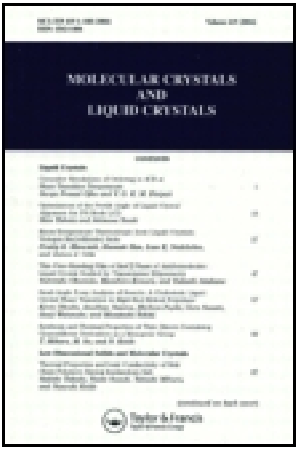

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Electronic Structure of $TiSe_2$ and $TiSe_2$ Intercalated with Eu

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Electronic Structure of $TiSe_2$ and $TiSe_2$ Intercalated with Eu

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We report on a PE study of the electronic structure of pristine $TiSe_2$. The experimental data are compared with results of band-structure calculations. It is confirmed that $TiSe_2$ reveals semimetallic properties. For the first time rare-earth metals were attempted to be incorporated *in situ* into $TiSe_2$. It is found that divalent Eu can be easy intercalated, whereas deposition of trivalent Gd leads to strong interfacial reactions. The electronic structure of the Eu-intercalation compound cannot be simply described within a rigid-band approach assuming charge transfer from Eu to unoccupied Ti *d* states. In a more elaborated approach hybridization phenomena have to be taken into consideration.

Keywords: photoemission; intercalation and rare-earth compounds

There has currently been considerable interest to transition-metal dichalcogenides (TMDC's) and their intercalation compounds (IC's) [1,2]. TMDC's consist of covalently bound sandwiches of the type DC-TM-DC, which are combined together by only weak van der Waals interaction. These quasi-two dimensional (2D) compounds serve as model systems to study the electronic structure of low-dimensional solids, transitions from 3D to 2D properties of electron states, and low-energy collective excitations like charge-density waves, which were observed in a number of TMDC's (TaS_2, $TaSe_2$, $TiSe_2$, $NbSe_2$) [2,3]. Detailed studies of the electronic structure of some TMDC's (e.g., dichalcogenides of Ti exploited as intercalation batteries and solar cells) lead, however, to inconsistent results. While $TiTe_2$ was shown to be a semimetal, TiS_2 is assumed to be an intrinsic semiconductor [4]. For $TiSe_2$ some band structure calculations conclude metallic behavior with a considerable overlap between Ti *d* and Se *p* orbitals, while other calculations tend to prove a narrow-gap semiconducting behavior. Photoemission (PE) results have been interpreted as indicating either semimetallic [4] or semiconducting properties [5].

TMDC's are known to intercalate species into the van der Waals gap [1]. Apart from conceivable applications as anisotropic conductors or highly ordered magnetic systems, the obtained IC's are of high importance to study basic phenomena relating to, e.g., an interplay between ionic and covalent chemical bondings upon intercalation. Quasi-2D structures can be tentatively used as rigid matrixes to fix guest atoms at certain distances from each other in order to follow a transition from bandlike to localized properties of their electronic states that is in particularly relevant for 4*f* and 5*f* elements [6]. The intercalation may be carried out by exposing the samples at elevated temperatures to metal vapors in closed ampoules. Spontanious intercalation of alkalies takes place if the species are deposited on top of TMDC's in UHV conditions [7].

We report on a PE study of the electronic structure of $TiSe_2$. The data are compared with results of a full-potential nonorthogonal local-orbital minimum-basis band-structure calculations [8]. It is confirmed that $TiSe_2$ reveals semimetallic properties with electronic bands crossing the Fermi level (E_F) at the $\overline{\Gamma}$ and $\overline{M}$ points in the Brillouin zone (BZ). For the first time rare-earth's (RE's) were attempted to be incorporated *in situ* into $TiSe_2$. It is found that similar to alkalies divalent Eu can be easy intercalated into the TMDC, whereas deposition of trivalent Gd leads to a strong interfacial reaction between Gd and Se. The electronic structure of the Eu-IC cannot be interpreted simply in terms of a rigid-band approach assuming charge transfer from Eu to Ti *d* states. In a more elaborated model hybridization effects have to be taken into account.

The measurements were performed at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSYI) using radiation from the TGM4 and SX/700 II beamlines. Valence-band and core-level PE spectra were taken with a hemispherical electron energy analyzer (ARIES-VSW) tuned to an energy resolution of 150 meV and an angle resolution of 1°. Similar to our studies of RE-graphite IC's [6,9], for the *in-situ* intercalation of Eu and Gd a method of thermal deposition of thick layers of intercalant (100 Å) onto the TMDC surface followed by a step-by-step annealing was exploited. In both cases the deposition at room temperature resulted in nonordered interfaces. Several stages of annealing (up to 700°C) of the systems led in case of Eu/$TiSe_2$ to a recovering of a crystalline structure with a sharp TMDC-like hexagonal LEED pattern.

Energy distribution curves (EDC's) taken along the $\overline{\Gamma}$ - $\overline{K}$ direction in the

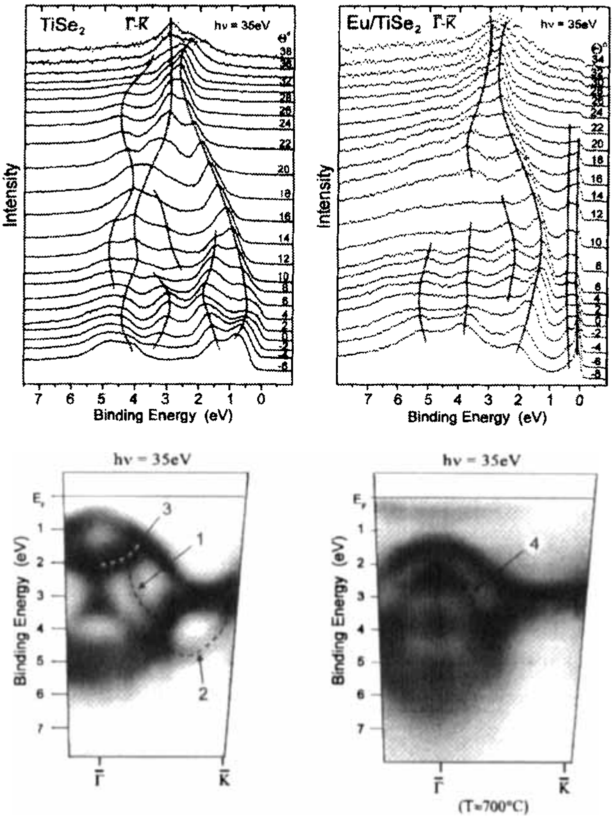

FIGURE 1 PE response of $TiSe_2$ and Eu-IC in form of EDC's and 2D plots visualizing intensity along the $\overline{\Gamma}$ - $\overline{K}$ direction.

surface BZ of $TiSe_2$ are shown in Fig. 1. The experimental data measured along this and other high symmetry directions are compared with the calculated bulk band structure projected onto the surface of the TMDC (Fig. 2). We emphasize a good correspondence between experimental and theoretical results particularly in the region of the $\bar{K}$ and $\bar{M}$ points, where both measured and theoretical bands reveal predominantly 2D behavior. In the region of the $\bar{\Gamma}$ point electronic bands are found to be clearly three dimensional. There are only two places in the BZ: the $\bar{\Gamma}$ and $\bar{M}$ points, with nonzero density of states at E_F. In both cases the semimetallic properties arise from hybridization between Se 4*p* [highly dispersive upper valence bands (VB's)] and Ti 3*d* (flat bands

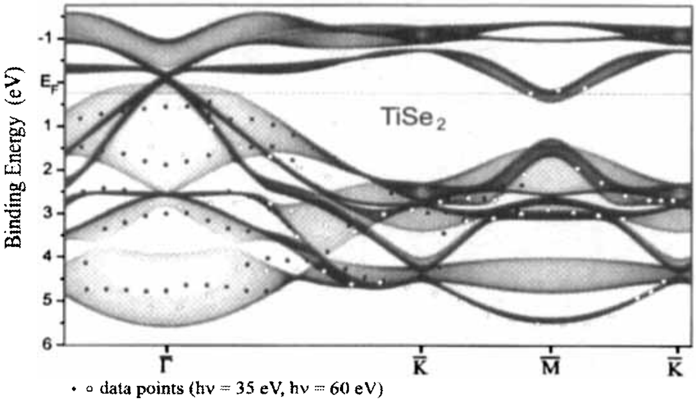

FIGURE 2 Projected band structure (calculated E_F is marked by a light horizontal line) in comparison to the experiment data points.

at the conduction band bottom) orbitals originating from neighboring layers.

EDC's measured from the Eu/$TiSe_2$ system after annealing at 700°C are shown in the right top panel of Fig. 1. At first glance the two sets of PE spectra in Fig. 1 replicate each other with the main difference that the EDC's presented in the right panel are shifted in average by about 0.8 eV toward higher binding energies (BE's) as expected for intercalated TMDC [10]. Additional structures appearing at E_F at any angle of analyzing can be assigned to the flat Ti $3d_{z^2}$ band, which is filled in the IC due to a charge transfer from Eu atoms.

A simple rigid-band model, however, is not appropriate for the Eu-IC. As seen from the 2D representations visualizing the PE intensities of $TiSe_2$ and the IC along the $\bar{\Gamma}$-$\bar{K}$ direction in the surface BZ of $TiSe_2$ (Fig. 1) there are a number of $TiSe_2$ bands (marked by numbers), which have no clear counterparts in the Eu-IC and *vise versa*. The latter points to a change of chemical interaction in the IC caused by hybridization between chemically active 5*d* states of Eu and 4*p* states of Se. Chemical interactions are not that dramatic for the divalent RE with only slight admixture of the *d* character to the VB as may be concluded from the Se 3*d* core-level spectrum that do not show chemical shifts upon intercalation [Fig. 3(a)]. The difference in the PE branching ratio for the two spectra measured for $TiSe_2$ and Eu-IC can be explained by an in-

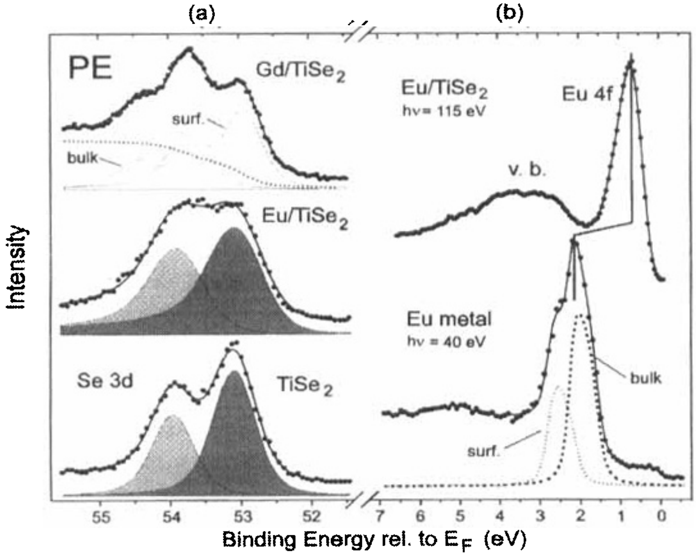

FIGURE 3 (a) Se 3*d* PE spectra. Shadowed subspectra simulate contributions from $3d_{3/2}$ (left) and $3d_{5/2}$ (right) components; (b) Eu 4*f* PE spectra.

crease of line asymmetry due to electron-hole excitations in the metallic compound. A least-squares fit of the data applying Doniach - Sunjic line-shapes [11] with different asymmetry parameters shows that both BE and branching ratio of the Se 3*d* emission are not changed in the compound.

Much stronger chemical interactions were observed upon deposition of trivalent Gd onto $TiSe_2$ followed by annealing at 700°C. As seen in Fig. 3(a) in contrast to the Eu/$TiSe_2$ system the Se 3*d* spectrum of the Gd compound reveals a triplet structure, which can be simulated [12] assuming two components assigned to bulk and surface contributions from Gd selenide. The chemical interaction destroys the $TiSe_2$ matrix resulting in a nonordered interface as it is also concluded from the LEED experiment.

As follows from analysis of the 4*f* PE spectra [Fig. 3(b)], Eu remains divalent in the IC. A shift of the 4*f* signal toward E_F in the IC as compared to its position in Eu metal, which is similar to that observed in Eu-graphite IC [9], can be understood by the increase of the cohesive energy upon intercalation.

Acknowledgments

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