

***Ab Initio* Study of Deep Defect States in Narrow Band-Gap Semiconductors: Group III Impurities in PbTe**

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(Received 22 November 2005; published 8 February 2006)

The nature of deep defect states, in general, and those associated with group III elements (Ga, In, Tl) in narrow band-gap IV–VI semiconductors (PbTe and PbSe), in particular, have been of great interest over the past three decades. We present *ab initio* electronic structure calculations that give a new picture of these states compared to the currently accepted model in terms of a negative- U Hubbard model. The Fermi surface pinning and why In-doped PbTe and related compounds show excellent high temperature thermoelectric behavior can be understood within the new picture.

DOI: [10.1103/PhysRevLett.96.056403](https://doi.org/10.1103/PhysRevLett.96.056403)

PACS numbers: 71.55.-i, 71.20.Nr, 71.23.An

Lead chalcogenide salts PbTe and PbSe are IV–VI narrow band-gap semiconductors whose study over several decades has been motivated by their importance in infrared detectors, light-emitting devices, infrared lasers, thermophotovoltaics, and thermoelectronics [1–3]. The potential for using PbTe as good high temperature thermoelectric material is well established [3]. Novel bulk quaternary systems $\text{AgPb}_m\text{SbTe}_{m+2}$ with special m values [4] and PbSeTe/PbTe quantum dot superlattices [5] have recently been found to give a large thermoelectric figure of merit, $ZT \sim 2$ in the temperature range (400–800 K). There are also attempts to improve ZT of PbTe through functional grading and by taking advantage of the specific features of In as the dopant element [6]. It appears that there is a great potential for achieving high ZT values in In-doped PbTe compared to the conventional PbI_2 -doped n -type compounds.

Indium and other group III impurities (gallium and thallium) in IV–VI semiconductors have been known to exhibit anomalous behavior [6,7]. For example, they are n -type in PbTe and p -type in SnTe. When PbTe is doped with group III impurities, one observes the pinning of the Fermi energy and mixed-valence behavior. The same impurity can be either donor or acceptor depending on the specific composition of the semiconductor. The Fermi-level stabilization within the band gap is essential for understanding the unusual behavior of these systems and also for their practical application. According to the current theoretical picture, the group III impurities exist in two valence states in the solid, one trivalent and the other monovalent (referred to as s^0p^3 and s^2p^1 states, respectively, where s refers to an impurity s state and p refers to a band p state), an inhomogeneous mixed-valence picture [8,9]. The divalent impurity state (s^1p^2) is an excited state. The trivalent and monovalent states (two holes or two electrons in the impurity s state) are stabilized by the negative correlation energy [8,9] as in the well-known negative- U Anderson model [10]. This results in the Fermi-level stabilization in the gap. In this Letter, we

propose a different picture for the observed Fermi-level stabilization and the mixed-valence behavior using the results of our *ab initio* electronic structure calculation of group III impurities in PbTe. We find that in case of In, two “localized” bands of states appear, one below the valence-band minimum and the other above the valence-band maximum, in the band gap. We identify these two states as deep defect states associated with the In impurity. They are strongly hybridized In s and neighboring Te p states. The spectral weights associated with both of these two localized bands of states are two (including spin degeneracy) per impurity. In this process, the valence band (predominantly of Te p character) loses one state (without spin degeneracy) per impurity. This picture naturally leads to the pinning of the Fermi energy in the band gap. For Ga and Tl, the upper localized band moves towards the valence band and appears to merge with it. Because of the strong hybridized nature of both the upper and lower localized bands, photoexcitation to the conduction band from these states can lead to strong electronic and lattice relaxation, which are needed to explain the observed slow relaxation process in photoconductivity studies [7].

The problem of deep defect states (DDS) in narrow band-gap semiconductors with large electronic dielectric constants such as PbTe is an old but interesting one. Simple effective mass theories that give an excellent description of shallow impurity states in large band-gap semiconductors are inadequate to describe the physics of these DDS. A local description of the impurity states is more appropriate. Although earlier theoretical attempts to understand the DDS by local orbital concepts and qualitative arguments [7,9,11,12] have been made, a fundamental microscopic understanding of these states is presently lacking. We present here the results of our *ab initio* density functional calculations of group III impurity-induced states in PbTe using a periodic supercell model. Our calculations shed new light on the nature of the DDS occurring both below the valence band and in the band gap in terms of their origin, parentage, and degree of localization.

To model the substitutional impurities, we have used $2 \times 2 \times 2$ ($3 \times 3 \times 3$) supercells containing 64 (216) atoms. Each contain 1 In atom, 31 (107) Pb atoms, and 32 (108) Te atoms. We have also carried out calculations using 2 In atoms and 30 Pb atoms in the $2 \times 2 \times 2$ supercell to see if there is a charge transfer between the two In impurities, i.e., whether a negative- U picture is adequate. Similar calculations were carried out for the other two trivalent impurities Ga and Tl. Electronic structure calculations have been performed within density functional theory (DFT) using all-electron full-potential linearized augmented plane-wave (FPLAPW) plus the local orbital method [13] incorporated in WIEN2K [14], and the projector augmented-wave (PAW) [15] method incorporated in the *Vienna Ab-initio Simulation Package* (VASP) [16]. We have used the generalized-gradient approximation (GGA) [17] for the exchange and correlation potential.

Before discussing our results, let us briefly summarize the basic physics of In impurities in PbTe. Nominally, Pb is divalent; it gives two electrons to fill the valence band, which is predominantly Te p with some hybridization with Pb $6p$. The Pb $6s$ state is strongly bound and lies below the valence band. Indium metal is nominally trivalent, and hence when In replaces a divalent Pb, one expects an n -type donor. This assumes that the number of states in the Te p band does not change when an In impurity is present. If the In s state is strongly bound and lies below the valence p band, then In will behave as an acceptor because it gives only one electron to the Te- p band instead of the needed two. In fact, the current theoretical models for the DDS in In present a different picture [7–9,11]; two In impurities after giving two electrons each to the Te- p valence band (thus becoming two In^{2+} sites—which correspond to one valence electron per In site occupying the In s state) dissociate into In^{3+} and In^{1+} . This charge disproportionation with subsequent localization of two electrons at one of the two In sites and two holes at the other In site is stabilized by attractive intrasite interaction [10]. Thus, half of the In impurities are trivalent and the other half are monovalent. The Fermi level gets pinned between the empty and doubly occupied single particle defect states. As we discuss below, our *ab initio* calculations give a different picture of the DDS.

In Figs. 1(a) and 1(b), we plot, respectively, the total density of states (DOS) obtained in FPLAPW calculations [18] for PbTe and $\text{InPb}_{31}\text{Te}_{32}$ and the difference (after making a small relative rigid shift by -0.654 eV so that the Pb $6s$ core state and the highest peak in the valence-band match). Clearly, we see a band of states split off below the valence-band minimum and a band of states split off above the valence-band maximum (VBM) and lying in the band-gap region. The integrated DOS in both these bands of states is 2 (including spin degeneracy). The width of these two bands is ~ 0.25 eV. We refer to these bands as localized bands. What is most interesting is that the Fermi energy (at 0 eV) is at the middle of the upper localized band (the one in the gap). This can easily be understood if

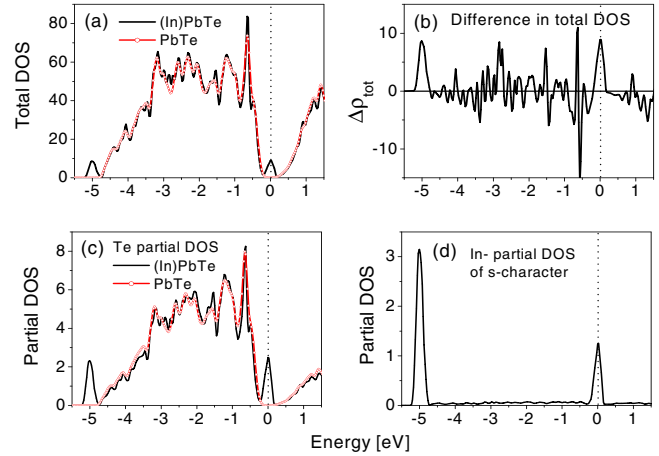


FIG. 1 (color online). (a) Total DOS of $\text{Pb}_{32}\text{Te}_{32}$ and $\text{InPb}_{31}\text{Te}_{32}$ and (b) their difference $\Delta\rho_{\text{tot}}$, (c) partial DOS associated with nearest neighbor Te atoms of the In impurity, and (d) In partial DOS of s character. Results obtained in FPLAPW calculations. The Fermi level is at 0 eV.

the Te- p valence band loses one state per In impurity. Naively, one can say that the In $5s$ state is strongly bound and appears below the valence-band minimum and is occupied by two In valence electrons. If the number of states in the valence band remained the same as in PbTe, then the third In valence electron will go to this band. Since Pb gives two electrons to fill the valence band in PbTe, the Fermi energy will be in the valence band giving one hole per In. The only way the Fermi energy can move to the upper localized band in the gap is if the valence band loses one state (two including spin). This is precisely what happens, and the reason for the observed Fermi surface pinning in the band gap in In-doped PbTe is a strong interaction between In and neighboring Te orbitals, which removes one state from the valence band and gives rise to a new hybridized state in the gap, a classic example of a DDS.

In order to understand the parentage of the two localized bands, we plot in Fig. 1(c) the partial DOS associated with Te atoms that are neighbors of In. Clearly, the Te p valence band of PbTe has changed dramatically in the presence of In. The two new “localized bands” have nearly similar Te p character. In Fig. 1(d), we show the In s character that contributes primarily to the “localized bands,” the lower one has more In s character. In addition, in FPLAPW calculations there is a substantial contribution to the charge density from the interstitial regions. The atomic radii have been chosen to be 1.53 Å for both In and Te, and the distance between In and its nearest neighbor Te is 3.23 Å, leaving a substantial interstitial charge distribution. The upper localized band has a more interstitial contribution; hence it is more diffused. Thus, the localized bands consist of strongly hybridized In s and Te p states and clearly exhibit mixed-valence behavior.

To see the effects of lattice relaxation and spin-orbit interaction (SOI), we have carried out PAW calculations

[19]. Our results are shown in Fig. 2(a), where we give results with SOI (with ionic relaxation) and without SOI (with and without ionic relaxation). The major effect of SOI is to shift the conduction-band minimum downwards and the VBM upwards, the former being much larger since it comes from the Pb p states. There is a reduction in the band gap by more than 0.5 eV. The DOS near the valence-band minimum is hardly affected. SOI does not affect the lower localized band much and reduces the width of the upper localized band by a small amount. The major effect of ionic relaxation is to stabilize the lower localized band (centered at -4.9 eV) by about 0.25 eV with respect to the bottom of the valence band. Thus, the relaxation energy (including both electronic and ionic degrees of freedom) is less than 0.5 eV. Relaxation has a slightly smaller effect on the upper localized band, of the order of ~ 0.125 eV, the major change being a lowering of the energy of the states near the VBM. The distance between In and the neighboring Te decreases by about 0.05 Å after relaxation (the average distance being 3.28 Å). Thus the relaxation effects are there but not very large.

To find out what happens when two In impurities are closer or farther than 13.16 Å, we have studied $\text{In}_2\text{Pb}_{31}\text{Te}_{32}$, where one In is located at the corner and the other at the center of the $2 \times 2 \times 2$ supercell, and $\text{InPb}_{107}\text{Te}_{108}$, where the only In is located at the corner of the $3 \times 3 \times 3$ supercell. In case of $\text{In}_2\text{Pb}_{31}\text{Te}_{32}$, since the impurity states have s symmetry and the overlap between two impurity states comes through Te- p and Pb- p orbitals, one expects the hopping amplitude between the two impurity states (in an effective tight-binding model) to be small due to 90° relative arrangement. Thus, if one of the impurities likes to be in the s^0 and the other in the s^2 state, we should see some hint of this, although DFT-GGA may not be adequate for this purpose. Our results for the 2-impurity are essentially that for two noninteracting 1-impurities and the Fermi energy is pinned at the “upper” localized band. Since the impurity states are quite diffuse, the relaxation energy associated with zero and double occupancies are not large enough to give rise to a

negative- U effect. Yet at the same time the positive- U may be quite small in magnitude so that the doubly occupied state is lower in energy than the singly occupied state with the other electron in the conduction band. In Fig. 2(b), we plot the total DOS of $\text{InPb}_{31}\text{Te}_{32}$ ($2 \times 2 \times 2$ supercell) and $\text{InPb}_{107}\text{Te}_{108}$ ($3 \times 3 \times 3$ supercell) obtained in PAW calculations (without SOI and ionic relaxation, using the experimental lattice constant of PbTe, which is 6.454 Å), where the DOS of the latter shows two peaks at -4.9 and 0 eV, which are much sharper than those of the former, as one should expect.

For Ga and Tl, the upper localized band overlaps the top of the valence band; the peak in Ga is slightly lower in energy than that for Tl. This nonmonotonic behavior in going from Ga to In to Tl can be understood by realizing that the relativistic effects are strongest for Tl; in their absence the Tl peak would have been at a higher energy than In. Because of this difference between In and the other two group III impurities In shows anomalous behavior.

In summary, our *ab initio* electronic structure calculations suggest a model for the group III impurities in PbTe that is dramatically different from the one currently accepted [7,9,11]. Instead of half the impurities in the trivalent and the other half in the monovalent state (an inhomogeneous mixed-valence scenario), all the impurities have the same electronic configuration, two electrons occupy a localized state whose energy is below the valence-band minimum and one electron occupies a localized state in the gap (in case of In) or a resonant state at the top of the valence band (in case of Ga and Tl). The impurity states are of s symmetry but strongly hybridized In s and neighboring Te p states. In contrast to the inhomogeneous mixed-valent picture where the impurity centers are diamagnetic, in our homogeneous mixed-valent picture, the impurity centers should be paramagnetic. Electron paramagnetic resonance experiments in systems without Pb vacancies can distinguish between these two different models. Finally, due to the presence of the half-filled In impurity level in the gap, electrons from this level can annihilate minority carriers and also trap electrons, which can be excited at high temperatures to the conduction band. Both these effects can lead to enhanced thermoelectric behavior [6].

This work was partly supported by MURI Grant No. N00014-03-10789 from the Office of Naval Research. We acknowledge stimulating discussions with Professor M. G. Kanatzidis and Dr. J. Androulakis.

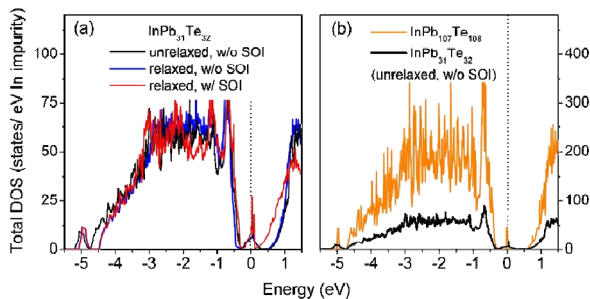


FIG. 2 (color online). Total DOS of (a) $\text{InPb}_{31}\text{Te}_{32}$ with SOI (with ionic relaxation) and without SOI (with and without ionic relaxation), and (b) $\text{InPb}_{31}\text{Te}_{32}$ and $\text{InPb}_{107}\text{Te}_{108}$ (without ionic relaxation, without SOI). Results obtained in PAW calculations. The Fermi level is at 0 eV.

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