

Electronic structure of $(\text{Tl}_{0.125}\text{Pb}_{0.875})\text{Te}$

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Abstract

We present an ab-initio supercell calculation of electronic band structures of $(\text{Tl}_\delta\text{Pb}_{1-\delta})\text{Te}$ with $\delta = 0$ and 0.125. PbTe is to be a very small gap semiconductor, and Tl doping induces a quasi-impurity band in this in-gap state. A local relaxation based on ionic model is discussed.

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Thallium is one of several elements known as ‘valence skipper’, which means that Tl forms the compounds in valence states Tl^{1+} and Tl^{3+} (corresponding to $(6s)^2$ and $(6s)^0$ outermost electron configuration, respectively), and naturally does not take Tl^{2+} state. If Tl atoms are forced to take Tl^{2+} valence state on average in a compound, they spontaneously dissipate to Tl^{1+} and Tl^{3+} . This situation corresponds to negative Hubbard U model, and if the outermost orbital of this ion is the s-orbital, the ground state becomes diamagnetic (no Curie term) [1]. Negative- U impurity can induce superconducting pairing interaction [1–3]. In this point of view, superconductivity found in slightly Tl-doped PbTe [4,5] is newly enlightened by Matushita et al. by careful control of the Tl-content [6]. They found that PbTe becomes superconducting with maximum $T_c \sim 1.5$ K by Tl-doping, on the other hand, all dopants except Tl bring about superconducting state below 0.01 K if at all, which is naturally anticipated by comparison with similar semiconducting materials, such as SnTe, GeTe and InTe. In these points of view, Tl-doped PbTe is a hopeful material that has negative- U center, which is expected to have new fruitful physics, such as charge-Kondo effect,

superconductivity, and possible reentrance of normal state in extremely low temperature [7]. For understanding this fascinating feature, reliable energy-level scheme is indispensable. However, there is no report of band structure calculation for Tl-doped PbTe as we know.

In this paper we performed an ab initio band calculation for non-doped and Tl-doped PbTe. In order to investigate the polarization effect which is a possible origin for the negative- U [6], we also examined the effects of lattice relaxation by Tl doping. We assumed that Tl takes Tl^{1+} (or Tl^{3+}) valence state, and the six nearest-neighbor Te atoms move away from (or toward) Tl atom. The ionic radius of Tl is usually $r(\text{Tl}^{1+}) = 1.59 \text{ \AA}$ and $r(\text{Tl}^{3+}) = 0.895 \text{ \AA}$, respectively [8]. The ionic radii of Pb^{2+} and Te^{2-} are $r(\text{Pb}^{2+}) = 1.19 \text{ \AA}$ and $r(\text{Te}^{2-}) = 2.11 \text{ \AA}$, respectively. We assumed that the averaged Tl–Te distance is the same as the Pb–Te distance in Pb–Te, which is $a_0 = 3.219 \text{ \AA}$. Thus we may determine the Tl–Te distances by

$$d_1 = (r(\text{Tl}^{1+}) + r(\text{Te}^{2-})) * c_0 = 3.568 \text{ \AA}$$

$$d_3 = (r(\text{Tl}^{3+}) + r(\text{Te}^{2-})) * c_0 = 2.916 \text{ \AA}$$

Here $c_0 = a_0 / (r(\text{Pb}^{2+}) + r(\text{Te}^{2-})) = 0.939$ is the scaling factor. However, due to the valence fluctuation and strong elastic force in the host lattice, such a large shift of Te atom may not be realized. We tentatively reduced the difference

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between d_1 and d_3 by factor $2/3$, and thus we set $d_1 = 3.48 \text{ \AA}$ and $d_3 = 3.03 \text{ \AA}$. We take a $2 \times 2 \times 2$ superlattice, i.e., fcc lattice with $a = 4a_0$, containing TlPb_7Te_8 in a primitive cell. We replace one of the Pb atoms with Tl atom, corresponding to 12.5% Tl doping. By this replacement, the other seven Pb atoms occupy the 24d-site and 4b-site in space group $\text{Fm}\bar{3}\text{m}$. Eight Te atoms also occupy the 24e-site and 8c-site. The 24e-site has a free parameter x

such as $(x,0,0)$, and we consider the relaxation of Te atom in 24e-site. Using above estimations, the position of Te atom is at $x = 0.235$ for Tl^{3+} , and $x = 0.27$ for Tl^{1+} . We investigated three cases, $x = 0.235$, 0.25 (no relaxation), and 0.27.

The scheme we used in our calculations is the standard full-potential augmented plane wave (FLAPW) method. The present energy-band calculation was performed using

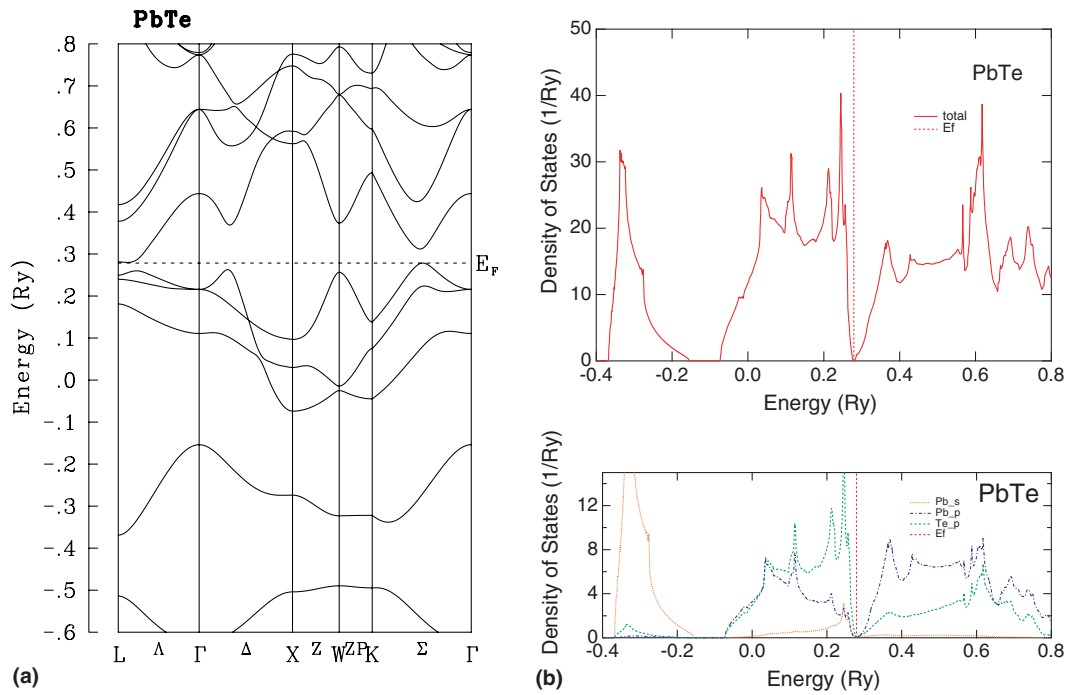


Fig. 1. (a) Band structure and (b) density of states (DOS) curve for PbTe.

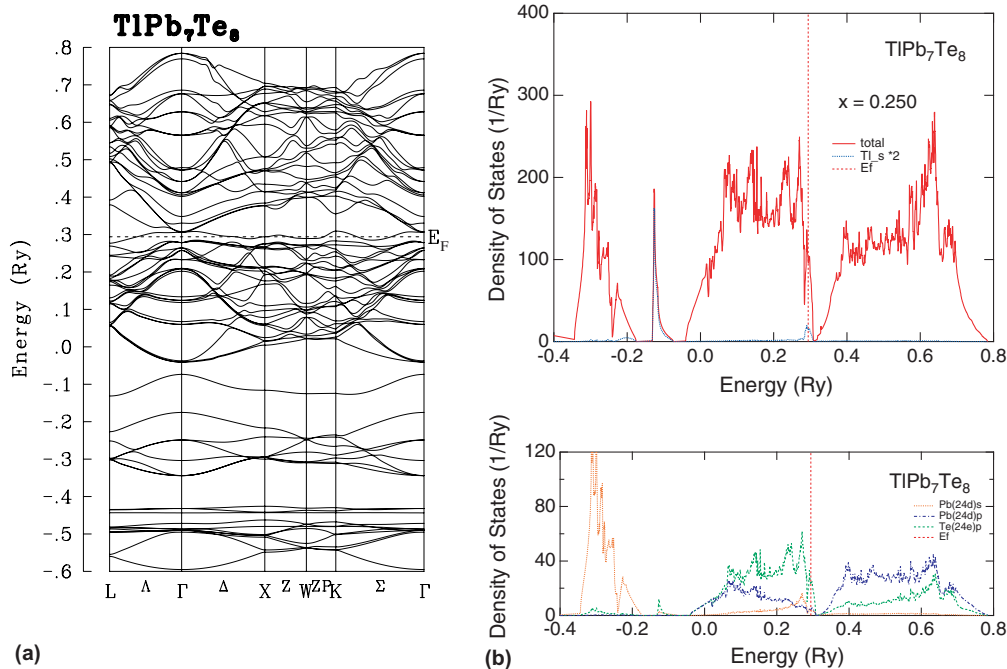


Fig. 2. (a) Band structure and (b) density of states (DOS) curve for TlPb_7Te_8 ($x = 0.25$).

the computer code KANSAL-94 and TSPACE [9]. For the exchange-correlation potential we adopted the local-density approximation (LDA), according to Gunnarson and Lundqvist [10]. The muffin-tin (MT) radii are set as 1.43 Å for Tl/Pb, 1.16 Å for Te. For plane wave basis functions we used are about 180 and 1400 LAPWs for PbTe and TlPb_7Te_8 , respectively. Spin-orbit interaction is included within the second-variational procedure [11]. The self-consistent potentials are calculated at 56 k -points in the irreducible Brillouin zone (IBZ, 1/48th of the BZ). The density of states (DOS) are deduced from the eigenstates at 489 points in the same IBZ by the ordinary tetrahedron method.

The energy band dispersions and the density of states (DOS) curve of PbTe are shown in Fig. 1. Overall band structure of PbTe is similar to the previous calculation [12]. However, in the present calculation we obtained an indirect gap (namely from Σ point to Λ point, very near the L point) $\Delta \sim 0.025$ eV. This is in contrast to the previous result, namely, a direct gap $\Delta \sim 0.17$ eV at L point. This result may show the importance of using full-potential approach. Nevertheless, this band gap is nearly a pseudo-gap, and a clear “band gap” is seen the DOS curve. The role of the spin-orbit interaction (SOI) is crucial. Without SOI, the band gap increases to 0.7 eV, inconsistent with previous calculations and experiments. Fig. 2 shows the energy band dispersions and the DOS curves of TlPb_7Te_8 . Because of the different unit cell it is difficult to compare the bands of PbTe and TlPb_7Te_8 . However, it is found that in TlPb_7Te_8 the band gap is vanished, and a narrow band state is appeared. The Fermi level (E_F) is pinned on this band. From the DOS curve we can see that this band is mainly composed of the mixture of the Tl-s and the Te-p orbitals. Hereafter we call this state as “Tl-s band”. In fact this is the antibonding state of Tl-s and Te-p orbitals, and the bonding state is seen at energy ~ -0.1 Ry. This Tl-s like narrow band is located just on the top of the valence band, suggesting that Tl atom works as an acceptor in the low concentration limit. We also performed the band calculation for TlPb_3Te_4 (25% doped case, not shown), and confirmed that the position of the Tl-s band mostly unchanged, though the band width gets larger due to the higher concentration of Tl. Similarly the calculation for InPb_3Te_4 [13] shows that the In-s level is almost at the midpoint of the band gap, which is also suggested by atomic calculation [5].

Total and partial density of states (MT-sphere-projected DOS) near E_F of TlPb_7Te_8 for $x = 0.235$, 0.25 and 0.27 are shown in Fig. 3. Total energy calculations shows that $x = 0.25$ has the lowest energy among these three cases, which means the lattice hardly relaxes spontaneously. This is possibly because our approximation that only the nearest-neighbor Te atoms relax is too crude. For going beyond this approximation we have to consider larger unit cell, and it is not yet feasible. As expected, the overall shape of the bands resemble between these three cases. However, there are two distinct differences as follows: First, in $x = 0.235$ the narrow

Tl-s band is split from the Te-p band, while in the other two cases these bands are overlapped. This is because the narrow Tl-s band is an antibonding state, thus when Tl-Te distance get smaller, the energy of this state increases. Second, the Tl-s partial DOS at E_F clearly decreases when x increases. This is also because when Tl-Te distance increases, the hybridization between Tl-s and Te-p orbitals decreases, and also the portion of Tl-s contribution of this band decreases. We also found that the occupation number of Tl-s orbitals in the MT sphere (which is equal to the integrated partial DOS up to E_F) increases, when x increases. This means that large x corresponds to the small valence, which is consistent with the above discussions.

In summary, we calculated the electronic energy band structure of $(\text{Pb}_{1-\delta}\text{Tl}_\delta)\text{Te}$ with $\delta = 0$ and 0.125. PbTe is a semiconductor with an indirect small gap, and Tl doping

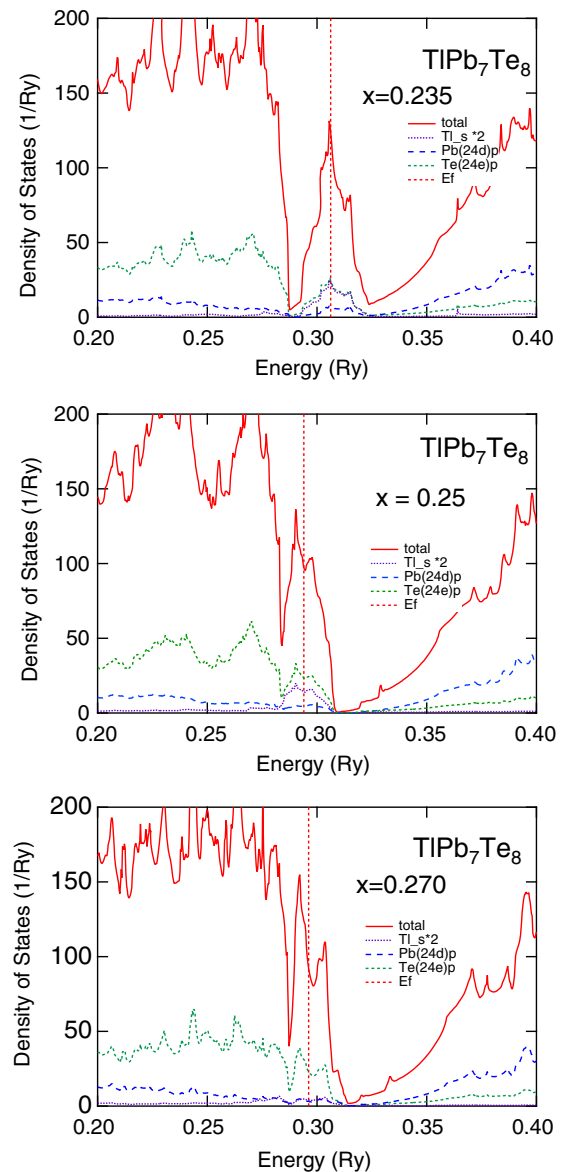


Fig. 3. Density of states (DOS) curve for TlPb_7Te_8 with $x = 0.235$, $x = 0.25$ and $x = 0.27$.

induces a narrow quasi-impurity band in this in-gap state. This band consists of the mixture of Tl-s and Te-p orbitals. A local lattice polarization around Tl can change the character of this band, and also the valency of Tl.

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