Correlation Effects in the Semimetal FeSb$_2$: From Bulk Properties to Spectroscopy

*Peijie Sun, Michael Baenitz, Andrei Gippius, Alexander Herzog, Bo Brummerstedt Iversen[1],
Simon Johnsen[1], Niels Oeschler, Jörg Sichelschmidt, and Frank Steglich*

Introduction

The class of strongly correlated semiconductors, particularly those that are usually referred to as Kondo insulators, has been of great fundamental and practical interest for more than a decade [1]. Many-body renormalization of the bands makes them an ideal playground for exploring electron-electron correlations that are absent in classic band insulators. Meanwhile, there are high expectations on these systems for practical applications such as spintronics and thermoelectrics.

FeSb$_2$ was identified as a new *d*-based correlated semiconductor, like FeSi. Band calculations within the local density approximation show a narrow gap opening at the Fermi level with narrow bands and enhanced density of states (DOS) at the edges [2]. FeSb$_2$ crystallizes in the orthorhombic marcasite-type FeS$_2$ structure. The resistivity exhibits semiconducting behavior below room temperature [3]. The magnetic susceptibility yields a non-magnetic ground state for the 3*d* electrons of Fe. The susceptibility is temperature independent up to 50 K and becomes paramagnetic at higher temperatures [4]. This feature was described by two narrow, renormalized bands with certain band width and gap size. However, direct evidence for strong correlation effects is highly desired. The correlation gap is to be probed by both electrical transport properties and microscopic spectroscopy, such as NMR, NQR and optical conductivity. Indeed, strong indications of electron-electron correlations are revealed in these measurements. For instance, the optical spectral weight suppressed due to the gap opening is recovered only above 1 eV, a rather high energy relative to the gap. Furthermore, an extremely large thermoelectric power is reported in this system at temperatures below 30 K [5]. This appears to be highly feasible for thermoelectric application in this temperature range. Materials with rather high thermoelectric performance have been found only for temperatures near or above room temperature. However, at cryogenic temperatures (below 77 K) no systems with thermoelectric properties sufficiently high for possible application have been discovered so far.

The thermoelectric performance of substances is given by the dimensionless figure of merit $ZT=TS^2\sigma/\kappa$ where S represents the thermoelectric power, σ the electrical conductivity and κ the thermal conductivity [1]. For applications, ZT values of the order of 1 or larger are required. Among the heavy fermion systems, CeB$_6$ was successfully used to build a simple Peltier cooler with a maximum $S(T)$ of 120 µV/K at 9 K and an effective cooling of 0.2 K at 4.5 K ($ZT = 0.3$ at 7 K) [6].

Further enhancement of ZT seems to be possible only for the case of a *semiconducting* system with strong correlations like FeSb$_2$. In rare cases, the hybridization leads to a gap opening below the characteristic Kondo temperature. Those systems are referred to as Kondo insulators. Well studied compounds within this class are Ce$_3$Bi$_4$Pt$_3$, YbB$_{12}$ and SmB$_6$ [7]. They exhibit an activated conductivity at low temperatures due to the formation of a hybridization gap. The thermoelectric power may reach values beyond 100 µV/K. For the 3*d*-electron system FeSi the thermoelectric power exhibits maximum values up to 500 µV/K at 50 K [8]. However, in all these materials the ZT value is small due to the high (phonon-dominated) thermal conductivity of high-quality crystals.

Transport properties of FeSb$_2$

Here, we present transport and thermotransport results on single crystalline FeSb$_2$. The thermotransport properties of FeSb$_2$ exceed those of FeSi by far and mark the record power factor $S^2\sigma$ among all materials [5]. Thus, FeSb$_2$ has remarkable potential for application in thermoelectric refrigeration.

Single crystalline samples of FeSb$_2$ were grown by the chemical vapor transport technique with Br as a transport agent [9]. Large single crystals of

high purity were obtained with lengths of almost 5 mm. Resistivity and Hall effect are measured using a standard ac setup in a commercial PPMS (Quantum Design) in the temperature range between 1.5 K and 300 K. The thermal conductivity and thermoelectric power measurements were performed with the thermal transport option in a PPMS by means of a relaxation method with one heater and two thermometers.

The resistivity of $FeSb_2$ follows a semiconducting behavior below room temperature with two regions of thermal activation separated by a plateau around 20 K (Fig. 1). The gap sizes obtained by $\rho = \rho_0 \exp(E_g/2T)$ are estimated to 320 K for the high-T part and 54 K for the low-T side [9]. These values are in good agreement with previous reports [5].

The Hall effect confirms the activated behavior below room temperature. The inset of Fig. 1 shows the Hall coefficient $R_H = \rho_{xy}/B$ at $B = 1$ T. Below 30 K, the Hall coefficient is negative. At low T, $|R_H|$ increases towards a maximum at 7 K. In a single-band model the carrier concentration at 10 K is estimated to $n = 0.6 \cdot 10^{22}$ m^{-3} [9]. The Hall effect provides evidence for the existence of multiple bands at the Fermi surface with electron-like and hole-like character. Calculations within a two-band model by Hu et al. yielded a huge carrier mobility [10].

The thermoelectric power of $FeSb_2$ is displayed in Fig. 2. Extremely large values in the order of -30 mV/K at 10 K are observed. These values agree well with previously reported results on single crystals grown by a self-flux technique [11]. As the Hall coefficient, the thermopower exhibits negative values below 30 K, i.e., the temperature at which the smaller gap opens. The maximum
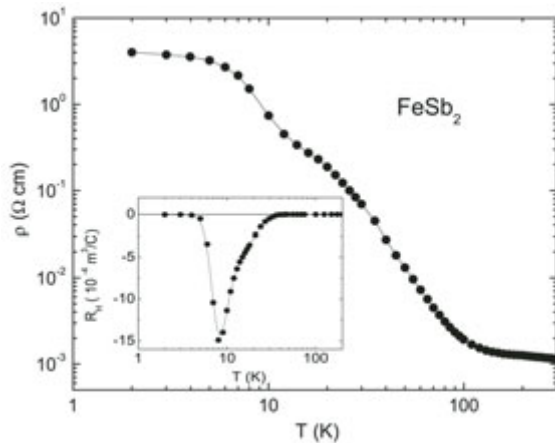
values of $|S|$ are largely enhanced compared to the thermopower of related systems, e.g. FeSi. Such a large thermopower cannot be ascribed to the phonon drag which is commonly observed in the same temperature range.

First, the Nernst effect, i.e., the transverse thermoelectric response (inset of Fig. 2), exhibits a distinct temperature dependence with two maxima related to the two energy gaps, without an apparent phonon drag contribution [11].

Second, the thermopower of the reference system $RuSb_2$ is one order of magnitude smaller, though its thermal conductivity is even higher than that of $FeSb_2$ [9].

NQR spectroscopy on $FeSb_2$ and $RuSb_2$

NQR is a very useful microscopic tool to probe the semimetallic behavior in $FeSb_2$ and $RuSb_2$. NQR experiments were performed utilizing the home-built phase-coherent pulsed spectrometer in the temperature range of 2 – 200 K. The Sb-NQR spectrum consists of three lines of the ^{123}Sb isotope (nuclear spin $^{123}I = 7/2$) and two lines of the ^{121}Sb isotope ($^{121}I = 5/2$) [12].

Here, we report the temperature dependence of $1/T_1$ for the $^{123}\nu_2$ NQR-line ($|\pm 3/2\rangle \leftrightarrow |\pm 5/2\rangle$ transition) in $FeSb_2$ and $RuSb_2$. The temperature dependence of $^{123}(1/T_1)$ consists of two distinct intervals (Fig. 3). At temperatures above 40 K, $^{123}(1/T_1)$ increases rapidly with increasing temperature but differently for $FeSb_2$ and $RuSb_2$. In the low temperature region, below 40 K, both compounds show surprisingly similar temperature dependencies with a smooth maximum at around 10 K
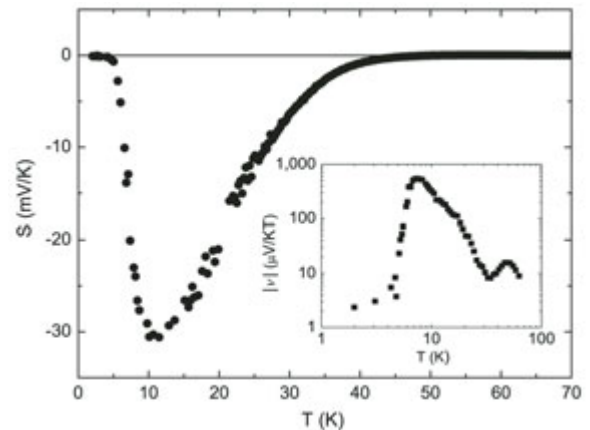

Fig. 1: Resistivity ρ of $FeSb_2$ vs. T. Inset: Hall coefficient R_H of $FeSb_2$ vs T.

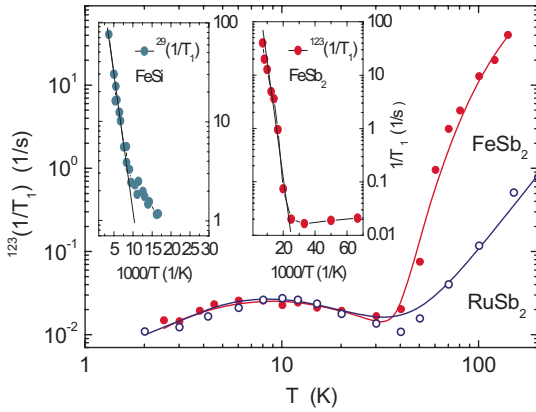Fig. 2: Thermo power S of $FeSb_2$ vs. T. Inset: Nernst coefficient ν of $FeSb_2$ vs T at B=0.5 T.

Fig. 3: $^{123}(1/T_1)$ of FeSb$_2$ and RuSb$_2$ as a function of temperature. Solid lines represent a calculation based on the in-gap-states model explained in the text. Insets show the Arrhenius plots for FeSb$_2$ and FeSi (^{29}Si-NMR data taken from Corti et al. [13]) to highlight the activated type of behavior (solid line) at high temperatures.

where the thermopower $S(T)$ peaks. This might be attributed to the presence of residual in-gap states. Above 40 K, $^{123}(1/T_1)$ for FeSb$_2$ is fitted with a simple exponential behavior ($1/T_1 \propto \exp\{-\Delta/k_BT\}$) similar to FeSi (solid line in inset of Fig 3, $^{29}(1/T_1)$ data by Corti et al. [13]). Unexpectedly, the non-magnetic homologue RuSb$_2$ does not exhibit an exponential behavior.

Here, the dependence of $^{123}(1/T_1)$ is close to a T^2 behavior characteristic for the phonon relaxation mechanism driven by the two-phonon (Raman) scattering. Such behavior was found earlier in other semimetals like Te [14]. To analyze the low temperature behavior of the Sb nuclear spin-lattice relaxation rate $1/T_1$ we propose a model of temperature dependent in-gapstates. Such a model was successfully applied to other correlated semimetals like SmB$_6$ [15] and CeRu$_4$Sn$_6$ [16]. In our case, these states might originate from an inherent Sb-deficiency and form a narrow and split band (total bandwidth ω and gap δ) around the Fermi level in both FeSb$_2$ and RuSb$_2$. In this scenario, for FeSb$_2$ a small number of Fe^{3+} ions exist which have one unpaired d_{xy} electron ($3d^5$ low-spin state) [12].

Applying the corresponding DOS model (plus a phonon driven relaxation mechanism for RuSb$_2$) one is able to consistently describe $^{123}(1/T_1)$ for both FeSb$_2$ and RuSb$_2$ in the entire temperature range (cf. solid lines in Fig. 3). For the large gap we found $\Delta/k_B = 400$ K, and for the small gap we obtained $\delta/k_B = 4$ K [17].

Optical conductivity of FeSb$_2$ compared with RuSb$_2$

Far-infrared optical spectroscopy has proved to be one of the key methods to investigate the formation of charge-excitation gaps of the order of 10 meV. For instance, for U$_2$Ru$_2$Sn we found a strongly temperature dependent suppression of the optical reflectivity below 60 meV [18] which indicates canonical heavy-fermion semiconductor behavior, i.e., the formation of a narrow energy gap due to strong electron correlations.

We investigated the far-infrared optical conductivity σ_1 of FeSb$_2$ and its non-magnetic homologue RuSb$_2$ in the energy range 3 meV - 30 eV at 10 K $< T <$ 295 K, see Fig. 4 [19].

Both FeSb$_2$ and RuSb$_2$ display a typical semiconducting optical response along all crystal axes. Except for $T = 10$ K, the low energy σ_1 spectra agree well with the zero energy DC values (see Fig. 4: square symbols and the extrapolation of the reflectivity prior to the Kramers-Kronig calculation of σ_1). For $T < 300$ K, FeSb$_2$ shows a pro-
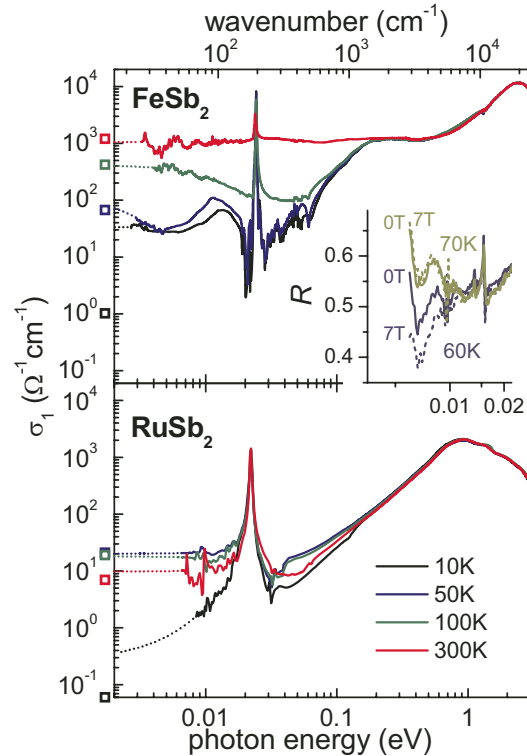

Fig. 4: Optical conductivity σ_1 of FeSb$_2$ and RuSb$_2$ for electric field along the c-axis. Dotted lines represent an extrapolation towards σ_{DC} (open squares). The inset shows the optical reflectivity R of FeSb$_2$ at the indicated temperature and magnetic fields (B||c-axis).

nounced decrease of σ_1 below 0.13 eV which corresponds to *direct* interband electronic excitations. A weakly temperature dependent *indirect* gap could also be identified which increases from 0.02 eV (at $T = 100$ K) to 0.03 eV (at $T = 10$ K). For RuSb$_2$ with a direct gap at 0.78 eV, the spectra display a much weaker temperature dependence and, in contrast to FeSb$_2$, they do not show a Drude-like increase towards low photon energies. The size of the indirect gap of FeSb$_2$ agrees with the high-temperature values derived from electrical resistivity and ^{123}Sb NQR results (see above). Another gap feature at 10 meV appears below 100 K and is most pronounced below 50 K. The onset of the σ_1 suppression clearly *increases* with decreasing temperature resembling the behavior of a gap that forms due to strong electronic correlations. The Seebeck coefficient, exhibiting colossal values related to strong electronic correlations [5] is connected to an energy gap with a similar size. However, the optical gap feature at 10 meV being related to Kondo-type interactions is questionable: As shown in the inset of Fig. 4, we found a clear *decrease* of the reflectivity (R) around 6 meV upon applying a magnetic field, in contrast to what is expected in a common Kondo semiconductor scenario. As for the NQR results, we propose temperature-dependent residual in-gap states forming a narrow and split band to be the origin of this gap feature. Nevertheless, strong electronic correlations are indicated by a temperature-dependent spectral weight redistribution up to energies as large as 1 eV.

Conclusion

FeSb$_2$ meets the requirements for high thermoelectric performance. It is a semimetal with a very low concentration and a high mobility of the charge carriers. The thermopower at low temperature is extremely large. Strong correlations associated with the small gap seem to cause the drastic enhancement of the thermopower. Evidence for correlations is primarily deduced from optical spectroscopy and thermotransport. The NQR results indicate that the in-gap states possibly filled by paramagnetic Fe^{3+} ions are essential for the extraordinary low-T properties.

Thus far, the phonon-dominated thermal conductivity of the single crystals is much too high to obtain large *ZT* values. However, the power factor $PF=S^2\sigma$ assumes record values of up to 2300 μW/cmK^2 below 30 K [5]. The aim of achieving high *ZT* values is pursued by minimization of the phononic mean free path. First studies on doped FeSb$_2$ revealed a reduced thermal conductivity. However, concomitantly the electronic properties changed drastically. Thin-film and nanoparticle growth of pure FeSb$_2$ appears, therefore, to be more promising routes towards application in Peltier cooling at cryogenic temperatures.

References

[1] *P.S. Riseborough,* Adv. Phys. **49** (2000) 257.
[2] *A. Bentien et al.,* Phys,. Rev. B **74** (2006) 205105.
[3] *C. Petrovic et al.,* Phys. Rev. B **67** (2003) 155205.
[4] *C. Petrovic et al.,* Phys. Rev. B **72** (2005) 045103.
[5] *A. Bentien, S. Johnsen, G.K.H. Madsen, B.B. Iversen and F. Steglich,* Europhys. Lett. **80** (2007) 17008.
[6] *S. R. Harutyunyan et al.,* Appl. Phys. Lett. **83** (2003) 2142.
[7] *G. Aeppli and Z. Fisk,* Comments Condens. Matter, **16** (1992) 155.
[8] *B.C. Sales et al.,* Phys. Rev. B **50** *(1994) 8207.*
[9] *P. Sun, N. Oeschler, S. Johnsen, B.B. Iversen and F. Steglich,* J. Phys.: Conference Series 150 (2009) 012049.
[10] *R. Hu et al.,* Appl. Phys. Lett. **92** (2008) 182108.
[11] *P. Sun, N. Oeschler, S. Johnsen, B.B. Iversen and F. Steglich,* Phys. Rev. **B** (2009) accepted.
[12] *A.A. Gippius, K. S. Okhotnikov, M. Baenitz, A.V. Shevelkov,* Solid State Phenomena **152-153** (2009) 287.
[13] *M. Corti, M. Fanciulli, F. Tabak,* J. Appl. Phys. **87** (2000) 6280.
[14] *B. Günther, O. Kanert,* Phys. Rev. B **31** (1985) 20.
[15] *T. Caldwell, et al.,* Phys. Rev. B **75** (2007) 075106.
[16] *M. Brando, E.M. Brüning, M. Baenitz, R. Sarkar, A.A. Gippius, R. Walstedt, and F. Steglich,* to be published (2009).
[17] *M. Baenitz, A.A. Gippius, K.S. Okotnikov, A.V. Shevelkov, S. Johnsen, B.B. Iversen, and F. Steglich,* to be published (2009).
[18] *J. Sichelschmidt, V. Voevodin, J. A. Mydosh and F. Steglich,* J. Magn. Magn. Mat. **310** (2007) 434.
[19] *A. Herzog, J. Sichelschmidt, M. Marutzky, S. Kimura, A. Bentien, S. Johnsen, B. B. Iversen and F. Steglich,* to be published (2009); A. Herzog, Diploma thesis, TU Dresden (2008).

―――――
[1] Department of Chemistry, University of Aarhus, Århus, Denmark