Journal of Electron Spectroscopy and Related Phenomena 189S (2013) 35–39

Contents lists available at ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

journal homepage: www.elsevier.com/locate/elspec

Spin orbit splitting in the valence bands of ZrS_xSe_{2-x}: Angle resolved photoemission and density functional theory

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ARTICLE INFO

Article history:
Available online 14 January 2013

Keywords:
Growth from vapour
Semiconductor compounds
Angle-resolved photoemission spectroscopy
Synchrotron radiation
Band structure
Density functional theory

ABSTRACT

Angle-resolved photoelectron spectroscopy using synchrotron radiation has been performed on 1*T*–ZrS_xSe_{2-x}, where x varies from 0 to 2, in order to study the influence of the spin-orbit interaction in the valence bands. The crystals were grown by chemical vapour transport technique using Iodine as transport agent. A characteristic splitting of the chalcogen p-derived valence bands along high symmetry directions has been observed experimentally. The size of the splitting increases with the increase of the atomic number of the chalcogenide, e.g. at the A point of the Brillouin zone from 0.06 eV to 0.31 eV with an almost linear dependence with x, as progressing from ZrS_2 towards $ZrSe_2$, respectively. Electronic structure calculations based on the density functional theory have been performed using the model of Tran–Blaha [1] and the modified version of the exchange potential proposed by Becke and Johnson [2] (TB–MBJ) both with and without spin-orbit (SO) coupling. The calculations show that the splitting is mainly due to spin-orbit coupling and the degeneracy of the valance bands is lifted.

1. Introduction

In the context of electronic structure theory, the spin-orbit (SO) interaction is well known to be responsible of the splitting of degenerate electron energy levels in atoms, molecules, and solids [3,4]. This influence is found to be most pronounced for the valence band maxima. It plays a significant role in developing a more refined description of the band structure of semiconductors and recently in the elucidation of various splittings of surface states [5–7]. The SO interaction is a relativistic effect and can be explained on the atomic level by the interaction of the magnetic momentum of the electron (spin) with the magnetic field viewed by this electron due to its movement in the electrostatic field of the proton. The Hamiltonian of the SO interaction for an isolated atom takes the form $H_{SO} = (h/4m^2c^2)(\nabla V \times p) \cdot \sigma$ where V is the potential energy of the electron, p is the momentum, and σ is the Pauli spin operator. It can also be written as $H_{SO} \sim L \cdot S$ where L and S are the angular and spin momenta, respectively [3].

Here we report on high-resolution angle-resolved photoemission spectroscopy (ARPES) measurements performed on zirconium dichalcogenide compounds of ZrS_xSe_{2-x}. ARPES is one of the most powerful tools for the electronic structure investigation of solids and their surfaces, especially when applied in conjunction with synchrotron radiation as a tunable photon source [8,9].

ZrS_xSe_{2-x} compounds belong to the large family of the layered transition metal dichalcogenides (TMDCs). These materials have been attracting much interest due to their suitability for a number of potential applications. For instance, recently, electrical transport properties and prototype optoelectronic devices based on individual ZrS_2 nanobelts have been discussed [10]. Additionally, the energy gaps of these materials match well the solar spectrum [11]. The size of the band gaps of the ternary ZrS_xSe_{2-x} semiconductor series was found to vary almost linearly with the composition parameter x [12]. The materials are discussed as promising candidates for third generation photovoltaic applications [12].

The general formula of the dichalcogenides is MX_2 (M is the metal and X is the chalcogenide) where M here represents Zr and X is Se or S. The most significant structural property of these compounds is that they crystallize in a quasi two-dimensional (2D) structure consisting of a sheet of metal atoms lying between two sheets of chalcogens forming X–M–X layers or sandwiches. Inside the layers, the bonding is of strong mixed covalent-ionic character depending on the electronegativity $x$of the elements, while the adjacent layers are loosely coupled to each other by a relatively weak Van der Waals (VdW) forces [13,14]. Based on the stacking sequence of the successive X–M–X sandwiches, a number of crystal structures or polytypes can be obtained. ZrS_xSe_{2-x} compounds

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http://dx.doi.org/10.1016/j.elspec.2012.12.010

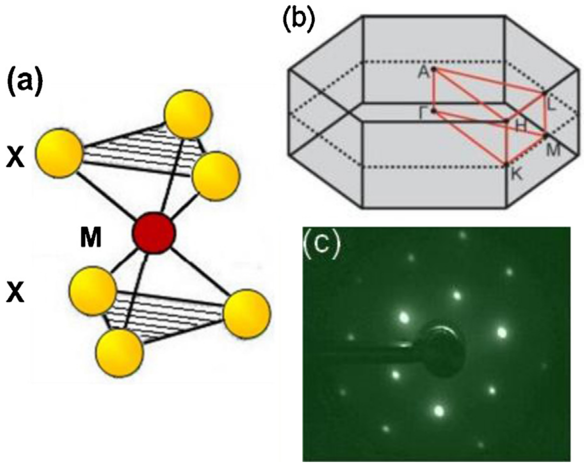

Fig. 1. 1-*T* crystal structure. (b) Corresponding Brillouin zone (BZ) with different high symmetry points and directions. (c) LEED pattern of ZrS_2 taken at an electron energy of 102 eV.

crystallize in a layered 1*T* structure in which the transition metal is octahedral coordinated by six chalcogenide atoms as shown in Fig. 1(a). This 2D bonding character has been found to be responsible for the marked anisotropy observed in a number of their physical properties [15,16]. Due to the weak VdW bonding, the samples display good cleavage along the interlayer gap presenting an ideal clean surface suitable for surface sensitive analysis techniques like, e.g. the photoemission spectroscopy which is employed in this study. In ideal cases, perfect dangling bond-free surfaces can be obtained by peeling off an adhesive tape attached to a crystal.

The electronic band structure calculations of the two end members of the ZrS_xSe_{2-x} series, i.e. $ZrSe_2$ and ZrS_2 have been reported by many authors using different techniques. The first calculated band structures of $ZrSe_2$ and ZrS_2 have been reported by Murray et al. in [17,18], obtained by the semi-empirical tight binding (TB) linear combination of atomic orbitals (LCAO) method. However there are many different TB variants, ranging from completely semi-empirical to first-principles-based versions [19]. The relationship between the semi-empirical TB method with the first-principles method has been discussed comprehensively in [20]. Bullett [21] reported on the calculation based on the chemical pseudopotential method, however, the pseudopotential method ignores the dynamics of the core electrons and replaces their effects by an effective potential [22]. Other methods like self-consistent symmetrized orthogonalised plane wave are reported by Isomaki et al. [23,24]. Recent calculations are given for $ZrSe_2$ and ZrS_2 using the WIEN97 code [25] by Reshak and Auluck [26] based on the density functional theory (DFT) method. Most recently, Ghafari et al. [27] have reported on DFT calculations using the accurate exchange-correlation energy from the WIEN2k code [28]. The results revealed that the materials are semiconductors with an indirect band gap, sharing the common features of a p-like valence band with a maximum located at the Brillouin zone (BZ) centre (and a conduction band with a minimum located around the BZ boundary L. Fig. 1(b) illustrates the BZ of the crystals with points of high-symmetry.

In this paper, we focus on the chalcogen p-derived valence bands where a distinct splitting of the top valence bands, for the series of ZrS_xSe_{2-x} crystals, is observed by angle-resolved photoemission spectroscopy (ARPES). The ARPES results have been performed at the A point of the Brillouin zone, because due to overlapping bands the splitting is hardly to be resolved at the Γ point. The analysis shows that the size of the splitting increases from ZrS_2 to $ZrSe_2$. For the interpretation of this splitting, electronic structure calculations of ZrS_2 and $ZrSe_2$ as well as the ternary compound ZrSSe have been performed with and without the inclusion of the spin-orbit (SO) coupling by implementation of the package WIEN2K code [28]. Our calculations show that the degeneracy of the topmost valence bands is removed when we consider spin-orbit coupling in the calculation for the three compounds. The size of the SO splitting increases with the atomic number of the chalcogenide, i.e. from ZrS_2 to $ZrSe_2$. Comparison between theory and experimental results reveals also good quantitative agreement for the splitting at the A point. This is due to the fact that the origin for the splitting is dominantly due to spin-orbit interactions.

2. Experiments and calculations

Single crystals of ZrS_xSe_{2-x} used for this study were grown by the chemical vapor transport technique (CVT) using iodine as the transport agent [29]. Details of the parameters and conditions of the crystal growth are found in [12]. The crystals obtained by this technique had natural clean mirror-like faces, they were thick enough enabling good cleavage in ultra high vacuum in the direction perpendicular to the crystallographic *c*-axis. The stoichiometric composition of the grown crystals was determined using energy dispersive X-ray emission (EDX).

For a qualitative determination of the crystal structure we used the low energy electron diffraction (LEED) technique which showed a very clear hexagonal array of points. A LEED pattern of ZrS_2 taken at electron energy of 102 eV is given in Fig. 1(c). The sharpness of the diffraction patterns reflects the high quality of the single crystals. LEED in addition to the Laue diffraction patterns were used to orientate the crystals for the ARPES measurements. The specimens were mounted to the sample holder by silver-filled epoxy resin and a clean surface was obtained by cleavage *in situ* using adhesive tape. Cleaved surfaces proved to be of high quality and chemically inert, as well as of other TMDCs, due to the absence of dangling bonds as the cleavage done at the van der Waals gaps.

High resolution photoemission spectra were measured at the Helmholtz–Zentrum Berlin (HZB) at the synchrotron radiation source BESSY II in Berlin, Germany. The measurements were performed at room temperature under ultrahigh vacuum conditions in the measurement chamber ($p \leq 2 \times 10^{-10}$ mbar) on the 5 m normal incidence monochromator of the beamline (BEST) [30]. The resulting photoelectrons were energy analyzed using a hemispherical analyser SCIENTA SES2002 analyser. A resolution of 20 meV was found sufficient to resolve the essential details.

The electronic structure of ZrS_2 and $ZrSe_2$ as well as the ternary compound ZrSSe was calculated by the full-potential linearized augmented plane wave method due to Singh [31], which is implemented in the package WIEN2K code [28]. Within the exchange-correlation energy functional, the new semilocal potential that combines the modified Becke–Johnson potential [2] and the LDA correlation potential (TB–MBJ) as recently proposed by Tran and Blaha [1] is used. For more details about the calculations the reader may refer to [27]. G_{max} and R_{MT} are optimized within the experimental lattice parameters. R_{MT} represents the smallest muffin tin radius, K_{max} is the maximum of the reciprocal lattice vectors, and G_{max} is the maximum magnitude of the largest vector in the charge density Fourier expansion. In the next step the theoretical lattice constants were extracted by total energy minimization to the volume in the PBE functional [27]. Values are collected in Table 1.

3. Results and discussion

The photoemission measurements have been carried out for several different compositions of the ZrS_xSe_{2-x} series. For the normal emission spectra ($K_{||} = 0$), EDC spectra have been recorded using different photon energies in the range of $15 \leq hv \leq 27$ ev.