

NEW MODEL FOR VACANCY STATES IN PbTe†

Nelson J. Parada and George W. Pratt, Jr.

Department of Electrical Engineering and Center for Materials Science and Engineering,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 2 December 1968)

We present new results that the states associated with Pb or Te vacancies in PbTe lie well up in the conduction band and that no localized states appear in the valence-conduction band gap. Holes and electrons due to Pb or Te vacancies cannot freeze out even at 0°K giving PbTe the character of a metal at very low temperatures.

It is well known¹ that PbTe is made *n*- or *p*-type by altering its stoichiometry. Pb-rich material is *n*-type and Te-rich is *p*-type. The role of interstitials, although perhaps important, is not considered here. The principal source of holes and electrons is taken to be the Pb and Te vacancies. The perturbing potential due to a vacancy is approximately the negative of the potential normally associated with the vacancy site. Since a vacancy has no net charge, the corresponding perturbing potential $U(r)$ is highly localized. It falls off rapidly as compared with the potential due to an acceptor or donor impurity where one has a screened Coulomb potential. The vacancy potential is very strong, going to $+\infty$ at the site as $1/r$.

The localized nature of $U(r)$ makes it convenient to expand the impurity wave function ψ as a linear combination of Wannier functions $a_n(r-R_q)$ summed over bands n and sites R_q :

$$\psi = \sum_{n, R_q} A_n(R_q) a_n(r-R_q), \quad (1)$$

where

$$(\mathcal{H}_0 + U)\psi = E\psi. \quad (2)$$

Following the Koster-Slater² theory for impurity states, one is led to a secular equation in matrix form,

$$\det|1 - G(E)U| = 0. \quad (3)$$

U is the matrix of the vacancy potential between Wannier functions

$$U_{n', n}^{i', i}(R_p, R_q) = \int d\vec{r} a_{n', i'}^*(n-R_p) U(n) a_{n, i}(n-R_q), \quad (4)$$

and the Green's function matrix $G(E)$ is

$$G_{n', n}^{i', i}(R_p, R_q, E) = \frac{1}{N} \sum_k \frac{\exp[i\vec{k} \cdot (R_p - R_q)]}{E - E_n(k)} \delta_{nn'} \delta_{ii'}, \quad (5)$$

where n and i denote the i th partner of the n th band whose energy is $E_n(k)$.

In order to construct the Wannier functions and set up the $G(E)$ and U matrices, it is necessary to know the Bloch functions and corresponding energies for all of the bands of interest over the entire Brillouin zone. This was done using a $\vec{k} \cdot \vec{p}$ interpolation scheme. First a relativistic augmented-plane-wave (APW) calculation was carried out at $k=0$ where accurate energies, wave functions, and interband momentum matrix elements were found. The solutions at $k=0$ were used to set up the $\vec{k} \cdot \vec{p}$ secular equation

$$\det \left[\left[E_m(k=0) + \frac{\hbar^2 k^2}{2m} - \frac{\hbar^4}{8m^3 c^2} k^4 - E_n(k) \right] \times \delta_{nm} \delta_{ij} + \frac{\hbar}{m} \vec{k} \cdot \vec{\pi}_{n, m}^{i, j} \right] = 0, \quad (6)$$

where

$$\vec{\pi} = \vec{p} + \frac{\hbar}{4mc^2} (\vec{\sigma} \times \nabla \vec{V}) - \frac{1}{2m^2 c^2} p^2 \vec{p} - \frac{1}{2m^2 c^2} (\vec{p} \cdot \vec{p}) \vec{p} - \frac{1}{4m^2 c^2} p^2 \vec{P}, \quad (7)$$

with $\vec{P} = \vec{p} + e\vec{A}/c$. The size of the secular determinant (6) was 32×32 . This was solved over the entire zone and the bands determined in this way agreed with APW calculations at numerous check points in the zone to within a few percent.

The $\vec{k} \cdot \vec{p}$ information allows one to set up the secular equation (3) for the impurity levels. The interaction of the five valence bands and four conduction bands, arising primarily from Pb and Te *s*- and *p*-like one-electron functions, was considered. For each pair of bands, five different values of $R_p - R_q$ were considered in the G and U matrices. The evaluation of the G matrix involves a sum over k space. This was done using 1000 points in 1/48th of the zone via the Conroy³ integration technique which is considerably more accurate than the Monte Carlo method.

The results are shown in Figs. 1 and 2. The

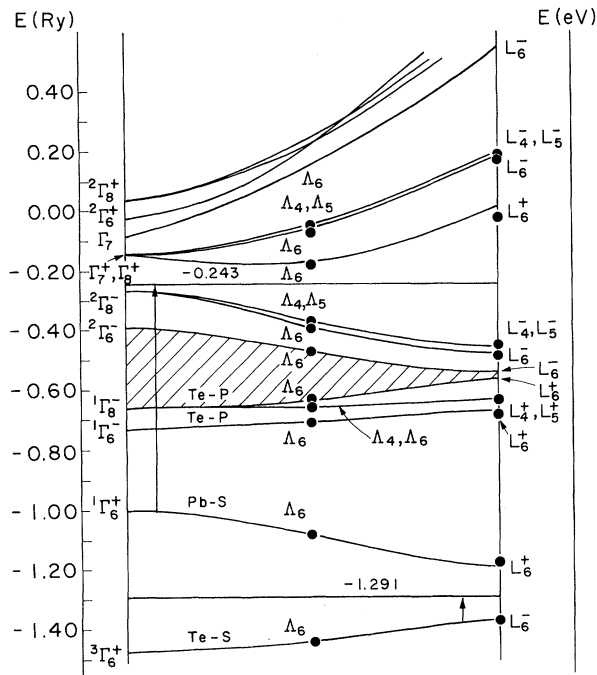


FIG. 1. A level due to a Pb vacancy splits off from the Pb s valence band and appears at -0.243 Ry. The bands shown are in the (111) direction and the energy is given in Rydbergs vertically. The shaded region is the gap between the valence and conduction bands. No other levels are split from the valence bands.

lowest valence band is primarily a Te s band. It lies about 2 eV below an essentially Pb s band which in turn lies about 1 eV below a band which is formed mainly from Te p functions. These valence bands have $10N$ levels in all where N is the number of unit cells in the crystal.

The solid circles in both figures denote the band energies found at that point by a full APW calculation⁴ and are inserted here to indicate the agreement obtained by the $\vec{k}\cdot\vec{p}$ scheme described above.

The ionicity of PbTe is not accurately known and the APW calculation of Ref. 4 used neutral-atom potentials to construct the crystal potential. Since the net charge within a Pb or Te APW sphere is very nearly zero in this model, the perturbing potential due to a missing atom lacks a long-range Coulomb tail. Also, although the valence bands in Figs. 1 and 2 are labeled Pb s , Te s , and Te p , this should not be taken to mean that the corresponding charge densities add up to two electrons about a Pb site and eight electrons about a Te site in a unit cell. Actually the Te s and Te p valence bands have an admixture of Pb s and Pb p charge, enough to correspond to

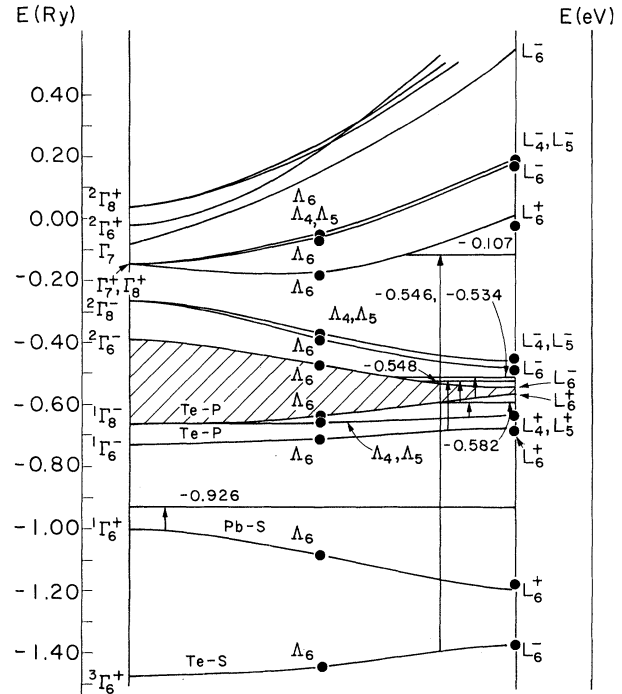


FIG. 2. A level due to a Te vacancy splits off from the Te s valence band and appears at -0.107 Ry. A level splits away from the Pb s band due to the Te vacancy and appears at -0.926 Ry between the Pb s and upper Te p valence bands. Another level separates from the lowest Te p band appearing above the gap at -0.548 Ry, only 0.002 Ry above the conduction-band minimum at the (111) edge. A level separates from the L_4^+, L_5^+ Te p valence band but at -0.582 Ry which is below the gap. Finally, two levels split away from the highest Te p valence band, both appearing across the gap at -0.546 and -0.534 Ry.

approximately four electrons per Pb site. Similarly, some of the Te p charge density appears in the conduction bands. Although the Te s and Te p bands do contribute to the charge about a Pb site, the matrix components of the Pb-vacancy potential for these bands are not large enough to split off a state.

A Pb vacancy strongly perturbs the Pb s band driving one doubly degenerate level out of that band through the upper Te p band, across the gap between the valence and conduction bands, and into the conduction-band system. Since the Green's function $G_{n,n}(E)$ [Eq. (5)] is only defined for energies outside of those lying in the n th band, it is not possible to locate the energy of the Pb vacancy level if it lies within any of the interacting bands. To a first approximation, we can consider only the Pb s band. Doing this and considering contributions to the $U_{mm}^{ii'}(R_p, R_q)$ matrix from Wannier functions located at the site of the

vacancy and at sites in the 12 surrounding unit cells, the Pb vacancy level was found to lie 0.758 Ry above the top of the Pb *s* band or about 0.24 Ry above the bottom of the conduction band. This doubly degenerate level will, of course, be empty and we can say it is removed from the $10N$ levels in the valence-band complex. A level is driven out of the lowest Te *s* valence band, but only 0.094 Ry above the top of this band. This level will be filled and regarded as still belonging to the valence-band levels. A Pb vacancy is not strong enough to drive any levels out of the Te *p* valence bands. Therefore, the valence bands contain $10N-2$ levels if there is a single Pb vacancy. However, a vacancy removes four electrons from the valence band since the missing Pb atom has a configuration $6s^26p^2$. Consequently there are $10N-4$ electrons in a band system with $10N-2$ levels, and hence two holes must be present. They will appear at the top of the valence-band complex which is the Te *p* band. Of special note is the fact that these holes cannot be frozen out even at 0°K. This metal-like behavior is in accord with experiment.⁵

As shown in Fig. 2, a Te vacancy strongly perturbs the lowest Te *s* band driving one doubly degenerate level 1.278 Ry above the top of that band which is far above the bottom of the conduction band. This doubly degenerate level is, therefore, removed from the valence-band complex. Again, this is a single-band result using contributions to the *U* matrix from the Wannier functions at the vacancy site and from the nearest 12 unit cells. The Te vacancy does push a level 0.075 Ry above the Pb *s* band and this will always be filled and not considered as removed from the valence bands. Next a level is driven above the lowest Te *p* band by 0.139 Ry, which places it 0.012 Ry above the bottom of the conduction band. This doubly degenerate level will be lost from the valence bands. The Te vacancy does not push a level from the middle Te *p* band

across the gap but to an energy 0.058 Ry above the top of that band. This overlaps the highest Te *p* valence band so that this level will be normally occupied. Finally, two levels each doubly degenerate are pushed from the highest Te *p* band by 0.039 and 0.027 Ry, which places them above the bottom of the conduction band, which lies 0.023 Ry above the top of the valence band.

We see that a Te vacancy leaves the valence band with $10N-8$ levels. Each Te vacancy removed takes six electrons with it since neutral Te has the configuration $5s^25p^4$. Therefore, two electrons will appear at the bottom of the conduction band for each Te vacancy. Again, there is no possibility of these electrons becoming bound even at 0°K. This metallic character is also in accord with experiment.

There are many interesting implications of this new type of impurity level. Assuming vacancies are the principal source of electrons or holes, *p*- or *n*-type PbTe can be thought of as a dilute metal. One can obtain carrier densities over a wide range and perhaps at some appropriate concentration the electrons or holes will form a lattice as suggested by the Wigner model of a low-density electron gas.⁶ The ground state may be antiferromagnetic or ferromagnetic.

A detailed account of this work will be published.

†Work supported by U. S. Army Research Office (Durham).

¹A. J. Crocker, *J. Phys. Chem. Solids* **28**, 1903 (1967).

²G. F. Koster and J. C. Slater, *Phys. Rev.* **96**, 1208 (1954).

³J. Conroy, *J. Chem. Phys.* **47**, 5307 (1967).

⁴J. B. Conklin, Jr., L. E. Johnson, and G. W. Pratt, Jr., *Phys. Rev.* **137**, A1282 (1965).

⁵R. S. Allgaier and W. W. Scanlon, *Phys. Rev.* **111**, 1029 (1958).

⁶W. J. Carr, Jr., *Phys. Rev.* **122**, 1437 (1961).