An Optical Determination of the Ground-State Splittings of Group V Impurities in Germanium*

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A method is described by which direct and accurate values are obtained for the energy separations, 4Δ, of the singlet and triplet ground states of Group V impurities in germanium. The method relies on measuring the energy difference between optical absorption lines which are due to transitions from both ground states to the same excited state of an impurity. With the values of 4Δ so found and the values of $4\Delta/E_2$ given by other workers, values of the shear deformation potential constant E_2 are obtained. Also observed for each impurity is a shift of the triplet state to an energy which is lower than that given by the effective-mass formalism. This shift is found to be almost the same for all the Group V impurities.

I. INTRODUCTION

IT is well known[1,2] that the ground state of a Group V impurity in germanium is more complicated than is predicted by the effective mass formalism.[1] If electron spin is ignored, the lowest two-energy states of such an impurity are one and threefold degenerate and transform according to the A_1 and T_1 irreducible representations the symmetry group T_d, the point group which characterizes the Group V substitutional impurities. The degree to which the actual ground-state levels differ from the value given by the effective mass theory depends largely on the species of the Group V impurity. It has been usual[1,2] to consider the correction to the effective mass potential as a perturbation whose effect is confined to the immediate vicinity of the donor impurity and hence only affects the s-like energy states. This effect has been considered most recently by Appel,[3] who has also treated the relativistic corrections to the ground state and included the electron spin.

In the effective mass treatment, the ground state is fourfold degenerate (neglecting spin) and is represented by the energy $-E_0$ in Fig. 1. Each of the four wave functions is constructed by taking the product of a Bloch function from one of the four conduction band minima and the effective mass wave function associated with the same minimum.[1] If one now adds a perturbation which separates the ground state into a onefold and a threefold degenerate level, the correct zero-order linear combinations of the four-valley wave functions can be obtained by requiring that these combinations have the transformation properties of A_1 and T_1 of T_d. In general, such a perturbation will produce a shift of the center of gravity of the original level as well as a splitting.[4] This is shown in Fig. 1. The center of gravity shift Λ is the expectation value of the perturbation in the ground state while the splitting, 4Δ, is due to the off-diagonal matrix elements each of whose magnitude is Δ.

It is the purpose of the present paper to present the results of the most direct experimental procedure[5] for the determination of the quantities Λ and Δ and to compare these results with those of other experimenters. The experimental procedure is simple and is readily understood by reference to Fig. 1. For Group V impurities in germanium, it is possible to attain a temperature at which the upper ground state can be sufficiently populated so that well-defined transitions can be induced from both ground states to the same excited states. Symmetry considerations show that electric dipole transitions of both types are allowed. Thus, experimentally, two series of absorption lines should be observed
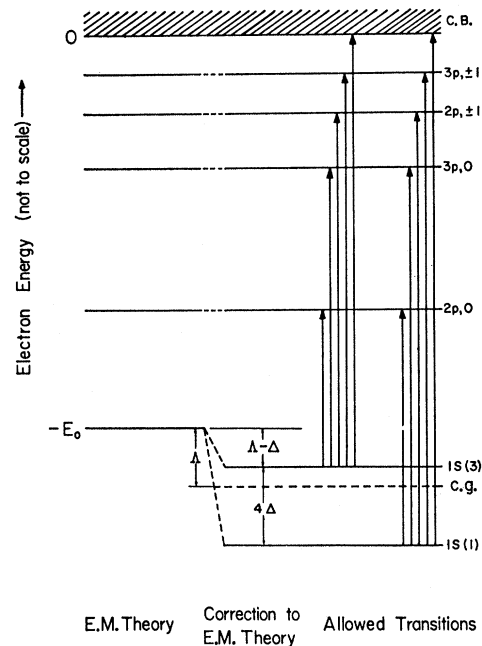

FIG. 1. The energy level scheme (not to scale) of a Group V impurity in germanium showing how a general perturbation affects the effective mass ground state. Shown also are the possible transitions between the two ground states and the excited p states.

[1] W. Kohn, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 257.
[2] P. J. Price, Phys. Rev. **104**, 1223 (1956).
[3] J. Appel, Phys. Rev. **133**, A280 (1964).
[4] R. W. Keyes, IBM J. Res. Develop. **5**, 266 (1961).

[5] P. Fisher, Phys. Chem. Solids **23**, 1346 (1962); J. H. Reuszer and P. Fisher, Bull. Am. Phys. Soc. **9**, 61 (1964).

TABLE I. Energy spacings of the excitation lines of bismuth impurity in germanium. Units are millielectron volts.

Effective mass theory		Experimental[a]		
$\epsilon(3p, \pm1) - \epsilon(2p, \pm1) = 0.75 \pm 0.08$	$\epsilon(A_1) - \epsilon(B_1) = 0.64$	$\epsilon(A_3) - \epsilon(B_3) = 0.68$	$\epsilon(A_1) - \epsilon(A_3) = 2.85$
$\epsilon(2p, \pm1) - \epsilon(3p, 0) = 0.75 \pm 0.23$	$\epsilon(B_1) - \epsilon(C_1) = 0.88$	$\epsilon(B_3) - \epsilon(C_3) = \cdots$	$\epsilon(B_1) - \epsilon(B_3) = 2.89$
$\epsilon(2p, \pm1) - \epsilon(2p, 0) = 2.90 \pm 0.23$	$\epsilon(B_1) - \epsilon(E_1) = 3.08$	$\epsilon(B_3) - \epsilon(E_3) = 3.07$	$\epsilon(E_1) - \epsilon(E_3) = 2.88$

[a] Experimental error in all spacings is ±0.02 unit.

separated in energy 4Δ. Identification of those lines which belong to a given series is made by observing the temperature dependence of their intensities. The determination of which lines in the two series have common excited states is made by a comparison of the line spacings in one series with those in the other series. Thus the energy difference between those lines in the two series which have common excited states will be 4Δ. An estimate of Λ-Δ, and hence Λ, is obtained by subtracting the effective mass energy, $E_0 - E(2p, \pm1)$, from the energy of the transition $1s(3) \rightarrow 2p, \pm1$. This is possible as the present and previous results[6] show that the effective mass calculations predict the energies of the excited states quite accurately.

II. EXPERIMENTAL PROCEDURE

The transitions to be excited occur in the range 80 to 260 μ. For this purpose a far-infrared grating spectrometer was used, the calibration being performed by the use of the values recently given by Pyler et al.[7] for the energies of the pure rotational spectrum of atmospheric water vapor. The sample to be examined was first ground to a suitable thickness and then etched. During the grinding procedure, a wedge was given to the sample to suppress interference fringes. A carbon thermometer was then glued to the sample and these attached to the sample block of an optical cryostat.[8] The major experimental difficulty was to obtain samples which contained only that impurity whose spectrum was to be investigated. As will be seen, the values obtained for Λ-Δ (see Fig. 1) do not differ greatly from one Group V impurity to another, thus the presence of more than one such impurity in a given sample would not give a low-energy series of lines characteristic of an individual impurity. It was possible to determine which neutral Group V impurities were present in a particular sample by noting whether or not the strongest line of the high-energy series of lines of a given impurity was observed.[9] It was found that arsenic was the most difficult impurity to isolate.

[6] H. Y. Fan and P. Fisher, Phys. Chem. Solids 8, 270 (1959).
[7] K. Narahari Rao, R. V. de Vore, and Earle K. Plyler, J. Res. Natl. Bur. Std. 67, 351 (1963).
[8] P. Fisher, W. H. Haak, E. J. Johnson, and A. K. Ramdas, Proceedings of the Eighth Symposium on the Art of Glassblowing (The American Scientific Glassblowers Society, Gwinhurst, Wilmington, Delaware 1953), p. 136.
[9] The success of this technique has demonstrated that this method of analysis is far more sensitive than the more conventional methods. It is estimated that concentrations as low as 10^{13} cm^{-3} can be detected by this means.

III. EXPERIMENTAL RESULTS

A. Bismuth Impurity

In Fig. 2 is shown the excitation spectrum of bismuth impurity in germanium for various sample temperatures. The geometrical spectral slitwidth used for the experiment is indicated in several regions of the energy range encompassed. It is seen that the intensities of those absorption lines which are designated by the subscript 3 decrease drastically as the sample temperature is lowered. Thus these lines have the upper or threefold degenerate ground state as the initial state. The lines labeled by the subscript 1 show possibly a small intensity increase as the temperature is decreased indicating that these lines are due to transitions that originate from impurities which have bound electrons in the lower ground state. The lines have been lettered such that the transitions which have common excited states are designated by the same letter. This can be verified by an examination of the data given in Table I. These data show that the energy spacing between the lines A_1 and B_1 is the same as the spacing between A_3 and B_3 while the spacing between B_1 and E_1 is the same as that between B_3 and E_3. For the sample used, the intensity of the C_3 line was apparently too small for this transition to be observed. Shown in the last column of Table I are the energy spacings between those lines which have common excited states. These spacings then give the value of 4Δ, the ground-state splitting.

An attempt was made to measure the intensity of the B_3 line as a function of sample temperature. For temperatures below about 12°K, it is adequate to assume that the population of the lower ground state remains essentially constant. This follows from the magnitude of 4Δ and agrees with the experimental results shown in Fig. 2. Hence the intensity of B_3 should change with temperature as $\exp(-4\Delta/kT)$. A plot was made of $\ln\alpha(B_3)$ versus T^{-1}, where α is the absorption coefficient. The slope of the straight line which was fitted to the data points gave a value of 4Δ which was within a factor of two of the value given in Table I.

The lettering of the lines is the same as that used previously.[6] In this latter work, a correlation was made between the experimentally determined excited state spacings and those calculated by the effective mass formalism.[1] For completeness this correlation is also included in Table I. Shown in Table II are the energies of the various transitions. The absorptions designated by $I_1(?)$ and $I_3(?)$ in Fig. 2 are presumed to be due to
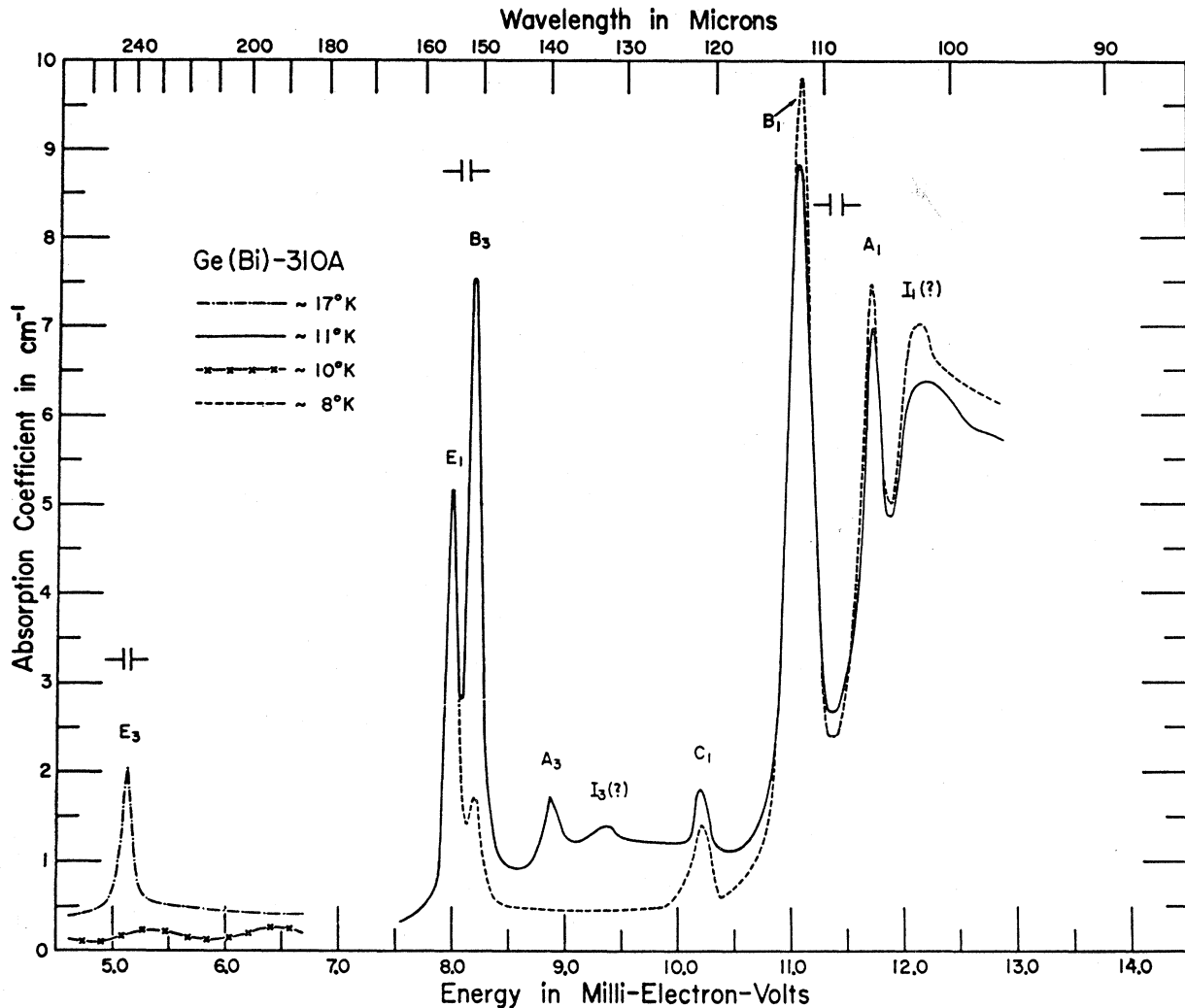
Fig. 2. The excitation spectrum of bismuth impurity in germanium for different sample temperatures. $N_D \simeq 4 \times 10^{14}$ cm^{-3}.

photoionization of the impurity atoms or to transitions to excited states higher in energy than $3p, \pm 1$. The question mark following the letter I indicates this uncertainty. The letter I was originally chosen[6] to indicate that that absorption was due to ionization of the impurity.

B. Arsenic Impurity

The excitation spectrum of arsenic impurity in germanium is shown in Fig. 3. The two series of lines have been labeled in the same manner as for bismuth. Comparison of the energy spacings for lines in the two series is given in Table III where also shown are the various values obtained for 4Δ. The energies of the transitions are given in Table II. The position of $I_3(?)$ as determined from $I_1(?)$ and 4Δ coincides with the position of E_1 as is indicated in Fig. 3. This accounts for the large background absorption observed for E_1 at $T \simeq 12°$K. The small line designated by "Phosphorus B_1" is interpreted as being due to the presence of $\sim 3 \times 10^{13}$ cm^{-3}

Table II. Energies of transitions observed for neutral Group V impurities in germanium. Units are millielectron volts.[a]

Impurity	$\epsilon(I_1)$	$\epsilon(A_1)$	$\epsilon(B_1)$	$\epsilon(C_1)$	$\epsilon(E_1)$	$\epsilon(I_3)$	$\epsilon(A_3)$	$\epsilon(B_3)$	$\epsilon(E_3)$	ϵ_i[b]
Bi	12.15	11.72	11.08	10.20	8.00	9.37	8.87	8.19	5.12	12.68
As	13.65	13.15	12.44	11.61	9.44	⋯	8.91	8.23	5.19	14.04
P	12.36	11.84	11.16	10.33	8.15	9.49	9.03	8.34	5.30	12.76
Sb	9.66	9.29	8.59	7.75	5.58	⋯	8.96	8.28	5.26	10.19

[a] Experimental error in all values except $\epsilon(I_1)$ and $\epsilon(I_3)$ is ± 0.01 unit. The error in $\epsilon(I_1)$ and $\epsilon(I_3)$ is ± 0.05 unit.
[b] Error in ϵ_i is ± 0.04 unit and is mainly due to the uncertainty in the position of the $2p, m=1$ level (see Table I).
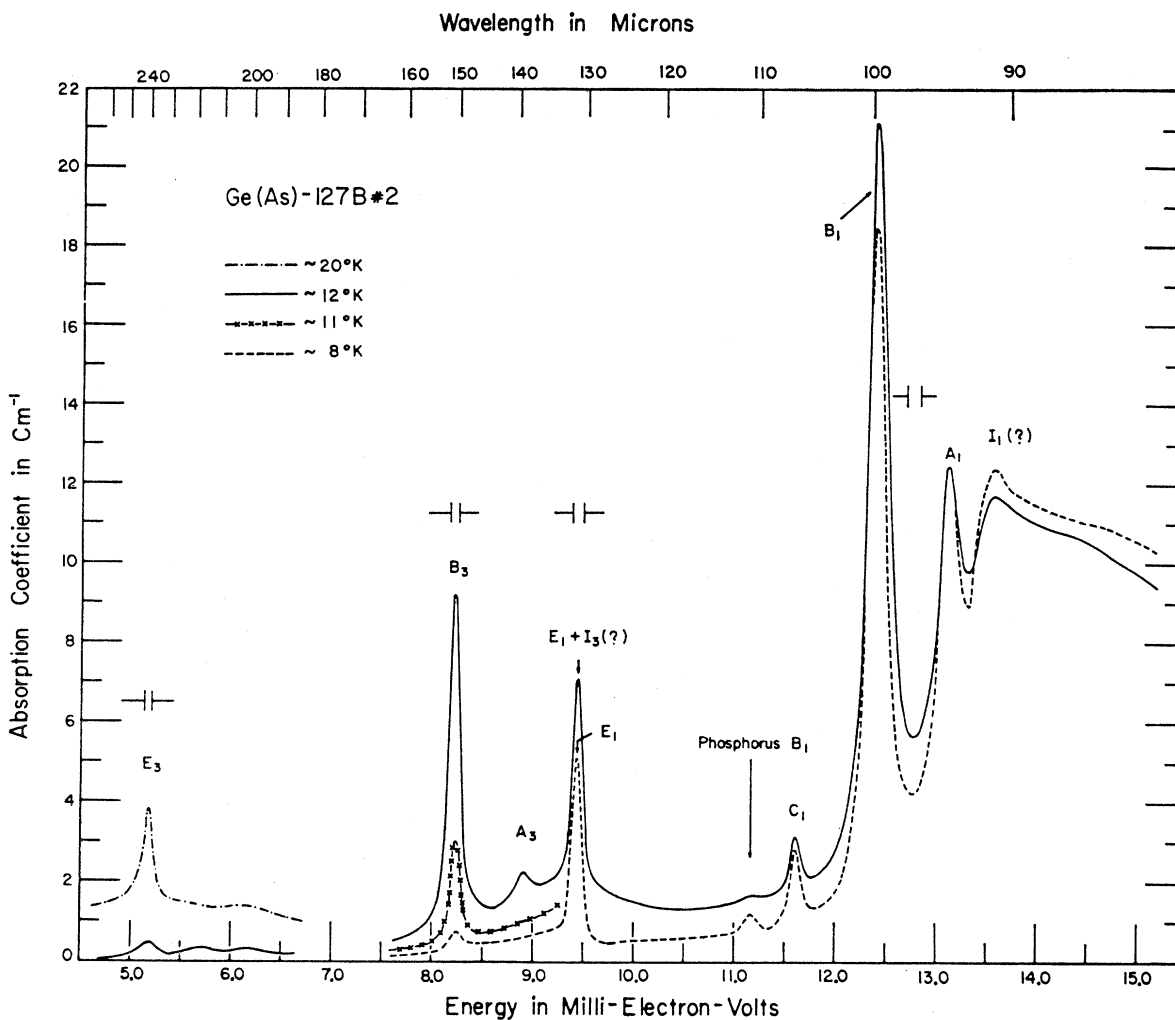
FIG. 3. The excitation spectrum of arsenic impurity in germanium for different sample temperatures. $N_D \simeq 1 \times 10^{15}$ cm^{-3}.

neutral phosphorus impurities "contaminating" the sample. It is interesting to note that the line called F in Ref. 6 occurred at an energy equal to that of the B_3 line shown in Fig. 3. Previously,[6] line F was interpreted as being due to contaminating antimony, this was justified at that time by comparing the intensity of the F line with that of the E line using samples cut from different ingots. There now seems to be little doubt that the F lines observed were B_3 lines and that the variations in its relative intensity from sample to sample were due to variations in the temperatures of the different samples.

TABLE III. Experimental energy spacings of the excitation lines of arsenic impurity in germanium. Units are millielectron volts.[a]

$\epsilon(A_1) - \epsilon(B_1) = 0.71$	$\epsilon(A_3) - \epsilon(B_3) = 0.68$	$\epsilon(A_1) - \epsilon(A_3) = 4.24$
$\epsilon(B_1) - \epsilon(C_1) = 0.83$	$\epsilon(B_3) - \epsilon(C_3) = \cdots$	$\epsilon(B_1) - \epsilon(B_3) = 4.21$
$\epsilon(B_1) - \epsilon(E_1) = 3.00$	$\epsilon(B_3) - \epsilon(E_3) = 3.04$	$\epsilon(E_1) - \epsilon(E_3) = 4.25$

[a] Experimental error is ±0.02 unit.

C. Phosphorus Impurity

A spectrum, similar to those shown in Figs. 2 and 3, is shown in Fig. 4 for phosphorus impurity. The pertinent energy spacings are shown in Table IV while the

TABLE IV. Experimental energy spacings of the excitation lines of phosphorus impurity in germanium. Units are millielectron volts.[a]

$\epsilon(A_1) - \epsilon(B_1) = 0.68$	$\epsilon(A_3) - \epsilon(B_3) = 0.69$	$\epsilon(A_1) - \epsilon(A_3) = 2.81$
$\epsilon(B_1) - \epsilon(C_1) = 0.83$	$\epsilon(B_3) - \epsilon(C_3) = \cdots$	$\epsilon(B_1) - \epsilon(B_3) = 2.82$
$\epsilon(B_1) - \epsilon(E_1) = 3.01$	$\epsilon(B_3) - \epsilon(E_3) = 3.04$	$\epsilon(E_1) - \epsilon(E_3) = 2.85$

[a] Experimental error is ±0.02 units.

energies of the various transitions are included in Table II. In the interpretation of the results shown in Fig. 4, it is assumed that when the sample temperature is changed from 10 to 12°K, the B_3 line has so increased in either intensity or width or both that a substantial
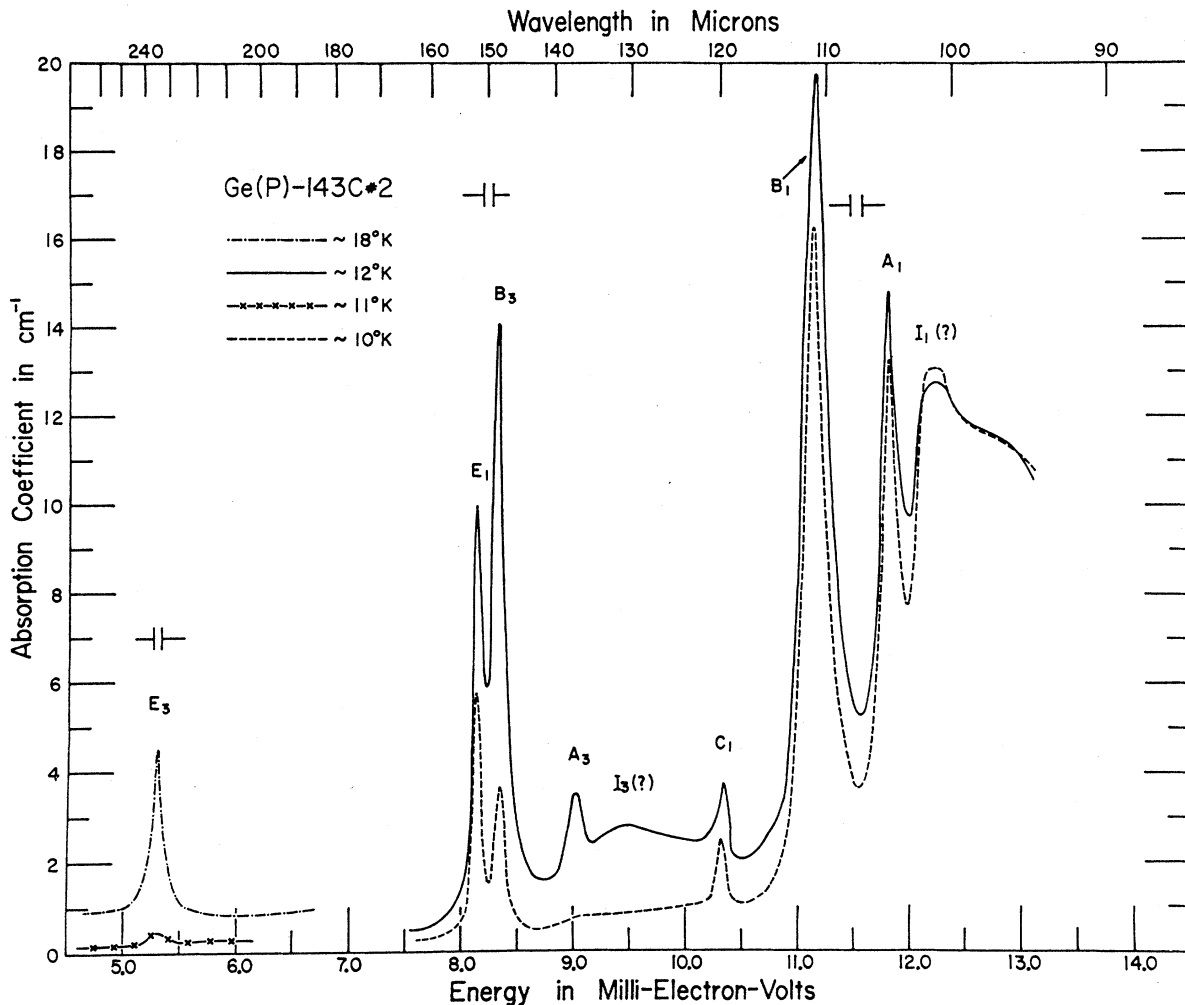
FIG. 4. The excitation spectrum of phosphorus impurity in germanium for different sample temperatures. $N_D \simeq 8 \times 10^{14}$ cm^{-3}.

background results for the E_1 line at the higher temperature. The magnitudes of the E_1 line at the two temperatures are about the same when the appropriate backgrounds are subtracted. Qualitative observations have shown that the B lines broaden with temperature more rapidly than do the E lines. Again, as for arsenic (see Sec. IIIB), previous investigations had indicated the existence of the phosphorus B_3 line as can be seen in Table I of Ref. 6.

D. Antimony Impurity

The current results for antimony are included here to clarify some uncertainties that were discussed previously in Ref. 5. At the time of this latter work, the origin of the shoulders designated as b_1 and b_3 was unknown. Subsequent examination of the same sample showed that both arsenic and phosphorus were present in the specimen. The shoulder b_3 occurred at the same energy as does the E_1 line of phosphorus. This would

then account for the persistence of the b_3 shoulder even to the lowest temperatures. During the course of some recent measurements on the spectra of Group III impurities in germanium,[10] it was found necessary to improve the purity of the light beam of the monochromator. Measurements made using the purer beam clearly indicated that the shoulder b_1 was spurious. Figure 5 shows part of the spectrum of an antimony-"doped" sample cut from an ingot grown specifically to minimize the concentration of other Group V impurities. The low-energy region of the antimony spectrum was not repeated. The previous observations[5] in this energy range were made at temperatures low enough that the E_3 lines of the other Group V impurities present in the sample would not be of sufficient intensity to distort the antimony spectrum. The energies of the transitions observed for antimony impurity are included in Table II.

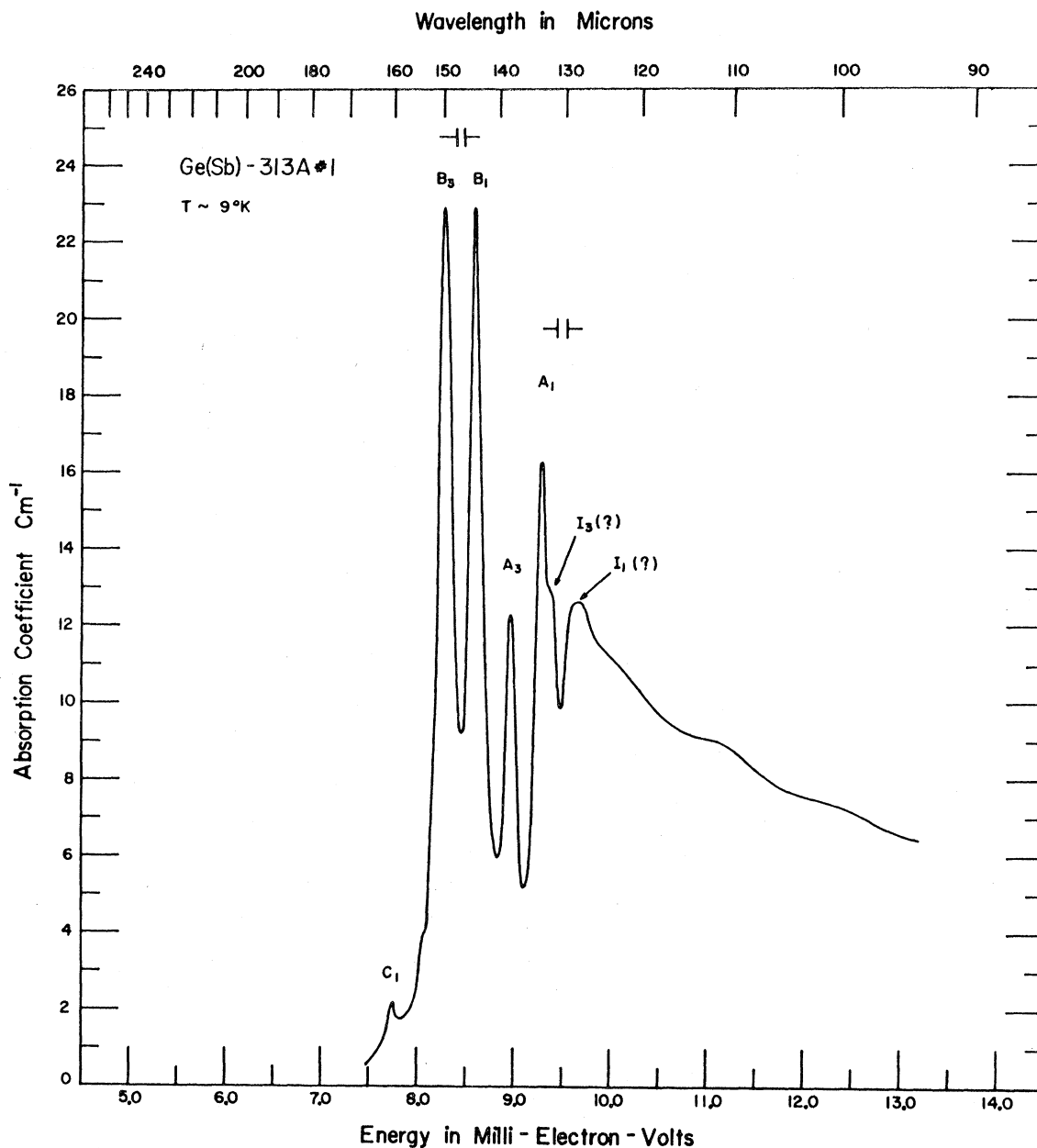[10] Rex L. Jones and P. Fisher (to be published).

FIG. 5. Part of the excitation spectrum of antimony impurity in germanium. $N_D \simeq 7 \times 10^{14}$ cm^{-3}.

E. Determination of Λ

Shown in Fig. 6 is the energy scheme of Group V impurities in germanium as given by the effective mass approximation and by the present experiments. In the effective mass scheme of Fig. 6, the widths of the levels indicate the errors in the calculated energies. The most precisely calculated binding energy is seen to be that given for the $2p,\pm 1$ level. Thus the correlation between experiment and theory has been made such that the final state of the B_1 and B_3 transitions coincides precisely with the calculated position of the $2p,\pm 1$ level.

The values of Λ-Δ have been determined, then, by using only the B_3 line rather than all the lines from the upper

TABLE V. Splittings and shifts of the ground states of Group V impurities in germanium. Units are millielectron volts.[a]

	4Δ	$\Lambda - \Delta$[b]	Λ
Bi	2.87	0.59	1.31
As	4.23	0.63	1.69
P	2.83	0.74	1.45
Sb	0.32	0.68	0.76

[a] Experimental error in 4Δ is ± 0.02 unit.
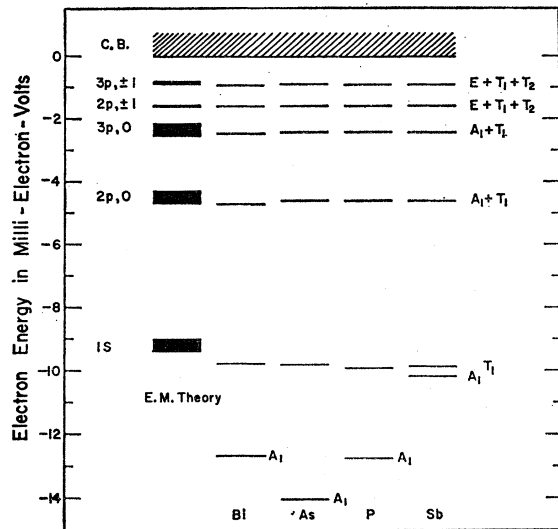[b] $\Lambda - \Delta$ estimated using $|E_{1s} - E_{2p,\pm 1}|_{e.m.} = 7.6 \pm 0.23$ unit.

FIG. 6. The diagram shows the part of the energy level scheme of each Group V impurity in germanium as determined by optical absorption measurements. Shown also is the scheme as determined by the effective mass formalism. For the latter, the width of the levels indicates the uncertainties in the positions of the levels. The various levels are labeled in two ways: (1) according to the magnetic quantum number, m, associated with the envelope wave functions and (2) according to the irreducible representations of the point group T_d to which the full wave functions belong.

ground state. The method of finding Λ-Δ is given in Sec. I. These values are summarized in Table V along with the values of 4Δ and Λ. The uncertainties in the values of Λ-Δ and Λ arise mainly from the uncertainties in the variational calculation for the ground-state energy.

IV. DISCUSSION

The interpretation of the results has been based on the conclusion that the same excited states participate in the transitions from the two ground states. This may not be quite correct. When a symmetry classification is made of the various excited states, it is found[11] that, for example, the wave functions of the $2p,\pm 1$ state form a basis for the E, T_1, and T_2 irreducible representations of T_d and not for just one such representation. Hence this state is, strictly speaking, a multiplet of three states of different energies. The separations between these three states will depend upon the magnitudes of any corrections which need to be applied to the effective mass theory just as does the separation of the effective mass ground state, $A_1 + T_1$. Similar multiplicities also occur for the other excited states. The labeling of the states according to their symmetries is given in Fig. 6. The selection rules allow electric dipole transitions from the lower ground state A_1 to occur only to those p substates characterized by T_1 whereas such transitions can occur from the upper ground state T_1 to

all those p substates characterized by A_1, E, T_1, and T_2. Thus, for example, it is not possible to say that the two B lines have the same final substate. Similarly for the other pairs of lines. However, in view of the close agreement obtained between the line spacings in the high-energy series and those in the low-energy series, for all the impurities, it can be concluded that either the separations of the substates in each excited state is smaller than the experimental precision or the largest transition probability between the upper ground state and each excited state occurs in all cases for that excited substate which belongs to T_1. In either case, the values obtained for 4Δ and Λ-Δ remain unchanged.

From the results given in Table V and illustrated in Fig. 6, it is seen that there is a depression of the upper ground state below the effective mass value and that this shift is nearly independent of the chemical species. This suggests that the corrections to the effective mass theory are of two types: (a) a correction that is independent of the chemical species and gives rise to a depression of the center of gravity of the ground state and a splitting of this state and (b) a correction that is species-dependent which is only important for those states in which the electron spends a large amount of its time in the immediate vicinity of the impurity atom and hence only produces a chemical shift of the totally symmetric ground state. Part of the species-dependent effect may be of the type introduced by Appel.[3]

The values obtained for 4Δ by other workers,[12–17] and from the present investigation, are given in Table VI. With the exception of the present values, all others have been obtained by observing the effect of uniaxial stress on one property or another of samples containing Group V impurities. The stress dependence of the property under examination is then analyzed on the basis of Price's[2] perturbation calculation except for the electron spin resonance measurements,[15–17] where the calculations are extended to give the new wave functions of the ground state. In all cases, it is seen that there is satisfactory agreement between the different methods when 4Δ is large, viz., bismuth, arsenic, and phosphorus but not for antimony. It is not understood why the value obtained by Fritzsche[13] for this latter impurity differs so greatly from the present results.

Of the various methods used by other workers, the piezo-optical measurements[14] are the most direct as the values of 4Δ obtained do not depend on a knowledge of

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[11] A. K. Ramdas, P. M. Lee, and P. Fisher, Phys. Letters 7, 99 (1963).

[12] H. Fritzsche, Phys. Rev. 115, 336 (1959).
[13] H. Fritzsche, Phys. Rev. 120, 1120 (1960).
[14] G. Weinreich and H. G. White, Bull. Am. Phys. Soc. 5, 60 (1960); and G. Weinreich, *Proceedings of the International Conference on Semiconductor Physics, Prague 1960* (Czechoslovak Academy of Sciences, Prague, 1961), p. 360.
[15] D. K. Wilson and G. Feher, Bull. Am. Phys. Soc. 5, 60 (1960); and G. Feher, *Proceedings of the International Conference on Semiconductor Physics, Prague 1960* (Czechoslovak Academy of Sciences, Prague, 1961), p. 579.
[16] D. K. Wilson, Phys. Rev. 134, A265 (1964).
[17] R. E. Pontinen and T. M. Sanders, Jr., Bull. Am. Phys. Soc. 6, 426 (1961).

TABLE VI. Values of 4Δ obtained by various methods. Units are millielectron volts.

Impurity	Piezoresistance method	Piezo-optical method	Piezoelectron spin resonance	Present method
Bi	⋯	⋯	2.8[d]	2.87±0.02
As	4.10±0.15[a]	3.9±0.6[c]	4.2[d]	4.23±0.02
P	⋯	3.0±0.3[c]	2.9[d]	2.83±0.02
Sb	0.57±0.03[b]	⋯	0.404[e]	0.32±0.02

[a] See Ref. 12.
[b] See Ref. 13.
[c] See Ref. 14.
[d] See Ref. 16.
[e] See Ref. 17.

either the applied stress or the deformation potential constant. However, this method does assume that the centers of gravity of all the energy states of the impurity shift by the same amount. In the case of the piezo-electron-spin-resonance technique, the quantity measured is not 4Δ but $4\Delta/E_2$, where E_2 is the shear deformation potential constant for the conduction band as defined by Brooks.[18] The values given in column four of Table VI for bismuth, arsenic, and phosphorus were obtained by Wilson[16] using a value of $E_2 = 19$ eV while that for antimony, given by Pontinen and Sanders,[17] was deduced apparently using $E_2 = 19.5$eV. From the values of $4\Delta/E_2$ given by these workers and with the present results for 4Δ, an evaluation of E_2 has been made. The values obtained are shown in Table VII together with the measured values of $4\Delta/E_2$. It is seen that for bismuth, arsenic, and phosphorus the

TABLE VII. Values of E_2 obtained from the present values of 4Δ and the piezo-electron spin resonance values of $4\Delta/E_2$.

Impurity	$4\Delta/E_2 \times 10^4$	E_2 (eV)
Bi	1.47±0.09[a]	19.5±1.3
As	2.20±0.13[a]	19.2±1.2
P	1.53±0.12[a]	18.5±1.6
Sb	0.208±0.004[b]	15.4±1.3[c]

[a] See Ref. 16.
[b] See Ref. 17.
[c] If Fritzsche's value of $4\Delta = (0.57 \pm 0.03) \times 10^{-3}$ eV for antimony is used: $E_2 = 27.4 \pm 2.0$ eV.

[18] H. Brooks, *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press Inc., New York, 1955), Vol. 7, p. 85.

values of E_2 are in satisfactory agreement with the value of (19.2 ± 0.4) eV obtained by Fritzsche[12] for arsenic impurity. The value of E_2 for antimony obtained in this manner appears to be unreasonable. If the value $4\Delta = 0.57$ meV[13] is used instead of the present value, then $E_2 = 27.4$ eV (see Table VII), a value which is even more unreasonable.

Finally, the ionization energies ϵ_i for the various impurities are included in Table II along with the energies corresponding to the absorptions $I_1(?)$ and $I_3(?)$. The ionization energies were obtained by adding to the energy of the B_1 lines the value calculated by Kohn[1] for the binding energy of the $2p,\pm 1$ state. It is seen that the values of ϵ_i and $\epsilon(I_1)$ are not the same. In view of the excellent agreement between theory and experiment for the level spacings, it is reasonable to assume that the values calculated for the actual binding energies are correct and that ϵ_i gives the ionization energy. The absorptions $I_1(?)$ and $I_3(?)$, then, are presumably due to transitions from the two ground states to excited states higher in energy than the $3p,\pm 1$ state. An examination of samples of lower impurity concentration, under higher resolution and, for $I_1(?)$, at lower temperatures, would probably clarify this point.