PHYSICAL REVIEW B VOLUME 35, NUMBER 2 15 JANUARY 1987-I

Electronic structure of the "chain" chalcogenide $TlInSe_2$

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(Received 18 August 1986)

We used synchrotron-radiation photoemission to study the valence band of $TlInSe_2$, a prototype crystal in the family of "chain" layered materials. The observed electronic structure was interpreted in terms of the inequivalent sites for the two cations by comparison with the analogous single-cation binary compounds TlSe and InSe. Measurements on germanium-covered $TlInSe_2$ were used to establish the position of the band structure of the material on an absolute scale.

I. INTRODUCTION

We investigated the electronic structure of $TlInSe_2$ with synchrotron-radiation photoemission spectroscopy. This experiment extends electronic structure studies of layered compounds[1] to a very interesting and largely unexplored class of "chain" ternary crystals.[2] The results were analyzed in terms of the two different cation coordinations in this class of materials.[2] They indicate that previous interpretations of the photoemission spectra of related binary chalcogenides should be revised.[3] We also extended to this material our systematic measurement of the absolute valence-band-edge positions in semiconductors.[4] This was derived from photoemission spectra taken after covering the materials with thin Ge overlayers.[4]

For many years, the properties of layered crystals have constituted a major research area in solid-state physics. In particular, photoemission spectroscopy with synchrotron radiation has been used extensively to study the electronic structure of different families of layered compounds.[2] Conversely, layered crystals were used to test some of the most advanced techniques in modern photoemission.[2] Until now, this approach was not applied to the chain binary and ternary chalcogenides containing thallium.[1] In fact, very little is known about the electronic structure of these materials. This is in sharp contrast with the extensive experiments dedicated to other physical properties.[5-10] The interest in these materials is stimulated not only by their fundamental properties, but also by possible practical applications.[5-10]

$TlInSe_2$ is the most widely investigated ternary material in this class. The chain character of its structure derives from the presence of two inequivalent cation sites.[1] This is evident from Fig. 1, where we view the crystal structure from the [001] direction. Notice the different coordination of the anions around the In and Tl sites, emphasized by the shadowed areas. In is in a tetrahedral site, while Tl is in an octahedral site. The In atoms and the surrounding Se atoms form strongly bonded, covalent chains along the [001] direction. These chains are held together by weaker ionic bonds through the octahedrally coordinated

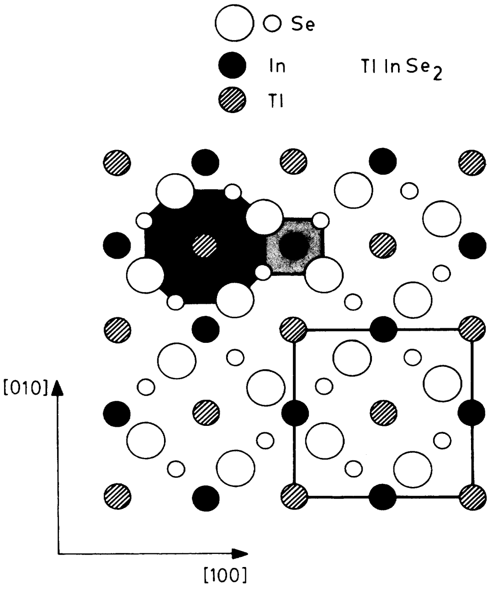

FIG. 1. View of the crystal structure of $TlInSe_2$ from the [001] direction. The structure is tetragonal, and its space group is D_{4h}^{18} (*I4/mcm*). The square at the lower right of the figure shows the projection of the unit cell. Three planes of atoms are visible. Their distances from the top plane, relative to the magnitude of the *c* lattice vector, are as follows: 0 for the top Se plane, $-\frac{1}{4}$ for the cation plane, and $-\frac{1}{2}$ for the next Se plane. A second cation plane at a distance $-\frac{3}{4}$ has atoms in the same positions as those of the cation plane at $-\frac{1}{4}$, and therefore is concealed in the figure. Likewise, the next Se plane at -1 is concealed by the top Se plane. The structure of $TlInSe_2$ is analogous to that of the binary compound TlSe, with In atoms substituting for half of the Tl atoms. In TlSe, the cations are in two inequivalent sites, corresponding to the sites emphasized by shadowing in this figure. Notice the coordination of anions around each site, i.e., tetrahedral in one case and octahedral in the other. It is commonly assumed that in $TlInSe_2$ all In atoms are in tetrahedral sites, and all Tl atoms are in octahedral sites, as shown here.

Tl atoms. This gives a natural (110) cleavage plane.

As for other layered compounds, the electronic properties of $TlInSe_2$ are strongly influenced by its nearly molecular character. The compound can be written[11] as $Tl^{1+}(In^{3+}Se_2^{2-})$. This emphasizes that the crystal contains chains of trivalent indium covalently bound to selenium, which in turn are ionically bound to monovalent thallium. The corresponding TlSe formula $Tl^{1+}(Tl^{3+}Se_2^{2-})$ contains both monovalent and trivalent thallium.

One certainly expects this dual role of thallium to influence the electronic structure of TlSe. In fact, Porte and Tranquard[3] interpreted features of their TlSe photoemission spectra as due to the atomic orbitals of Tl atoms in the two inequivalent sites. The interpretation of our $TlInSe_2$ spectra agrees with this general philosophy. However, our findings suggest that changes are necessary in the detailed assignment of spectral features to tetrahedral and octahedral Tl in Ref. 3, or, alternatively, that a fraction of the In atoms in $InTlSe_2$ are in octahedral sites.

II. CRYSTAL PREPARATION AND EXPERIMENTAL PROCEDURE

$TlInSe_2$ single crystals were grown from the melt by the Bridgman-Stockbauer technique. The silica glass crucible with a tip at the bottom was cleaned and degassed by the usual procedure. A carbon liner was deposited by benzol or penthane pyrolysis at 1000 °C and the elements were introduced in the crucible in stoichiometric ratio. The whole ampul was heated in a temperature gradient so that selenium condensed at the cold end and slowly reacted with the heated metals at the hot end.

The growth itself was achieved in a zone furnace. The crucible was lowered from the hot side at 850 to the cold side at 400 °C at a speed of 0.15 mm/h. In order to avoid the formation of holes in the crystal, 100-Torr argon was added before sealing the reaction crucible. In the cold zone, the crystal was cooled down slowly within a couple of days. A boule has been obtained consisting of a few large single crystalline pieces from which the investigated samples were cleaved off.

In the present experiment, $TlInSe_2$ was cleaved *in situ* under ultrahigh vacuum conditions, at a pressure $<1\times10^{-9}$ Torr. Like other layered crystals, cleaved $TlInSe_2$ has limited chemical reactivity.[2] The working pressure was sufficient to keep the sample free of detectable contamination for the duration of the experiment. Photoemission spectra of the clean surface were taken with a double-pass cylindrical mirror electron energy analyzer. The photons were emitted by the storage ring Tantalus I of the University of Wisconsin Synchrotron Radiation Center (SRC) at Stoughton, and filtered in energy by an aluminum Seya-Namioka monochromator.

After completing the study of the clean surface, we performed experiments on Ge overlayers deposited *in situ* on $TlInSe_2$. These experiments had the purpose of measuring the relative position of the valence-band edges of $TlInSe_2$ and Ge. Ge was deposited by evaporation from a tungsten basket. The equivalent thickness of the overlayer was estimated with a quartz crystal oscillator. Valence-band and core-level photoemission spectra were taken for different overlayer thicknesses, ranging up to 40 Å.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The bottom solid curve in Fig. 2 shows the valence-band photoemission spectrum of $TlInSe_2$ taken with a photon energy $h\nu=18$ eV. In analyzing the data, we could not rely on theoretical calculations of the electronic structure. Only one such calculation has been performed for $TlInSe_2$, with pseudopotential techniques.[12] The results were used to interpret optical data.[13] However, they provide no indication on the nature of peaks in the local density of states.

Much more helpful in analyzing the data were previous photoemission data. These included spectra of TlSe, InSe, and ionic Tl compounds such as TlCl and TlBr.[3,14] The middle (solid) curve and the top (dashed) curve of Fig. 2 shows the photoemission spectra of TlSe and of InSe, from Refs. 3 and 14. The TlSe curve was aligned with the bottom spectrum so as to have their main peaks in the same position. This peak is 1.4 eV below the top of the $TlInSe_2$ valence band E_v, which sets the zero of the energy scale for all the spectra in this article. The nature of the peak is easily identified (see Ref. 3), and it corresponds primarily to Se $4p$ states.

Both spectra in Fig. 2 exhibit a second structure at larger binding energies, 5—7 eV below E_v. However, its position is different for TlSe and for $TlInSe_2$. This structure is primarily due to Tl $6s$ states. We have seen that

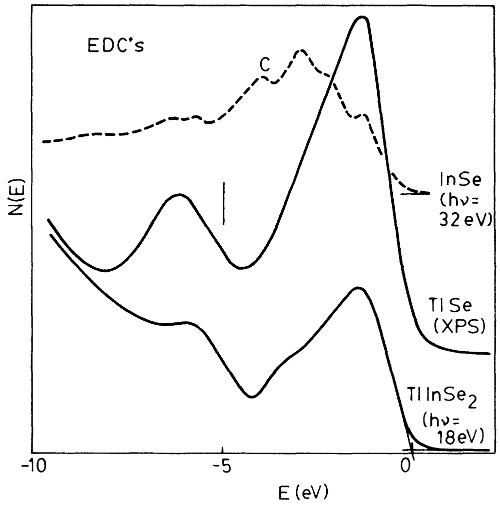

FIG. 2. Bottom solid line: photoelectron energy distribution curve (EDC) of $TlInSe_2$, taken with a photon energy of 18 eV. Middle curve: x-ray photoemission (XPS) EDC of TlSe from Ref. 3, taken with Al $K\alpha$ photons. The vertical line indicates the position of a weak feature in the TlSe spectrum, as discussed in the text. Dashed line: EDC of InSe, taken with photon energy of 32 eV (Ref. 14). The letter C labels one of the features of this spectrum. The horizontal scale for this and for all other spectra in this article is referred to the top of the clean $TlInSe_2$ valence band E_v.

there are two inequivalent cation sites in TlSe, which actually correspond to two different cationic species for $TlInSe_2$. Does this affect the cation s structure in the spectra? According to Porte and Tranquard's analysis,[3] it does.

Specifically, they observe a weak component representative of this fact, approximately 1.2 eV above the Tl 6s peak. This weak feature is not readily visible in Fig. 2, and it was identified in Ref. 3 by comparing spectra taken for TlSe and TlS. Its position is marked in the figure by a vertical line. Porte and Tranquard[3] identify the weak feature with tetrahedrally coordinated Tl, and the main cation s peak with octahedrally coordinated Tl. They arrive at this conclusion by comparing the TlS and TlSe spectra with those of the strongly ionic Tl compounds TlCl and TlBr. After aligning the Tl 5d peaks, they find that the cation s peak of TlBr or TlCl is in the same position as the main cation s peak of TlSe or TlS.

Our present data, however, cast doubts on this interpretation. If we assume that all In atoms in $TlInSe_2$ are in tetrahedral sites, then the tetrahedral-Tl component of the cation s feature should disappear on going from the TlSe spectrum to the ternary spectrum. On the contrary, we see that the position of the Tl 6s peak for $TlInSe_2$ is closer to the weak TlSe feature than to the main Tl 6s peak. This suggests that the interpretation of the TlSe cation s feature in terms of octahedral and tetrahedral coordinations should be inverted.

There is, however, an alternate possible interpretation of the data of Fig. 2. We can see that the peak of the Tl 6s feature for $TlInSe_2$ does not exactly coincide with either the peak or the weak structure of the cation s feature of TlSe—but it has an intermediate position. This could be interpreted as evidence that both octahedral and tetrahedral Tl atoms are present in $TlInSe_2$. This does not imply that Tl and In atoms are evenly distributed among sites of different coordination. Even if a fraction of the indium atoms are in a trivalent position, it is likely that most of them occupy tetrahedral sites. In fact, the 5s^2 shells of indium are less stable than the 6s^2 shells of thallium. Thus, Tl is more likely than In to be in a univalent state.[5]

Conversely, most (if not all) of the In atoms are covalently bound. Thus, their hybridized orbitals should contribute to the valence-band photoemission spectra. We see in Fig. 2 a feature 3.5 eV below E_v for $TlInSe_2$, which is not present for TlSe. On the other hand, a similar feature is present in the InSe photoemission spectra, peak C in Fig. 2 and in Ref. 14. That feature is due to hybridized p_x, p_y states related to In—Se bonds. Thus, we tentatively interpret the −3.5-eV feature of $TlInSe_2$ as due to hybridized In and Se orbitals.

The bottom spectrum of Fig. 3 shows the Tl 5d and In 4d core-level peaks of clean $TlInSe_2$, at a photon energy of 29 eV. The peak positions are −12.15, −14.4 eV for Tl 5d and −16.7, −17.5 eV for In 4d. For comparison,[3] the Tl 5d positions for TlSe are −12.9, −15.1 eV. The discrepancy with respect to the position in $TlInSe_2$ is in qualitative agreement with the replacement of trivalent Tl with trivalent In. A quantitative interpretation is made impossible by the strong covalent component of the bonds involving trivalent Tl in TlSe. The In 4d level positions in $TlInSe_2$ are close to those[14] in InSe, −16.9 and −17.7 eV. This is further evidence that most In atoms in $TlInSe_2$ are involved in the formation of covalent bonds with Se, like indium in InSe.

Following a procedure described in Ref. 4, we deposited Ge on $TlInSe_2$ to measure the position in energy of its valence-band structure in an absolute scale. The scale is conventionally referred to the top of the valence band of Ge, E_v^{Ge}. In particular, we estimated the position in the absolute scale of the top of the $TlInSe_2$ valence-band edge E_v. This information is important, for example, in predicting in first approximation the valence-band discontinuities at interfaces between two semiconductors. This problem is discussed in detail in Ref. 4.

The position of E_v with respect to E_v^{Ge} was determined from the photoemission spectra taken on Ge-covered $TlInSe_2$ for different nominal overlayer thicknesses—see

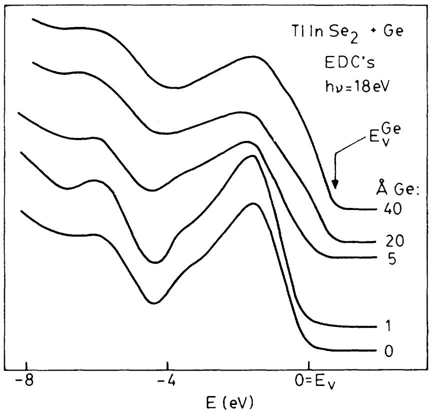

FIG. 3. Core-level EDC's taken at a photon energy of 29 eV on clean $TlInSe_2$ (bottom curve) and on Ge-covered $TlInSe_2$. The nominal thickness of the Ge overlayer is shown at the right-hand side of each curve. The spectra include contributions from the In 4d and Tl 5d core levels.

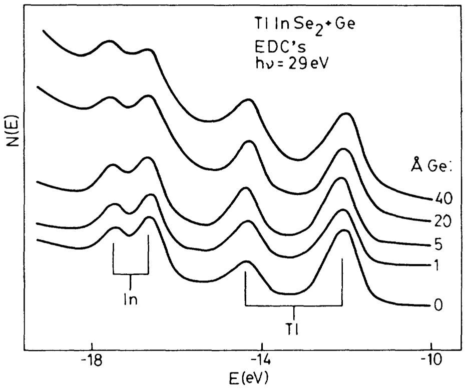

FIG. 4. Valence-band EDC's taken on clean and Ge-covered TlInSe.$_2$. The leading spectral edge for thick Ge coverage corresponds to the Ge valence-band edge E_v^{Ge}.

Fig. 4. As the overlayer becomes thicker, the leading spectral edge moves to lower binding energies. This is due to the formation of Ge valence-band states overlapping the lower portion of the $TlInSe_2$ valence band. For thick coverages, the leading spectral edge corresponds to the Ge valence-band edge E_v^{Ge}.

We see from Fig. 4 that the difference in energy between the *initial* position of the $TlInSe_2$ valence-band edge and E_v^{Ge} is 0.9 eV. This does *not* directly give the position of the $TlInSe_2$ valence-band edge with respect to E_v^{Ge}. One must, in fact, take into account the overlayer-induced change of the substrate band bending.[4] This was estimated by comparing the core-level peaks of clean and Ge-covered $TlInSe_2$—see Fig. 3.

We see that both the In 4*d* and Tl 5*d* peaks exhibit a small, common shift on going from clean $TlInSe_2$ to a thick Ge overlayer. The behavior of these peaks is similar to that observed for valence-band features at low Ge coverages. This indicates that the cation *d* levels are not affected by overlayer-induced chemical shift changes—and therefore that their spectral shifts track the changes in band bending. A similar conclusion has been reached for almost all the semiconductor-semiconductor interfaces investigated with this technique.[4]

The total Ge-induced shift deduced from Fig. 3 is approximately 0.05 eV towards lower binding energy. With this band-bending correction, we deduce a valence-band discontinuity $\Delta E_v = 0.9 - 0.05 = 0.85$ eV. This also corresponds to the position of the $TlInSe_2$ edge in the absolute scale.

Since the forbidden gap of $TlInSe_2$ has a width of 1.1 eV and the gap of Ge is 0.67 eV, the above value of ΔE_v is larger than the magnitude of the gap difference between the two semiconductors. This means that the conduction-band discontinuity for the $TlInSe_2$-Ge interface has a negative value, approximately -0.4 eV. This interface, therefore, provides one of the rare examples of "staggered-gap" band lineup.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (NSF), under Grant No. DMR-84-21292. The Synchrotron Radiation Center (SRC), Stoughton, of the University of Wisconsin—Madison is also supported by the NSF, under Grant No. DMR-86-01349.

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