complish this task, but the bond is readily broken and the probability of a successful experiment is thus lowered. Finally when two or more extremal orbits exist for a given crystal-field orientation the RFSE method is definitely superior since the signals are either resolved, or maybe disentangled using the frequency variation techniques described in Ref. 20. On the other hand, the UA method yields periodic signals which must be separated by analyzing the signal curves and this proves to be tedious and susceptible to large inaccuracy.

ACKNOWLEDGMENTS

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Piezotransmission Measurements of Phonon-Assisted Transitions in Semiconductors. I. Germanium

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The strain-optical constants of Ge have been determined in the vicinity of the first indirect band gap 0.60–0.74 eV. The experiments were performed at room temperature and consisted of straining single crystals of Ge in an oscillatory manner and observing the amplitude modulation which was thereby impressed upon the transmitted beam. Single-crystal samples were used, allowing the full specification to be made. The results show both sharp structure and a relatively slowly varying background signal. The structure is discussed in terms of the strain-induced changes of the various threshold energies for indirect transitions expected on the basis of the deformation-potential model. The shape of the observed structure is in agreement with this simple model and the phonon energies are in excellent agreement with earlier determinations. The general features of the experimental results are explained in terms of indirect transitions taking place via the $\Gamma_{2'}$ intermediate state. A detailed calculation of the strain-optical constants made on the basis of the deformation-potential model indicates that direct transitions to $\Gamma_{2'}$ may also be important in this energy range.

I. INTRODUCTION

WHEN stress is applied to a solid, the optical properties of the material are altered. These changes may be measured and the results utilized to obtain information about the band structure and other fundamental properties of the solid. This paper describes a sensitive method for measuring these changes, which utilizes a periodically applied stress. The results of measurements made in the vicinity of the indirect optical-absorption edge of germanium are presented. A second paper will give the results of a similar measurement for silicon. A preliminary account of the Ge results has been presented previously.[1]

Periodic stress modulation of the reflectivity of semiconductors[2,3] and metals[2,4,5] has been shown to be a sensitive and useful technique. In principle, if these data are taken over a sufficiently wide energy range, they will yield, after a Kramers-Kronig analysis,[4,5] information concerning the changes in the optical constants of the solid caused by the strain. Piezoreflectivity, like the reflectivity itself, however, is quite insensitive to the relatively weak indirect optical transitions. The structure associated with the phonon-assisted transitions at the indirect edge of Ge, for example, is not observed in reflection. These weak processes must be observed in transmission. Piezotransmission measurements using static stress have recently been made[6] but because of lack of sensitivity, the phonon structure was not observed. The deformation potentials of silicon and germanium have recently been measured through the application of large static stresses and the use of the transmitted beam having a periodically oscillating wavelength.[7] The present experiment involves straining single-crystal samples of Ge in an oscillatory manner, thereby impressing some modulation upon the transmitted beam. This strain-modulated beam clearly shows the phonon and exciton

[1] W. E. Engeler, M. Garfinkel, and J. J. Tiemann, Phys. Rev. Letters **16**, 239 (1966).
[2] W. E. Engeler, H. Fritzsche, M. Garfinkel, and J. J. Tiemann, Phys. Rev. Letters **14**, 1069 (1965).
[3] G. W. Gobeli and E. O. Kane, Phys. Rev. Letters **15**, 142 (1965).
[4] W. E. Engeler, M. Garfinkel, J. J. Tiemann, and H. Fritzsche, in *Proceedings of the International Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965*, edited by F. Abeles (North-Holland Publishing Company, Amsterdam, 1966).
[5] M. Garfinkel, J. J. Tiemann, and W. E. Engeler, Phys. Rev. **148**, 695 (1966).
[6] E. Adler and E. Erlbach, Phys. Rev. Letters **16**, 87 (1966); **16**, 927 (1966).
[7] I. Balslev, Phys. Rev. **143**, 636 (1966).

structure associated with the indirect absorption edge even at room temperature.

II. EXPERIMENTAL PROCEDURE

Figure 1 shows a block diagram of the over-all experimental equipment. It is similar to that previously described.[1,2,5] A tungsten bulb is used as a source and its radiation is chopped at frequency f_1. The radiation is sent through a grating monochromator after which it is polarized, passed through the sample, and is incident onto a detector. The sample, which is the central leg of a three-post yoke shown in Fig. 2, undergoes periodic strain at the frequency f_2. The sample is driven by two matched lead-zirconate-titanate–type transducers which comprise the other two legs of the yoke. The signal received at the detector is analyzed for both frequencies f_1 and f_2 by means of two phase-sensitive lock-in amplifiers. The voltage proportional to the signal at f_1, $A(f_1)$, is compared to a fixed voltage. The difference is fed back to a servoamplifier which controls the angular positioning of a second polarizer. In this manner the signal at f_1 received by the detector is held constant. To first order, the ratio of the amplitude of the signals at f_2 and f_1 is

$$A(f_2)/A(f_1)=\sqrt{2}t\Delta\alpha. \tag{1}$$

Here t is the thickness of the sample and $\Delta\alpha$ is the change of the absorption constant which has been induced by the strain.[8] This ratio was recorded.

The germanium used in the experiment was single-crystal 3-cm n type. Samples were crystallographically oriented and mechanically polished to the desired thickness of 0.5 mm. In order that the sample always remain in tension throughout the oscillating stress cycle, a small steady stress was applied to the sample. Care was taken to insure that both the static and the oscillatory stress were applied uniformly throughout the sample. This was checked by means of metal-foil strain gauges mounted directly onto the sides of the sample, and by observation of the strain-induced birefringence. These gauges also were used to calibrate the measurements. Two sample configurations were used. Light was incident normally onto a (100) surface with the stress in one case in the [010] direction and in the other case along the [011] axis. The sample strains as measured in the stress direction for these two situations were 4.4×10^{-5} for [010] stress and 3.3×10^{-5} for [011] stress.

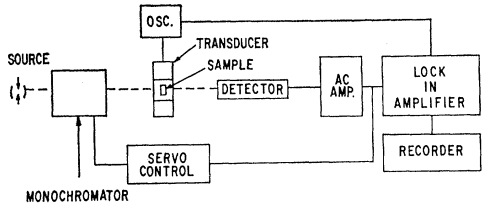

FIG. 1. Block diagram of experimental arrangement.

[8] ac quantities are quoted as rms values throughout.

III. METHOD OF ANALYSIS

The changes in the optical properties of a solid caused by strain can be completely expressed in terms of the changes in the real and imaginary part of the dielectric constant. Since the dielectric constant $\epsilon_1+i\epsilon_2$ and the strain e are both symmetric second-rank tensors, the relationship of these changes to the applied strain is given by a fourth-rank tensor $\mathbf{W}$ defined by the relation[1,3,5]

$$(\Delta\epsilon_1+i\Delta\epsilon_2)_{pj}=(\mathbf{W}_1+i\mathbf{W}_2)_{pjkl}e_{kl}. \tag{2}$$

Because of symmetry, only six independent constants are needed to completely specify the effect of general strain on the optical properties of Ge. This general relation may be written in the usual reduced notation,[9] with the six independent components $(W_1)_{11}$, $(W_2)_{11}$, $(W_1)_{12}$, $(W_2)_{12}$, $(W_1)_{44}$, and $(W_2)_{44}$.[10] The transmission experiment is sensitive primarily to changes in $\Delta\epsilon_2$, and only the imaginary portion of the $\mathbf{W}$ tensor may conveniently be measured in this way. Because of the relatively small absorption coefficient, however, the change in the real part of the dielectric constant $\Delta\epsilon_1$ can be obtained from a measurement of the change in the index of refraction. As was previously noted,[1,5] measurements made upon two samples with (100) surfaces, pulled uniaxially in either the [011] or the [010] directions and measured with light polarized parallel and perpendicular to the stress direction are sufficient to specify the three real or imaginary independent components of the $\mathbf{W}$ tensor. For stress in the [010] direction,

$$\Delta\epsilon_{11}=\left[W_{11}+2\frac{S_{12}}{S_{11}}W_{12}\right]e, \tag{3}$$

$$\Delta\epsilon_{\perp}=\left[\frac{S_{12}}{S_{11}}W_{11}+\left(1+\frac{S_{12}}{S_{11}}\right)W_{12}\right]e, \tag{4}$$

where $\Delta\epsilon_{11}$ and $\Delta\epsilon_{\perp}$ are the observed changes of the dielectric constant for polarization vector parallel and perpendicular, respectively, to the stress axis, e is the strain measured along the stress direction, and S_{11} and S_{12} are the usual elastic compliances. For stress in the [011] direction

$$\Delta\epsilon_{11}=\left[\frac{(S_{11}+S_{12})W_{11}+(S_{11}+3S_{12})W_{12}+S_{44}W_{44}}{S_{11}+S_{12}+\frac{1}{2}S_{44}}\right]e, \tag{5}$$

[9] J. F. Nye, *Physical Properties of Crystals* (Oxford University Press, London, 1957).

[10] In this notation the stress tensor is replaced by a six-element column matrix with the usual definitions $e_j=e_{jj}$ and $e_4=2e_{23}$, etc. The elements of $\Delta\epsilon$ are $\Delta\epsilon_{ii}=\Delta\epsilon_i$, $\Delta\epsilon_{23}=\Delta\epsilon_4$, $\Delta\epsilon_{13}=\Delta\epsilon_5$, and $\Delta\epsilon_{12}=\Delta\epsilon_6$. With these definitions $W_{44}=W_{xyxy}$. This convention differs from that used in Ref. 5 where $e_4=e_{23}$, etc., and $W_{44}=2W_{xyxy}$.

$$\Delta\epsilon_{\perp}=\left[\frac{(S_{11}+S_{12})W_{11}+(S_{11}+3S_{12})W_{12}-S_{44}W_{44}}{S_{11}+S_{12}+\frac{1}{2}S_{44}}\right]e. \quad (6)$$

It is noteworthy that the sum $\Delta\epsilon_{11}+\Delta\epsilon_{\perp}$ for [010] stress as obtained from Eqs. (3) and (4) is proportional to $\Delta\epsilon_{11}+\Delta\epsilon_{\perp}$ for [011] stress as obtained from Eqs. (4) and (5). The proportionality factor $\frac{1}{2}(1+S_{12}/S_{11}+S_{44}/2S_{11})$ arises from the different compliances of the two different configurations and is wavelength independent. Its value for germanium is 0.75. Equations (3), (4), (5), and (6) may be solved for the components of the **W** tensor, yielding for the [010] stress direction

$$W_{11}=\frac{1}{e}\left[\frac{(S_{11}+S_{12})\Delta\epsilon_{11}-2S_{12}\Delta\epsilon_{\perp}}{(S_{11}+S_{12})-2S_{12}^2/S_{11}}\right], \quad (7)$$

$$W_{12}=\frac{1}{e}\left[\frac{S_{11}\Delta\epsilon_{\perp}-S_{12}\Delta\epsilon_{11}}{S_{11}+S_{12}-2S_{12}^2/S_{11}}\right], \quad (8)$$

and for stress in the [011] direction

$$W_{44}=\frac{(S_{11}+S_{12}+\frac{1}{2}S_{44})(\Delta\epsilon_{11}-\Delta\epsilon_{\perp})}{2eS_{44}}. \quad (9)$$

The basic definition of the **W** tensor implies that a linear relation exists between the strain and the change in dielectric constant. In the vicinity of sharp structure, however, this condition is satisfied for only the smallest strains. Larger periodic strains will cause a reduction in the sharpness of the observed structure, and if a static strain is applied in addition to the periodic strain, a more complex situation results. If the splittings caused by the static strain are less than the width of the structure, the relation remains linear and no problem occurs. In the vicinity of very sharp structure, however, it is relatively easy for the splittings to exceed the width of the structure thereby producing significant nonlinear contributions. This situation will be discussed more fully in a later section.

In a given experiment, the light intensity transmitted by the crystal, I, is given by

$$I=\frac{I_0(1-R)^2e^{-\alpha t}}{1-R^2e^{-2\alpha t}}, \quad (10)$$

where I_0 is the incident intensity, R the reflection coefficient, α the absorption constant, and t the thickness. When the crystal is strained,

$$\frac{\Delta I}{I}=\left[\frac{-2R}{(1-R)}+\frac{2R^2e^{-2\alpha t}}{1-R^2e^{-2\alpha t}}\right]\frac{\Delta R}{R}-\left[\frac{1+R^2e^{-2\alpha t}}{1-R^2e^{-2\alpha t}}\right](t\Delta\alpha+\alpha\Delta t). \quad (11)$$

The contributions to $\Delta I/I$ caused by the change in reflectivity due to the stress modulation of the index of refraction and the change in thickness due to Poisson's ratio are small and may be considered as corrections to the measurements of the absorption-coefficient change $\Delta\alpha$. For these corrections to be made, Δn, the elastically induced change in the index of refraction, and the elastic constants of the material must be known. $\Delta\epsilon_2$ may then be determined from the relation

$$\Delta\epsilon_2=(\lambda/2\pi)(n\Delta\alpha+\alpha\Delta n). \quad (12)$$

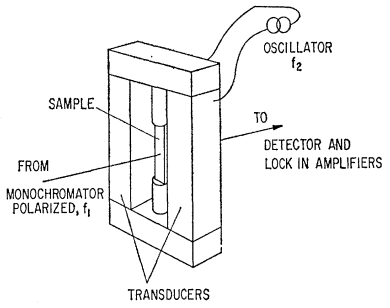

FIG. 2. Schematic view of experimental apparatus.

Measurements of $\Delta\epsilon_1$ were made by an interferometric technique.[11] The results of the measurement at 0.722 eV are $(W_1)_{11}=54$, $(W_1)_{12}=63$, and $(W_1)_{44}=19$. These values, which were used in the calculation of the corrections necessary to obtain $\Delta\epsilon_2$ as outlined above, are consistent with previous birefringence measurements[12,13] but disagree with earlier measurements of the change of the index of refraction of Ge with hydrostatic pressure.[14]

IV. EXPERIMENTAL RESULTS

This section discusses the experimental results obtained at room temperature. Figure 3 shows the measured curves of $\Delta I/I$ for the two samples for light polarized parallel and perpendicular to the stress direction. These data may be reduced to the components of the strain-optical tensor **W** as outlined above. The results for $(W_2)_{11}$, $(W_2)_{12}$, and $(W_2)_{44}$ are shown in Fig. 4. The values $(W_2)_{11}$ and $(W_2)_{12}$ were obtained from sample 1 and $(W_2)_{44}$ was obtained from sample 2. These results differ from those previously reported[1] because of a recalibration of the experiment. All of the coefficients show structure of two types. First there is a general background which starts near 0.63 eV and increases with increasing photon energy. Second, sharp structure may be seen near 0.63 and 0.69 eV.

As we have previously noted,[1] the observed sharp structure may be understood in terms of the shift of threshold energies of the various phonon-assisted indirect transitions. The peaks in the vicinity of 0.63

[11] W. E. Engeler and M. Garfinkel (to be published).
[12] K. J. Schmidt-Tiedemann, J. Appl. Phys. 32, 2058 (1961).
[13] A. Feldman, Ph.D. thesis, University of Chicago (unpublished).
[14] M. Cardona, H. Brooks, and W. Paul, J. Phys. Chem. Solids 8, 204 (1959).

TABLE I. Phonon energies in germanium at L (given in millielectron volts). The tabulated values for piezotransmission are obtained directly from Figs. 5 and 6. The mean energies $\bar{E}$ corresponding to transitions between a given conduction-band–valence-band pair are also given (in electron volts). In the case of the LA phonon, the splittings due to the static stress are partially resolved and the $\bar{E}$ due to two components are listed. For the other phonons the splittings are unresolved and the structure is assumed to be due to transitions from both valence bands to the lowest conduction band. These $\bar{E}$ were corrected for the shifts due to the static strain and the exciton binding energy of 2.7×10^{-3} eV. The resulting values for the indirect gap at 298°K, E_g, are given in the last column.

Phonon	Piezotransmission (298°K) [010]	[011]	Electro-absorption[a] (Room temp.)	Tunneling[b] (Room temp.)	Tunneling[c] (1.8°K)	Optical[d] (291°C)	$\bar{E}$	E_g
TA	7.6	7.7	7.3±0.5	7.6	7.805±0.006	7.6	0.6582	0.6641
LA	27.7	28.1	27.7±0.1	27.5	27.49±0.01	27.3	0.6584($\Xi^-,\frac{3}{2}$)	0.6643
							0.6626(Ξ^+)	0.6643
LO				31.6	30.55±0.02	30.7		
TO	35.4	35.9		36.0	36.04±0.01	36.7	0.6584	0.6643

[a] A. Frova, P. Handler, F. A. Germano, and D. G. Aspnes, Phys. Rev. **145**, 575 (1966).
[b] A. G. Chynoweth, R. A. Logan, and D. E. Thomas, Phys. Rev. **125**, 877 (1962).
[c] See Ref. 17.
[d] See Ref. 23.

and 0.69 eV are caused by the transitions involving either the emission or the absorption of a longitudinal acoustic (LA) phonon. In addition to these sharp peaks, smaller peaks may also be observed corresponding to the transverse optic (TO) phonon. The transverse acoustic (TA) phonon transitions, however, are characterized by steps in the background rather than by peaks. This is clearly shown in Fig. 5. The sum $(\Delta\epsilon_2)_{\parallel}+(\Delta\epsilon_2)_{\perp}$ is shown so that polarization effects may be ignored temporarily. The threshold energies for the various transitions are shown. A similar curve was obtained for the [010] sample and is shown in Fig. 6.

The phonon energies may be obtained by taking half the difference between the threshold energies for emission and absorption of each phonon. These energies together with the energies previously measured by optical and tunneling experiments are tabulated in Table I. In addition, the average energy $\bar{E}$ corresponding to the emission and absorption of each phonon is tabulated. Because of the strong peak associated with the LA phonon transition, the weak longitudinal optic (LO) phonon is not observed. Its expected location is shown by a dotted arrow.

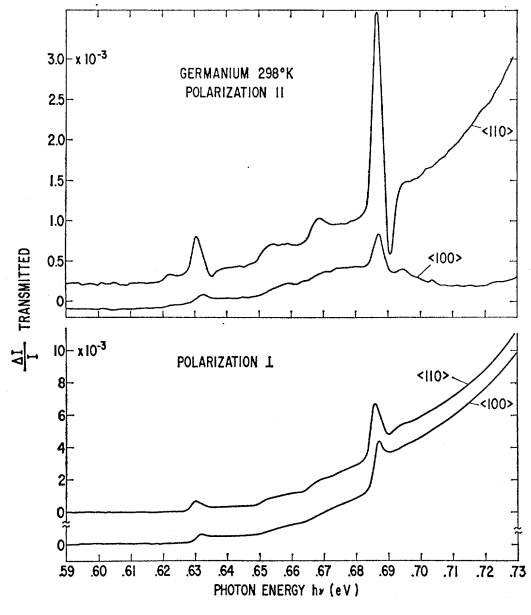

FIG. 3. Stress-induced changes in the transmission of Ge at 298°K. Sample 1 is stressed along a ⟨010⟩ direction and sample 2 is stressed along a ⟨011⟩ direction. Both samples presented a {100} face to the beam and were 0.53-mm thick. The light polarization directions are parallel and perpendicular to the stress axis. The sample strains as measured along the stress direction are 4.4×10^{-5} and 3.3×10^{-5} for samples 1 and 2, respectively.

V. INTERPRETATION OF RESULTS

The interpretation of the curves is made most conveniently with the help of the deformation potential model. For the conduction band the energy shift of each

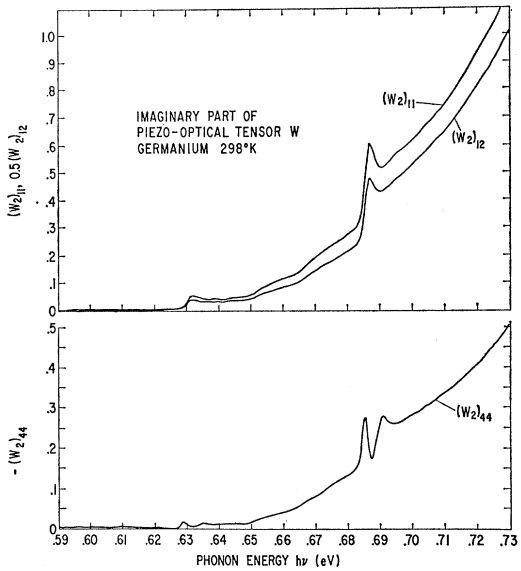

FIG. 4. (a) Spectral dependence of the imaginary parts of the complex strain optical tensor **W**. $(W_2)_{12}$ is shown one-half the scale of $(W_1)_{11}$. (b) Spectral dependence of the imaginary parts of the complex strain optical tensor **W**. $(W_2)_{44}$ is negative and is shown inverted.

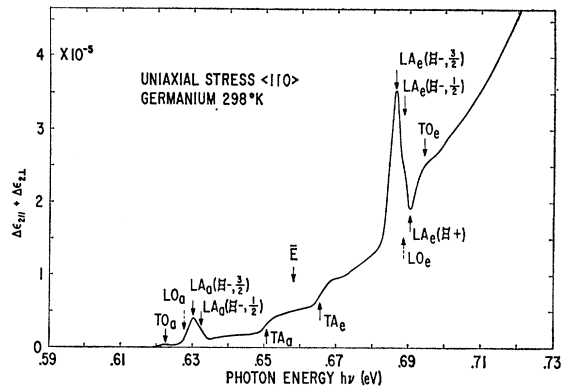

FIG. 5. $(\Delta\epsilon_2)_{\parallel}+(\Delta\epsilon_2)_{\perp}$ showing phonon assignments for the sample stressed along [011].

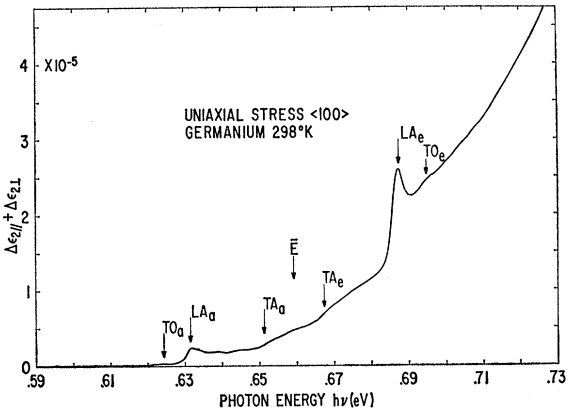

FIG. 6. $(\Delta\epsilon_2)_{\parallel}+(\Delta\epsilon_2)_{\perp}$ showing phonon assignments for the sample stressed along [010].

of the valleys in Ge is[15]

$$\Delta E_c^{(i)}=\mathbf{n}^{(i)}\cdot\{E_{1C}(\mathrm{Tr}\mathbf{e})\mathbf{1}+E_2[\mathbf{e}-\tfrac{1}{3}(\mathrm{Tr}\mathbf{e})\mathbf{1}]\}\cdot\mathbf{n}^{(i)}, \quad (13)$$

where $\mathbf{n}^{(i)}$ is a unit vector in the direction of the ith valley, $\mathbf{1}$ is the unit tensor, and E_{1C} and E_2 are the conduction-band deformation potentials. A tension T along the [010] direction as in sample 1 causes no splitting of the valleys but causes a shift given by

$$\Delta E_c^{(i)}=\Delta E_c=\frac{(S_{11}+2S_{12})}{S_{11}}E_{1C}e, \quad (14)$$

where e is the dilatation along the stress axis. The static tension applied in the [011] direction as in sample 2 causes, in addition to an average shift of

$$(\Delta E_c)=\left[\frac{4(S_{11}+2S_{12})E_{1C}}{2(S_{11}+S_{12})+S_{44}}\right]e, \quad (15)$$

a splitting of the $\langle 111\rangle$ valleys. Two move to higher energies and two move more strongly to lower energy. The separation of these pairs of valleys is given by

$$\Delta E_c^{(u)}-\Delta E_c^{(l)}=\frac{4}{3}\frac{S_{44}E_2e}{2(S_{11}+S_{12})+S_{44}}. \quad (16)$$

When uniaxial stress is applied to the crystal, the valence band is also affected. This band not only shifts its position but the originally fourfold degenerate band at $k=0$ is split into two twofold bands.[16] The average shift is given by

$$\Delta E_v=a\ \mathrm{Tr}\mathbf{e} \quad (17)$$

and the splitting of the states labeled $m_j=\frac{1}{2}$ and $m_j=\frac{3}{2}$ is, in the case for [010] stress, given by $2\epsilon_0$, where

$$\epsilon_0=b(S_{11}-S_{12})e/S_{11}. \quad (18)$$

For uniaxial stress in the [111] direction, the eigenfunctions of the diagonalized Hamiltonian may still be characterized by the eigenvalues $m_z=\frac{1}{2},\frac{3}{2}$, where z is the stress axis. A splitting of $2\epsilon_0'$ results, where

$$\epsilon_0'=\frac{\sqrt{3}}{2}d\frac{S_{44}e}{(S_{11}+2S_{12}+S_{44})}. \quad (19)$$

In Eqs. (17), (18), and (19), a, b, and d are the valence-band deformation potentials. For uniaxial stress in the [011] direction, the eigenvalues of $\langle J_z\rangle$ along the stress axis are no longer good quantum numbers and the split states are admixtures of the $m_j=\frac{1}{2}$ and $m_j=\frac{3}{2}$ levels. An approximate splitting is given by $2\epsilon''$, where[17]

$$\epsilon''=(\epsilon_0^2+3\epsilon_0'^2)^{1/2} \quad (20)$$

and ϵ_0 and ϵ_0' are given for equal tension. For large strain, particularly in Si,[7,18] it is necessary to take account of the closely lying spin-orbit split-off band. For Ge, however, the strains are small enough so that this band may be neglected. The indirect optical transitions may proceed via an intermediate state at Γ. In germanium, the lowest-lying conduction band at Γ is the one-dimensional $\Gamma_{2'}$ band. This band will also shift its energy with strain, with the shift given by

$$\Delta E_d=E_{1d}\mathrm{Tr}\mathbf{e}. \quad (21)$$

The parameters E_{1C}, E_2, E_{1d}, a, b, d specify the motion of the various bands. The shift of the threshold energies for optical transitions between the two valence-band maxima and the various conduction-band minima due to stress-induced changes in the energy separations of the corresponding conduction-band–valence-band pairs may thus be calculated if these deformation potentials are known.

[15] H. Brooks, in *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press Inc., New York, 1955), Vol. 17, p. 85.

[16] G. E. Pikus and G. L. Bir, Fiz. Tverd. Tela **1**, 154 (1959); **1** 1642 (1959) [English transls.: Soviet Phys.—Solid State **1**, 136 (1959); **1**, 1502 (1959)].

[17] J. C. Hensel and G. Feher, Phys. Rev. **129**, 1041 (1963).

[18] H. Hasegawa, Phys. Rev. **129**, 1029 (1963).

Values of $(E_{1C}-a)$[19] and E_2[7,15,20] have been measured and have values of

$$(E_{1C}-a)=E_1=-4 \text{ eV}$$

and

$$E_2=16 \text{ eV}.$$

The values of b and d have also been measured. A value for $|b|$ of 1.8 ± 0.4 eV was obtained by Balslev[7] which is somewhat lower than the values of 2.1 ± 0.2 and 2.7 ± 0.3 eV obtained by Hall[21] and Glass,[22] respectively. For $|d|$, these same authors obtain 3.7 ± 0.4[7], 7.0[21], and 4.7 ± 0.5 eV.[22] We will use the value of -2.0 eV for b and -4.3 eV for d in our calculations, as being reasonable averages of the existing data. For the case of uniaxial stress in the [010] direction there are only two distinct conduction-band–valence-band energy gaps. These correspond to transitions from the split $m_z=\frac{1}{2}$ and $m_z=\frac{3}{2}$ valence bands to the shifted but unsplit conduction band. Using Eqs. (19) and (18) and the above values for the deformation potentials we obtain

$$\Delta(E_c-E_v)=-(1.7+2.6)e, \quad m_z=\tfrac{1}{2}$$
$$\Delta(E_c-E_v)=-(1.7-2.6)e, \quad m_z=\tfrac{3}{2}. \qquad (22a)$$

For stress along the [011] axis the conduction band is also split. In this case, there are four distinct thresholds corresponding to transitions from each of the split valence bands to each of the two sets of conduction bands. In this case, we have

$$\Delta(E_c-E_v)=-(2.3\pm5.6\pm2.9)e, \qquad (22b)$$

where the ±5.6 is due to the conduction-band splitting and the ±2.9 is due to the splitting of the valence band. It should be emphasized here that Eq. (22) describes the changes in the energy gaps for *stress* along the given axis. The strain e is in each case the dilatation as measured along the stress axis.

The optical absorption due to allowed phonon-assisted transitions to the indirect exciton has the form[23]

$$(\epsilon_2)_{\text{allowed}}=C(E-E_t)^{1/2}, \qquad (23a)$$

and that due to forbidden transitions has the form

$$(\epsilon_2)_{\text{forbidden}}=C'(E-E_t)^{3/2}, \qquad (23b)$$

where $E_t=E_g-E_{\text{ex}}\pm E_{\text{phonon}}$ is the threshold energy for the transition, and E is the photon energy. Stress will in general change C, and as outlined above will also modulate the threshold energy. The portion of the signal produced by the threshold changes is proportional to the derivatives of the absorptions given in Eqs. (23) and is given by

$$(\Delta\epsilon_2)_{\text{allowed}}=-\tfrac{1}{2}C(E-E_t)^{-1/2}(dE_t/de)e \qquad (24)$$

and

$$(\Delta\epsilon_2)_{\text{forbidden}}=-\tfrac{3}{2}C'(E-E_t)^{1/2}(dE_t/de)e. \qquad (25)$$

The signal due to the modulation of C, on the other hand, is proportional to the absorption itself and is in general more slowly varying. If we confine our attention for the moment to the structure near the thresholds, only the variation of E_t need be considered. Thus, the allowed transitions give rise to peaks while the forbidden transitions give rise to thresholds with no local maxima. The shapes of the observed structure agree with the expected shapes. Transitions involving the LA and TO phonons appear as peaks, while those involving the TA phonon produce thresholds. The identification of LA as allowed and TA as forbidden agrees with previous observations, and the identification of TO as an allowed transition confirms the expectation based on group theory.[24,25] The LO transition, which is not observed, should be forbidden.

It is interesting to note that while the indirect optical absorption involving the LA phonon is allowed via the low-lying $\Gamma_{2'}$ band as an intermediate state, the transition involving the TO phonon is allowed only through the relatively deep-lying $L_{3'}$ intermediary. The TO phonon would thus be expected to contribute a much smaller signal, as is observed.

According to Eq. (22), uniaxial stress will cause each phonon-assisted transition to be split into a number of transitions. Two transitions are obtained for [010] stress, due to the splitting of the valence band, and four are obtained for the [011] stress, due to the splitting of both valence and conduction bands. Equations (24) and (25) show that the magnitude of the signal expected from these various transitions depends on the differences between the shifts of the bands involved. These differences are given in Eqs. (22a) and (22b). In each case, one of the expected transitions should contribute much more weakly to $\Delta\epsilon_2$ than the others as the net change in one threshold energy is accidentally very small. For [010] therefore, only one transition is expected to contribute strongly, and it should produce structure of positive sign. This is observed in Fig. 5. In the case of [011] stress three transitions contribute strongly. Two give rise to positive structure in $\Delta\epsilon_2$ and one to negative. These transitions will be split by the static stress applied to the sample. Since the static stress is in the same direction as the ac stress, the positive structure will be moved to lower energy and the negative structure to higher energy. A positive signal due to the first two transitions should be followed at higher

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energy by a negative signal due to the latter. This is observed in the structure associated with the LA phonon. The first two transitions are not clearly resolved, however, as the second positive transition shows up only as a small shoulder on the larger signal and is thus masked by it. These transitions are shown in Fig. 4 and are labeled LA($\Xi-$, $\frac{3}{2}$), LA($\Xi-$, $\frac{1}{2}$), and LA($\Xi+$), respectively.

These splittings caused by the static strain, while useful in enumerating the various transitions, cause errors in the W_2 curves, as was mentioned previously. The sum of $\Delta\epsilon_{11}$ and $\Delta\epsilon_{\perp}$ of Fig. 5 and that of Fig. 6 would be proportional to each other as discussed above if $\Delta\epsilon_2$ were a linear function of strain. However, since the structure splits differently for the different orientations the combinations leading to the W_2 curves do not match up. The discrepancy shows that the region near the sharp structure must be disregarded when considering the magnitude of the components of W. In regions where no sharp structure exists, Figs. 5 and 6 are in good agreement, and in these regions the curves for $(W_2)_{11}$, $(W_2)_{12}$, and $(W_2)_{44}$ are correct.

The amplitude of the structure associated with the emission of a phonon is expected to be larger than that associated with its absorption by the ratio

$$(N+1)/N=\exp(E_p/kT)\,,$$

where N is the phonon occupation number.

In addition, a second factor ρ arises due to the differences in the energy denominators of the second-order processes associated with the emission and absorption of the phonons.[23,26] Calling the difference between the energy required for a vertical transition to the intermediate state and the indirect energy gap Δ, the energy denominator for phonon emission is $(\Delta-E_p)$, while for absorption it is $(\Delta+E_p)$. If the phonon energy depends on strain a third factor β may be introduced. β is given by

$$\beta=(\Delta E_g+\Delta E_p)/(\Delta E_g-\Delta E_p)\,, \tag{26}$$

where ΔE_p is the change of phonon energy with stress. This change of phonon energy with stress may be calculated using the phonon deformation potentials. The ratio of the size of the structure associated with emission to that associated with absorption is then given by

$$\frac{P_e}{P_a}=\beta\rho\exp\left(\frac{E_p}{kT}\right)=\frac{(\Delta+E_p)^2}{(\Delta-E_p)^2}\beta\exp\left(\frac{E_p}{KT}\right). \tag{27}$$

The germanium-phonon deformation potentials have been measured at low temperatures[27] and, for the LA phonon, have the values $E_1=-14\pm2$ meV and $E_2=40\pm10$ meV. Since these constants are more than two orders of magnitude smaller than the deformation potentials of the bands, β may be set equal to unity. Using the value 0.14 eV[23] for Δ one obtains from Eq. (27) for the LA-phonon transition at 298°C a ratio of 6.4 and for the TA phonon a ratio of 1.6. The experimental values for the ratio of the emission to absorption amplitudes for the data shown in Fig. 5 are 5.2 and 1.4, respectively, corresponding to a Δ of about 0.19 eV. This apparent increase in Δ might be caused by the static splitting or it may be due to transitions via intermediate states lying above the band minima. This latter possibility may be particularly important for the TA phonon since these transitions are forbidden at the band minima.

Thus far we have discussed the features of the data associated with the sharp structure, and have shown that it is caused by changes in the threshold for indirect transitions to the first exciton level accompanied by either the emission or the absorption of a phonon. At phonon energies greater than the threshold, transitions to the higher-lying states of the exciton, band-to-band transitions, and matrix element changes will all contribute to $\Delta\epsilon_2$. The sharp structure should thus be followed by a background contribution to $\Delta\epsilon_2$ whose energy variation is relatively smooth. We now turn our attention to this background and to the polarization dependence of the signals.

If matrix element changes are neglected and only the motion of nondegenerate levels $E(k)$ are considered, the following relationships between the various components of the W tensor may be deduced directly from symmetry arguments: (1) The motion of the conduction band at L causes equal contribution to W_{11} and W_{12}. (2) The motion of bands at Δ such as are important in silicon produces no contribution to W_{44}. (3) Band motion at Γ makes no contribution to W_{44} and equal contributions to W_{11} and W_{12}.

These results are easily obtained by reference to Fig. 7. Figure 7(a) schematically shows the experimental configuration by means of which W_{11} and W_{12} are determined. The ellipses indicate the L-type symmetry. Configuration (1) with the strain axis perpendicular to the polarization vector yields W_{12} and (2) with the strain parallel to the polarization yields W_{11}. For the L symmetry shown, however, the changes induced by the strain in each of the four valleys are the same independent of whether the strain axis is [001] or [010]. The results of these two experiments are therefore identical and our conclusion that the strain-induced motion of bands at L contribute equally to W_{11} and W_{12} follows immediately. The difference between the results of the two experiments shown schematically in Fig. 7(b) is proportional to W_{44}. Bands having Δ symmetry are, in this instance, not all treated alike. The bands numbered 1, 2, 3, and 4 all move one way while the two labeled 5 and 6 move differently. Although these two motions are different from each other

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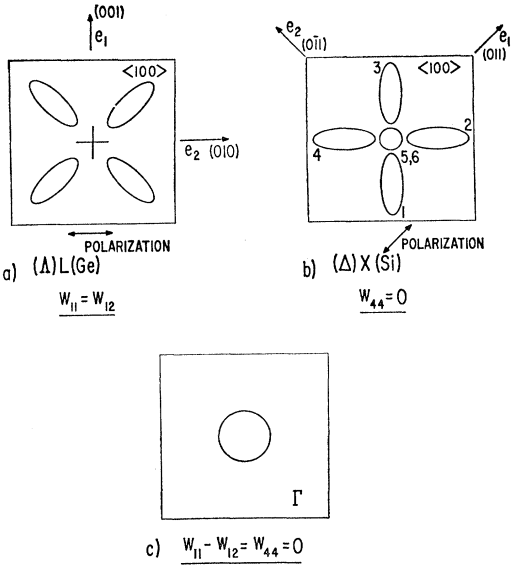

FIG. 7. Schematic diagram of band structure showing relations among the strain optical tensor components for transitions involving nondegenerate bands at various locations in the Brillouin zone.

each is the same whether the strain is along [011] or [01$\bar{1}$]. The band motions are the same for the strain axis either parallel or perpendicular to the polarization direction. The two experiments are thus equivalent, yielding the result that band motions along Δ make no contribution to W_{44}. Relationship (3) follows immediately from the isotropy of Γ.

These simple relations break down, however, if one of the bands involved in the transition is degenerate, and if this degeneracy is removed by the stress. It is then necessary to consider the transition selection rules in detail. Recently, Adler and Erlbach[6] have calculated the selection rules for transitions from the $m_j=\frac{1}{2}$ and $m_j=\frac{3}{2}$ states of the Γ_{25}' valence band to the $\Gamma_{2'}$ intermediate state for stress in the [111] and the [100] direction. Since both $\Gamma_{2'}$ and L_1 are one-dimensional representations, the allowed phonon transitions proceed equally to each valley. In a way analogous to Eqs. (23) and (24) we may write

$$(\epsilon_2)_{11}=C\sum_i c_{i11}\frac{f(E-E_t{}^i)}{(\Delta^i\pm E_p)^2} \tag{28}$$

and

$$(\epsilon_2)_{1}=C\sum_i c_{i1}\frac{f(E-E_t{}^i)}{(\Delta^i\pm E_p)^2}, \tag{29}$$

where i is summed over the transitions involved. In Eqs. (28) and (29) C is the matrix element for the transition, f is the appropriate threshold function, and c_{i11} and c_{i1} are the normalized matrix element coefficients for transitions involving light polarized parallel and perpendicular to the stress, respectively. As above, Δ^i is the difference between the intermediate state and the indirect energy gap now dependent upon the specific band involved in the transition. The changes in ϵ_2 due to strain induced changes in the threshold energies are

$$(\Delta\epsilon_2)_{11}=-C\sum_i c_{i11}\frac{f'(E-E_t{}^i)}{(\Delta^i\pm E_p)^2}\frac{dE_t{}^i}{de}e \tag{30}$$

and

$$(\Delta\epsilon_2)_{1}=-C\sum_i c_{i1}\frac{f'(E-E_t{}^i)}{(\Delta^i\pm E_p)^2}\frac{dE_t{}^i}{de}e. \tag{31}$$

Ignoring the effects of static stress and using Eqs. (7), (8), (14), (17), and (18), the contribution of the threshold changes to $(W_2)_{11}$ and $(W_2)_{12}$ are

$$(W_2)_{11}=-C\frac{f'(E-E_t)}{(\Delta\pm E_p)^2}[E_1+b(c_{211}-c_{111})] \tag{32}$$

and

$$(W_2)_{12}=-C\frac{f'(E-E_t)}{(\Delta\pm E_p)^2}[E_1+b(c_{21}-c_{11})]. \tag{33}$$

In addition to these contributions to the strain optical tensor from the variation of the threshold energy, an additional contribution due to the variation of the energy denominator must be included. This term is important for germanium, but may be neglected for silicon. With this term included, Eqs. (32) and (33) may be written as

$$(W_2)_{11}=-C\sum_p \frac{f(E-E_t)}{(\Delta\pm E_p)^2}\left[\frac{f'}{f}[E_1+b(c_{211}-c_{111})]+2\frac{E_{1d}-E_{1c}}{\Delta\pm E_p}\right] \tag{32'}$$

and

$$(W_2)_{12}=-C\sum_p \frac{f(E-E_t)}{(\Delta\pm E_p)^2}\left[\frac{f'}{f}[E_1+b(c_{21}-c_{11})]+2\frac{E_{1d}-E_{1c}}{\Delta\pm E_p}\right], \tag{33'}$$

where the summation is over both the emission and absorption of all phonons whose thresholds lie below the energy under consideration. For high energies this may be approximated by taking only the largest term. The ratio $(W_2)_{11}$ to $(W_2)_{12}$ is then

$$\frac{(W_2)_{11}}{(W_2)_{12}}=\frac{(\Delta-E_p)f'(E-E_t)[E_1+b(c_{211}-c_{111})]+2f(E-E_t)(E_d-E_1)}{(\Delta-E_p)f'(E-E_t)[E_1+b(c_{21}-c_{11})]+2f(E-E_t)(E_d-E_1)}, \tag{34}$$

where c_1 refers to the transitions from the $m_j=\frac{1}{2}$ and c_2 refers to the transitions from the $m_j=\frac{3}{2}$ levels. These values are $c_{111}=1$, $c_{211}=0$, $c_{11}=\frac{1}{4}$, and $c_{21}=\frac{3}{4}$.[6] The value of the ratio f'/f may be obtained directly from the absorption-coefficient measurements[23] and has the value 32.9 $(\text{eV})^{-1}$ at 0.71 eV. Using the values for E_1, Δ, and b quoted previously and the value of 10 eV for E_d,[28] the ratio of Eq. (34) is equal to 0.62 at 0.71 eV, which compares reasonably well with the measured ratio of 0.56 at the same energy. $(W_2)_{44}$ may be similarly calculated. In this case, the variation of the energy denominator makes no contribution and $(W_2)_{44}$ may be obtained directly from Eqs. (30) and (31). The result is

$$(W_2)_{44}=-C\frac{f'(E-E_t)}{(\Delta+E_p)^2}\frac{d}{2\sqrt{3}}(c'_{211}-c'_{111}-c'_{21}+c'_{11}), \tag{35}$$

and the ratio $(W_2)_{11}/(W_2)_{44}$ becomes

$$\frac{(W_2)_{11}}{(W_2)_{44}}=\frac{E_1+b(c_{211}-c_{21})+2f(E-E_t)(E_{1d}-E_{1c})/(\Delta\pm E_p)}{(d/2\sqrt{3})(c'_{211}-c'_{111}-c'_{21}+c'_{11})}. \tag{36}$$

In Eqs. (35) and (36) the c' constants are the normalized coefficients for light polarized parallel and perpendicular to the [111] direction. These coefficients are numerically equal to the corresponding coefficients for the [100] direction.[6] Using these values and the value $d=4.3$ eV quoted previously, a ratio of -2.8 is calculated. This compares quite well with the measured value of -2.7 obtained at 0.71 eV.

It is interesting to note that most of the optical absorption is caused by transitions proceeding via the $\Gamma_{2'}$ intermediate state. The phonon transitions from this state to the various conduction-band minima at L are all equally probable, and are independent of the polarization of the light. The shape of $(W_2)_{11}$ and $(W_2)_{12}$ due to these transitions should therefore be identical. The TO phonon on the other hand proceeds via the L_3 intermediate state. This causes the structure due to the transition accompanied by this phonon to be more pronounced in $(W_2)_{11}$ than in $(W_2)_{12}$.

We have shown that the ratios of the various components of the strain optical tensor agree with calculated values when both the influence of the changes of threshold energies and the changes in the energy denominator are considered. This theory should also predict the absolute magnitude of $(W_2)_{11}$, $(W_2)_{12}$, and $(W_2)_{44}$. However, when Eqs. (32′), (33′), and (36) are evaluated at 0.71 eV, the calculation shows that the processes considered above account for only one-third of the observed signal. The remaining signal must thus have some other origin. The additional processes responsible for this extra signal must involve transitions which have similar selection rules to the ones discussed. This is necessary in order that the resulting calculated ratios between the components of the strain optical tensor agree with those observed. As will be shown below, signals resulting from direct optical transitions from the valence band at Γ to the conduction band at Γ have this desired property.

In semiconductors having a direct energy gap, it has long been known that the absorption associated with the direct edge persists to energies well below that edge. For many materials at sufficiently high temperatures, this absorption is described by Urbach's[29] rule, i.e., the absorption decreases exponentially with energy. Optical absorptions of this type have recently been considered theoretically[30] and may be explained by considering the optical-phonon-induced absorptions, and their temperature broadening. One-phonon transitions of this type were first considered by Dumke[31] and were used to explain the absorption edge of InSb. More recently this theory was extended by Segall[32] to two-phonon processes and the results used to explain the absorption edge of CdTe.[33] In addition, impurity and other broadening effects may also be important at this low level of absorption. If we assume that a portion of the optical absorption in the vicinity of the indirect gap of Ge may be coupled to the conduction band at Γ by one of the above processes, and if we assume further that this coupling is independent of strain, then the contribution of this absorption to the strain optical tensor may be calculated. The calculation proceeds exactly as in Eqs. (28) through (33) except that there is no energy denominator term and the threshold is that for the direct transitions at Γ. The results are as follows:

$$(W_2)_{11}(\text{direct})=-C_2[f_2'(E-E_t)E_{1d}+b(c_{211}-c_{111})], \tag{37}$$

$$(W_2)_{12}(\text{direct})=-C_2[f_2'(E-E_t)E_{1d}+b(c_{21}-c_{11})], \tag{38}$$

and

$$(W_2)_{44}(\text{direct})=-C_2f_2'(E-E_t)(d/2\sqrt{3})\times(c_2'_{11}-c'_{111}-c'_{21}+c'_{11}). \tag{39}$$

Using the values of the constants quoted previously, the ratios $(W_2)_{11}/(W_2)_{12}=0.73$ and $(W_2)_{11}/(W_2)_{44}=-4.3$ are obtained for the absorptions associated with the direct transitions. While these ratios are somewhat

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larger than those observed, they are of the correct general magnitude. If a deformation potential of 7 eV were used in place of 10 eV for E_{1d} then the agreement would be very close. Paul and Warschauer[34] and Fan *et al.*[35] have measured the shift of the optical-absorption edge with hydrostatic pressure and find a shift which saturates at a value of approximately 9×10^{-12} eV/dyn/cm^2) for photon energies greater than that corresponding to $\alpha=30$ cm^{-1}. At the lower energies Paul and Warschauer deduce a value closer to the one measured by piezoresistance.[36] This pressure dependence of 9×10^{-12} eV/dyn/cm^2 corresponds to an apparent deformation potential of 7 eV. This is exactly the value needed to account for our observations on the basis of the model discussed immediately above. Changes of the coupling with strain might produce this apparent reduction of the deformation potential, or still other additional absorptive processes may be important. Other possible sources of additional signal are surface damage and/or impurity-induced optical absorption analogous to the impurity-induced tunneling[37] observed in Ge. However, since the crystal used was only lightly doped with Sb, this last mechanism appears to be unlikely. On balance, we are forced to conclude that the exact cause of this excess signal remains uncertain. Experiments carried out at low temperatures should improve our understanding of these processes, by indicating whether the phonon-assisted direct transitions are important in this energy range.

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VI. CONCLUSIONS

We have shown that the sharp structure observed by means of the piezotransmission technique may be explained in terms of motion of the conduction-band edge and motion and removal of valence-band degeneracies caused by the applied stress. The structure distinguishes transitions which are allowed from those which are forbidden. The phonon energies and their observed selection rules agree with the expected values. The background absorption is quite dependent upon the stress axis and the polarization direction and appears to come from several sources. The measured ratios of the components of the strain optical tensor agree quite closely with those calculated on the basis of the deformation-potential model using the optical selection rules and the values $E_1=-4$, $b=-2$, and $d=-4.3$ eV for the various deformation potentials. The absolute magnitude of this background signal, however, depends on additional processes which have not been entirely explained.

These data and calculations show that the measured piezooptical constants are consistent with negative values for the constants b and d. This is consistent with the previous cyclotron resonance observations of Hensel and Feher[17] but does not agree with previous conclusions drawn from piezoabsorption measurements in the [100] direction, where an apparent positive b was observed.[6]

ACKNOWLEDGMENTS

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