

Relativistic Band Structure and Electronic Properties of SnTe, GeTe, and PbTe†

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The electronic energy band structures of SnTe, GeTe, and PbTe are calculated including spin-orbit interactions. The resulting band structures are used to discuss some of the electronic properties of these crystals and to calculate the intervalley deformation potential for electron-phonon scattering in SnTe. The value obtained for the deformation potential is consistent with the value used to explain the superconducting properties of SnTe.

WE have calculated the electronic energy band structure of SnTe, GeTe and PbTe using the empirical pseudopotential method¹ (EPM). Spin-orbit interactions are included and the resulting energy bands are in good agreement with the results of experimental investigations of the electronic structure of these compounds as will be discussed. In addition we have calculated the intervalley electron-phonon deformation potential ξ for SnTe based on the band-structure results. Because of our model, the results for ξ are approximate; the value obtained is consistent with the value of ξ which was used to fit² the carrier concentration dependence of the superconducting transition temperature of SnTe.

The IV-VI compounds have been extensively studied experimentally. Measurements of the de Haas-Shubnikov effect,^{3,4} tunneling spectroscopy,⁵ optical spectroscopy,⁶ and various transport coefficients have been made. These experiments have raised several interesting questions about the electronic structure near the band edge (L point of the fcc Brillouin zone) and away from the band edge. In particular, it has been suggested⁷ that the ordering of the energy levels at the top of the valence band reverses as one goes from SnTe to PbTe. A previous pseudopotential band structure⁸ was obtained for SnTe to analyze the experimental optical data; however, spin-orbit effects were not included in that calculation and the ordering of the levels near the gap was therefore not determined accurately. Here we incorporate spin-orbit effects into the calculation and analyze the electronic structure close to the band edge

and away from the band edge. We chose a band structure consistent with the band inversion scheme for PbTe and SnTe, and illustrate that the changes in going from SnTe to PbTe both through the kinetic energy and the potential energy terms gives a model consistent with the inversion picture. Our model also gives the same ordering at L for GeTe as in SnTe.

Both SnTe and PbTe have fcc crystal structures while GeTe is face-centered rhombic; however, the distortion from fcc is small, and we have assumed the fcc crystal structure for all three materials. The lattice constants were taken to be 6.313 Å, 5.996 Å, and 6.454 Å for SnTe, GeTe, and PbTe, respectively. The description of the application of the EPM without spin-orbit interactions for the rocksalt structure has been given⁹; we therefore proceed immediately to the addition of spin-orbit effects using the model introduced by Weisz¹⁰ for white tin and modified by Bloom and Bergstresser¹¹ for grey Sn and InSb. The total pseudo-Hamiltonian matrix element in the plane-wave representation then becomes

$$\mathcal{H}_{\mathbf{k}'s',\mathbf{k}s} = (p^2/2m)\delta_{\mathbf{k}'\mathbf{k}}\delta_{s's} + S(\mathbf{k}-\mathbf{k}') \times [V(|\mathbf{k}'-\mathbf{k}|)\delta_{s's} - i\lambda_1(\hat{\mathbf{k}}' \times \hat{\mathbf{k}}) \cdot \boldsymbol{\sigma}_{s's}], \quad (1)$$

where S is the structure factor, V is the usual pseudopotential, and $\boldsymbol{\sigma}$ represents the Pauli spin matrices. The last term is the spin-orbit contribution to the Hamiltonian arising from the p -core electrons. In this calculation we retain only the core-core contribution since this is several orders of magnitude larger than the core-planewave and planewave-planewave contributions. For this case, λ_1 is essentially a product of two orthogonal integrals $B_{n1}(k)$ and $B_{n1}(k')$ multiplied by an adjustable numerical parameter. Tabulated Hartree-Fock-Slater orbitals¹² are used for the radial wave functions of the core in order to evaluate these integrals. To extend Weisz's model to binary compounds, it is convenient to decompose λ_1 into a symmetric part λ^S and an antisymmetric part λ^A in the same fashion as one

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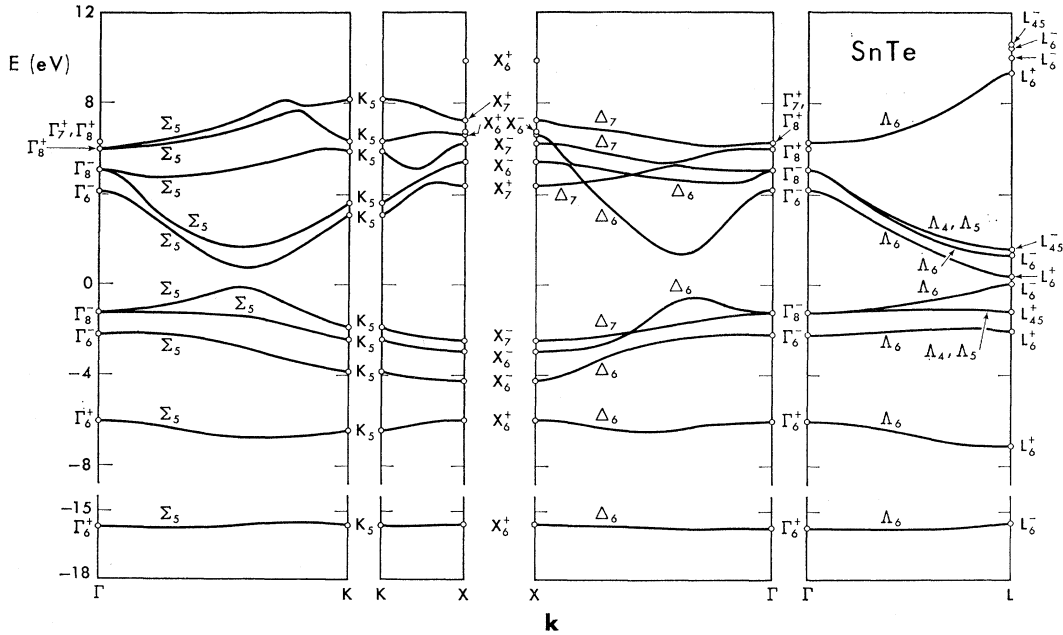


FIG. 1. Electronic energy band structure of SnTe.

decomposes the pseudopotential form factors. Equation (1) then becomes

$$\begin{aligned} \mathfrak{H}_{\mathbf{k}'s',\mathbf{k}s} = & (p^2/2m)\delta_{\mathbf{k}'\mathbf{k}}\delta_{s's} + S^S(\mathbf{k}-\mathbf{k}') \\ & \times [V^S(|\mathbf{k}-\mathbf{k}'|)\delta_{ss'} - i\lambda^S(\hat{\mathbf{k}}' \times \hat{\mathbf{k}}) \cdot \boldsymbol{\sigma}_{s's}] \\ & + iS^A(\mathbf{k}-\mathbf{k}') [V^A(|\mathbf{k}-\mathbf{k}'|)\delta_{s's} \\ & - i\lambda^A(\hat{\mathbf{k}}' \times \hat{\mathbf{k}}) \cdot \boldsymbol{\sigma}_{s's}], \quad (2) \end{aligned}$$

where S^S and S^A are the symmetric and antisymmetric structure factors.¹³ We estimate the splitting in the crystal from atomic splittings¹⁴ and assume the valence band splitting at Γ to be 0.98, 0.77, and 1.82 eV for SnTe, GeTe, and PbTe, respectively. The numerical parameters in λ^S and λ^A are chosen to give the estimated splitting at Γ and the ratio of these parameters is taken to be consistent with the ratio of atomic spin-orbit splittings of the two types of atoms.

The potentials are chosen in the following way: For SnTe, we start with the same set of symmetric form factors used in the previous EPM calculation,⁸ and vary the two antisymmetric form factors to give a few of the principal gaps. The symmetric form factors are then varied slightly in an attempt to get even closer agreement with the experimental splittings. The form factors chosen were $V^S(G^2=4) = -0.232$ Ry, $V^S(8) = -0.024$, $V^S(12) = 0.018$, $V^A(3) = 0.055$, and $V^A(11) = 0.023$.

¹³ This decomposition is strictly valid only if the k dependence of orthogonal integrals $B_{n1}(k)$ is identical for the fourth-column and the sixth-column elements in the IV-VI compounds. In the cases of SnTe, GeTe, and PbTe, these integrals are similar so that it is an excellent approximation to take an average of the $B_{n1}(k)$ k dependence for both λ^S and λ^A .

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These are almost identical with the form factors of Lin *et al.*⁸; the largest variation is 0.004 Ry in the symmetric potential and 0.02 Ry in the antisymmetric potential. For GeTe, the starting set of form factors was taken as an average of the Sb and As form factors extracted from the symmetric and antisymmetric form factors of InSb¹ and GaAs¹ (with appropriate scaling factors to account for the lattice constant changes). After this set was chosen, the form factors were varied slightly to give some of the observed gaps. The GeTe form factors are $V^S(4) = -0.245$ Ry, $V^S(8) = -0.022$, $V^S(12) = 0.032$, $V^A(3) = 0.060$, and $V^A(11) = 0.017$.

The form factors for PbTe are obtained in a slightly different fashion from those of SnTe and GeTe. As a first attempt, we merely scaled the SnTe form factors to the PbTe lattice as a test to explore the possibility of a band inversion at the L point going from SnTe to PbTe. The ordering in SnTe is L_6^- for the valence-band maximum and L_6^+ for the conduction-band minimum with a splitting $L_6^+ - L_6^- = 0.33$ eV. The minimum gap for SnTe is not at L ; the extrema for both the valence and conduction bands lie in the hexagonal face of the Brillouin zone, slightly away from L . (We will still refer to this gap as the L gap.) Tunneling measurements⁵ give 0.3 eV at 4.2°K for this gap. The result of the scaling is that the L_6^- and L_6^+ levels move within 0.08 eV of each other, but the ordering has not yet reversed. If we had started with a slightly smaller SnTe gap, the inversion would have taken place. The final form factors for PbTe were chosen to give the gap at L to be $L_6^- - L_6^+ = 0.18$ eV.¹⁵ These form factors were only slightly different from the scaled values from SnTe; the changes were -0.01 Ry in V^S ($G^2=4$) and -0.003 Ry in V^S ($G^2=8$).

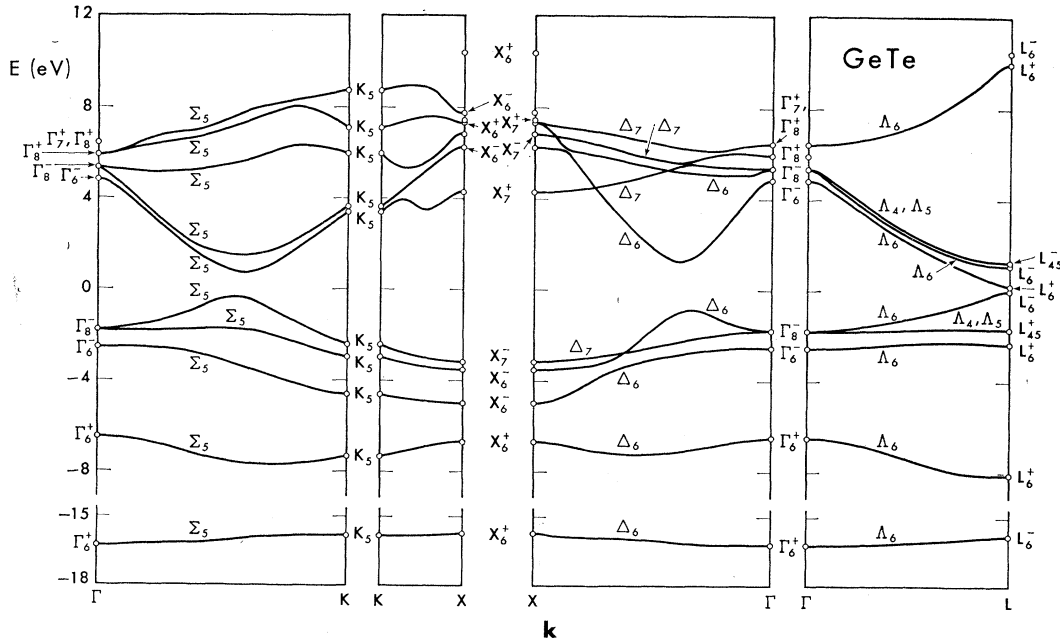


FIG. 2. Electronic energy band structure of GeTe.

The values for the form factors are $V^S(4) = -0.241$ Ry, $V^S(8) = -0.0352$, $V^S(12) = 0.017$, $V^A(3) = 0.052$, and $V^A(11) = 0.021$. This shift from the scaled values is consistent with the differences between the Pb and Sn potentials as calculated by Animalu and Heine.¹⁶ Their calculated Pb potential is more negative for small G 's than the Sn potential. We conclude, therefore, that the band inversion at L results both from the lattice constant change and from the difference in the Sn and Pb crystal potentials.

The band structures of SnTe, GeTe, and PbTe are given in Figs. 1–3. The results are similar to those obtained by Lin and Kleinman for the lead salts.²⁵ All three crystals have the valence maximum and conduction minimum near L . The L gap for SnTe and PbTe is given above; for GeTe, $L_6^+ - L_6^- = 0.23$ eV, which is consistent with the tunneling value of 0.2 eV.⁵ Both SnTe and PbTe have a second valence maximum along the Σ axis (although Fig. 2 seems to indicate the same for GeTe, we are guided by a critical-point analysis which gives only a saddle point along Σ rather than an absolute maximum for GeTe). There is experimental evidence for the existence of a second valence maximum in these two crystals,^{4,17–22} and the Σ axis is a possible

choice⁸ for this maximum. The second-band maximum is 0.15 and 0.3 eV below the L valence maximum in SnTe and PbTe, respectively. In our calculation we implicitly assume zero temperature values for the fundamental gaps for all three crystals. This gap has a negative temperature coefficient for SnTe²³ and a positive coefficient for PbTe.²⁴ We therefore expect that at room temperature the L_6^+ maximum will move closer to the second maximum in PbTe than the L_6^- maximum in SnTe will move to its second maximum.

The imaginary part of the frequency-dependent dielectric function $\epsilon_2(\omega)$ for all three band structures has been computed in order to analyze the optical properties of these crystals, and fairly good agreement with experiment⁶ is found. The results are similar to that given in Ref. 8.

Both SnTe and GeTe are superconductors and a recent calculation² of the superconducting transition temperature as a function of carrier concentration has been made. This calculation involves one adjustable parameter ξ , the deformation potential which measures the strength of electron-phonon coupling when electrons are scattered from one Fermi-surface pocket near L to another by exchanging a short wavelength phonon. The inversion symmetry of the rocksalt

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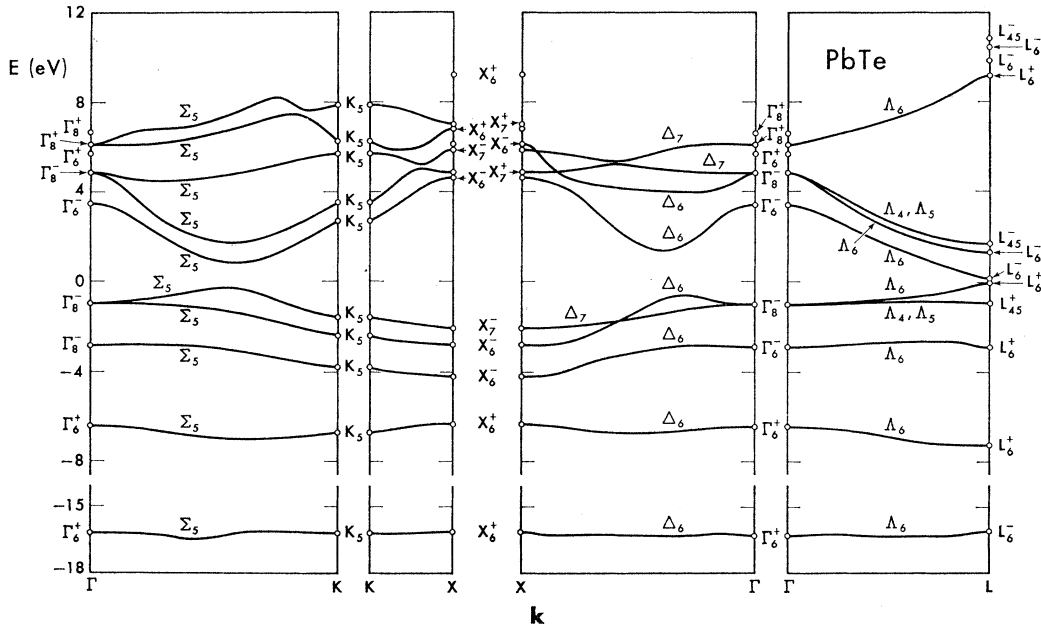


FIG. 3. Electronic energy band structure of PbTe.

structure forbids nonzero electron-phonon matrix elements connecting electrons from one L point to another in the Brillouin zone. We have therefore investigated the matrix elements between electronic states in the L valleys near the L point. We take our band-structure pseudopotential and a rigid ion model for the electron-phonon interaction

$$\mathcal{H}'_{e-ph} = \sum_{l,\alpha} \nabla_{l,\alpha} V_{l,\alpha}(\mathbf{r} - \mathbf{r}_{l,\alpha}^0) \cdot \delta \mathbf{R}_{l,\alpha}, \quad (3)$$

where $V_{l,\alpha}(\mathbf{r} - \mathbf{r}_{l,\alpha}^0)$ is the pseudopotential about the atom core in its equilibrium position with lattice index l , and basis index α , $\delta \mathbf{R}_{l,\alpha}$ is the displacement of the core. The displacement $\delta \mathbf{R}_{l,\alpha}$ may be expanded in phonon operators and the matrix elements between the pseudowave functions of the electron states are evaluated. Our calculation gives typical values of between 1–3 eV for random \mathbf{k} points in the vicinity of the L points. The

high-wave-vector tail of the pseudopotential contributes in a positive way to the value of ξ ; however, this high-wave-vector part is not necessary for the band-structure calculation, and the potentials are cut off around $G^2 = 12$ in computing the energy bands. Since we use the same potential in both calculations, the value of ξ should be considered to be approximate and to be at least a lower bound. The values obtained $\xi \approx 1-3$ eV are consistent with the value $\xi = 2.35-2.63$ eV obtained² from the superconducting properties of SnTe.

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