PHYSICAL REVIEW B VOLUME 8, NUMBER 10 15 NOVEMBER 1973

Temperature Dependence of the HgTe Band Gap*

Charles S. Guenzer† and Arthur Bienenstock
Department of Applied Physics, Stanford University, Stanford, California 94305

(Received 26 February 1973)

Hg and Te Debye-Waller factors in HgTe have been measured using x-ray diffraction. These have been combined with a previously published pseudopotential to calculate the temperature dependence of the band gap within the Brooks-Yu theory. The calculated value has approximately one-half the magnitude and the opposite sign of the experimental value. A detailed analysis indicates the Debye-Waller factors are not likely to be the cause of the discrepancy, but that the pseudopotential may be. A further analysis shows that when interband matrix elements are included for normal electron-phonon processes in a rough self-energy calculation, the correct sign is obtained. The magnitude has not, however, been determined. It is also shown, though, that a self-energy band calculation neglects significant terms if only the bands closest to the gap are included. We conclude that our understanding of the temperature dependence of semiconductor band gaps is somewhat weaker than many are claiming on the basis of moderate agreement with experiment.

INTRODUCTION

In recent years, a number of workers have presented calculations of the temperature dependence of semiconductor band gaps using the Brooks-Yu[1,2] theory. In this theory, the temperature dependence is obtained through temperature-dependent pseudopotentials. The effective strength of each ionic pseudopotential is reduced by the appropriate ionic Debye-Waller factor, a measure of the amplitude of thermal vibration of that ion.

In the first such published calculation, Keffer, Hayes, and Bienenstock[3,4] investigated PbTe. They used a number of pseudopotentials, each of which gave reasonable agreement with experimental results. Subsequently, Tsang and Cohen[5] used their own local pseudopotential to produce very good agreement between experiment and the Brooks-Yu theory. Tsang and Cohen's calculation for SnTe and Tsay *et al.*'s[6] calculations for a number of zinc-blende structure compounds have strengthened the conclusion that, with sufficiently accurate pseudopotentials and Debye-Waller factors, the Brooks-Yu theory can predict the temperature dependence of the band gap. As Tsay *et al.* stated, "Agreement of calculated values are within 30% of the experimentally determined values... It is reasonable to expect that it can be corrected by better zero-temperature pseudopotential form factors as well as more accurate Debye-Waller factors."

It is our belief that the understanding of band-gap temperatures dependences is significantly less complete than these calculations would indicate. We support this belief with the historical introduction which concludes this section of the paper, and then with a detailed experiment and calculations on HgTe. The experiment is the measurement of the ionic Debye-Waller factors in HgTe. The calculations are of both the Brooks-Yu terms and portions of the self-energy terms which contribute to the band-gap temperature dependence. Let us proceed, therefore, with the historical survey, which is quite revealing in itself.

The first significant theory of the explicit temperature dependence of the gap (i.e., that due to electron-phonon interaction at constant volume, rather than that due to thermal expansion) was presented by Fan.[7] It is a self-energy theory carried to second order in the mixing of electron and phonon states. As a result of the mixing, the Bloch vectors associated with the one-electron states are no longer good quantum numbers. This, of course, is a partial representation of the fact that the instantaneous one-electron potential is not periodic as a result of the thermal vibrations. Using a simplified model of the band structures and phonon dispersion relations, Fan obtained good agreement with the temperature dependence of Si, but less satisfactory agreement with that of Ge.

Later, Cohen[8] obtained extremely good agreement for Ge using a more sophisticated band structure and phonon dispersion relations within the Fan theory. Although this good agreement was obtained through adjustment of unknown deformation potential parameters, the parameters chosen appear quite reasonable. Hence, on the basis of the Fan and Cohen calculations, one might have concluded that the Fan theory is quite valid and contains the dominant terms in the explicit band-gap temperature dependence.

It became apparent, however, with experimental studies on PbS, PbSe, and PbTe that this was not the case. In these materials, the direct, fundamental band gaps increase with increasing temperature. The Fan theory, on the other hand, necessarily predicts a decrease. The discrepancy could not be explained through the effects of thermal expansion. Something was wrong.

With this in mind, Brooks and Yu undertook a reexamination of the electron-phonon interaction and showed that there is one more effect which must be taken into account. This is the modification of the pseudopotential by the Debye-Waller factors. That these two effects are quite different can be seen without a detailed theoretical analysis. The Brooks-Yu theory involves only temperature dependences of the pseudopotentials at the reciprocal lattice points. Hence, if only this theory is applied, the Bloch vectors of the one-electron states remain good quantum numbers. This is in distinct contrast to the situation in the Fan theory. From Yu's more detailed theoretical analysis, it appeared as if the two effects were additive.

Yu also calculated the contributions of the Fan and Brooks-Yu effects in Ge and concluded that the Fan contribution is quite small compared to the Brooks-Yu contribution and the experimentally observed values. Since the calculation was never published, though, there was no published analysis of why the Yu estimate of the self-energy contribution is so much smaller than those of Fan and Cohen.

General acceptance of the Brooks-Yu theory started when Keffer *et al.*[3,4] showed that it did yield the increase of the PbTe band gap with increasing temperature. They did find, however, that the "best" calculation yielded twice the observed magnitude. These workers might have concluded the self-energy contribution is, therefore, of the opposite sign and one-half of the magnitude, but they lacked sufficient confidence in their pseudopotential. The subsequent Brooks-Yu calculation of Tsang and Cohen,[4] which yielded extremely good agreement with experiment, appeared to negate the possibility that the self-energy terms are appreciable. This conclusion was reinforced by the apparent success of other Brooks-Yu–type calculations.

Nevertheless, in one more unpublished work, Mostoller[9] reexamined the theory and the Ge calculations. He concluded that the Fan and Brooks-Yu effects are additive and are of the same order of magnitude. He showed that Yu's calculation of the self-energy terms was incorrect.

Then, there came our earlier report[10] that the Brooks-Yu theory yielded the wrong sign for the HgTe negative band-gap temperature dependence. This result, too, should have been taken as justification for concern about the general applicability of the theory.

In fact, when viewed in this historical manner, one cannot help but conclude that the view that only better pseudopotentials and better Debye-Waller factors are needed to obtain complete agreement with experiment through the Brooks-Yu theory is completely unjustified when previous calculations have shown that the self-energy terms are so large.

Since the previously reported[10] calculation on HgTe becomes rather important in this context, it is presented in more detail, and with more analysis here, so that its limitations and strengths are apparent.

Section I describes our method of measuring the Debye-Waller factors. The resultant Debye temperatures agree fairly well with other recent work. We feel the method described is capable of accurately measuring temperature-independent Debye temperatures.

With the experimental Debye-Waller factors we then calculate the Brooks-Yu temperature coefficient. The coefficient is of half the right magnitude and of the wrong sign. In the hope of understanding this discrepancy, we give further results that generalize upon the simple temperature coefficient. We also give a critique of the available HgTe pseudopotential.

Since the Brooks-Yu theory has not provided a coefficient agreeing with experiment, we have further developed the self-energy theory for band-gap changes with temperature. While little originality is claimed for the general result, we have put the terms into a much more tractable form. The resultant expression needs more parameters than available for HgTe, but by making some normal process approximations, we can make a rough calculation of the sign of this self-energy terms for HgTe. The sign of this calculation is that of the experiment, though the magnitude of the coefficient is unknown. The calculation also shows the importance of including all states in the self-energy theory.

II. DETERMINATION OF DEBYE-WALLER FACTORS

The determination of Debye-Waller factors from x-ray experiments relies on the reduction of atomic scattering factors by Debye-Waller factors. The integrated intensity of a Bragg peak of wave vector $\vec{k}$ from a mosaic crystal is given by

$$I(\vec{k}) = D(\vec{k}) \left| \sum_{\alpha} f_\alpha(k) e^{i\vec{k}\cdot\vec{\tau}_\alpha} e^{-M_\alpha(\vec{k})} \right|^2 , \qquad (1)$$

where f_α is the x-ray scattering factor, τ_α the position vector of the α-type atom, and $e^{-M_\alpha(\vec{k})}$ is the atomic Debye-Waller factor. $D(\vec{k})$ is a slowly varying geometric factor.

The symmetry of a zinc-blende structure implies that the thermal motion is isotropic, so that

$$M_\alpha(\vec{k}) = \tfrac{1}{2}k^2 u_\alpha^2 \quad , \qquad (2)$$

where u_α^2 is the time averaged mean square displacement of the α atom along an arbitrary axis.

Thermal diffuse scattering (TDS) has been neglected in these equations. Approximate TDS corrections were applied directly to the data.

For a zinc-blende structure, the position vectors can be defined such that the phase factor is unity for the Hg atom and some power of i for Te. However, in order to more easily separate the effects of the two Debye-Waller factors, only those reflections were used for which the Te phase factor was ± 1; so the general form for peak intensity is

$$I(k) = D(k) \left| f_{\mathrm{Hg}}(k) e^{-M_{\mathrm{Hg}}(k)} \pm f_{\mathrm{Te}}(k)\, e^{-M_{\mathrm{Te}}(k)} \right|^2 . \quad (3)$$

If the wave vectors corresponding to the various reflections are represented as vector multiples of the basic reciprocal-lattice spacing $(lmn)2\pi/a$, where the l's, m's, and n's are integers, then the sum reflections correspond to wave vectors $(4l, 4m, 4n)$, while the difference reflections correspond to the wave vectors $(2l, 2m, 2n)$, with the sum wave vectors excluded.

To determine the effect of the Debye-Waller factors upon intensity, the temperature dependence of integrated intensity was measured for several reflections from a single crystal of $\mathrm{Hg}_{0.968}\mathrm{Cd}_{0.032}\mathrm{Te}$.[11] The work of Bublik *et al.*[12] indicates that the small degree of Cd alloying should have little effect upon the Debye-Waller factors. A 0.6×1.0×1.2-mm chip was cut approximately on the (001) face and then chemically etched. The sample was then glued to the cooling finger of an Electronics and Alloys x-ray camera in which the flow of liquid nitrogen provided cooling.

Mo K_α radiation was used so that the (006), (008), and (0012) Bragg peaks with relatively large k values could be studied. The sample was realigned at each temperature and adjusted so that the peak profile was symmetric during the angular scanning. The peak was then scanned in ω; that is, the crystal was rotated about the axis of the diffractometer while the detector was held at the Bragg angle.

The resulting temperature dependence of the integrated intensities is shown by the circles in Fig. 1. TDS corrections were applied with the XTDS2 program of Walker and Chipman.[13] Elastic constants were taken from Alper and Saunders.[14] The resulting corrections ranged from 0.15 to 1.4%, and altered the final effective Debye temperatures used to describe the mean square displacements by less than 1%.

To eliminate the dependence of the intensity on the angular factor $D(k)$ of Eq. (1), the data reduction was performed on the ratio of intensities of peaks measured at two temperatures. That is, analysis was performed on the quantity $R(k, T_1, T_2)$ given by the equation

$$R(k, T_1, T_2) = \frac{I(k, T_1)}{I(k, T_2)} = \left| \frac{f_{\mathrm{Hg}} \exp[-\frac{1}{2} u_{\mathrm{Hg}}^2(T_1) k^2] \pm f_{\mathrm{Te}} [-\frac{1}{2} u_{\mathrm{Te}}^2(T_1) k^2]}{f_{\mathrm{Hg}} \exp[-\frac{1}{2} u_{\mathrm{Hg}}^2(T_2) k^2] \pm f_{\mathrm{Te}} [-\frac{1}{2} u_{\mathrm{Te}}^2(T_2) k^2]} \right|^2 \quad (4)$$

To obtain ionic mean square displacements from the experimentally determined R values, it was assumed that the temperature dependence of these displacements is well described by a Debye relation,

$$u_\alpha^2(T) = \frac{3\hbar^2}{M_\alpha k_B} \frac{T}{\Theta_\alpha^2} \left[\Phi\left(\frac{\Theta_\alpha}{T}\right) + \frac{1}{4} \frac{\Theta_\alpha}{T} \right] \quad (5)$$

with a separate temperature-independent Debye temperature Θ_α for each ionic species. Here, M_α is the ionic mass, $\hbar$ is Planck's constant, k_B is Boltzmann's constant, and $\Phi(z)$ is a Debye integral of order one. For T greater than or of the order of Θ, the expression in brackets is quite close to unity. While this expression rests upon the Debye approximation, we note that mean square displacements obtained from sophisticated normal mode eigenvector and eigenvalue calculations are well described by Eq. (5) above low-temperature extremes.[15]

Equation (4) shows that $R(k, T_1, T_2)$ is dependent, when coupled with Eq. (5), on the two Debye temperatures since known atomic scattering factors and the structure determine all other variables. Hence, the Debye temperatures were determined by iterative solutions of pairs of transcendental equations resulting from the combination of Eqs. (4) and (5) with intensity ratios between two temperatures for two peaks. Appendix A gives an analysis indicating that derived parameter errors are minimized by using a sum and a difference peak and by using reflections of large scattering vector.

In these calculations, the real parts of the atomic scattering factors were obtained from the calculations of Cromer and Mann[16] for the neutral free Hg, Cd, and Te atoms. Since the reflections considered involve large values of k, the differences between the scattering factors of the neutral and ionized species are negligible. The factors of Hg and Cd were combined to reflect the alloying. The complex parts of the scattering factors were obtained from the International Tables for X-Ray Crystallography.[17] In the iteration process associated with each pair of equations, a number of initial solutions were attempted to determine the

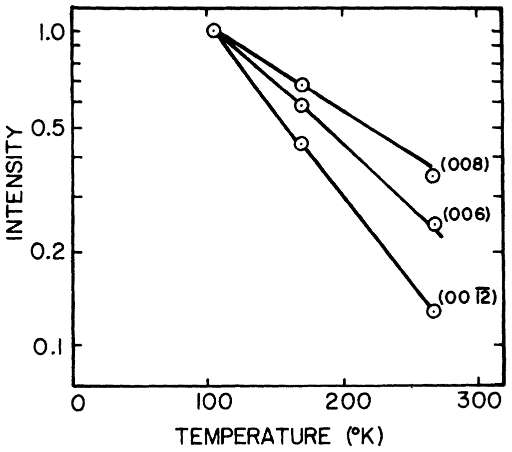

FIG. 1. X-ray diffraction intensities for the (006), (008), and (00$\bar{1}\bar{2}$) reflections of HgTe as a function of temperature. All intensities normalized to 104°K intensities. The circles represent experimental values. The solid lines represent values calculated with derived Debye temperatures.

uniqueness of the solutions. In each case, the iteration process led to the solutions presented in Table I or diverged.

Table I gives the derived parameters for various combinations of peaks and temperatures. Θ_{Hg} varies from 70.5 to 76.6 °K while Θ_{Te} varies from 112 to 136 °K.

Average values are taken of

$$\Theta_{Hg} = (75 \pm 1.5)\,°\mathrm{K} \quad \text{and} \quad \Theta_{Te} = (130 \pm 5)\,°\mathrm{K}\ . \qquad (6)$$

The errors in the temperatures correspond to a 3% error in any experimental intensity.

Figure 1 compares the experimental intensities with those calculated with the Debye temperatures presented above. It is seen that satisfactory agreement is obtained. Figure 2 presents the mean square displacements of Hg and Te, as calculated with Eq. (5), using the parameters presented in Eq. (6).

Much work has been published recently on determination of the separate Debye temperatures for HgTe. Our previous published results[10] are superceded by those presented here.

Skelton, Radoff, Bolsaitis, and Verbalis[18] performed an x-ray experiment which required a complete knowledge of the angular dependence, the $D(k)$ of Eq. (1), but yielded temperature-dependent Debye temperatures. For mercury, the Debye temperature shifts from 63.4 to 86 °K as the sample temperature changes from 32 to 296 °K. The corresponding tellurium values are 89.5 and 127.6 °K. These results are in fairly good agreement with those presented here.

Bublik *et al.*[12,19] used a similar procedure to arrive at values of 75 and 109 °K for the Hg and Te, respectively. Their Debye temperatures are relatively temperature insensitive.

Ivanov-Omskii *et al.*[20] have measured a single average Debye temperature by a method similar to ours. For a pure sample, they determined a Debye temperature of 130 °K. However for a sample with acceptor concentration of 3×10^{18} cm^{-3}, they claim a drop in Debye temperature to 110 °K. This strong impurity dependence may cause some of the disparity in published results.

Vetelino, Gaur, and Mitra[21] have done a theoretical lattice dynamics calculation for HgTe. Their temperature-dependent amplitudes can be well represented by Debye temperatures of 106.4 °K for the Hg and 97.5 °K for the Te. Given the simplicity of their model, the disagreement between their calculation and this experiment, as well as that of Skelton *et al.*,[18] cannot be taken as serious cause for concern about the validity of the experimental conclusions.

Given the reasonable good agreement between the measurements presented here and those of Skelton *et al.*, we tend to believe that the measured Debye-Waller factors are reliable.

III. BROOKS-YU TEMPERATURE DEPENDENCE

The Brooks-Yu[1,2] theory provides a straightforward method of calculating temperature-dependent eigenenergies. If the zero-temperature electronic energies are calculated as a function of a weak potential or pseudopotential

$$E(\vec{k}) = E(\vec{k}, \{w_\alpha(\vec{G})\}) \ , \qquad (7)$$

TABLE I. Debye temperatures (in °K) for Hg and Te ions in HgTe derived from x-ray experiment. Two Bragg reflections at two temperatures were used for each set of values. These pairs are given on the left-hand side. The bottom line gives Debye temperatures derived from a single reflection at three temperatures.

	Θ_{Hg}	Θ_{Te}
267–170 °K (006)–(008)	70.5	112.2
170–104 °K (006)–(008)	75.7	131.9
267–104 °K (006)–(008)	72.5	118.9
267–170 °K (006)–(00$\bar{1}\bar{2}$)	74.7	127.4
170–104 °K (006)–(00$\bar{1}\bar{2}$)	76.6	136.1
267–104 °K (006)–(00$\bar{1}\bar{2}$)	75.5	130.6
267–170–104 °K (006)	71.5	114.0

where $\{w_\alpha(\vec{G})\}$ represents the complete set of Fourier components of the ionic potentials or pseudopotentials, then the Brooks-Yu temperature dependence is calculated by reducing each Fourier component by the Debye-Waller factors associated with the respective ion,

$$E(\vec{k}, T) = E(\vec{k}, \{w_\alpha(\vec{G})\, e^{-M_\alpha(\vec{G})}\}) \quad . \tag{8}$$

The Debye-Waller factor is the same factor used in x-ray scattering theory,

$$M_\alpha(\vec{G}) = \tfrac{1}{2}\langle |\vec{u}_\alpha(T)\cdot\vec{G}|^2\rangle \quad , \tag{9}$$

where a time average is taken of the temperature-dependent vibration.

The Brooks-Yu theory does not describe all temperature effects. The thermal expansion effects are accounted for below. The self-energy terms of coupling of electron-phonon states are described in Sec. IV. The Brooks-Yu theory represents a time average of energies in a distorted lattice. To obtain the simple result, multiple scattering terms and terms corresponding to x-ray thermal diffuse scattering are neglected. The condition of small potential necessitates working within the pseudopotential formalism.

Let us briefly describe the band structure of HgTe before pursuing its temperature dependence. HgTe has a zinc-blende crystal structure common to many group-IV, -III-V, and -II-VI semiconductors. However, its electronic band structure differs from almost all of these in that its Γ_6 level is depressed to an energy between the spin-split Γ_7 and Γ_8 levels as indicated in Fig. 3. At zero temperature, the intrinsic Fermi level lies at the double (quadruply including all spin states) degenerate Γ_8. Thus the true band gap is zero by symmetry considerations, and HgTe is a semimetal.

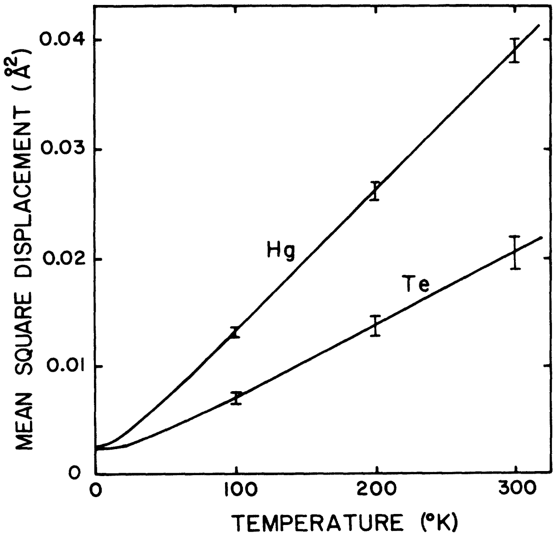

FIG. 2. Temperature-dependent mean square displacements for the two atomic species in HgTe calculated according to Debye formula with derived Debye temperatures. The error bars represent a 3% error in any intensity.

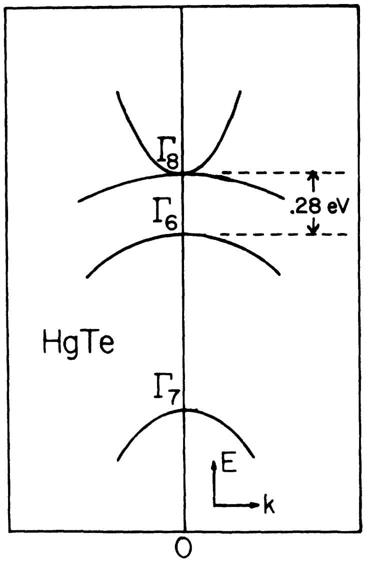

FIG. 3. Electronic band structure for HgTe near the zone center. The intrinsic zero-temperature Fermi level lies at Γ_8.

The Γ_6-Γ_8 separation is referred to as the negative band gap in analogy to the positive gap between these two bands in many zinc-blende semiconductors;

$$E_g(\text{HgTe}) = E(\Gamma_6) - E(\Gamma_8) = -|E_g| \quad . \tag{10}$$

Recent work[22-24] has determined the band gap to be near the value

$$E_g = -0.28 \text{ eV} \quad . \tag{11}$$

The temperature coefficient of this negative gap is more uncertain, with estimates for $d|E_g|/dT$ ranging from -3.6×10^{-4} [22,23] to -8.5×10^{-4} eV/°K.[24] The most reliable result is probably that of Pidgeon and Groves[25] which, in the temperature range 60–77 °K, is

$$\frac{d|E_g|}{dT} = -6.1\times10^{-4} \text{ eV/°K} \quad . \tag{12}$$

The effect of thermal expansion can be accounted for explicitly using the relation

$$\frac{dE_g}{dT} = \left.\frac{\partial E_g}{\partial T}\right|_V + \left.\frac{\partial E_g}{\partial V}\right|_T \frac{dV}{dT} \quad . \tag{13}$$

The second set of terms can be expressed in terms of the lattice temperature coefficient α, the bulk modulus B, and the experimentally observed pressure dependence of the band gap;

$$\left.\frac{\partial E_g}{\partial V}\right|_T \frac{dV}{dT} = -3\alpha B \left.\frac{\partial E_g}{\partial P}\right|_T . \qquad (14)$$

Measured[14,24,26] values of these parameters yield a maximum dilatational effect of $+7\times10^{-5}$ eV/°K, which is an order of magnitude smaller than the observed temperature dependence.

The temperature coefficient for the band gap is obtained by calculating the temperature-dependent band energies according to Eq. (8). The Debye temperatures given in Eq. (6) are used to calculate the ionic mean square displacements according to Eq. (5). However the second term in Eq. (5), the zero point motion term, was excluded in order to force agreement at zero temperature with the non-temperature-dependent band structure calculations. As long as we consider only high-temperature behavior, i.e., above the Debye temperature, the difference is small.

To obtain ionic pseudopotentials, we started with the sum $(w_A + w_B)$ and difference $(w_A - w_B)$ pseudopotentials obtained for HgTe by Bloom and Bergstresser (BB).[27] Their calculated band structure agrees qualitatively with the relativistic Korringa-Kohn-Rostoker (KKR) calculation of Overhof,[28] although some calculated gaps differ by up to factors of two. Ambiguities associated with the atomic species to be associated with A and B and loss of data owing to sums or differences rendered unnecessary by symmetry were resolved by a rederivation of BB's initial estimates of the pseudopotentials from data for each of the two species.

Calculation of the relevant aspects of the band structure at each temperature from the ionic pseudopotentials and the Debye-Waller factors was accomplished through a computer program prepared by us. This program is essentially identical, in its mathematical and numerical analysis, to that used by BB. It does, however, allow for automatic treatment of the Debye-Waller effects on all terms, including the appropriate spin-orbit parameters, given the effective ionic Debye temperatures and the temperatures at which the band structure is to be calculated.

The resultant calculated temperature coefficient of the HgTe negative gap, in the temperature range 0–300 °K, is

$$\frac{\partial |E_g|}{\partial T} = +2.7\times10^{-4}\ \mathrm{eV/°K} . \qquad (15)$$

This result is about half the right magnitude but of the wrong sign.

It will help in discussions of the validity of this result to consider some results that generalize on the calculated temperature dependence. The temperature coefficient of the band gap is deduced from the variations of the Γ point energies with temperature. The temperature-dependent band energies are shown in Fig. 4.

An informative result possible with the Brooks-Yu approach is to calculate the bands as a function of arbitrary mean square displacement. We define two variables: One, S, is the sum of mean square displacements of the two species,

$$S = u_{\mathrm{Hg}}^2 + u_{\mathrm{Te}}^2 , \qquad (16)$$

while the other is the fraction of this sum arising from Te motion,

$$\zeta = u_{\mathrm{Te}}^2/(u_{\mathrm{Hg}}^2 + u_{\mathrm{Te}}^2) . \qquad (17)$$

This decomposition is made because S is more accurately determined than ζ. The levels's dependences upon arbitrary amplitude are given in Fig. 5. S_0 is the amplitude sum at 104 °K determined by the x-ray experiments. The experimentally determined fraction is $\zeta = 0.32$. The horizontal lines are the zero temperature bands, i.e., $S = 0$.

We see a strong linear dependence, which can be shown to be equivalent to a linear dependence upon u_{Hg}^2 and u_{Te}^2; that is, the Brooks-Yu temperature effect is, to a good approximation, a first-order expansion about the zero-temperature bands. Also, the independence of Γ_7 and Γ_8 from Hg motion, and the relatively strong dependence upon Te motion is in agreement with the association of these levels with Te atomic states. This is a general association in the III-V and II-VI compounds and does not depend on the fine structure of the potential. It does not, therefore, prove the validity of the potential.

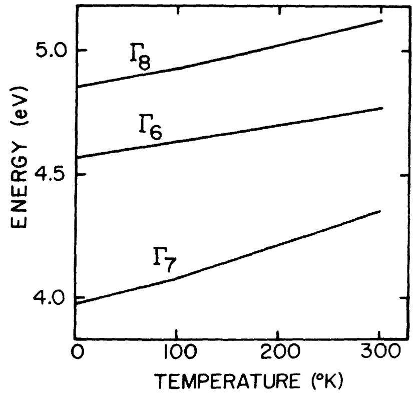

FIG. 4. Temperature-dependent band energies of HgTe at the zone center calculated according to the Brooks-Yu theory. The zero of energy scale results from a zero $V(k=0)$.

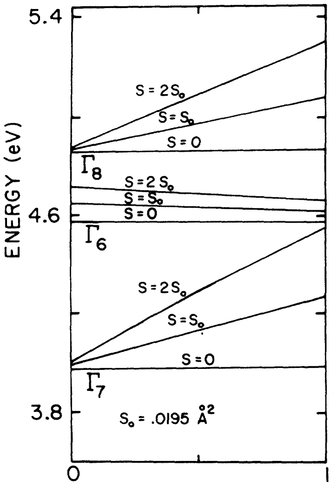

FIG. 5. Dependence of HgTe zone center on arbitrary mean square amplitudes of the ions. Calculated with Brooks-Yu theory. S represents the sum of Hg and Te mean squared amplitudes. ζ is fraction of this sum arising from Te motion. S_0 is our x-ray determined value at 104 °K. $\zeta = 0.32$ is our experimental fraction.

The disagreement between the experimental and calculated values of the temperature coefficient is very serious. There are three possible causes for the discrepancy: (a) inaccuracies of the Debye-Waller factors; (b) inaccuracies in the pseudopotential; (c) inadequacy of the Brooks-Yu theory. The first two of these are discussed immediately below, and the third in Sec. VI.

To determine the sensitivity of the calculation to the Debye-Waller factors, the data in Fig. 5 have been used to determine the values which would give the correct change of the gap between 0 and 100 °K for S equal to S_0 and $2S_0$. These are $\zeta = 0.19$ and 0.12, respectively. These correspond to values of $u^2_{\mathrm{Hg}}/u^2_{\mathrm{Te}}$ equal to 4.3 and 7.3, respectively, at 100 °K. Since the value of S_0 is considered to be quite reliable, it would appear as if the ratio must be significantly larger than 4.3, and close to 7.3, to obtain agreement with experiment through alteration of the Debye-Waller factors. Such a ratio seems unlikely on physical grounds and disagrees strongly with all estimates presented thus far. Hence we do not feel that the Debye-Waller factors are the source of the discrepancy.

The zero-temperature pseudopotential calculation which we use as a base for our calculation has serious shortcomings. Bloom and Bergstresser[27] have used a truncated local pseudopotential in their calculation. Examination of their ionic pseudopotentials show a good correspondence with Animalu and Heine's[29] ionic pseudopotentials for those form factors used. However BB truncate their pseudopotential at a wave vector less than that corresponding to the positive maxima of Animalu and Heine's results. This neglect is especially serious in a Debye-Waller-type form factor reduction since, as pointed out by Shay,[30] the large wave vector components suffer a much stronger temperature reduction.

A more general criticism of this band structure calculation is the local approximation for the non-spin-orbit pseudopotential, i.e.,

$$\langle \vec{k}_1 | w | \vec{k}_2 \rangle = w(|\vec{k}_1 - \vec{k}_2|) \ . \qquad (18)$$

If we use a Slater-type approximation for the core states, $R_{nl} \propto r^{n-1} e^{-\rho r}$, the core partition is expressible in analytic form. It can then be shown that the pseudopotential is local in the sense of Eq. (18) only for small values of $|\vec{k}_1|$ and $|\vec{k}_2|$. To determine the meaning of small, we used an optimized pseudopotential with zero conduction level energy. Herman and Skillman's[31] tables were used for the radii and energies of the core states. It was found that if the matrix elements were required for only small wave vectors, $k < 2.5$ Å^{-1}, then the partition of core s states dominates, and in this region the s partition is mostly local. However, for large wave vectors, the p, d, and f partitions dominate. These partitions have significant nonlocal contributions, with the nonlocality increasing with wave vector.

Thus only for small wave vectors is the local approximation valid. Selection of a nonoptimized pseudopotential to emphasize the s partition would not solve the problem since such a pseudopotential would need more basis states, i.e., larger wave vectors, and the s partition goes nonlocal for large wave vectors, approximately corresponding to the core state radius.

In the HgTe pseudopotential band gap calculation, the states of interest arise mainly from the $\langle 111 \rangle$ pseudo-plane waves for which $k = 1.7$ Å^{-1}. Therefore the interaction among these states, and also with the $\langle 002 \rangle$ states, is reasonably local, but matrix elements involving any other basis state are not properly local. BB's calculation includes basis states extending out to $k = 4.8$ Å^{-1}. The extension of the basis set beyond that of a very simple calculation is valid only if the pseudopotential is made nonlocal.

Hence, it is possible that the source of the discrepancy between theory and experiment is due to inaccuracies of the pseudopotential. In the course of this research, we learned that other pseudopotentials were being derived by another group and that these pseudopotentials would be used with the Brooks-Yu theory. Rather than duplicate their efforts, we turned our attention to the self-energy terms.

IV. SELF-ENERGY CONTRIBUTIONS

We have already noted that some electronic temperature effects have been neglected in the Brooks-Yu[1] theory. One of these is the self-energy of an electron in phonon field. This effect was the basis of Fan's[7] attempt to explain the temperature dependences of band gaps. However, Fan's results have not been rigorously calculated, and the approximations used limit the theory's applicability.

In this section, we will give a more general expression for the self-energy term than previously used. The resulting expression is involved, but by using the result from Appendix B for evaluation of deformation potential matrix elements and by restricting the interaction to normal phonon processes, one can calculate the self-energy contribution for a well characterized material. We also show that by calculating only the electronic band structure of a material we can determine the sign of this contribution. For HgTe, the sign is shown to be such that the magnitude of the gap decreases, i.e., opposite to the Brooks-Yu effect as calculated in Sec. III.

Fan wrote the second-order perturbation energy of all electrons in a crystal with the electron-phonon interaction, ΔV, as

$$\Delta E = \sum_{k\sigma} \sum_{q\sigma'} \frac{|\langle \psi(k \pm q, \sigma')\chi(n_q \mp 1)|\Delta V|\psi(k,\sigma)\chi(n_q)\rangle|^2}{\epsilon(k,\sigma) - \epsilon(k \pm q, \sigma') \mp \hbar\omega_q} \quad . \tag{19}$$

$\psi(k,\sigma)$ is the one-electron state with wave vector k in band σ. $\chi(n_q)$ is the phonon state of n_q quanta of energy $\hbar\omega_q$. $\epsilon(k,\sigma)$ is the zero-temperature electronic energy. The summation (k,σ) is over occupied electron states. The summation (q,σ') is over unoccupied states.

Fan identified the thermal band-gap change with the change of energy of Eq. (19) by promoting an electron across the band gap, i.e., by reevaluating Eq. (18) with a different occupation set. If the valence maximum and conduction minimum states are denoted by (k_v, v) and (k_c, c), respectively, the self-energy contribution to thermal change of band gap is

$$\begin{aligned}\Delta E_g = &\sum_{q\sigma'} \frac{|\langle \psi(k_c \pm q, \sigma')\,\chi(n_q \mp 1)|\Delta V|\psi(k_c, c)\,\chi(n_q)\rangle|^2}{\epsilon(k_c, c) - \epsilon(k_c \pm q, \sigma') \pm \hbar\omega_q}\\ &- \sum_{k\sigma} \frac{|\langle \psi(k \pm q = k_c, c)\chi(n_q \mp 1)|\Delta V|\psi(k,\sigma)\chi(n_q)\rangle|^2}{\epsilon(k,\sigma) - \epsilon(k \pm q = k_c, c) \pm \hbar\omega_q} - \sum_{q\sigma'} \frac{|\langle \psi(k_v \pm q, \sigma')\chi(n_q \mp 1)|\Delta V|\psi(k_v, v)\chi(n_q)\rangle|^2}{\epsilon(k_v, v) - \epsilon(k_v \pm q, \sigma') \pm \hbar\omega_q}\\ &+ \sum_{k\sigma} \frac{|\langle \psi(k \pm q = k_v, v)\chi(n_q \mp 1)|\Delta V|\psi(k,\sigma)\chi(n_q)\rangle|^2}{\epsilon(k,\sigma) - \epsilon(k \pm q = k_v, v) \pm \hbar\omega_q} \quad .\end{aligned} \tag{20}$$

We will avoid Fan's approximation of eliminating all interband terms, $\sigma_1 \neq \sigma_2$. As Keffer, Hayes, and Bienenstock[4] pointed out, the effect of the energy denominator for interband terms for narrow gap semiconductors is not necessarily larger than for intraband terms. In evaluating Eq. (20) for HgTe, we believe four bands a minimum for the set of interacting states.

The light Γ_8 band is the conduction band while the Γ_6 band is the valence band of this discussion. The heavy Γ_8 band is a necessary addition arising from the semimetal character of HgTe. The remaining band Γ_7 is split from Γ_8 at the zone center only by spin-orbit interaction and is close to the valence band. We will use this four-band approximation and the approximation that the Γ_7, Γ_6, and $\Gamma_{8,\text{heavy}}$ band are full while the $\Gamma_{8,\text{light}}$ band is empty. This occupation set is inaccurate for an undoped sample only where the Γ_8 bands are within kT of each other. We will suppress the labeling of phonon states and the distinction between addition and subtraction of phonon momentum. Bands will be denoted by simple digits: $\Gamma_7 = 1$, $\Gamma_6 = 2$, $\Gamma_{8,\text{heavy}} = 3$, and $\Gamma_{8,\text{light}} = 4$. The result for the change in magnitude of the HgTe band gap is given by

$$\begin{aligned}\Delta E_g = \sum_k \Bigg(&- \frac{|\langle \psi(k,4)|\Delta V|\psi(0,4)\rangle|^2}{\epsilon(k,4) - \epsilon(0,4) - \hbar\omega_k} - \frac{|\langle \psi(0,2)|\Delta V|\psi(k,2)\rangle|^2}{\epsilon(0,2) - \epsilon(k,2) - \hbar\omega_{-k}} + \frac{|\langle \psi(0,4)|\Delta V|\psi(k,2)\rangle|^2}{\epsilon(0,4) - \epsilon(k,2) - \hbar\omega_{-k}}\\ &+ \frac{|\langle \psi(k,4)|\Delta V|\psi(0,2)\rangle|^2}{\epsilon(k,4) - \epsilon(0,2) - \hbar\omega_k} + \frac{|\langle \psi(0,4)|\Delta V|\psi(k,3)\rangle|^2}{\epsilon(0,4) - \epsilon(k,3) - \hbar\omega_{-k}} + \frac{|\langle \psi(0,2)|\Delta V|\psi(k,3)\rangle|^2}{\epsilon(k,3) - \epsilon(0,2) + \hbar\omega_{-k}}\\ &+ \frac{|\langle \psi(0,4)|\Delta V|\psi(k,1)\rangle|^2}{\epsilon(0,4) - \epsilon(k,1) - \hbar\omega_{-k}} - \frac{|\langle \psi(0,2)|\Delta V|\psi(k,1)\rangle|^2}{\epsilon(0,2) - \epsilon(k,1) - \hbar\omega_{-k}} \Bigg) \quad .\end{aligned} \tag{21}$$

If the curvatures are simply given by Fig. 3, if the phonon energy is negligible, and if band energies are not degenerate aside from Γ_8, then the signs of the contributions are as given. We can identify the first two terms as Fan's intraband terms; the second pair, as Keffer, Hayes, and Bienenstock's positive interband contribution (KHB term). The third pair give a positive contribution from the semimetal band. The last pair arise from the extra band and has both positive and negative parts as will any other band far reremoved from the band gap, whether above or below.

If we use the result from Appendix B for normal phonon processes, the matrix element of the deformation potential is

$$\langle\psi(0,i)|\Delta V|\psi(\vec{k},j)\rangle = i\,\frac{a_{ji}(\vec{k})}{N}\sum_{\alpha s}\delta\vec{R}_\alpha(\vec{k},s)\cdot\vec{k}v_\alpha(\vec{k})\ , \tag{22}$$

where $v_\alpha(k)$ is the Fourier component of the potential of the α-type ion, $\delta\vec{R}_\alpha(k,s)$ is the Fourier component of the thermal displacement of the α-type ion in the s mode, $\delta\vec{R}$ describes the phonon system, and $a_{ji}(\vec{k})$ is the projection of the Bloch function $u_j(\vec{k},r)$ upon the zone center, $k=0$, Bloch function $u_i(r)$.

Then in the normal process approximation, the self-energy contribution to thermal band change is

$$\Delta E_g = \sum_k \frac{1}{N^2}\left|\sum_{\alpha,s}\delta\vec{R}_\alpha(\vec{k},s)\cdot\vec{k}v_\alpha(\vec{k})\right|^2\cdot H(\vec{k})\ , \tag{23}$$

where $H(\vec{k})$ is the eightfold sum corresponding to the terms in Eq. (21);

$$\begin{aligned} H(\vec{k}) = &-\frac{|a_{44}(k)|^2}{\epsilon(k,4)-\epsilon(0,4)-\hbar\omega_k}-\frac{|a_{22}(k)|^2}{\epsilon(0,2)-\epsilon(k,2)-\hbar\omega_{-k}}+\frac{|a_{24}(k)|^2}{\epsilon(0,4)-\epsilon(k,2)-\hbar\omega_{-k}}+\frac{|a_{42}(k)|^2}{\epsilon(k,4)-\epsilon(0,2)-\hbar\omega_k} \\ &+\frac{|a_{34}(k)|^2}{\epsilon(0,4)-\epsilon(k,3)-\hbar\omega_{-k}}+\frac{|a_{32}(k)|^2}{\epsilon(k,3)-\epsilon(0,2)+\hbar\omega_{-k}}+\frac{|a_{14}(k)|^2}{\epsilon(0,4)-\epsilon(k,1)-\hbar\omega_{-k}}-\frac{|a_{12}(k)|^2}{\epsilon(0,2)-\epsilon(k,1)-\hbar\omega_{-k}}\ . \end{aligned} \tag{24}$$

The quantities δR_α and v_α are often available for well characterized materials. For HgTe, the phonon modes have never been measured and the factor between the bars in Eq. (23) must remain unknown. However, since the magnitude squared is always positive, the sign of each term in the summation over $\vec{k}$ is determined by the sign of $H(\vec{k})$.

$H(\vec{k})$ is determined by the electronic eigenstates and their eigenenergies and can thus be determined by any band structure and associated eigenvector calculation. If the calculation is done by the $\vec{k}\cdot\vec{p}$ method, the expansion coefficients are immediately available from the solution of equations for the energies $\epsilon(k,\sigma)$.

We have attempted such a $\vec{k}\cdot\vec{p}$ calculation for HgTe. The four-band model of Kane[32] yields a very poor band structure. Gorzkowski's[33] model has seven bands but contains more atomic parameters than are experimentally available. We were guided by Bloom and Bergstresser's[27] band energies at the zone center and found that interband atomic matrix elements needed to be as large as intraband elements to assure sufficient interaction yielding the usual type of curvature. Around the zone center $\vec{k}\cdot\vec{p}$ energies compare favorably with those calculated by BB and by Overhof.[28] However, owing to the severely truncated basis set of seven states, away from the zone center the quality rapidly deteriorates, and the bands are much too wide.

Nonetheless we used this calculation to evaluate the separate parts of $H(\vec{k})$ as defined in Eq. (24). The phonon energy was set at a constant 0.01 eV. The calculation was made along the Γ-X symmetry axis. The results are given in Fig. 6 and are weighted by k^2 to simulate the contributions from the entire Brillouin zone. The labeling is as in the description of the generalized Fan theory. The semimetal term has an integrable singularity and change of sign owing to degeneracy with the valence band maximum.

We note that the KHB term in Eq. (24) is larger than the original Fan term. Also, the extra term is larger than the sum of the Fan and KHB terms.

The sum of these eight terms is negative except at the unimportant semimetal singularity. We have been calculating the thermal change in the magnitude of the gap so this result yields an effect opposite in sign to that calculated for the Brooks-Yu theory, and with the same sign measured experimentally.

We must emphasize that we have not calculated the magnitude of this effect and so have no idea if it would balance off the Brooks-Yu terms. In addition, the Umklapp terms, which could be important, have been neglected. Nonetheless, this agreement in sign makes the self-energy contribution worthy of a more detailed calculation. For reasons discussed immediately below, however, that calculation will not be without difficulties.

The significant contribution of the interband matrix elements calls to question the limitation

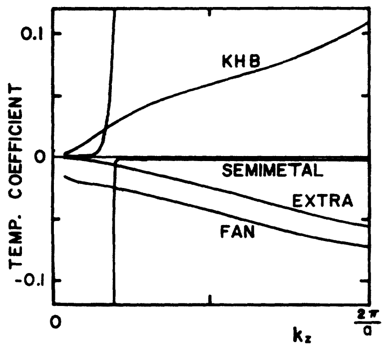

FIG. 6. Temperature coefficient for magnitude of HgTe band gap of the form of Eq. (24) weighted by $(ka/2\pi)^2$. Calculated along the Γ-X symmetry axis. Units for temperature coefficient are $(\mathrm{eV})^{-1}$.

of the summations to the bands close to the gap. We show that it is probably necessary to include all bands in the self-energy summation.

Consider a typical matrix element in Eq. (19):

$$\frac{|\langle\psi(k\pm q,\sigma')|\Delta V|\psi(k,\sigma)\rangle|^2}{\epsilon(k,\sigma)-\epsilon(k\pm q,\sigma')\mp\hbar\omega_q} \; . \tag{25}$$

For longitudinal acoustic mode scattering, the numerator varies roughly with q as[7]

$$|\langle\psi(k\pm q,\sigma')|\Delta V|\psi(k,\sigma)\rangle|^2 \propto q^2 n_q/\omega_q \; . \tag{26}$$

Taking $\omega_q \propto q$, this means

$$|\langle\psi(k\pm q,\sigma')|\Delta V|\psi(k,\sigma)\rangle|^2 \propto q n_q \underset{\sim}{\propto} q^0 \; . \tag{27}$$

Now, switching to an extended zone scheme for simplicity, it is easily seen that the denominator varies, for large q, as q^2. It should be noted however, that the number of final states in a spherical shell of radius q around the initial state also varies as q^2. Hence, each such spherical shell will yield roughly the same contribution to the interband summation of Eq. (20). Hence, it would appear as if there is no justification for neglecting bands, which are quite separated in energy from the gap in the summation of Eq. (20).

On the other hand, it should be noted that any such spherical shell interacts with both the conduction and valence bands in Eq. (20). Moreover, the contributions of the corresponding terms are of opposite sign. Hence, these terms tend to cancel. Nevertheless, the completeness of the cancellation remains to be determined.

This analysis indicates that a complete study of the self-energy terms would involve a great deal more effort than any published so far.

SUMMARY AND CONCLUSIONS

In this work, we have measured the ionic Debye-Waller factors in HgTe and combined them with the BB pseudopotential to calculate the temperature dependence of the band gap within the Brooks-Yu theory. That calculation yielded a temperature dependence which is approximately one-half the magnitude and of the opposite sign of the experimental result.

In an effort to understand this discrepancy, we have examined the sensitivity of the calculation to the Debye-Waller factors and find they are not the cause. Our measured values are sufficiently close to others obtained recently by different experiments or calculation so that they are not sufficiently in doubt to be considered a cause of the discrepancy.

Our examination of the pseudopotential, on the other hand, leads to some concern about its validity, especially for this type of calculation in which the large reciprocal lattice vector components are most changed with temperature. Hence, the inadequacy of the pseudopotential *may* be a cause of the failure.

We note after some calculation, though, that the discrepancy may be due to inadequacies of the Brooks-Yu theory, both in its approximations and in the neglect of the self-energy terms. Our simple calculation, which includes only normal processes and considers only the valence and lowest conduction bands explicitly, yields a sign agreeing with experiment. Unfortunately, we have not been able to determine the magnitude of these terms.

Finally, we note that all published self-energy-type calculations have neglected interband terms which, our calculations and analysis show, must be included.

We conclude, therefore, that our understanding of the temperature dependence of semiconductor band gaps is somewhat weaker than many are claiming on the basis of moderate agreement with experiment.

We end this paper with the feeling that the pseudopotential problem should have been further explored, leading to a more valid potential and that the self-energy term should have been calculated more completely. In the end, it seemed best to leave these problems to those who are more prepared for the extensive calculations required.

APPENDIX A: OPTIMIZATION OF DEBYE-WALLER EXPERIMENT

We wish to establish which experimental conditions will minimize the effect of intensity inaccuracies upon derived Debye-Waller factors in the x-ray experiment in which the intensities of Bragg reflections are measured at two temperatures and then the Debye-Waller factors are numerically fit to a series of ratios of intensities at the two temperatures. For our sum and difference reflections in a zinc-blende structure, the intensity ratio depends on the Debye-Waller factors as in Eq. (A1.1);

$$\frac{I(\theta, T_1)}{I(\theta, T_2)} = \left| \frac{f_x e^{-M_x(\theta, T_1)} \pm f_y e^{-M_y(\theta, T_1)}}{f_x e^{-M_x(\theta, T_2)} \pm f_y e^{-M_y(\theta, T_2)}} \right|^2 . \qquad \text{(A1)}$$

θ and T denote the Bragg angle and temperature, respectively. The f's are angle-dependent x-ray scattering factors. The M's are the ionic Debye-Waller factors, depending on both angle and temperature. The choice of sign depends on type of reflection. The two atomic types are represented by x and y.

The variables in the Debye-Waller factor are separable;

$$M_x(\theta, T) = \psi u_x^2(T) , \qquad \text{(A2)}$$

where we have defined the angular variable ψ,

$$\psi = 8\pi^2 \sin^2\theta/\lambda^2 . \qquad \text{(A3)}$$

We will restrict ourselves to the high temperature limit (of the order of the Debye temperature or above) so the mean squared amplitude u^2 is proportional to temperature. The temperature-reduced scattering factor is given by $f_x(\psi)e^{-B_x T\psi}$. The experiment thus determines the temperature coefficient B for each atomic type.

If we restrict the experiment to temperatures for which the scattering amplitude does not change sign, that is, we avoid regions in which the temperature-reduced scattering factors cancel for a difference peak, then the intensity ratio equations can be expressed as

$$\left(\frac{I(\psi, T_1)}{I(\psi, T_2)} \right)^{1/2} = \frac{f_x e^{-B_x T_1 \psi} \pm f_y e^{-B_y T_1 \psi}}{f_x e^{-B_x T_2 \psi} \pm f_y e^{-B_y T_2 \psi}} . \qquad \text{(A4)}$$

Now define variables describing the fraction of scattering amplitude arising from each species:

$$S_x(\psi, T) = \frac{f_x e^{-B_x T \psi}}{f_x e^{-B_x T \psi} \pm f_y e^{-B_y T \psi}} , \qquad \text{(A5)}$$

$$S_y(\psi, T) = \pm \frac{f_y e^{-B_y T \psi}}{f_x e^{-B_x T \psi} \pm f_y e^{-B_y T \psi}} , \qquad \text{(A6)}$$

where S_y has included an over-all sign depending on type of reflection. The square root of the intensity ratio equals the sum of S_x and S_y.

Now introduce small variations b_x and b_y in the proportionality constants B_x and B_y. These variations correspond to a fractional increase η in the left-hand side of Eq. (A4). If the right-hand side of Eq. (A4) is then expanded to first order in the parameter variations, these error quantities are related by

$$\eta = b_x [T_2 \psi S_x(\psi, T_2) - T_1 \psi S_x(\psi, T_1)] + b_y [T_2 \psi S_y(\psi, T_2) - T_1 \psi S_y(\psi, T_1)] . \qquad \text{(A7)}$$

Equation (A7) could be used directly to relate intensity errors to parameter errors, but interpretation is eased if we make the approximation that the S's are temperature independent, i.e., each species contributes a constant fraction of the scattering amplitude. Two equations of this type for reflections at ψ_a and ψ_b can be easily solved to yield

$$b_x = \frac{1}{T_2 - T_1} \frac{1}{S_x(\psi_a)S_y(\psi_b) - S_y(\psi_a)S_x(\psi_b)} \times \left(\eta_a \frac{S_y(\psi_b)}{\psi_a} - \eta_b \frac{S_y(\psi_a)}{\psi_b} \right) \qquad \text{(A8)}$$

with an analogous equation for b_y.

If we accept the intensity errors η as given, then variation in the derived parameter is minimized by using a large temperature difference and a large ψ which corresponds to high-order reflections.

The S's are larger for a difference reflection. The S denominators can be made larger by making one S_y positive and the other negative, that is, one sum and one difference reflection.

APPENDIX B: DEFORMATION POTENTIAL MATRIX ELEMENTS

In this appendix, we will derive an expression for the deformation potential matrix element between one-electron states. The final result will be in terms of Bloch functions, phonon eigenstates, and atomic potentials. If the normal phonon process approximation is made, the result greatly simplifies. Detailed knowledge of the Bloch functions is not then needed.

The deformation potential is the increase in the local potential caused by the displacement of the ions from their equilibrium positions. The rigid ion, one-electron deformation potential is a sum of displaced ionic potentials with the equilibrium potential subtracted out. Let vector notation be understood in this appendix. To first order in displacements, the deformation potential ΔV is given by

$$\Delta V(r) = - \sum_{j\alpha} \delta R_{j\alpha} \cdot \nabla v_\alpha (r - R_j - \tau_\alpha) . \qquad \text{(B1)}$$

This includes a summation over the lattice sites R_j and a summation over the atoms located at τ_α within the unit cell. v_α is the atomic potential of that atom or ion. $\delta R_{j\alpha}$ is the displacement of the (j, α) ion.

We immediately take Fourier transforms. The transform of the potential is continuous and normalized by the unit cell volume Ω_0. For a crystal, the transform of the displacement is a discrete sum over reduced wave vector q and phonon branch s and is normalized by the number of lattice sites N. The spatial differentiation is easily performed on the Fourier transform

$$\Delta V(r)=i\frac{\Omega_0}{N(2\pi)^3}\sum_{j\alpha}\sum_{qs}\delta R_\alpha(q,s)e^{-iq(R_j+\tau_\alpha)}$$
$$\times\int d^3k\,kv_\alpha(k)e^{-ik(r-R_j-\tau_\alpha)}\;. \qquad \text{(B2)}$$

The sum over lattice sites is sharply peaked at values of the reciprocal lattice vectors $\{G\}$. As long as the rest of the integrand varies slowly on a scale of $k=2\pi(N\Omega_0)^{-1/3}$ we may make the substitution,

$$\sum_j e^{-ikR_j}=\frac{(2\pi)^3}{\Omega_0}\sum_G\delta(k-G)\;, \qquad \text{(B3)}$$

where δ is the three-dimensional Dirac δ function. The integral is thus transformed to a summation, and the final form of the deformation potential is

$$\Delta V(r)=\frac{i}{N}\sum_{qs}\sum_G\sum_\alpha\delta R_\alpha(q,s)\cdot(q+G)$$
$$\times v_\alpha(q+G)e^{iG\tau_\alpha}e^{-i(q+G)r}\;. \qquad \text{(B4)}$$

The general matrix element of the deformation potential is

$$\langle\psi_{2,k_2}|\Delta V|\psi_{1,k_1}\rangle\;, \qquad \text{(B5)}$$

where ψ_{1,k_1} is a one-electron eigenfunction of reduced wave vector k_1 located in energy band 1. Now express the electronic state in terms of a Bloch function,

$$\psi_{1,k_1}=u_1(k_1,r)e^{ik_1r}\;. \qquad \text{(B6)}$$

The integral implied by the matrix element of (B5) is over all space, but let us split it into a sum of integrals over unit cells (u. c.);

$$\langle\psi_{2,k_2}|\Delta V|\psi_{1,k_1}\rangle=\sum_{R_j}\int_{\text{u.c.}}d^3r\,u_2^*(k_2,r)u_1(k_1,r)$$
$$\times\Delta V(r+R_j)e^{i(k_1-k_2)(r+R_j)} \qquad \text{(B7)}$$

The extra R_j term has dropped from the u_1 because of the Bloch function's periodicity. The form for $\Delta V(r+R_j)$ is available from Eq. (B4). There result factors of the form $e^{i(k_1-k_2-q)R_j}$. The phonon wave vector, q, has been restricted to the first Brillouin zone. k_1-k_2 can have values in the second Brillouin zone, but this exponential term is simply summed over lattice sites R_j and thus results in a δ function of k_1-k_2-q if k_1-k_2 is assumed reduced to the first zone. The matrix element becomes

$$\langle\psi_{2,k_2}|\Delta V|\psi_{1,k_1}\rangle=i\sum_G\int_{\text{u.c.}}d^3r\,u_2^*(k_2,r)u_1(k_1,r)e^{iGr}$$
$$\times\sum_{s\alpha}\delta R_\alpha(k_1-k_2,s)\cdot(k_1-k_2+G)v_\alpha$$
$$\times(k_1-k_2+G)e^{iG\tau_\alpha}\;. \qquad \text{(B8)}$$

Let us now specialize to the case for which k_2 is zero and then expand the other electronic Bloch function in terms of the zone center, $k=0$, Bloch functions;

$$u_j(k,r)=\sum_n a_{jn}(k)u_n(r)\;. \qquad \text{(B9)}$$

The final rigorous result becomes

$$\langle\psi_{i0}|\Delta V|\psi_{jk}\rangle=i\sum_n a_{jn}(k)\sum_G\int_{\text{u.c.}}d^3r\,u_i^*(r)u_n(r)e^{iGr}$$
$$\times\sum_{s\alpha}\delta R_\alpha(k,s)\circ(k+G)v_\alpha(k+G)e^{iG\tau_\alpha}\;. \qquad \text{(B10)}$$

If we restrict the result to normal phonon processes, i.e., $G=0$, the spatial integral of the Bloch functions becomes an overlap integral, aside from a factor of N, between the zone center Bloch functions, which are identical to the orthogonal electronic eigenstates. The normal approximation for the deformation potential matrix element becomes

$$\langle\psi_{i0}|\Delta V_{\text{norm}}|\psi_{j\vec{\mathrm{k}}}\rangle=i\frac{a_{ji}(k)}{N}\sum_{s\alpha}\delta R_\alpha(k,s)\cdot kv_\alpha(k)\;. \qquad \text{(B11)}$$

The electronic eigenstate part $a_{ji}(k)$ is separated from the lattice dynamic parts and is calculated from a $\vec{\mathrm{k}}\cdot\vec{\mathrm{p}}$ band structure calculation at k expanded about the zone center. The vibrational amplitude $\delta R_\alpha(k,s)$ is a product of the normalized phonon eigenstate for that ion and the Bose-Einstein occupation function, which depends on temperature and phonon energy. It is insufficient to use simply the free atomic potentials since the electrons are reacting to the movements of atoms distant by the interatomic spacing or more. The potential required is related to crystal binding potentials.

---

*Work partially supported by the National Science Foundation through Grant No. GK-2967 and by both the National Science Foundation and the Advanced Research Projects Agency through the Center for Materials Research, Stanford University. This work constituted part of a Ph.D. thesis research program of C.S.G.

†Present address: U. S. Naval Research Laboratory, Washington, D.C. 20375.

[1] S. C. Yu and H. Brooks (unpublished); S. C. Yu, Ph.D. thesis (Harvard University, 1964) (unpublished).

[2] Similar though less rigorous results are available in R. V. Kasowski, Phys. Rev. **187**, 891 (1969).

[3] C. Keffer, T. M. Hayes, and A. Bienenstock, Phys. Rev. Lett. **21**, 1676 (1968).

[4] C. Keffer, T. Hayes, and A. Bienenestock, Phys. Rev. B **2**, 1966 (1970).

[5] Y. W. Tsang and M. L. Cohen, Phys. Rev. B **3**, 1254 (1971).

[6] Y. F. Tsay, B. Gong, S. S. Mitra, and J. F. Vetelino, Phys. Rev. B **6**, 2330 (1972).

[7] H. Y. Fan, Phys. Rev. **82**, 900 (1951).

[8] M. L. Cohen, Phys. Rev. **128**, 131 (1962).

[9] M. E. Mostoller, Ph.D. thesis (Harvard University, 1964) (unpublished).

[10] C. S. Guenzer and A. Bienenstock, Phys. Lett. A **34**, 172 (1971).

[11] The crystal was supplied by D. Long of Honeywell, Inc. through the assistance of W. Paul of Harvard.

[12] V. T. Bublik, S. S. Gorelik, and M. D. Kapustina, Izv. Vyssh. Uchebn. Zaved. Fiz. **11** (11), 142 (1968) [Sov. Phys. J. **11** (11), 128 (1968)].

[13] C. B. Walker and D. R. Chipman, Acta Crystallogr. A **26**, 447 (1970).

[14] T. Alper and G. A. Saunders, J. Phys. Chem. Solids **28**, 1637 (1967).

[15] R. Banerjee and Y. P. Varshni, Can. J. Phys. **47**, 451 (1969).

[16] D. T. Cromer and J. B. Mann, Acta Crystallogr. A **24**, 321 (1968).

[17] *International Tables for X-ray Crystallography*, edited by K. Lonsdale (Kynoch, Birmingham, England, 1965), Vol. 3.

[18] E. F. Skelton, P. L. Radoff, P. Bolsaitis, and A. Verbalis, Phys. Rev. B **5**, 3008 (1972).

[19] V. T. Bublik, S. S. Gorelik, M. D. Kapustina, A. D. Fishel, and G. E. Shpichinetskii, Fiz. Tverd. Tela **12**, 2513 (1970) [Sov. Phys.-Solid State **12**, 2021 (1971)].

[20] V. I. Ivanov-Omskii, B. T. Kolomiets, L. I. Kleshchinskii, and K. P. Smekalova, Fiz. Tverd. Tela **10**, 3106 (1968) [Sov. Phys.-Solid State **10**, 2447 (1969)].

[21] J. F. Vetelino, S. P. Gaur, and S. S. Mitra, Phys. Rev. B **5**, 2360 (1972).

[22] C. Verie, Phys. Status Solidi **17**, 889 (1966).

[23] C. Verie, in *II-VI Semiconducting Compounds, 1967 International Conference*, edited by D. G. Thomas (Benjamin, New York, 1967), p. 1124.

[24] R. Piotrzkowski and S. Porowski, in Ref. 23, p. 1090.

[25] C. R. Pidgeon and S. H. Groves, in Ref. 23, p. 1080.

[26] L. Sniadower, M. Psoda, and R. R. Galazka, Phys. Status Solidi **28**, K121 (1968).

[27] S. Bloom and T. K. Bergatresser, Phys. Status Solidi **42**, 191 (1971).

[28] H. Overhof, Phys. Status Solidi B **43**, 221 (1971;)Phys. Status Solidi B **45**, 315 (1971).

[29] A. O. E. Animalu and V. Heine, Philos. Mag. **12**, 1249 (1965).

[30] J. L. Shay, Phys. Rev. B **4**, 1385 (1971).

[31] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J., 1963).

[32] E. O. Kane, J. Phys. Chem. Solids **1**, 249 (1957).

[33] W. Gorzkowski, Phys. Status Solidi **11**, K131 (1965).