

# The bulk band structure and inner potential of layered $\text{In}_4\text{Se}_3$

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## Abstract

The layered  $\text{In}_4\text{Se}_3$  system does have a bulk band structure (i.e. discernable and significant band dispersion) perpendicular to the cleavage plane. Band widths (the extent of dispersion) of 300 meV or more are observed, for In-p and Se-p weighted bands within the valence region, and is indicative of a bulk band structure. Two-dimensionality of state is clearly not conserved, and there must exist interactions between layers sufficient to support a bulk band structure.

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## 1. Introduction

Narrow band gap layered insulators have possible applications as the thin gate dielectric in tunnel junctions and other related structures. Recently, non-oxide layered materials like hexagonal boron nitride have been considered [1]. At issue is whether such materials are truly two-dimensional, as is generally implied [2–4] or exhibit a bulk band structure perpendicular to the cleavage plane. The studies of  $\text{In}_4\text{Se}_3$  semiconductor crystal cleavage surfaces and interface formation are interesting from this point of view as this material crystallizes in a layered structure with, in principle, weak interaction of van der Waals type between the layers and strong covalent–ionic interactions within the layer. The quasi two-dimensionality (2D) of layered crystals and, consequently, absence of free unsaturated electron bonds on the cleavage surfaces, does not quite apply as the layers are not perfectly flat but warped [5–8].  $\text{In}_4\text{Se}_3$  as in fact is dominated by an  $(\text{In}_3)^{5+}$  multivalent clusters bonded with selenium through ionic

covalent bonds (see Fig. 1).  $\text{In}_4\text{Se}_3$  seems to be less studied among the layered chalcogenides crystals [2,3], yet continues to attract attention as a natural low dimensional 2D material in much the same way as occurs with layered systems with flat layers, held together with van der Waals forces.

Here we show that this  $\text{In}_4\text{Se}_3$  system does have a bulk band structure (i.e. discernable and significant band dispersion) perpendicular to the cleavage plane and thus is not two-dimensional.

## 2. Experimental details

The layered crystal structure of  $\text{In}_4\text{Se}_3$  allows one to obtain cleaved (1 0 0) surface (Fig. 1). The crystals were grown by Czochralski method, and then cleaved *in situ*. Surface order was established by low energy electron diffraction.

Angle-resolved photoemission spectra were obtained using plane polarized synchrotron light dispersed by a 3 m toroidal grating monochromator [9,10], at the Center for Microstructures and Devices (CAMD) [11]. The measurements were made in a UHV chamber employing a hemispherical electron analyzer with an angular acceptance of  $\pm 1^\circ$ , as described elsewhere [9,10]. The combined resolution of the electron

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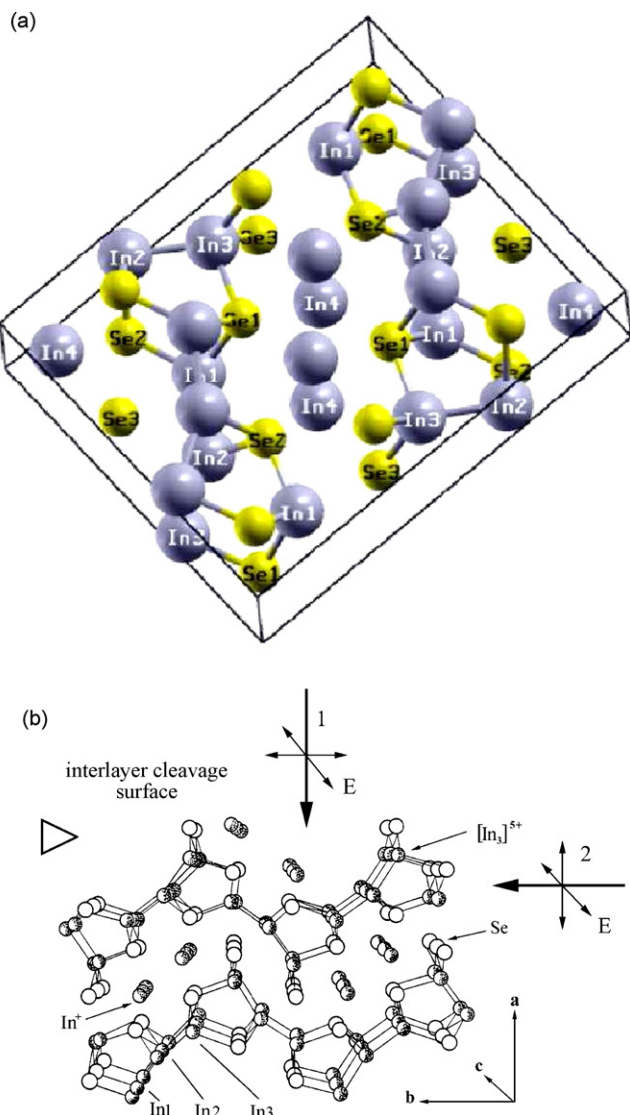


Fig. 1. The schematic crystal structure for  $\text{In}_4\text{Se}_3$  is presented top. The lattice constants of the crystal structure are:  $a = 15.296(1) \text{ \AA}$ ;  $b = 12.308(1) \text{ \AA}$ ;  $c = 4.0806(5) \text{ \AA}$ ; space group  $P_{nmm}$  [5–8], dominated by an  $(\text{In}_3)^{5+}$  multivalent clusters bonded with selenium through ionic covalent bonds. The cleavage direction is indicated at the bottom, by the triangle in the upper left.

energy analyzer and monochromator is 120–150 meV for higher photon energies (50–120 eV), but higher resolution (about 80 meV) is obtained at lower photon energies of 15–40 eV. The photoemission experiments were undertaken with a light incidence angle of  $45^\circ$  with respect to the surface normal and with the photoelectrons collected along the surface normal, to preserve the highest point group symmetry and eliminate any wave vector component parallel with the surface. All binding energies are referenced to the Fermi level, as determined from clean gold. The bulk band mapping was undertaken at room temperature, well above the Curie temperature.

### 3. Theory and structure

The  $\text{In}_4\text{Se}_3$  crystal structure according to [5–8] (projection of  $(0 0 1)$  plane) is shown in Fig. 1. The measured lattice constants

of the crystal structure are:  $a = 15.297(1) \text{ \AA}$ ;  $b = 12.308(1) \text{ \AA}$ ;  $c = 4.0810(5) \text{ \AA}$  in the orthorhombic space group  $P_{nmm}$ , obtained by X-ray diffraction using  $\text{Cu K}\alpha$  radiation. These values are in agreement with the published values of  $a = 15.296(1) \text{ \AA}$ ;  $b = 12.308(1) \text{ \AA}$ ;  $c = 4.0806(5) \text{ \AA}$ ; also in the space group  $P_{nmm}$  [8]. The interlayer cleavage plane  $(1 0 0)$  of  $\text{In}_4\text{Se}_3$  is normal to the axis of crystal growth  $a$ . The triangle in the upper left shows the cleavage direction (Fig. 1b).

We have performed FP-LAPW calculations of  $\text{In}_4\text{Se}_3$  within the density functional theory (DFT), in the form implemented in the WIEN2k code [12]. As part of our treatment, we have used the so-called generalized gradient approximation (GGA) [13,14], in the formal parameterization scheme of Perdew–Burke–Ernzerhof (PBE) [15]. Our calculations were performed on the basis of structural information taken from Schwarz et al. [8]. We have used 120 irreducible  $k$ -points in the Brillouin zone for the self-consistent calculation, with an  $R_{\text{MT}}K_{\text{max}}$  product of 7, here  $R_{\text{MT}}$  is the smallest of all atomic sphere radii and  $K_{\text{max}}$  is the plane-wave cut-off. The system has 28 (i.e.  $7 \times 4$ ) atoms in the unit cell with seven crystallographically inequivalent sites (four indium and three selenium), each of which occupying four equivalent positions (see Fig. 1a). In general, our results are comparable with prior calculations [16].

The electronic structure of  $\text{In}_4\text{Se}_3$  can be understood as five main bundles of bands (four below and one above the Fermi energy). There are flat isotropic occupied bands due to the In-4d orbitals between  $-15.00$  and  $-13.73$  eV binding energies, followed by a less “populated” band due to Se-4s and also (though less significant) In-4d orbitals between  $-13.59$  and  $-11.91$  eV binding energy. Then there is an empty (unoccupied) region between  $-11.91$  and  $-7.17$  eV below the Fermi level, where the bottom of the valence band begins. The valence band maximum is dominated by In-5s, In-5p, Se-4p, while at  $-1.5$  eV binding energy the band is more dominated by In-5p. The bands at  $-2.5$  to  $-4.5$  eV binding energy are dominated by the In-5p and Se-4p orbitals. The calculated density of occupied states, within the valence band region, is seen to be in good agreement with the photoemission, as indicated in Fig. 2.

The conduction band is mainly p-like (with both In and Se contributions). However there is a sharp peak of In-s orbitals near the bottom of the conduction band. A similar situation holds for the narrow In-s states near the valence band maximum. These s-cation states, hybridized with their p-cation and anion counterparts, are very important for the physical properties of this material, since they define the band gap.

### 4. The bulk band structure

Fig. 3 illustrates the dependence of the normal emission photoemission spectra on photon energy from 15 to 40 eV. From the dispersion of the bands, evident in the photoemission spectra as a function of photon energy, we have been able to construct a band structure mapping along the  $\Gamma Z$  line (along the surface normal). The perpendicular component of the crystal wave vector ( $k_{\perp}$ ), however, is not conserved across the solid vacuum interface because of the crystal truncation at the

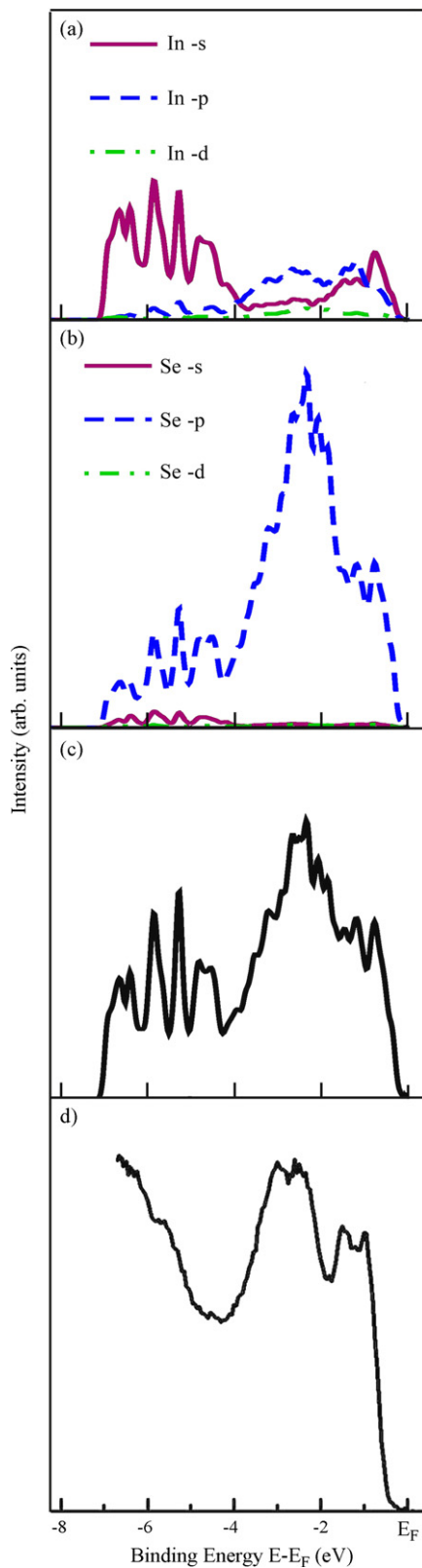


Fig. 2. The partial In (a) and Se (b) occupied density of states provide a total density of states (c) that are compared to the photoemission (d). The photoemission spectra were taken with a combined instrumental resolution of 70 meV, at a photon energy of 15 eV, with a light incidence angle of  $45^\circ$  with respect to the surface normal and with the photoelectrons collected along the surface normal.

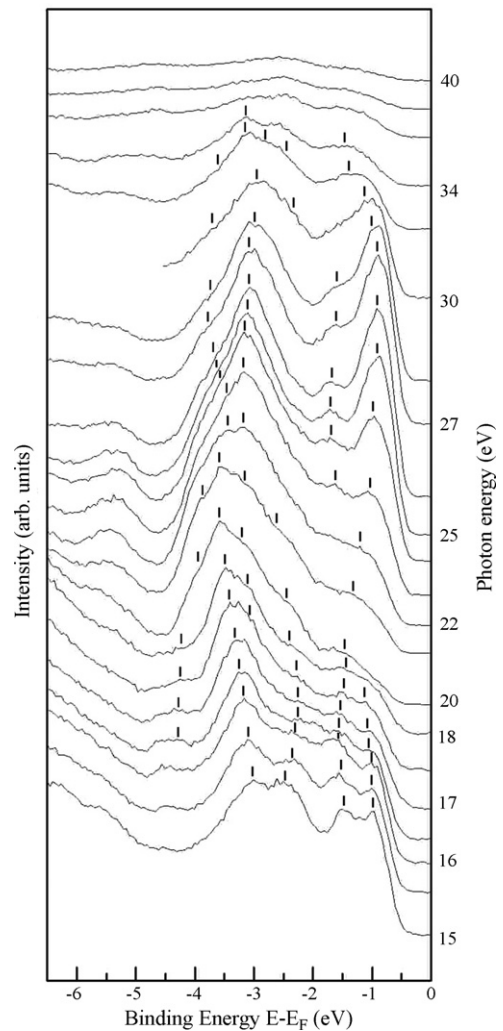


Fig. 3. The photoemission spectra of  $\text{In}_4\text{Se}_3(0\ 0\ 1)$  for photon energies from 14 to 40 eV, taken at normal emission ( $k_\perp = 0$ ).

surface. Thus the perpendicular wave vector in the crystal can be determined using

$$k_\perp = \left[ \left( \frac{-2m}{\hbar^2} \right) E_{\text{kin}} [\cos(\theta)]^2 + U_{\text{in}} \right]^{1/2} \quad (1)$$

where  $\theta$  is the emission angle of the photoelectron and  $U_{\text{in}}$  is the inner potential of the solid [17,18].

Following Eq. (1), the resulting experimental band structure has been plotted in Fig. 4 along the  $(0\ 0\ 1)$  direction, or from  $\Gamma$  to Z of the bulk Brillouin zone (along the surface normal). At photon energies of 14 and 27 eV, where the band at the valence band maximum has the least binding energy, should be the photon energies where the wave vectors correspond to the  $\Gamma$  point in the  $k$  vector space. This corresponds to a  $\Gamma$  point occurring at  $2.35\ \text{\AA}^{-1}$ , while the zone edge occurs at  $1.91$  and  $2.76\ \text{\AA}^{-1}$ . This suggests a lattice constant of  $7.4\ \text{\AA}$ , or about the expected lattice constant of  $15.3\ \text{\AA}$ . This is different from the in plane band dispersion, where the critical points are consistent with both expectation and the low energy electron diffraction as will be discussed in detail elsewhere [19].

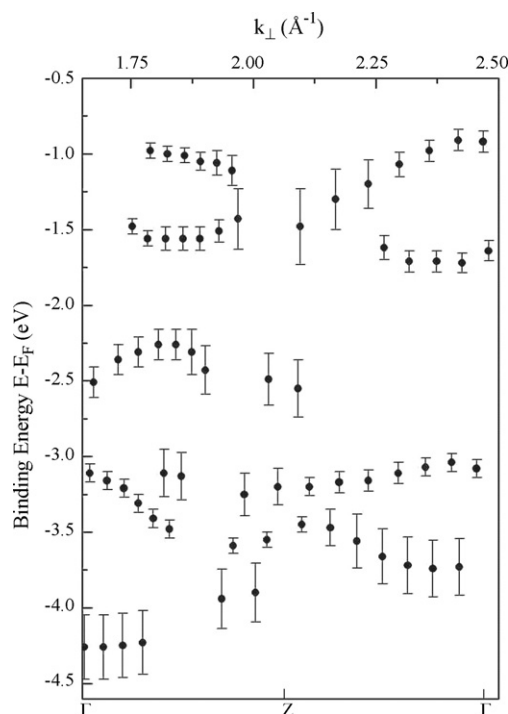


Fig. 4. Experimental bulk band structure of  $\text{In}_4\text{Se}_3$  along the  $(0\ 0\ 1)$  direction. From the experimental data, both critical points and the experimental wave vectors are identified.

Though the Z point in Fig. 4 should designate another  $\Gamma$  point in the bulk band structure, surprisingly, it does not appear to do so. We may understand this smaller than expected lattice constant in the bulk band structure if both “a” and “b” cleavage surfaces are present at the surface (separated by a unit cell along the surface normal or about  $7.65\ \text{\AA}$ ). By superposition, the bulk band structure may now resemble the bulk band structure of a crystal with a glide plane symmetry, as in  $\text{CoS}_2$  [20]. This increase in the effective Brillouin zone, due to superposition of different facets or cleavage surfaces, along the surface normal would tend to diminish the extent of the band dispersion measured, making the observation of bulk band structure even more significant. If we now assume an effective lattice constant along the surface normal of  $15.3\ \text{\AA}/2$  (although not the correct lattice constant), we can estimate that the inner potential  $U$  of about 2.5 eV if the critical point at  $2.35\ \text{\AA}^{-1}$  is the “effective”  $\Gamma_3$  and about 21 eV if this is the effective  $\Gamma_4$  critical point. Neither value would be expected for a conventional narrow band gap insulator.

## 5. Summary

The downward dispersion (towards greater binding energy) of the band at the valence band maximum, away from the  $\Gamma$  point, can be understood as this band is dominated by In-s and Se- $p_y$  while band at  $-1.5\ \text{eV}$  binding energy has strong  $p_y p_z$  components. In any case the band widths (the extent of

dispersion) of 300 meV or more, for bands within the valence region, is well more than the instrumental resolution and is indicative of a bulk band structure. Two-dimensionality of state is clearly not conserved; there must therefore exist interactions between layers sufficient to support a bulk band structure.

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