist(maxerr)).gt.small) go to 90
   nrmax = nrmax+1
50 continue
perform extrapolation.

60 numr12 = numr12 + 1
   rlist2(numr12) = area
   call dqelg(numr12,rlist2,reseps,abseps,res3la,ntes)
   ktmnin = ktmmin + 1
   if(ktmin.gt.5.and.abserr.lt.0.1d-02*errsum) ier = 5
   if(abseps.ge.abserr) go to 70
   ktmnin = 0
   abserr = abseps
   result = reseps
   correc = erlarg
   ertest = dmax1(epsabs,epsrel*dabs(reseps))
   if(abserr.le.ertest) go to 100

prepare bisection of the smallest interval.

70 if(numr12.eq.1) noext = .true.
   if(ier.eq.5) go to 100
   maxerr = iord(1)
   errmax = elist(maxerr)
   nmax = 1
   extrap = .false.
   small = small*0.5d+00
   erlarg = errsum
   go to 90
80 small = 0.375d+00
   erlarg = errsum
   ertest = errbnd
   rlist2(2) = area
90 continue

   set final result and error estimate.
   -----------------------------

100 if(abserr.eq.oflow) go to 115
   if((ier+ierro).eq.0) go to 110
   if(ierro.eq.3) abserr = abserr+correc
   if(ier.eq.0) ier = 3
   if(result.ne.0.0d+00.and.area.ne.0.0d+00) go to 105
   if(abserr.gt.errsum) go to 115
   if(area.eq.0.0d+00) go to 130
   go to 110
105 if(abserr/dabs(result).gt.errsum/dabs(area)) go to 115

test on divergence

110 if(ksig.eq.(-1).and.dmax1(dabs(result),dabs(area))le.
   * defabs*0.1d-01) go to 170
   if(0.1d-01.gt.(result/area).or.(result/area).gt.0.1d+03.
   * or.errsum.gt.dabs(area)) ier = 6
   go to 130

   compute global integral sum.

115 result = 0.0d+00
   do 120 k = 1, last
      result = result + rlist(k)
120 continue
   abserr = errsum
130 neval = 30*last-15
   if(inf.eq.2) neval = 2*neval

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if (ierr.gt.2) ierr=ierr-1
999 return
end

subroutine dqk61(f,a,b,result,abserr,resabs,resasc)
c***begin prologue  dqk61

c***date written  800101  (yymmd)
c***revision date  830518  (yymmd)
c***category no.  h2a1a2

c***keywords  61-point gauss-kronrod rules

c***author  piessens,robert,appl.math. & progr. div. - k.u.leuven

c de doncker,elise,appl. math. & progr. div. - k.u.leuven

c***purpose  to compute i = integral of f over (a,b) with error

c estimate

c j = integral of dabs(f) over (a,b)

c***description

Integration rule
standard fortran subroutine
double precision version

parameters
on entry

  f  - double precision
      function subroutine defining the integrand
      function f(x). the actual name for f needs to be declared extern a l in the calling program.

  a  - double precision
      lower limit of integration

  b  - double precision
      upper limit of integration

on return

  result  - double precision
      approximation to the integral i
      result is computed by applying the 61-point kronrod rule (resk) obtained by optimal addition of abscissae to the 30-point gauss rule (rewg).

  abserr  - double precision
      estimate of the modulus of the absolute error,
      which should equal or exceed dabs(i-result)

  resabs  - double precision
      approximation to the integral j

  resasc  - double precision
      approximation to the integral of dabs(f-i/(b-a))

***references (none)
***routines called  dimach
***end prologue  dqk61

double precision i,dabsc,abaerr,b,centr,dabs,dhignt,dmax1,dmin1,
  dimach,epmach,f,f1,fc,fsum,fval1,fval2,fv1,fv2,hignt,resabs,resasc,
  resg,rewk,revk,rewg,uflow,wg,vgk,xgk
integer j,jtw,jtwml

external f
the abscissae and weights are given for the
interval (-1,1). Because of symmetry only the positive
abscissae and their corresponding weights are given.

xgk  - abscissae of the 61-point kromron rule
xg(2), xg(4) ... abscissae of the 30-point
gauss rule
xgk(1), xgk(3) ... optimally added abscissae
to the 30-point gauss rule

wgk - weights of the 61-point kromron rule

wg - weights of the 30-point gauss rule

c gauss quadrature weights and kromron quadrature abscissae and weights
as evaluated with 80 decimal digit arithmetric by l. w. fuller-ton.
c bell labs, nov. 1981.

data wg ( 1 ) / 0.0079681924 9616660561 546583474 674 d0 /
data wg ( 2 ) / 0.0184664681 1109959514 2302211912 047 d0 /
data wg ( 3 ) / 0.0287847078 8132336934 9719176611 292 d0 /
data wg ( 4 ) / 0.0387991925 6962704959 6081936446 348 d0 /
data wg ( 5 ) / 0.0484026278 3059405290 2938140422 808 d0 /
data wg ( 6 ) / 0.0574931552 1761906648 1721689402 956 d0 /
data wg ( 7 ) / 0.0659742298 8218049512 8128515115 962 d0 /
data wg ( 8 ) / 0.0737559747 3770520626 8243850022 191 d0 /
data wg ( 9 ) / 0.0807558952 2942021535 4694938460 530 d0 /
data wg (10) / 0.0868997872 0108297980 2387520715 126 d0 /
data wg (11) / 0.0921225222 3778612871 7632707087 619 d0 /
data wg (12) / 0.0963687371 7464425963 9468826351 810 d0 /
data wg (13) / 0.0995934205 8679526706 2780282103 569 d0 /
data wg (14) / 0.1017623897 4840505049 6428952168 554 d0 /
data wg (15) / 0.1028526528 9355984034 1285636705 415 d0 /

data xgk ( 1 ) / 0.9994844100 5049067357 1325895705 811 d0 /
data xgk ( 2 ) / 0.9969234840 7464954027 1630059180 695 d0 /
data xgk ( 3 ) / 0.9916309968 7040459485 8628356109 486 d0 /
data xgk ( 4 ) / 0.9836681232 7974720997 0032581605 663 d0 /
data xgk ( 5 ) / 0.9731163225 0112626837 4693848423 707 d0 /
data xgk ( 6 ) / 0.9600218649 6830751221 6871025581 798 d0 /
data xgk ( 7 ) / 0.9443744447 4855997941 5831324037 439 d0 /
data xgk ( 8 ) / 0.9252200047 2927432587 9324277080 474 d0 /
data xgk ( 9 ) / 0.9055730376 9907797854 6522558825 958 d0 /
data xgk (10) / 0.8825605357 9205268154 1110462530 226 d0 /
data xgk (11) / 0.8570252335 4606109895 8658510658 944 d0 /
data xgk (12) / 0.8295657623 8276839744 299811973 502 d0 /
data xgk (13) / 0.7997278358 2183908301 3689942322 683 d0 /
data xgk (14) / 0.7677774321 0409619491 7977340974 503 d0 /
data xgk (15) / 0.7337900624 5322608047 6171131369 528 d0 /
data xgk (16) / 0.6978504947 9331579693 2292388026 640 d0 /
data xgk (17) / 0.6600610541 2662696137 0053668149 271 d0 /
data xgk (18) / 0.6205261829 8924265114 0477556431 189 d0 /
data xgk (19) / 0.5793452358 2636196175 6024932172 540 d0 /
data xgk (20) / 0.5366214481 4201989926 4169791311 073 d0 /
data xgk (21) / 0.4924804678 6177857499 3693061207 709 d0 /
data xgk (22) / 0.4470337695 3808917678 060990322 854 d0 /
data xgk (23) / 0.4040412548 4303493253 5476211542 661 d0 /
data xgk (24) / 0.3527047255 3087811347 1037207089 374 d0 /
data xgk (25) / 0.3040730220 7362507737 2677107199 257 d0 /
data xgk ( 26) / 0.2546369261 6788982643 9805129817 805 d0 /
data xgk ( 27) / 0.2045251166 8230989143 8957670102 025 d0 /
data xgk ( 28) / 0.153869136 0858354696 394672743 256 d0 /
data xgk ( 29) / 0.1028069379 6673703014 7069751318 091 d0 /
data xgk ( 30) / 0.0514718425 5531769587 3025213366 723 d0 /
data xgk ( 31) / 0.0000000000 0000000000 0000000000 000 d0 /
data wqk ( 1) / 0.0013890136 986770762 4551591226 760 d0 /
data wqk ( 2) / 0.0038904611 2709988405 1267201844 516 d0 /
data wqk ( 3) / 0.0066307039 1593129217 319826363 750 d0 /
data wqk ( 4) / 0.0092732796 5951770342 8441146892 024 d0 /
data wqk ( 5) / 0.0118230152 5349634174 2222898853 251 d0 /
data wqk ( 6) / 0.0143697295 0704580481 2451432443 580 d0 /
data wqk ( 7) / 0.0169208951 8905327262 7572289420 372 d0 /
data wqk ( 8) / 0.0194141411 9394238117 3408951050 128 d0 /
data wqk ( 9) / 0.0218280358 2160919229 7167485738 339 d0 /
data wqk (10) / 0.0241911620 7408060136 5686370725 232 d0 /
data wqk (11) / 0.0265099548 8233310161 0601709335 075 d0 /
data wqk (12) / 0.0287540487 6504129284 3978785354 334 d0 /
data wqk (13) / 0.0309072575 6238776247 2882525943 092 d0 /
data wqk (14) / 0.0332981447 0748372603 1841910168 854 d0 /
data wqk (15) / 0.0349793380 2806002241 7499670793 468 d0 /
data wqk (16) / 0.0366823466 5182122922 3911065516 136 d0 /
data wqk (17) / 0.0383878946 2472759295 0348651532 281 d0 /
data wqk (18) / 0.0400745389 5153695911 1995279752 468 d0 /
data wqk (19) / 0.0419698102 1516424614 7147541285 970 d0 /
data wqk (20) / 0.0434525397 0135606931 6831728117 073 d0 /
data wqk (21) / 0.0448418001 3316266319 2355551616 723 d0 /
data wqk (22) / 0.0460592382 7100698811 6271735559 374 d0 /
data wqk (23) / 0.0471855465 6929915394 5261478191 099 d0 /
data wqk (24) / 0.0481858617 5708712214 0779422298 305 d0 /
data wqk (25) / 0.0490554345 5502977888 7528165367 230 d0 /
data wqk (26) / 0.0497956934 2707420635 7811569379 942 d0 /
data wqk (27) / 0.0504059214 0278234684 0893085653 585 d0 /
data wqk (28) / 0.0508917958 8974960649 2297473049 805 d0 /
data wqk (29) / 0.0512215478 4925877217 0656282604 944 d0 /
data wqk (30) / 0.0514261285 3745902593 3862879216 781 d0 /
data wqk (31) / 0.0514947294 2945156755 8340433647 099 d0 /

list of major variables
-----------------------

centr - mid point of the interval
hlght - half-length of the interval
dabs - absissa
fval* - function value
resg - result of the 30-point gauss rule
resk - result of the 61-point kronrod rule
reskh - approximation to the mean value of f
        over (a,b), i.e. to 1/(b-a)

machine dependent constants
---------------------------

epmach is the largest relative spacing.
uflow is the smallest positive magnitude.

epmach = dimach(4)
uflow = dimach(1)

centr = 0.5d+00*(b-a)
hlght = 0.5d+00*(b-a)
dhight = dabs(hight)

c
compute the 61-point kronrod approximation to the
integral, and estimate the absolute error.
c
***first executable statement dqk61
resg = 0.0d+00
fc = f(center)
resk = wsgk(31)*fc
resabs = dabs(resk)
do i0 j=1,15
jtw = j*2
dabsc = hight*xgk(jtw)
fval1 = f(center-dabsc)
fval2 = f(center+dabsc)
fv1(jtw) = fval1
fv2(jtw) = fval2
fsum = fval1+fval2
resg = resg+wgk(j)*fsum
resk = resk+wgk(jtw)*fsum
resabs = resabs+wgk(jtw)*(dabs(fval1)+dabs(fval2))
10 continue
continue
10 do 15 j=1,15
jtwl1 = j*2-1
dabsc = hight*xgk(jtwl1)
fval1 = f(center-dabsc)
fval2 = f(center+dabsc)
fv1(jtwl1) = fval1
fv2(jtwl1) = fval2
fsum = fval1+fval2
resk = resk+wgk(jtwl1)*fsum
resabs = resabs+wgk(jtwl1)*(dabs(fval1)+dabs(fval2))
15 continue
reskh = resk*0.5d+00
resasc = wsgk(31)*dabs(fc-reskh)
do 20 j=1,30
resasc = resasc+wgk(j)*(dabs(fv1(j)-reskh)+dabs(fv2(j)-reskh))
20 continue
result = resk+hight
resabs = resabs*dhight
resasc = resasc*dhight
abser = dabs(resc-resg)*hight
if(resasc.ne.0.0d+00.and.abser.ne.0.0d+00)
* abser = resasc*dml(0.1d+01,0.2d+03)*abser/resasc)**1.5d+00
if(resabs.gt.ultflow/(0.5d+02*epmach)) abser = dmax1
* ((epmach*0.5d+02)*resabs, abser))
return
end

subroutine dgsrt(limit, lea, maxerr, ermax, elist, iord, nrmax)
c***begin prologue dgsrt
c***refer to dgsge, dgsple, dgspsle, dgswe
c***routines called (none)
c***revision date 810101 (yyymmdd)
c***keywords sequential sorting
c***author piessens, robert, appl. math. & progr. div. - k.u.leuven
c de doncker, elise, appl. math. & progr. div. - k.u.leuven

c***purpose this routine maintains the descending ordering in the
c list of the local error estimated resulting from the

c interval subdivision process. at each call two error
c estimates are inserted using the sequential search
c method, top-down for the largest error estimate and
c bottom-up for the smallest error estimate.

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ordering routine
standard fortran subroutine
double precision version

parameters (meaning at output)
   limit  - integer
       maximum number of error estimates the list
       can contain
   last   - integer
       number of error estimates currently in the list
   maxerr - integer
       maxerr points to the nmax-th largest error
       estimate currently in the list
   ermax  - double precision
       nmax-th largest error estimate
       ermax = elist(maxerr)
   elist  - double precision
       vector of dimension last containing
       the error estimates
   iord  - integer
       vector of dimension last, the first k elements
       of which contain pointers to the error
       estimates, such that
       elist(iord(1)), ..., elist(iord(k))
       form a decreasing sequence, with
       k > last if last .ge. (limit/2+2), and
       k = limit+1-last otherwise
   nmax  - integer
       maxerr = iord(nmax)

double precision elist, ermax, errmax, ermin
integer i, ibeg, iido, iord, isucc, j, jbound, jupbn, k, last, limit, maxerr.
* nmax
   dimension elist(last), iord(last)

    check whether the list contains more than
    two error estimates.

first executable statement dqpsrt
   if(last.gt.2) go to 10
      iord(1) = 1
      iord(2) = 2
   go to 90
   this part of the routine is only executed if, due to a
   difficult integrand, subdivision increased the error
   estimate. in the normal case the insert procedure should
   start after the nmax-th largest error estimate.

10 errmax = elist(maxerr)
   if(nmax.eq.1) go to 30
      iido = nmax-1
do 20 i = 1, lds
   isucc = iord(nrmax-1)
c*** jump out of do-loop
   if(errmax.le.elist(isucc)) go to 30
   iord(nrmax) = isucc
   nrmax = nrmax-1
20 continue

compute the number of elements in the list to be maintained
in descending order. This number depends on the number of
subdivisions still allowed.

10 jupbn = last
   if(lst.gt.(limit/2+2)) jupbn = limit+3-last
   errnin = ealist(last)
   c*** insert errmax by traversing the list top-down,
   starting comparison from the element ealist(iord(nrmax+1)).
   c
   jbdn = jupbn-1
   lbdn = nrmax+1
   if(lbdn.gt.jbdn) go to 50
   do 40 l = lbdn, jbdn
      isucc = iord(l)
c*** jump out of do-loop
      if(errmax.ge.elist(isucc)) go to 60
      iord(l-1) = isucc
50 continue
   40 iord(jbdn) = maxerr
   iord(jupbn) = last
   go to 90
   c*** insert errmin by traversing the list bottom-up.
   c
   60 iord(l-1) = maxerr
      k = jbdn
   do 70 j = 1, jbdn
      isucc = iord(k)
c*** jump out of do-loop
      if(errmin.lt.elist(isucc)) go to 80
      iord(k+1) = isucc
50 continue
   70 iord(1) = last
   go to 50
   80 iord(k+1) = last
   c
   set maxerr and errmax.
   c
   90 maxerr = iord(nrmax)
      errmax = ealist(maxerr)
      return
end

DOUBLE PRECISION FUNCTION DIMACH(1)

DOUBLE PRECISION MACHINE CONSTANTS

DIMACH( 1) = B**(EMIN-1), THE SMALLEST POSITIVE MAGNITUDE.

DIMACH( 2) = B**EMAX*(1 - B**(-T)), THE LARGEST MAGNITUDE.

DIMACH( 3) = B**(-T), THE SMALLEST RELATIVE SPACING.
D1MACH(4) = B**(-1-T), THE LARGEST RELATIVE SPACING.
D1MACH(5) = LOG10(B)

TO ALTER THIS FUNCTION FOR A PARTICULAR ENVIRONMENT,
THE DESIRED SET OF DATA STATEMENTS SHOULD BE ACTIVATED BY
REMOVING THE C FROM COLUMN 1.
ON RARE MACHINES A STATIC STATEMENT MAY NEED TO BE ADDED.
(BUT PROBABLY MORE SYSTEMS PROHIBIT IT THAN REQUIRE IT.)

FOR IEEE-ARITHMETIC MACHINES (BINARY STANDARD), ONE OF THE FIRST
TWO SETS OF CONSTANTS BELOW SHOULD BE APPROPRIATE.

WHERE POSSIBLE, DECIMAL, OCTAL OR HEXADECIMAL CONSTANTS ARE USED
TO SPECIFY THE CONSTANTS EXACTLY. SOMETIMES THIS REQUIRES USING
EQUIVALENT INTEGER ARRAYS. IF YOUR COMPILER USES HALF-WORD
INTEGERS BY DEFAULT (SOMETIMES CALLED INTEGER*2), YOU MAY NEED TO
CHANGE INTEGER TO INTEGER*4 OR OTHERWISE INSTRUCT YOUR COMPILER
TO USE FULL-WORD INTEGERS IN THE NEXT 5 DECLARATIONS.

INTEGER SMALL(2)
INTEGER LARGE(2)
INTEGER RIGHT(2)
INTEGER DIVER(2)
INTEGER LOG10(2)
INTEGER SC

DOUBLE PRECISION D1MACH(5)

EQUIVALENCE (D1MACH(1), SMALL(1))
EQUIVALENCE (D1MACH(2), LARGE(1))
EQUIVALENCE (D1MACH(3), RIGHT(1))
EQUIVALENCE (D1MACH(4), DIVER(1))
EQUIVALENCE (D1MACH(5), LOG10(1))

MACHINE CONSTANTS FOR IEEE ARITHMETIC MACHINES, SUCH AS THE AT&T
3B SERIES AND MOTOROLA 68000-BASED MACHINES (E.G. SUN 3 AND AT&T
PC 7300), IN WHICH THE MOST SIGNIFICANT BYTE IS STORED FIRST.

DATA SMALL(1), SMALL(2) / 1048576, 0 /
DATA LARGE(1), LARGE(2) / 2146435071, -1 /
DATA RIGHT(1), RIGHT(2) / 1017118720, 0 /
DATA DIVER(1), DIVER(2) / 1018167296, 0 /
DATA LOG10(1), LOG10(2) / 1070810171, 1352628735, 0, SC/987/

MACHINE CONSTANTS FOR IEEE ARITHMETIC MACHINES AND 8087-BASED
MICROS, SUCH AS THE IBM PC AND AT&T 6300, IN WHICH THE LEAST
SIGNIFICANT BYTE IS STORED FIRST.

DATA SMALL(1), SMALL(2) / 0, 1048576 /
DATA LARGE(1), LARGE(2) / -1, 2146435071 /
DATA RIGHT(1), RIGHT(2) / 0, 1017118720 /
DATA DIVER(1), DIVER(2) / 0, 1018167296 /
DATA LOG10(1), LOG10(2) / 1352628735, 1070810171, 0, SC/987/

MACHINE CONSTANTS FOR AMDahl MACHINES.

DATA SMALL(1), SMALL(2) / 1048576, 0 /
DATA LARGE(1), LARGE(2) / 2147483647, -1 /
DATA RIGHT(1), RIGHT(2) / 856688592, 0 /
DATA DIVER(1), DIVER(2) / 971463809, 0 /

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DATA LOG10(1), LOG10(2) / 1091781651, 1352628735 /, SC/987/

MACHINE CONSTANTS FOR THE BURROUGHS 1700 SYSTEM.

DATA SMALL(1) / ZC00800000 /
DATA SMALL(2) / Z00000000 /
DATA LARGE(1) / ZDFPFPFPFP /
DATA LARGE(2) / ZFPFPFPFPFP /
DATA RIGHT(1) / ZCC5800000 /
DATA RIGHT(2) / Z000000000 /
DATA DIVER(1) / ZCC6000000 /
DATA DIVER(2) / Z000000000 /
DATA LOG10(1) / Z200E730E7 /
DATA LOG10(2) / ZC77800DC0 /, SC/987/

MACHINE CONSTANTS FOR THE BURROUGHS 5700 SYSTEM.

DATA SMALL(1) / O17770000000000000000 /
DATA SMALL(2) / O00000000000000000000 /
DATA LARGE(1) / O07777777777777777777 /
DATA LARGE(2) / O00000000000000000000 /
DATA RIGHT(1) / O14610000000000000000 /
DATA RIGHT(2) / O00000000000000000000 /
DATA DIVER(1) / O14510000000000000000 /
DATA DIVER(2) / O00000000000000000000 /
DATA LOG10(1) / O1157163034761674 /
DATA LOG10(2) / O0006677466732724 /, SC/987/

MACHINE CONSTANTS FOR THE BURROUGHS 6700/7700 SYSTEMS.

DATA SMALL(1) / O17770000000000000000 /
DATA SMALL(2) / O77770000000000000000 /
DATA LARGE(1) / O77777777777777777777 /
DATA LARGE(2) / O77777777777777777777 /
DATA RIGHT(1) / O14610000000000000000 /
DATA RIGHT(2) / O00000000000000000000 /
DATA DIVER(1) / O14510000000000000000 /
DATA DIVER(2) / O00000000000000000000 /
DATA LOG10(1) / O1157163034761674 /
DATA LOG10(2) / O0006677466732724 /, SC/987/

MACHINE CONSTANTS FOR PTN4 ON THE CDC 6000/7000 SERIES.

DATA SMALL(1) / 00564000000000000000 /
DATA SMALL(2) / 00000000000000000000 /
DATA LARGE(1) / 37757777777777777777 /
DATA LARGE(2) / 3715577777777777774B /
DATA RIGHT(1) / 15624000000000000000 /

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DATA RIGHT(2) / 00000000000000000000B /
DATA DIVER(1) / 15634000000000000000R /
DATA DIVER(2) / 00000000000000000000B /
DATA LOG10(1) / 1716464202324117517B /
DATA LOG10(2) / 16367571421742254654B /, SC/987/

MACHINE CONSTANTS FOR FTNS ON THE CDC 6000/7000 SERIES.

DATA SMALL(1) / 0'05640000000000000000* /
DATA SMALL(2) / 0'00000000000000000000* /
DATA LARGE(1) / 0'37757777777777777777* /
DATA LARGE(2) / 0'37157777777777777777* /
DATA RIGHT(1) / 0'15624000000000000000* /
DATA RIGHT(2) / 0'00000000000000000000* /
DATA DIVER(1) / 0'15634000000000000000* /
DATA DIVER(2) / 0'00000000000000000000* /
DATA LOG10(1) / 0'1716464202324117517* /
DATA LOG10(2) / 0'16367571421742254654* /, SC/987/

MACHINE CONSTANTS FOR CONVEX C-1

DATA SMALL(1), SMALL(2) / '001000000'X, '000000000'X /
DATA LARGE(1), LARGE(2) / '7FFFFFFF'X, 'FFFFFFF'X /
DATA RIGHT(1), RIGHT(2) / '3CC00000'X, '00000000'X /
DATA DIVER(1), DIVER(2) / '3CD00000'X, '00000000'X /
DATA LOG10(1), LOG10(2) / '3F34413'X, '509F799F'X /, SC/987/

MACHINE CONSTANTS FOR THE CRAY 1, XMP. 2. AND 3.

DATA SMALL(1) / 20135400000000000000B /
DATA SMALL(2) / 000000000000000000003B /
DATA LARGE(1) / 57776777777777777777B /
DATA LARGE(2) / 00007777777777777777B /
DATA RIGHT(1) / 37643400000000000000B /
DATA RIGHT(2) / 00000000000000000000B /
DATA DIVER(1) / 37644400000000000000B /
DATA DIVER(2) / 00000000000000000000B /
DATA LOG10(1) / 37774644202324117517B /
DATA LOG10(2) / 00007571421742254654B /, SC/987/

MACHINE CONSTANTS FOR THE DATA GENERAL ECLIPSE S/200

SMALL, LARGE, RIGHT, DIVER, LOG10 SHOULD BE DECLARED INTEGER SMALL(4), LARGE(4), RIGHT(4), DIVER(4), LOG10(4)

NOTE - IT MAY BE APPROPRIATE TO INCLUDE THE FOLLOWING LINE -
STATIC Dmach(5)

DATA SMALL/20K,3*0/, LARGE/77777K,3*177777K/
DATA RIGHT/31420K,3*0/, DIVER/32020K,3*0 /
DATA LOG10/46423K,42023K,50237K,74776K/, SC/987/
MACHINE CONSTANTS FOR THE HARRIS SLASH 6 AND SLASH 7

DATA SMALL1, SMALL2 / '20000000, 00000201 /
DATA LARGE1, LARGE2 / '37777777, 37777577 /
DATA RIGHT1, RIGHT2 / '20000000, 00000333 /
DATA DIVER1, DIVER2 / '20000000, 00000334 /
DATA LOG10(1), LOG10(2) / '23210115, 10237777, SC/987/

MACHINE CONSTANTS FOR THE HONEYWELL DPS 8/70 SERIES.

DATA SMALL1, SMALL2 / 04024000000000, 00000000000000 /
DATA LARGE1, LARGE2 / 037677777777, 077777777777 /
DATA RIGHT1, RIGHT2 / 06344000000000, 00000000000000 /
DATA DIVER1, DIVER2 / 06940000000000, 00000000000000 /
DATA LOG10(1), LOG10(2) / 07744440202824, 017751775714, SC/987/

MACHINE CONSTANTS FOR THE IBM 360/370 SERIES.

THE XEROX SIGMA 5/7/9 AND THE SEL SYSTEMS 85/86.

DATA SMALL1, SMALL2 / 200000000, 2000000000 /
DATA LARGE1, LARGE2 / 27FFFFF, ZFFFFF1FF /
DATA RIGHT1, RIGHT2 / 233100000, 2000000000 /
DATA DIVER1, DIVER2 / 234300000, 2000000000 /
DATA LOG10(1), LOG10(2) / 241134413, 25997997FF, SC/987/

MACHINE CONSTANTS FOR THE INTERDATA 8/32.

WITH THE UNIX SYSTEM FORTRAN 77 COMPILER.

FOR THE INTERDATA FORTRAN VII COMPILER REPLACE
THE Z'S SPECIFYING HEX CONSTANTS WITH Y'S.

DATA SMALL1, SMALL2 / Y'00100000', Y'00000000' /
DATA LARGE1, LARGE2 / Y'7EFFFFF', Y'FFFFF1FF'/
DATA RIGHT1, RIGHT2 / Y'33100000', Y'0000000000' /
DATA DIVER1, DIVER2 / Y'34130000', Y'00000000' /
DATA LOG10(1), LOG10(2) / Y'41134413', Y'5097997F', SC/987/

MACHINE CONSTANTS FOR THE FDP-10 (KA PROCESSOR).

DATA SMALL1, SMALL2 / '033400000000, '000000000000 /
DATA LARGE1, LARGE2 / '377777777777, '344777777777 /
DATA RIGHT1, RIGHT2 / '113400000000, '000000000000 /
DATA DIVER1, DIVER2 / '114400000000, '000000000000 /
DATA LOG10(1), LOG10(2) / '177464202024, '14117571776, SC/987/

MACHINE CONSTANTS FOR THE FDP-10 (KI PROCESSOR).

DATA SMALL1, SMALL2 / '00400000000, '000000000000 /
DATA LARGE1, LARGE2 / '377777777777, '377777777777 /
DATA RIGHT1, RIGHT2 / '103400000000, '000000000000 /
DATA DIVER1, DIVER2 / '104400000000, '000000000000 /
DATA LOG10(1), LOG10(2) / '177464202024, '047674776746, SC/987/

MACHINE CONSTANTS FOR PDP-11 FORTRAN SUPPORTING
32-BIT INTEGERS (EXPRESSED IN INTEGER AND OCTAL).

DATA SMALL1, SMALL2 / 8388608, 0 /
DATA LARGE1, LARGE2 / 2147483647, -1 /
DATA RIGHT1, RIGHT2 / 612368384, 0 /
DATA DIVER1, DIVER2 / 620756992, 0 /
DATA LOG10(1), LOG10(2) / 1067065498, -206387208, SC/987/
DATA SMALL(1), SMALL(2) / 000000000000, 000000000000 /
DATA LARGE(1), LARGE(2) / 037777777777, 077777777777 /
DATA RIGHT(1), RIGHT(2) / 0170540000000, 000000000000 /
DATA DIVER(1), DIVER(2) / 0170640000000, 000000000000 /
DATA LOG10(1), LOG10(2) / 0177746420212, 041175717572 /
, SC/987/

MACHINE CONSTANTS FOR THE VAX UNIX FT7 COMPILER

DATA SMALL(1), SMALL(2) / 128, 0 /
DATA LARGE(1), LARGE(2) / -32768, -1 /
DATA RIGHT(1), RIGHT(2) / 9344, 0 /
DATA DIVER(1), DIVER(2) / 9472, 0 /
DATA LOG10(1), LOG10(2) / 546979738, -805796613 /
, SC/987/

MACHINE CONSTANTS FOR THE VAX-11 WITH
FORTRAN IV-PLUS COMPILER

DATA SMALL(1), SMALL(2) / Z00000000, Z00000000 /
DATA LARGE(1), LARGE(2) / ZFFFF7FFF, ZFFFF7FFF /
DATA RIGHT(1), RIGHT(2) / Z00000000, Z00000000 /
DATA DIVER(1), DIVER(2) / Z00000000, Z00000000 /
DATA LOG10(1), LOG10(2) / 2209A3P9A, ZCF884F8 /
, SC/987/

MACHINE CONSTANTS FOR VAX/VMS VERSION 2.2

DATA SMALL(1), SMALL(2) / '80'X, '0'X /
DATA LARGE(1), LARGE(2) / 'FFFF77FFF'X, 'FFFF77FFF'X /
DATA RIGHT(1), RIGHT(2) / '2400'X, '0'X /
DATA DIVER(1), DIVER(2) / '2500'X, '0'X /
DATA LOG10(1), LOG10(2) / '209A3P9AX', 'CF884F8X' /
, SC/987/

*** ISSUE STOP 779 if ALL DATA STATEMENTS ARE COMMENTED...
IF (SC .NE. 987) STOP 779

*** ISSUE STOP 776 IF ALL DATA STATEMENTS ARE OBVIOUSLY WRONG...
IF (DMACH(4) .GE. 1.0D0) STOP 778
IF (I .LT. 1 .OR. I .GT. 5) GOTO 999
DIMACH = DMACH(1)
RETURN

999 WRITE(*,999) I
1999 FORMAT('DIMACH = I OUT OF BOUNDS', (I10))
STOP
END

subroutine dqelgn(s, epstab, result, abserr, res3la, res3c)
c**begin prologue dqelgn
subroutine dqelgn
***refer to dqagle, dqagse, dqagpe, dqagse
***routines called dimach
***revised date 830518 (yymmdd)
***keywords epsilon algorithm, convergence acceleration,
***author biessens, robert, appl. math. & progr. div. - k.u.leuven
***summary the routine determines the limit of a given sequence of
approximations, by means of the epsilon algorithm of
p-wyn. an estimate of the absolute error is also given.
the condensed epsilon table is computed. only those
elements needed for the computation of the next diagonal
are preserved.
***description
\epsilon (epsilon) algorithm
* standard fortran subroutine
* double precision version
parameters
n     - integer
      epstabl(n) contains the new element in the
      first column of the epsilon table.

c epstab - double precision
      vector of dimension 52 containing the elements
      of the two lower diagonals of the triangular
      epsilon table. the elements are numbered
      starting at the right-hand corner of the
      triangle.

c result - double precision
      resulting approximation to the integral

c abserr - double precision
      estimate of the absolute error computed from
      result and the 3 previous results

c res3la - double precision
      vector of dimension 3 containing the last 3
      results

c nres - integer
      number of calls to the routine
      (*should be zero at first call*)

***end prologue dqelg***

double precision abserr, dabs, delta1, delta2, delta3, dmax1, dimach.
* epmach, epsint, epstab, error, err1, err2, err3, e0, e1, e1abs, e2, e3,
  * oflow, res, result, res3la, ss, to11, to12, to13
integer i, ib, ib2, ie, indx, k1, k2, k3, limexp, n, newelm, nres, num
dimension epstab(52), res3la(3):

list of major variables
----------------------

e0        - the 4 elements on which the computation of a new
e1        - element in the epsilon table is based
  e2
  e3
  e3        - e2  new
      e1

newelm - number of elements to be computed in the new
diagonal
error - error = abs(e1-e0)+abs(e2-e1)+abs(new-e2)
result - the element in the new diagonal with least value
  of error

machine dependent constants
----------------------

epmach is the largest relative spacing.
oflow is the largest positive magnitude.
limexp is the maximum number of elements the epsilon
table can contain. if this number is reached, the upper
diagonal of the epsilon table is deleted.

***first executable statement dqelg
 .epmch = dimach(4)

251
oflow = dimach(2)
nres = nres+1
abserr = oflow
result = epsstab(n)
if (n.lt.3) go to 100
limexp = 50
epsstab(n+2) = epsstab(n)
newelm = (n-1)/2
epsstab(n) = oflow
num = n
k1 = n
do 40 i = 1,newelm
   k2 = k1-1
   k3 = k1-2
   res = epsstab(k1+2)
e0 = epsstab(k3)
e1 = epsstab(k2)
e2 = res
   elabs = dabs(e1)
delta2 = e2-e1
err2 = dabs(delta2)
tol2 = dmax1(dabs(e2),elabs)*epmach
delta3 = e1-e0
err3 = dabs(delta3)
tol3 = dmax1(elabs,dabs(e0))*epmach
if (err2.ge.tol2.or.err3.ge.tol3) go to 10
   c
   if e0, e1 and e2 are equal to within machine
   c
   accuracy, convergence is assumed.
   c
   result = e2
   c
   abserr = abs(e1-e0)+abs(e2-e1)
   c
   result = res
   abserr = err2+err3
   c
   ***jump out of do-loop
   go to 100
40  
   e3 = epsstab(k1)
   epsstab(k1) = e1
delta1 = e1-e3
erri = dabs(delta1)
tol1 = dmax1(elabs,dabs(e3))*epmach
   c
   if two elements are very close to each other, omit
   c
   a part of the table by adjusting the value of n
   c
   if (err1.le.tol1.or.err2.le.tol2.or.err3.le.tol3) go to 20
   ss = 0.1d+01/delta1+0.1d+01/delta2-0.1d+01/delta3
   epsinf = dabs(ss*e1)
   c
   test to detect irregular behaviour in the table, and
   c
   eventually omit a part of the table adjusting the value
   c
   of n.
   c
   if (epsinf.gt.0.1d-03) go to 30
   n = i+1-1
   c
   ***jump out of do-loop
   go to 50
20  
   c
   compute a new element and eventually adjust
   c
   the value of result.
   c
   30  res = e1+0.1d+01/ss

252
epstab(k1) = res
k1 = k1-2
error = err2+dabs(res-e2)+err3
if(error.gt.abserr) go to 40
abserr = error
result = res
40 continue

shift the table.

50 if(n.eq.limexp) n = 2*limexp/2
   ib = 1
   if((num/2)*2.eq.num) ib = 2
   ie = newelm+1
   do 60 i=1,ie
       lb2 = ib+2
       epstab(lb2) = epstab(ib2)
       ib = lb2
   60 continue
   if(num.eq.n) go to 80
   indx = num-n+1
   do 70 i = 1,n
       epstab(i) = epstab(indx)
       indx = indx+1
   70 continue
80 if(nres.ge.4) go to 90
   res3la(nres) = result
   abserr = oflow
   go to 100

compute error estimate

90 abserr = dabs(result-res3la(3))+dabs(result-res3la(2))
   *+dabs(result-res3la(1))
   res3la(1) = res3la(2)
   res3la(2) = res3la(3)
   res3la(3) = result
100 abserr = dmax1(abserr, 0.5d0*epmach*dabs(result))
   return
end

A.2.2 Sample Inputs to the Programs

The controlling input file:

dll1.aux
dll1.f1d
dll1.out

The meanings of the lines are

<table>
<thead>
<tr>
<th>Filename of the parameter file</th>
<th>Filename of the displacement file</th>
<th>Filename of the output</th>
</tr>
</thead>
<tbody>
<tr>
<td>Described below</td>
<td>Generated by the program in the last section</td>
<td>To be used by the program in the next section</td>
</tr>
</tbody>
</table>

The content of the parameter file:

1.757798 1.340138 0.760752 3.598952 151 201 11 31 6 101
40.0 40.0 1.75 0.20 0.30 1.0 1.0 1.0 300.0 500.0
1 0.450000

253
\[
\begin{array}{ccc}
1.000000 & 1.000000 & 1.000000 \\
0.004330 & 0.000000 & -0.000000 \\
-1.000000 & 1.000000 & 0.000000 \\
0.000000 & 0.004330 & 0.000000 \\
-1.000000 & -1.000000 & 2.000000 \\
-0.000000 & 0.000000 & -0.158097 \\
-1499.795288 & 0.000000 & 0.000000 \\
0.000000 & -1499.795532 & 0.000000 \\
0.000000 & 0.000000 & -3195.950328 \\
\end{array}
\]

Meanings of the parameters:

\[
\begin{array}{ccc}
c_{11} & c_{12} & c_{44} \\
a & b & c \end{array}
\]

Lattice parameter \hspace{1cm} Do not change these \hspace{1cm}

\[
\begin{array}{ccc}
a_{31} & a_{32} & a_{33} \\
C_p - C_0 \end{array}
\]

Don’t change \hspace{1cm} Don’t change \hspace{1cm}

where, \( \epsilon_{ij} \) is the final strain inside the ellipsoid, and \( d_{ij} \) is the dipole tensor, which is given by

\[
d_{ij} = \frac{4\pi}{3} abc \epsilon_{ij}^2.
\]

The program accepts the first mentioned input file from the standard input and outputs the results according to the content of this file. This program also needs to be run once for each non-equivalent direction.

### A.3 Quasiline

#### A.3.1 Programs

```fortran
implicit none
double precision phirr(302), phiri(302), phiq(302), prq(302)
double precision conc, a, b, c, vc, ca, rfin, rstep, lac, dspac, pi
double precision q(302), dacos, k(3), landa, frs, const, pcons
double precision theta2, epsi, pshift, thetac, r(302), tmp5
double precision prrr(302), prri(302), tmp1, tmp2, tmp3, tmp4
double precision qsrr(302), qsri(302), qsprr(302), qspri(302)
double precision quasim(302), quasip(302), rpaf, epsil, epsav
double precision yo, am, pa, ttlad(302), ttlqs(302), ttlbg(302)
double precision dgamma, dexp, dcos, dsin, dabs, phiqq, prqqqq
double precision weight(4)
character*40 quafile, outfile(4), phifile, allfile
integer i, j, nrp1, nrp, numfiles
read(*,*) numfiles
do 89 i=1, numfiles
```

254
read(*,'(a9,f30.0)')outfile(i),weight(i)
89 continue
read(*,'(a)')quafile
read(*,'(a)')phiffile
read(*,'(a)')allfile
open(7,file=quafile,status='old')
open(10,file=phiffile,status='unknown')
open(11, file=allfile, status='unknown')
READ(7,*)LAC,NRP,RFIN,K(1),K(2),K(3),LAMDA,A,B,C,EP$AV,CA,FRS,RPAF
READ(7,*)PA,AM

C
PI=DCOS(-1.0d+00)
DSPAC=LAC/DSQRT(K(1)**2+K(2)**2+K(3)**2)
CONST2=2.*PI/LAMDA*DSQRT(1.-LAMDA**2/4./DSPAC**2)
PCONS=180./PI
THETA2=DSIN(LAMDA/2./DSPAC)*PCONS/2.
VC=LAC**3/4.
RSTEF=RFIN/(NRP-1.)
NRP1=RPAF/RSTEF+1
CONCA=CONC*FRS/AS/VC/3.*VC
EPSI=CONCA/VC**.3.*PI**A*B*C*EP$AV
PHSHIFT=-EP$AV/CTAN(THETA2/2./PCONS)*PCONS/2.
THETAS=THETA2+PHSHIFT

C.................integration grid................
C
DO 86 i=1,NRP
   r(i)=rstep*dfloat(i-1)
86 continue
C................convert phi(q3) and pr(q3) to dimensionless........
C
DO 98 i=1,302
   phii(i)=0.0d+00
   pr(i)=0.0d+00
98 continue
DO 567 j=1,numfiles
   OPEN(8, file=outfile(j), status='old')
   DO 99 i=1,302
      READ(8,*)Q(I),tmp1,tmp2
      phii(i)=phii(i)+tmp1*weight(j)
      pr(i)=pr(i)+tmp2*weight(j)
   99 continue
   CLOSE(8)
567 continue
DO 97 i=1,302
   phii(i)=phii(i)*conc/vc
   pr(i)=pr(i)*conc/vc
97 continue
C...............Find phir(r)................
C
DO 13 J=1,NRP
   phir(J)=0.0d+00
   phir(J)=0.0d+00
   DO 12 I=2,302
      tmp1=-Q(I)*r(J)
      tmp2=-Q(I-1)*r(J)
      tmp3=DCOS(tmp1)
      tmp4=DSIN(tmp1)
   12 continue
   phir(J)=PHSHIFT+2*PI*(R(I)*tmp3)/(1./2.*TAN(THETA2/2.))
13 continue
tmp1 = dc\cos(tmp2)
tmp2 = dsin(tmp2)
Tmp5 = (q(1)-q(l-1))*0.5d+00
phirr(j) = phirr(j) + (phiq(i)*tmp3+phiq(i-1)*tmp1)*tmp5
phiri(j) = phiri(j) + (phiq(i)*tmp4+phiq(i-1)*tmp2)*tmp5

12 continue
phirr(j) = phirr(j)/(2.0d+00*pi)
phiri(j) = phiri(j)/(2.0d+00*pi)

13 continue

WRITE(10,'(1X,3e15.5;)') R(J),PHIR(J),PHIR(J),J=1,NRP

C............This is e^{(-2M)(e^{\phi(t)}-1)\phi(t)}

C
C
C
C EPHI=EXP(-phirr(1))
C
C............Calculate e^{(-2M)(e^{\phi(t)}-1)\phi(t)}

C DO 23 J=1,NRP
Qsrr(j) = ephii*(dexp(phirr(j))*dcos(phiri(j))-1.0d+00-phirr(j))
Qsri(j) = ephii*(dexp(phirr(j))*dsin(phiri(j))-phiri(j))

23 continue

C............Find P(t) and calc e^{(-2M)(e^{\phi(t)}-1)P(t)}

C DO 77 J=1,NRP1
Prrr(j) = 0.0d+00
Pprri(j) = 0.0d+00
DO 79 I=2,302

tmp1 = -q(1)*r(j)
tmp2 = -q(l-1)*r(j)
tmp3 = dc\cos(tmp1)
tmp4 = dsin(tmp1)
tmp2 = dc\os(tmp2)
tmp2 = dsin(tmp2)

25 continue

79 continue

Prrr(j) = Prrr(j)/(2.0d+00*pi)
Pprri(j) = Pprri(j)/(2.0d+00*pi)

77 continue

C
C
C
C do 24 I=1,302
Quasim(i) = 0.0d+00
Quasii(i) = 0.0d+00
DO 25 J=1,NRP

tmp1 = q(j)*r(j)
tmp2 = 2.0d+00*(dcos(tmp1)*qsrr(j)-dsin(tmp1)*qsrri(j))
if (j.eq.1.or.j.eq.NRP) tmp2=tmp2*0.5d+00
Quasim(i) = Quasim(i)+tmp2

25 continue

Quasim(i) = Quasim(i)*rstep
DO 26 J=1,NRP1

tmp1 = q(j)*r(j)
tmp2 = 2.0d+00*(dcos(tmp1)*qsprri(j)-dsin(tmp1)*qsprri(j))
if (j.eq.1.or.j.eq.np) tmp2=tmp2*0.5d+0
    quasip(i) = quasip(i)+tmp2
26  continue
    quasip(i) = quasip(i)*rstep
24  continue

/*
  total, scaling and all that....
*/

y0=dsqrt(1.0d+00/pi/am)/pa*dgamma(a)/dgamma(a-0.5)*ephi1/vc
1     8.*pi**3*pcons
      y0=ephi1/vc*8.*pi**3*pcons/pa/dsqrt(pi)

do 68 i=1,302
  ttlsd(i) = ephi1*(phiq(i)+prq(i))*const*(2.0d+00*pi)**2/vc
  ttlqs(i) = (quasim(i)+quasip(i))*const*(2.0d+00*pi)**2/vc
   c
  ttlbg(i) = y0/(1.0d+00+(q(i)*pcons/consta)**2/am)**am
  ttlbg(i) = y0*delta(-q(i)*pcons/consta)**2)
68  continue

/*
  Output...
*/

write(11,'(5e15.5e3)')(q(i)*pcons/consta,ttlxd(i),ttlqs(i),
  1      ttlbg(i),ttlxd(i)+ttlqs(i)+ttlbg(i),i=1,302)
END

A.3.2 Sample Inputs to the Programs

The controlling input file:

1
1111.out  1.000000
1111.qua
1111.phi
1111.all

The meanings:

<table>
<thead>
<tr>
<th>n</th>
<th>Number of non-equivalent directions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input intermediate filename</td>
<td>Weight for one non-equivalent direction</td>
</tr>
<tr>
<td>Repeat once for each non-equivalent dir</td>
<td></td>
</tr>
<tr>
<td>Parameter filename</td>
<td></td>
</tr>
<tr>
<td>Output filename for $\Phi(\beta_3)$ data</td>
<td></td>
</tr>
<tr>
<td>Output filename for profile data</td>
<td></td>
</tr>
</tbody>
</table>

The input intermediate filenames are the names of the output files from the program in the last section. There is one for each non-equivalent direction. The weight of each non-equivalent direction is the relative multiplicity of the direction. The sum of the weights should be equal to 1.

The contents of the parameter file:

3.598952 101 503. 1. 1. 1. 1.540510 40. 40. 1.75 -0.039675 0.0616 0.5 40. 0.070000 10.000000

Meanings:

Lattice parameter  Don't change  Don't change  $a_31$  $a_32$  $a_33$  $\lambda$  $a$  $b$  $c$  $\epsilon_{av}$  $C$  $C_p$  $a$
$P_d$  $P_m$
where

$$
\epsilon_{avg} = \frac{1}{3}(2\epsilon_{11}^T + \epsilon_3^T),
$$

and $C$ is the concentration of the precipitates in the material, and, $P_a$ and $P_m$ are the Pearson VII parameters for the Bragg peak.

This program accepts the controlling input from the standard input and outputs the results according the data in this file. For the $\Phi(R_0)$, the data are arranged in three columns. The first is the value of $R_0$, and the second and the third columns are the real and imaginary part of $\Phi(R_0)$. For the output profile, the first column is the $2\theta$ value relative to the matrix Bragg peak position, and the second column is the unscaled intensity value. The intensity should be transformed according to the descriptions at the end of Chapter 6.

This data files given in the appendices are those for the sample aged for 16 hours at 200°C.
Vita

The author was born on October 16, 1966 in Guangzhou, Guangdong, China. He attended Zhixin Middle School of Guangzhou. At age 14, he was admitted to the University of Science and Technology of China (in Hefei, Anhui, China) under a special program designed for gifted children. In July 1986, he was awarded the Bachelor of Science degree in Physics. He came to the U.S. in September 1986 through the CUSPEA (China-US Physics Examination and Application) Program, and started his graduate study in the Department of Physics at Virginia Tech. After finishing his Master of Science degree in Physics in May 1989, he entered the Materials Engineering Science Program at Virginia Tech and began studies for his Ph. D. degree under the guidance of Dr. C. R. Houska. The author's interests are in the design, testing and manufacturing of VLSI chips and devices.

Chyi Wu