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¹⁵Using standard estimates for R^S (Refs. 5 and 14), the condition $|R^S| < 2|\gamma^S|N^S$ is satisfied (in order of magnitude sense) provided $(T_i/T_e)[\int N_{\Delta\vec{k}}^S \omega_{\Delta\vec{k}}^S d(\Delta\vec{k})]/n_0 k_B T_e \ll (\pi^3 m/2M)^{1/2}$. With $N_{\Delta\vec{k}}^S \approx -S_{\Delta\vec{k}}^S/2\gamma_{\Delta\vec{k}}^S$, the above inequality imposes a restriction on $S_{\Delta\vec{k}}^S$ for which nonlinear Landau damping effects may be neglected in Eq. (11).

¹⁶With $G(k, k', t=0) = \delta(k-k')$.

¹⁷G. N. Watson, A Treatise on the Theory of Bessel Functions (University Press, Cambridge, England, 1962), 2nd ed., p. 77.

PbTe DEBYE-WALLER FACTORS AND BAND-GAP TEMPERATURE DEPENDENCE*†

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Experimentally verified, calculated Debye-Waller factors have been combined with a modified Lin-Kleinman pseudopotential and formalism to compute the temperature dependence of the PbTe direct band gap. The band-gap increase of 0.008 Ry between 100 and 300°K is in fair agreement with an experimental estimate of the explicit increase.

This Letter reports a relatively successful calculation of the positive explicit temperature dependence of the fundamental band gap E_g of PbTe. This temperature dependence ($\Delta E_g/\Delta T$) was calculated using the theory of Brooks and Yu,¹ combined with a slightly modified Lin-Kleinman² pseudopotential calculation.

Brooks and Yu¹ have shown that the dominant portion of the explicit temperature dependence of the one-electron band structure is obtained by replacing each ionic pseudopotential form factor $V_i(K)$ with a temperature-dependent form factor $V_i(K, T)$, which is given by

$$\begin{aligned} V_i(K, T) &= V_i(K) \exp[-W_i(K, T)] \\ &\equiv V_i(K) \exp[-2\pi^2 \langle u_i^2(T) \rangle / d^2(K)]. \end{aligned} \quad (1)$$

In Eq. (1), the subscript i labels ions, $W_i(K, T)$ is the appropriate Debye-Waller factor associated with the mean square thermal displacement $\langle u_i^2 \rangle$ of the i th ion, and $d(K)$ is the interplanar spacing associated with K .

The W_i were obtained initially by measurements of the temperature dependences of a number of Bragg x-ray diffraction peaks, under the assumption that the W_i are proportional to temperature in the region between 80 and 300°K. These measurements gave the unexpected result that the Pb mean square displacement is significantly greater than that of Te over the measured

temperature range. To check the validity of this result, the $\langle u_i^2 \rangle$ were calculated using vibrational eigenvalues and eigenvectors supplied by Cowley for PbTe. These were computed by Cochran et al.³ in an analysis of their neutron-diffraction measurements of the vibrational frequencies. The calculated $\langle u_i^2 \rangle$, which are in reasonable agreement with the experimental measurements, are shown in Fig. 1. Examination of the $\langle u_i^2 \rangle$ calculation indicates that the Pb motion dominates most of the acoustic modes, whereas the Te motion dominates most of the optical modes. Since the acoustic modes have lower vibrational frequencies, their thermal weighting is greater than that of the optical modes. As a result,

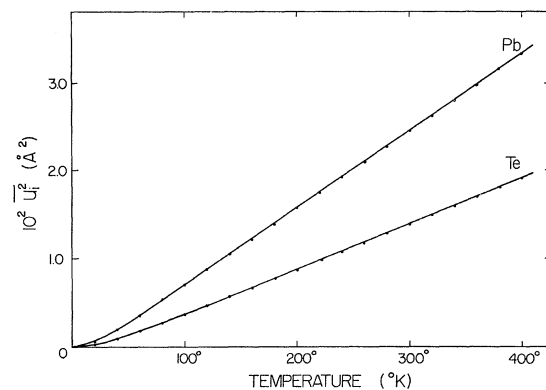


FIG. 1. Calculated mean square displacements of Pb and Te in PbTe as a function of temperature.

$$\langle u_{\text{Pb}}^2 \rangle > \langle u_{\text{Te}}^2 \rangle.$$

This result leads immediately to an increase with temperature of certain Fourier coefficients of the PbTe pseudopotential. The first five pseudopotential coefficients of Lin and Kleinman are considerably larger in magnitude than the remainder, and $|V_{\text{Te}}| > |V_{\text{Pb}}|$ for them. In addition, both the Pb and Te coefficients are negative. Since the structure is fcc, the Miller indices describing the reciprocal lattice vectors are all even or all odd. For the odd vectors,

$$V(K, T) = V_{\text{Te}}(K) \exp[-W_{\text{Te}}(K, T)] - V_{\text{Pb}}(K) \exp[-W_{\text{Pb}}(K, T)]. \quad (2)$$

At 0°K, a decrease in $|V_{\text{Pb}}|$ would result in an increase in $|V(K, 0)|$. As the temperature is increased, the decrease in the Debye-Waller factor of Pb is sufficiently larger than the corresponding decrease in the Te factor that these $V(K, T)$ increase in magnitude with temperature.

This positive temperature dependence of certain $V(K, T)$ gives a clue to the origin of the positive $\Delta E_g/\Delta T$ within the Brooks-Yu theory. When E_g is very small compared with the dominant Fourier coefficients of the ionic pseudopotentials, there must be strong cancellations among the terms. As a result, $\Delta E_g/\Delta T$ depends sensitively upon the relative temperature dependences of terms contributing positively and negatively. In particular, its sign depends upon the detailed nature of the system. The relatively important differences in the temperature dependences of the significant pseudopotential coefficients in PbTe suggested to us the possibility of a successful calculation of $\Delta E_g/\Delta T$ in this instance.

Our initial attempts to calculate $\Delta E_g/\Delta T$ involved the use of the Lin-Kleinman² formalism and pseudopotential parameters. For reasons to be described in detail elsewhere, it became apparent that both would have to be modified slightly. Since modifications were required, the band structure in the vicinity of the gap was adjusted in the direction of agreement at the symmetry point L with the more recent calculation of Herman *et al.*⁴ The positions of the relevant levels in the two calculations are shown in Fig. 2.

The remainder of Fig. 2 exhibits the calculated positions of the relevant bands for 100, 200, and 300°K. These were obtained by recalculating the modified Lin-Kleinman band structure at each temperature using potential form factors as

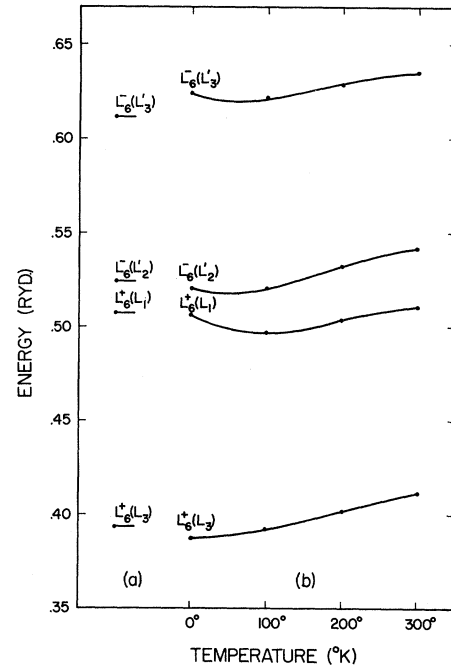


FIG. 2. Energy levels at L in the region of the PbTe band gap. (a) As calculated by Herman *et al.* (b) As calculated here as a function of temperature.

determined according to Eq. (1) with the calculated $\langle u_i^2 \rangle$. The positive sign of $\Delta E_g/\Delta T$ is apparent from this graph. The magnitude of the calculated shift is 0.008 Ry from 100 to 300°K, as compared with an experimental value⁵ of 0.004 Ry for the explicit shift. It is apparent from this calculation that the magnitude of the shift is quite sensitive to the form of the pseudopotential. Indeed, reasonable modifications in the pseudopotential have changed the magnitude of the calculated shift by a factor of 2 in either direction, but have not changed its sign.

The magnitude and sign of $\Delta E_g/\Delta T$ are also sensitive to the dynamics of the system. This has been verified by calculations with different $\langle u_i^2 \rangle$. Indeed, interchanging the $\langle u_i^2 \rangle$ changes the sign of the calculated shift.

In addition, the relative ordering of the levels is quite important in determining $\Delta E_g/\Delta T$. That is, the $L_6^-(L_2')$ level must be above the $L_6^+(L_1)$ level in PbTe. As shown in Fig. 2, the effect of temperature is more pronounced on $L_6^-(L_2')$ than on $L_6^+(L_1)$, leading to the increase in the gap. If their ordering were reversed but their temperature dependences to remain as shown, the gap would decrease. This inversion of levels and the corresponding change in the sign of $\Delta E_g/\Delta T$ have been suggested by Dimmock, Melngailis, and

Strauss⁶ for SnTe and have been partially verified by the band-structure calculations of Herman *et al.*⁴

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