History, Smithsonian Institution, Washington, D. C. (Catalog Nos. R402, 91779, and C288).

[6]G. Hass, J. Opt. Soc. Am. 45, 945 (1955).

[7]The 470-cm^{-1} frequency replaces the less accurate value of 466 cm^{-1} which was given in an earlier paper (see Ref. 2).

[8]M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford U. P., London, England, 1966) Sec. 10, p. 121.

[9]R. Loudon, Advan. Phys. 13, 423 (1964).

[10]I. F. Chang, S. S. Mitra, J. N. Plendl, and L. C. Mansur, Phys. Status Solidi 28, 663 (1968).

[11]R. H. Lyddane, R. G. Sachs, and E. Teller, Phys. Rev. 59, 673 (1941).

[12]B. L. Evans and P. A. Young, Proc. Roy. Soc. (London) A284, 402 (1965).

[13]R. F. Frindt and A. D. Yoffe, Proc. Roy. Soc. (London) A273, 69 (1963).

[14]R. Bailly, Am. Mineralogist 33, 519 (1948).

[15]The authors previously reported (see Ref. 2) a Raman line at 519 cm^{-1}, which has since been shown to be spurious. However, a very weak line at 287 cm^{-1} has been discovered that has the correct polarization properties.

[16]R. A. Bromley, Phys. Letters 33A, 242 (1970).

[17]Because of the low mobility ($\approx 10^2$ cm/V sec) and high carrier concentration ($\approx 10^{17}$ cm^{-3}), free-carrier absorption in MoS_2 saturates well before free-carrier dispersion in the index of refraction becomes appreciable. Moreover, the free-carrier effective mass is thought to be large and the relaxation time short. This explains why the reflectivity of MoS_2 shows no plasma dispersion at low photon energies.

[18]R. Fivaz and E. Mooser, Phys. Rev. 163, 743 (1967).

[19]T. J. Wieting and A. D. Yoffe, Phys. Status Solidi 37, 353 (1970).

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Detailed Study of the Γ_{15} Conduction-Band Minimum in Germanium by Photoemission and Transverse Electroreflectance

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Direct transitions occurring at the center of the Brillouin zone can be unambiguously identified by photoemission and transverse electroreflectance methods. In a material whose valence-band maximum lies at Γ, such transitions produce structure on the leading edge of the energy distribution curve (EDC) of photoemitted electrons. In transverse electroreflectance (TER), the absence of polarization dependence associated with multivalley effects provides a signature of transitions having Γ symmetry. In this paper we report three independent studies of direct transitions near 3 eV in germanium; namely, photoemission EDC, energy-derivative EDC, and polarization-dependent TER. Both photoemission experiments yield a value 2.92 $\pm$0.05 eV for the minimum separation $\Gamma_6^- - \Gamma_8^+$ at 300 °K. The TER experiment can only be performed at 80 °K or below, and gives 3.00 $\pm$ 0.05 eV for the same gap at 80 °K. The agreement among all three is perfect, assuming a temperature coefficient of -4×10^{-4} eV/°K. The spin-orbit splitting of the conduction band is observed directly in the TER spectra; we find $\Delta(\Gamma_{15}) \equiv \Gamma_8^- - \Gamma_6^- = 0.191 + 0.005$ eV. The present results are compared with recent band calculations and previous experiments.

I. INTRODUCTION AND SUMMARY

The energy position of the Γ_{15} conduction-band minimum in germanium is a sensitive testing ground for band-structure calculations. The interband energy $\Gamma_{15} - \Gamma_{25'}$ represents the lowest critical-point transition which has not been reliably fitted to experiment in the various theoretical methods, so variations in the predicted values provide a basis for critical evaluation of the calculated band structures. Such evaluation has not been possible up to now, because of the tentative nature of prior experimental determinations of $\Gamma_{15} - \Gamma_{25'}$.

We present here the results of three completely independent spectroscopic studies of single-crystal germanium which pertain to the Γ_{15} conduction band. In two of these, the energy distribution curves (EDC) of photoemitted electrons[1] were obtained for several photon energies near 3 eV; in the more recent of the two, the energy derivative of the EDC was also recorded directly,[2] allowing more accurate location of weak structure. In the third experiment, polarization-dependent transverse electroreflectance (TER) spectra[3] were recorded from 2.8 to 3.6 eV for the three principal crystallographic orientations of the electric field. Both types of experiment provide unambiguous identification of direct transitions originating at

the center of the Brillouin zone (BZ), as discussed below.

The results of all three experiments clearly indicate a Γ transition at 2.92 ± 0.05 eV (300 °K). The three independent values for the transition energy agree to within 0.01 eV. We conclude that this transition represents the minimum separation of $\Gamma_{15} - \Gamma_{25'}$ ($\Gamma_6^- - \Gamma_8^+$ in double-group notation), based on a direct-transition analysis of the EDC and selection-rule arguments applied to the TER multiplet spectrum. The TER measurement also reveals the spin-orbit splitting of the Γ_{15} level:

$$\Delta(\Gamma_{15}) = 0.191 \pm 0.005 \text{ eV}.$$

The two phenomena exploited in this work, photoemission and electroreflectance, provide complimentary tools for band-structure spectroscopy. Structure in photoemission is enhanced by a large density of states,[4] or interband effective mass, while electroreflectance amplitudes are greater the smaller the mass.[5] The agreement obtained between the two methods in the current work is indeed gratifying, and tends to increase confidence in both.

In Secs. II and III we briefly discuss the analyses and give experimental results for photoemission and TER, respectively. Comparison of our results with recent theoretical predictions and previous experiments is given in Sec. IV.

II. PHOTOEMISSION

Photoemission data, particularly energy distributions of photoemitted electrons (EDC) from semiconductors,[1] have been successfully analyzed in terms of energy-band calculations and optical selection rules. Energy positions of peaks and shoulders in the EDC, taken as a function of photon energy, are related directly to the energies of the initial and final states involved in the optical transitions. Using this approach the threshold for transitions occurring at the center of the zone (where the valence-band maximum occurs) can be easily identified by an increase in the number of photoelectrons in the leading edge of the EDC.[6] This will cause a change in the curvature of the EDC near the leading edge, which can most easily be picked up in the energy derivative of the EDC.[2] Direct transitions originating in the highest filled levels will appear in the highest-energy positions of the EDC. Since no competing transitions from other regions of the BZ occur here, the assignment of both the transition energy and location in the BZ in the special case of γ transitions is completely unambiguous.

EDC measured at 300 and 80 °K for a photon energy $h\nu = 3.1$ eV and normalized to the photoelectric yield are shown in Fig. 1.[7,8] The curves are from a p-type crystal that was cleaved, cesiated, and measured in ultrahigh vacuum. Details of the normalization procedure and method of energy scale calibration, as well as the cleaving and measuring techniques, have been described before.[7,8] A strong shoulder is seen near the leading edge of the distribution at 300 °K and this shoulder is enhanced at 80 °K. The shoulder first appears abruptly between $2.9 \leq h\nu \leq 3.0$ eV. This is seen clearly in the insert to Fig. 1, where the number of electrons in the distribution (in arbitrary units) is plotted versus the retarding potential (in volts) applied to the collector can, with the sample, the emitter in a photodiode configuration. Similar behavior is observed with other samples including an intrinsic crystal and a more heavily doped p-type crystal. Detailed measurements establish the threshold energy as 2.92 ± 0.05 eV.[7,8]

The structure of Fig. 1 is enhanced by electronically recording the derivative of the EDC during measurement.[8] Derivatives of EDC are shown in Fig. 2 for a p-type crystal ($\sim 10^{19}/\text{cm}^3$) with $2.9 \leq h\nu \leq 3.0$ eV. The lowest photon energy where the derivative shows the change in curvature associated with the appearance of the shoulder is 2.93 ± 0.05 eV. The value determined for three crystals falls within these limits. We assign this transition energy to the minimum separation $\Gamma_6^- - \Gamma_8^+$ for the reasons mentioned above. The spin-orbit splitting of the initial state is resolved in higher-photon-energy distributions and is equal to 0.27 ± 0.05 eV.[9] The temperature dependence of the threshold has not been accurately determined in these experiments but the shift is less than 0.1 eV from 300 to 80 °K.

III. TRANSVERSE ELECTROREFLECTANCE

The symmetry analysis of TER has been discussed by several authors.[10–12] The modulating field $\vec{F}$ lies in the reflecting plane, so the normal incidence spectrum can be obtained with polarization vector $\vec{e}$ either parallel or perpendicular to $\vec{F}$. A strong differentiation is predicted between transitions originating at the zone center and those occurring off $\vec{k} = 0$. The TER spectrum of a Γ transition is independent of polarization for any field direction, while off-center transitions exhibit varying degrees of polarization anisotropy depending on the $\vec{F}$ direction and interband mass tensor.[12] Transitions of [111] or [100] symmetry yield isotropic TER spectra with $\vec{F} \| [100]$ and [111], respectively, but not otherwise. These predictions have been verified in several instances where the symmetry is known from other experiments. For germanium, the E_0, $E_0 + \Delta_0$ (Γ symmetry),[13] and E_1, $E_1 + \Delta_1$ (essentially Λ symmetry)[3,14] transitions have been studied in detail. Anisotropies not exceeding 8% were observed at E_0 and interpreted in terms of the light-heavy hole degeneracy of the

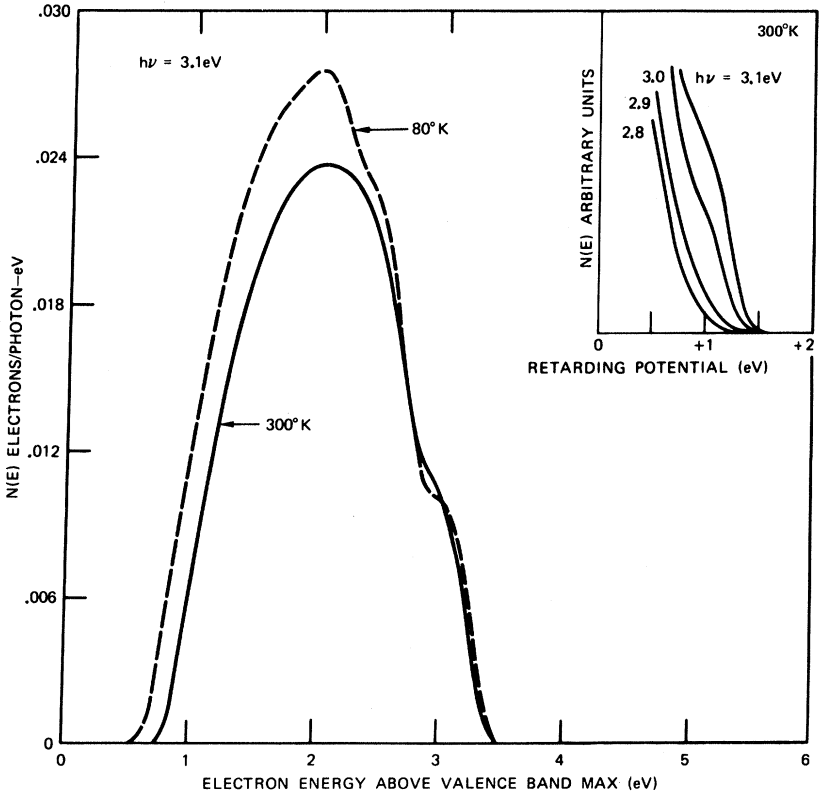

FIG. 1. Energy distribution curves (EDC) for cleaved cesiated p-type Ge measured at 300 and 80 °K. The shoulder at 3.0 eV is due to transitions near Γ_{15}. The insert clearly shows the onset of the Γ transition for $2.9 \leq h\nu \leq 3.0$ eV at 300 °K.

initial state; the nondegenerate $E_0+\Delta_0$ transition was found to be isotropic to within a few percent. With $\vec{F}\parallel\langle 111\rangle$, ~30% anisotropy was observed for E_1 and $E_1+\Delta_1$.

In Fig. 3 we present polarization-dependent TER from 2.8 to 3.6 eV, taken at 85 °K with $\vec{F}\parallel\langle 100\rangle$; solid (dashed) curves denote $\vec{e}\perp(\parallel)\vec{F}$. The experimental method is discussed elsewhere.[14] Three down-up structures are observed, superposed on a broad "background"; the minima are located at 3.00, 3.19, and ~3.5 eV. Measured with respect to the background, these three structures are independent of polarization direction to within 10%. Similar results are obtained with $\vec{F}\parallel\langle 111\rangle$ and $\langle 110\rangle$. Based on the previously verified predictions of the analysis, we conclude that these three peaks originate from critical points of Γ symmetry.

The polarization-dependent background suggests the presence of additional off-center transitions in this energy region. The "background" increases more rapidly with increasing $|F|$ than the three down-up structures. The surface-barrier method of electroreflectance[15] provides maximum field strengths 10–100 times as large as in Fig. 3; surface-barrier electroreflectance spectra of the 2.8–4.0 eV region are extremely complex and cannot be reliably interpreted.[16]

The assignment of the three peaks in Fig. 3 to specific transitions is shown in Fig. 4, where we

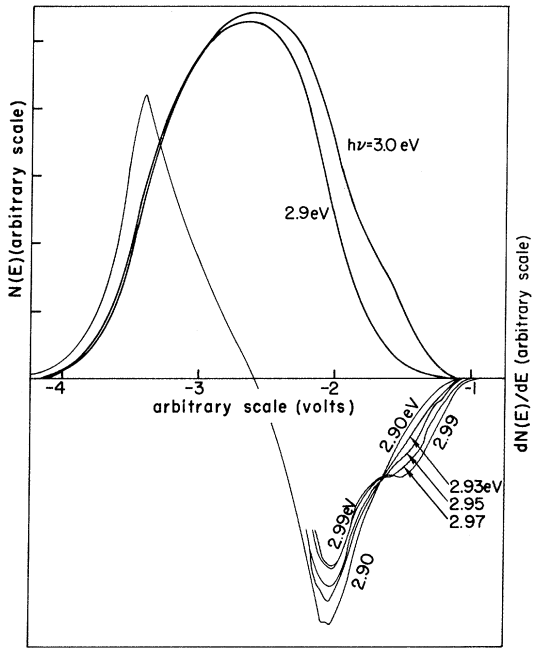

FIG. 2. EDC for a more highly doped p-type crystal at $h\nu = 2.9$ and 3.0 eV. Plotted using the same arbitrary energy scale are derivatives of EDC measured at closer intervals. The change in curvature of the leading edge which we associate with the Γ_{15} threshold is first seen in the $h\nu = 2.93$-eV derivative curve.

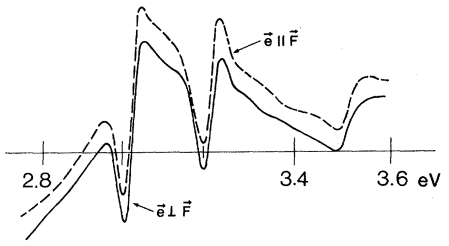

FIG. 3. Polarization-dependent TER spectrum ($\Delta R/R$ vs photon energy) of Ge at 80 °K; $\vec{F} \sim 6$ kV/cm $\parallel \langle 100 \rangle$. Solid (dashed) curves denote $\vec{e} \perp (\parallel) \vec{F}$, respectively. The structures observed at 3.00, 3.19, and ~3.5 eV are independent of polarization when measured with respect to the broad "background."

include the spin-orbit splitting of initial and final states. All transition energies are at 80 °K; results for the fundamental edge have been reported previously.[3] We assign gap energies to the positions of the negative peaks, as at the fundamental edge:

$$\Gamma_6^- - \Gamma_8^+ = 3.00 \pm 0.05 \text{ eV},$$

$$\Gamma_8^- - \Gamma_8^+ = 3.19 \pm 0.05 \text{ eV}.$$

The uncertainty is associated primarily with ambiguities in line-shape interpretation and allows for possible many-body effects.[17] The spin-orbit splitting of the Γ_{15} state can be read out very accurately; we find $\Delta(\Gamma_{15}) \equiv \Gamma_8^- - \Gamma_6^- = 0.191 \pm 0.005$ eV. The 3.5-eV peak is assigned to $\Gamma_8^- - \Gamma_7^+$, consistent with the known $\Gamma_{25'}$ splitting of 0.29 eV.[15]

The absence of a fourth peak at ~3.3 eV in the spectrum of Fig. 3 justifies the assignment of $\Gamma_{15}(\Gamma_6^-, \Gamma_8^-)$ as the final state. Such a peak is energetically possible, since $\Delta(\Gamma_{15}) \neq \Delta(\Gamma_{25'})$, but is dipole forbidden if the initial- and final-state symmetries are Γ_7^+ and Γ_8^-, respectively.[18]

IV. DISCUSSION

The basic results of this study are

$$\Gamma_6^- - \Gamma_8^+ (80\,^\circ\text{K}) = 3.00 \pm 0.05 \text{ eV}$$

from TER, and

$$\Gamma_6^- - \Gamma_8^+ (300\,^\circ\text{K}) = 2.92 \pm 0.05 \text{ eV}$$

from photoemission. Assuming the same temperature coefficient as the fundamental direct gap,[15] the TER result scales to 2.92 ± 0.05 eV at 300 °K, in excellent agreement with the photoemission value.

Optical structure around 3 eV (labeled E_0', $E_0' + \Delta_0'$) has been attributed to Δ [the (100) direction] in the past.[16,19] We assign the structure shown in Figs. 1–3 to Γ rather than Δ for the following reasons: (i) The structure is located within 0.2 eV of the leading edge of the EDC, so the initial state must be within 0.2 eV of the top of the valence band. From the known heavy-hole mass along (100),[20] the initial state must therefore lie between $\vec{k} = 0$ and $\vec{k} = 0.2\,\vec{k}_{max}$. (ii) The valence-band splitting observed in both experiments further localizes the initial state to within $0.1\vec{k}_{max}$.[21] (iii) The absence of a peak at 3.3 eV in TER (Fig. 3) indicates Γ_{15} symmetry for the final state. (iv) The lack of polarization dependence is compatible with either Γ symmetry or an M_0 or M_3 critical point along Δ having equal transverse and longitudinal masses.[3,12] The latter has not been suggested by any band calculation.

Experimental results up to 1968 have been exhaustively reviewed by McElroy.[16] In the top half of Table I we list the results of Potter[22] and Ghosh[19] along with our own. The first column gives the minimum separation, which is presumably the experimentally observed quantity. The second column gives the final-state splitting $\Delta(\Gamma_{15})$ as observed in the various experiments. The third column lists the single-group equivalent (or center of mass), obtained by adding $\frac{1}{3}\Delta(\Gamma_{25'})$ and $\frac{2}{3}\Delta(\Gamma_{15})$ to the minimum separation.[23]

Potter[22] observes four spectral features in the optical constants measured via the pseudo-Brew-

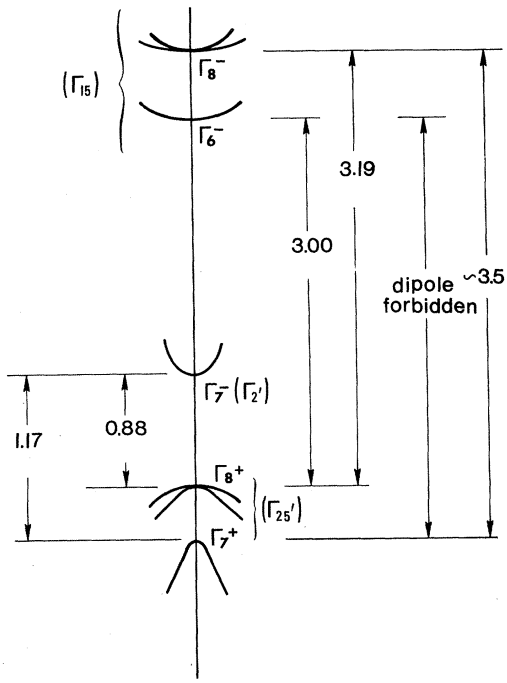

FIG. 4. Schematic representation of the energy bands of Ge near $\vec{k} = 0$. The bands are labeled by the usual double-group notation to include spin-orbit splitting; single-group equivalents are indicated in parentheses. Transition energies are at 80 °K; the three peaks in Fig. 1 are assigned to transitions from the split valence band to the (second) split conduction band. (The $\Gamma_7^+ \rightarrow \Gamma_6^-$ transition, labeled "dipole forbidden," is not observed.)

ster angle method which he assigns to the $\Gamma_{15} - \Gamma_{25'}$ quartet. Neither the observed structure nor Potter's interpretation has been confirmed in detail by comparable experiments.[24] Ghosh[19] obtained electrolyte electroreflectance spectra under modulation conditions which are known to induce chemical and photochemical reactions at the Ge-aqueous electrolyte interface[25]; he also finds four peaks which he interprets as $\Gamma_{15} - \Gamma_{25'}$, at energies ~0.15 eV higher than Potter. In both cases, inclusion of four peaks in the interpretation is inconsistent with the selection rules discussed in Sec. III. Ghosh also measured polarization dependence on a (110) face ($\vec{e}$ always $\perp \vec{F}$, $\vec{e} \parallel [1\bar{1}0]$ or [001], $\vec{F} \parallel [110]$). Large polarization effects were observed from 2.8 to 4.0 eV, which are inconsistent with results obtained on the same crystal geometry using thin-film metal-oxide-semiconductor (MOS) samples.[26]

An indirect measure of $\Delta(\Gamma_{15})$ is obtained from the combined resonance experiments of Hensel and Suzuki at 1.4 °K.[27] By analyzing their results in terms of the Luttinger effective-mass Hamiltonian (neglecting core states and including only the first term in the summation), they deduce

$$\Delta(\Gamma_{15}) = 0.051 E_g \pm (0.03 \text{ eV}) , \quad (1)$$

where E_g is the center of mass of the final state minus the highest-energy initial state, namely, $\Gamma_{15} - \Gamma_8^+$. Computing E_g from our results (scaled to 1.4 °K) gives $\Delta(\Gamma_{15}) = 0.16 \pm 0.03$ eV, which agrees with the directly observed TER value within the errors of the two experiments.

In the bottom half of Table I we present a sampling of band-theory results; no attempt has been made to include every calculation in existence. Numbers in parentheses are experimental inputs to empirical theories or adjustment schemes; any resemblance to the present results is purely coincidental. Compared to our experimental value for $\Gamma_6^- - \Gamma_8^+$, the only two calculations[28,29] which explicitly include spin-orbit coupling are ~0.3–0.4 eV too low.[30] The truncation scheme used in the Fourier method[28] requires $\Delta(\Gamma_{15}) = \Delta(\Gamma_{25'}) = 0.29$ eV, which is clearly inadequate; Saravia and Brust[29] calculate 0.21 eV, in good agreement with our measured value.

We turn now to calculations which neglect spin-orbit splitting, listed in the third column of Table I. The early pseudopotential value is ~0.5 eV too high.[31] Cardona and Pollak use $\Gamma_{15} - \Gamma_{25'} = 3.15$ eV as an input to their $\vec{k} \cdot \vec{p}$ calculation[32]; the experimental origin of their value is not clear[33] but it agrees very well with ours. Their calculated splitting is 0.36 eV, clearly too high. Recently, Saravia and Casamayou[34] used the pseudopotential method to calculate ECD; they obtained 3.2 eV for the center of mass, in good agreement with the results.

TABLE I. Experimental and theoretical values for the minimum separation $\Gamma_6^- - \Gamma_8^+$, the conduction-band splitting $\Delta(\Gamma_{15})$, and the center of mass $\Gamma_{15} - \Gamma_{25'}$. No attempt at completeness has been made.

		$\Gamma_6^- - \Gamma_8^+$(300 °K)	$\Delta(\Gamma_{15})$	$\Gamma_{15} - \Gamma_{25'}$ (300 °K)[a]
Potter[b]		2.63	0.12	2.84
Ghosh[c]		2.80	0.13	2.98
Hensel and Suzuki[d]		•••	0.16 ± 0.03	•••
Present work	EDC	2.92 ± 0.05	•••	3.13 ± 0.05
	derivative EDC	2.93 ± 0.05	•••	3.14 ± 0.05
	TER	2.92 ± 0.05[e]	0.191 ± 0.005	3.13 ± 0.05
Early pseudopotential[f]		•••	•••	(3.6)[g]
Fourier expansion[h]		2.55	0.29	2.84
Recent pseudopotential[i]		2.60	0.21	•••
Full zone $\vec{k} \cdot \vec{p}$ [j]		(2.83)[k]	0.36	(3.15)[g]
OPW + two parameters[l]		•••	0.21	2.53, 2.70, 2.94
OPW + three parameters[m]		•••	•••	(2.91)[g]
Pseudopotential EDC[n]		•••	•••	3.2
OPW unadjusted[o]		•••	•••	2.98

[a] Derived from $\Gamma_6^- - \Gamma_8^+$ and $\Delta(\Gamma_{15})$.
[b] See Ref. 23.
[c] See Ref. 19.
[d] See Ref. 27.
[e] Adjusted to 300 °K from low-temperature result. See text.
[f] See Ref. 31.
[g] ( ) denotes experimental input to empirical model or correction; agreement of such values with the present results is of no theoretical significance.
[h] See Ref. 28.
[i] See Ref. 29.
[j] See Ref. 32.
[k] See Ref. 30.
[l] See Ref. 35.
[m] See Ref. 36.
[n] See Ref. 34.
[o] See Ref. 37.

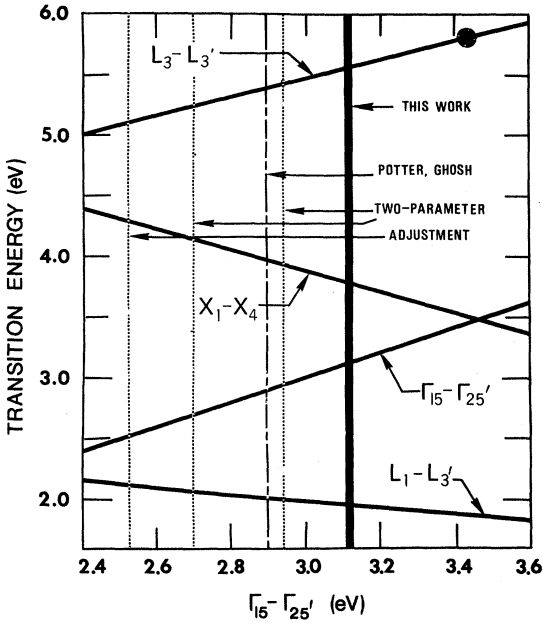

FIG. 5. Dependence of three energy gaps on the $\Gamma_{15}-\Gamma_{25'}$ separation, from the first principles theory of Herman *et al.* Five choices for $\Gamma_{15}-\Gamma_{25'}$, and their implications on other gaps, are shown as vertical lines. The three dotted lines are values predicted by three separate two-parameter adjustments. The dashed line is the average of Potter's and Ghosh's experimental results. The heavy black line is the present result, 3.13 ±0.05 eV. With respect to the other four, our value of $\Gamma_{15}-\Gamma_{25'}$ improves agreement between first-principles theory and experiment *vis a vis* L_3-L_3' (the large black dot is the experimental value) but not L_1-L_3'. The X_1-X_4 gap is not known experimentally.

The most detailed calculations of the Ge band structure have been performed by Herman and coworkers. In their latest method, the final band structure is obtained by small corrections based on experiment. In 1967 Herman *et al.* used experimental values for the direct and indirect gaps in three different two-parameter adjustment procedures,[35] which predicted three separate values for $\Gamma_{15}-\Gamma_{25'}$: 2.53, 2.70, and 2.94 eV. The highest of these three is 0.2 eV below our value. They later admitted the Ghosh and Potter results, using the experimental average 2.91 ± 0.07 eV to generate a unique three-parameter correction scheme.[36] In a very recent first principles calculation (*no* experimental adjustment), a value 2.98 eV was obtained[37]; this is within 0.15 eV of our value.

The $\Gamma_{15}-\Gamma_{25'}$ transition energy forms the cornerstone of Herman's two-parameter adjustment scheme; that is, other transitions are very sensitive to the value specified for $\Gamma_{15}-\Gamma_{25'}$. Figure 5 is a replot of Fig. 2, Ref. 35, in which the L_3-L_3', X_1-X_4, and L_1-L_3' first-principles energies are plotted versus $\Gamma_{15}-\Gamma_{25'}$. The three vertical dotted lines represent the three values predicted from two-parameter adjustments (the two experimental parameters being the fundamental indirect and direct gaps). The dashed line is the average of the Potter and Ghosh results which was used in a unique three-parameter fit and generated the most recently published band structure of Herman and coworkers.[36] We note two implications of our $\Gamma_{15}-\Gamma_{25'}$ value (heavy line on Fig. 5). First, L_3-L_3' increases to 5.6 eV from a maximum of 5.4 eV predicted by the other $\Gamma_{15}-\Gamma_{25'}$ values, improving agreement with the 5.8 eV determined from photoemission[7,8] and (tentative) electroreflectance[38] measurements. This latter value is denoted by the large dot on the L_3-L_3' line in Fig. 5. Second, L_1-L_3' decreases to 1.9 eV from a maximum of 2.2 eV; the commonly accepted experimental value is 2.2 eV,[16] so the agreement is worse for this transition. There is no clearcut experiment value for X_1-X_4.[3]

V. FURTHER CONFIRMATION OF RESULTS AND ASSIGNMENTS

Electroreflectance is extremely sensitive to weak structure, being essentially the third derivative of the optical spectrum with respect to photon energy. With careful techniques, comparable sensitivity can be achieved in the first derivative.[39] In fact, Sell has obtained $(dR/dE)/R$ spectra which agree extremely well with the TER spectrum of Fig. 3; sharp peaks are observed at 3.00 and 3.19 eV, and a broader dip occurs at 3.5 eV. Furthermore, the response of the lower-energy doublet to uniaxial stress (energy position, polarization dependence) unambiguously confirms the assignment to transitions of Γ symmetry.[40] This removes the possibility, left open by the TER polarization dependence, of a spherical M_0 or M_3 critical point along Δ.

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[1]W. E. Spicer and R. C. Eden, *Proceedings of the Ninth International Conference on the Physics of Semiconductors* (Nauka, Leningrad, 1969), p. 65.

[2]L. W. James, R. C. Eden, J. L. Moll, and W. E. Spicer, Phys. Rev. 174, 909 (1968).

[3]J. E. Fischer, Atomic Energy Commission Report No. CONF 700801, 1970 (unpublished), p. 427.

[4]C. N. Berglund and W. E. Spicer, Phys. Rev. 136,

1044 (1964).

[5]D. E. Aspnes and J. E. Rowe, Solid State Commun. 8, 1145 (1970), and references cited therein.

[6]J. L. Shay and W. E. Spicer, Phys. Rev. 161, 799 (1967).

[7]T. M. Donovan, Ph. D. thesis (Stanford University, Stanford, Calif., 1970) (unpublished); see also W. E. Spicer and T. M. Donovan in Ref. 3, p. 677.

[8]T. M. Donovan, J. Matsuzaki, and W. E. Spicer (unpublished).

[9]J. Matsuzaki, T. M. Donovan, and W. E. Spicer, Bull. Am. Phys. Soc. 15, 1600 (1970).

[10]F. Aymerich and F. Bassani, Nuovo Cimento B56, 295 (1968).

[11]R. A. Forman, D. E. Aspnes, and M. Cardona, J. Phys. Chem. Solids 31, 227 (1970).

[12]N. Bottka and J. E. Fischer, Phys. Rev. B (to be published).

[13]J. E. Fischer and N. Bottka, Phys. Rev. Letters 24, 1292 (1970).

[14]J. E. Fischer, D. S. Kyser, and N. Bottka, Solid State Commun. 7, 1821 (1969).

[15]B. O. Seraphin, R. B. Hess, and N. Bottka, J. Appl. Phys. 36, 2242 (1965).

[16]A comprehensive review is given by P. T. McElroy, Ph. D. thesis (Harvard University, Boston, Mass., 1968), available as Technical Report No. HP-21 (unpublisted); J. P. Walter and M. L. Cohen, Phys. Rev. 183, 763 (1969); R. R. L. Zucca and Y. R. Shen, Phys. Rev. B 1, 2668 (1970); and other references given in these two papers.

[17]M. Cardona, *Modulation Spectroscopy* (Academic, New York, 1968).

[18]The polarization vector for any orientation transforms as Γ_4^- in the point group O_h. The selection rules for initial states of Γ_7^+ and Γ_8^+ symmetry are $\Gamma_7^+ \times \Gamma_4^- \rightarrow \Gamma_7^- + \Gamma_8^-$ and $\Gamma_8^+ \times \Gamma_4^- \rightarrow \Gamma_6^- + \Gamma_7^- + 2\Gamma_8^-$. Thus a transition with Γ_6^- final- and Γ_7^+ initial-state symmetries is forbidden [see, for example, G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the* 32 *Point Groups* (MIT, Cambridge, Mass., 1963)]. (We are grateful to J. Treusch and N. Bottka for discussions on this point.) In principle, the electric field breaks the symmetry so that the transition becomes allowed (see Refs. 12, 13, and 16), but it is expected to be very weak compared to the other three peaks at the field strengths employed (Ref. 13).

[19]A. K. Ghosh, Phys. Rev. 165, 888 (1968).

[20]G. Dresselhaus, A. F. Kip, and C. Kittel, Phys. Rev. 98, 368 (1955).

[21]The valence-band splitting increases rapidly in all directions from $\vec{k}=0$; see, for example, Fig. 2 in M. Cardona, K. L. Shaklee, and F. H. Pollak, Phys. Rev. 154, 696 (1967).

[22]R. F. Potter, Phys. Rev. 150, 562 (1966).

[23]The center of mass is obtained from spin-split bands by weighting each member of a degenerate set equally; see Ref. 35.

[24]Structure in "unperturbed" optical experiments (as opposed to piezo- or electroreflectance) in this energy region is an open question; see Ref. 16.

[25]D. E. Aspnes and A. Frova, Phys. Rev. B 2, 1037 (1970).

[26]J. E. Fischer (unpublished).

[27]J. C. Hensel, Phys. Rev. Letters 21, 983 (1968); J. C. Hensel and K. Suzuki, *ibid.* 22, 838 (1969).

[28]G. Dresselhaus and M. S. Dresselhaus, Phys. Rev. 160, 649 (1967).

[29]L. R. Saravia and D. Brust, Phys. Rev. 176, 915 (1968).

[30]McElroy (Ref. 16) quotes a spin-orbit-split $\vec{k} \cdot \vec{p}$ calculation by Cardona *et al.* [Phys. Rev. 154, 696 (1967)], which gives 2.83 eV for the minimum separation. This is only 0.1 eV below our value, but is probably an experimental input to the calculation.

[31]M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966), and references cited therein.

[32]M. Cardona and F. H. Pollak, Phys. Rev. 142, 530 (1966).

[33]M. Cardona, J. Phys. Chem. Solids 24, 1543 (1963).

[34]L. Saravia and L. Casamayou (unpublished).

[35]F. Herman, R. L. Kortum, and C. D. Kuglin, Intern. J. Quantum Chem. 15, 533 (1967).

[36]F. Herman, R. L. Kortum, C. D. Kuglin, and J. P. VanDyke, *Methods of Computational Physics* (Academic, New York, 1968), Vol. 8.

[37]F. Herman and I. Ortenberger (private communication).

[38]B. J. Parsons and H. Piller, *Proceedings of the Density of States Conference*, 1969 (Natl. Bur. Std., U. S. GPO, Washington, D. C., to be published).

[39]D. D. Sell and S. E. Stokowski, in Ref. 3, p. 417.

[40]D. D. Sell and E. O. Kane (unpublished).