Debye-Waller Factors and the PbTe Band-Gap Temperature Dependence*†

Charles Keffer‡

Department of Physics, Harvard University, Cambridge, Massachusetts 02138

and

Timothy M. Hayes§ and Arthur Bienenstock

Department of Materials Science, Stanford University, Stanford, California 94305

(Received 18 February 1970)

Measurements of the temperature variation of x-ray diffraction peak intensities have been used to show that the mean-square thermal displacement of Pb in PbTe is approximately twice that of Te. This phenomenon is explained, using a calculation of the mean-square displacements from vibrational eigenvalues and eigenvectors, in terms of the heavy thermal weighting of the acoustic modes relative to the optical. The Pb motion dominates in the acoustic modes, whereas the Te motion dominates in the optic modes. Debye-Waller factors obtained from the calculated mean-square displacements have been associated with a modified Lin-Kleinman pseudopotential to obtain a theoretical estimate of the temperature dependence of the band gap. The modifications are necessary because of errors associated with their treatment of spin-orbit interaction. The calculated band-gap increase of 0.008 Ry between 100 and 300 °K is in fair agreement with an experimental estimate of the explicit increase. It is shown that the magnitude of the shift is quite sensitive to adjustable parameters in the gap calculation as well as to the Debye-Waller factors. The sign of the shift is dependent on the relative ordering of levels and the relative mean-square displacements of the ions but not, otherwise, on the details of the calculation.

I. INTRODUCTION

The fundamental one-electron band gaps of most semiconductors and insulators decrease as the temperature increases. Explanations of this negative temperature dependence are usually based upon the consideration of two primary effects: an explicit dependence through the electron-phonon interaction, to be evaluated with the volume held constant, and an implicit dependence through the volume thermal expansion of the material. In the initial attempt at a quantitative estimate of the explicit effect, Fan[1] expressed the electron self-energies to second order in the electron-phonon interaction and obtained the following equation for the thermally induced explicit shift in the energy gap:

$$\Delta E_g = \sum_{\vec{q}} \frac{|\langle \psi(\vec{k}_b \pm \vec{q}, c) \, \chi(n_q \mp 1)| \Delta u |\psi(\vec{k}_b, c) \, \chi(n_q)\rangle|^2}{\epsilon(\vec{k}_b, c) - \epsilon(\vec{k}_b \pm \vec{q}, c) \pm \hbar \omega_q}$$

$$+ \sum_{\vec{q}} \frac{|\langle \psi(\vec{k}_t, v) \, \chi(n_q \mp 1)| \Delta u |\psi(\vec{k}_t \mp \vec{q}, v) \, \chi(n_q)\rangle|^2}{\epsilon(\vec{k}_t \mp \vec{q}, v) - \epsilon(\vec{k}_t, v) \pm \hbar \omega_q} . \quad (1)$$

In this expression, the electron-phonon interaction is represented by Δu. The electron wave function and energy corresponding to a reduced wave vector $\vec{k}$ and band n in the undistorted lattice are denoted by $\psi(\vec{k}, n)$ and $\epsilon(\vec{k}, n)$. The extrema of the valence and conduction bands are represented by $\vec{k}_t$ and $\vec{k}_b$, respectively, while v and c refer to the bands

themselves. Corresponding to the lattice vibrational state with phonon wave vector $\vec{q}$, $\chi(n_q)$ is the ionic wave function, n_q is the occupation number, and ω_q is the vibrational frequency. It has been noted by many authors that the Fan expression must contribute a negative term to this temperature dependence since the numerators of Eq. (1) are positive and increase with temperature, while the denominators are negative.

PbTe is one of a few semiconductors which show positive temperature dependences of the band gaps. Prakash measured the pressure dependence of its fundamental absorption edge[2] and found that the implicit effect is insufficient to cause the observed increase in the band gap. As indicated in the previous paragraph, however, the Fan theory is incapable of producing a positive dependence of the band gap. This dilemma has troubled many people in the field since its observation.

Recently, however, we[3] reported a calculation which yielded a positive temperature dependence for the explicit effect, based on the Brooks-Yu[4] theory of temperature-dependent band energies. The purpose of this paper is to present the details of that calculation and related experiments as well as their limitations. In addition, it is shown that a self-energy theory of the Fan type is capable, in principle, of predicting a positive temperature dependence when all of the second-order terms are included.

The paper is organized in the following manner. The Brooks-Yu theory indicates that the most important effect of the electron-phonon interaction on the band structure can be represented by the association of the usual Debye-Waller factor with each Fourier coefficient of the pseudopotential. Thus, the first portion of the paper describes x-ray diffraction measurements of the ionic Debye-Waller factors in lead telluride. These measurements yielded the unexpected result that the Pb mean-square thermal displacement is approximately twice that of the Te. Since this result was unexpected, we proceeded to calculate the Debye-Waller factors using vibrational eigenvectors and eigenvalues obtained by Cochran $et al.$[5] in an analysis of their inelastic neutron scattering data. This calculation and its results are presented in Sec. II.

The last sections of the paper deal with a calculation of the temperature dependence of the band gap, based on the Lin and Kleinman[6] (LK) pseudopotential. Unfortunately, the LK work contains a faulty computational procedure. A result of this error is the establishment of an incorrect relationship between the parameters characterizing their pseudopotential and the band structure. Our use of the correct relationship necessitated the revision of their parameters. Consequently, the LK procedure and its modifications are discussed in detail. Then, the results of the calculation of the temperature dependence of the PbTe band gap are presented and discussed. Finally, a revised Fan theory, capable, in principle, of yielding a positive temperature dependence of the band gap, is presented in an appendix.

II. MEASUREMENT OF DEBYE-WALLER FACTORS

Samples for the x-ray diffraction study were prepared by grinding polycrystalline PbTe of greater than 99.999% purity[7] until it passed through a 200-mesh screen. The resultant powder was pressed into a copper sample holder under moderate pressures. The sample was annealed for 24 h at approximately 150 °C.

The temperature dependences of the intensities of of the (331) and (420) reflections were measured in an Electronics and Alloys high-temperature camera, whose sample chamber was evacuated, on a General Electric XRD-5 diffractometer. A doubly bent LiF crystal served as a diffracted beam analyzer. The half-wavelength components were eliminated by means of a pulse-height analyzer. Integrated intensities of the diffraction peaks were obtained at 20 and 102.5 °C, as measured with a chromel-alumel thermocouple. The ratio of the intensity of the (331) reflection at 102.5 °C to that at 20 °C is 0.68. The corresponding ratio for the (420) reflection is 0.86.

ing ratio for the (420) reflection is 0.86.

In order to avoid the problems which would arise if the crystallites showed preferred orientation, the Debye-Waller factors were extracted from the ratios of intensities measured at two different temperatures. Specifically, the ratio of the intensities of a single reflection from PbTe at two temperatures is given by

$$\frac{I(T_2)}{I(T_1)} = \frac{[f_{Pb}e^{-W_{Pb}(T_2)} \pm f_{Te}e^{-W_{Te}(T_2)}]^2}{[f_{Pb}e^{-W_{Pb}(T_1)} \pm f_{Te}e^{-W_{Te}(T_1)}]^2} . \quad (2)$$

In this expression, the + and − signs apply to reflections whose Miller indices are even and odd, respectively. The f_κ are the appropriate x-ray scattering factors, while the exponentials are the Debye-Waller factors for Pb and Te. The thermal effects are contained within the $W_\kappa(T)$, which are related to the mean-square displacements of the atoms of type κ, denoted by $\langle u_\kappa^2 \rangle$, through the equation

$$W_\kappa(T) = 2\pi^2 S^2 \langle u_\kappa^2 \rangle / \lambda^2 . \quad (3)$$

In this expression, S is the x-ray scattering vector, whose magnitude is $2\sin\theta$, θ is the Bragg scattering angle, and λ is the x-ray wavelength.

The determination of the $\langle u_\kappa^2 \rangle$ is complicated by the fact that the data yield two ratios of intensities of the form of Eq. (3), whereas four W_κ appear as unknowns to be determined. In the harmonic approximation, however, W_κ is proportional to T at temperatures above the Debye temperature, which is roughly 140 °K for PbTe.[8] Therefore, since each atom occupies a site of cubic symmetry, Eq. (3) can be written as

$$W_\kappa(T) = A_\kappa T \sin^2\theta . \quad (4)$$

Equation (2) can then be written as

$$\frac{I(T_2)}{I(T_1)} = \frac{(f_{Pb}e^{-A_{Pb}T_2 \sin^2\theta} \pm f_{Te}e^{-A_{Te}T_2 \sin^2\theta})^2}{(f_{Pb}e^{-A_{Pb}T_1 \sin^2\theta} \pm f_{Te}e^{-A_{Te}T_1 \sin^2\theta})^2} . \quad (5)$$

The two A_κ may be determined with ease from the two ratios using iterative techniques. The resultant $\langle u_\kappa^2 \rangle$ are presented in Table I.

Although these results show quite clearly that the mean-square displacement of Pb is approximately twice that of Te, their reliability is limited in two respects. First, no correction was made for diffuse scattering under the Bragg peak, except as it could be described by a linear background

TABLE I. Experimental vibrational amplitudes in PbTe at 300 °K.

Atom	$\langle u_\kappa^2 \rangle$ (10^{-16} cm^2)
Pb	0.0351
Te	0.0196

correction beneath the peak. Order-of-magnitude calculations indicated that the additional corrections should be small, but not negligible. In addition, the method of determining the $\langle u_\kappa^2 \rangle$ does not lend itself to evaluation at low temperature, since the approximation of a linear temperature dependence was made. Accordingly, it was decided to calculate the $\langle u_\kappa^2 \rangle$ directly. Such a calculation can also be expected to yield some insight into the cause of the relative values. This calculation is described in Sec. III.

III. CALCULATION OF THE DEBYE-WALLER FACTORS

In the harmonic approximation, the Debye-Waller factor has the form e^{-W_κ} for the κth atom in the unit cell, where[8]

$$W_\kappa = (2\pi^2/NM_\kappa\lambda^2)\sum_{\vec{q}, j} [\vec{S} \cdot \vec{e}(\kappa \,|\, \vec{q}, j)]^2 E(\vec{q}, j) \quad (6)$$

and

$$E(\vec{q}, j) = [\hbar/2\omega_j(\vec{q})] \coth[\hbar\omega_j(\vec{q})/2k_B T] . \quad (7)$$

In this expression, N is the number of unit cells in the crystal, and M_κ is the mass of the κth atom. The polarization vector and the angular frequency associated with the jth mode of wave vector q are denoted by $\vec{e}(\kappa \,|\, \vec{q}, j)$ and $\omega_j(\vec{q})$, respectively. The $\vec{e}(\kappa \,|\, \vec{q}, j)$ are the eigenvectors of the dynamical matrix which satisfy the following orthogonality conditions:

$$\sum_{\kappa, \alpha} e_\alpha^*(\kappa \,|\, \vec{q}, j) e_\alpha(\kappa \,|\, \vec{q}, j) = \delta_{jj'} ,$$

$$\sum_{j} e_\beta^*(\kappa' \,|\, \vec{q}, j) e_\alpha(\kappa \,|\, \vec{q}, j) = \delta_{\alpha\beta} \delta_{\kappa\kappa'} . \quad (8)$$

Since each atom sits in a site of cubic symmetry, Eq. (6) can be rewritten as

$$W_\kappa = \frac{4\pi^2 \hbar \sin^2\theta}{3N\lambda^2 M_\kappa} \sum_{\vec{q}, j, \alpha} \frac{e_\alpha^2(\kappa \,|\, \vec{q}, j) \coth[\hbar\omega_j(\vec{q})/2k_B T]}{\omega_j(\vec{q})} , \quad (9)$$

where the summation over α includes the components of the eigenvectors associated with atom κ. This sum was evaluated numerically at a number of temperatures, using eigenvalues and eigenvectors obtained by Cochran *et al.*[5] in an analysis of their inelastic neutron scattering data. Throughout most of the Brillouin zone, the sampling procedure of Kellerman[9] was used, with 48 points in the summation over $\frac{1}{48}$ of the Brillouin zone. The contribution of the elastic modes was, however, evaluated using Houston's[10] method of expansion in Kubic harmonics, with a sphere of equal volume replacing the central rhombohedron associated with the Kellerman sampling procedure. The resultant $\langle u_\kappa^2 \rangle$ are shown in Fig. 1 along with the experimentally obtained values.
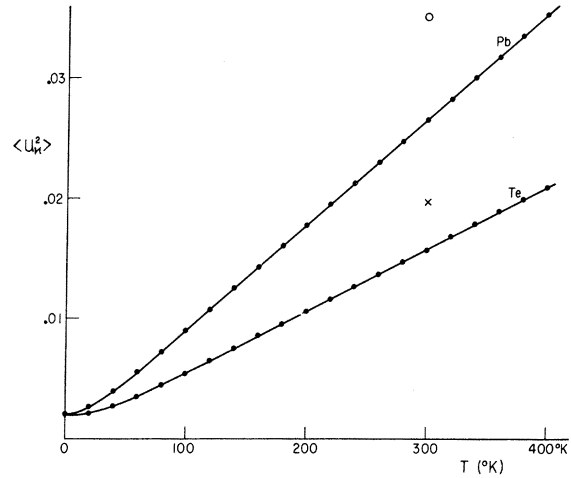

FIG. 1. Vibrational amplitudes $\langle u_\kappa^2 \rangle$ for lead and tellurium as a function of temperature. Heavy curve connects the calculated values. Experimental values are indicated by O for Pb and by × for Te.

Three features of these results merit discussion. The first, and most significant, is that the calculation confirms that the motion of the Pb atoms is larger than that of the Te. This is most easily understood through an examination of the acoustical and optical contributions to the mean-square displacements, as represented in Table II. It is seen that Pb motion dominates the acoustic modes, whereas Te motion dominates the optic modes. Since nearly all of the acoustic modes are of lower frequency than the optic modes, the former are weighted much more heavily in W_κ through the thermal factor of Eq. (7). This thermal weighting of

TABLE II. Calculated vibrational amplitudes for PbTe $- \langle u_\kappa^2 \rangle$ (10^{-16} cm^2).

Temperature	Pb acoustical	Te accustical	Pb optical	Te optical	Pb total	Te total
0.00	0.0018	0.0007	0.0002	0.0012	0.0020	0.0019
20.00	0.0024	0.0009	0.0002	0.0012	0.0026	0.0021
40.00	0.0038	0.0015	0.0002	0.0012	0.0040	0.0027
60.00	0.0054	0.0022	0.0002	0.0014	0.0056	0.0036
80.00	0.0070	0.0028	0.0002	0.0017	0.0072	0.0045
100.00	0.0087	0.0035	0.0003	0.0020	0.0090	0.0055
120.00	0.0104	0.0042	0.0u03	0.0023	0.0107	0.0065
140.00	0.0121	0.0049	0.0004	0.0026	0.0125	0.0075
160.00	0.0138	0.0056	0.0004	0.0030	0.0142	0.0086
180.00	0.0155	0.0062	0.0004	0.0033	0.0159	0.0095
200.00	0.0172	0.0069	0.0005	0.0036	0.0177	0.0105
220.00	0.0189	0.0076	0.0005	0.0040	0.0194	0.0116
240.00	0.0206	0.0083	0.0006	0.0043	0.0212	0.0126
260.00	0.0223	0.0090	0.0006	0.0046	0.0229	0.0136
280.00	0.0240	0.0097	0.0007	0.0050	0.0247	0.0147
300.00	0.0257	0.0104	0.0007	0.0053	0.0264	0.0157
320.00	0.0274	0.0111	0.0008	0.0057	0.0282	0.0168
340.00	0.0291	0.0118	0.0008	0.0060	0.0299	0.0178
360.00	0.0308	0.0125	0.0009	0.0064	0.0317	0.0189
380.00	0.0325	0.0132	0.0009	0.0067	0.0334	0.0199
400.00	0.0342	0.0138	0.0010	0.0070	0.0352	0.0208

the low-frequency modes in the Debye-Waller factor persists to high temperatures in spite of equipartition. Indeed, the high-temperature limit of Eq. (7) is

$$E(\vec{q}, j) \cong k_B\, T/\omega_j^2(\vec{q}) \ . \tag{10}$$

The second feature of these results is the disagreement between the theoretical and experimental predictions of the mean-square displacements. The discrepancy may be regarded as a measure of the uncertainties associated with both results. The reliability of the interpretation of the measurements has already been discussed. The calculation suffers from the approximate nature of the eigenvectors, which are not expected to be as reliable as the eigenvalues. In addition, the use of the harmonic approximation itself is open to question at the high temperatures where theory and experiment can be compared. In the work that follows, we have treated the calculated $\langle u_\kappa^2 \rangle$ as approximate and tested the sensitivity of any conclusions about band-gap effects to variations in them.

Finally, it should be noted that the mean-square displacements are linear with temperature down to approximately $100°$K. This justifies, within the harmonic approximation, the linear temperature dependence assumed in the temperature region of the experimental measurements.

IV. ZERO-TEMPERATURE CALCULATION

Recently, LK[6] presented a pseudopotential calculation of the band structures of PbTe, PbSe, and PbS. In the original plan of this research, we expected to modify their pseudopotential matrix elements for PbTe with the appropriate Debye-Waller factors in order to obtain the temperature dependence of the band gap. Our initial attempts to reproduce their calculations were unsuccessful, however, as a result of an error in their treatment of the spin-orbit interaction. In effect, this error results in the establishment of an incorrect relationship between their parameters and the band structure, which they correlated with experiment. In order to achieve an acceptable band structure using the correct relationship, it was necessary for us to change some of the adjustable parameters involved. This, for reasons which will become evident, lessens our confidence in the reliability of the pseudopotential used here. Accordingly, the LK procedure will be discussed in more detail than might otherwise be fruitful.

LK search for solutions, corresponding to the valence and conduction hands, of the one-electron Schrödinger equation

$$(T + W + H_{so})\, \psi_{\vec{k}} = (E_{\vec{k}} + E_{so})\, \psi_{\vec{k}} \ , \tag{11}$$

where T and W are the kinetic-energy and the po-

tential-energy operators, respectively. H_{so} is the spin-orbit part of the Hamiltonian, which has the form

$$H_{so} = (\hbar^2/4m^2 c^2)(\vec{\nabla}\, W \times \vec{p} \cdot \vec{\sigma}) \ , \tag{12}$$

and E_{so} is the contribution of this interaction to the energy eigenvalue E_k. Their pseudopotential is constructed by means of the substitution

$$\psi_{\vec{k}} = \phi_{\vec{k}} - \sum_t (\Phi_{\vec{k}t},\ \phi_{\vec{k}})\, \Phi_{\vec{k}t} \ , \tag{13}$$

where $\phi_{\vec{k}}$ denotes the smooth part of the crystal wave function, $\Phi_{\vec{k}t}$ represents a core state, and the sum is over all core states, as represented by the index t. The substitution of Eq. (13) into Eq. (11) yields the equation

$$(T + V_p + V_{so} + H_{so})\, \phi_{\vec{k}} = (E_{\vec{k}} + E_{so})\, \phi_{\vec{k}} \ , \tag{14}$$

for $(E_{\vec{k}} + E_{so})$ and $\phi_{\vec{k}}$, where

$$V_p = W + \left\{ -\sum_t (\Phi_{\vec{k}t},\ \phi_{\vec{k}})\, [(\Phi_{\vec{k}t}|H|\Phi_{\vec{k}t}) - E_{\vec{k}}]\, \Phi_{\vec{k}t} \right\}/\phi_{\vec{k}} \tag{15}$$

and

$$V_{so} = -\sum_t (\Phi_{\vec{k}t}, \phi_{\vec{k}})\, [(\Phi_{\vec{k}t}|H_{so}|\Phi_{\vec{k}t}) - E_{so}]\Phi_{\vec{k}t}/\phi_{\vec{k}} \ . \tag{16}$$

In their treatment, LK separate V_p into a local part V and a correction for nonlocality V_s known as the s shift. V is expressed as a superposition of individual atomic pseudopotentials of the form

$$\begin{aligned} V_{eff} &= 0 \ , & r &< r_0 \\ V_{eff} &= \frac{2Z}{r}\, (1 - e^{-\beta(r - r_0)}), & r &\geqslant r_0 \ . \end{aligned} \tag{17}$$

where β, r_0, and Z are adjustable parameters. Values for r_0 are obtained by considering Slater's[11] analytical atomic wave functions

$$\begin{aligned} \chi_{5p}^{Pb} &= 381.8\ r^3 e^{-6.088r} \ , \\ \chi_{4p}^{Te} &= 461.3\ r^{2.7} e^{-6.544r} \ , \end{aligned} \tag{18}$$

and solving

$$\chi(r_0) = \max[\chi(r)] \ , \tag{19}$$

where $\chi(r)$ is the outermost p-core orbital of the atom. β is determined by the relation

$$\beta = 1/(r_1 - r_2) \ , \tag{20}$$

where

$$\chi(r_1) = \chi(r_0)/2e$$

and

$$\chi(r_2) = \chi(r_0)/2 \ . \tag{21}$$

The appropriate values of r_0 and β for lead and tellurium are given in Table III. This procedure leaves one adjustable parameter Z for each kind of atom. While the parameters r_0 and β obtained by LK have been used in this calculation, it has

TABLE III. Some parameters for the lead telluride band-structure calculation.

$r_0^{Pb} = 0.493\, a_0$
$r_0^{Te} = 0.412\, a_0$
$\beta^{Pb} = 3.228\, a_0^{-1}$
$\beta^{Te} = 3.597\, a_0^{-1}$
Lattice constant $= 12.21\, a_0$
$E_{5s}^{Pb} = -9.030$ Ry [a]
$E_{4s}^{Te} = -11.899$ Ry [a]

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

been necessary to adjust the Z values in a manner and for reasons described below.

In analogy with Eq. (15) the s-shift potential of LK has the form

$$V_s = -\sum_t \alpha_t (\Phi_{\vec{K}t}^*, \phi_{\vec{K}}) E_t \Phi_{\vec{K}t}^* / \phi_{\vec{K}} . \quad (22)$$

In this expression, the sum is over the outermost s-core states, and the E_t are the associated s-core state energies, as listed in Table III. The α_{Pb} and α_{Te} are two adjustable parameters, whose values we have found it necessary to change.

In their treatment of the spin-orbit part of Eq. (14), LK neglect H_{so}. In addition, Eq. (16) for V_{so} is modified by the neglect of E_{so} and by the truncation of the sum over core states to include only the outermost p and d levels of each atom. The final form for V_{so} is

$$V_{so} = -\alpha_{so} \sum_t (\Phi_{\vec{K}t}^*, \phi_{\vec{K}}) (\Phi_{\vec{K}t} | H_{so} | \Phi_{\vec{K}t}^*) / \phi_{\vec{K}} , \quad (23)$$

where α_{so} is an adjustable parameter intended to compensate for these approximations.

The solution of Eq. (14) involves expressing the $\phi_{\vec{K}}$ as linear combinations of the members of some suitable complete set of functions, called the basis functions. For this purpose, LK choose the set of symmetrized plane waves $|\vec{K}_I^\alpha\rangle$, which transform according to the single-group irreducible representation Γ^α of the cubic point group. The spin index is suppressed as long as possible. These functions are

$$\langle \vec{r} | \vec{K}_I^\alpha \rangle = (N\Omega)^{-1/2} \sum_j C_{Ij}^\alpha \exp[i(\vec{K} + \vec{K}_j) \cdot \vec{r}] , \quad (24)$$

where N denotes the number of units cells, Ω represents the volume of the primitive unit cell, and the $\vec{K}_j$ are reciprocal lattice vectors. The C_{Ij}^α are determined by symmetry. For a given $\vec{k}$ and I, the sum over j includes only those vectors $\vec{k} + \vec{K}_j$ which are related by the group of $\vec{k}$. When this set of basis functions is used, the resultant secular determinant involves matrix elements of the type

$\langle \vec{K}_I^{\alpha'} | T + V_p + V_{so} | \vec{K}_M^\alpha \rangle$. The evaluation of the matrix elements of $T + V_p$ is simplified by the fact that there is no mixing of single-group representations, as expressed by

$$\langle \vec{K}_I^{\alpha'} | T + V_p | \vec{K}_M^\alpha \rangle = \langle \vec{K}_I^\alpha | T + V_p | \vec{K}_M^\alpha \rangle \delta_{\alpha'\alpha} . \quad (25)$$

Although our evaluation of the matrix elements of $T + V_p$ follows that of LK, our treatment of V_{so} differs and will accordingly be discussed in detail.

The important matrix elements of V_{so} which appear in the secular determinant for the eigenvalues of Eq. (14) are

$$\langle \vec{K}_I^{\alpha'} | V_{so} | \vec{K}_M^\alpha \rangle$$
$$= -\alpha_{so} \sum_t \langle \vec{K}_I^{\alpha'} | \Phi_{\vec{K}t}^* \rangle \langle \Phi_{\vec{K}t}^* | H_{so} | \Phi_{\vec{K}t} \rangle \langle \Phi_{\vec{K}t} | \vec{K}_M^\alpha \rangle$$
$$\equiv -\alpha_{so} D_{IM}^{\alpha'\alpha} , \quad (26)$$

where the α now includes a spin index. In the work that follows, we assume that the spin-orbit interaction and the p- and d-core wave functions are sufficiently localized that the interatomic interaction terms can be neglected. In this case, the $\Phi_{\vec{K}t}$ can be constructed from atomic core states of a particular atomic species with fixed $|L|$, $|J|$, and m_J. These are denoted by

$$\langle \vec{r} | \mu, L, J, m_J \rangle = N^{-1/2} \sum_{I\mu} \chi_{\mu, L, J, m_J}$$
$$\times (\vec{r} - \vec{r}_{I\mu}) \exp(i\vec{k} \cdot \vec{r}_{I\mu}) , \quad (27)$$

where the label $\vec{k}$ has been suppressed on the left-hand side and the sum is over the sites of the species μ. Using these core wave functions, $D_{IM}^{\alpha'\alpha}$ can be expressed as follows:

$$D_{IM}^{\alpha'\alpha} = \sum_{\mu, L, J, m_J} \langle \vec{K}_I^{\alpha'} | \mu, L, J, m_J \rangle$$
$$\times \langle \mu, L, J, m_J | H_{so} | \mu, L, J, m_J \rangle$$
$$\times \langle \mu, L, J, m_J | \vec{K}_M^\alpha \rangle . \quad (28)$$

In treating the matrix elements of H_{so}, we make the approximation that

$$\chi_{\mu, L, J, m_J} (\vec{r}) = \chi_{\mu, L} (\vec{r}) \langle \vec{r} | J, m_J \rangle , \quad (29)$$

where $\langle \vec{r} | J, m_J \rangle$ is the appropriate one-center spinor eigenfunction. The matrix elements can then be written as

$$\langle \mu, L, J, m_J | H_{so} | \mu, L, J, m_J \rangle$$
$$= \tfrac{1}{2} [J(J+1) - L(L+1) - \tfrac{3}{4}] \xi_{\mu, L} , \quad (30)$$

where

$$\xi_{\mu, L} = (2m^2 c^2)^{-1} \int_0^\infty \chi_{\mu, L}^2 (r) (1/r) (\partial V/\partial r) r^2 \, dr \quad (31)$$

and is obtainable from atomic splittings, as indicated by LK. As a result, Eq. (28) can be written in the form

$$D_{IM}^{\alpha'\alpha} = \tfrac{1}{2}\sum_{\mu,L}\xi_{\mu,L}\sum_{J}\left[J(J+1)-L(L+1)-\tfrac{3}{4}\right]$$

$$\times\sum_{m_J}\langle\vec{K}_I^{\alpha'}\,|\,\mu,L,J,m_J\rangle\langle\mu,L,J,m_J\,|\,\vec{K}_M^{\alpha}\rangle\ . \tag{32}$$

Further evaluation of the $D_{IM}^{\alpha'\alpha}$ requires the explicit consideration of spin. With an obvious expansion of the notation, the substitution of Eq. (24) into the last factor of Eq. (32) yields

$$\sum_{m_J}\langle\pm\vec{K}_I^{\alpha'}\,|\,\mu,L,J,m_J\rangle\langle\mu,L,J,m_J\,|\,\vec{K}_M^{\alpha}\,\pm\rangle$$

$$= \sum_{m_J,j',j}C_{Ij'}^{\alpha'*}C_{Mj}^{\alpha}\langle\pm\vec{K}_{j'}\,|\,\mu,L,J,m_J\rangle$$

$$\times\langle\mu,L,J,m_J\,|\,\vec{K}_j\,\pm\rangle, \tag{33}$$

where $\langle\mu,L,J,m_J\,|\,\vec{K}_j\,\pm\rangle$ represents the overlap of the state $\langle\mu,L,J,m_J\,|$ with the normalized product of a plane wave $\vec{k}+\vec{K}_j$ and a spin function. After some algebraic manipulation, it is easily shown that a major portion of Eq. (32) can be put in the form

$$\sum_{J}\left[J(J+1)-L(L+1)-\tfrac{3}{4}\right]\sum_{m_J}\langle+\vec{K}_I^{\alpha'}\,|\,\mu,L,J,m_J\rangle\langle\mu,L,J,m_J\,|\,\vec{K}_M^{\alpha}+\rangle$$

$$= (4\pi)^2\sum_{j,j'}C_{Ij'}^{\alpha'*}C_{Mj}^{\alpha}R_{\mu L}(K_{j'})R_{\mu L}(K_j)\sum_{m=-L}^{L}mY_{Lm}^{*}(\hat{K}_j)Y_{Lm}(\hat{K}_{j'})$$

$$= \begin{cases}12\pi i\sum_{j,j'}C_{Ij'}^{\alpha'*}C_{Mj}^{\alpha}R_{\mu L}(K_{j'})R_{\mu L}(K_j)(\vec{K}_j\times\vec{K}_{j'})_z/K_jK_{j'} & (L=1)\\[2mm] 60\pi i\sum_{j,j'}C_{Ij'}^{\alpha'*}C_{Mj}^{\alpha}R_{\mu L}(K_{j'})R_{\mu L}(K_j)(\vec{K}_j\cdot\vec{K}_{j'})(\vec{K}_j\times\vec{K}_{j'})_z/K_j^2K_{j'}^2 & (L=2)\end{cases} \tag{34}$$

and

$$\sum_{J}\left[J(J+1)-L(L+1)-\tfrac{3}{4}\right]\sum_{m_J}\langle+\vec{K}_I^{\alpha'}\,|\,\mu,L,J,m_J\rangle\langle\mu,L,J,m_J\,|\,\vec{K}_M^{\alpha}-\rangle$$

$$= (4\pi)^2\sum_{j,j'}C_{Ij'}^{\alpha'*}C_{Mj}^{\alpha}R_{\mu L}(K_{j'})R_{\mu L}(K_j)\sum_{m=-L}^{L}[(L+m+1)(L-m)]^{1/2}Y_{L,m+1}^{*}(\hat{K}_j)Y_{L,m}(\hat{K}_{j'})$$

$$= 12\pi\sum_{j,j'}C_{Ij'}^{\alpha'*}C_{Mj}^{\alpha}R_{\mu L}(K_{j'})R_{\mu L}(K_j)[(\vec{K}_j\times\vec{K}_{j'})_y+i(\vec{K}_j\times\vec{K}_{j'})_x]/K_jK_{j'} \qquad (L=1)\ . \tag{35}$$

In these expressions

$$R_{\mu L}(K_j)=\int_0^{\infty}r^2dr\,\chi_{\mu L}(r)\,j_L(K_jr)\ , \tag{36}$$

and $j_L(K_jr)$ is a spherical Bessel function. The reversal of both spins in Eq. (34) leads to a change of sign. Only the $L=1$ portion is presented in Eq. (35), as the $L=2$ term does not contribute to any of the levels of interest in this calculation. The parameters $R_{\mu L}$ are easily evaluated using the procedure described by LK, while the C_{Mj}^{α} are tabulated by Luehrmann.[12] Accordingly, although it should be noted that Luehrmann quantizes spin along the $\langle 111\rangle$ direction, the procedure for the numerical evaluation of Eqs. (34), (35), and, hence, (32) is well defined.

The band calculation proceeds in a straightforward manner once the necessary matrix elements have been prescribed. Those matrix elements represented by Eq. (26) which do not mix the single-group representations are included with those represented by Eq. (25) and treated in a direct diagonalization of the associated secular determinant. Following the procedure of LK, the mixing matrix elements of Eq. (26) are treated as perturbations on the resultant eigenstates. Of the six distinct energy levels in the region of the gap, only the L_6

levels were calculated since the L_{45} levels do not mix with the L_6 levels.

Our initial calculations yielded energy levels at the symmetry point L which differ considerably from those of LK, even though their values of the adjustable parameters were used. A detailed analysis[13] of that portion of the LK calculation[14] which is based upon Eq. (26) indicates that the contributions of terms of the form of the $L=2$ portion of Eq. (34) and of terms which mix single-group representations had been calculated incorrectly. These errors cast doubt upon the general reliability of their band-structure calculation.

In order to proceed with our calculation, we needed an acceptable pseudopotential. Accordingly, the five adjustable parameters of LK were varied systematically until reasonable agreement was obtained with the level structure at L computed by Herman et al.[15] The parameters used here, as well as those of LK, are listed in Table IV. The energy levels obtained here are compared with those of Herman et al. in Table V. The good agreement with Herman et al. should not lead the reader to the conclusion that we have demonstrated that the pseudopotential constructed here is an accurate representation of the potential in PbTe. Such a

TABLE IV. Comparison of parameters in original and modified LK band-structure calculation.

Parameter	Lin and Kleinman	This work
Z_{Pb}	2.9	3.1
Z_{Te}	3.2	3.5
α_{Pb}	0.125	0.122
α_{Te}	0.17	0.109
α_{so}	−0.78	−1.55

demonstration would necessarily involve a calculation of the entire band structure and a detailed comparison with experiment. We have not gone through this lengthy procedure. Instead, as discussed below, we have tested the sensitivity of the calculated band-gap temperature dependence of the parameters used.

V. TEMPERATURE DEPENDENCE OF THE BAND GAP

The calculation of the temperature dependence of the band gap is also straightforward. By using symmetrized combinations of plane waves, all matrix elements are eventually expressed as plane-wave matrix elements coming from individual ions. To include the temperature dependence, each of these matrix elements is multiplied by the Debye-Waller factor associated with the difference of the two plane waves, and the energy level calculation repeated. For this purpose, the calculated Debye-Waller factors, with the zero-point motion removed, were used initially, and band gaps calculated at 100, 200, and 300 °K. The L-point level structure and associated band gaps thus calculated as a function of temperature are shown in Figs. 2 and 3, respectively, and are tabulated in Table VI. These results show quite conclusively that the Brooks-Yu theory is capable of yielding an increase of the band gap with temperature despite the fact that the individual ionic contributions to the pseudo-potential decrease with temperature.

TABLE V. Comparison of energy levels near the band gap for our modified LK calculation and the band structure of Herman et al. (0 °K) (energies in Ry).

Level	Modified Lin and Kleinman	Herman et al.[a]
$L_6^-(L_3')$	0.6242	0.6134
$L_6^-(L_2')$	0.5202	0.5251
$L_6^+(L_1)$	0.5060	0.5067
$L_6^+(L_3)$	0.3869	0.3940

[a]F. Herman, R. L. Kortum, I. B. Ortenburger, and J. P. Van Dyke, J. Phys. (Paris) 29, 62 (1968). Their energy levels have been adjusted by +0.4242 Ry.
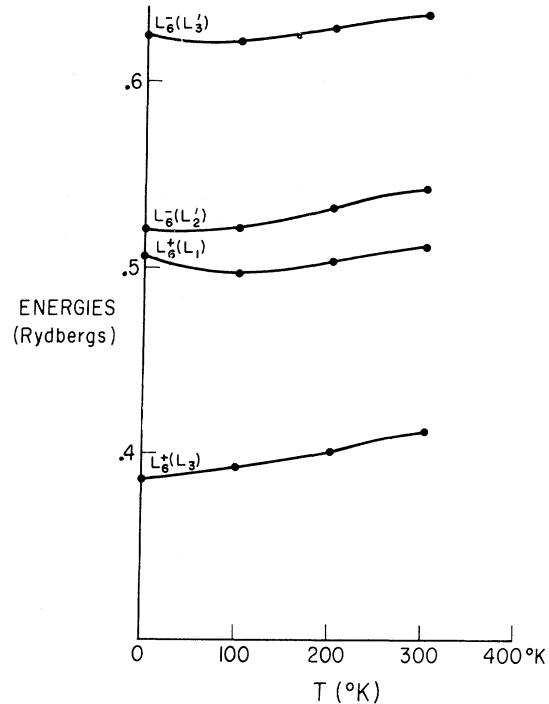

FIG. 2. Energy levels at the band gap in PbTe as a function of temperature.

These results may be compared with the experimental observations of Prakash.[2] Qualitative agreement is obtained in the sense that the gap increases with temperature, while the temperature coefficient itself decreases with temperature. Prakash presents an average explicit temperature dependence of $+2.0 \times 10^{-5}$ Ry/°K over the temperature interval 90–295 °K, while our average coefficient over this range is $+4.0 \times 10^{-5}$ Ry/°K. Thus, it appears as if the calculation is incorrect by roughly a factor of 2. In light of the discussion at the end of Sec. IV, however, this is not surprising. In order to test the sensitivity of the calculation to the adjustment of parameters, a number of other calculations were performed.

The first of these involved using all of Lin and Kleinman's original parameters, but with the V_{so} matrix elements calculated in the correct manner as described above. We refer to this result as calculation A. Table VI displays the level orderings as well as the size of the band gap at temperatures from 0 to 300 °K. Even though the gap is initially larger by a factor of about 3 and is made up of a different pair of energy states, a positive temperature dependence is still obtained. The size of the temperature coefficient in the region from 100 to 300 °K is $+0.72 \times 10^{-5}$ Ry/°K.

The second form of band structure was obtained by maintaining the same order of levels as in cal-
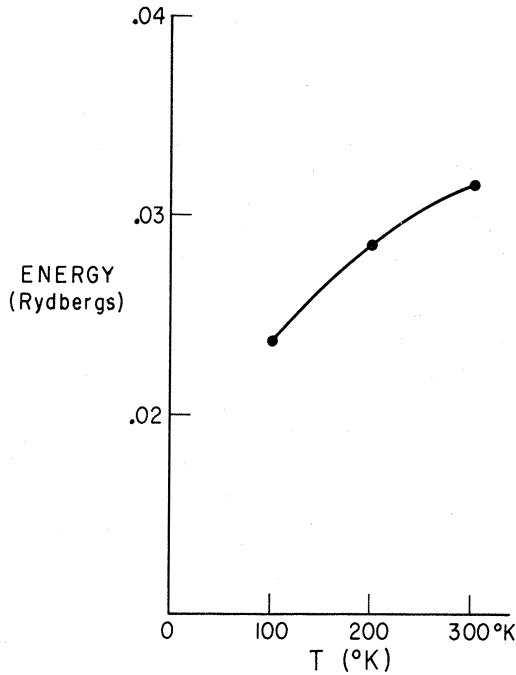
FIG. 3. Temperature dependence of the energy-band gap in PbTe.

These results indicate that the *sign* of the temperature coefficient is not sensitive to the size of the gap or the values of the arbitrary parameters, as long at the $L_6^+(L_1)$ level forms the valence band and the Debye-Waller factors are held constant. On the other hand, the *size* of the temperature coefficient is quite dependent on the nature of the pseudopotential. Because of this latter fact, we conclude that our results for the temperature dependence of the band gap in lead telluride have the correct sign. Since we have not done a complete band structure, we have no reason to believe that the pseudopotential parameters finally obtained in the previous section correctly describe the band structure at all points in $\vec{k}$ space. Consequently, our calculation of the magnitude of the temperature coefficient could easily be in error by a factor of 2 or more.

As discussed at the end of Sec. III, it was also necessary to test the sensitivity of the calculation to the Debye-Waller factors. In these two calcu-

culation A, but changing Lin and Kleinman's parameters to obtain a value of the band gap at 0 °K which is closer to the experimental value of 0.014 Ry. We refer to this result as calculation B. Table VI displays the level orderings as well as the size of the band gap at temperatures from 0 to 300 °K for this calculation. In this case, likewise, a positive temperature dependence is obtained at all temperatures. The size of the temperature coefficient in the region from 100 to 300 °K is $+3.1 \times 10^{-5}$ Ry/°K.

Three additional calculations were performed to test the sensitivity of the final results to the starting parameters of the band structure. These are tabulated in Table VI for 0 and 300 °K. The first calculation (C) involves a change of about 10% in the strength of the pseudopotential for both lead and tellurium. This displaces all the levels downward in energy with the L_1 and L_3 levels experiencing a larger shift. Consequently, the relative positioning of the levels and the size of the band gap does not agree with the results of Herman *et al.* The second calculation (D) involves a change in the spin-orbit parameter by about 30%. This also causes the relative positions of the levels to change and gives rise to a very large band gap. The final calculation (E) is due to a change of 60% in the Te s-shift parameter. The change affects only the $L_{2'}$ level directly and gives rise to an increased band gap. In all cases, the gap increases with increasing temperature.

TABLE VI. Temperature dependence of band gap for various calculations (energies in Ry).

Calculation	Level	0 °K	100 °K	200 °K	300 °K
Modified	L_1	0.506 02	0.496 78	0.503 59	0.510 23
(LK) (0 °K)	L_3	0.386 87	0.392 20	0.401 87	0.411 16
agrees with	$L_{2'}$	0.520 21	0.520 46	0.532 18	0.541 78
Herman *et al.*	$L_{3'}$	0.624 16	0.621 41	0.628 47	0.635 48
	gap	0.014 19	0.023 68	0.028 59	0.031 55
A	L_1	0.562 20	0.550 37	0.556 20	0.561 82
	L_3	0.478 72	0.482 69	0.489 13	0.495 29
	$L_{2'}$	0.650 12	0.592 88	0.599 97	0.605 77
	$L_{3'}$	0.601 69	0.641 42	0.648 11	0.654 55
	gap	0.039 49	0.042 51	0.043 77	0.043 95
B	L_1	0.564 78	0.553 90	0.559 36	0.564 65
	L_3	0.469 05	0.472 07	0.479 06	0.485 77
	$L_{2'}$	0.649 58	0.570 65	0.579 91	0.587 51
	$L_{3'}$	0.575 21	0.640 67	0.646 49	0.652 21
	gap	0.010 43	0.016 75	0.020 55	0.022 86
C	L_1	0.437 54			0.446 42
	L_3	0.317 41			0.347 51
	$L_{2'}$	0.593 89			0.509 41
	$L_{3'}$	0.474 75			0.606 80
	gap	0.037 21			0.062 99
D	L_1	0.499 86			0.499 90
	L_3	0.403 92			0.425 53
	$L_{2'}$	0.547 07			0.559 22
	$L_{3'}$	0.617 92			0.639 35
	gap	0.047 21			0.059 32
E	L_1	0.506 02			0.510 23
	L_3	0.386 87			0.411 16
	$L_{2'}$	0.638 56			0.555 85
	$L_{3'}$	0.531 90			0.640 58
	gap	0.025 88			0.045 62
F	L_1	0.506 02			0.516 39
	L_3	0.386 87			0.424 73
	$L_{2'}$	0.520 21			0.534 04
	$L_{3'}$	0.624 16			0.628 65
	gap	0.014 19			0.017 65
G	L_1	0.506 02			0.522 45
	L_3	0.386 87			0.437 96
	$L_{2'}$	0.520 21			0.525 73
	$L_{3'}$	0.624 16			0.621 96
	gap	0.014 19			0.003 28

lations we used the final parameters obtained in Sec. IV. In the first, denoted by F, the individual Debye-Waller factors for lead and tellurium have been replaced by an average Debye-Waller factor for both lead and tellurium. Table VI exhibits the level orderings as well as the size of the band gap at temperatures of 0 and 300 °K for this calculation. We note that the size of the gap still increases, but the magnitude of the increase +0. 09×10⁻⁵ Ry/°K is the smallest yet encountered in any of our calculations.

In the second of these calculations, denoted by G, the Debye-Waller factors of the individual atoms have been reversed. Table VI displays the levels and band gap at 0 and 300 °K for this trial. These results show a *decrease* in the size of the band gap as temperature increases from 0 to 300 °K.

We can conclude from these last two calculations that the size and, more importantly, the sign of the temperature coefficient of the band-gap energy do depend on the specific vibrational properties of lead telluride.

There is one additional consideration that enters into the nature of the temperature dependence of a given band structure which is evident from the results given above. Examination of Fig. 2 reveals that the reason why the band gap increases as temperature increases is that the $L_6^-(L_{2'})$ level has, initially, a smaller shift with temperature than the $L_6^+(L_1)$ level, and both are going down in energy. At higher temperatures, the $L_6^-(L_{2'})$ level has a larger shift with temperature than the $L_6^+(L_2)$, and both are going up. In both cases, the nature of the individual effects on the two levels is such as to increase their separation as the temperature increases. Suppose, however, tha the levels were reversed; namely, suppose the $L_6^+(L_1)$ level occurred above the $L_6^-(L_{2'})$ level. We have performed a calculation like this by adjusting the s-shift parameter on the lead atom until the $L_6^+(L_1)$ and $L_6^-(L_{2'})$ levels have been reversed. The results are shown in Table VII for 0 and 300 °K. They clearly show that the individual levels exhibit the same kind of temperature dependence as in the prior calculation, and consequently we obtain a

net decrease in the size of the energy gap with temperature. This calculation appears to indicate that, with fixed Debye-Waller factors, each level has a characteristic temperature dependence which is roughly independent of the ordering at the gap. The importance of the Debye-Waller factor is, however, made evident by calculation G.

This characteristic temperature dependence of the levels is interesting because of much recent work on SnTe and alloys of SnTe with the lead salts. SnTe is known to have a negative temperature coefficient of the band gap like most materials.[16] Dimmock *et al.*[17] have observed that the band gap in $Pb_xSn_{1-x}Te$ alloys exhibits a compostion dependence of such a nature that they postulate a band structure for SnTe which has the levels comprising the band gap inverted from those of PbTe. In other words, they suggest that their experimental observations can be explained by assuming that the $L_6^-(L_{2'})$ level is the valence-band edge, and the $L_6^+(L_1)$ level is the conduction-band edge in SnTe. Recent work of Herman *et al.*[15] on the theoretical side supports this assignment for the levels that make up the band gap in tin telluride, although the calculations of Tung and Cohen[18] complicate the picture somewhat. The modification of the ordering of the levels through a change in the s-shift parameter represents our attempt to simulate the band structure of SnTe through the simplest possible adjustment of the parameters of the band structure. Although we have no measurements of the Debye-Waller factors for tin telluride and no pseudopotential calculation of the band structure, it appears reasonable on the basis of the above calculation to expect that we would obtain a negative temperature coefficient of the band gap for tin telluride. This expectation rests on the assumption that the temperature dependence of the individual levels would remain about the same as in PbTe even though the levels have a different ordering and that the Debye-Waller factors would show that the vibrational amplitude of the tin atom is larger than that of the tellurium atom.

VI. CONCLUSION

This work shows quite clearly that the Brooks-Yu theory is capable of yielding an increase of the band gap with increasing temperature, in spite of the fact that the individual ionic effective pseudopotentials decrease with increasing temperature. However, because of the uncertainties associated with the pseudopotential band calculation we have used, it cannot be called a definitive calculation of the temperature dependence of the PbTe band gap. The good agreement with experiment within a factor of 2 with no adjustable parameters indicates that much of the physics associated with the ex-

TABLE VII. Temperature dependence of the band gap for the case where the L_1 and L_2' levels are interchanged (energies in Ry). (Change α_{Pb} from − 1.1 to − 1.5.)

Level	0 °K	300 °K
L_1	0.539 89	0.540 13
L_3	0.390 46	0.414 21
L_2'	0.520 21	0.541 78
L_3'	0.624 16	0.635 48
gap	0.019 68	0.001 65

plicit effect in PbTe is contained within the theory. Nevertheless, it should be clear that in order to obtain a more complete understanding, ours should not be the last calculation.

ACKNOWLEDGMENTS

We are deeply indebted to W. Paul for drawing our attention to this problem and for helpful discussions, to P. J. Lin-Chung for considerable detailed aid in our efforts to understand the Lin-Kleinman calculation, to R. Cowley for supplying the vibrational eigenvectors and eigenvalues, to J. P. Van Dyke and F. Herman for supplying the results of their band-structure calculation in advance of publication, and to F. Molea for aid in the experimental aspects of the problem.

APPENDIX

In this appendix we report on an examination of the Fan[1] theory of temperature dependence of the band gap in semiconductors. This investigation has indicated that it may be possible to obtain a positive temperature dependence of the band gap in

some semiconductors using Fan's theory in a more complete form.

We will proceed by reiterating Fan's derivation of the temperature dependence of semiconductor band gaps and in the process indicate where a more complete development might be called for. Fan writes the change in the electron-lattice interaction energy due to the lattice distortion as

$$\Delta u = \sum_{\vec{q}} [a(\vec{q}) e^{i\vec{q}\cdot\vec{r}} + a^*(\vec{q}) e^{-i\vec{q}\cdot\vec{r}}] f(\vec{q}) , \tag{A1}$$

where r represents the coordinates of the electron and $a(\vec{q})$ is the time-dependent amplitude of the normal mode having wave number $\vec{q}$. The Bloch wave functions for electrons in the periodic lattice ψ are characterized by a reduced wave vector $\vec{k}$ and an index σ which takes on the values "c" and "v" for conduction and valence bands, respectively. The wave function for the ions χ is a product of harmonic oscillator wave functions, one for each normal mode. It can be specified by a set of quantum numbers n for the various modes. Following Fröhlich,[19] Fan writes the second-order approximation for the interaction energy of the whole crystal as

$$\Delta E = \sum_{\vec{k};\sigma} \sum_{\vec{q},\sigma'} \frac{|[\psi(\vec{k}\pm\vec{q},\sigma')\chi(n_q\mp 1)|\Delta u|\psi(\vec{k},\sigma)\chi(n_q)]|^2}{\epsilon(\vec{k},\sigma) - \epsilon(\vec{k}\pm\vec{q},\sigma')\pm\hbar\omega_q} , \tag{A2}$$

where ϵ is the electron energy in the undistorted lattice, and ω_q is the angular frequency of the normal mode $\vec{q}$. The summation over $\vec{k}$ and σ covers all the occupied states, whereas the summation over $\vec{q}$ and σ' is limited by the requirement that $(\vec{k}\pm\vec{q},\sigma')$ must be an unoccupied state. In the analysis which follows, Fan neglects terms for which $\sigma\neq\sigma'$ because the associated energy denominators are large enough to make the corresponding terms negligible for the semiconductors of interest to him at that time. Our present analysis differs from his only in that such terms are retained.

When an electron is shifted from a state near the top of the valence band $(\vec{k}_t, v)$ to a state near the bottom of the conduction band $(\vec{k}_b, c)$, the change in the interaction energy is

$$\Delta E_q = \sum_{\vec{q},\sigma'} \frac{|[\psi(\vec{k}_b\pm\vec{q},\sigma')\chi(n_q\mp 1)|\Delta u|\psi(\vec{k}_b,c)\chi(n_q)]|^2}{\epsilon(\vec{k}_b,c) - \epsilon(\vec{k}_b\pm\vec{q},\sigma')\pm\hbar\omega_q} - \sum_{\vec{k},\sigma} \frac{|[\psi(\vec{k}\pm\vec{q}=\vec{k}_b,c)\chi(n_q\mp 1)|\Delta u|\psi(\vec{k},\sigma)\chi(n_q)]|^2}{\epsilon(\vec{k},\sigma) - \epsilon(\vec{k}\pm\vec{q}=\vec{k}_b,c)\pm\hbar\omega_q}$$

$$- \sum_{\vec{q},\sigma'} \frac{|[\psi(\vec{k}_t\pm\vec{q},\sigma')\chi(n_q\mp 1)|\Delta u|\psi(\vec{k}_t,v)\chi(n_q)]|^2}{\epsilon(\vec{k}_t,v) - \epsilon(\vec{k}_t\pm\vec{q},\sigma')\pm\hbar\omega_q} + \sum_{\vec{k},\sigma} \frac{|[\psi(\vec{k}\pm\vec{q}=\vec{k}_t,v)\chi(n_q\mp 1)|\Delta u|\psi(\vec{k},\sigma)\chi(n_q)]|^2}{\epsilon(\vec{k},\sigma) - \epsilon(\vec{k}\pm\vec{q}=\vec{k}_t,v)\pm\hbar\omega_q} . \tag{A3}$$

As stated by Fan, "The first two terms are due to the introduction of an extra electron into the state $(\vec{k}_b,c)$ and the last two terms are due to the removal of an electron from the states $(\vec{k}_t, v)$." Since only a small number of states of the valence and conduction bands are empty and filled, respectively, we may approximate these bands as full and empty, respectively. In that case, in the first term there are only contributions when $\sigma' = c$. Similarly, contributions to the second term come only when $\sigma = v$, and so on. As a result, Eq. (A3) may be rewritten as

$$\Delta E_g = \sum_{\vec{q}} \frac{|[\psi(\vec{k}_b\pm\vec{q},c)\chi(n_q\mp 1)|\Delta u|\psi(\vec{k}_b,c)\chi(n_q)]|^2}{\epsilon(\vec{k}_b,c) - \epsilon(\vec{k}_b\pm\vec{q},c)\pm\hbar\omega_q} - \sum_{\vec{k}} \frac{|[\psi(\vec{k}\pm\vec{q}=\vec{k}_b,c)\chi(n_q\mp 1)|\Delta u|\psi(\vec{k},v)\chi(n_q)]|^2}{\epsilon(\vec{k},v) - \epsilon(\vec{k}\pm\vec{q}=\vec{k}_b,c)\pm\hbar\omega_q}$$

$$- \sum_{\vec{q}} \frac{|[\psi(\vec{k}_t\pm\vec{q},c)\chi(n_q\mp 1)|\Delta u|\psi(\vec{k}_t,v)\chi(n_q)]|^2}{\epsilon(\vec{k}_t,v) - \epsilon(\vec{k}_t\pm\vec{q},c)\pm\hbar\omega_q} + \sum_{\vec{k}} \frac{|[\psi(\vec{k}\pm\vec{q}=\vec{k}_t,v)\chi(n_q\mp 1)|\Delta u|\psi(\vec{k},v)\chi(n_q)]|^2}{\epsilon(\vec{k},v) - \epsilon(\vec{k}\pm\vec{q}=\vec{k}_t,v)\pm\hbar\omega_q} . \tag{A4}$$

The first and fourth terms of Eq. (A4) are those obtained by Fan. They always contribute negatively because the denominators are negative for all terms. The second and third terms are the contributions of this work. These terms always contribute positively to the shift because their denominators are also negative. Thus, the sign of the shift of the gap with temperature can be viewed as a competition between the interband and intraband terms. Only if the band gap is relatively small, or if there are unusual circumstances which make the interband very much larger than the intraband matrix elements, can we admit the possibility of an increase of the band gap with temperature.

Since the band gap in PbTe is rather small, it is possible that these self-energy contributions will also contribute positively to the temperature dependence. We have not evaluated them numerically. Because of the difficulties discussed above with the pseudopotential used here, such a calculation seemed inappropriate.

*This work constituted part of a Ph. D. thesis submitted to Harvard University by CK, Cambridge, Mass.

†Work supported in part by the National Science Foundation under Grant No. GK-2967, by the Advanced Research Projects Agency through the Center for Materials Research, Stanford University, Stanford, Calif., and by Contract No. SD-88, as well as the Division of Engineering and Applied Physics, Harvard University, Cambridge, Mass.

‡Present address: Department of Physics, University of Scranton, Scranton, Pa. 18510.

§Present address: Research Laboratories, Xerox Corporation, Rochester, N. Y. 14603.

[1]H. Y. Fan, Phys. Rev. 78, 808 (1950); 82, 900 (1951).

[2]V. Prakash, Ph. D. thesis, Harvard University, 1967 (unpublished).

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

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

[5]W. Cochran, R. A. Cowley, G. Dolling, and M. M. Elcombe, Proc. Roy. Soc. (London) A293, 433 (1966).

[6]P. J. Lin and L. Kleinman, Phys. Rev. 142, 478 (1966).

[7]Samples were obtained from Electronic Space Products Inc., 854 So. Robertson Blvd., Los Angeles, Calif. Purity based on their analysis.

[8]A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic, New York, 1963).

[9]E. W. Kellerman, Phil. Trans. Roy. Soc. London A238, 513 (1940).

[10]W. V. Houston, Rev. Mod. Phys. 20, 161 (1948).

[11]J. C. Slater, Phys. Rev. 36, 57 (1930).

[12]A. W. Luehrmann, Ph. D. thesis, University of Chicago, 1967 (unpublished); see also, A. W. Luehrmann, Advan. Phys. 17, 1 (1968).

[13]C. Keffer, Ph. D. thesis, Harvard University, 1969 (unpublished).

[14]P. J. Lin-Chung (private communication).

[15]F. Herman, R. L. Kortum, I. B. Ortenburger, and J. P. Van Duke, J. Phys. (Paris) 29, 62 (1968).

[16]L. Esaki and P. J. Stiles, Phys. Rev. Letters 16, 1108 (1966).

[17]J. O. Dimmock, I. Melngailis, and A. J. Strauss, Phys. Rev. Letters 16, 1193 (1966).

[18]Y. W. Tung and M. L. Cohen, Phys. Letters 29A, 236 (1969).

[19]H. Fröhlich, Phys. Rev. 79, 845 (1950).