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Author
Tsang, Y.W.

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Y. W. Tsang and Marvin L. Cohen

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Electronic Charge Density in PbTe*

Y. W. Tsang and Marvin L. Cohen
Department of Physics, University of California
and
Inorganic Materials Research Division, Lawrence Berkeley Laboratory
University of California, Berkeley, California 94720

Abstract

The electronic charge density for PbTe is computed as a function of position in the unit cell on two different planes. A rough estimate of the charge about each atom is made. The charge density for the top valence and bottom conduction bands are given for the L point of the Brillouin Zone. The influence of the L-point charge distribution on the temperature dependence of the fundamental gap is discussed.

In this note we present a calculation of the electronic charge density as a function of position in the unit cell for PbTe, which is a IV-VI semiconductor with the rocksalt structure. It is known that ionic compounds favor the rocksalt structure whereas the more covalent semiconductor compounds usually crystallize in the four-fold coordinated crystal structures like the zincblende structure. The charge density of the zincblende structure has been examined by Walter and Cohen[1] and the covalent nature of these compounds was displayed. Here we present the first calculation for the electronic charge density for a six-fold coordinated diatomic compound.

The charge density

$$\rho_n(r) = \frac{e}{\Omega} \sum_k \psi^*_{nk}(r)\,\psi_{nk}(r) \qquad (1)$$

is computed band by band for all the valence bands and the first conduction band. The summation is over all available states k in the Brillouin Zone for each band n, e is the electronic charge and Ω is the primitive cell volume. The wavefunction used in Eq. (1) is derived from the same set of pseudopotential form factors used[2] in previous band structure calculations using the Empirical Pseudopotential Method.[3] Spin-orbit interactions are not taken into account in this calculation. Following Walter and Cohen[1] we compute the charge density at about 1600 and 2400 points respectively in two different planes described below. The first plane is a $(1\bar{1}0)$ plane which is the same as reference 1. This plane contains Pb at (0,0,0)a and Te at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$a, where a is the lattice constant. The second plane is a (100) plane which contains Pb at (0,0,0)a and Te at $(\frac{1}{2},0,0)$a.

We have investigated contours of constant $\rho_n(r)$ in both planes for each band. These contours indicate that in the first valence band, the electronic charge density is spherical (s-like) and it piles up almost exclusively around Te; presumably the two s electrons crowd around the Te atom to balance the positive Te core. In the second valence band, the roles of Pb and Te are interchanged; the charge distribution is nearly spherical and primarily around the Pb atom. The charge density contours of the three upper valence bands all show p-character around both Pb and Te; however, because of the heavier concentration near the Te atom, only a few contours appear around Pb. We also note that there is very little build-up of electronic charge between neighboring atoms.

A crude attempt was made to evaluate the charge about each atom. To do this, the $\rho_n(r)$ is integrated to the outermost closed contour around each atom, given an estimate of the total charge around each type of atom. In integrating, we use a spherical approximation, i.e. the radius of any given contour is taken to be the weighted average of radii along the three symmetry direction: [100], [110], and [111]. The charge density is then linearly interpolated between neighboring contours. The spherical approximation used above is reasonable since the contours are very nearly circular about each atom. For the five valence bands, the computed charge around Pb and Te are respectively 1.93e and 6.43e. These numbers are only approximate for the following reasons. Firstly, we use the pseudowavefunction $\psi_{nk}(r)$ in computing the charge density; these wavefunctions are of course more suited to describe the properties of the crystal away from the core, e.g. in the bond as in reference 1. In this work the integration scheme includes the less reliable core region. In addition, our integration scheme underestimates the amount of charge outside the core region around each atom. This arises from the fact that the values for contours of constant $\rho_n(r)$ in the drawings are chosen to be equally spaced, and all the $\rho_n(r)$'s away from the cores that have values smaller than the minimum contour chosen will not be included in our integration. Taking the above into consideration we still conclude that our results unmistakably display the ionic nature of the six-fold coordinated PbTe.

Apart from the basic interest in correlating ionicity of a compound to its crystal structure, we are also interested in the role of the charge distribution of PbTe in the temperature dependence[4] of the fundamental gap. In working with the temperature dependence of the L gap in PbTe, we found that the symmetry of the energy levels at L plays an interesting role in the temperature coefficient of the gap. For the temperature coefficient arising from the thermal motion of the ions, or the so-called Debye-Waller effect, every energy level moves up in energy with increasing temperature. One expects the p-like wavefunction to be sensitive to the thermal motion since the jiggling of the ion core brings it into contact with the charge density away from the origin.

The top valence band in PbTe has the L_6^+ symmetry (L_1 in the absence of spin orbit interaction). The bottom conduction band has the L_6^- symmetry (L_2 in the absence of the spin-orbit interaction). Group theory[5] indicates that L_1 is s-like about Pb, p-like about Te, while L_2' is p-like about Pb and s-like about Te. In PbTe, the Pb ion has a bigger mean squared displacement than the Te ion;[6] this together with the expected sensitivity of the p-like wavefunction appears to explain the positive gap temperature in PbTe.[4]

Because of the above remark, it would be interesting to see whether the pseudo-wavefunctions in real space indeed correspond to what is assumed in the discussion of temperature calculation. We therefore compute

$$\rho_L(r) = \frac{e}{\Omega} \psi^*_L(r)\, \psi_L(r) \qquad (2)$$

where L refers to the $L(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ point of the Brillouin zone. Eq. (2) can be calculated for the top valence band and the bottom conduction band at the L point of the Brillouin zone. Fig. 1 displays contours of constant $\rho_L(r)$ in the $(1\bar{1}0)$ plane. Fig. 1a gives contours for the top valence band (L_1 symmetry). Fig. 1b gives contours for the bottom conduction band (L_2' symmetry). It is clear that the charge density is indeed s-like about Pb, p-like about Te in the top valence band and vice-versa in the bottom conduction band. The angular variation of the p-like $\rho_L(r)$ accounts[4] for the sensitivity of each level to the thermal motion. If the Kleinman ordering[7] is assumed, the results are essentially unchanged since the parent levels for the L_6^+ and L_6^- states would still have the s and p character described here. However, the details of the charge distribution would be different.

Acknowledgements

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References

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1. J.P. Walter and M. L. Cohen, Phys. Rev. B4, 1877 (1971).
2. Y. W. Tung and M. L. Cohen, Phys. Rev. 180, 823 (1969).
3. M. L. Cohen and V. Heine, Solid State Physics 24, (Academic Press, Inc., New York, N. Y., 1970), p. 37.
4. Y. W. Tsang and M. L. Cohen, Phys. Rev. B3, 1254 (1971).
5. D. G. Bell, Rev. Mod. Phys. 26, 311 (1954).
6. C. Keffer, T. M. Hayes, and A. Bienenstock, Phys. Rev. B2, 1966 (1970).
7. Y. W. Tsang and M. L. Cohen, Solid State Commun. 9, 261 (1971).

Figure Captions

1a. Contours of constant charge density in the $[1\bar{1}0]$ plane for states in the top valence band at the L point of the Brillouin Zone.

1b. Contours of constant charge density in the $[1\bar{1}0]$ plane for states in the bottom conduction band at the L point of the Brillouin Zone.

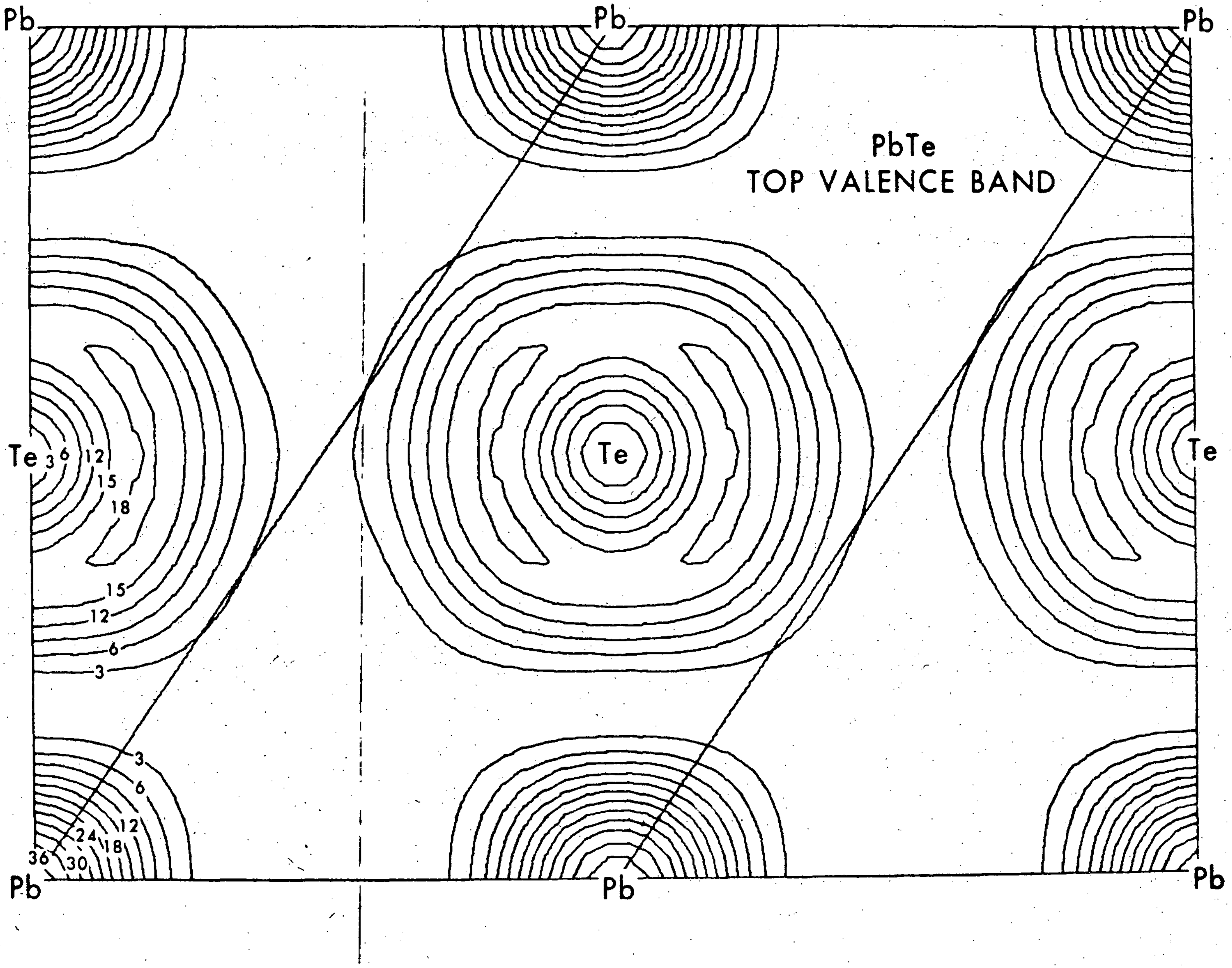
PbTe
TOP VALENCE BAND
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Fig. 1a

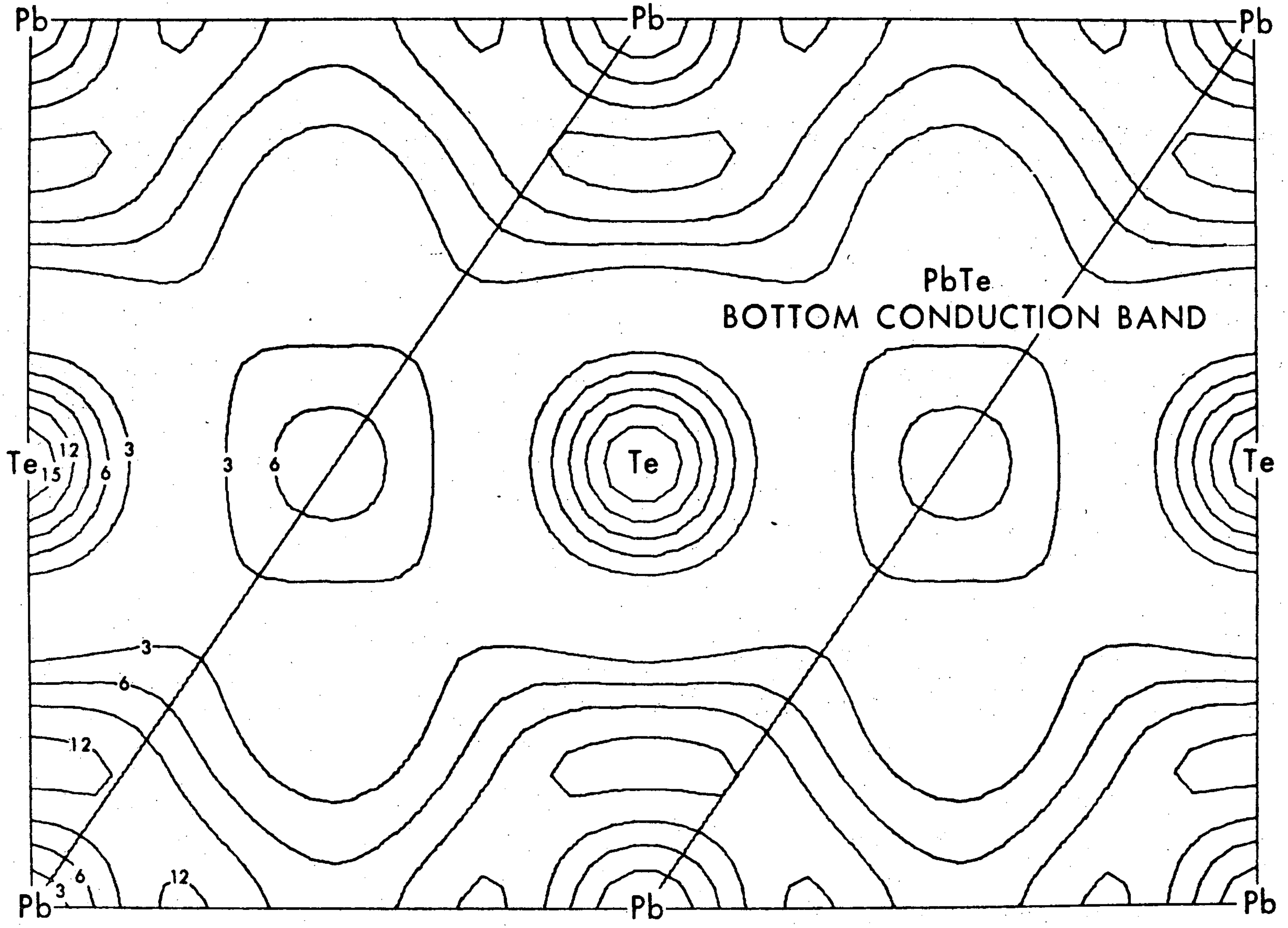
PbTe
BOTTOM CONDUCTION BAND
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Fig. 1b

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