

## Magnetism and Spin States of FeSb<sub>2</sub>

Peijie Sun, Nils Hollmann, Zhi Wei Hu, Walter Schnelle, Micheal Baenitz, Simon Johnsen<sup>1</sup>, Martin Søndergaard<sup>1</sup>, Bo Brummersted Iversen<sup>1</sup>, Julio Criginski Cezar<sup>2</sup>, Nick B. Brookes<sup>2</sup>, Liu Hao Tjeng, and Frank Steglich

The prototype *d*-electron based correlated semiconductor FeSi continues to attract significant interest in the field of solid state physics due to its unusual magnetic and thermodynamic properties [1]. FeSb<sub>2</sub>, a newly identified narrow-gap semiconductor, is also receiving attention because of its striking similarities to FeSi [2,3,4]. Part of our interest in this class of materials stems from their potential as thermoelectric materials in the cryogenic range. In particular, FeSb<sub>2</sub> exhibits a colossal thermopower amounting to  $-45\text{mV K}^{-1}$  at around 10 K [5, 6]. The two compounds have rather close energy scales: for example, the crossover from diamagnetism to enhanced paramagnetism occurs at  $\sim 100$  K in both systems; the main transport gap in FeSb<sub>2</sub> and FeSi is roughly 30 meV and 50 meV, respectively.

To capture the significant many body effects found in these systems, different theoretical approaches have so far been proposed including the Kondo insulator [7] and the nearly magnetic semiconductor [8] scenarios, as well as the recently suggested correlated band insulator model [9], i.e., a more general physical treatment starting from the picture of a classical semiconductor including many-body renormalizations. While each model can more or less explain the observed main features in both systems, a consistent interpretation of the magnetic, transport, optical and thermodynamic properties in a unified framework is still lacking.

We report on our experimental investigations of the magnetism and Fe spin-state configurations of FeSb<sub>2</sub>, which provides a basis for the interpretation of the unusual physical properties observed in this material. This contribution is a follow-up of our previous scientific report [10], where transport properties, NMR and optical properties have been presented.

### Magnetic properties

FeSb<sub>2</sub> crystallizes in the orthorhombic marcasite type structure. Its magnetic susceptibility  $\chi(T)$  was realized already four decades ago to be distinctly differ-

ent from that of other semiconductors of this family [11]. As shown in Figure 1,  $\chi(T)$  of FeSb<sub>2</sub> is characterized by a crossover from low-temperature diamagnetism to a largely enhanced paramagnetism at  $T > 100$  K. After passing through a broad maximum at around 400 K,  $\chi(T)$  smoothly decreases with temperature up to 750 K. Further increase of the temperature results in a more rapid decrease of  $\chi(T)$ .

By assuming correlated conduction and valence bands, Goncalves da Silva was able to theoretically interpret the peculiar enhancement of  $\chi(T)$  above 100 K [12]. By contrast, after the recognition of the strong similarities in magnetic properties between FeSb<sub>2</sub> and FeSi [4,13], the Kondo insulator [4] and the nearly magnetic semiconductor [14] models were also applied to FeSb<sub>2</sub> in analogy with FeSi. A description of the  $\chi(T)$  employing a narrow-band, narrow-gap scheme (inset of Fig. 1), which is compatible to the Kondo insulator description, requires an unrealistically narrow band width  $W$  (the dash-line calculation shown in Figure 1 is based on  $W = 59.5$  meV, roughly the same size as the employed energy gap,  $E_g = 57.8$  meV). For FeSi, this has been taken as a proof supporting the Kondo insulator scenario [15]. Notice, however, that the fit of this model

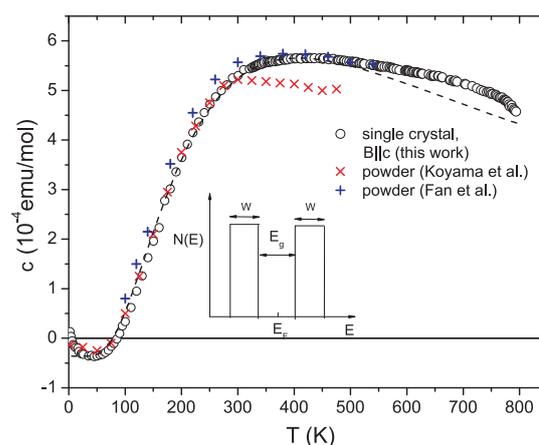


Fig. 1: Magnetic susceptibility of FeSb<sub>2</sub> up to 800 K in comparison to the reported values in literatures [7,11]. The dash line is a calculation based on a simple narrow-band narrow-gap model (inset). Notice that the high-temperature part does not fit well to this model.

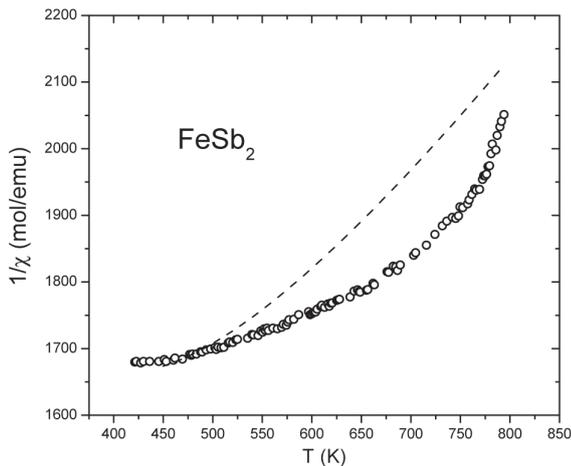


Fig. 2: Inverse magnetic susceptibility of  $\text{FeSb}_2$  in the temperature range 400 K – 800 K, with the diamagnetic contribution subtracted from the raw data. No clear CW behavior is observed in this range. By contrast, the dash line based on the same calculation as shown in Figure 1, is CW like at high temperatures.

to  $\text{FeSb}_2$  yields considerable discrepancy at temperatures above the  $\chi(T)$  maximum (cf. Figs. 1 and 2).

Extending the temperature range of the reported magnetic susceptibility [4,11,14] up to 800 K enables one to check the applicability of the Curie-Weiss (CW) law at higher temperatures, which is anticipated by the Kondo insulator and the nearly magnetic semiconductor scenarios and has been experimentally observed for  $\text{FeSi}$  [13]. As seen in Figure 2, the inverse magnetic susceptibility exhibits a positive curvature; a linear variation of  $1/\chi(T)$  as expected by the CW law cannot be identified in any temperature range between 400 K and 800 K, in contrast to the CW like behavior of the calculated curve based on the narrow band model. One possible reason accounting for the absence of CW behavior lies in the complex electronic structure in the vicinity of the Fermi level, as revealed by various electronic structure calculations [3,16]. As far as the magnetic properties are concerned, it seems that the correlated band insulator scenario [9], which starts from a realistic band structure and takes significant many body effects into account, is more flexible to describe the unusual magnetic, as well as the transport, optical, and thermodynamic properties [2].

### X-ray absorption spectroscopy and Fe spin states

It is perhaps also helpful to investigate the intriguing electronic and magnetic properties from a local viewpoint, since the rise in magnetization with temperature could be explained by a spin-state transition of the Fe  $3d$  electrons. In an early paper, Goodenough [17] proposed an electron occupation close to  $3d^4$  at the iron sites, where the electrons form a non-magnetic low-spin state with  $S=0$ . When the temperature is increased, the rise in magnetization could be caused by a thermal population of an excited magnetic spin state. However, band structure calculations predict that the electron occupation is close to  $3d^6$  for Fe [3]. No direct experimental evidence for the electronic occupation of the Fe  $3d$  shell and the possibility of a spin-state transition existed so far.

We have performed X-ray absorption spectroscopy on the Fe  $L_{2,3}$  edge, a technique that is highly sensitive to the local electronic structure, both in terms of occupation numbers and spin states. In Figure 3 we show the spectrum for  $\text{FeSb}_2$  along with other iron compounds as references:  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$  are ionic-like and strongly correlated  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  high-spin systems, respectively,

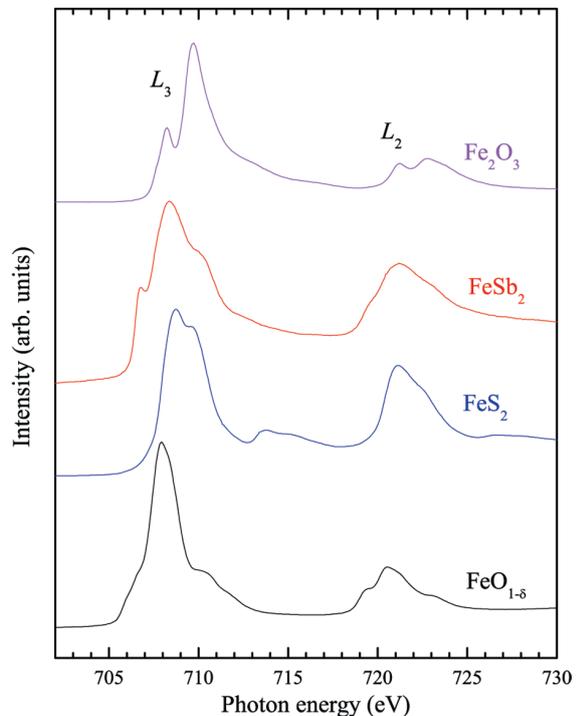


Fig. 3: X-ray absorption on the Fe  $L_{2,3}$  edge of  $\text{FeSb}_2$  and references.

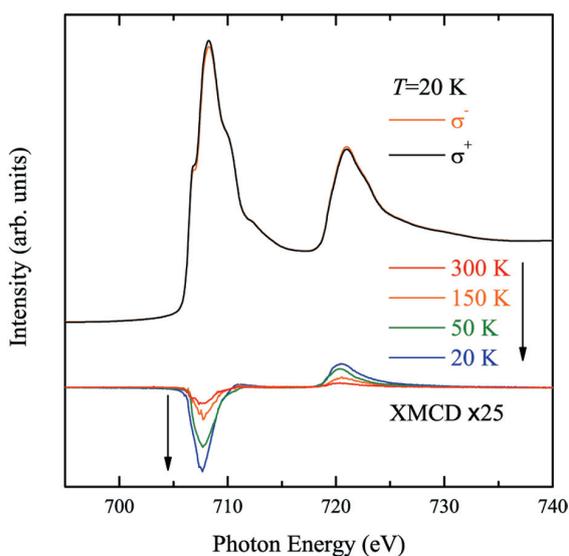


Fig. 4: X-ray magnetic circular dichroism of FeSb<sub>2</sub>.

while FeS<sub>2</sub> is a rather covalent system with a low-spin configuration. From comparison to the spectrum of FeSb<sub>2</sub>, we can draw three significant conclusions. (1) The absolute energy position and the line shape show that the occupation is indeed close to  $3d^6$  as predicted by band structure calculations. (2) The FeSb<sub>2</sub> XAS spectrum shows very distinct features reminiscent of multiplet structures. This means that electron correlations are important in FeSb<sub>2</sub>, and that the system is far away from a band material. (3) The spectral weight distribution between the  $L_2$  and  $L_3$  lines (the branching ratio) is a good indication for the spin state of Fe. For FeSb<sub>2</sub>, we find a clearly enhanced spectral weight at the  $L_2$  line, like for the low-spin FeS<sub>2</sub> reference. The branching ratio thus indicates a predominant low-spin state for FeSb<sub>2</sub>.

Interestingly, we also see features in the FeSb<sub>2</sub> spectrum which are not present in FeS<sub>2</sub>, for example the low energy peak at 707 eV and the shoulder at 720 eV. Such features are present in the FeO spectrum, suggesting that there is also a high-spin contribution in FeSb<sub>2</sub>.

To investigate this issue in more detail, we have also performed X-ray magnetic circular dichroism (XMCD) measurements of the Fe  $L_{2,3}$  edge of FeSb<sub>2</sub>. The results are shown in Figure 4. A small dichroic signal is found at the low energy side of the  $L_3$  and  $L_2$  lines, which is the part of the spectrum that is suspected to indicate a high-spin contribution and which has a more atomic-like lineshape. Surprisingly, this XMCD signal increases with

decreasing temperature, approximately with a Curie-law. This means that the local magnetism picked up in the XMCD experiment is in stark contrast to the behavior observed in the bulk magnetic susceptibility in Figure 1. We attribute the high-spin signal of FeSb<sub>2</sub> to surface effects. It is well-known that the electronic structure of correlated materials at the surface can be quite different from the bulk due to differences in the local coordination. This is especially true if the system is close to an instability, e.g. close to a low-spin to high-spin transition like it has been proposed for FeSb<sub>2</sub>. We therefore speculate that the Fe in the near surface region of FeSb<sub>2</sub> is in the high-spin state while the Fe in the bulk is in the low-spin state, and that we are able to pick up this high-spin signal because of the XAS probing depth of about 50 Å only. In the near future we plan further investigations using bulk-sensitive X-ray inelastic scattering in order to confirm our conjectures and to determine the temperature dependence of the spin state in the bulk of FeSb<sub>2</sub>.

## References

- [1] *N. Manyala, J. F. DiTusa, G. Aeppli, and A. P. Ramirez*, *Nature* **454** (2008) 976.
- [2] For a recent review on FeSb<sub>2</sub>, see *P. Sun, M. Søndergaard, B. Iversen, and F. Steglich*, accepted for publication by *Annalen der Physik*.
- [3] *A. Bentien et al.*, *Phys. Rev. B* **74** (2006) 205105.
- [4] *C. Petrovic et al.*, *Phys. Rev. B* **72** (2005) 045103.
- [5] *A. Bentien et al.*, *Europhys. Lett.* **80** (2007) 17008.
- [6] *P. Sun et al.*, *Phys. Rev. B* **79** (2009) 153308.
- [7] *G. Aeppli and Z. Fisk*, *Comments Condens. Matter Phys.* **16** (1992) 155.
- [8] *Y. Takahashi and T. Moriya*, *J. Phys. Soc. Jpn.* **46** (1979) 1451.
- [9] *J. Kunes and V. I. Anisimov*, *Phys. Rev. B* **78** (2008) 033109.
- [10] *P. Sun et al.*, Scientific Report 2006-2008 (MPI-CPfS, Dresden Germany, March 2009, p.37ff).
- [11] *A. K. L Fan et al.*, *J. Solid State Chem.* **5** (1972) 136.
- [12] *C. E. T. Goncalves da Silva*, *Solid State Commun.* **33** (1980) 63.
- [13] *V. Jaccarino, G. K. Wertheim, J. H. Wernick, L. R. Walker, and A. Araj*, *Phys. Rev.* **160** (1967) 476.
- [14] *T. Koyama, H. Nakamura, T. Kohara, and Y. Takahashi*, *J. Phys. Soc. Jpn.* **79** (2010) 093704.
- [15] *D. Mandrus et al.*, *Phys. Rev. B* **51** (1995) 4763.
- [16] *A. V. Lukoyanov et al.*, *Eur. Phys. J. B* **53** (2006) 205.
- [17] *J. B. Goodenough*, *J Solid State Chem.* **5** (1972) 144.

<sup>1</sup> Department of Chemistry, University of Aarhus, Denmark

<sup>2</sup> European Synchrotron Research Facility, Grenoble, France