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The anisotropic band structure of layered $In_4Se_3(001)$

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There is discernable and significant band dispersion along both high symmetry directions for cleaved ordered surfaces of the layered $In_4Se_3(001)$. The extent of dispersion of approximately 1 eV is observed along the surface chain rows, and about 0.5 eV perpendicular to the surface "furrows," consistent with theoretical expectations. A possible surface state exists at the surface Brillouin zone edge, in the direction perpendicular to the chains, in a gap of the projected bulk band structure. Excluding the possible surface state, the experimental hole mass is 5.5 times greater along the chains than perpendicular to the chains, but the dispersion is easier to discern. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3000453]

I. INTRODUCTION

The band structure of quasi-one-dimensional systems has attracted considerable attention[1,2] in part because of the very anisotropic band structure such systems provide.[3,4] While a common approach to the study of such systems is to study atomic chains and wires on stepped and "furrowed surfaces," bulk crystals with quasi-one-dimensional chains also exist like the molybdenum and tungsten bronzes[5–13] and $(TaSe_4)_2I$.[12–14] In_4Se_3 is a semiconductor, unlike the quasi-one-dimensional conductors, and is thus not susceptible to change density wave effects[15] although the band structure should be highly anisotropic.[16]

The In_4Se_3 semiconductor crystal forms a layered structure characterized by, in principle, weak interaction of van der Waals type between the layers and strong covalent-ionic interactions within the layer, but the (001) surface is not "smooth." The quasi-two-dimensionality (2D) of layered crystals and, consequently, absence of free unsaturated electron bonds on the cleavage surfaces, do not quite apply here as the layers are not perfectly flat but corrugated,[16–20] resulting in quasi-one-dimensional chain structures at the semiconducting $In_4Se_3(001)$ surface. In_4Se_3 is, in fact, dominated by $(In_3)^{5+}$ multivalent clusters bonded with selenium through ionic covalent bonds. The layered crystal structure of In_4Se_3 allows one to obtain cleavage (001) surfaces,[16–20] as shown in Fig. 1. The surface of In_4Se_3 provides an opportunity to study the electronic structure of In chains in the presence of strong bonding with Se atoms.[16]

In prior studies, we have shown that there is strong dispersion along the chain direction of the $In_4Se_3(001)$ surface[16] as well as demonstrated the presence of a bulk band structure in spite of the layered nature of $In_4Se_3(001)$.[21] Here we show that the perpendicular to the chains in the $In_4Se_3(001)$ surface is characterized by a weaker but nonetheless discernable dispersion perpendicular to both the chain direction and the cleavage plane. We also identify a band near the valence band maximum that falls into a gap of the projected bulk band structure at the surface Brillouin zone (BZ) edge that may well be a surface state.

II. EXPERIMENTAL DETAILS

The layered crystal structure of In_4Se_3 allows one to obtain cleavage (001) surfaces (Fig. 1). The crystals were grown by Czochralski method and then cleaved *in situ*. The surface order was established by low energy electron diffraction (LEED), as seen in Fig. 2, and scanning tunneling microscopy (STM).[20] The In_4Se_3 crystal structure was found to be in agreement with prior structural determinations[17–20] with measured lattice constants of the crystal structure: $\boldsymbol{a}=15.297(1)$ Å, $\boldsymbol{b}=12.308(1)$ Å, and $\boldsymbol{c}=4.0810(5)$ Å in the orthorhombic space group P_{nnm} obtained by x-ray diffraction using Cu $K\alpha$ radiation. These values are in agreement with the published values.[20] The interlayer cleavage plane (001) of In_4Se_3 is normal to the axis of crystal growth $\boldsymbol{a}$. The triangle in the upper left shows the cleavage direction [Fig. 1(b)].

Angle-resolved photoemission spectra along the chain direction were obtained using plane polarized synchrotron light dispersed by a 3 m toroidal grating monochromator[22,23] at the Center for Microstructures and Devices (CAMD).[24] The measurements were made in a UHV chamber employing a hemispherical electron analyzer with an angular acceptance of $\pm 1°$, as described elsewhere.[16,21–23] The combined resolution of the electron energy analyzer and monochromator is 120–150 meV for high kinetic photon energies (50–120 eV), but higher resolution (about 80 meV) is obtained at lower photon energies of 15–40 eV. The photoemission experi-

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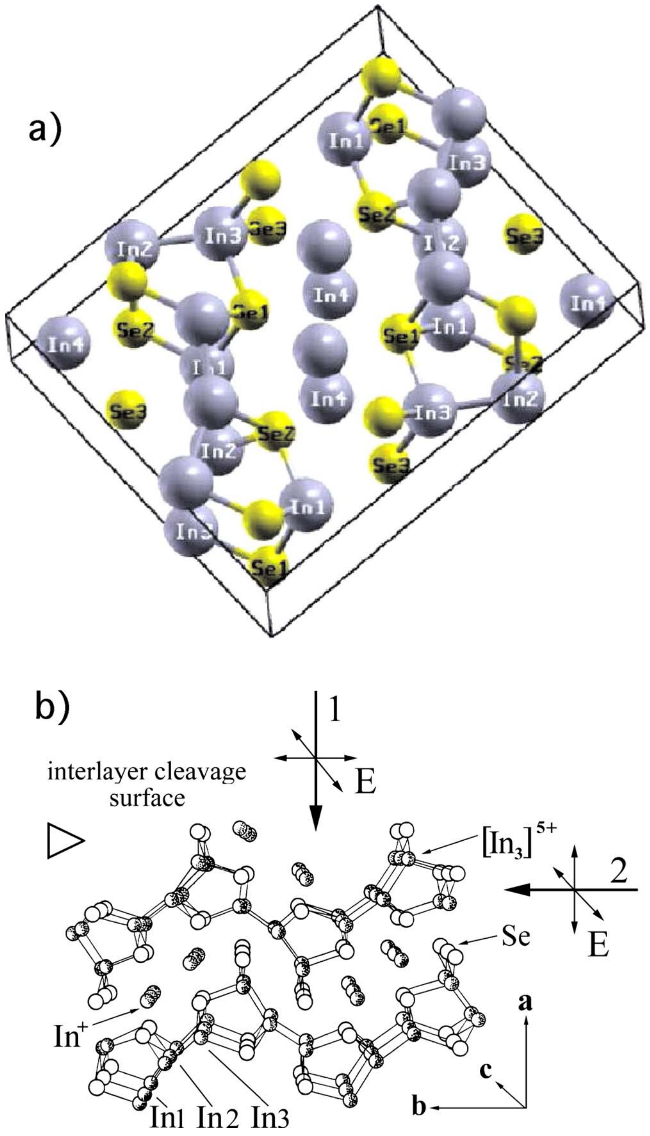

FIG. 1. (Color online) The schematic crystal structure for In_4Se_3 is presented top. The lattice constants of the crystal structure are $\boldsymbol{a}=15.296(1)$ Å, $\boldsymbol{b}=12.308(1)$ Å, $\boldsymbol{c}=4.0806(5)$ Å and space group P_{nnm} (Refs. 16–21) dominated by an $(In_3)^{5+}$ multivalent clusters bonded with selenium through ionic covalent bonds. The cleavage direction is indicated at the bottom by the triangle in the upper left.

ments were undertaken with a light incidence angle of 45° 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. For the band dispersion perpendicular to the chain direction, the dispersion was significantly smaller and the band mapping measurements were complemented by high resolution photoemission.

The high resolution photoemission studies were carried out on the 3m normal incidence beamline that consists of water cooled ellipsoidal entrance mirror with a 70 mrad acceptance angle of horizontal radiation from a dipole magnet at CAMD,[25] as described elsewhere.[26] This normal incidence monochromator is combined with an angle-resolved ultraviolet photoemission endstation, which consists of a magnetic field shielded UHV chamber with the electron energy analyzer (Scienta SES200 electron energy analyzer).[25] Both gas phase resolution tests and solid state sample show that the combined resolution (including beamline and analyzer) is 9 meV or less for the Fermi edge of gold films at the lowest possible temperature we have obtained using He I radiation. The measured Fermi edge broadening of gold films at about of 30 K appears to be less than 15 meV.[25]

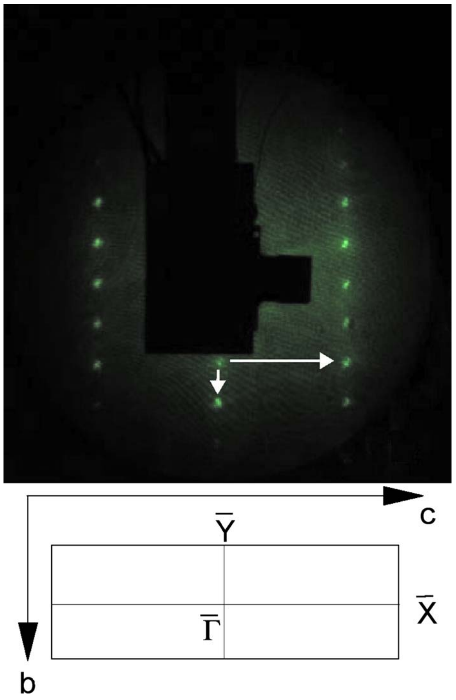

FIG. 2. (Color online) The LEED of the crystal structure for the $In_4Se_3(001)$ surface at room temperature. The electron beam energy for LEED is 76 eV. The corresponding surface BZ is shown at the bottom, adapted from Ref. 16.

III. COMPUTATIONAL DETAILS

We have performed full potential linearized augmented plane waves (FP-LAPW) calculations of In_4Se_3 within the density functional theory in the form implemented in the WIEN2k code.[27] As part of our treatment, we have used the so called generalized gradient approximation[28,29] in the formal parametrization scheme of Perdew–Burke–Ernzerhof.[30] Our calculations, briefly described in Refs. 16 and 21, were performed on the basis of structural information taken from Schwarz *et al.*[20] We have used 120 irreducible $\boldsymbol{k}$ points in the BZ for the self-consistent calculation, with a $R_{MT}K_{\max}$ product of 7. Here R_{MT} is the smallest of all atomic sphere radii and $K_{\max}$ is the plane-wave cutoff. The system has 28 (i.e., 7×4) atoms in the unit cell with seven crystallographically inequivalent sites (four indium and three selenium), each of which occupying four equivalent positions [see Fig. 1(a)]. In general, our results are comparable with prior calculations.[16,21,31]

A. Calculated bulk band structure and density of states

The electronic structure of In_4Se_3 can be understood as four main bundles of valence bands and one of conduction

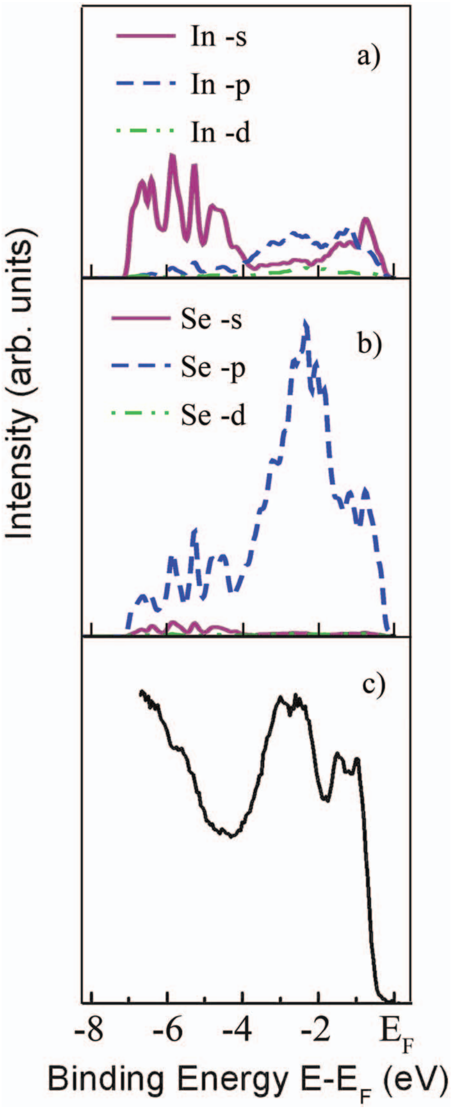

FIG. 3. (Color) The partial (a) In and (b) Se occupied DOSs are compared to the (c) photoemission. The photoemission spectra were taken with a combined instrumental resolution of 70 meV, at a photon energy of 15 eV, with a light incidence angle of 45° with respect to the surface normal and with the photoelectrons collected along the surface normal.

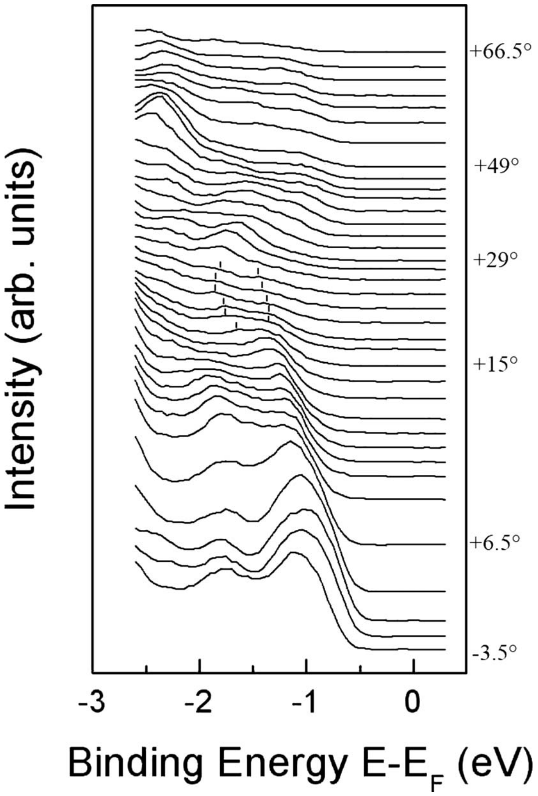

FIG. 4. Angle-resolved photoemission spectra taken at photon energy of 25 eV for $k_{\|}$ lying in the $\overline{\Gamma X}$ direction for In$_4$Se$_3$(001) at about 150 K. The separate weak bands in the region of the BZ edge are indicated above the spectra, adapted from Ref. 16.

bands (see Figs. 3–5). There is a flat isotropic band mostly due to the In *d* orbitals between −15.00 and −13.73 eV binding energies and a much more minor contribution of Se *s* states (see Fig. 4). This higher binding energy band between −15.00 and −13.73 eV binding energy has a fine structure of three peaks, the first of which is almost entirely due to In4 atoms (see Fig. 1 for the atomic number assignments) showing a rather low hybridization. This band is followed by a less "populated" band resulting from Se *s* but also from the In *d* orbitals (though with a less significant contribution) between −13.59 and −11.91 eV binding energies. 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. At the bottom of the valence, we find four noticeable peaks due to similar contributions from In *s* and Se *p* electrons. The valence band maximum is mostly formed by In *s* and Se *p*, while at −1.5 eV the band is more dominated by In *p*. The bands at −2.5 to −4.5 eV binding energy are dominated by the Se *p* and In *p* orbitals. As general observation, we note that crystallographically each of the nonequivalent Se atoms contribute an almost identical density of state (DOS) (see second panel of Fig. 5), while In atoms show some differences, especially In4 atoms with respect to the other In atoms. Our calculated density of occupied states, within the valence band region, is generally seen to be in good agreement with our photoemission data, as indicated in Fig. 6, as well as with the DOS indicated by STM spectroscopy, as described in Ref. 16.

The conduction band is mainly *p*-like (with both In and Se contributions). However there is a sharp peak in the DOS due to the 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.

B. The "chain" band structure

In spite of the fact that In$_4$Se$_3$(001) is clearly a semiconductor, the dispersion along the chains, for the bands near the valence band maximum, is quite significant, as noted previously.[16] Figure 7 illustrates the emission dependence of the angle resolved photoemission spectra along the chain direction. From the dispersion of the bands, evident in the photoemission spectra as a function of emission angle, we have been able to construct a band structure mapping along

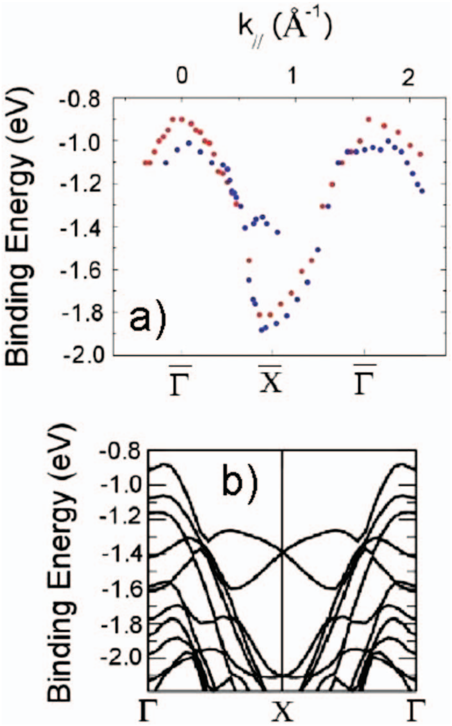

FIG. 5. (Color) (a) The experimental band structure along the $\overline{\Gamma X}$ chain direction has been plotted, with critical points and experimental wave vectors identified, measured at room temperature (red dots), and at 150 K (blue dots) using a photon energy of 25 eV. (b) The theoretical band structure along the chains is shown for comparison. The bands have been rigidly shifted to higher binding energies by about 0.84 eV, so as to theory more readily comparable with experiment, adapted from Ref. 16.

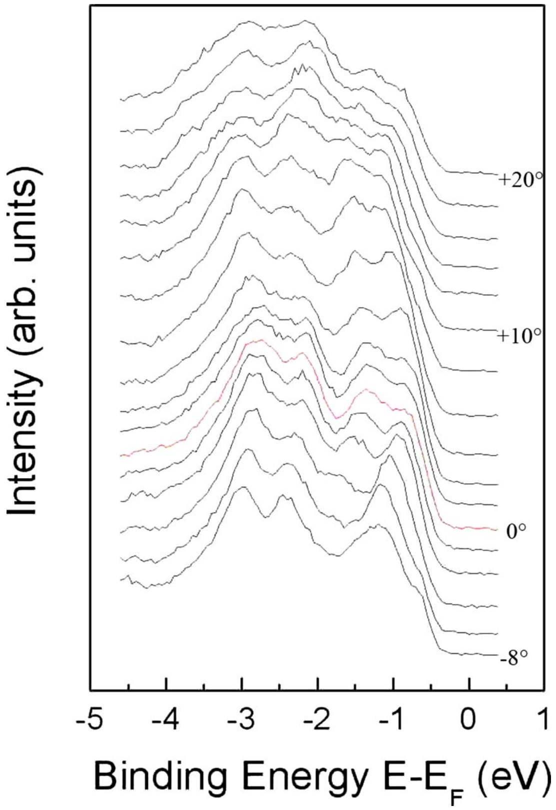

FIG. 6. (Color online) Angle-resolved photoemission spectra, taken at photon energy of 15.5 eV for $k_\parallel$ lying perpendicular to the chain direction, in the $\overline{\Gamma Y}$ direction for $In_4Se_3(001)$.

the $\overline{\Gamma X}$ line (along the surface chains) and $\overline{\Gamma Y}$ line (perpendicular to the surface chains but in the plane of the surface) using

$$k_\parallel = \left[\left(\frac{2m}{\hbar^2}\right)E_{\mathrm{kin}}\right]^{1/2}\sin(\theta), \qquad (1)$$

where θ is the emission angle of the photoelectron.[32,33] The resulting experimental band structure has been plotted in the inset of Fig. 8 along the chain direction. This band dispersion is somewhat photon energy dependent; some variations in the extent of the band dispersion along the surface chains (with photon energy) occur because the 2D of state is not conserved in this otherwise largely layered system.[21] There exist interactions between layers sufficient to support a bulk band structure,[21] and this is a complication that cannot be strictly ignored.

The band dispersion of about 0.4 eV along the chains, for the In *s*, In *p*, and Se *p* band at the valence band maximum is largely in agreement with our theoretical expectations,[16] as seen in Fig. 8. The main bands near the Fermi level, however, have band dispersion of about 1 eV, indicative of a significant band width. The two theoretical bands crossing the "valley" about $\overline{X}$ [Fig. 8(b), in the region of the BZ edge] are weak in intensity in the experimental data, but many basic features of the calculation are found in the experimental band structure.[16] Even with the smaller band dispersion of about 0.5 eV (from theory) to 0.4 eV (experiment), it is clear that a strongly hybridized indium chain can provide considerable band dispersion even if the system is semiconducting and not metallic.[16] In the region of $\bar{\Gamma}$, the experimental downward dispersion of the band at the top of the valence band suggests an effective mass of roughly −2.3 that of the electron mass.

Perpendicular to the chain direction there is also dispersion, but the band width is rather less significant. According

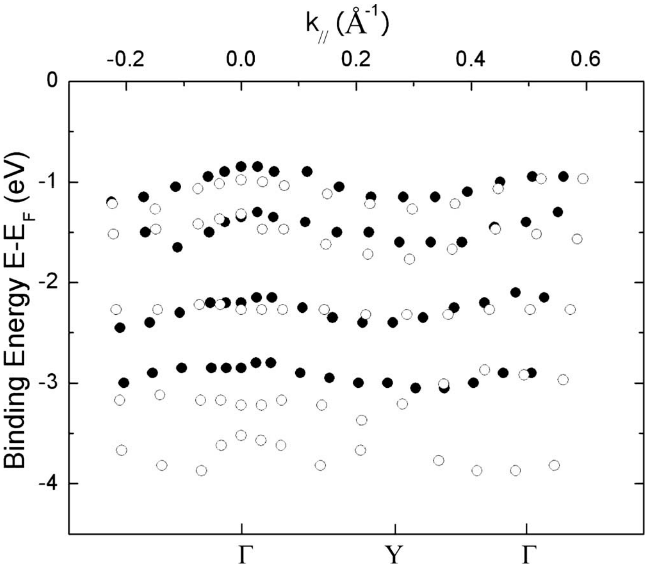

FIG. 7. The experimental band structure perpendicular to the chain direction, but in the plane of the surface ($\overline{\Gamma Y}$), has been plotted with critical points and experimental wave vectors identified, measured at two photon energies of 15.5 (filled dots) and 23 eV (open dots).

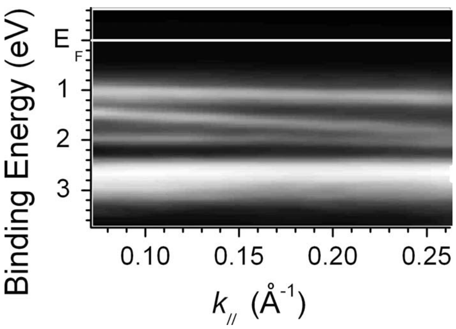

FIG. 8. The 2D image of surface state band dispersion of $\mathrm{In_4Se_3}$(001) taken with a photon energy of 16 eV perpendicular to the chain direction but in the plane of the surface ($\overline{\Gamma Y}$).

to our band structure calculations (Fig. 3, the band dispersion is of 0.32 eV along the $\overline{\Gamma Y}$ line in the BZ (to be compared with the 1.25 eV band width in the directions of the chains, as seen in Fig. 8). In the more conventional angle-resolved photoemission, the wave vector dependence of the bands is more difficult to discern (Figs. 9 and 10). In high resolution photoemission, the band dispersion is far more evident, as seen in Fig. 11. Yet in both theory and experiment, there is some band dispersion; in experiment, for bands near the valence band maximum and perpendicular to the chain direction, this amounts to some 0.4 eV, very close to our theoretical expectations of 0.32 eV. In the region of $\bar{\Gamma}$, the experimental downward dispersion of the band just below the top of the valence band suggests an effective mass of roughly -0.4 that of the electron mass, while the band at the top of the valance band is -1.2 to -1.3 that of the electron mass.

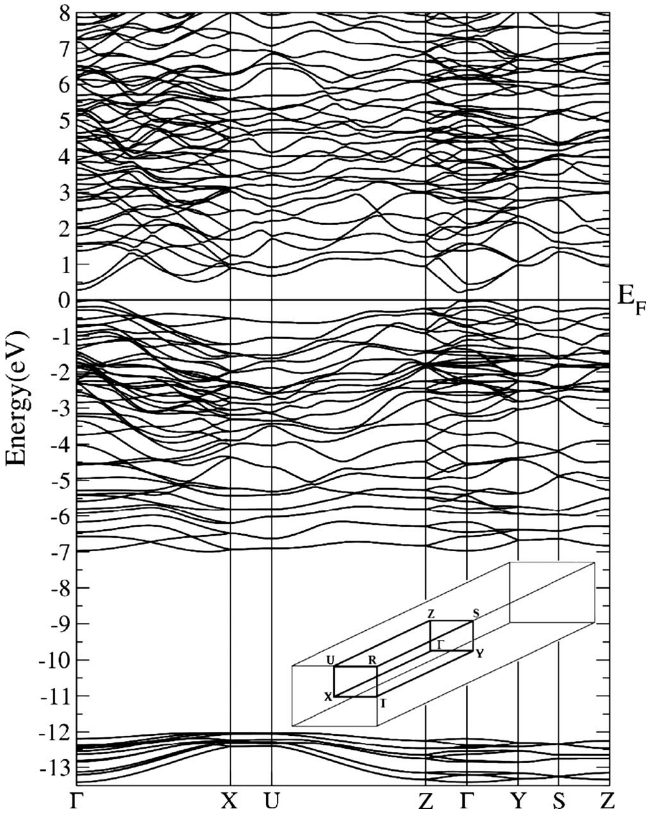

FIG. 9. Band structure of bulk $\mathrm{In_4Se_3}$ in a wide energy range along high symmetry lines of the BZ.

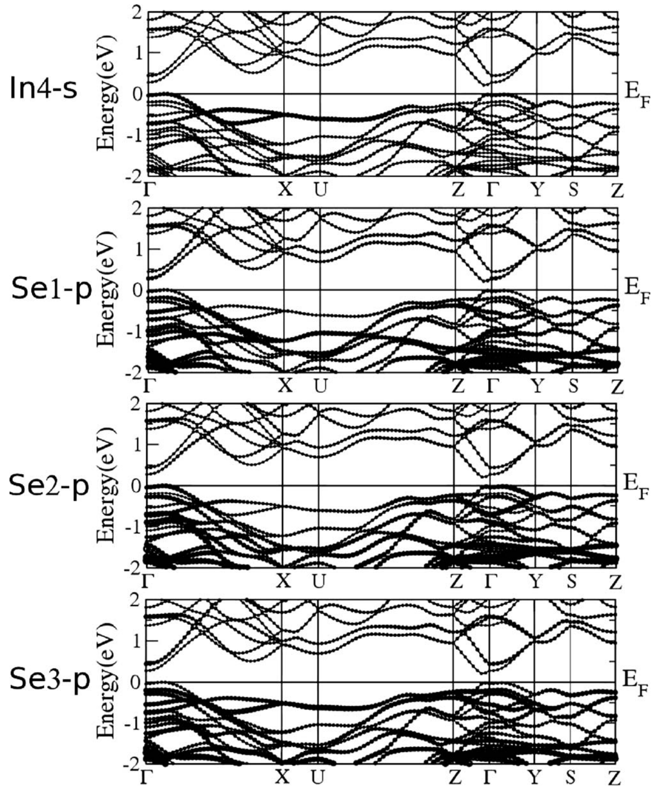

FIG. 10. Element-resolved orbital-weighted bands near the gap; we show only the main contributors to the definition of the top of the valence band: In 4*s* and Se (1, 2, and 3)-*p*.

In order to thoroughly study the origin of the states revealed by our photoemission experiments and to assess in detail the system's anisotropy near the energy gap, we performed atom-resolved orbital-weighted band calculations. These calculations gave us further understanding of what the DOS had already yielded, i.e., that the top of the valence band is dominated by Se *p* and In 4*s* states. In Fig. 5, "character" bands for In 4*s*, Se 1*p*, Se 2*p*, and Se 3*p* are plotted between -2 and 2 eV (following the atomic site labeling scheme of Fig. 1); filled dots indicate a relatively higher contribution from the corresponding atom-orbital states (the higher the contribution, the bigger the dots). It can be seen that the bands crossing the "valley" are mainly due to In 4*s* and Se 3*p*, while Se 1*p* and Se 2*p* make a smaller contribution (again following the atomic site labeling scheme of Fig. 1). In the direction perpendicular to the chain (on the surface) and perpendicular to the surface ($\overline{\Gamma Y}$ and ΓZ, respectively), the dispersion of the top of the valence band is less significant than that in the direction of the chain $\overline{\Gamma X}$, as mentioned above, and is mostly due to Se 2*p* and In 4*s*.

The distance from the center of one surface BZ (the $\bar{\Gamma}$ point) to the next is some 1.60 ± 0.05 Å^{-1} along the chain direction, while the zone edge occurs at 0.81 ± 0.05 Å^{-1}. This suggests a lattice constant of 3.92 ± 0.1 Å, or about the expected lattice constant of 4.08 Å along the chain direction, as determined from x-ray diffraction and LEED. The band dispersion perpendicular to the chains, in the plane of the

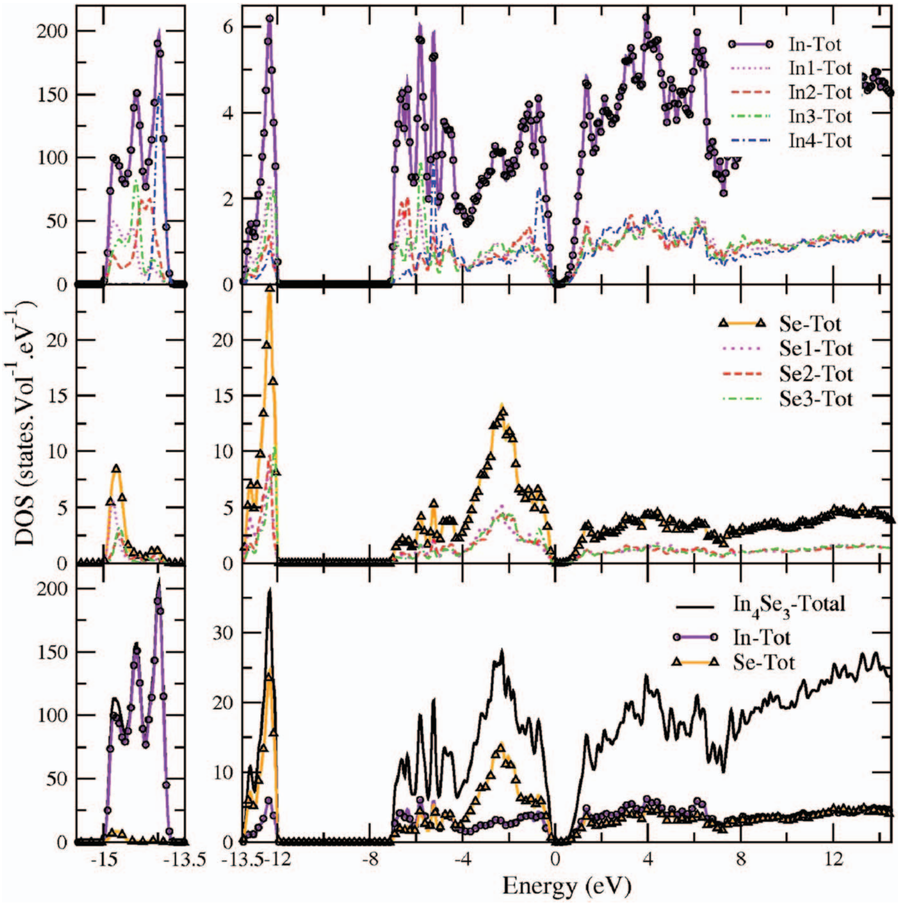

FIG. 11. (Color) Element-resolved calculated densities of states.

surface, is much smaller as is the distance to the next BZ center; a value of 0.51 ± 0.2 Å^{-1} can be determined from the critical points of the experimental band structure corresponding to a representative of a lattice constant of 12.2 ± 0.1 Å, or about the expected lattice constant of 12.31 Å, again determined from x-ray diffraction and LEED.

C. A possible surface state

In Fig. 11, we find evidence of a very weakly dispersing band at about 1 eV binding energy perpendicular to the chains but in the plane of the surface. Toward the BZ edge at about 0.255 Å^{-1}, this band falls into a gap of the projected bulk band structure (Fig. 3). As such this band toward the valence band maximum may be a surface state. As yet, we have not yet tested this state for conservation of 2D of state or tested the surface character of this band by adsorption. As such, assignment of this state as a surface state remains somewhat speculative. As indicated above, the dispersion of this band with wave vector suggests a band three times greater (negative) mass than the distinct bulk band at slightly greater binding energy (1.4 ± 0.1 eV binding energy). This heavier negative effective mass is also consistent with a surface state or resonance.

As discussed in detail elsewhere,[21] from the dispersion of the bands, evident in the photoemission spectra as a function of photon energy, In$_4$Se$_3$(001) has a bulk band structure mapping along the ΓZ line (along the surface normal). The 2D of state is clearly not conserved; there must therefore exist interactions between layers sufficient to support a bulk band structure. Thus identification of true surface states does hold some importance here as otherwise the states cannot be assumed to be two-dimensional.

IV. SUMMARY

The downward dispersion (toward greater binding energy) of the band at the valence band maximum, away from the Γ point, can be understood as this band is dominated by In s and Se p_y, while the band at −1.5 eV binding energy has strong $p_y p_x$ components. In any case the band widths (the extent of the dispersion) of 300–400 meV perpendicular to the chain direction or 1.25 eV along the chain direction, for bands within the valence region, are in line with the expectations from the calculated band structure. The effective mass of the bands at the valence band maximum is negative in both symmetry directions. The dispersion along the chains suggests a hole mass about 5.5 times greater than perpendicular to the chains, but the dispersion perpendicular to the chains is more difficult to discern because of the smaller distance to the BZ edge and the close proximity of a possible surface state or surface resonance.

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