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Transport properties of FeSi

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Abstract

We have measured thermoelectric power, thermal conductivity and electric resistivity on FeSi samples, single crystal and polycrystals, with different qualities. Our data can be understood in terms of classic semiconductor physics. Good agreement is found with the results from recent band structure calculations.

Keywords: FeSi; Kondo insulators; Thermoelectric power; Transport properties

FeSi is a small gap semiconductor [1] which has been studied for more than 30 years owing mainly to its unconventional magnetic properties. In the last years, a Kondo insulator description has become popular to account for these properties [2, 3], but recent band structure calculations invoking spin fluctuations at higher temperatures [4] were also able to explain most of the magnetic properties.

The transport properties of FeSi were found to be strongly sample-dependent, presumably due to the extended homogeneity range $Fe_{1+x}Si_{1-x}$ [5]. Commonly, small Si-excess is used for the sample preparation to avoid ferromagnetic impurity-phases [6]. In order to separate the intrinsic from the impurity effects, we have measured thermoelectric power, thermal conductivity and resistivity between 1.5 and 300 K on a single crystal (sc) as well as on stoichiometric, off-stoichiometric and Ge-doped polycrystalline (pc) samples.

Polycrystalline samples were obtained by argon arc-melting the pure elements with 5 N (Fe) and 6 N (Si, Ge) purity. All samples were annealed in high vacuum at 1000°C for 120 h. The single crystal investigated was obtained by zone-melting. X-ray patterns of the polycrystalline samples showed reflections belonging to the FeSi-structure only. However, both the stoichiometric samples and the samples rich in Fe contain a minor amount of ferromagnetic impurity. The lattice parameter a is almost independent from exact stoichiometry for undoped samples and increases from 4.49 to 4.53 Å for the sample doped with 25% Ge.

Thermoelectric power (TEP) and thermal conductivities were measured using a steady-state method with one end of the samples thermally anchored to the cold plate of a commercial He^4-cryostat whose temperature could be varied between 1.5 and 300 K. Small temperature gradients

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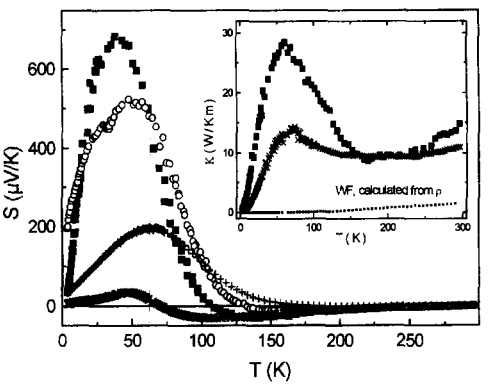

Fig. 1. TEP versus temperature for stoichiometric pc (■), sc (O), $Fe_{0.98}Si_{1.02}$ (+) and $Fe_{1.01}Si_{0.99}$ (x). Inset: Thermal conductivity for pc and $Fe_{1.01}Si_{0.99}$. Dashed line shows electronic contribution as calculated from the resistivity of the stoichiometric sample using WF law.

(typically 50 mK) were provided by a heater fixed to the other end of the samples and were measured using AuFe versus Chromel thermocouples. The DC-resistivity was measured in the same run.

First, we want to address the effects of stoichiometry variations on the low-temperature properties. As already pointed out by Wolfe et al. [6], TEP of FeSi is highly sensitive to sample quality. Fig. 1 depicts the TEP measured on polycrystalline samples $Fe_{1-x}Si_{1+x}$ with x (0.02, 0, − 0.01) and on the single crystal. Both the stoichiometric pc and the sc show a behavior rather similar to that reported in [6], with a small positive TEP at high temperature, a first zero-crossing around 280 K, a shallow minimum around $T_1 = 150$ K and a huge positive maximum at low temperatures. The maximum value S_{max} around $T_2 = 50$ K, which can be taken as a measure of the inverse impurity concentration, is substantially larger in our samples compared to [6], pointing to a good sample quality. This magnitude is strongly reduced in the off-stoichiometric samples. Both characteristic temperatures T_i are shifted to lower values for the Fe-rich sample and to higher values for the Si-rich sample. Compared to the stoichiometric pc, the sc has slightly higher T_i's and smaller S_{max} pointing to a little Si-excess. The overall dependences of both the magnitudes and the T_i on the impurity concentrations are in very good agreement with the diffusion TEP calculated from band structure [4].

For all samples, the TEP decreases as A/T as temperature is raised above T_2. This $1/T$ dependence holds up to T_1. Assuming that the diffusion TEP alone is responsible for this temperature dependence, the value of the semiconducting gap can be estimated from A to be 900 and 820 K for the pc and the sc, respectively. These values are between those deduced from fits of the resistivity [3, 7, 8, 9] and those from modelling the susceptibility [3, 10]. Sales et al. [10] claimed a strongly enhanced phonon-drag contribution for the large maximum. The peak position which is expected around $0.15\theta_D$, ($\theta_D = 313$ K [11]) corresponds rather well to this description, but a $1/T$ dependence should show up only at temperatures above θ_D.

At low temperatures the TEP increases linearly with T at least up to 15 K consistent with a variable range hopping (VRH) mechanism as deduced from the resistivity ρ which follows $\rho = \rho_0 \exp(T/T_0)^{1/4}$ in the same temperature range. VRH conductivity is commonly observed for pure FeSi [9] as well as for doped pc material [8]. An activated behavior can be fitted for any sample in a rather small temperature range between 100 and 200 K. Gap values obtained from these fits are smaller than those from TEP (app. 630 K for stoichiometric samples), but in good agreement with values reported, e.g., in Ref. [8]. Resistance data are depicted in Fig. 2. Room temperature resistivities vary between 180 and 500 μΩ cm.

As expected from the low carrier concentration in FeSi, the thermal conductivity is dominated by phonons in the whole temperature range investigated (cf. inset Fig. 1) with a peak around 50 K which is much more pronounced for the stoichiometric pc and sc than for other samples. The dashed line indicates the electronic contribution as calculated from the resistivity using the Wiedemann–Franz law.

Doping with 5% Ge leads to rather small changes of the TEP at higher temperatures (cf. Fig. 3), but the T_i are shifted to slightly lower temperatures and the minimum gets more pronounced. In contrast to the linear T-dependence at low T in undoped samples the TEP is clearly proportional to T^3 up to 25 K (cf. inset Fig.3), indicating a dominating

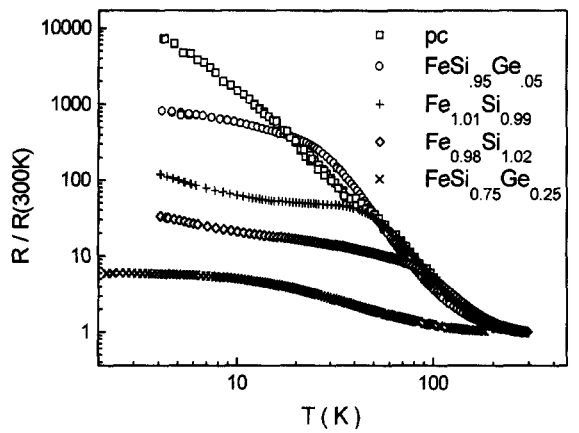

Fig. 2. Electric resistivities normalised to room temperature values versus temperature for different samples (see legend). Data for sc are very close to that of stoichiometric pc and have been omitted for clarity.

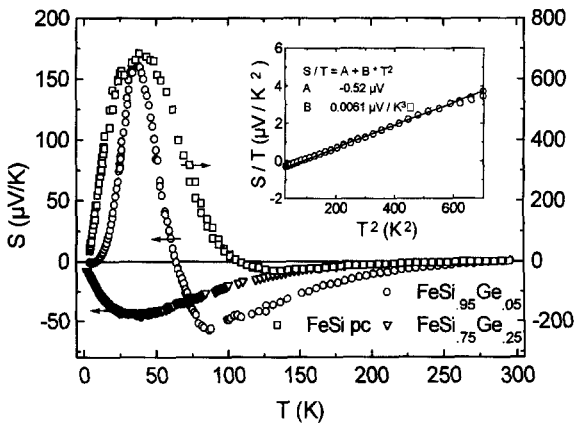

Fig. 3. TEP versus temperature for $FeSi_{1-x}Ge_x$ ($x = 0.05, 0.25$: left scale, $x = 0$: right scale). Inset shows S/T versus T^2 for $x = 0.05$ from 2 to 25 K.

phonon-drag mechanism in this temperature range. Since in this case $S = C_v\,(N\,e)^{-1}$, one can calculate the carrier number to $N = 5 \times 10^{21}$/mol using $\theta_D = 313$ K for the lattice specific heat.

Larger amounts of Ge lead to a complete suppression of the low-T maximum and a TEP that is negative in the whole temperature range, indicating n-type conductivity. As the gap deduced from ρ is reduced to only 88 K, it is likely that the characteristic T_i are strongly shifted towards lower T.

In summary, thermopower, thermal conductivity and resistivity data presented here can be understood applying classical semiconductor physics. Very good agreement is found with the calculations presented in [4]. Stoichiometry variations within the homogeneity range of FeSi dramatically influence all properties discussed. Although the 1 : 1 pc contains a small ferromagnetic impurity, this sample shows the most pronounced features in general, indicating that this composition most closely matches pure FeSi.

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