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Deep defect states in narrow band-gap semiconductors

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Abstract

The nature of defect states associated with group III impurities (Ga, In, and Tl) in PbTe, a narrow band-gap semiconductor, has been studied within density functional theory and supercell model. For all three impurities (both substitutional—at the Pb site and interstitial—at the tetrahedral site), there is a hyper-deep defect state which lies about 0.5–1.0 eV below the valence band. It is a highly localized bonding state between the impurity s-orbital and the surrounding p-orbitals of the Te atoms. The corresponding anti-bonding state, denoted as the deep defect state, lies in the band-gap region. Its precise position *vis-à-vis* the conduction- and valence-band extrema controls the unusual properties exhibited by these defects.

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1. Introduction

Lead chalcogenides (PbTe, PbSe, and PbS) are IV–VI narrow band-gap semiconductors whose studies over several decades have been motivated by their importance in infrared devices, photovoltaics, and high temperature thermoelectrics. PbTe in particular is the end-compound of several ternary and quaternary high performance high temperature thermoelectric materials [1]. Since transport and optical properties of semiconductors are dominated by the electronic states in the neighborhood of the band gap, it is important to understand the nature of these states and how they change in the presence of defects. In PbTe one usually has deep defect states (DDSs) (rather than the shallow ones which are described by a hydrogenic model) dominated by the short-range atomic-like defect potential and changes in the local bonding [2]. The problem of defect states in bulk PbTe has been theoretically studied by numerous authors using different methods [3–10]. Our *ab initio* calculations carried out recently for a large class of substitutional impurities and vacancies on the Pb and Te sites have shown that the electronic density of states (DOS) near the top of the valence band and the bottom of the conduction band get significantly modified for most of the defects [9]. Also how these defect states change in going to PbTe thin films has been studied [11].

In this paper we discuss the nature of defect states associated with Ga, In, and Tl impurities in PbTe. These impurities have been studied during the last several decades [12]. They show interesting properties, e.g., amphoteric nature (both donor and acceptor-like behavior—for In), Fermi surface pinning (for all three), and superconductivity with large T_C (for Tl). These properties have been explained in terms of a mixed-valence model where the divalent state of the impurity (say In^{2+}) is unstable towards the coexistence of trivalent (In^{3+}) and monovalent (In^{1+}) states. These latter two valence states are stabilized by electronic and ionic relaxation. We have carried out extensive studies of these defect states using *ab initio* density functional theory (DFT) and supercell models. We see two types of defect states. One is a doubly occupied hyper-deep defect state (HDS) lying below the valence-band bottom, about 5 eV below the Fermi level. The other is a DDS in the neighborhood of the narrow band gap. We

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will explore the physics of these defect states and see how they can help understand the experiments. As we will argue later, these calculations do not support the energetic possibility of the trivalent state.

2. Computational details

Structural optimization, total energy and electronic structure calculations were performed within the DFT formalism, using the generalized-gradient approximation (GGA) [13] and the projector-augmented wave (PAW) [14] method as implemented in VASP [15]. We treated the outermost s and p electrons of Pb, Te, and group III (Ga, In, Tl) impurities as valence electrons and the rest as cores; scalar relativistic effects (mass–velocity and Darwin terms) were included. Spin–orbit interaction (SOI) was included in some calculations. The energy cutoff was set at 200 eV, and the convergence was assumed when the total energy difference between consecutive cycles was within 10^{-4} eV. The optimized lattice constant of bulk PbTe, $a = 6.55$ Å, was used to set up the initial structure for defect calculations.

3. DDSs in PbTe

3.1. Bulk

We modeled the impurities in bulk PbTe using ($2 \times 2 \times 2$) or ($3 \times 3 \times 3$) supercells containing 64 or 216 atoms, respectively. One impurity atom substituted the Pb atom at the center of the supercell (substitutional impurity) or was added to one of the tetrahedral sites (interstitial impurity). The impurity–impurity distance of the ($2 \times 2 \times 2$) supercell is ~13 Å, whereas that of the ($3 \times 3 \times 3$) is ~20 Å. All atomic coordinates were allowed to relax; the optimized structure was then used to calculate energy and electronic DOS.

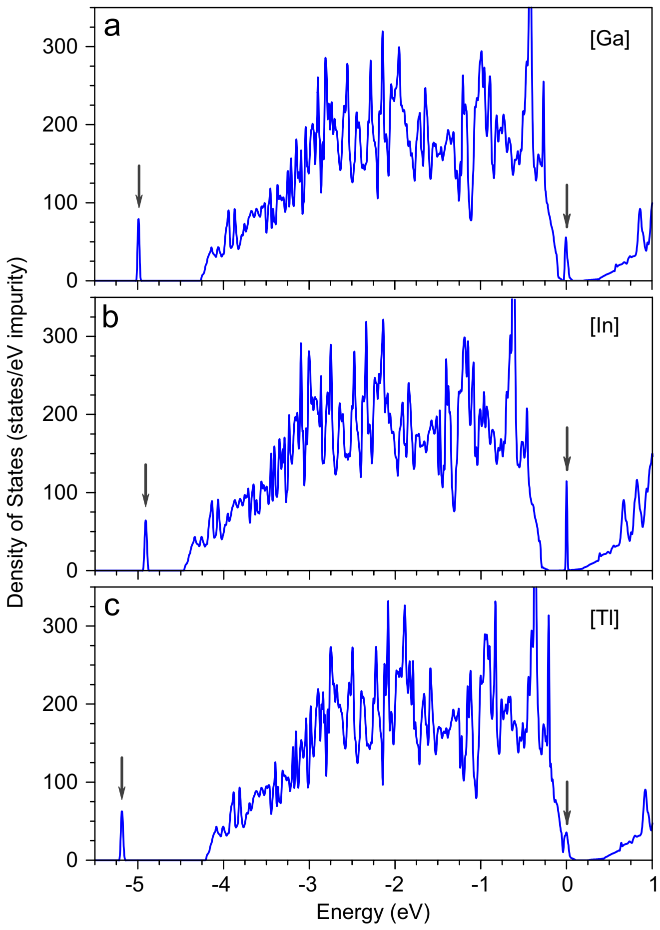

Fig. 1. Density of states (DOS) of bulk PbTe doped with (a) Ga, (b) In, and (c) Tl substitutional impurities. The results were obtained in calculations using the ($3 \times 3 \times 3$) supercell; spin–orbit interaction (SOI) was included. HDS and DDS are marked by arrows. The zero of the energy is set to the highest occupied state.

We show in Figs. 1(a)–(c) the DOS of PbTe doped with group III substitutional impurities obtained in calculations using ($3 \times 3 \times 3$) supercells. The large supercell helps reduce the impurity–impurity interaction thereby narrowing the width of the localized bands formed by HDS and DDS. SOI reduces the band gap of PbTe with a large downward shift (~0.5 eV) in energy of the bottom of the conduction band (predominantly Pb 6p) and a smaller upward shift (~0.1 eV) of the top of the valence band (predominantly Te 5p). As seen in the figures, the DDS in case of In and Ga are localized states near the bottom of the conduction band and near the top of the valence band, respectively; whereas the DDS of Tl is a resonant state near the top of the valence band. HDS is filled (with two electrons), whereas DDS is half-filled (with one electron) and the Fermi level is pinned in the middle of the localized band formed by the DDS. Our calculated results are in the right trend with experiments where it is found that the impurity level is 70 meV above the conduction-band bottom in the case of (In)PbTe, 65–60 meV below the conduction-band bottom in the case of (Ga)PbTe, and 0.15–0.25 eV below the top of the light-hole valence band in the case of (Tl)PbTe [12].

In Figs. 2(a)–(c), we show the DOS of PbTe doped with group III interstitial impurities obtained in calculations using ($2 \times 2 \times 2$) supercells (see Ref. [11] for the DOS of the substitutional ones using the same supercell size). There are also HDS and DDS, similar to the substitutional case. An interstitial impurity at the tetrahedral site has four Te and four Pb atoms as the nearest neighbors (instead of six Te atoms as in the case of the substitutional impurity at the Pb site). This reflects in the changes of the position and the shape of the localized bands formed by HDS and DDS. HDS is shifted downward in energy (towards the band predominantly formed by Pb 6s) by ~0.4 eV (Ga and In) or 0.3 eV (Tl); whereas DDS is shifted upward (towards the conduction-band bottom predominantly formed by Pb 6p) by ~0.2 eV (Ga), 0.02 eV (In), or 0.1 eV (Tl). DDS is filled and the Fermi level lies in the conduction band, in contrast to the substitutional case where the Fermi energy is pinned to the DDS, which is half-filled. Each interstitial atom introduces one electron to the conduction band and the

Fermi level is shifted upward as one adds more interstitial atoms into the supercell. This means that the group III interstitial impurities cannot lead to Fermi level pinning.

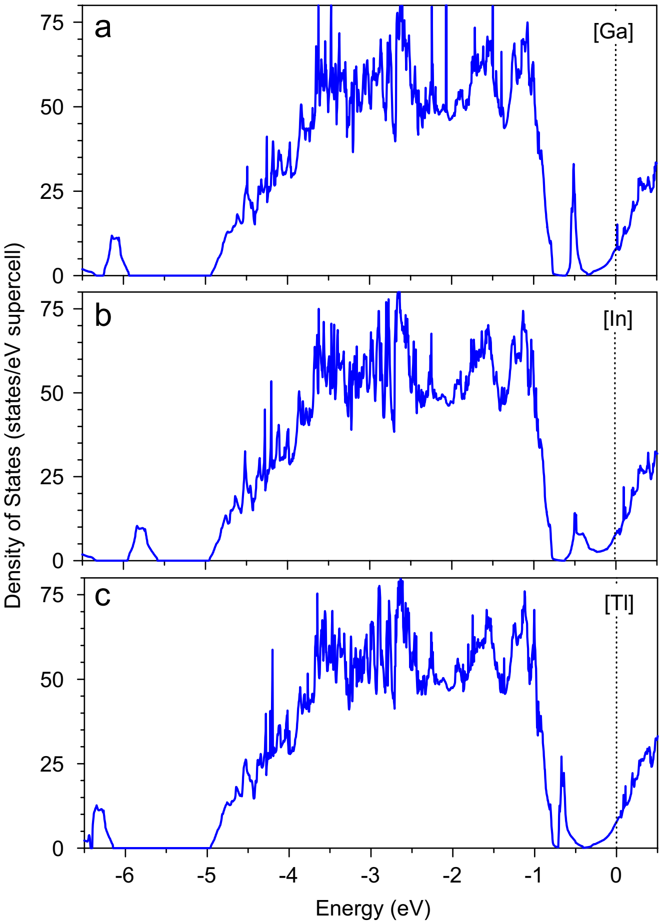

Fig. 2. Density of states (DOS) of bulk PbTe doped with (a) Ga, (b) In, and (c) Tl interstitial impurities at the tetrahedral sites. The results were obtained in calculations using the (2 × 2 × 2) supercell; spin–orbit interaction (SOI) was included. The zero of the energy is set to the highest occupied state.

Experimentally, it was found that the interstitial In atoms were neutral and did not contribute to the carrier concentration [17]. This can be understood if both substitutional and interstitial impurities are present simultaneously [18].

In order to see the nature of the DDSs, we show in Figs. 3(a) and (b) the partial charge densities associated with HDS and DDS, respectively, formed by a substitutional In impurity. As seen in the figures, HDS and DDS are the bonding and anti-bonding states of the In 5s and its neighboring Te 5p and are strongly localized within ~6 Å around the impurity atom. The HDS is predominantly In 5s, whereas the DDS has more contribution from Te 5p. These strongly bound states are similar to the electrically inactive "hyper-deep level" and the electrically active "deep level" proposed by Hjalmarson et al. [16].

3.2. Thin films

PbTe films doped with group III (Ga, In, Tl) impurities have been studied both experimentally and theoretically (see Ref. [11] and references therein). Experimental studies have revealed some of the interesting features that had been seen in the bulk, such as Fermi level pinning and, in the case of Tl, superconductivity. We have recently carried out *ab initio* calculations in PbTe thin films [11] using slab models and found that the defect states associated with different substitutional impurities and native defects that were found in PbTe bulk are preserved in the film geometry. HDS and DDS have been identified in group III (Ga, In, and Tl) doped PbTe films, similar to those in PbTe bulk. Anomalies are usually found in connection with the defects in the first and the second layer of the slab due to the special local environment of the defects, resulting from surface relaxation. These modifications in the defect states, which usually occur in the neighborhood of the band gap, should have an impact on the properties of the systems. However, we expect that some of their main characteristics will be preserved in the films.

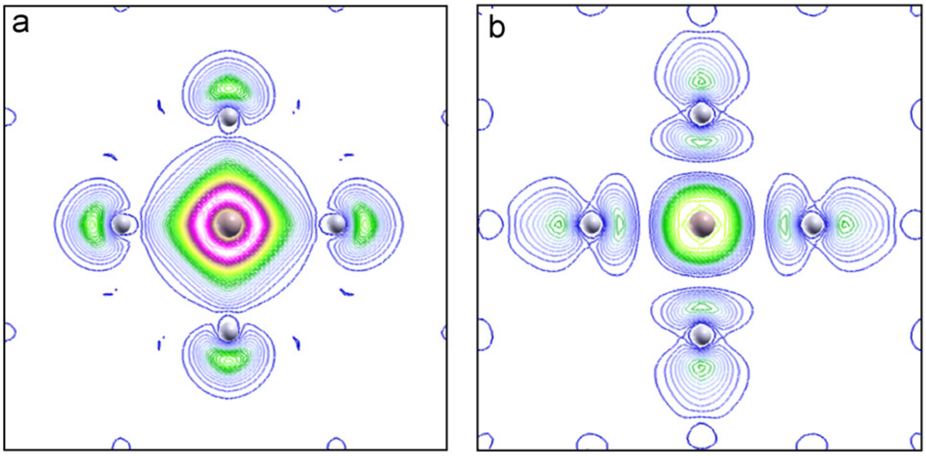

Fig. 3. Partial charge density associated with (a) HDS (bonding) and (b) DDS (anti-bonding) created by an In substitutional impurity in PbTe [in the (1 0 0) plane containing the impurity]. The results were obtained in calculations using the (3 × 3 × 3) supercell; spin–orbit interaction (SOI) was not included. The isolines in the two figures were plotted with the same scale. Large balls (at the centers) are for In, small balls are for its neighboring Te atoms.

3.3. Nanoclusters

PbTe has been used not only as bulk and films, but also as colloidal and embedded nanocrystals [19,20]. In order to see how robust the defect states are in different geometries, we have studied PbTe nanoclusters doped with group III substitutional impurities. A 216-atom stoichiometric cubic-shaped PbTe cluster (~1.6 nm in size) was constructed as a cube cut from the bulk. In a supercell model, the clusters from the neighboring supercells were separated by a vacuum of ~10 Å in thickness. An impurity atom was introduced into the system at the Pb site in the middle of the cluster. All atoms were allowed to relax to their minimum energy position.

We show in Figs. 4(a)–(c) the DOS of the PbTe cluster doped with Ga, In, and Tl substitutional impurities. The DOS structure of the cluster resembles very well that of the bulk counterpart. There are defect states, one is the highest occupied state and the other ~5 eV below the former, which can be easily identified as DDS and HDS, respectively, as had been seen in bulk PbTe and films. In going from the bulk to the cluster, the HDS–DDS distance increases in the case of Ga (~ 5.5%) and In (~ 2.0%) and decreases by ~2.3% in the case of Tl. This indicates that HDS and DDS are extremely robust. There are surface “resonant states” near the top of the valence band and at the bottom of the conduction band. The surface “resonant states” on the valence-band top overlaps with the DDS in the case of Tl.

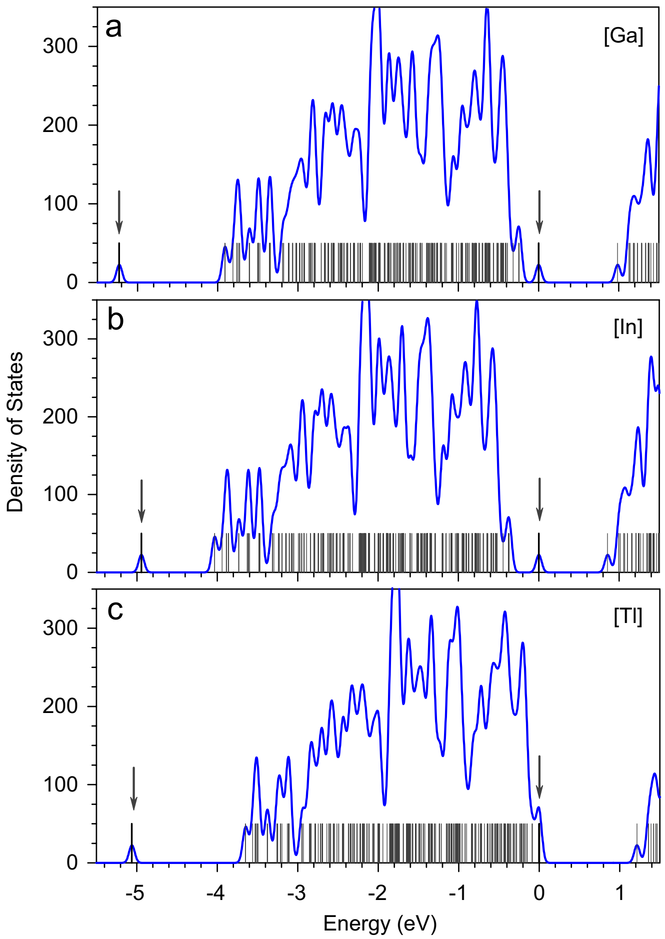

Fig. 4. Density of states (DOS) of the 216-atom cubic-shaped PbTe nanocluster doped with (a) Ga, (b) In, and (c) Tl substitutional impurities. The states have been Gaussian broadened by 0.05 eV. HDS and DDS are marked by arrows. The dashes are the eigenvalues of the cluster. Spin–orbit interaction (SOI) was not included. The zero of the energy is set to the highest occupied level.

4. Conclusion

Our extensive *ab initio* DFT studies show that the three trivalent impurities Ga, In, and Tl in PbTe give rise to two types of defect states. Both are DDSs in the sense that they are localized near the impurity and its neighboring Te atoms and their energy depends on the covalent bonding (anti-bonding) of the impurity s-orbital and p-orbitals of the neighboring Te atoms. One of the defect state (bonding) is strongly bound and lies about 5 eV below the valence-band maximum. It is doubly occupied and does not take part in transport or low-energy physics. We call this state as the HDS. The other (anti-bonding) lies about 5 eV above the HDS and its precise position with respect to the conduction-band minimum might not be given accurately by the DFT due to the DFT related difficulties with the band gap [21]. Also due to the localized nature of this state (denoted as deep defect state—DDS), Coulomb correlation effects may be important in understanding the experiments involving the DDS. This will be investigated in the future. DDS is half-filled if the impurity is substitutional at the Pb site and fully filled if interstitial at the tetrahedral site. According to this picture, group III interstitial impurities cannot lead to the Fermi level pinning. We also find that both the DDS and DDS preserve their characteristic behaviors in different types of geometry such as films and clusters, the only difference being the possibility of overlap between these defect states and the surface states of PbTe films and clusters.

Acknowledgments

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