Electronic structure of shandite Co$_3$Sn$_2$S$_2$

Yu S Dedkov$^{1,*}$, M Holder$^1$, S L Molodtsov$^1$ and H Rosner$^2$

$^1$Institut für Festkörperphysik, Technische Universität Dresden, 01062 Dresden, Germany
$^2$Max-Planck-Institut für Chemische Physik fester Stoffe, 01187 Dresden, Germany

E-mail: dedkov@physik.phy.tu-dresden.de

Abstract. The electronic structure of shandite Co$_3$Sn$_2$S$_2$ was determined by photoelectron spectroscopy and compared with ab initio band structure calculations. Presented results give evidence that this compound has half-metallic ferromagnetic properties.

Field of spintronics is concerned with search for highly spin-polarized materials with the aim of enhancing tunneling magnetoresistance of magnetic tunnel junctions, which are active members of magnetic random access memory elements [1]. The second application of spintronics is spin transistors and the underlying basic concept of spin injection. Injection of a spin polarized current from a ferromagnet into a semiconductor is also necessary in order to carry out qubit (quantum bit) operations required for quantum computing. The first theoretical demonstration of a spin Field Effect Transistor was done by Datta and Das in 1990 [2]. It has not yet been realized in experiments, mainly because it requires spin injection from a ferromagnetic metal (for example Fe) into a semiconductor. This has been shown to be practically impossible due to the large conductivity mismatch between a metal and a semiconductor [3]. The use of ferromagnetic materials with a spin polarization as large as possible can help to efficient injection of spin into semiconductor [3]. The half-metallic ferromagnets (HMF) are the ultimate materials in this respect since 100% spin polarization is expected from these materials [4].

The concept of a half-metallic ferromagnet was introduced by de Groot et al. [4], based on their electronic structure calculations for Heusler systems NiMnSb and PtMnSb. HMFs are solids that are metals with the Fermi surface in one spin-channel, and insulators or semiconductors in the other spin-channel. They give rise to 100% spin polarization at the Fermi energy, $E_F$, which makes them ideal materials for spin-dependent devices and spin injection. A broad classification scheme of half-metallic ferromagnets, encompassing localized and itinerant electron systems as well as possible semimetals and semiconductors, was proposed by Coey and Venkatesan [5], based on the electronic structure.

In the present paper, we present for the first time a theoretical and experimental electronic structure study of the recently reinvestigated shandite Co$_3$Sn$_2$S$_2$ [6]. Previous experimental results from magnetic susceptibility, specific heat, and resistivity measurements on powder samples showed a phase transition to a ferromagnetic metallic state at 177 K with a saturation moment of 0.87 $\mu_B$/f.u. [7]. Full potential electronic structure calculations within the local spin density approximation (LSDA) result in a half-metallic ferromagnetic ground state with a moment of 1 $\mu_B$/f.u. and a tiny gap in the minority spin channel. Presented experimental results obtained on polycrystalline Co$_3$Sn$_2$S$_2$ samples

$^*$ To whom any correspondence should be addressed.
by means of ultraviolet as well as x-ray photoelectron spectroscopies (UPS as well XPS, respectively) were compared with LSDA band structure calculations. Extracted from the experimental spectra, partial and total density of states, are in good agreement with presented theoretical results and give evidence that this compound can be related to the class of half-metallic ferromagnets.

Co$_3$Sn$_2$S$_2$ samples were prepared by high temperature synthesis [8]. Stoichiometric amounts of the elements were heated in a sealed quartz tube to 950°C. After two days, the temperature was decreased stepwise, and at 500°C the tube was quenched in cold water. Composition, structure and thermal properties of the samples were characterized by x-ray powder diffraction, scanning electron microscopy (SEM), energy dispersive x-ray diffraction (EDX), differential thermal analysis (DTA) and differential scanning calorimetric (DSC) methods. The structure determination was performed at 298 K on an imaging plate system equipped with an Oxford cryostat system. From the crystalline product, only a single phase was identified that exhibits the composition Co$_3$Sn$_2$S$_2$. The determined lattice parameters are in agreement with the literature [8].

The photoelectron spectroscopy experiments were carried out in the experimental station consisting of two separated chambers: preparation and analysis (base pressure: 8×10^{-11} mbar). The photoelectron spectra (hν=21.2 eV, 40.8 eV, and 1486.6 eV) were recorded at room temperature in angle-integrated mode by a 180° hemispherical energy analyzer (SPECS). The energy resolution was set to 100 meV and 800 meV for UPS and XPS, respectively. The light was incident at an angle of 30° with respect to the sample surface. Samples have been scratched in situ in preparation chamber by using a diamond file. Surface contamination has been monitored by the eventual presence of C 1s and O 1s core levels signal in the XPS spectra. The Fermi level of sample was referenced to a copper polycrystalline foil in electrical contact to sample.

Co$_3$Sn$_2$S$_2$ is a ternary chalcogenide with a shandite structure (Fig. 1) [8]. The shandite structure is an interesting structural variant which contains transition metals M (M=Co, Ni, Rh, Pd), main group elements M' from Groups 3 and 4 (M'=In, Tl, Sn, Pb), as well as sulfur and/or selenium. The overall

![Figure 1. Crystal structure of shandite Co$_3$Sn$_2$S$_2$.](image1)

![Figure 2. Non spin-resolved total and partial density of states for Co$_3$Sn$_2$S$_2$. Inset shows the corresponding spin-resolved density of states in the vicinity of the Fermi level.](image2)
Figure 3. (a) Co 2p_{3/2,1/2}, (b) Sn 3d_{5/2,3/2}, (c,d) S 2p_{3/2,1/2} XPS spectra of Co$_3$Sn$_2$S$_2$. Fit procedure (d) gives two photoemission components with binding energies marked in the figure.

The calculated total and partial densities of states (DOS) of Co$_3$Sn$_2$S$_2$ are shown in Fig. 2. At room temperature, where the spectra have been measured, the system is not magnetically ordered. Therefore, here we restrict ourselves to the non spin polarized solution. The system exhibits a valence band of about 10 eV bandwidth. The low lying states (between -7 eV and -10 eV) are predominantly due to bonding Sn 5s states (see Fig. 2) that hybridize with the S 3p states. The region between about -3 eV and -7 eV, separated by pseudogaps from the rest of the valence band, is dominated by the S 3p states. The low lying states between -3 eV and the Fermi level are strongly dominated by the Co 3d electrons. Whereas most of the Co 3d (between about -0.5 eV and -2.5 eV) hybridize only weakly with the Sn an S states, a considerable admixture of Sn 5p and S 3p states is observed for the low lying Co 3d states. This covalency is important for the formation of the narrow peak at the Fermi level that responsible for the ferromagnetism in this system [7]. This peak is separated from the rest of the valence band by a narrow gap of about 300 meV.

Figure 3 shows XPS spectra of Co$_3$Sn$_2$S$_2$ obtained with Al Kα emission line. All spectra represent well-known core-level multiplets of Co, Sn, and S. The binding energy (BE) of Co 2p$_{3/2}$ line [Fig. 3(a)] is 778.4 eV and is close to ones in Co monochalcogenides and dichalcogenides: 778.7 eV for CoSe [9], 778.3 eV for CoSe$_2$ [10], and 778.3 eV for CoS$_2$ [10]. The binding energy of Sn 3d$_{5/2}$ line [Fig. 3(b)] is 485.45 eV and is also close to ones in Sn monochalcogenides: 485.6 eV for SnTe and 485.7 eV for SnS and SnSe [11].

XPS spectra of sulfur [Fig. 3(c) and (d)] were used to determine its valence state. The position of S 2p spin-orbit doublet is at 162.5 eV of BE that can confirm the S$^2-$ state [12]. The same results were obtained in the recent work for the Ni$_3$Sn$_2$S$_2$ compound [13]. In this work authors try to clarify the question of the valence states of Ni, Sn, and S in ternary chalcogenide Ni$_3$Sn$_2$S$_2$, which has the same sandsite crystal structure as the compound studied in the present work. They employed XPS as well as $^{61}$Ni and $^{119}$Sn Mössbauer spectroscopy. Experimental results were compared with band structure calculations on the basis of linear-muffin-tin-orbitals (LMTO) procedure. The Ni$_3$Sn$_2$S$_2$ compound was found to be a paramagnet in the ground state and the valence electron configuration from experimental and theoretical data was determined to be (Ni$^{3+}$)$_3$(Sn(1)$^{2+}$)(Sn(2)$^{2+}$)(S$^2-$)$_2$. Additionally in
Figure 4. Valence band photoelectron spectra of shandite Co$_3$Sn$_2$S$_2$ obtained at different photon energies in comparison with calculated DOS convoluted with corresponding Gaussian distribution, which simulates the experimental resolution (full width $\Delta$). Inset in the upper panel shows the result in the vicinity of the Fermi level.

In our case of S 2$p$ XPS spectrum we can resolve the second photoelectron doublet at 164.5 eV of BE. According to [12] this line can be assigned to the S$^0$ state of sulfur and it can be explained by some imperfections arising from ex situ sample preparation and sulfur segregation on the sample surface due to in situ cleaning procedure.

Investigation of the valence-band electronic structure of Co$_3$Sn$_2$S$_2$ was performed by means of photoelectron spectroscopy with different photon energies. The obtained results were compared with band structure calculations on the basis of LSDA formalism.

Fig. 4 shows the photoelectron spectra of Co$_3$Sn$_2$S$_2$ obtained with He I (open circles, upper panel), He II (open squares, middle panel), and Al K$\alpha$ (open diamonds, lower panel) radiations in comparison with calculated paramagnetic DOS multiplied by the Fermi-Dirac distribution function and convoluted with Gaussian functions, which simulates the corresponding experimental resolution. Considering the photoionization cross section [14], a broad feature with some weak structures located at 3-8 eV BE is ascribed to the S 3$p$ states, while a sharp peak located in the region $E_F$–2 eV is attributed to the Co 3$d$ state (the cross section of Sn 5$p$ valence state is significantly lower). We find in Fig. 4 that the spectra have clear Fermi-edge cutoff indicative of metallic nature of compound, consistent with the electrical resistivity measurement [7]. Presented experimental data show a good agreement with calculated band structure and DOS. One has to note that feature near Fermi level is well described by electronic calculations. The spin-resolved DOS reveals the half-metallic nature of this feature at low temperature.

In conclusion, the electronic structure of shandite Co$_3$Sn$_2$S$_2$ was calculated on the basis of LSDA formalism. The obtained theoretical results were compared with experimentally determined partial and total DOS. Extracted from the experimental spectra, partial and total density of states, are in good agreement with presented theoretical results and give indirect evidence that this compound can be related to the class of half-metallic ferromagnets.

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