

AN INFRARED ABSORPTION STUDY OF THE BISMUTH

DONOR IN SILICON

by

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I. INTRODUCTION

When phosphorus, arsenic, antimony, or bismuth, all Group V atoms, are added to silicon, four of the valence electrons complete bonds with neighboring silicon atoms. The remaining valence electron is then in the Coulomb field of the remaining charge (reduced by the dielectric constant of the material) and is so loosely bound that it may be thermally excited to the conduction band at temperatures well below room temperature. Thus one may say that these impurities "donate" an electron to the crystal and thus obviously affect its electrical properties. These donor states fall into two categories, the "deep" donor states and the "shallow" donor states. The deep donor state is one in which the extra electron is bound very tightly (~ 0.5 ev) to the impurity ion while in the shallow donor state the extra electron is bound rather loosely (0.01 to 0.1 ev). In the effective mass theory (12), a shallow donor impurity ion and its loosely bound electron are treated as a hydrogenic system in a dielectric medium. The crystal field effects upon the system are concealed in the dielectric constant of the crystal and in the effective mass of the donor electron within the crystal.

At liquid helium temperature the donor electrons populate the ground state of the system in much larger numbers than the other states of the system. Infrared radiation, for example, may then be used to induce transitions from the ground state to the excited states and continuum and this will, in turn, yield information about the energies of the excited levels relative to the ground state level, the level

widths, and the relative transition probabilities.

Optical studies that have been made on shallow donors in silicon show that the effective mass theory accounts very well for the excited states but does not for the ground state (2, 3, 7, 15). This has been attributed to the neglect of effects near the donor ion.

Kohn and Luttinger (13) have shown that the six-fold degenerate ground state in reality splits into singly, doubly, and triply degenerate $1s$ levels.

Although transitions from the upper $1s$ levels to the excited states have been observed for some impurities in silicon (1), this thesis reports research which includes the first observation of transitions from the lowest-lying $1s$ level to the upper $1s$ levels in any semiconductor; in particular, we have observed transitions from the lowest-lying $1s$ level to the upper $1s$ levels in bismuth-doped silicon.

II. REVIEW OF LITERATURE

Since Kohn has given an extensive treatment of shallow donor theory (12), we shall present here only those points basic to a somewhat qualitative understanding of the theory.

Let us consider a donor state as a neutral impurity atom, introduced into the lattice of a perfect crystal, from which one electron has been removed leaving behind a positive, singly charged ion. The ion will polarize the semiconductor and at large distances from the ion the electrostatic potential may be written

$$V(r) = e/\kappa r \quad (1.1)$$

where r is the distance from the ion to the electron and κ is the static dielectric constant of the medium. The static dielectric constant is used because the frequency of the impurity electron in its orbit is much lower than that of the other electrons in the crystal whose polarization gives rise to κ in a homopolar material (12). When the electron is brought back, two possibilities arise for the interaction between it and the impurity ion. First, it may be energetically favorable for the electron to spend most of its time near the impurity ion. This describes the deep donor state, a state whose structure is not very well understood. In contrast to this, the electronic orbit may be so large that, even in the ground state, (1.1) applies. It is in such a shallow donor state that we are interested.

In the field of the impurity ion, the potential energy of the electron is

$$U(r) = -e^2/\kappa r. \quad (1.2)$$

Treating this as a perturbation one can show that the Schroedinger equation for shallow donor states is

$$\left[-\frac{\hbar^2}{2m^*} \nabla^2 - \frac{e^2}{kr} \right] F(r) = E F(r). \quad (1.3)$$

Note that this is identical to the Schroedinger equation for the hydrogen atom except that k has been introduced and the free electron mass, m , has been replaced by the so-called effective mass, m^* , which is generally not the same as the free electron mass. Actually, the effective mass depends on the wave vector, \vec{k} , but for small wave vector displacements about the bottom of the conduction band it may be considered constant. The eigenvalues of (1.3) are the well-known

$$E(n) = - \frac{m^*(e^2/k)^2}{2 \hbar^2 n^2} \quad (1.4)$$
$$n = 1, 2, 3, \dots$$

and the normalized ground state eigenfunction is

$$F(r) = (\pi a^{*3})^{-1/2} \exp(-r/a^*) \quad (1.5)$$

where

$$a^* = \frac{\hbar^2 k}{e^2 m^*}. \quad (1.6)$$

Using $k = 12.0$ and the scalar approximation $m^* \approx 0.25m$ for silicon, the first Bohr orbit radius is found to be $a^* \approx 20\text{\AA}$. Since silicon has a lattice constant of 5.43\AA , we see that the electron does spend most of its time in the region where (1.1) applies.

The preceding analysis, while illuminating, has failed to provide a detailed picture of donor states in silicon. Specifically, it neglected the anisotropy of the effective mass of the electron in the silicon lattice and the detailed structure of the silicon conduction

band. In silicon there are six equivalent conduction band minima in k -space located at $(k_0, 0, 0)$, $(-k_0, 0, 0)$, $(0, k_0, 0)$, \dots , $(0, 0, -k_0)$. Near any one of these minima the energy of the electron may be written in the form (13)

$$E = \frac{\hbar^2}{2m_l} (k_z - k_0)^2 + \frac{\hbar^2}{2m_t} (k_x^2 + k_y^2) \quad (1.7)$$

where the longitudinal and transverse effective mass parameters have the values (4)

$$m_l = 0.98m \quad m_t = 0.19m \quad (1.8)$$

m being the free electron mass.

Using the effective Hamiltonian corresponding to (1.7), $F(r)$ is found to satisfy an equation of the type

$$\left[-\frac{\hbar^2}{2m_l} \frac{\partial^2}{\partial z^2} - \frac{\hbar^2}{2m_t} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) - \frac{e^2}{Kr} \right] F(r) = EF(r). \quad (1.9)$$

This equation has been solved (10, 13) by variational methods using trial functions similar to hydrogenic eigenfunctions. For example, the ground state hydrogenic eigenfunction is

$$C \exp \left[-(x^2/a^2 + y^2/a^2 + z^2/a^2)^{1/2} \right] \quad (1.10)$$

while the ground state trial function is

$$C \exp \left[-(x^2/A^2 + y^2/A^2 + z^2/B^2)^{1/2} \right] \quad (1.11)$$

where C is a constant and A and B are used to minimize the energy.

Although the solutions are different from the hydrogenic ones, it is customary to label them by the atomic notation of the hydrogenic functions into which they go when $m_l = m_t$. It is evident that, because of the six equivalent minima of the conduction band in silicon, the

solutions exhibit six-fold degeneracy.

For states having large orbits and small amplitudes near the impurity ion (indicating orbits which do not penetrate the immediate vicinity of the impurity ion) the effective mass theory and experiment agree very well. For states having smaller orbits and large amplitudes near the impurity ion, in particular the ground states in silicon, experiment and theory agree poorly. By making corrections to the potential for small distances from the impurity ion and using symmetry arguments, Kohn and Luttinger (13) have shown that, for substitutional impurities, the six-fold degenerate ground state is split into a non-degenerate $1s$ level, which is the ground state, and doubly and triply degenerate $1s$ levels.

Figure 1 indicates a theoretical energy level diagram of a phosphorus donor. Here the doubly and triply degenerate $1s$ levels have been lumped into a five-fold degenerate $1s$ level. The effective mass theory predicts and experiment has shown (3, 7, 15) that the energies of the excited states do not depend on which impurity is present in the crystal. This is indicated in Figure 2. Because of this fact, one would expect an energy level diagram of a bismuth donor to resemble Figure 1 except for the ground state, $1s(A_1)$. The excited states of bismuth-doped silicon have been investigated (7) and tend to substantiate the theory but the transitions from the state $1s(A_1)$ to the states $1s(E)$ and $1s(T_1)$ have not been reported.

Aggarwal (1) recently reported research in which the $1s$ state split was observed in antimony-, arsenic-, and phosphorus-doped silicon.

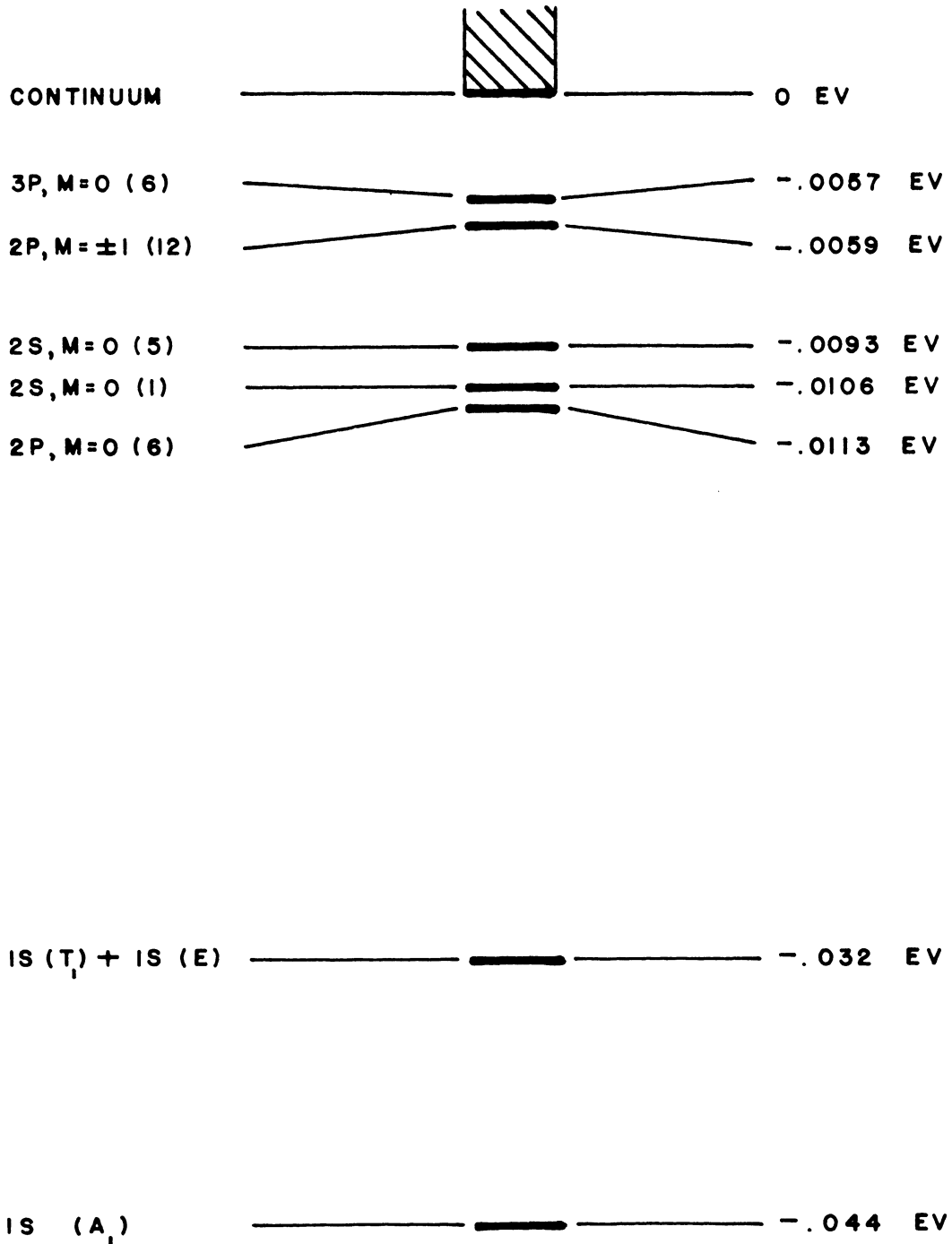


Figure 1. Energy levels of bound states due to a phosphorus donor. Numbers in parentheses indicate the number of approximately degenerate states; spin degeneracy is not included. Theoretical predictions are due to Kohn and Luttinger (13).

The experiments were performed at liquid nitrogen temperature with the result that the $1s(E)$ and $1s(T_1)$ levels were populated sufficiently so that transitions from these states to the higher excited states could be observed. The results of that investigation will be discussed in section IV of this thesis.

Using silicon samples that have been rather heavily doped with bismuth, we were able to observe transitions from the $1s(A_1)$ level to the levels $1s(E)$ and $1s(T_1)$.

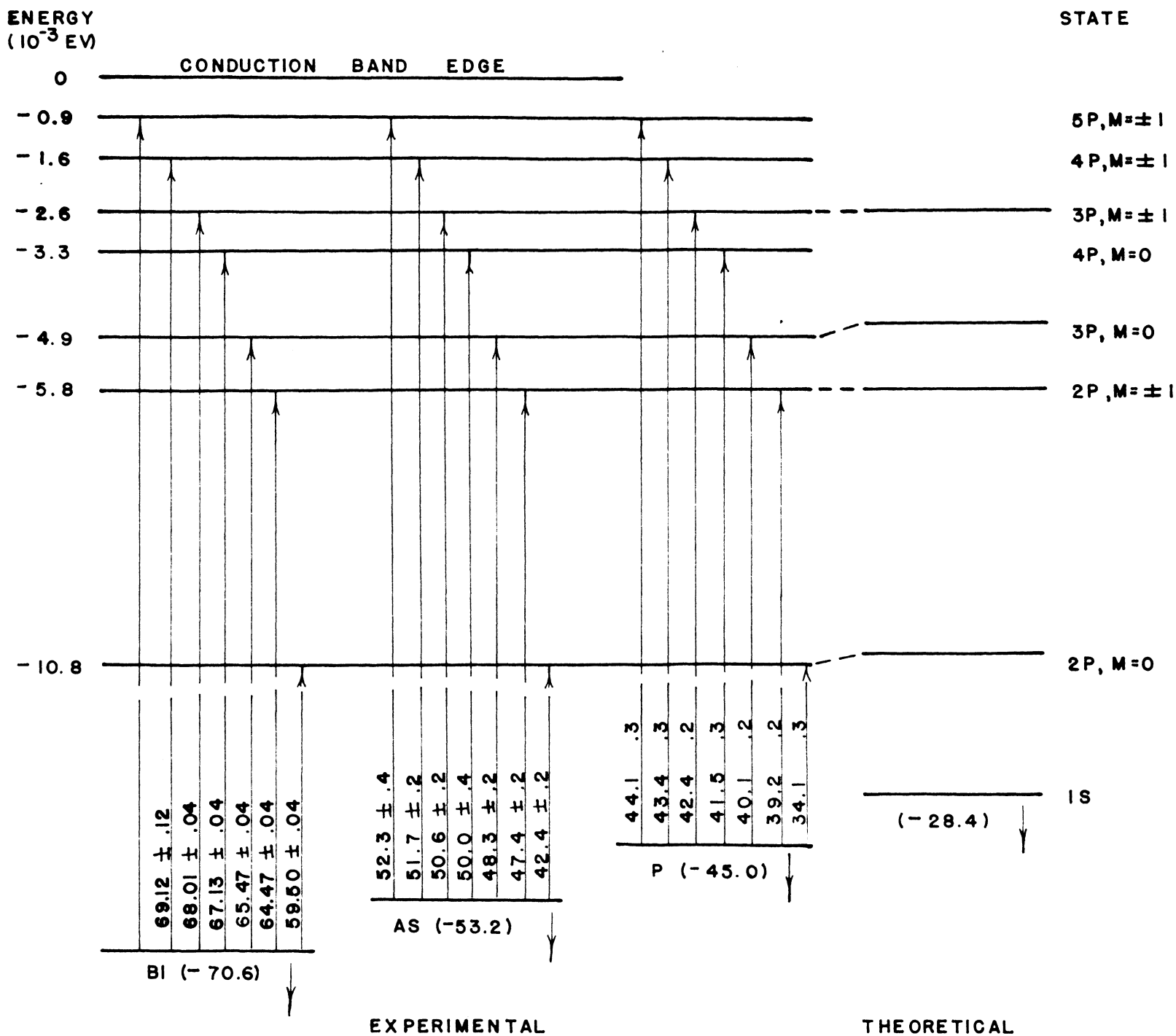


Figure 2. Energy level diagram for bismuth, arsenic, and phosphorus in silicon. Experimental bismuth levels are due to Hrostowski and Kaiser (7), experimental arsenic and phosphorus levels are due to Richard and Giles (3), and theoretical predictions are due to Kleiner (10).

III. EXPERIMENTAL DETAILS

Sample Characteristics

The samples used in this investigation were supplied by Dr. R. H. Kaiser of the Bell Telephone Laboratories, Murray Hill, New Jersey. The impurity type of each of the samples was determined by the thermoelectric probe method of Dunlap (5). Resistivity measurements were made by the four probe method as outlined by Valdes (17) using a probe spacing of 4.5 mm. These resistivity measurements were used in conjunction with the data of Irvin (9) to determine the concentration of bismuth atoms in the silicon samples. The important data for each sample used in this investigation are listed in Table 1.

Sample Preparation

The sample wafers were cut from the boules on a converted surface grinder with a diamond saw. The wafers were then ground with varying grades of carborundum and alundum abrasives on glass plates to achieve parallel surfaces. After the final grinding operation with number 600 alundum abrasive, a mirror-like surface was achieved by polishing with number 600 alundum abrasive on Gamal cloth supported by a glass plate. Water was used as a lubricant during all grinding and polishing operations. The surfaces resulting from this procedure were such that one could distinguish certain objects when viewed from near normal incidence. Finally, a flat was ground into the periphery of each sample so that a germanium resistance thermometer could be attached to the sample.

Table 1

Sample Data

Sample	Crystal Type	Thickness (mm)	Donor Conc. (cm^{-3})
BL-1	Pulled from melt	3.70	$\geq 10^{16}$
BL-2B	Pulled from melt	6.00	$\sim 10^{17}$
M-1S	Floating zone	3.50	Undoped Sample

Experimental Procedure

Figure 3 shows the details of mounting the sample and thermometer in the mounting block. The mounting block was, in turn, bolted to the bottom of the copper liquid helium container of a cryostat as indicated. A thin film of silicone grease was used to enhance thermal contact between the various items. With this arrangement sample temperatures in the neighborhood of 20° K were routine.

A Model 112, Perkin-Elmer spectrometer which had been converted to a grating instrument by Bell (2) was used in this investigation. It was calibrated over the wavelength range 28 to 55 microns using the water vapor absorption lines determined by Randal et al (16).

The samples were placed in the cryostat so that the faces were centered in and perpendicular to the infrared beam. The entire spectrometer was purged during and two hours prior to the transmission measurements with dry nitrogen gas to eliminate water vapor absorption lines from the data.

Data Reduction

The intensity of the spectrometer beam after it has passed through a sample is given by

$$I = I_0 \left[\frac{(1 - R)^2 \exp(-\alpha t)}{1 - R^2 \exp(-2\alpha t)} \right] \quad (2.1)$$

where I_0 is the initial beam intensity, R is the sample surface reflectivity, α is the sample absorption coefficient, and t is the sample thickness. Writing such an expression for a doped and an undoped sample and then taking ratios, we have

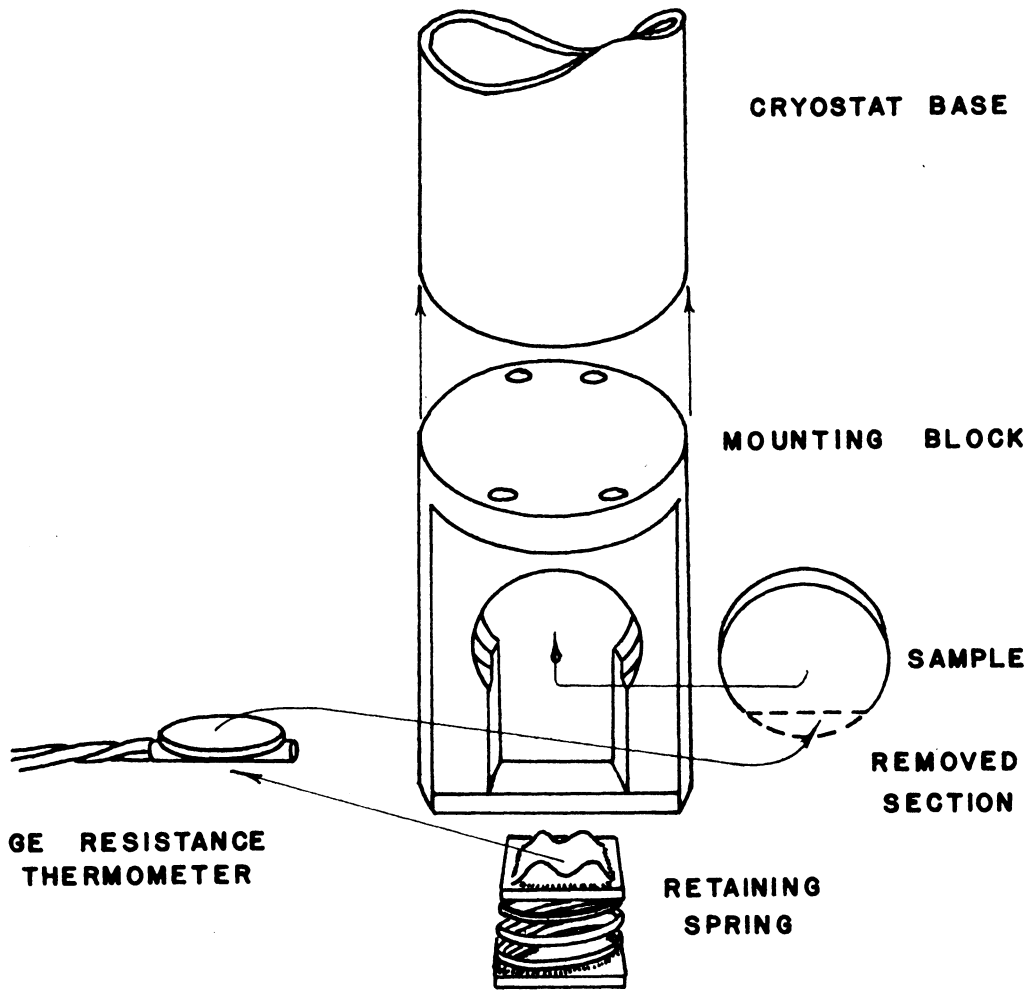


Figure 3. Assembly of Sample, Thermometer, Mounting Block, and Cryostat Base.

$$\frac{I_d}{I_s} = \frac{1 - R^2 \exp(-2\alpha_s t_s)}{1 - R^2 \exp(-2\alpha_d t_d)} \exp(\alpha_s t_s - \alpha_d t_d) \quad (2.2)$$

where the subscript s refers to the undoped silicon sample and the subscript d refers to the doped sample. We may write the absorption coefficient of the doped sample as the sum of the absorption coefficient of the silicon and that of the added impurity. Thus

$$\alpha_d = \alpha_s + \alpha_i \quad (2.3)$$

where α_i is the absorption coefficient of the impurity. Using (2.3), we may rewrite (2.2) in the following form:

$$\alpha_i = \frac{\ln(I_s/I_d)}{t_d} + \alpha_s \frac{t_s - t_d}{t_d} - \frac{1}{t_d} \ln \left[\frac{1 - R^2 \exp(-2\alpha_d t_d)}{1 - R^2 \exp(-2\alpha_s t_s)} \right]. \quad (2.4)$$

Over the range in which we are interested the absorption coefficient α_s and the reflectivity R are essentially constant and have the approximate values of 0.12 cm^{-1} and 0.3 respectively. The second term in (2.4) is negligible for approximately equal thicknesses of doped and undoped samples while the third term corrects α_i by at most -0.3 cm^{-1} . Therefore, the first term in (2.4) is the only one used in the calculations of this investigation.

A determination of the error involved in making the calculations would be a rather formidable undertaking not only because there were so many points that had to be analyzed but also there were some wavelength ranges where the measurements of I_s and/or I_d were comparable to the uncertainty of the background signal. However, these

uncertainties in calculating the absorption coefficient have almost nothing to do with the placing of the absorption resonances because of the critical dependence of the resonance upon the photon wavelength.

IV. RESULTS AND CONCLUSIONS

The data presented here is in the form of absorption spectra in which the absorption coefficients are due only to the impurities introduced into the silicon lattice during the doping process. While bismuth is the desired dopant, we leave open the possibility that other impurities may be present. The instrumental band width (full width at half maximum) is indicated for the regions in which the absorptions occur.

In Figure 4 we see the absorption spectra of the bismuth donor in silicon. We note in both curves prominent absorption peaks at 316.5 cm^{-1} and at 275.3 cm^{-1} . The probable explanation of the non-symmetric character of these peaks is that water vapor remained in the system in spite of the fact that the system was purged with dry nitrogen gas. This is substantiated by the fact that water vapor absorptions do occur at approximately 279 cm^{-1} and 322 cm^{-1} . The rather weak peaks at 342.5 cm^{-1} and at 348 cm^{-1} are also in the region of water vapor absorptions; no conclusion can be reached at this time about the relatively weak peak at 294 cm^{-1} .

Kaiser (8) observed the absorption at 316.5 cm^{-1} and suggested that, since it coincides with an antimony absorption, the sample was contaminated with antimony. In view of the fact that there is another antimony absorption, almost twice as intense as the one at 316.5 cm^{-1} , at 294 cm^{-1} it seems very unlikely that our sample contained significant antimony.

According to the data of Richard and Giles (3), there are

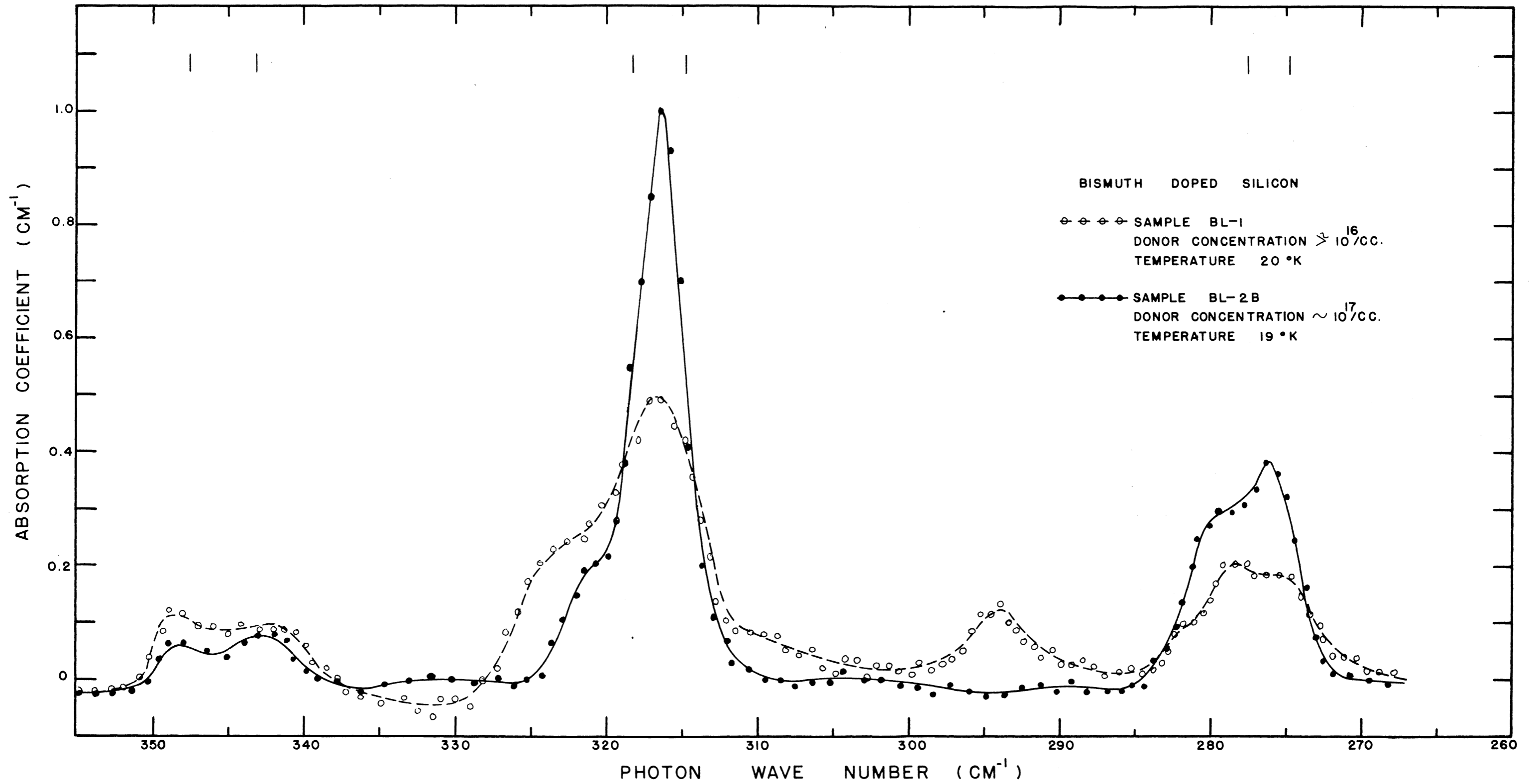


FIGURE 4. ABSORPTION SPECTRA OF BISMUTH DOPED SILICON

phosphorus absorptions occurring at approximately the same locations as the prominent absorptions in Figure 4 leading one to suspect that phosphorus may be present in the sample. However, there are three rather strong phosphorus absorptions occurring in the range 324 to 350 cm^{-1} . Since none of these is present in our spectra, we can only conclude that the samples are not contaminated with phosphorus. Since there are no arsenic absorptions in the range under investigation (15), arsenic contamination would have no effect on our results. Table 2 summarizes the foregoing remarks by listing the locations of the absorptions of the suspected contaminants.

We are thus led to the conclusion that the observed absorptions must be due to the bismuth in the samples. The excited states of bismuth in silicon have been investigated by Hrostowski and Kaiser (7, 8). The results of their investigation are listed in Table 3. Comparing their data with that obtained in this investigation, we conclude that the absorptions in Figure 4 represent transitions from the ground state, $1s(A_1)$, to the states $1s(E)$ and $1s(T_1)$. To further strengthen this statement, one immediately notes that the energies of these absorptions agree quite well with the theoretical spectrum of phosphorus as shown in Figure 1. Figure 5 illustrates a comparison of the predicted phosphorus spectrum and the observed bismuth spectrum.

Aggarwal (1) has reported observing the $1s$ state split in antimony-, arsenic-, and phosphorus-doped silicon. His data are listed in Table 4. While we are unable to determine the ordering of the

Table 2

Principal Absorptions of Several Donors in Silicon

Donor	Principal Absorptions (cm^{-1})
Phosphorus ¹	276
	316
	324
	343
	350
Antimony ²	322
	294
Arsenic ²	341
	381
	408
	420

¹ Data due to Richard and Giles (3).

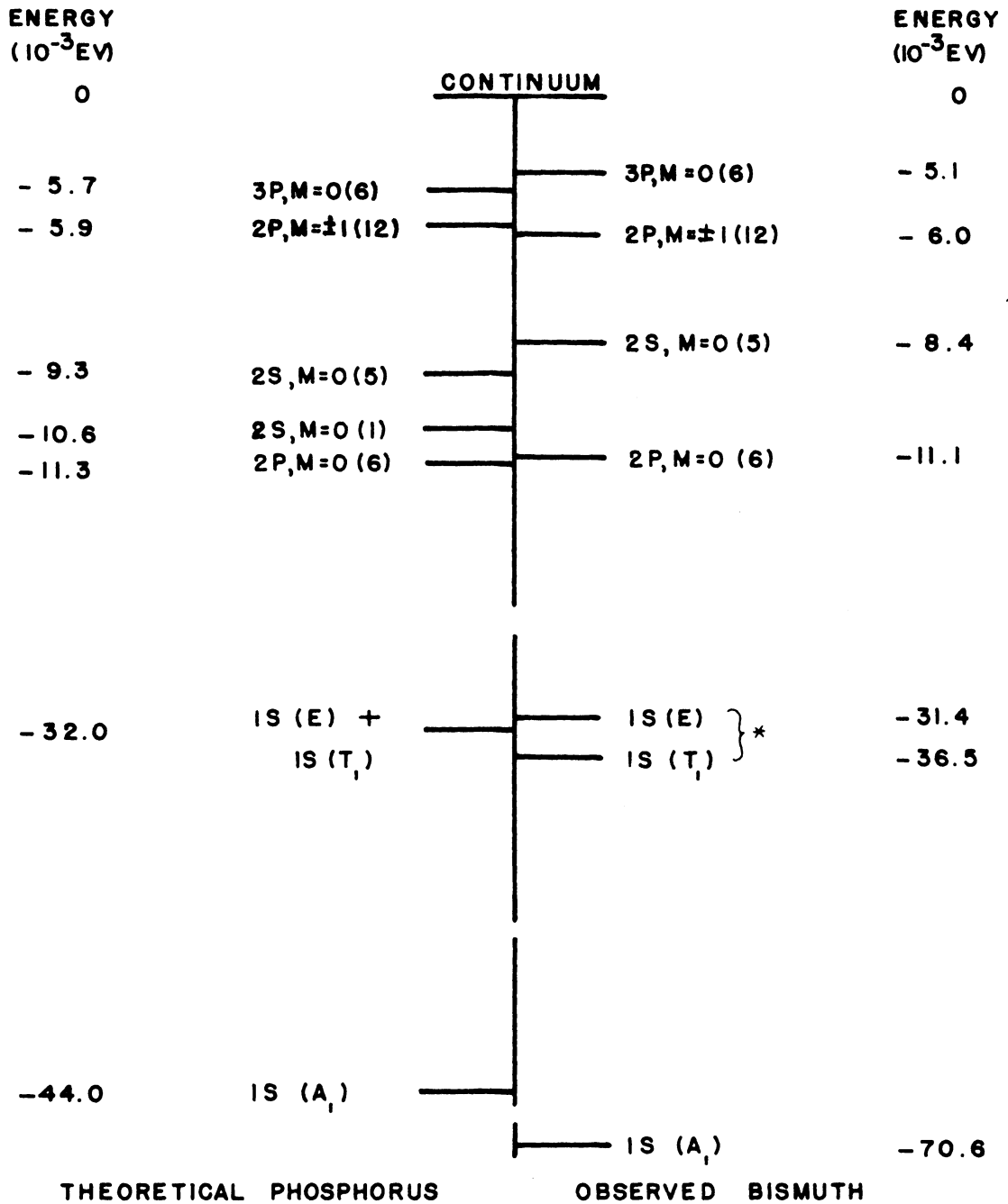
² Data due to Picus, Burstein, and Henvis (15).

Table 3

Data of Hrostowski and Kaiser on Bismuth Doped Silicon (7)

Transition	Energy (ev x 10 ³)*
1s to 2p, m=0	59.50
1s(1) to 2s(5)	62.19
1s to 2p, m=+1	64.57
1s to 3p, m=0	65.47
1s to 4p, m=0 (?)	67.13
1s to 3p, m=+1	68.01
1s to 4p, m=+1, 5p, m=0	69.12 ± 0.12

* Except where noted, experimental error is less than 4×10^{-5} ev.



* The ordering of these levels is uncertain.

Figure 5. Comparison of theoretical phosphorus spectrum (13) and observed bismuth spectrum (7).

states $1s(E)$ and $1s(T_1)$ from our data, we are able to show that the separation of the two states is 5.1×10^{-3} ev which is of the same order of magnitude as the results in Table 4. The separation of the ground state, $1s(A_1)$, from the lowest-lying upper $1s$ level in our data is 34.1×10^{-3} ev. That this is larger than the values in Table 4 is to be expected because of the large donor ionization energy of bismuth in silicon.

We conclude then that the $1s$ state of the bismuth donor in silicon does split into a nondegenerate level, the ground state, $1s(A_1)$, a two-fold degenerate level, $1s(E)$, and a three-fold degenerate level, $1s(T_1)$, as predicted by the effective mass theory. The observed transitions fall very close to or coincide with absorption peaks of other impurities. By comparing the spectra of those impurities with the spectra obtained in this investigation, we are able to show that no significant undesired impurities are present in our samples.

Table 4

Energy Spacings of 1s Donor States in Silicon in meV (1)

States	Antimony	Phosphorus	Arsenic
$1s(T_1) - 1s(A_1)$	9.94	11.85	21.15
$1s(E) - 1s(T_1)$	2.50	1.35	1.42

Experimental error in all spacings is ± 0.05 units.

V. ACKNOWLEDGEMENTS

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ABSTRACT

It has been known for some time that the experimentally determined energies of the excited states of donors in silicon agree favorably with the values predicted by the effective mass theory due to Kohn (3). However, the experimentally determined energies of the ground states in silicon differ from the predicted value by at least 3.5 mev (2). This has been attributed to the neglect of effects near the impurity ion. By making corrections to the potential for small distances from the impurity ion and using symmetry arguments, it has been shown (4) that the ground state in reality splits into a non-degenerate level, $1s(A_1)$, which is the ground state, and doubly and triply degenerate $1s$ levels, $1s(E)$ and $1s(T_1)$ respectively. Recent work in this area has shown evidence of the $1s$ state split in antimony-, arsenic-, and phosphorus-doped silicon (1).

At liquid helium temperature the ground state is the only state significantly populated so that, by using infrared radiation, for example, transitions may be induced from the ground state to the excited states and continuum. Thus the energies of the excited states relative to the ground state may be determined.

Our data shows evidence that the $1s$ state split occurs for bismuth-doped silicon with the upper $1s$ levels having energies of -31.4 mev and -36.5 mev relative to the bottom of the conduction band. This shows that the lowest-lying upper $1s$ level is separated from the ground state by 34.1 mev and the two upper $1s$ levels are separated by 5.1 mev. The latter agrees very favorably with the data of Aggarwal (1), however, we are unable to determine the ordering of

these states from our data. That the former is larger than the values found by Aggarwal is to be expected because of the large donor ionization energy of bismuth in silicon.

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