

ATOMIC SIZE FACTOR AND THE Cr O-TYPE COMPOUND
3
IN THE Cr-Si-Sn TERNARY SYSTEM

by

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INTRODUCTION

The Cr_3O -type structure frequently occurs in various binary alloy systems involving transition elements. In approximately forty binary alloy systems Cr_3O -type compounds are found. However, little is known concerning the factors that govern the formation of these compounds.

Investigators have reported two different sets of "derived radii" for the elements which form the Cr_3O -type compounds. Each of these sets of radii predicts the lattice parameter to an acceptable degree of accuracy. However, the equations used with either set of radii do not necessarily follow from geometrical considerations of the unit cell.

Other investigators have found that size factor seems to play an important role in the stability of these compounds. Some of these compounds also exhibit unusual electrical properties at low temperatures.

As almost all of the observations regarding the Cr_3O -type compounds had been made from binary systems, the Department of Metallurgical Engineering under the sponsorship of the Atomic Energy Commission began an investigation to determine the effect of size factor on the stability of these compounds in ternary alloy systems.

The first phase of the investigation dealing with the V-Si-Sn system did not rule out the concept of size factor playing an important role in the stability of the Cr_3O -type compounds. The second phase of the investigation, with which this thesis deals, was conducted to further test the effect of size factor in the Cr-Si-Sn system.

LITERATURE REVIEW

Introduction. Historically, the element tungsten was once thought to have an allotropic modification isomorphous with the structure of the Cr_3O -type phases. (1) Hagg and Schonberg were able to show that this so-called "Beta Tungsten" modification was actually a compound of tungsten and oxygen (W_3O) with oxygen atoms randomly distributed in the available atomic sites. A corresponding compound Cr_3O is isomorphous with W_3O , but in this compound the oxygen atoms occupy specific ordered positions resulting in an ordered structure. Therefore, in the literature these compounds are referred to as either the Beta Tungsten-type or the Cr_3O -type. The Cr_3O -type nomenclature is preferred by some, as these (2) intermetallic phases are also ordered.

In some instances these Cr_3O -type compounds are designated by the formula A_3B . This usage is sometimes ambiguous, as only the stoichiometry is indicated. In this thesis the formula A_3B will be used to denote the Cr_3O -type structure in general when no particular chemical elements are specified.

Geometrical Considerations. The Cr_3O -type phases have the Space-Group $\text{Oh}^3\text{-Pm}3\text{n}$, belonging to the cubic system.

The unit cell contains eight atoms whose coordinates for the ordered structure are:

6 A Atoms	1/4, 0, 1/2;	1/2, 1/4, 0;	0, 1/2, 1/4
	3/4, 0, 1/2;	1/2, 3/4, 0;	0, 1/2, 3/4
2 B Atoms	0, 0, 0;	1/2, 1/2, 1/2	

In considering the coordination of the atoms of the ordered structure, it is found that:

(3)

Each A atom is coordinated to:

Two A atoms at distance $1/2 a_0$
Eight A atoms at distance $1/4 a_0 \sqrt{6}$
Four B atoms at distance $1/4 a_0 \sqrt{5}$

Each B atom is coordinated to:

Twelve A atoms at distance $1/4 a_0 \sqrt{5}$
Eight B atoms at distance $1/2 a_0 \sqrt{3}$

The unit cell of the Cr_3O -type structure is shown in Figure 1.

Using the popular concept of atoms being hard touching spheres, Laves (4) has shown:

If A touches A and B atoms, $R_a/R_b = 0.81$

If B touches B and A atoms, $R_a/R_b = 0.29$

If R_a/R_b is greater than 0.81, only (A-A) contact is present.

If R_a/R_b is greater than 0.29 and less than 0.81, only (A-B) contact is present.

If R_a/R_b is less than 0.29, only (B-B) contact is present.

Atomic Size and Lattice Parameters of the Cr₃O-type

Phases. In dealing with the "Size" of atoms in a structure, (3)(4)(5)(6)(7)(8) an area of controversy is entered.

An examination of Figure 2 indicates that if A-A contacts are present, the relation between atomic radius and lattice parameter is:

$$4 R_a = a_o \tag{1}$$

R_a = radius of "A" atoms

a_o = parameter of unit cells

and does not depend on the radius of the B atom.

Further examination indicates that if (A-B) contacts are present the relation becomes--

$$a_o = 4/\sqrt{5} (R_a + R_b) \tag{2}$$

Equations (1) and (2) are consistent when:

$$4 R_a = a_o \quad 4/5 (R_a + R_b)$$

$$4 R_a = 4/\sqrt{5} (R_a + R_b)$$

dividing by $4 R_a$ --

$$1 = 1/\sqrt{5} (1 + R_b/R_a)$$
$$\sqrt{5} = 1 + R_b/R_a$$
$$R_b/R_a = 1/\sqrt{5} - 1 = 1/1.236 - 1 = 0.81$$

as was shown by Laves.

As a basis for discussing the relative size of an atom, it is often convenient to use the Goldschmidt Coordination Number 12 Radii. It is known that for different crystal structures the Atomic Radius of a given element usually varies when the Coordination Number (number of nearest neighbors) changes for the various crystal structures.

In general, with a decrease in Coordination Number, the size of the atom tends to decrease according to:
(9)

Change in Coordination Number	% Contraction
(12) \longrightarrow (8)	3 %
(12) \longrightarrow (6)	4 %
(12) \longrightarrow (4)	12 %

The Goldschmidt Coordination Number 12 Radii, in effect, give the size which an atom would exhibit in a Coordination Number 12 environment. There are two crystal structures commonly found in metals which have a

Coordination Number 12 environment. The first is the face-centered cubic structure, and the second is the hexagonal close-packed structure. If one uses the concept of atoms having a spherical shape and touching each other, the Coordination Number 12 Radii are probably adequate for comparison purposes. This can be seen by considering the face-centered cubic structure in which each atom has identical surroundings consisting of twelve equidistant neighbors whose directions are more or less equally distributed in space. This face-centered cubic structure also represents one of the two "closest packing" arrangements of equal diameter spheres in space.

The Coordination Number of an atom in a given crystal structure does not necessarily define the valence. Pauling, (1) by observing the change in the inter-atomic distance of the carbon atom with change in the number of carbon bonds formed, formulated the relation:

$$D_n = D_1 - 0.70 \log n$$

D_n = inter-atomic distance between
atom with n bonds

D_1 = inter-atomic distance between
atoms with 1 bond

n = number of bonds between atoms

From this relation and his theory of resonating covalent bonds for metals, Pauling modified the relation such that:

$$D_n = D_1 - 0.60 \log n$$

D_n = inter-atomic distance between atoms with n bonds

D_1 = inter-atomic distance between atoms with 1 bond (also called the univalent radii)

n = $\frac{\text{bonding electrons}}{\text{Coordination Number}}$

Pauling indicates this relation holds very well in metallic structures.

(3)

Geller, using the relation $a_0 = 4/5 (R_a + R_b)$ for the A-B contacts, derived a set of Coordination Number 12 Radii for metals in B-Wolfram structures which predict the lattice parameter of these compounds. He also indicates Pauling's resonating-valence-bond theory of intermetallic compounds does not apply.

(5)

In reply, Pauling modifies the equation of Geller such that:

$$a_0 = 1.788 (3/2 R_a + 1/2 R_b)$$

This modification gives the A atom three times the weight of a B atom in determining the lattice parameter in accordance with the stoichiometric formula, A_3B . Pauling then proposes, "A set of effective metallic radii for use in compounds with the B-Wolfram structure."

(6)

Geller objects to Pauling's paper in the following areas: 1) does the resonating-valence-bond theory apply? 2) if not, what technique is used to obtain the new radii? and 3) are the new radii an improvement over the original ones by Geller?

(7)

Pauling replies again in defense of his radii and reports the results of a least squares evaluation which shows the weighing factor to be 2.45/1, closer to his 3/1 factor than Geller's 1/1 relation.

(8)

To this, Geller states his position as being clear and no further discussion is necessary.

By using the Goldschmidt Coordination Number 12 Radii of the elements and calculating the R_a/R_b ratio, (10) Nevitt found the binary Cr_3O -type compounds to lie in a "favorable" R_a/R_b ratio range between 0.84 and 1.11. Nevitt also points out the strong tendency of vanadium, niobium, and chromium to act as A elements and for the third long period of Group VIII elements to act as B elements.

(12)

Scope of Work. Work by Van Reuth on the V-Si-Sn system had indicated the feasibility of substituting Sn atoms for Si atoms in "B" atom sites. If the atomic size of the atoms were the governing factor in the formation of Cr_3O -type compounds, Sn atoms should substitute for Si atoms in ternary systems which have an "A" element other than vanadium.

In the Cr-Si-Sn system, Cr_3Si is known to exist, the R_a/R_b ratio being 0.96 which is within the "favorable" range observed by Nevitt. (10) However, no Cr_3O -type compound has been reported in the Cr-Sn binary. If such a compound did exist, then its R_a/R_b ratio of 0.81 would fall outside Nevitt's "favorable" range.

If Sn atoms could be substituted for Si atoms in Cr_3Si structure, the effective radius ratio would vary linearly from 0.96 at 25 per cent Si, 75 per cent Cr to 0.81 at 25 per cent Sn, 75 per cent Cr. As Cr_3Sn is not known to exist, a one phase field extending across the ternary Cr-Si-Sn diagram from Cr_3Si toward the Cr-Sn binary should terminate within the ternary diagram. From the terminating point of the one phase field the effective R_a/R_b ratio could be determined. If the derived R_a/R_b limiting ratio coincided with Nevitt's observed value of 0.84, this would be evidence that size factor exerts a strong influence on the stability of the Cr_3O -type compounds.

From these considerations, the proposed object of this thesis was to measure the extent of substitution of Sn atoms for Si atoms in the compound Cr_3Si and to determine the lower effective Coordination Number 12 radius ratio below which the $\text{Cr}_3(\text{Si},\text{Sn})$ phase is not stable.

EXPERIMENTAL

Experimental Procedure. Facilities for arc melting of the alloys were not available in the Department of Metallurgical Engineering at the beginning of this investigation. Therefore, six alloys in the Cr-Si-Sn system of constant 75 atomic per cent Cr were weighed out in 30-gram samples and sent to Battelle Memorial Institute of Columbus, Ohio for melting.

The method of arc melting employed at Battelle was the popular inert gas-cold-mold technique. In this operation an inert gas atmosphere (Helium) protects the molten metal which rests on a water cooled copper hearth; thus contamination of the melt is prevented. As the portion of the sample in contact with the mold was not 100 per cent molten, the samples were inverted and re-melted approximately six times to insure homogeneity.

After the melting operations, a weighing of the samples indicated the losses during melting were too high to be commensurate with the accuracy desired. These losses were attributed to the high vapor pressure of Sn as compared to Cr and Si.

To avoid such losses it was decided to use powder metallurgy techniques to prepare the alloys in the Cr-Si-Sn system.

A powder compact of 25 atomic per cent Si and 75 atomic per cent Cr was prepared. The compact was sealed in vacuo in fused quartz tubing. The pressure when sealed was less than one micron of mercury as indicated by a National Research Corporation thermo-couple gauge. Sealing of the fused quartz was accomplished without difficulty using an oxidizing oxygen-acetylene flame.

Annealing of this compact for eight hours at approximately 1100 degrees Centigrade produced a specimen containing an estimated 85 per cent of the Cr_3Si phase. The measured lattice parameter of this phase was in good agreement with the values reported in the literature. The interplanar spacings and intensities of the diffracted rays of Cr_3Si are shown in Table I.

A second powder compact of 20 atomic per cent Si, 5 atomic per cent Sn, and 75 atomic per cent Cr was prepared. This compact was sealed in vacuo and sintered at 1100 degrees Centigrade for 72 hours. X-Ray examination of this alloy indicated the presence of Cr_3Si , Cr, and Sn. The lattice parameter of the Cr_3Si phase had not changed, indicating Sn was not substituting for Si in the structure.

A third similar compact was sintered at 1100 degrees Centigrade for 500 hours. X-Ray examination of the specimen still indicated no evidence of Sn substituting for Si in the structure.

A fourth similar compact was sintered at 1100 degrees Centigrade for 2000 hours, and again the desired substitution did not occur. However, a complex phase did form which could not be identified. The "d" spacings and observed intensities from the X-Ray pattern of the alloy containing this phase are reported in Table II.

While the sintering of the above compacts proceeded, the arc melted alloys were examined. Though the compositions of these arc melted alloys were estimated to be in error by about five atomic per cent, the presence of a Cr_3O -type phase whose lattice parameter was not the same as Cr_3Si would indicate that a Cr_3O -type solid solution was possible in the Cr-Si-Sn system. The Cr_3Si phase was found in each of three arc melted alloys examined, and in each case the lattice parameter corresponded to that of the binary Cr_3Si phase.

From these attempts it seems reasonable to assume that Sn atoms will not substitute for Si atoms in the compound Cr_3Si .

DISCUSSION

From the Cr-Sn and Si-Sn binary phase diagrams, (13)
one might expect that Sn would not alloy readily with Cr
or Si. However, this would not exclude an alloying of Sn
with Cr_3Si , and such an alloy might be expected in light
of the work done by Van Reuth in the V-Si-Sn system.

The inability of Sn to substitute for Si in the
compound Cr_3Si leads to the contention that factors
other than size must be considered when discussing the
stability of the Cr_3O -type compounds.

If atomic size is not the only factor in the forma-
tion of these compounds, another factor to be considered
is the electron configuration of the elements involved.
As outlined previously, Nevitt (10) has shown the location
in the periodic chart of the elements forming Cr_3O -type
compounds. As these compounds involve transition ele-
ments, it would not be surprising to find that the "usual"
chemical valences do not hold true. (14)

The two models proposed by Geller (3) and Pauling (5)
for relating the lattice parameter of the Cr_3O -type com-
pounds to the size of the atoms involved have one point
in common. Each model has a given element exhibiting a
constant size in all of the Cr_3O -type compounds in which
it forms.

Geller's model based on the equation $a_0 = \frac{4}{5} (R_a + R_b)$ is geometrically correct for the A-B atom contacts. However, the R_a/R_b ratio using his formulated radii varies for the different Cr_3O -type compounds.

Likewise, the model of Pauling which lists the "effective metallic radii" for each element assumes a constant radius for each element in all Cr_3O -type compounds. The equation used by Pauling relating the lattice parameter to the atomic size of the elements is essentially the same as Geller's except that Pauling gives the "A" element three times the weight of the "B" element in establishing the lattice parameter. Though this weighing procedure seems reasonable, the resulting equation has no relationship to the geometry of the unit cell.

Using the radii of either Pauling or Geller, the R_a/R_b ratio varies from one compound to another. From geometrical considerations these variable R_a/R_b ratios fall within a range such that only A-A contact is permitted, and the B atoms "rattle" in their positions. This "rattling" of the B atoms does not seem reasonable.

(15)
Nevitt has shown in a survey of the known types of intermetallic phases that the Cr_3O -type compounds represent one of the more "efficient" methods of filling space. Considering the efficient filling of space to be a factor in the formation of these compounds, the idea of "rattling" B atoms does not seem likely. If the B atoms did

"rattle" changing the "B" atoms should not change the lattice parameter if the R_a/R_b ratio were greater than 0.81. However, the lattice parameter does vary as the "B" element is varied.

Therefore, it seems that R_a/R_b ratios greater than 0.81 do not follow from the observations of these compounds.

A radius ratio of 0.81 appears more reasonable in several aspects. As noted in the Geometrical Considerations section of this thesis, a R_a/R_b radius ratio of 0.81 allows A-A contacts and A-B contacts. The lattice parameter then can be expressed:

$$a_0 = 4R_a \sqrt[4]{5} (R_a + R_b)$$

Such a model would provide an efficient filling of space in accordance with Nevitt's (15) observations. Also the problem of "rattling" B atoms would not exist.

R_a/R_b ratios less than 0.81 would permit A-B contacts only. The filling of space would not be as efficient as at a ratio of 0.81 until the very low ratio of 0.29 was reached. The Coordination Number 12 R_a/R_b ratios for these compounds, as are the derived R_a/R_b ratios of Geller and Pauling, are all greater than 0.81. Therefore, it would seem unreasonable that ratios less than 0.81 would exist. Such low ratios would eliminate the A-A contacts which exist at R_a/R_b ratios of 0.81 and greater.

If a constant R_a/R_b radius ratio of 0.81 is assumed for the Cr_3O -type compounds the radius of a given atom must change with lattice parameter from compound to compound. Though the Coordination Number remains constant for the "A" or "B" atoms, such a change in size is possible as evidenced by departures from Vegard's Law. Vegard's Law states that the lattice parameter of a solid solution is a linear function of the atomic per cent of solute atoms in solution, and implies that the atoms exhibit a constant size in a given crystal structure.

Proposed Model of the Cr_3O -type Compounds. From the above considerations a model of the Cr_3O -type compounds is proposed. The model is based on the following assumptions:

- 1) The atoms approximate a spherical shape in the Cr_3O -type compounds.
- 2) The R_a/R_b ratio is equal to 0.81 in these compounds.
- 3) The atoms change size in accordance with Pauling's Equation, $R_n/R_1 = 0.3 \log n$ such that assumption number 2 above holds true.

The following is implied in assumption number 2:

- 1) The lattice parameter, a_o equals--
 $4R_a$ and also equals $4/\sqrt{5} (R_a + R_b)$: $a_o = 4R_a = 4/\sqrt{5} (R_a + R_b)$.

- 2) Each "B" atom is in contact with 12 "A" atoms.
- 3) Each "A" atom is in contact with 2 "A" atoms and 4 "B" atoms.

From this model the "bonding electrons" per unit cell of a known Cr_3O -type compound can be calculated using the following procedure:

- 1) Using $a_0 = 4R_a$ and the value of a_0 for the compound, R_a can be calculated.
- 2) From $R_a/R_b = 0.81$ and the value of R_a , R_b can be calculated.
- 3) Using the Pauling univalent radii for the "B" element and the value of R_b from above in the equation:

$$R_n = R_i - 0.3 \log n$$

where: R_n = radius of B element R_b

R_i = Pauling univalent
metallic radii

$$n = \frac{\text{bonding electrons}}{\text{Coordination Number}} = \frac{e_b}{12}$$

The number of "bonding electrons," e_b per B atoms can be calculated. This value of electrons does not imply that they are being contributed by the B atom, only that they are associated with a B atom through the A-B contact.

4) Using the same equation for the A element the value of n can be calculated. In this case n has two components which add together to give the bonding associated with the A elements. The first component deals with the bonding electrons associated with the A atom through the two A-A contacts. The second component deals with the bonding electrons associated with the A atoms through the four A-B contacts. As the bonding electrons associated with the B atoms through the A-B contacts are also associated with the A atoms through the same contacts, the second component can be evaluated using the value of e_b from number 3 above.

Thus n for the A atoms becomes:

$$n = \frac{e_a}{2} + \frac{e_b}{4}$$

where: $b =$ bonding electrons associated with B atoms

$a =$ bonding electrons associated with the A atoms

then: $2 \times e_b + 6 \times e_a$ number of "bonding electrons per unit cell"

The values of $2 \times e_b$ and $6 \times e_a$ for the Cr_3O -type

compounds of Cr, Nb, and V are listed in Table III.

A plot of "bonding electrons per unit cell," as derived from above, versus lattice parameter of the Cr₃O-type compounds gives a rather interesting relationship. As the number of bonding electrons increases, the lattice parameters of the compounds involving a given A element tend to decrease in a somewhat linear manner. This is shown in Figure 3.

This relationship is consistent with the concept of stronger bonding producing a smaller atomic size as reflected by the lattice parameter. That the compounds Nb₃B, V₃B and Cr₃B fall on three separate lines, follows from a consideration of three times as many A atoms being present as there are B atoms. The A atoms determine the lattice parameter through the A-A contacts, and the number of bonding electrons determines the "size" of the A atoms.

Objections to the above model may arise in the area of the calculation of the number of "bonding electrons" as the nature of the bonding in these compounds is not known. The above calculations are based on Pauling's equation, $R_n = R_i - 0.3 \log n$ and his "univalent metallic radii." The coefficient 0.3 in the term $0.3 \log n$ is empirical and applies to metallic bonding. Deviations from linearity may be due to several factors such as inaccuracy of the lattice parameters reported in the literature and possible unknown departures from stoichiometry of the compounds.

Perhaps therefore, the values of "bonding electrons per unit cell" should be considered as an approximation and only the trend is significant.

Data reported from the V-Sn binary system tend to support a model of this type. Koster and Haug⁽¹⁶⁾ report V_3Sn occurring at 21.2 atomic per cent Sn with a lattice parameter of 5.104 Å. Geller et.al.⁽¹⁷⁾ seem to have found V_3Sn at the stoichiometric composition, 25 atomic per cent Sn, with a lattice parameter of 4.94 Å. As the atomic radius of vanadium is commonly thought to be less than that of Sn, substitution of a smaller V atom for a Sn atom in a B atom site should produce a decrease in the lattice parameter. However, the converse is true.

With the proposed model in mind, consider the substitution of a V atom for a Sn atom in a stoichiometrically correct V_3Sn compound with a lattice parameter of 4.94 Å. As the V atom is smaller than the Sn atom, it would contribute less bonding electrons than Sn in assuming the required R_a/R_b ratio of 0.81. The smaller number of bonding electrons should result in a larger lattice parameter according to the proposed model. As noted above, the lattice parameter does increase with increasing V content.

The above illustration is not intended to imply that gross substitutions of smaller atoms in the B sites would

produce larger and larger lattice parameters. The above effect would only apply to very dilute concentrations of smaller B atoms substituting for larger B atoms in an A_3B phase.

In light of the above model, a possible explanation of the inability of Sn to substitute for Si in the compound Cr_3Si can be found. Consider the lattice parameter of Cr_3Si which is 4.555 \AA . Using $a_0 = 4R_a$ and $R_a/R_b = 0.81$ from the model, a R_b value of 1.408 is calculated. Substituting a Sn atom into a B site of this size and using Pauling's equation, the number of bonding electrons that would have to be associated with the Sn atom is 13.4. As the number of nearest neighbors to the Sn atoms is equal to twelve, such a substitution of a Sn atom for a Si atom would require that a double bond be formed. Perhaps the inability of a double bond to form between the Cr and Sn atoms explains the inability of Sn to substitute for Si in the compound Cr_3Si . It is noted in Table III that the values of e_b are much less than twelve in all cases. In the compound V_3Si , whose lattice parameter is 4.722 \AA , a substitution of a Sn atom for a Si atom requires 9.1 bonding electrons, and this substitution does occur. (12) It will be noted that the number of bonding electrons associated with an atom does not have to be contributed by that particular atom. Thus, the

required number of electrons could be contributed by other atoms in the structure.

That the above model may be an oversimplification of the problem is admitted. However, the general principles involved are commensurate with the observations of the Cr_3O -type compounds.

CONCLUSION AND SUMMARY

From size factor considerations of the Cr_3O -type compounds, Sn atoms should substitute to a measurable extent for Si atoms in the compound Cr_3Si . However, experimental attempts to produce this substitution were unsuccessful.

In the literature two sets of "effective" radii of the elements can be found which predict the lattice parameter of the Cr_3O -type compounds. The equations used with these radii appear to be based on A to B atom contacts. Upon examination of the radii reported, it is found that these radii do not allow A to B atom contacts.

A model which allows A to A and A to B atom contacts to be present seems to follow from observations of these compounds. The model, based on a constant R_a/R_b ratio of 0.81, seems to explain the inability of Sn to substitute for Si in Cr_3Si . Such a substitution would require the formation of a double bond, which in these compounds may be impossible.

SAMPLE CALCULATION

of

Bonding Electrons Per Unit Cell

for the Compound V_3Si

$$a_o = 4.722$$

$$R_1 \text{ for } V = 1.224$$

$$R_1 \text{ for } Si = 1.173$$

using $a_o = 4 R_a$ and $R_a/R_b = 0.81$

$$R_a = 1.1805$$

$$R_b = 1.4591$$

$$R_b = R_1 - 0.3 \log n$$

$$1.4591 = 1.173 - 0.3 \log e_b/12$$

$$-0.2861 = 0.3 \log e_b/12$$

$$-0.9536 = \log e_b/12$$

$$0.1113 = e_b/12$$

$$e_b = 1.335$$

$$R_a = R_1 - 0.3 \log n$$

$$1.1805 = 1.224 - 0.3 \log (e_b/4 + e_a/2)$$

$$0.0435 = 0.3 \log (e_b/4 + e_a/2)$$

$$0.1450 = \log (e_b/4 + e_a/2)$$

$$1.396 = e_b/4 + e_a/2$$

$$1.396 = 1.335/4 + e_a/2$$

$$e_a = 2.122$$

$e_a \times 6 + e_b \times 2 =$ bonding electrons per unit
cell

$$12.73 + 2.67 = 15.40$$

TABLE I

X-Ray Diffraction Data
for Cr₃Si. Filtered(Cr K_α)

Interplanar Spacings in Angstrom Units	Intensity	Reflecting Plane h k l
3.218	50	110
2.279	60	200
2.041	100	210
1.863	80	211
1.612	10	220
1.442	10	310
1.317	50	222
1.264	80	320
1.220	100	321
1.141	10	400

TABLE II

Interplanar Spacings and Observed Intensities
from X-Ray Diffraction Pattern of a 75 Atomic %
Cr, 20 Atomic Per Cent Sn, 5 Atomic Per Cent Si Alloy
which had been Annealed 2000 Hours at 1100° C.

Line Number	Spacing in Å ^o	Observed Intensities
1	3.063	V V W
2	2.891	V V W
3	2.798	V V W
4	2.318	W
5	2.281	V W
6	2.225	S
7	2.158	V W
8	2.064	W
9	2.045	W
10	2.035	V W
11	2.002	V S
12	1.884	S
13	1.857	W
14	1.630	W
15	1.597	M
16	1.579	V V W
17	1.448	W
18	1.420	V V W
19	1.366	V W
20	1.328	W
21	1.320	W
22	1.311	W
23	1.300	W
24	1.295	W
25	1.275	W
26	1.269	S
27	1.264	V W
28	1.229	W
29	1.218	W
30	1.215	W
31	1.204	V V W
32	1.158	S

Key to Observed Intensities: M Medium; S Strong;
W Weak; V S Very Strong; V W Very Weak;
V V W Very Very Weak.

Note: Pattern from 114.6 mm Norelco X-Ray diffraction
camera using filtered Cr K_a radiation.

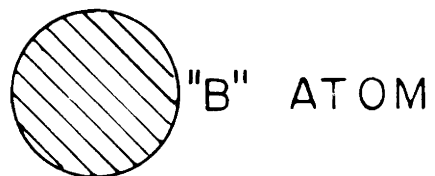
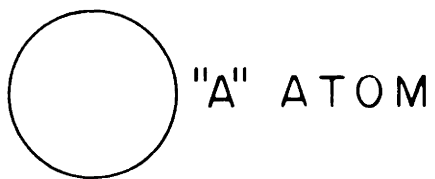
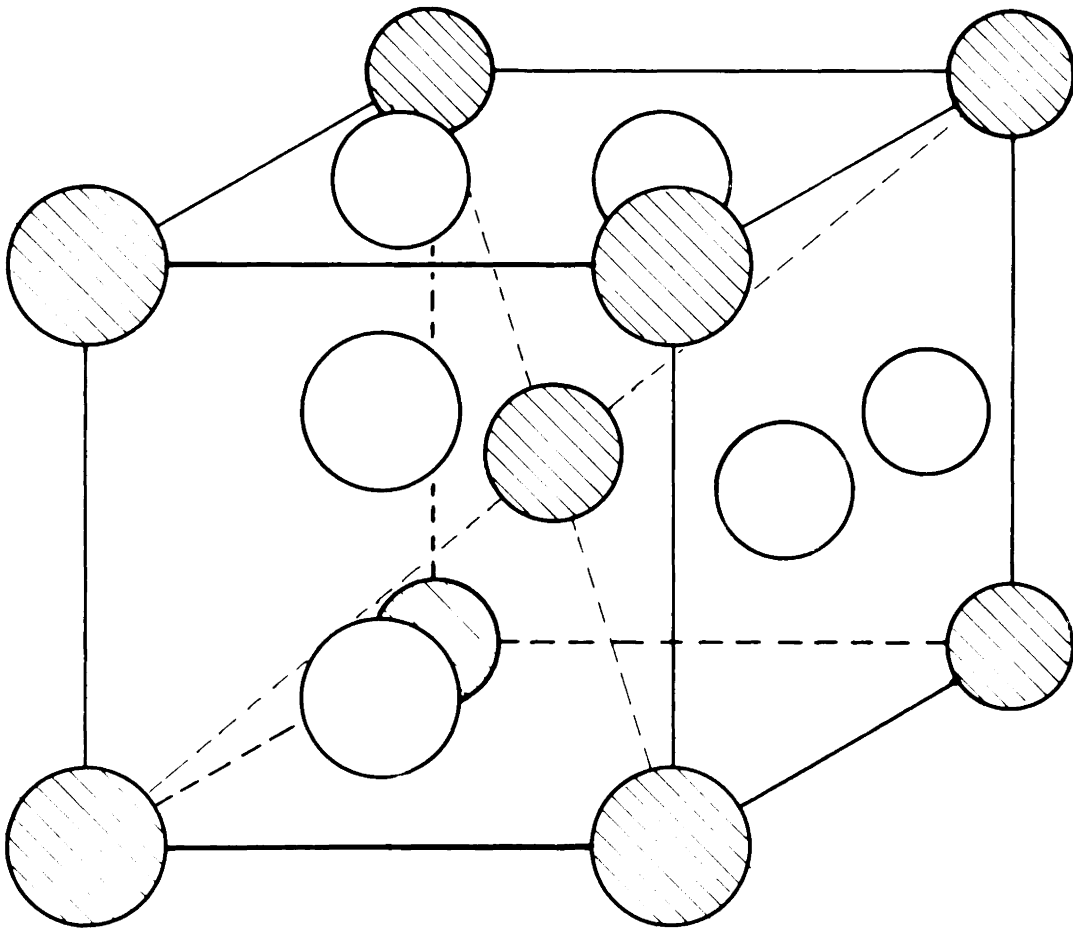
TABLE III

Lattice Parameter and "bonding electrons" Per Unit Cell of the Cr₃O-Type Compounds Involving Cr, V, and Nb

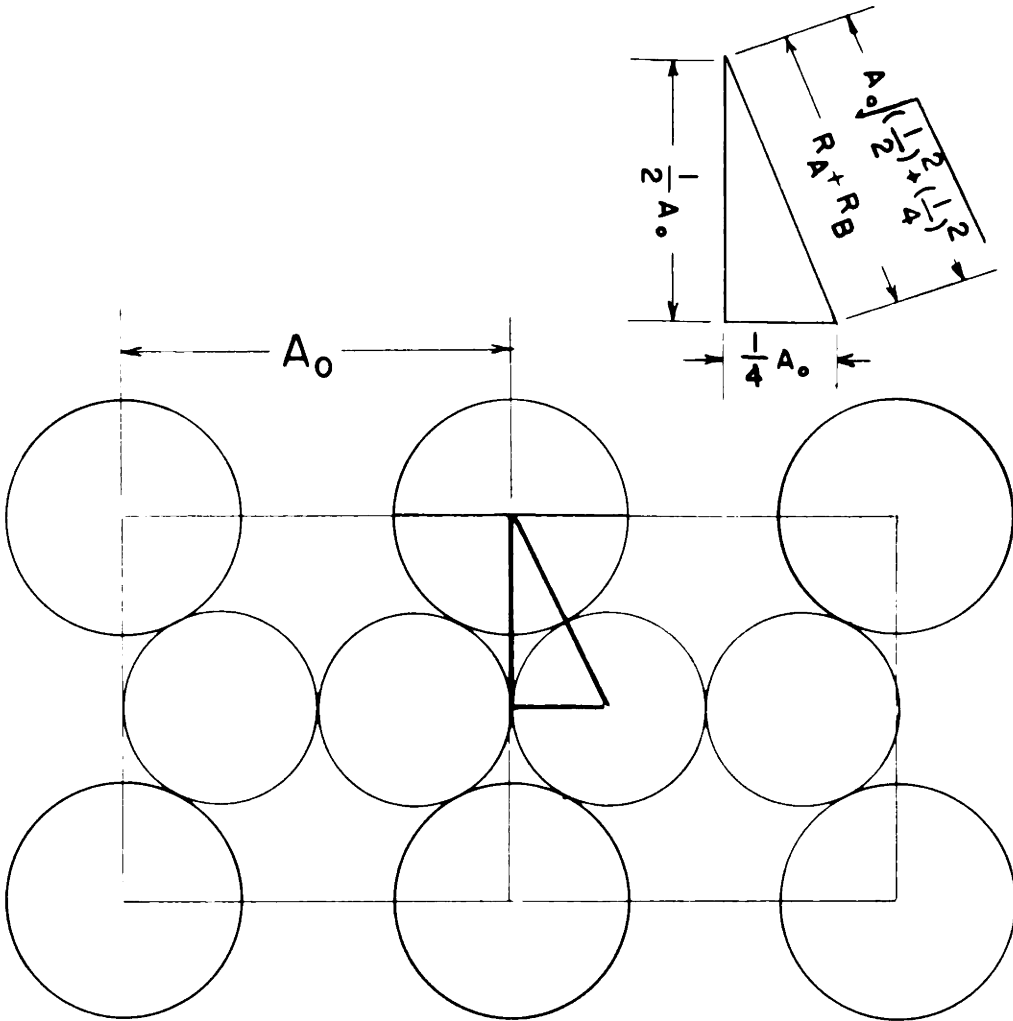
Compound	a _o	e _b x 2	e _a x 6	"bonding electrons" Per Unit Cell
Cr ₃ Si	4.555	3.94	10.12	14.06
Cr ₃ Ge	4.623	5.73	6.53	12.26
Cr ₃ Rh	4.656	5.72	5.62	11.34
Cr ₃ Os	4.678	5.80	4.92	10.72
Cr ₃ Ir	4.678	6.01	4.61	10.62
Cr ₃ Ru	4.683	5.13	5.79	10.92
Cr ₃ Pt	4.711	6.99	2.29	9.28
V ₃ Co	4.676	2.74	14.20	16.94
V ₃ Ni	4.710	2.37	13.60	15.97
V ₃ Si	4.722	2.67	12.73	15.40
V ₃ Rh	4.767	4.40	8.77	13.17
V ₃ Ge	4.769	4.05	10.43	14.48
V ₃ Ir	4.785	4.66	7.85	12.51
V ₃ Pt	4.815	5.46	5.82	11.28
V ₃ Au	4.88	6.56	1.34	7.90
V ₃ Sb	4.932	8.70	-1.86	6.84
V ₃ Sn	4.948	10.42	-5.04	5.38
Nb ₃ Rh	5.115	1.93	16.61	18.54
Nb ₃ Os	5.121	2.02	16.25	18.27
Nb ₃ Ir	5.131	2.05	15.84	17.89
Nb ₃ Pt	5.153	2.45	14.46	16.91
Nb ₃ Au	5.21	3.00	11.63	14.63
Nb ₃ Sn	5.289	4.67	6.97	11.64

FIGURE 1. UNIT CELL OF THE Cr_3O -TYPE COMPOUNDS

Note: "A" atoms in rear faces omitted for clarity



UNIT CELL OF THE " Cr_3O " TYPE
COMPOUNDS



$$A_0 = 4 R_A$$

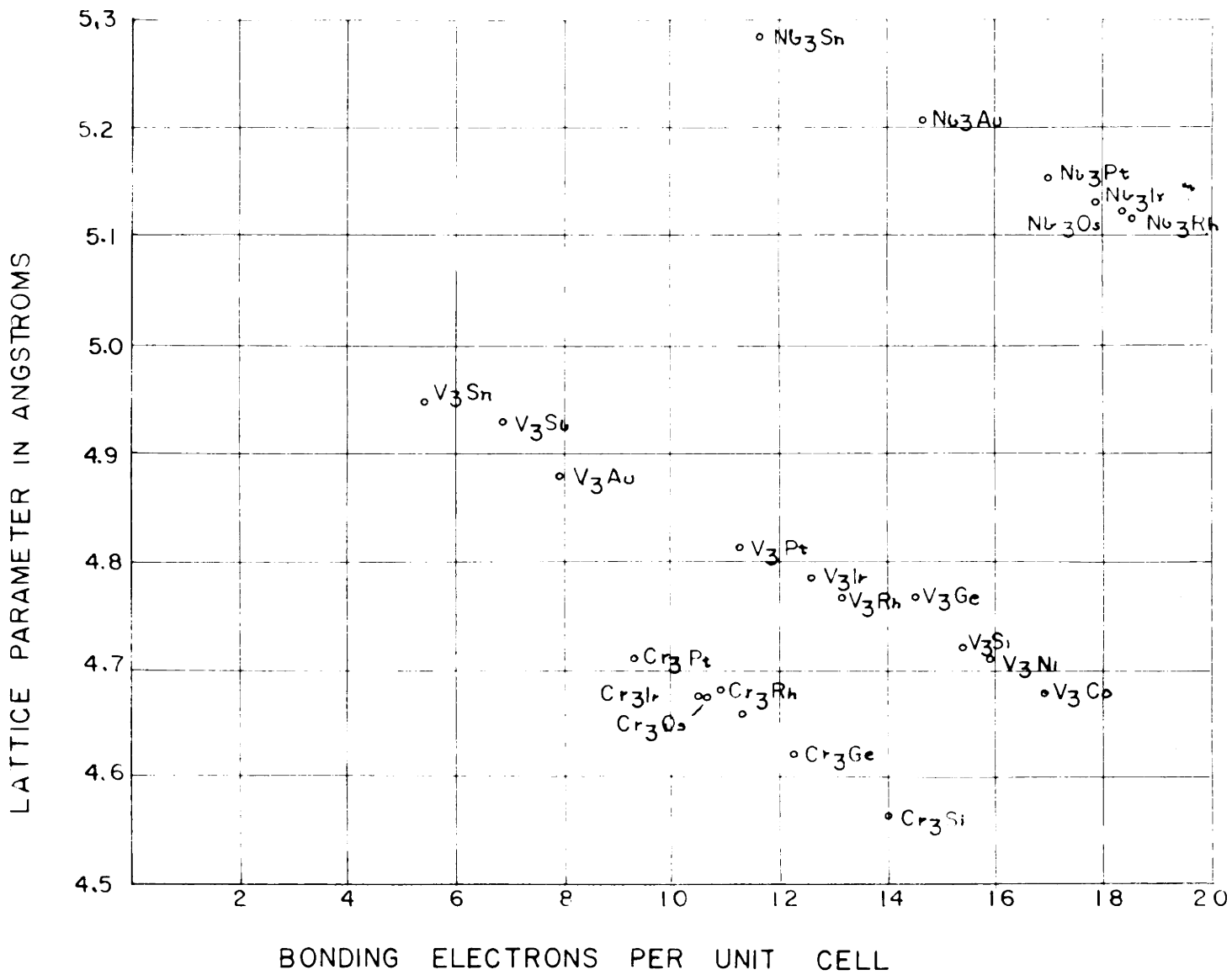
$$A_0 = 4/\sqrt{5} (R_A + R_B)$$

$$R_A / R_B = .81$$

100 PLANE OF TWO UNIT CELLS

FIGURE 2

FIGURE 3. PLOT OF LATTICE PARAMETER VERSUS "BONDING ELECTRONS" PER UNIT CELL.



BIBLIOGRAPHY

1. Hagg, G. and Schonberg, N.: B-Tungsten as a Tungsten Oxide, Acta Crystallographica, Vol 7, p. 351 (1954).
2. Greenfield, P. and Beck, P. A.: Intermediate Phases in Binary Systems of Certain Transition Elements, Transactions of A.I.M.E., Vol 206, p. 265 (1956).
3. Geller, S.: A Set of Effective Coordination Number (12) Radii for the B-Wolfram Structure Elements, Acta Crystallographica, Vol 9, p. 885 (1956).
4. Laves, F.: Crystal Structure and Atomic Size, Transactions A.S.M., Vol 48 A, p. 124 (1956).
5. Pauling, L.: A Set of Effective Metallic Radii for Use in Compounds with the B-Wolfram Structure, Acta Crystallographica, Vol 10, p. 374 (1957).
6. Geller, S.: Comments on Pauling's Paper of Effective Metallic Radii for use in the B-Wolfram Structure, Acta Crystallographica, Vol 10, p. 380 (1957).
7. Pauling, L.: Use of Atomic Radii in the Discussion of Interatomic Distances and Lattice Constants of Crystals, Acta Crystallographica, Vol 10, p. 685 (1957).
8. Geller, S.: Comments on the Preceding Paper by L. Pauling Entitled, "The Use of Atomic Radii, etc.", Acta Crystallographica, Vol 10, p. 687 (1957).
9. Hume-Rothery, William: The Structure of Metals and Alloys, The Institute of Metals Monograph and Report Series No. 2, London, England, p. 35 (1936).
10. Nevitt, M. V.: Atomic Size Effects in Cr₃O-Type Structure, Transactions A.I.M.E., Vol 206, p. 124 (1956).
11. Pauling, L.: The Electronic Structure of Metals and Alloys, Transactions A.S.M., Vol 48 A, p. 220 (1956).
12. Van Reuth, E.: Unpublished Thesis, V.P.I. June, 1960.

13. Hanson, M.: "Constitution of Binary Alloys,"
Mc Graw-Hill Co., New York, N. Y., 1958.
14. Pauling, L.: Electron Transfer in Intermetallic
Compounds-Proceedings of the National
Academy of Sciences, Vol 36, p. 533 (1950).
15. Nevitt, M. V.: Personal Communication, April, 1961.
16. Koster, W. and Haug, K.: Ternary System Titanium-
Vanadium-Tin, Z. Metallkunde, Vol 48, p. 327
(1957).
17. Geller, S., Matthias, B. T., and Goldstein, R.:
Some New Intermetallic Compounds with B-
Wolfram Structure, Journal American Chemical
Society, Vol 77, p. 1507 (1955).

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ABSTRACT

An investigation was conducted to determine if Sn atoms could be substituted for Si atoms in the compound Cr_3Si .

From size factor considerations, the feasibility that this substitution should occur seemed reasonable. However, attempts to make the substitution were unsuccessful.

A model of the Cr_3O -type compounds, of which Cr_3Si is a representative, is proposed. From this model substitution of a Sn atom for a Si atom would require the formation of a double bond. The possibility of this double bond being unable to form may explain the unsuccessful attempts to make the above substitution.