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Pressure and temperature dependence of electronic energy levels in PbSe and PbTe[†]

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Using recent highly accurate pseudopotential band structures of PbSe and PbTe, the variation of the smallest gap at L with hydrostatic pressure and with temperature has been calculated. The experimental values of the pressure coefficient can well be reproduced assuming reasonable slopes of the pseudopotential-form-factor curves. Combining these values with experimental compressibility and thermal-expansion coefficients, the anharmonic part of the temperature coefficient has been evaluated and found to contribute about 50% to the total experimental temperature coefficient. The remaining contribution arising from electron-phonon interactions has been analyzed using Brooks-Yu and Fan-like scattering theory. While the inclusion of a Debye-Waller factor yields reasonable results for the L gap in PbTe, it fails for the Σ-L gap and it predicts a temperature coefficient of the opposite sign for PbSe. A detailed analysis of the PbSe discrepancy is presented. It is proposed that Fan-type *intra*valley and *inter*valley scattering can resolve the dilemma. First-order estimates for Fan-type scattering contributions are presented.

I. INTRODUCTION

The semiconductors PbTe and PbSe show a small (~0.2 eV) direct gap at the point L of the Brillouin zone. The dependence of this gap on pressure and on temperature has been a puzzling question for some time. In contrast to most semiconductors, this gap *decreases* with hydrostatic pressure[1–3] and *increases* with temperature.[3–5] Though the effect of pressure could well be simulated by several band structure models,[6] its origin has not been clarified sufficiently so far. The calculations presented in this paper are based on recently developed band structure models of very high accuracy for PbSe and PbTe.[7,8] The calculations serve both as a check on the quality of the band-structure models and as an explanation of the nature of the negative pressure coefficient.

The situation with regard to the temperature variation of the gap is even less clear and has been the object of many studies.[9–11] Straightforward application of Fan's[12] theory fails because it always produces a negative temperature coefficient of the gap. However, as already pointed out by Keffer *et al.*,[11] Fan's theory might give a different result if reformulated without neglecting the potentially important interband terms. Brooks and Yu[13] have proposed a new theory of the temperature variation of electronic energy levels based on the introduction of a Debye-Waller-like factor in the calculation of band structures. This procedure was applied to PbTe by Keffer *et al.*[9,10] and by Tsang *et al.*[11] and yielded fair agreement with experiment. The band structures used in the two cases, however, were incorrect near the band gap, since they predicted an inverted band ordering at L, which on the basis of recent calculations is inconsistent with effective-mass anisotropies.[7] Moreover, recent Debye-Waller-type calculations of Guenzer *et al.*[14] on HgTe have failed to give good values for the temperature variation of the band gap. This seems to indicate that despite several successful applications,[9–11] the Debye-Waller-type treatment at finite temperatures may be incomplete. Using formal theory, it can also be argued that this is not unexpected.

We shall show in this paper that the Brooks-Yu theory applied to very accurate band models of PbTe and PbSe is only partially successful and that the additional inclusion of generalized Fan-type terms might give satisfactory results. In Sec. II, we shall analyze the variation of the gap in PbSe and PbTe with hydrostatic pressure, and in Sec. III, we shall discuss the gap variation with temperature.

II. PRESSURE COEFFICIENT

Both pressure and temperature effects appear as second-order corrections to the band structure. The most practical way to compute these effects is to evaluate directly the derivatives of the energy levels with respect to pressure or temperature. For the case of hydrostatic pressure, we can write for the change of a given electron level with pressure at constant temperature

$$\frac{\partial E_n}{\partial P}\bigg|_T = \frac{1}{\Omega}\frac{\partial \Omega}{\partial P}\bigg|_T \; \Omega\frac{\partial E_n}{\partial \Omega}\bigg|_T , \tag{1}$$

where Ω is the unit cell volume and

$$\frac{1}{\Omega}\frac{\partial \Omega}{\partial P}\bigg|_T = \kappa$$

is the compressibility of the material which is known experimentally.[15] The deformation potential $\Omega\,\partial E_n/\partial\Omega$ can be evaluated from band-structure data using perturbation theory:

$$\Omega \frac{\partial E_n}{\partial \Omega} = \Omega \langle \psi_n | \frac{\partial H}{\partial \Omega} | \psi_n \rangle . \tag{2}$$

The Hamiltonian we used to calculate the band structures of PbTe and PbSe is based on the pseudopotential scheme and contains the following terms[7]:

$$H = T + V_L + V_{\mathrm{NL}} + V_{\mathrm{SO}} . \tag{3}$$

The matrix elements of H between plane waves $\vec{\mathrm{K}} = \vec{\mathrm{k}} + \vec{\mathrm{G}}$ and $\vec{\mathrm{K}}' = \vec{\mathrm{k}} + \vec{\mathrm{G}}'$ and spin s and s' have the form for the kinetic energy

$$T = (K^2/m^*)\, \delta_{KK'} \delta_{ss'} ;$$

for the local pseudopotential

$$V_L = \sum_{\alpha} S_\alpha(\vec{\mathrm{K}} - \vec{\mathrm{K}}')\, V_\alpha(|\vec{\mathrm{K}} - \vec{\mathrm{K}}'|)\, \delta_{ss'} ; \tag{4}$$

for the nonlocal d-like pseudopotential

$$V_{\mathrm{NL}} = \sum_{\alpha} S_\alpha(\vec{\mathrm{K}} - \vec{\mathrm{K}}') \frac{(2l+1)4\pi}{\Omega} A_\alpha B^{\alpha}_{n,l}(|\vec{\mathrm{K}}|) \times B^{\alpha}_{n,l}(|\vec{\mathrm{K}}'|) P_l(\cos\theta)\, \delta_{ss'} \quad \text{for } l = 2 ;$$

for the p-like spin-orbit potential

$$V_{\mathrm{SO}} = \sum_{\alpha} S_\alpha(\vec{\mathrm{K}} - \vec{\mathrm{K}}')\, i \frac{(2l+1)4\pi}{\Omega} \lambda_\alpha B^{\alpha}_{n,l}(|\vec{\mathrm{K}}|) \times B^{\alpha}_{n,l}(|\vec{\mathrm{K}}'|) \frac{\vec{\mathrm{K}} \times \vec{\mathrm{K}}'}{|\vec{\mathrm{K}}|\, |\vec{\mathrm{K}}'|} \langle s | \sigma | s' \rangle \quad \text{for } l = 1 ,$$

where m^* is an effective-mass parameter introduced to simulate nonlocality to first order,[7] $S_\alpha(\vec{\mathrm{G}})$ is the structure factor, and $V_\alpha(|\vec{\mathrm{G}}|)$ is the local form factor of atom α. The nonlocal potential V_{NL} is used only for $l = 2$, the spin-orbit potential only for $l = 1$, their respective strength being described by the two parameters A_α and λ_α. $P_l(\cos\theta)$ is the Legendre polynomial of order l for an angle θ between the wave vectors $\vec{\mathrm{K}}$ and $\vec{\mathrm{K}}'$. The functions $B^{\alpha}_{n,l}(|\vec{\mathrm{K}}|) = \int_0^\infty R^{\alpha}_{n,l}(r) j_l(Kr) r^2 dr$ are slowly varying functions of $|\vec{\mathrm{K}}|$, depending on the atomic radial functions $R^{\alpha}_{n,l}(r)$ and on spherical Bessel functions $j_l(Kr)$. The quantity $\langle s | \vec{\sigma} | s \rangle$ represents the usual spin matrix element. Assuming the eigensolution for the energy E_n to be given by the following pseudo-wave-function:

$$\psi_n = \sum_{\vec{\mathrm{G}}} a^n_{\vec{\mathrm{G}}}(\vec{\mathrm{k}})\, e^{i(\vec{\mathrm{k}} + \vec{\mathrm{G}}) \cdot \vec{\mathrm{r}}} , \tag{5}$$

where the coefficients $a^n_{\vec{\mathrm{G}}}(\vec{\mathrm{k}})$ are spinors, we can evaluate the contributions to the matrix element in Eq. (2) arising from the different terms of Eq. (3). We find, for the kinetic-energy term,

$$\Omega \frac{\partial E^{\mathrm{kin}}_n}{\partial \Omega} = -\frac{2}{3} \sum_{\vec{\mathrm{G}}} \frac{|\vec{\mathrm{k}} + \vec{\mathrm{G}}|^2}{m^*} a^{n*}_{\vec{\mathrm{G}}} a^n_{\vec{\mathrm{G}}} = -\tfrac{2}{3} E^{\mathrm{kin}}_n \tag{6}$$

and for the local-potential term,

$$\Omega \frac{\partial E^{\mathrm{L}}_n}{\partial \Omega} = \sum_{\vec{\mathrm{G}}} \rho^n_{\mathrm{L}}(\vec{\mathrm{G}}) \Omega \frac{\partial V_L(\vec{\mathrm{G}})}{\partial \Omega} , \tag{7}$$

with the charge Fourier components

$$\rho^n_L(\vec{\mathrm{G}}) = \sum_{\vec{\mathrm{G}}'} a^{n*}_{\vec{\mathrm{G}}'} a^n_{\vec{\mathrm{G}}' + \vec{\mathrm{G}}} .$$

Equation (7) represents a novel very convenient way to express derivatives of local potentials in first-order perturbation. The intrinsic properties of a particular energy level $E_n(\vec{\mathrm{k}})$ can easily be analyzed by inspecting the various Fourier components of the charge density $\rho^n_{\vec{\mathrm{k}}}(\vec{\mathrm{G}})$ and their combination with the corresponding Fourier components of the potential derivative. The derivative of the local pseudopotential, with respect to volume can be obtained from

$$V_L(\vec{\mathrm{G}}) = \frac{1}{\Omega} \int e^{-i\vec{\mathrm{G}} \cdot \vec{\mathrm{r}}} V(\vec{\mathrm{r}})\, d\vec{\mathrm{r}} , \tag{8}$$

to be

$$\Omega \frac{\partial V_L(\vec{\mathrm{G}})}{\partial \Omega} = -V_L(\vec{\mathrm{G}}) \left(1 + \frac{|\vec{\mathrm{G}}|}{3} \frac{1}{V_L(\vec{\mathrm{G}})} \frac{\partial V_L(|\vec{\mathrm{G}}|)}{\partial |\vec{\mathrm{G}}|} \right) , \tag{9}$$

by neglecting contributions arising from the crystal surface. Pressure dependence as well as the temperature dependence of m^* have been neglected. For the nonlocal-potential term and the spin-orbit term we find

$$\Omega \frac{\partial E^{\mathrm{NL}}_n}{\partial \Omega} = \sum_{\vec{\mathrm{G}}} \sum_{\vec{\mathrm{G}}'} a^{n*}_{\vec{\mathrm{G}}'} a^n_{\vec{\mathrm{G}}} \Omega \frac{\partial V_{\mathrm{NL}}(\vec{\mathrm{K}}, \vec{\mathrm{K}}')}{\partial \Omega} \tag{10}$$

and

$$\Omega \frac{\partial E^{\mathrm{SO}}_n}{\partial \Omega} = \sum_{\vec{\mathrm{G}}} \sum_{\vec{\mathrm{G}}'} a^{n*}_{\vec{\mathrm{G}}'} a^n_{\vec{\mathrm{G}}} \Omega \frac{\partial V_{\mathrm{SO}}(\vec{\mathrm{K}}, \vec{\mathrm{K}}')}{\partial \Omega} , \tag{11}$$

respectively, where

$$\Omega \frac{\partial V_{\mathrm{NL}}(\vec{\mathrm{K}}, \vec{\mathrm{K}}')}{\partial \Omega} = -V_{\mathrm{NL}} \left(1 + \tfrac{1}{3} |\vec{\mathrm{K}}| \frac{1}{B_{nl}(|\vec{\mathrm{K}}|)} \frac{\partial B_{nl}(|\vec{\mathrm{K}}|)}{\partial |\vec{\mathrm{K}}|} + \frac{|\vec{\mathrm{K}}'|}{3} \frac{1}{B_{nl}(|\vec{\mathrm{K}}'|)} \frac{\partial B_{nl}(|\vec{\mathrm{K}}'|)}{\partial |\vec{\mathrm{K}}'|} \right) , \tag{12}$$

and similarly for V_{SO}.

In all derivatives of the potentials, the first term arises from the $1/\Omega$ scaling factor and the second term from the functional dependence of the potential on $\vec{\mathrm{K}}$, $\vec{\mathrm{K}}'$ which, in turn, depend on the volume. Due to its dependence on $\vec{\mathrm{K}} - \vec{\mathrm{K}}'$, the derivative of the local potential can be written in terms of charge-density Fourier components. This is not possible for the nonlocal d-like potential and for the spin-orbit potential. However, their contributions to the total deformation potential are small and

TABLE I. Symmetric V_S and and antisymmetric V_A form factors for PbSe and PbTe and their slopes $\partial V_S/\partial G$, $\partial V_A/\partial G$ as they are used to calculate the pressure coefficients. Potentials are given in rydbergs and G in units of $2\pi/a$, where a is the lattice parameter.

	G^2	3	4	8	11	12	16
PbSe	V_A	0.0590			−0.010		
	V_S		−0.2064	−0.0129		0.040	0.0688
	dV_A/dG	−0.050			−0.015		
	dV_S/dG		0.35	0.18		0.070	0.030
PbTe	V_A	0.0358			−0.0112		
	V_S		−0.238	−0.0168		0.0548	0.0668
	dV_A/dG	−0.035			−0.030		
	dV_S/dG		0.30	0.19		0.060	0.020

therefore can be neglected in discussing the physical origin of the pressure coefficient. From Eq. (9), we see that the result depends on additional parameters, i.e., on the slopes $\partial V_L(|\vec{G}|)/\partial|\vec{G}|$. It turns out, in practice, that the pressure coefficient is rather sensitive to the values of $\partial V_L(|\vec{G}|)/\partial|\vec{G}|$ and that the calculations can be used to determine the slopes of the local pseudopotential very accurately, rather than to check the quality of values $V_L(|\vec{G}|)$ of the pseudopotential itself. In Table I, we list the values of the local pseudopotential parameters $V_S(|\vec{G}|)$ and $V_A(|\vec{G}|)$ as used in Ref. 7 to calculate the band structures of PbSe and PbTe together with the slopes $\partial V_S/\partial|\vec{G}|$ and $\partial V_A/\partial|\vec{G}|$ determined by fitting the pressure coefficient of the L gap to experiment.

In Table II, we present the experimental and calculated[7] energies for the gap at L between $L(5)$ and $L(6)$ and the energy differences between a secondary valence maximum $\Sigma(5)$ (see Ref. 3) and the top of the valence bands $L(5)$. This second valence-band maximum has been considered by several authors[3] to explain anomalies in the experimental temperature dependence of the fundamental gap at L. The energy difference $L(5)-\Sigma(5)$ is found to be temperature dependent[4]; the values given in Table II are extrapolated to $T=0$. In Table II, we also list the pressure coefficients of the two energy gaps obtained experimentally and calculated in the manner described above. The experimental values have been derived from galvanomagnetic measurement, assuming a band-structure model with two valence-band maxima (at L and Σ) of type M_0.[3] From our band-structure calculations it follows, however, that $\Sigma(5)$ is an M_1 critical point as long as its energy is lower than $L(5)$. This fact might render the quoted experimental value of the pressure coefficient of $\Sigma(5)$ doubtful and account for the difference between experiment and calculations. It is worth noting that though the introduction of the slope values $\partial V_L/\partial|\vec{G}|$ added six new free parameters to the system, the ratio of the pressure coefficients of the two gaps $[L(6)-L(5)$ and $L(5)-\Sigma(5)]$ remains relatively independent of these parameters. We shall now discuss the origin of the negative pressure dependence of the fundamental gap at L. A detailed analysis shows that the negative coefficient arises from the anomalously strong deformation

TABLE II. Experimental (compiled in Ref. 3) and theoretical values for different gaps and their pressure dependence in PbSe and PbTe. $E_g=E[L(6)]-E[L(5)]$ stands for the fundamental gap at L while $Eg'=E[L(5)]-E[\Sigma(5)]$ denotes the energy difference between the topmost valence band and the M_1 critical point along Σ. Calculated pressure coefficients have been obtained by using the experimental (Ref. 15) compressibility values of $\kappa=(-2.1\pm0.2)\times10^{-6}$/bar for PbSe and $\kappa=(-2.5\pm0.2)\times10^{-6}$/bar for PbTe.

	E_g(eV)		E_g'(eV)		dE_g/dP (10^{-6} eV/bar)		dE_g'/dP (10^{-6} eV/bar)	
	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
PbSe	0.160	0.157	0.17–0.18	0.188	−8.6 ±0.2	−8.5	⋯	+3.25
PbTe	0.190	0.189	0.25–0.35	0.344	−7.4 ±0.2	−7.5	+7±0.5	+3.25

TABLE III. Calculated deformation potentials for volume changes for the $L(5)$, $L(6)$, and $\Sigma(5)$ bands in PbSe and PbTe. Contributions arising from the kinetic- and potential-energy terms are indicated separately. Also indicated are the calculated characters of the corresponding wave functions in terms of atomic angular functions.

		$\Omega\,\partial E/\partial\Omega$ (eV)		Angular character(%)					
				cation			anion		
		E_{kin}	V_{total}	s	p	d	s	p	d
	$L(5)$	-10.9	-4.2	73	0	2	0	25	0
PbSe	$L(6)$	-9.1	-2.2	0	72	0	14	0	14
	$\Sigma(5)$	-11.5	-2.2	59	0	3	0	38	0
	$L(5)$	-10.0	-1.3	59	0	3	0	38	0
PbTe	$L(6)$	-9.4	$+1.2$	0	83	0	4	0	13
	$\Sigma(5)$	-10.2	$+1.0$	44	0	3	0	53	0

potential of the $L(5)$ valence level.

Separating the contributions arising from the kinetic energy term and the potential terms, we note the dominant role of the kinetic-energy part (see Table III). Its contributions, however, are quite comparable for valence and conduction bands in PbTe and to a somewhat less extent in PbSe. Analyzing the potential contributions in the spirit of Eqs. (7) and (9), we find that $\partial V_L/\partial\Omega$ is largest for $|\vec{G}|^2 = 8$ and has a negative value. For smaller $|\vec{G}|^2$ values, $V_L(|\vec{G}|)$ is negative and cancels with the second term arising from the positive slope; for larger $|\vec{G}|^2$ values both, $V_L(|\vec{G}|)$ and the slopes become smaller. $V_L(|\vec{G}|)$ therefore changes most with volume for $|\vec{G}|$ values where the form-factor curve changes sign; translated into real space, this means that volume changes are felt by the electrons mostly through oscillations with wavelengths of the order of interatomic distances. With this result, we can approximate the potential contribution by

$$\rho^n_{\vec{k}}(|\vec{G}|^2 = 8)\,\frac{\partial V_L(|\vec{G}|^2 = 8)}{\partial\Omega}\ ,$$

indicating that sign and magnitude of $\rho^n_{\vec{k}}(|\vec{G}|^2 = 8)$ determine the effect of the potential on the pressure coefficient. This term adds to the negative kinetic term, if $\rho^n_{\vec{k}}(|\vec{G}|^2 = 8)$ is positive, and therefore increases the absolute value of the pressure coefficient of the energy level, and it subtracts from the kinetic-energy term if $\rho^n_{\vec{k}}(|\vec{G}|^2 = 8)$ is negative. As mentioned above $\rho^n_{\vec{k}}(|\vec{G}|^2 = 8)$, or more generally $\rho^n_{\vec{k}}(|\vec{G}_0|^2)$, where $|\vec{G}_0|^2$ is about the zero in the form factor curve, corresponds to charge-density fluctuations with wavelengths comparable to interatomic distances. Positive values of $\rho^n_{\vec{k}}(|\vec{G}_0|^2)$ pile up charge *at* the atomic sites and therefore correspond to s-like states; negative values of $\rho^n_{\vec{k}}(|\vec{G}_0|^2)$ pile up charge *between* the atoms and are found in p-like states (we choose the origin at an atomic site). This analysis shows that for approximately *equal* kinetic energy, s-like states increase in energy faster with pressure than do p-like states. Applying these arguments to PbSe and PbTe, we expect the $L(5)$ valence level to be more s like (and less p like) than the $L(6)$ conduction level. Calculations done by angular projection[7] confirm these ideas; the fractional theoretical values of s-, p-, and d-like character on cation and anion are indicated in Table III.

III. TEMPERATURE COEFFICIENT

In a similar approach to the pressure case which gives Eq. (1), the change of an electronic level with temperature under constant pressure can be written

$$\left.\frac{\partial E_n}{\partial T}\right|_P = \frac{1}{\Omega}\left.\frac{\partial\Omega}{\partial T}\right|_P\,\Omega\left.\frac{\partial E_n}{\partial\Omega}\right|_T + \left.\frac{\partial E_n}{\partial T}\right|_V . \tag{13}$$

The net change of E_n arises from two contributions: an anharmonic-lattice part given by the product of the thermal-expansion coefficient $\alpha = (1/3\Omega)(\partial\Omega/\partial T)_P$, and a deformation potential $3\Omega(\partial E_n/\partial\Omega)_T$, and from an electron-phonon interaction term $(\partial E_n/\partial T)_V$. The first term can easily be computed, knowing the deformation potential $\Omega\,\partial E_n/\partial\Omega$ from the pressure coefficient calculations (see Table III) and the thermal-expansion coefficients α from experiment.[16] The thermal-expansion coefficients are increasing functions of temperature up to about 150 °K where they reach the constant value of $\alpha = 2\times10^{-5}/^\circ\text{K}$ for both PbSe and PbTe. Thus, with the calculated deformation potentials of Table III, we find that the gap at L opens up due to the thermal-lattice expansion, with a linear coefficient of $(\partial E_g/\partial T)_{\text{anh}} = 1.8\times10^{-4}$ eV/°K for PbTe and $(\partial E_g/\partial T)_{\text{anh}} = 2.3\times10^{-4}$ eV/°K for PbSe for temperatures above 150 °K.

These values contribute about one half to the total experimental-temperature coefficient $(\partial E_g/\partial T)_{\text{expt}} \approx 4.3\times10^{-4}$ eV/°K for PbTe for temperatures between 150 and 450 °K, and to $(\partial E_g/\partial T)_{\text{expt}} \approx 4.4\times10^{-4}$ eV/°K for[4,5] PbSe for temperatures between 150 and 700 °K. Above 450 and 700 °K, respectively, the measured energy gaps become independent of temperature. For this region, there is experimental evidence[3] that the second valence-band maximum at Σ takes over the role of the top-most valence band at these temperatures and that it moves parallel to the first conduction band $L(6)$ with further increasing temperature. On the basis of the Debye-Waller theory , this model would suggest that the character of the $\Sigma(5)$ states resembles the character of the $L(6)$ states, which is not found in our calculations (see Table III). The experimental findings[3] therefore seem to suggest that the temperature dependence of the $\Sigma - L$ gap cannot satisfactorily be described by the Debye-Waller theory.

We shall now discuss possible approximations to the electron-phonon term of Eq. (13). Following the usual method[17] to describe the effect of lattice vibrations on the electronic band structure, we write the energy of an electronic state as a function of atomic displacements $\delta\vec{R}_{l,\alpha}$, where l labels the unit cell, and α labels the individual atom within this cell. If we displace each atom by $\delta\vec{R}_{l,\alpha}$, we can write the Hamiltonian H' for the energy change caused by the displacement as follows:

$$H' = \sum_l \sum_\alpha [V(r - \vec{R}_{l,\alpha} - \delta\vec{R}_{l,\alpha}) - V(r - \vec{R}_{l,\alpha})], \tag{14}$$

or expanding H' in powers of $\delta\vec{R}_{l,\alpha}$, we get

$$H' = \sum_l \sum_\alpha [\delta\vec{R}_{l,\alpha} \cdot \vec{\nabla} V(r - \vec{R}_{l,\alpha}) + \tfrac{1}{2}\delta\vec{R}_{l,\alpha} \cdot \delta\vec{R}_{l,\alpha}\vec{\nabla} \cdot \vec{\nabla} V(r - \vec{R}_{l,\alpha}) + \cdots].$$

The change of energy, accurate to second order in the displacement, is then given by

$$\Delta E_n(\vec{k}) = \frac{1}{2}\sum_l \sum_\alpha \langle n,\vec{k}|\vec{\nabla}^2_{l,\alpha} V|n,\vec{k}\rangle \delta\vec{R}_{l,\alpha} \cdot \delta\vec{R}_{l,\alpha} + \sum_{ll'} \sum_{\alpha\alpha'} \sum_{n',k'} \frac{\langle n,\vec{k}\,|\nabla_{l,\alpha}V|n',k'\rangle\langle n',k'|\nabla_{l',\alpha'}V|n,k\rangle}{E_n(\vec{k}) - E_{n'}(\vec{k}') \pm \hbar\omega_q} \times \delta\vec{R}_{l,\alpha} \cdot \delta\vec{R}_{l',\alpha'}, \tag{15}$$

for an arbitrary set of atomic displacements $\{\delta\vec{R}_{l,\alpha}\}$. We now assume that the temperature-dependent energy shift $\Delta E_n(\vec{k}, T)$ is obtained by thermally averaging over the products of the atomic displacements.

The first term, which is a first-order perturbation term of a two-phonon process, corresponds to the *instantaneous* emission and absorption of two phonons (i.e., of the same phonon if thermal average is assumed). It has been shown by Brooks and Yu[13] that contributions from this term can be obtained by introducing a temperature-dependent Debye-Waller factor e^{-w} into the band-structure calculation. This procedure, however, can lead to serious errors if *nonlocal* pseudopotentials are used in the band-structure calculation. The energy of an electronic level at $T=0$ in the presence of a local and a *nonlocal* potential has the form

$$E_n(\vec{k}, T=0) = \sum_{\vec{G},\vec{G}'} a^{*n}_{\vec{G}'}(\vec{k})\, a^n_{\vec{G}}(\vec{k}) \bigg(\frac{|\vec{k}+\vec{G}|^2}{m^*}\delta_{\vec{G},\vec{G}'} + \sum_\alpha S_\alpha(\vec{G}-\vec{G}')[V^\alpha_L(|\vec{G}-\vec{G}'|) + V^\alpha_{\mathrm{NL}}(\vec{G},\vec{G}',\vec{k})]\bigg), \tag{16}$$

where $a^n_{\vec{G}}(\vec{k})$ are the eigenspinor components of the state. For finite temperature, the structure factors $S_\alpha(\vec{G}-\vec{G}')$ are multiplied by the Debye-Waller factor $\exp[-\frac{1}{2}(\vec{G}-\vec{G}')^2\langle\delta\vec{R}^2_{\alpha,T}\rangle]$, which is equivalent to replacing V^α_L and V^α_{NL} by

$$V^{\alpha\prime}_L = V^\alpha_L \exp[-\tfrac{1}{2}(\vec{G}-\vec{G}')^2\langle\delta\vec{R}^2_{\alpha,T}\rangle],$$

and by

$$V^{\alpha\prime}_{\mathrm{NL}} = V^\alpha_{\mathrm{NL}} \exp[-\tfrac{1}{2}(\vec{G}-\vec{G}')^2\langle\delta\vec{R}^2_{\alpha,T}\rangle], \tag{17}$$

respectively. Since V_L depends only on the difference $(\vec{G}-\vec{G}')$, the energy can partially be written in terms of charge Fourier components $\rho^n_{\vec{k}}(\vec{G})$,

$$E_n(\vec{k}, T) = E_{\mathrm{kin}} + \sum_{\vec{G}} \rho^n_{\vec{k}}(\vec{G}) \sum_\alpha S_\alpha(\vec{G}) \exp(-\tfrac{1}{2}|\vec{G}|^2\langle\delta\vec{R}^2_{\alpha,T}\rangle) V^\alpha_L(|\vec{G}|) + \sum_{\vec{G},\vec{G}'} a^{n*}_{\vec{G}'}(\vec{k})\, a^n_{\vec{G}}(\vec{k}) \times \sum_\alpha S_\alpha(\vec{G}-\vec{G}') \exp(-\tfrac{1}{2}|\vec{G}-\vec{G}|^2\langle\delta\vec{R}^2_{\alpha,T}\rangle) V^\alpha_{\mathrm{NL}}(\vec{G},\vec{G}',\vec{k}). \tag{18}$$

As can be seen from Eq. (18), the inclusion of a Debye-Waller factor merely damps the higher Fourier components of the local potential $V^\alpha_L(|\vec{G}|)$, whereas it destroys the angular character of the nonlocal scattering potential $V^\alpha_{\mathrm{NL}}(\vec{G},\vec{G}',\vec{k})$ by introducing an additional angular dependence through the factor $\exp(-|\vec{G}|\,|\vec{G}'|\langle R^2_{\alpha,T}\rangle\cos\theta)$, where θ is the angle between $\vec{G}$ and $\vec{G}'$. In practice, this result can lead to serious errors; e.g., a nonlocal d-like potential which has been introduced into the $T=0$ band-structure calculation to control the position of higher d-like bands may at finite temperature operationally affect states which have *no d* character at all. In the calculation of the band structures of PbSe and PbTe at finite temperatures, we therefore only included Debye-Waller factors into the *local* potential. With regard to the d-like nonlocal potential used in the band-structure calculation, this procedure does not introduce significant errors since the states at the L or Σ gap contain only little d-like character. For the nonlocal spin-orbit potential, we have assumed that since it is of short range, it should, on the basis of the Born-Oppenheimer approximation, give only small contributions to temperature-dependent energy corrections arising from lattice vibrations. Thus considering only contributions from the local potential, we can express the change of energy with temperature due to the Debye-Waller term in first order,

$$\left.\frac{\partial E_n(\vec{\mathrm{k}})}{\partial T}\right|_{\mathrm{DW}} = -\frac{1}{2}\sum_{\vec{\mathrm{G}}} \rho^n_{\vec{\mathrm{k}}}(\vec{\mathrm{G}})\,|\vec{\mathrm{G}}|^2 \sum_{\alpha} S_\alpha(\vec{\mathrm{G}}) V^\alpha_L(|\vec{\mathrm{G}}|)\,F_\alpha\,, \tag{19}$$

where we assumed the linear temperature dependence of $\langle \delta\vec{\mathrm{R}}^2_{\alpha,T}\rangle = TF_\alpha$. Equation (19) can conveniently be written

$$\left.\frac{\partial E_n(\vec{\mathrm{k}})}{\partial T}\right|_{\mathrm{DW}} = \sum_{\alpha} \frac{\partial E_n}{\partial\langle \delta\vec{\mathrm{R}}^2_\alpha\rangle}\,F_\alpha \tag{20}$$

in order to emphasize the different contributions from different atoms α. The Debye-Waller "deformation" potentials $\partial E_n/\partial\langle\delta\vec{\mathrm{R}}^2_\alpha\rangle$ are listed in Table IV. Only contributions for $|\vec{\mathrm{G}}|^2 \le 16(2\pi/a)^2$ have been considered. Though the quantity $|\vec{\mathrm{G}}|^2\, V(|\vec{\mathrm{G}}|)$ is still important for higher $|\vec{\mathrm{G}}|^2$ values, their net effect on the final temperature coefficient is small, due to the drastic decrease of $\rho^n_{\vec{\mathrm{k}}}(\vec{\mathrm{G}})$ and cancellation effects through the atomic-structure factor. The main contribution arises from the $\vec{\mathrm{G}} = \langle 200\rangle$ and the $\vec{\mathrm{G}} = \langle 222\rangle$ sets of plane waves. The cutoff at $|\vec{\mathrm{G}}|^2 = 16(2\pi/a)^2$ therefore does not considerably influence the calculated values of the temperature coefficients. Combining these calculated values with the experimental and extrapolated values[18] of $F_{\mathrm{Pb}} \approx 1.1 \times 10^{-4}$ Å^2/°K and $F_{\mathrm{Se}} \approx 0.59 \times 10^{-4}$ Å^2/°K for PbSe, and $F_{\mathrm{Pb}} = 1.17\times 10^{-4}$ Å^2/°K and $F_{\mathrm{Te}} = 0.65 \times 10^{-4}$ Å^2/°K for PbTe, we obtain the following temperature coefficients for the gap at L:

$$\partial E_g/\partial T|_{\mathrm{DW}} = -3.6 \times 10^{-4}\ \mathrm{eV/°K} \quad \text{for the PbSe}$$

and

$$\partial E_g/\partial T|_{\mathrm{DW}} = +2.1 \times 10^{-4}\ \mathrm{eV/°K} \quad \text{for PbTe.}$$

Adding these results to the anharmonic lattice contribution, we find that the gap in PbSe closes with temperature with a coefficient of -1.3×10^{-4} eV/°K and that it opens in PbTe with a coefficient of $+3.9 \times 10^{-4}$ eV/°K. These values have to be compared to the experimental results of $(+4.4 \pm 0.2)\times 10^{-4}$ eV/°K for PbSe and $(+4.3 \pm 0.2)\times 10^{-4}$ eV/°K for PbTe. While for PbTe the results agree reasonably for PbSe, even the sign of the temperature coefficient cannot be reproduced.

TABLE IV. Calculated Debye-Waller deformation potentials for lattice vibrations for the $L(5)$, $L(6)$, and $\Sigma(5)$ bands in PbSe and PbTe. Contributions arising from cation and anion are indicated separately. The listed values have to be multiplied by the individual mean-square displacements to give the energy shift caused by lattice vibrations.

		$\frac{\partial E_n}{\partial\langle\partial R^2_\alpha\rangle}$	$\left(\frac{\mathrm{eV}}{\mathrm{\AA}^2}\right)$
		Pb	Se or Te
	$L(5)$	2.0	10.8
PbSe	$L(6)$	6.8	−4.2
	$\Sigma(5)$	0.4	14.5
	$L(5)$	1.1	12.2
PbTe	$L(6)$	11.1	−2.7
	$\Sigma(5)$	−0.4	14.5

It is interesting to compare these calculated coefficients to some erroneous values of $\partial E_g/\partial T|_{\mathrm{DW}}$, which would be obtained, if nonlocal and/or spin-orbit potentials are also scaled by Debye-Waller factors. The inclusion of the spin-orbit contribution would raise the coefficients by (100–200)%, whereas the inclusion of the nonlocal contribution would lower the coefficients by about 100% of the value obtained from the pure local contributions. This example indicates the scale of errors arising at incorrect use of Debye-Waller factors.

The $\Sigma(5) - L(5)$ energy difference is found to be only weakly temperature dependent with a coefficient of about 1×10^{-4} eV/°K for both salts which is *not* in agreement with the previously mentioned experiments.[3] Before we analyze the origin of the difference between the calculated values of $\partial E_g/\partial T$ for PbSe and PbTe, let us inspect how the sign of the temperature coefficients could be changed as a function of $\{F_\alpha\}$. Using the values of Table IV for the deformation potentials, we find for PbSe that $\partial E_g/\partial T > 0$ if

$$\frac{\langle\delta\vec{\mathrm{R}}^2_{\mathrm{Pb},T}\rangle}{\langle\delta\vec{\mathrm{R}}^2_{\mathrm{Se},T}\rangle} > 2.3\,,$$

and for PbTe that $\partial E_g/\partial T > 0$ if

$$\frac{\langle\delta\vec{\mathrm{R}}^2_{\mathrm{Pb},T}\rangle}{\langle\delta\vec{\mathrm{R}}^2_{\mathrm{Te},T}\rangle} > 1.1\,.$$

Even though the measured and extrapolated[18] and calculated[11] values of $\langle\delta\vec{\mathrm{R}}^2_{\alpha,T}\rangle$ show large fluctuations and uncertainties, it seems very unlikely that $\langle\delta\vec{\mathrm{R}}^2_{\mathrm{Pb},T}\rangle$ can exceed $\langle\delta\vec{\mathrm{R}}^2_{\mathrm{Se},T}\rangle$ by a factor of about 3.5 to give the correct temperature coefficient.

Let us now analyze the difference between the temperature coefficients of PbSe and PbTe for given values of $\langle\delta\vec{\mathrm{R}}^2_{\alpha,T}\rangle$. To do this we examine valence $L(5)$ and conduction $L(6)$ bands separately. In both compounds the $L(5)$ valence bands move up with temperature with about the same coefficients of 8.6×10^{-4} eV/°K for PbSe and 9.1×10^{-4} eV/°K for PbTe. Differences appear in the $L(6)$ conduction bands; both move up with temperature but at very different rates: 11.2×10^{-4} eV/°K for PbTe and only 5.0×10^{-4} eV/°K for PbSe. This difference originates (about 80%) from the *lead* contributions, which renders the uncertainty in the determination of the Se mean-square displacement relatively unimportant. From Table III, we see that $L(6)$ is pure p like around the lead atoms with 72% and 83% for PbSe and PbTe, respectively, of p character in the wavefunctions. All these differences have their origin in the band structure, or rather in the band ordering. While in PbSe the lowest conduction level, which has L_6^- symmetry including spin-orbit interaction is derived from a L_2^- level, in PbTe the L_6^- conduction band is derived from a L_3^- level. Moreover, the second L_6^- bands at higher energies, which in PbSe is derived from L_3^-, and in PbTe from L_2^-, show approximately reversed temperature coefficients. We can thus conclude that the different conduction-band ordering in PbSe and PbTe is responsible for the different signs of the Debye-Waller temperature coefficient of the gap. On the other hand, the different band ordering in the two compounds has been shown[7] to be the only possible ordering to account for the very different effective-mass anisotropies found experimentally for PbSe and PbTe.

We like to add that earlier calculations[6, 11] of the temperature effect on the band gap, based on band structures with "PbSe band ordering," also gave a positive coefficient. We believe that this was due to the use of different local pseudopotentials and to the inclusion of nonlocal and spin-orbit terms into the Debye-Waller-type calculation. Since the present band structures can be considered to be highly accurate, e.g., they accurately reproduce gaps, effective masses, photoemission data,[7] and various optical measurements in an energy range from 0 to about 20 eV,[8] we may conclude from our results for the $\Sigma - L$ gap in PbTe and for the PbTe and PbSe comparison of the L gap, that the effect of temperature on electronic levels is *not* sufficiently described by the Brooks-Yu[13] theory.

To extend the treatment of the effect of finite temperature on electronic energy levels, we go back to Eq. (15) and focus on the second term in the perturbation series. This term, introduced by Fan[12] corresponds to the scattering of an electron in state $|\vec{k}, n\rangle$ into another state $|\vec{k}', n'\rangle$ by emitting or absorbing a phonon of wave vector $\vec{q} = \vec{k}' - \vec{k} + \vec{G}^u$ followed by the reversed process. If $\vec{k}' - \vec{k}$ falls outside the first Brillouin zone, umklapp processes with wave vector $\vec{G}^u$ have to be considered. In his original paper, Fan only retained scattering terms with $n = n'$ (intraband terms) with the argument, that the energy denominator in (15) would be large enough to make the interband terms with $n \neq n'$ negligible for the semiconductors he considered. Within this approximation, the Fan term always *decreases* the gap and thus would only deteriorate the situation for PbSe. In the lead salts, however, the band gaps are relatively small and as already pointed out by Keffer *et al.*,[11] the (positive) *inter*band terms might overcompensate the (negative) *intra*band terms. The importance of Fan terms in the lead salts has also been discussed by Martinez.[3]

Expanding the atomic displacements $\delta\vec{R}_{l,\alpha}$ in phonon coordinates and considering the Bloch character of the electronic wave functions, we can write the second term of Eq. (15) as

$$\Delta E = \sum_{k',j} \sum_{n'} \frac{|M^{nn'}_{Q,j}(\vec{k}, \vec{k}')|^2}{E_n(\vec{k}) - E_{n'}(\vec{k}')} , \tag{21}$$

where we have neglected the phonon energy in the energy denominator and also occupation effects, and where the electron-phonon matrix elements for scattering involving *one* mode are given by

$$M^{nn'}_{\vec{Q},j}(\vec{k}, \vec{k}') = -i \left(\frac{\hbar}{2N\omega_{\vec{Q},j}}\right)^{1/2} \sum_{\alpha} \frac{1}{M_\alpha^{1/2}} \sum_{\vec{G}} S_\alpha(\vec{G}) \times [\hat{\epsilon}(\alpha|\vec{Q},j) \circ (\vec{Q} - \vec{G})] V^\alpha_L(|\vec{Q} - \vec{G}|) \rho^{nn'}_{\vec{k}\vec{k}'}(\vec{Q} - \vec{G}) . \tag{22}$$

Here

$$\Delta\vec{k} = \vec{k}' - \vec{k} = \vec{Q} + \vec{G}^u . \tag{23}$$

$\vec{G}^u$ is a reciprocal-lattice vector such that $\vec{Q}$ falls inside the first Brillouin zone, $\omega_{\vec{Q}j}$ is the phonon frequency of the mode with wave vector $\vec{Q}$ and polarization j, M_α is the atomic mass of atom α, N is the number of unit cells per crystal, and $\hat{\epsilon}(\alpha|\vec{Q},j)$ is the polarization unit vector of atom α for the mode $\vec{Q},j$. The electronic structure enters Eq. (22) through the structure factor $S_\alpha(\vec{G})$, the local pseudopotential $V^\alpha_L(|\vec{Q} - \vec{G}|)$, and through the Fourier components of the "generalized" charge densities

$$\rho^{nn'}_{\vec{k}\vec{k}'}(\vec{Q} - \vec{G}) = \sum_{\vec{G}'} a^{n'*}_{\vec{G}'}(\vec{k}') a^{n}_{\vec{G}'+\vec{G}}(\vec{k}) . \tag{24}$$

Normal ($\vec{G}^u = 0$) and umklapp ($\vec{G}^u \neq 0$) processes are treated the same way by Eq. (22), with the additional requirement that $\vec{Q}$ has to be determined by Eq. (23) for a given pair $\vec{k}, \vec{k}'$.

The thermal average of the self-energy equation (21) can be obtained by thermally weighting each phonon mode individually. The systematic evaluation of (21) requires a knowledge of the electron and the phonon spectrum, including eigenvectors over the entire Brillouin zone. Approximate solutions could be obtained by sampling the Brillouin zone with a grid of $\vec{k}$ points similar to density of states calculations.[7] Because of the very involved nature of this kind of calculations, we present here only some specific examples which already exhibit trends in comparing PbSe to PbTe. We thus have calculated matrix elements for $\vec{k} \approx \vec{k}'$ (*intra*valley) and for scattering from one L point to another *non*-equivalent L point (*inter*valley). Because of the energy denominator in Eq. (21), it is sufficient to include the three topmost valence bands which have even parity, and the lowest three conduction bands which have odd parity at L. For both cases (*intra*- and *inter*valley scattering), the contributing phonon modes have odd parity, if $\vec{k}$ and $\vec{k}'$ are exactly at the high symmetry points L and L', respectively. Due to these selection rules, ΔE is always positive for $\vec{k}' = \vec{k}$ (*intra*valley) and $\vec{k}' = \vec{k} - (1, 0, 0)$ (*inter*valley). If $\vec{k}'$ is slightly off the high symmetry points, the selection rules are relaxed and ΔE decreases. Let us explore the question of which phonons are involved in the $\vec{Q} \approx 0$ (*intra*valley) and $\vec{Q} \approx (\bar{1}, 0, 0)$ (*inter*valley) scattering processes. For $\vec{Q} \approx 0$, the anions and cations move in counterphase with amplitudes weighted by the inverse square root of their respective masses. All three optical modes (one longitudinal and two transverse modes) can be treated identically in the electronic scattering matrix elements, even though their energies differ considerably from each other for $\vec{Q} \neq 0$.[19] Since $\vec{Q} \approx 0$, the required pseudopotential-form factors $V_L(|\vec{Q} - \vec{G}|)$ are those used in the band-structure calculations. For the *inter*valley scattering $\vec{Q} \approx (\bar{1}, 0, 0)$, there are six phonon modes (two longitudinal and four transverse) available. These modes involve the motion of only *one* atom at the time. We therefore can classify the modes into A modes (only the Pb atoms move) and into B modes (only the Se or Te atoms move). If $\vec{k}'$ is not exactly at L′ but slightly off, the required phonon to scatter from $\vec{k}$ to $\vec{k}'$ can still be approximated by a pure $X(\bar{1}, 0, 0)$ phonon. Since $\vec{Q} = (\bar{1}, 0, 0)$ is not a reciprocal-lattice vector, we need to interpolate and to extrapolate the functional form of $V_L(|\vec{G}|)$. This introduces some arbitrariness, especially for higher arguments [the results are proportional to $\vec{Q}\, V_L(|\vec{Q}|)$]. However, in comparing the results for PbSe and for PbTe, these effects should be unimportant. In Table V, we list some typical deformation potentials Z obtained from *intra*valley and *inter*valley scattering. The values Z are defined for given $\vec{k}$ and $\vec{k}'$ through the relation

$$\Delta E_n(\vec{k}) = \sum_{n'} \frac{|\langle n\vec{k}|H'|n'\vec{k}'\rangle|^2}{E_n(\vec{k}) - E_{n'}(\vec{k}')} = \sum_{n'} \frac{\xi_{n'}^2}{\Delta E_{n'}} \frac{\hbar}{2\bar{M}N\omega_Q} = Z\,\frac{\hbar}{2\bar{M}N\omega_{\vec{Q}}}\ , \qquad (25)$$

where

$$\bar{M} = \tfrac{1}{2}[M_{\mathrm{Pb}} + M_{\mathrm{Se\ or\ Te}}].$$

N is the number of unit cells per crystal scaling $\Delta E_n(\vec{k})$ to the contribution arising from one phonon mode, and $\omega_{\vec{Q}}$ is the phonon frequency. The values of Table V are for $\vec{k}$ and $\vec{k}'$ at the exact high-symmetry points. If we move $\vec{k}'$ by $|\Delta\vec{k}'| \approx 0.05 \times 2\pi/a$ away from L′, the values for Z typically decrease by a factor of 5–10. These preliminary calculations show very interesting trends: (a) *inter*band ($n \neq n'$) contributions are strong and may lead to positive temperature coefficients for PbSe and PbTe; (b) *inter*valley $[\vec{k}' \approx \vec{k} - (100)]$ scattering on longitudinal X phonons can be the predominant scattering mechanism. The main contributions arise from scattering over the gap $L(5) \to L'(6)$; (c) B-mode scattering matrix elements (the anion vibrates, the cation is at rest) can exceed the A-mode scattering matrix elements by one order of magnitude; (d) contributions from scattering on *transverse* modes are appreciable, thus indicating the importance of umklapp processes. The magnitude of transverse mode scattering measures the *non*uniformity of the electronic charge density; (e) effects are always stronger in PbSe than in PbTe; in particular, the longitudinal B-mode scattering in PbSe exceeds the equivalent scattering in PbTe by a factor of 5. This might indicate the importance of Fan-type electron-phonon scattering in PbSe as compared to PbTe; and (f) absolute values of $\partial E/\partial T$ for *inter*valley Fan-type scattering can be estimated to be of the order of 10^{-4} eV/°K, based on known phonon frequencies[19] and on the variation of the calculated deformation potentials as a function of $\vec{k}'$.

TABLE V. Integrated deformation potentials Z as defined by Eq. (25) for *intra*- and *inter*valley scattering on optical phonons in PbSe and PbTe. For $Q \neq 0$ (*inter*valley) scattering the contributions arising from longitudinal and transverse mode scattering are indicated separately. Results are also separated according to mode A (only Pb atoms move) and mode B (only Se or Te atoms move) scattering.

		Z (eV/Å^2) $\vec{k}' = \vec{k}$ (*intra*valley) (interband)	Z (eV/Å^2) $\vec{k}' = \vec{k} - (100)$ (*inter*valley)			
			Longitudinal		Transverse	
			A	B	A	B
PbSe	$Z(L_5)$	−37	−3	−200	−5	−38
	$Z(L_6)$	68	3	200	4	51
PbTe	$Z(L_5)$	−28	−2	−41	−4	−20
	$Z(L_6)$	45	3	37	5	23

IV. CONCLUSIONS

The pressure coefficient of the smallest gap at L in PbSe and PbTe has been calculated on the basis of recent highly accurate pseudopotential band-structure models.[7,8] The experimental values for $(\partial E_g/\partial P)_T$ can be reproduced, assuming reasonable slopes of the form-factor curves $V_L(|\vec{G}|)$. Due to partial freedom in choosing the slopes $\partial V_L(|\vec{G}|)/\partial|\vec{G}|$, the absolute value of the calculated pressure coefficients cannot be taken as very strong tests for the band-structure models; the sign of the pressure coefficient, however, is strictly determined by the band-ordering at the gap. Combining the deformation potentials with experimental thermal-expansion coefficients, the anharmonic part in the temperature coefficient $(\partial E_g/\partial T)_P$ can be evaluated; it is positive and is responsible for about 50% of the total experimental temperature coefficient. The remaining contributions, which are due to the interaction of electrons with lattice vibrations, are analyzed by perturbation theory up to second order in the lattice vibrations. The inclusion of a Debye-Waller factor alone yields reasonable results for the L gap in PbTe but fails for the $\Sigma - L$ gap and predicts an opposite sign in the temperature coefficient for PbSe. Detailed analysis of the origin of the different energy shifts shows that the inverted *conduction-band* structure of PbSe as compared to PbTe[7] is responsible for the sign change in the Debye-Waller temperature coefficient. Uncertainties in the experimental mean-square displacements used are unlikely to cause the sign change. The contributions to the L gap from Fan-type electron-phonon scattering terms are calculated for *intra*valley ($\vec{Q} \approx 0$) and for *inter*valley [$\vec{Q} \approx (\bar{1}, 0, 0)$] scattering. In spite of their very preliminary nature, these calculations seem to indicate the tendency of Fan-type scattering to *open* the L gaps in PbSe and PbTe. At this point, no analysis has been made for the $\Sigma - L$ gap. The calculations also indicate that the effect is stronger in PbSe than in PbTe, which would be consistent with the need to compensate the negative Debye-Waller result for PbSe. Quantitative conclusions, however, can only be drawn on the basis of explicit calculations including thermally weighted scattering into states over the whole Brillouin zone.

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