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VI-3. A Piezo-Spectroscopic Determination of the Symmetries of Acceptor States in Silicon and Germanium*

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The effect of uniaxial stress on the excitation spectra of neutral zinc in germanium and Group III acceptors in silicon has been studied with compression along the simple directions ⟨111⟩, ⟨110⟩ and ⟨100⟩ using polarized light. A comparison of selection rules deduced from symmetry arguments with the observed polarization features and the energy spacings of the stress induced components is given.

§ 1. Introduction

In view of the inherent mathematical complexity of the theory of acceptor states[1~3] in silicon and germanium, a comprehensive experimental investigation of the optical excitation spectra of acceptors is clearly valuable. As in atomic spectroscopy, perturbing external fields can be used effectively to investigate the symmetry of the energy states. Magneto-spectroscopic[4~7] and piezo-spectroscopic[8~13] studies have already been reported for some acceptors in silicon and germanium. The object of the present paper is to discuss the results of recent experiments on the piezo-spectroscopic effects of neutral zinc in germanium and the Group III acceptors in silicon.

§ 2. Experimental Results

The excitation spectra to be described were obtained using grating monochromators, polarized light and the differential thermal compression technique of Rose-Innes.[14]

(i) *Neutral zinc in germanium*

In Fig. 1 is shown part of the excitation spectrum of neutral zinc in germanium. The upper curve, Fig. 1a, is for zero stress while Fig. 1b shows the effect of a compressive force, $\boldsymbol{F}$, applied along a ⟨100⟩ direction. It is clear from Fig. 1b that the B line has split into two components while the C and D lines each gives rise to three components. The components C_2 and D_2 occur at the zero stress positions.

The effect of compression along ⟨111⟩ is shown in Fig. 2. It can be seen that for this stress the B, C and D lines each give rise to two components. At a higher stress, the component labeled D_1+D_2, observed for the electric vector $\boldsymbol{E}$ perpendicular to $\boldsymbol{F}$, splits into two components; hence the designation D_1+D_2. Also, at higher stress, the lines labeled D_3 and D_4 become resolved.

Measurements have also been made for $\boldsymbol{F} \parallel [110]$ with the direction of light propagation, $\boldsymbol{q}$, either along $[1\bar{1}0]$ or [001]. For this direction of compression, at least two D, three C, and two B components have been observed.

(ii) *Neutral group III acceptors in silicon*

In Fig. 3 is shown the effect of a ⟨111⟩ compression on the excitation spectrum of neutral boron in silicon.[10,11,13] As indicated in the figure, the observed excitation lines are associated with the excited states derived from the $p_{3/2}$ and the $p_{1/2}$ valence bands.[7,11] The two insets in the figure show the effect of an increased stress on line 1 of the $p_{3/2}$ spectrum and line $2p'$ of the $p_{1/2}$ spectrum. The magnitude of the strain is gauged by the spacing of the two $2p'$ components.

The improved experimental conditions used for the present ⟨111⟩ measurements have enabled more details to be observed than previously.[10] This has necessitated relabeling the components. The presence of the component 1.2, observed for $\boldsymbol{E} \parallel \boldsymbol{F}$, shows that four stress induced components arise from line 1. At the lower stress used in the previous measurement, the components 4.1 and 4.2 shown in Fig. 3 merged to give the component previously labeled 4.1. Further, the present results show that the weak line 3 generates four components with a polarization pattern identical to that of line 1. This is seen clearly in Fig. 4 which shows the ⟨111⟩ stress dependence of part of the $p_{3/2}$ spectrum for a boron concentration higher than that of Fig. 3. Also, from Fig. 4, it is seen that line

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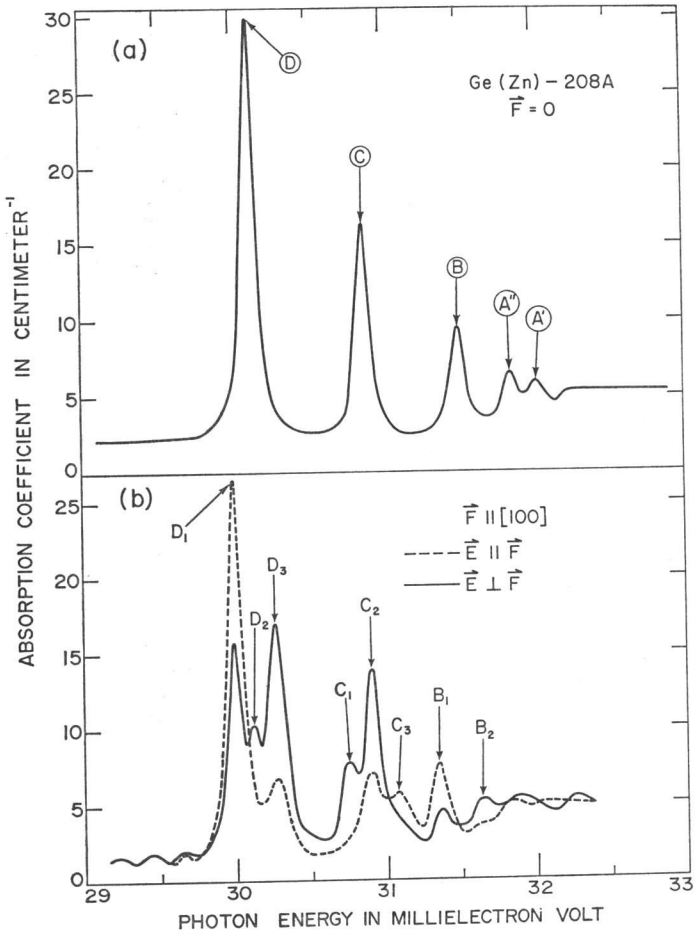

Fig. 1. Part of the excitation spectrum of neutral zinc in germanium measured with and without uniaxial stress. Liquid helium used as coolant. Room temperature resistivity~2.5 ohm-cm.

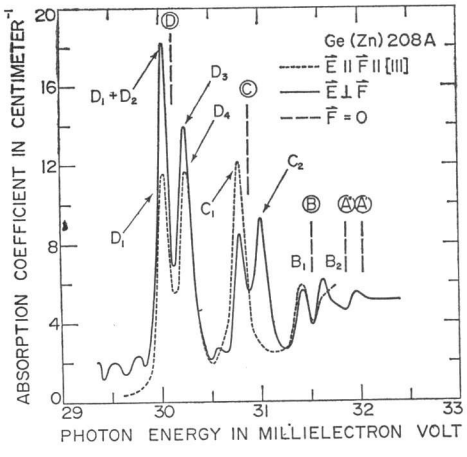

Fig. 2. Effect of a ⟨111⟩ compression on the excitation spectrum of neutral zinc in germanium. The vertical dashed lines indicate the positions of the zero stress lines.

5 behaves in much the same way as lines 1 and 3. Lines 6 and 7 appear to give two and three components, respectively. Little can be said regarding the behavior of lines 8 and 9.

The results for $\boldsymbol{F}||[110]$ are given in Figs. 5a and 5b for $\boldsymbol{q}||[1\bar{1}0]$ and [001], respectively. It is expected that the spectra should be identical for $\boldsymbol{E}||\boldsymbol{F}$ irrespective of $\boldsymbol{q}$. This is borne out by the present results in that the strong components 2.2, 4.3 and 4.4 are observed for both $\boldsymbol{q}$ with $\boldsymbol{E}||\boldsymbol{F}$. The relative intensities of 4.3 and 4.4 are, however, clearly different for the two cases; this is attributed to stress-dependent depopulation effects.

In the case of $\boldsymbol{F}||\langle 100\rangle$, the most striking feature is that little effect has been observed for line 2 even for comparatively large stresses, whereas lines 1, 3 and 4 do exhibit splittings.

The effect of stress on $2p'$, the strongest line

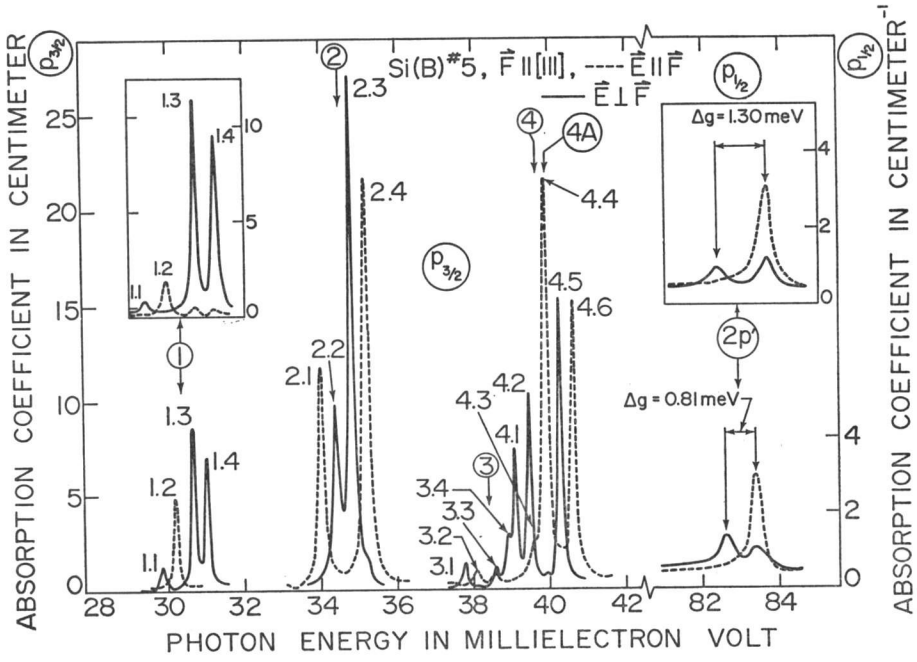

Fig. 3. The excitation lines 1–4A and $2p'$ of neutral boron impurity in silicon under a ⟨111⟩ compression. The encircled numbers together with the associated vertical arrows indicate the positions of the zero stress lines. The two insets show the effect of a larger stress on lines 1 and $2p'$. Room temperature resistivity ~12 ohm-cm.

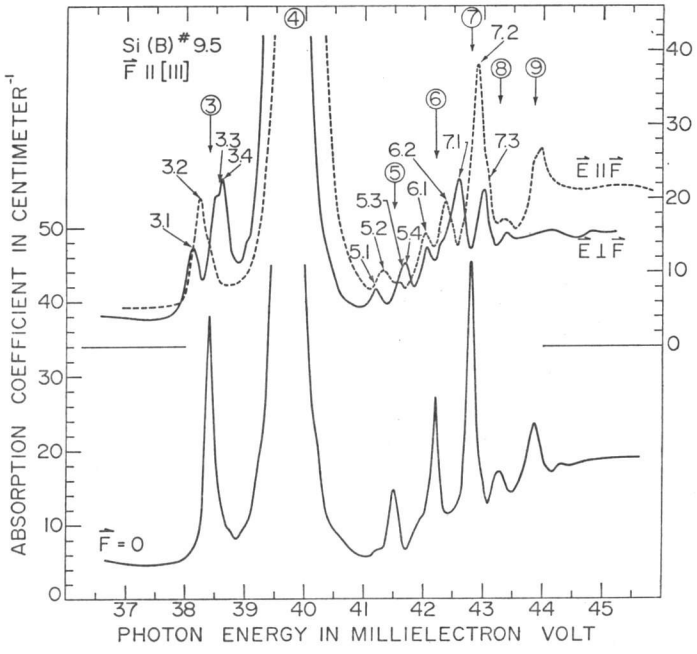

Fig. 4. The effect of a ⟨111⟩ compression on lines 3, and 5–9 of the excitation spectrum of neutral boron impurity in silicon (see upper half). The curve in the lower half is the zero stress spectrum. Room temperature resistivity ~1 ohm-cm.

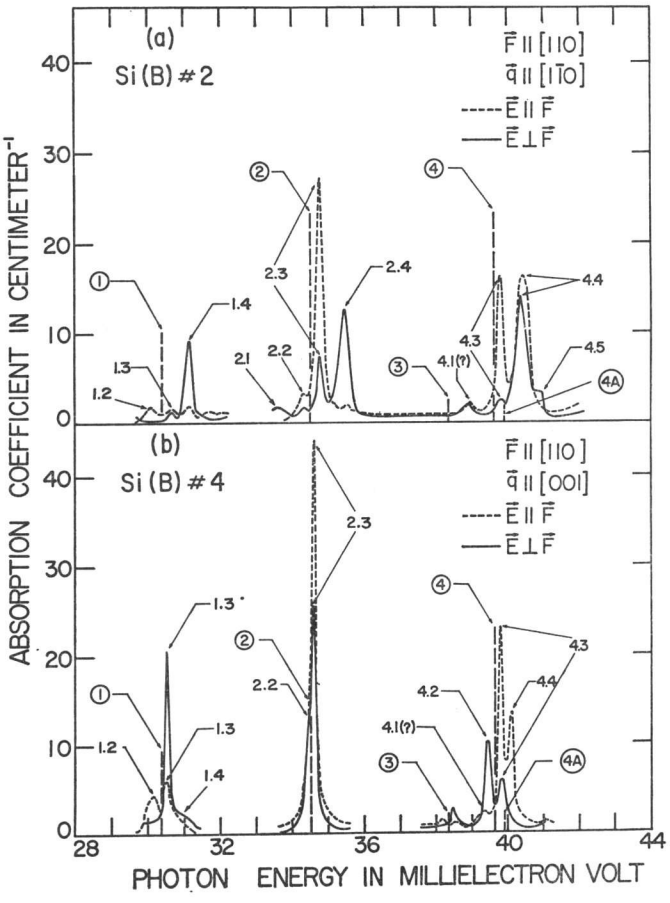

Fig. 5. Excitation spectrum of neutral boron in silicon with compression along [110], for $q \| [1\bar{1}0]$ and [001]. Room temperature resistivity~12 ohm-cm.

of the $p_{1/2}$ spectrum, is found to be identical for $\boldsymbol{F} \| \langle 111 \rangle$, $\langle 100 \rangle$ and $\langle 110 \rangle$. The remaining prominent line, $3p'$, of the $p_{1/2}$ spectrum[7] behaves exactly like $2p'$.

The behavior of gallium and aluminum impurities in silicon has also been examined under uniaxial stress. A comparison of the experimental results shows that the $2p'$ lines of boron, aluminum and gallium behave identically. Of the $p_{3/2}$ spectra, the lines of aluminum and gallium which correspond to line 1 of boron, behave similarly. This is also the case for line 2 of boron and aluminum. A more complete comparison of the entire excitation spectra under stress is in progress.

§ 3. Discussion

(i) *Symmetry considerations*

An impurity which replaces a germanium or silicon atom precisely, has the site symmetry T_d. The transformation properties of the impurity states, including spin, must conform to those of the irreducible representations Γ_6, Γ_7 and Γ_8 of the double group $\overline{T}_d$.[15] The behavior of such states under uniaxial stress is shown schematically in Fig. 6. Here it is assumed that for $\boldsymbol{F}=0$ the ground state belongs to Γ_8 as is predicted theoretically for Group III impurities.[1~3] The actual splittings of the Γ_8 states will be determined by the magnitudes and signs of the appropriate deformation potential constants which will also, of course, determine the ordering of these states.[16] The selection rules for electric dipole transitions for $\boldsymbol{F} \| \langle 111 \rangle$ and $\langle 100 \rangle$ are also shown.

In the case of $\boldsymbol{F} \| \langle 110 \rangle$, the Γ_8 states split into two levels. The selection rules, however, permit all transitions for both directions of polarization and of $\boldsymbol{q}$.

(ii) *Neutral zinc in germanium*

The energy spacings of the excitation lines of neutral zinc in germanium are identical to those

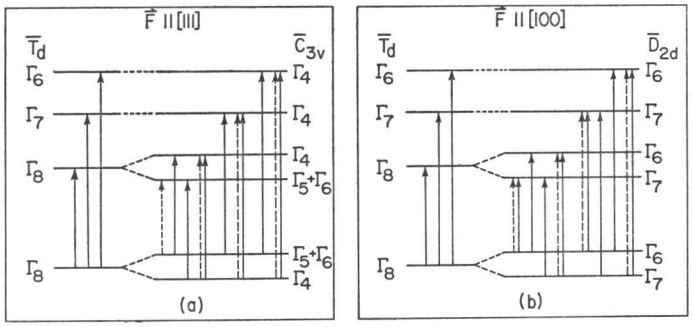

Fig. 6. The behavior of transitions from a Γ_8 ground state to Γ_6, Γ_7 and Γ_8 excited states of the double group $\overline{T}_d$ under uniaxial compression. The dashed arrows are for $\boldsymbol{E}||\boldsymbol{F}$ while the full arrows are for $\boldsymbol{E}\perp\boldsymbol{F}$.

of the Group III impurities.[5,17] Further, this is also true for the neutral impurities copper,[5] mercury[18] and beryllium[19] in germanium. The similarity of the line spacings for all these acceptors strongly suggests that the excited states involved in the optical transitions are essentially the same, in agreement with the effective mass approach. A comparison of the experimental energy spacings of the excited states of Group III impurities in germanium[17] with the theoretical values[3] clearly indicates that the upper state for the B transition belongs to Γ_7. Thus, this is also expected to be the case for neutral zinc. The low energy B component is observed for $\boldsymbol{E}||\boldsymbol{F}$, for both $\boldsymbol{F}||\langle 100\rangle$ and $\langle 111\rangle$. It is not clear for $\boldsymbol{F}||\langle 111\rangle$ if there is a high energy B component for $\boldsymbol{E}||\boldsymbol{F}$. This ambiguity appears to be a consequence of the proximity of the A components. The experimental results for the B components are consistent with the selection rules given in Fig. 6 if the ground states for $\boldsymbol{F}||\langle 100\rangle$ have the same order as that given in Fig. 6b while those for $\boldsymbol{F}||\langle 111\rangle$ have the opposite order to that shown in Fig. 6a. It is assumed that for neutral zinc the unperturbed ground state has Γ_8 symmetry.

The fact that the C line gives at least three components for $\boldsymbol{F}||[110]$, $\boldsymbol{q}||[001]$ and for $\boldsymbol{F}||\langle 100\rangle$ implies that the upper state for this transition must be at least four-fold degenerate.[20] The effective mass theory predicts the existence of two almost degenerate states, a Γ_7 and a Γ_8, which can account for the C line. The polarization and spacings of the stress induced C components are consistent with either the Γ_8 or the combination $\Gamma_7+\Gamma_8$ being the final state for this transition. The latter possibility is favored by Dickey and Dimmock[12] for Group III impurities.

The D line has been assigned to a $\Gamma_8\rightarrow\Gamma_8$ transition.[17] For $\boldsymbol{F}||\langle 111\rangle$, the polarizations and energies of the D components uniquely order the sub-states of both the ground and final state; this ordering is opposite to that shown in Fig. 6a. This is the same ground state ordering predicted above by the B components. For $\boldsymbol{F}||\langle 110\rangle$, the number of D components observed is consistent with a transition to a Γ_8 state. Also, for $\boldsymbol{F}||\langle 100\rangle$, the number of D components is not inconsistent with this assignment. However, it has not been possible to reconcile the selection rules with the observed energy spacings. It might be noted that if the final state of the B line is Γ_8, instead of Γ_7, this inconsistency is removed.

In the above discussion, a single particle description has been used *i.e.* no attempt has been made to take into account the fact that zinc is a double acceptor. Chapman and Estles[21] have recently considered this aspect for mercury in germanium.

(iii) *Neutral group III acceptors in silicon*

The $p_{1/2}$ spectra of the Group III impurities in silicon provide a measure of the ground state splitting. That this spectrum has a ground state in common with the $p_{3/2}$ spectrum is readily demonstrated by the occurrence of this spacing in all the stress induced multiplets of $p_{3/2}$. Also, the stress induced depopulation effects go hand in hand for the $p_{1/2}$ and $p_{3/2}$ spectra. The polarization features of the $p_{1/2}$ spectra are consistent with the final states for these lines having either Γ_6 or Γ_7 of $\overline{T}_d$ as their representation. The ordering of the stress induced ground states has been possible for $\boldsymbol{F}||\langle 111\rangle$ because both Γ_6 and Γ_7 of $\overline{T}_d$ become Γ_4 of $\overline{C}_{3v}$. For $\boldsymbol{F}||\langle 100\rangle$, however, Γ_6 and Γ_7 of $\overline{T}_d$ become Γ_6 and Γ_7 of $\overline{D}_{2d}$, respectively. Since measurements for $\boldsymbol{F}||\langle 111\rangle$ cannot determine the sym-

metries of the final states of the $p_{1/2}$ lines, it does not appear possible to arrive at a unique ordering of the ground states for $\boldsymbol{F} \| \langle 100 \rangle$ from symmetry considerations alone.

In the spectrum shown in Fig. 3, the behavior of line 1 can be understood on the basis of the selection rules given in Fig. 6a provided the sub-levels of the upper Γ_8 state are inverted. The only exception to this is the presence of the very weak 1.4 component observed for $\boldsymbol{E} \| \boldsymbol{F}$. The existence of this component, however, has not been established beyond doubt experimentally. The decrease in intensity of the two low energy components 1.1 and 1.2 with increasing stress, the latter being gauged by the splitting of the $2p'$ line, supports the above interpretation.

From Figs. 3 and 4, it can be seen that lines 3 and 5 follow the same stress pattern as line 1. Hence, the excited states for these transitions must also have Γ_8 symmetry with the same ordering of their stress induced sublevels as for line 1.

The polarization features and energy spacings of the components of line 2 in Fig. 3 conform to the selection rules depicted for the $\Gamma_8 \rightarrow \Gamma_8$ transition in Fig. 6a.

The complexity of the stress pattern for lines 4 and 4A makes it difficult to arrive at a unique assignment of final states for these lines. Further, the polarization features and the number of components for the lines 6 and 7 in Fig. 4 do not admit of a simple interpretation for the symmetries of the final states of these lines.

Acknowledgements

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References

1) W. Kohn and D. Schechter: Phys. Rev. **99** (1955) 1903; W. Kohn: *Solid State Physics* ed. F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957) Vol. 5, p. 257.
2) D. Schechter: J. Phys. Chem. Solids **23** (1962) 237.
3) K. Mendelson and H. M. James: J. Phys. Chem. Solids **25** (1964) 729.
4) P. Fisher and H. Y. Fan: Phys. Rev. Letters **2** (1959) 456.
5) P. Fisher and H. Y. Fan: Phys. Rev. Letters **5** (1960) 195.
6) S. Zwerdling, K. J. Button and B. Lax: Phys. Rev. **118** (1960) 975.
7) S. Zwerdling, K. J. Button, B. Lax and L. M. Roth: Phys. Rev. Letters **4** (1960) 173.
8) R. L. Jones and P. Fisher: Bull. Amer. Phys. Soc. **9** (1964) 237.
9) R.L. Jones and P. Fisher: Solid State Commun. **2** (1964) 369.
10) P. Fisher and A. K. Ramdas: Phys. Letters **16** (1965) 26.
11) A. Onton and A. K. Ramdas: Bull. Amer. Phys. Soc. **11** (1966) 51.
12) D. H. Dickey and J. O. Dimmock: Bull. Amer. Phys. Soc. **10** (1965) 1086.
13) M. W. Skoczylas and J. J. White: Canad. J. Phys. **43** (1965) 1388.
14) A. C. Rose-Innes: Proc. Phys. Soc. (London) **72** (1958) 514.
15) G. F. Koster, J. O. Dimmock, R. G. Wheeler and H. Statz: *Properties of the Thirty-two Point Groups* (M. I. T. Press, Cambridge, Mass., 1963).
16) See, for example, A. A. Kaplyanskii: Optika i Spektrosk. **16** (1964) 1031. translation: Opt. Spectrosc. **16** (1964) 557.
17) R. L. Jones and P. Fisher: J. Phys. Chem. Solids **26** (1965) 1125.
18) R. A. Chapman and W. G. Hutchinson: Solid State Commun. **3** (1965) 293; W. J. Moore: *ibid.* **3** (1965) 385.
19) W. J. Moore and R. Kaplan: Bull. Amer. Phys. Soc. **11** (1966) 206.
20) In the previous measurement (ref. 8)) for $\boldsymbol{F} \| [110]$, made with $q \| [1\bar{1}0]$, only two C components were observed; for $\boldsymbol{F} \| \langle 100 \rangle$ the stress was such that the origin of the component C_1 (Fig. 1b) was not clear.
21) R. A. Chapman, W. G. Hutchinson and T. L. Estle: Phys. Rev. Letters **17** (1966) 132.

DISCUSSION

Balslev, I.: Did you make any theoretical analysis of the absolute values of the observed energy shifts? This might be possible for high stresses when the valence bands become ellipsoidal.

Fisher, P.: We have to date confined ourselves mainly to the symmetry aspects of the problem. I agree that a quantitative investigation of the stress-dependent splittings and intensities of the lines is essential. Some progress in this direction is possible using a phenomenological approach as developed by Kaplyanskii for piezo-spectroscopic effects in general.