ENHANCED THERMOPOWER OF THE NARROW-GAP SEMICONDUCTOR $FeSb_2$

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The study of thermoelectric properties of semiconductors recently became an active field in condensed matter physics. Thus far, materials with high thermoelectric performance have been found for the temperature above room temperature. However, at cryogenic temperatures no systems with sufficiently high thermoelectric properties have been discovered for possible application. One of the routes to enhance their efficiency are semiconductors with enhanced low-temperature thermopower due to strong electronic correlation. The thermoelectric performance of substances are given by the dimensionless figure of merit $ZT=TS^2\sigma/\kappa$ where S depicts the thermoelectric power, σ the electrical conductivity and κ the thermal conductivity [1]. For applications ZT values larger than 1 are required. In a simple approach of neglected lattice thermal conductivity and the validity of the Wiedemann-Franz law the thermoelectric power can be estimated to be necessarily higher than $150\mu V/K$ for ZT=1.

Around room temperature doped Bi_2Te_3 as n-type and Sb_2Te_3 as p-type semiconductor are still the most commonly used materials for thermoelectric generators (TEG) [2]. Below room temperature a Bi-Sb alloy with small amounts of Sb as n-type semiconductor is found to be the most efficient substance [3]. Its maximum ZT lies in the temperature range of 150K to 300K. Effective cooling has been shown if Bi-Sb alloys are used for thermoelectric refrigeration. However, below that temperature no system with sufficiently high thermoelectric performance has been discovered.

Very promising material classes seem to be strongly correlated electron systems with partially filled $3d$ or $4f$ bands. In those systems the hybridization between the d or f electrons with the conduction bands lead to high effective masses of the quasiparticles below a characteristic temperature of some tens of Kelvin [4]. The specific heat of so-called heavy fermion systems reveals high Sommerfeld coefficients that are 100 or 1000 times higher than ordinary metals. Also the thermoelectric power is enhanced by some orders of magnitude than that of ordinary metals. Values of several tens of $\mu V/K$ are often observed for heavy fermion systems [5]. Among the heavy fermion systems CeB_6 was successfully used to build a simple Peltier cooler with a maximum $S(T)$ of $120\mu V/K$ at 9K and an effective cooling of 0.2K at 4.5K (ZT=0.3 at 7K) [6].

Further enhancement of ZT seems to be possible only for the case of a semiconducting system with strong correlation. In rare cases the hybridization leads to a gap opening below the characteristic temperature. Those systems are referred to as Kondo insulator. Well studied compounds are $Ce_3Bi_4Pt_3$, YbB_{12} and SmB_6 [7]. They exhibit a semiconducting conductivity at low temperatures due to the formation of a hybridization gap. The thermoelectric power reaches values above $100\mu V/K$ [8]. For the $3d$-electron system FeSi the thermoelectric power exhibit values up to $500\mu V/K$ at 50K [9]. However, in all the systems the ZT value is small due to the high thermal conductivity of high-quality crystals.

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 [10]. This material has remarkable potential for application as thermoelectric refrigeration.

$FeSb_2$ crystallizes in the orthorhombic marcasite-type FeS_2 structure. The Fe ions are surrounded by distorted octahedrals of Sb atoms. The magnetic susceptibility yields a non-magnetic ground state for the $3d$ electrons of Fe which could be the low spin state of the Fe^{4+} configuration. The susceptibility is diamagnetic and temperature independent up to 50K and shows thermally activated paramagnetic behavior at higher temperatures.

First, a description of sample preparation and characterization will be given. Second, the experimental results such as resistivity, thermoelectric power, Hall effect and thermal conductivity will be shown and discussed.

Single crystalline samples of $FeSb_2$ were grown by chemical vapor transport technique with Br as a transport agent. Large single crystals of high purity were obtained with lengths of almost 5mm. Two samples of different batches (S1 and S2) are presented here. Sample S1 was oriented along a and sample S2 along c by Laue diffraction. Resistivity and Hall effect are measured in a standard ac setup in a commercial PPMS machine (Quantum Design) in the temperature range between 1.5K and 300K. The thermal conductivity and thermoelectric power were performed with the thermal transport option in a PPMS by means of a relaxation method with one heater and two thermometers for S1 and with a home-built cryostat for S2.

The resistivity $\rho(T)$ of $FeSb_2$ follows a semiconducting behavior below room temperature with two regions of thermal activation separated by a plateau around 20K (Fig. 1). The gap sizes obtained by fitting $\rho=\rho_0 \exp(E_g/2T)$ are estimated to
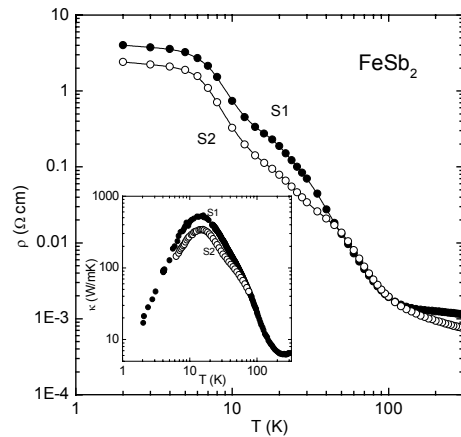

Fig. 1: Resistivity ρ of $FeSb_2$ vs T. Sample S1 and S2 are prepared by the same technique, however, from different batches. The inset shows the thermal conductivity κ.

320K (350K) for the high-T part and 54K (52K) for the low-T side for sample S1 (S2). These values are in good agreement with previous reports [11].

The Hall effect $R_H(T)$ confirms the activated behavior below room temperature. Fig. 2 shows the Hall effect $R_H=\rho_{xy}/B$ for $B=1T$. Below 30K the Hall effect $|R_H|$, R_H being negative at low T, increases to a maximum at 7K. In a single-band model the carrier concentration at 10K is estimated to $n=0.6\cdot10^{22}$ m^{-3} (S1) and $3.5\cdot10^{22}$ m^{-3} (S2). Towards higher temperatures the charge carrier concentration increases rapidly. For sample S1, a sign change is observed around 50K followed by a second sign change at 140K (Inset of Fig. 2). Such behavior is not observed for sample S2. Nonetheless, the Hall effect evidences the existence of multiple bands at the Fermi surface with electron-like and hole-like character. Calculation within a two-band model by Hu et al. derived a huge carrier mobility [12]. The differences between sample S1 and S2 are denoted by different resistivity values as well as different Hall coefficients at low temperatures. We conclude that the differing sample quality causes variations in the transport properties. Sample S2 contains a larger amount of
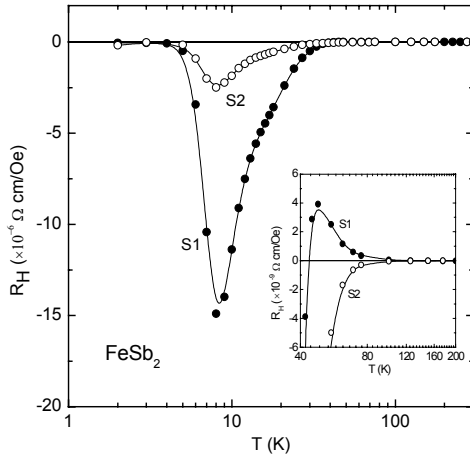
Fig. 2: Hall coefficient R_H vs T of FeSb$_2$. The inset shows the enlarged region between 30K and 200K.

Fig. 3: Thermopower S vs T for FeSb$_2$. The inset shows the enlarged region between 30K and 200K.

impurities or defects in the crystal than sample S1. However, it is most likely that the leveling of ρ for sample S1 is also due to a tiny impurity concentration.

The thermoelectric power $S(T)$ of FeSb$_2$ is displayed in Fig. 3. Extremely large values in the order of -30mV/K for sample S1 and -10mV/K for S2 at 10K are observed. These values agree well with previously reported results on single crystals grown by a self-flux technique [10]. As the Hall effect, the thermopower exhibits negative values below 30K at which the smaller gap opens. Also here, the thermopower of sample S1 shows the overshoot around 50K that was found in the Hall coefficient for the same sample. The maximum values of $|S|$ are largely enhanced compared to the thermopower of related systems. As mention above the system FeSi with similar underlying physics exhibits values of 0.5mV/K at slightly higher temperatures (50K) [9]. The sample dependence previously described also plays a role in the absolute values of $S(T)$. The thermopower of the sample with fewer impurities (S1) yields values that are a factor of 3 larger than that of S2.

The thermal conductivity κ of FeSb$_2$ is plotted in the inset of Fig. 1. It is dominated by a large peak around 20K. For a
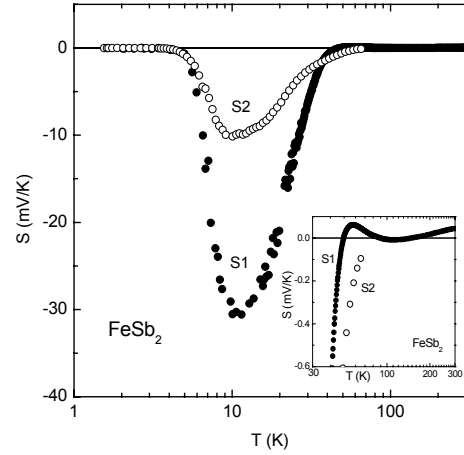
semiconductor with high mobility the large phononic mean free path yields a high thermal conductivity. At low temperatures the thermal conductivity is thus dominated by the heat transport by phonons. However, a T^3 dependence as expected for boundary scattering cannot be fit to the low-temperature data. Above the maximum Umklapp scattering leads to a decrease of κ. For Umklapp scattering, a temperature dependence of $1/T$ is expected. However, for FeSb$_2$ a shoulder around 50K is observed. At this temperature, also R_H and S show features like the sign change and the successive maximum at 50K, particularly in sample S1.

FeSb$_2$ meets the requirements for high thermoelectric performance. It is a semiconductor with very low charge carrier concentration and high mobility. The thermopower at low temperature is extremely large. However, in order to obtain large ZT values the thermal conductivity of the singe crystals exhibit too high values due to the large phononic contribution. If focused on the numerator of ZT – the so-called power factor $PF=S^2\sigma$ which is shown in Fig. 5, a broad maximum with high values below 30K is deduced. The values at the maximum of

$2600\mu W/cmK^2$ depict record values among all thermoelectric materials [10]. The aim of achieving high *ZT* values are 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 changes drastically. Isoelectronic substitution on the Sb site apparently varies the band structure resulting in a higher charge carrier concentration [13]. A strongly reduced thermopower is accompanied by a lower resistivity.

Causes for the huge thermopower values in $FeSb_2$ are still under debate. In many clean semiconductors like Ge the thermopower is dominated by the phonon drag effect which is responsible for a sharp peak in the thermopower around 10K to 50K. For $FeSb_2$ the temperature dependence indicate an additional effect which yields a broad minimum in $S(T)$. The structure of the thermopower with additional features around 50K cannot be explained by the phonon drag alone. The non-magnetic reference compound $RuSb_2$ which has been studied recently exhibits very similar resistivity and thermal conductivity. However, its thermopower is smaller by one order of magnitude than that of $FeSb_2$ [14]. Although the origin of the large thermopower in $FeSb_2$ is still under debate strong correlations seem a likely cause of the enhancement of S. The formation of hybridized states at the Fermi energy which lead to a steep peak of the density of states $N(E)$ at E_F would enhance the thermopower as it is given by $S=\mathrm{d}\ln N(E)/\mathrm{d}E\_E_F$. Furthermore the excitation of spins from the low spin to the high spin state in the intermediate temperature might lead to a large thermopower. The entropy connected to spin excitations results in an enhanced thermopower. Further investigations have to be performed in order to reveal the causes of the high thermopower.
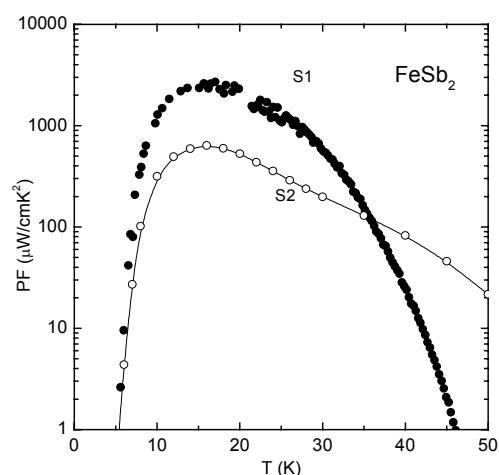

Fig. 4: Power factor PF vs. T for $FeSb_2$.

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