Thermoelectric properties of the narrow-gap semiconductors FeSb$_2$ and RuSb$_2$: a comparative study

P Sun$^1$, N Oeschler$^1$, S Johnsen$^2$, B B Iversen$^2$ and F Steglich$^1$

$^1$ Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Straße 40, 01187 Dresden, Germany
$^2$ Department of Chemistry, University of Aarhus, Langelandsgade 140, 8000 Aarhus C, Denmark

E-mail: Peijie.Sun@cpfs.mpg.de

Abstract. We report on the thermoelectric properties of FeSb$_2$ in comparison with the isostructural RuSb$_2$, both of which are narrow-gap semiconductors. Significant difference in the thermoelectric properties is found between the two systems. Despite similar charge carrier concentrations, the thermoelectric power factor differs as much as two orders of magnitude whereas the thermal conductivity is of the same order. The thermopower of strongly correlated FeSb$_2$ seems to possess a huge contribution due to correlated electrons that are absent in RuSb$_2$.

1. Introduction

Various approaches are being explored to improve the figure of merit of thermoelectric materials for practical electronic cooling and power generation [1]. Recent results of a narrow-gap semiconductor FeSb$_2$ [2] stimulate much more interest on the impact of correlation effects on thermoelectric performance. In this material, colossal values of the thermopower $S$ amounting to several tens of mV/K along with a huge power factor (PF = $S^2/\rho$) of 2300 $\mu$W/K$^2$cm were observed at around 10 K. Other physical properties like magnetic susceptibility [3], optical conductivity [4] reveal strong resemblance to the $d$-electron based strongly correlated semiconductor FeSi [5]. The thermal activation gap of FeSb$_2$ is $\sim$30 meV, even smaller than that of FeSi. This narrow gap is generally believed to be derived from hybridization between localized 3$d$ and conduction bands [6]. A smaller gap, therefore, suggests stronger many body effects. Band structure calculation [7] points out two enhanced narrow bands of 3$d$ character in the edge of a narrow gap at the Fermi level, indicative of an ideal playground for exploring electronic correlation effects as in FeSi.

In this work we report on a comparative study on iso-structural FeSb$_2$ and RuSb$_2$. In contrast to FeSb$_2$ that is being discussed as a strongly correlated semiconductor, RuSb$_2$ is more of a conventional band semiconductor. Band calculation gives an energy gap of 0.19 eV for RuSb$_2$[8] comparable to the calculated gap (0.1-0.3 eV) for FeSb$_2$ [7], the latter largely exceeding the observed thermal activation gap. Nevertheless, magnetic susceptibility of RuSb$_2$ is of Van-Vleck-like diamagnetism of inner core electrons in the whole temperature range measured up to 400 K except for a small Curie tail at low temperatures [9], in sharp contrast to the thermally...
activated behavior appearing from below 50 K in FeSb$_2$ (for FeSi with a larger gap, the activated magnetic susceptibility starts below 100 K [5]). Therefore, on the basis of the prevalent scenarios on correlated semiconductors [6], it is reasonable to consider RuSb$_2$ as a classical semiconductor. Our results show that the enhancement of thermopower in the FeSb$_2$ is accompanied by the onset of a lower energy gap of several tens of Kelvin, and is very different from a phonon drag enhancement seen in some elemental semiconductor like silicon and germanium [10]. A moderately enhanced effective electron mass indicates involvement of correlation effects in FeSb$_2$. On the other hand, thermopower of RuSb$_2$ has a less enhanced peak, probably dominated by normal phonon drag and narrow band-gap effects in the absence of correlated electrons. The power factor of FeSb$_2$ exceeds that of RuSb$_2$ by two orders of magnitude and is a testament to the influence of the strong correlation effects.

2. Experimental

Single crystal FeSb$_2$ employed here was prepared by chemical vapor transport technique, whereas RuSb$_2$ was synthesized using a self-flux method. Powder X-ray diffraction experiments confirmed the crystals are single phase with the proper marcasite structure. Laue diffraction was used to orient the samples. All the data shown below were obtained by measurements along the c axis of the orthorhombic lattice. Thermoelectric measurements were performed with the thermal transport option of a Quantum Design PPMS and our home-made cryostat in the temperature range of 1.5 to 300 K. The Hall coefficient was measured by isothermally sweeping the magnetic field. For comparison, the thermoelectric properties of one self-flux FeSb$_2$ single crystal, appearing in the previous work of Bentien et al. [2], are also shown together with the newly measured Hall coefficient on this particular sample.

3. Results and discussion

![Figure 1](image_url)

**Figure 1.** Electrical resistivity (a) and thermopower (b) of the two FeSb$_2$ and one RuSb$_2$ single crystals. The labels VT and SF denote vapor transport and self-flux, respectively. Data of the FeSb$_2$ (SF) was taken from reference [2].

Fig. 1(a) shows the electrical resistivity $\rho(T)$ and Fig. 1(b) the thermopower $S(T)$ as a function of temperature. Differences in $\rho(T)$ and $S(T)$ between the Fe- and Ru-based systems are immediately apparent. $\rho(T)$ of FeSb$_2$ is characterized by two activation regions and a shoulder like crossover at 20-50 K. The Arrhenius equation $\rho = \rho_0 \exp(E_g/2T)$ fits well the activation regions, leading to an energy gap of 50-80 K and 300-400 K in the low- and high-temperature regions, respectively. RuSb$_2$, on the other hand, is more resistive over the whole temperature range.
range. A metallic conduction with high resistivity at 50–280 K is observed, from below and above which, an energy gap of 165 K and 3400 K was derived, respectively. Similar $\rho(T)$ behavior is frequently observed in other semiconducting systems of relatively higher energy gap, e.g., Ru$_2$Si$_3$ [11], where the low-$T$ activation was ascribed to excitations from impurity states. This seems to be the case in RuSb$_2$, too. Both systems turn to a weakly $T$-dependent behavior below around 8 K, presumably dominated by a hopping conduction mechanism which will not be addressed in this work. For both FeSb$_2$ and RuSb$_2$, the thermopower is negative in the whole temperature range, with the values largely enhanced below around 60 K. However, the manners in which $S$ is enhanced are very different between them. Compared to $S$ above 100 K, FeSb$_2$(SF) is enhanced 3 orders of magnitude (at least 2 orders of magnitude for FeSb$_2$(VT)), while RuSb$_2$ only by a factor of 5, as temperature is decreased down to below the onset of the lower gap. The thermopower peak of RuSb$_2$ is small, relative to its larger resistivity and energy gap. The high resistivity and low thermopower in RuSb$_2$ contrast the low resistivity and high thermopower in FeSb$_2$.

A large thermopower along with low resistivity results in a huge thermoelectric PF at 10-30 K for FeSb$_2$ (Fig. 2(a)). Regarding the PF of optimized Bi$_2$Te$_3$ as a reference ($\sim 40$ $\mu$W/K$^2$cm), one notices immediately that the PF of FeSb$_2$ is unusually large while that of RuSb$_2$ is normal. Particularly, the power factor of the self-flux FeSb$_2$ crystal has a peak of almost two orders of magnitude larger than that of RuSb$_2$, in spite of their very close carrier concentrations derived from Hall effect measurements (Fig. 3) and the larger resistivity of the latter. A classical semiconductor has no large PF because a higher $S$ is only achieved at the cost of degrading its electrical conductivity. The thermal conductivity $\kappa(T)$, shown in Fig. 2 (b)), is dominated by the phonon contribution. $\kappa(T)$ of RuSb$_2$ exhibits a peak at 18 K with a value of 760 W/mK, even larger than that of FeSb$_2$, contrasting its much smaller $S$ peak again. The large $\kappa$ hinders realization of a large ZT in FeSb$_2$.

![Figure 2. Thermoelectric power factor (a) and thermal conductivity (b) of the two FeSb$_2$ and one RuSb$_2$ single crystals. Data of the FeSb$_2$ (SF) was taken from reference [2].](image)

The Hall coefficient $R_H(T)$ is shown Fig. 3 for the two systems. $R_H(T)$ is negative in the whole temperature range, pointing to electron dominated transport properties. Above 100 K, $R_H$ of FeSb$_2$ is 4 orders of magnitude smaller than that of RuSb$_2$. Below 30 K, close values were obtained for the FeSb$_2$(SF) and RuSb$_2$ samples, while that of FeSb$_2$(VT) is more than one order of magnitude smaller. Applying a simple one-band model for FeSb$_2$, the high carrier concentration $n (1/|R_H|e)$ at above 100 K and its drastic $T$-dependence on cooling evidence the narrow gap features with enhanced narrow bands at the edges. As was mentioned before, the same crystal structure and similar band structure hint at analog physical
properties of the two systems. Indeed the thermal conductivity and the Hall effect exhibit similar behaviors, while the PF of FeSb$_2$ exceeds that of RuSb$_2$ by two orders of magnitude. The very different thermopower and PF values in the two systems exclude a predominant phonon drag contribution alone in FeSb$_2$. Differences of the band gap are not able to account for the difference in thermoelectric, as well as in magnetic properties. Conventional theory gives a larger thermopower for semiconductors with a larger gap and less carriers, which is contrary to our observations. Therefore, it seems reasonable to relate the origin of the enhanced PF in FeSb$_2$ to the correlation effects, while other mechanisms related to the unusual magnetic properties could also be involved. In addition, a careful analysis of the fine structures of thermopower indicates an enhanced diffusion contribution [12]. Combining the Sommerfeld coefficient from the electronic specific heat and the one-band carrier model, we obtain a relatively large electron effective mass of 14 times that of free electron for FeSb$_2$. This enhanced value suggests a considerable involvement of strong correlation effects in the thermoelectric properties.

4. Conclusion
We compared transport and magnetic properties of the iso-structural FeSb$_2$ and RuSb$_2$ and confirmed the extremely large thermopower of FeSb$_2$. At low temperatures, the less enhanced thermopower and the small power factor in the RuSb$_2$ showing a similar carrier concentration evidence an extra contribution to the largely enhanced values of both thermopower and power factor in FeSb$_2$. The existence of correlated electrons that are absent in RuSb$_2$ is likely to be the origin of the extra contribution in FeSb$_2$. The correlation-enhanced thermoelectric power factor would be of great interest not only in application, but also in theoretical aspect for designing new thermoelectric materials particularly for low temperature operation.

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