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Impurity band conduction in $FeSi_{1-x}Al_x$

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Abstract

Precise resistivity and thermopower measurements across the metal insulator transition in Al doped correlated semiconductor FeSi are reported. Doping of carriers results in the emergence of electronic states at the Fermi level. For sufficient concentration of dopant, these states form into an impurity band. The properties of such systems are governed by this impurity band at low temperatures and the semiconducting bands at higher temperatures. Here we show the applicability of such a two-band structure to account for the temperature dependence of resistivity and thermopower in metals near the metal insulator transition.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

FeSi is a correlated non-magnetic semiconductor having an energy gap of about 50 meV. It has been attractive among the scientific community for more than three decades due to its unusual magnetic properties [1–5]. Insulator to metal transition is observed for substitution in both sites, Fe [6–9] and Si [10–12]. In the ligand site of Si, hole doping through aluminum leads to a heavy Fermi liquid metal with a critical concentration of $x_c = 0.005$. Metal insulator (MI) transition in $FeSi_{1-x}Al_x$ is identified to be similar to Si:P [11, 12]. Mass enhancement of carriers arises from the strong correlations involved. Substitution of carriers into a semiconductor will result in the appearance of electronic states at the Fermi level. As carrier doping increases, these electronic states form into a half filled impurity band leading to an MI transition. The temperature dependence of resistivity ρ shows a broad peak ($T_{\rho P}$) for metals near MI transition. As concentration of dopant increases, $T_{\rho P}$ shifts to higher temperatures and vanishes for metals far from the MI transition [11–13]. Below $T_{\rho P}$, ρ has a positive temperature coefficient corresponding to metallic behavior. While for $T > T_{\rho P}$ an exponential decrease in ρ is observed. Similarly thermopower S also shows a peak (T_{SP}) in its temperature dependence. Below T_{SP}, S has a linear temperature dependence, while above T_{SP}, S decreases as T^{-1}. The temperature dependence of ρ and S may be represented by a metal in parallel with that for a semiconductor. This two-band or parallel-resistor model was extensively used in describing high temperature superconductors [14] as well as Kondo semiconductor/semimetal CeNiSn [15]. However, such a quantitative attempt for metals derived by MI transition has not been reported in the literature.

In this paper, we report resistivity and thermopower measurements on Al doped FeSi across the MI transition. The temperature dependences of ρ and S in doped samples are described on the basis the model mentioned above.

2. Experimental details

Polycrystalline samples were prepared by taking elements of purity better than 99.95%. Ingredients in stoichiometric proportions were melted in an argon arc furnace. Ingots thus formed were drawn into rectangular rods. Samples were annealed in evacuated quartz ampoules at 1000 °C for one week to increase the homogeneity and to relieve strain. X-ray diffraction measurements were carried out using a Rigaku diffractometer with Cu Kα radiation. The absence of impurity peaks reveals that the samples were formed in a single phase. Resistivity measurements were carried out down to 2 K in the four probe configuration. Thermopower measurements were carried out by the differential sandwich method using a closed cycle refrigerator in the temperature range of 4–300 K with an in-house developed platform.

3. Results

Resistivity measurements down to 2 K are shown in figure 1. For FeSi, resistivity increases by four orders of magnitude

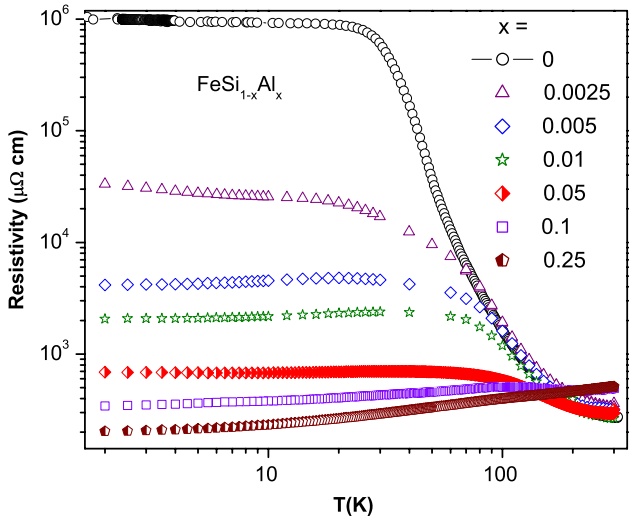

Figure 1. Resistivity measurements down to 2 K for $x = 0$–0.25 in $FeSi_{1-x}Al_x$.

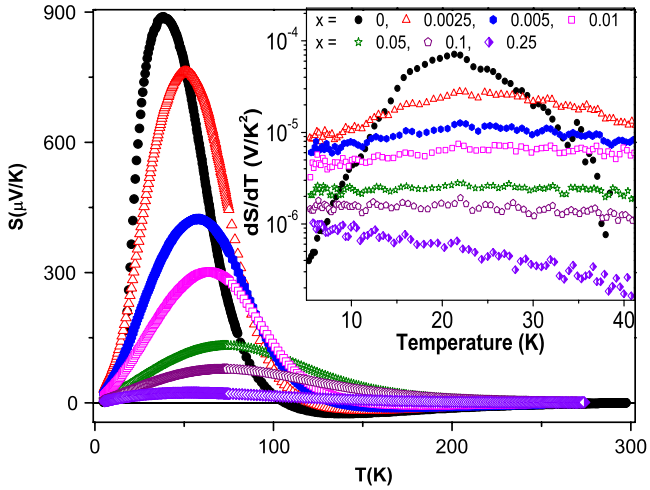

Figure 2. Thermopower of Al doped FeSi up to $x = 0.25$. As the concentration of carriers increases, the absolute thermopower at low temperatures decreases. High temperature negative thermopower becomes positive as Al concentration increases due to hole doping. (Inset) dS/dT showing linear S below 40 K for doped samples.

upon cooling from 300 to 2 K. Activated behavior is observed in the temperature range of 30–200 K with an activation energy ≈640 K. Slope change below 30 K is attributed to extrinsic conduction through variable range hopping. Resistivity is substantially reduced by a small amount of Al substitution. MI transition occurs for $x_c = 0.005$ which is on a par with the literature value [11, 12]. For $x = x_c$, a peak in resistivity is observed at $T_{\rho P} = 20$ K. As aluminum concentration increases, $T_{\rho P}$ shifts to high temperatures. For $x = 0.1$, $T_{\rho P} = 107$ K and vanishes for $x = 0.25$ (figure 3).

The thermopower down to ≈4 K is shown in figure 2. At 300 K, S for all the samples is very small, of the order of 1 μV K^{-1} or less. For FeSi, thermopower becomes negative when the temperature is decreased below 290 K. A negative peak of 25 μV K^{-1} is observed at 150 K. The manifestation of a gap in the density of states below 200 K results in a large

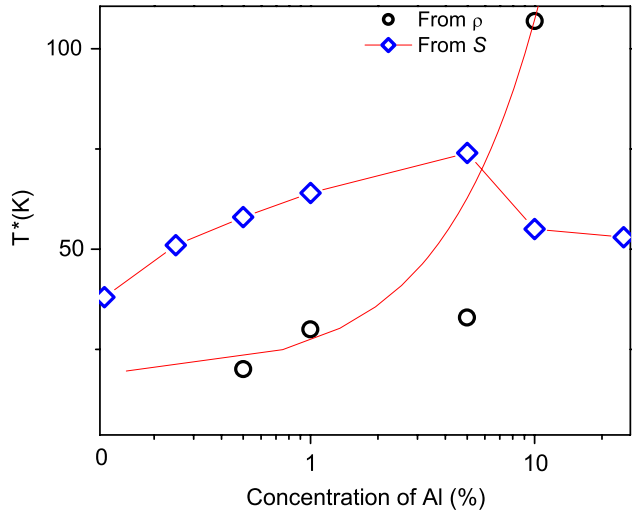

Figure 3. The temperature corresponding to the peak in resistivity and thermopower as a function of Al concentration. The peak shifts to higher temperature as concentration is increased. For the resistivity, the peak vanishes for $x = 0.25$. However, for thermopower we find a peak for $x = 0.25$.

positive peak at 35 K (figure 2). This low temperature peak may have an origin either from the phonon drag mechanism [6] or the correlations which makes S become zero [16]. As aluminum concentration increases, S above 150 K become more positive as compared to FeSi. For concentrations of 5% and above, S is positive over our temperature range of measurements. At low temperatures, a linear temperature dependence of S is observed. This is indicated by constant dS/dT (inset of figure 2). A huge increase in S at 5 K for a small amount of Al doping is observed. Again, S decreases for an increased amount of Al doping. It is to be noted that the FeSi has the lowest value of S at 5 K. Thus, the observed features are due to an increase in the number of carriers at the Fermi level resulting in a decrease of contributions from the phonon drag mechanism [17]. In figure 3, we show the temperature T_{SP} as a function of Al concentration along with $T_{\rho P}$. The peak shifts to high temperature as Al concentration increases and then decreases to lower temperatures for $x \geqslant 0.1$

4. Discussion

4.1. Description of the model

For a two-band conduction, the effective conductivity is given by

$$\sigma = \sigma_1 + \sigma_2 = 1/\rho. \quad (1)$$

The contributions from different bands add as the resistors are in a parallel configuration. The σ_1 is from the metallic impurity band. For simplicity, we assume the linear temperature dependence of resistivity for this band as $\sigma_1 = (\sigma_{01}^{-1} + aT)^{-1}$. σ_2 is the activated conduction from semiconducting bands as $\sigma_2 = \sigma_{02}\exp(-E_g/2k_BT)$, where E_g is the activation energy and k_B is the Boltzmann constant.

Thermopower for this configuration is derived using the Nordheim–Gorter rule [18] as

$$S = (S_1\sigma_1 + S_2\sigma_2)/(\sigma_1 + \sigma_2) \quad (2)$$

Table 1. Parameters of fitting of resistivity and thermopower using equations (1) and (2), respectively.

Concentration (%)	$1/\sigma_{01}$ ($\mu\Omega$ cm)	a ($\mu\Omega$ cm K^{-1})	$1/\sigma_{02}$ ($\mu\Omega$ cm)	$E_{g\rho}$ (K)	A (μV K^{-2})	C (μV K^{-1})	E_{gS} (K)
1	2323	0.913	0.02466	810	5.597	−347.4	813
5	687	0.249	0.00892	666	2.315	−425.7	645
10	367	1.908	0.00385	616	1.479	−375	475
25	199	3.367	0.00152	163	0.742	−204.6	209

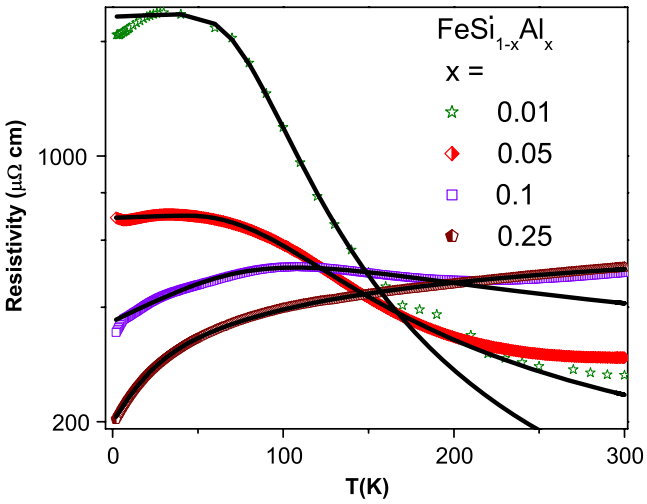

Figure 4. Resistivity for $x > x_c$ is fitted using equation (1). The fit improves over a larger temperature range at higher concentration due to the well formed impurity band. The parameters are tabulated in table 1.

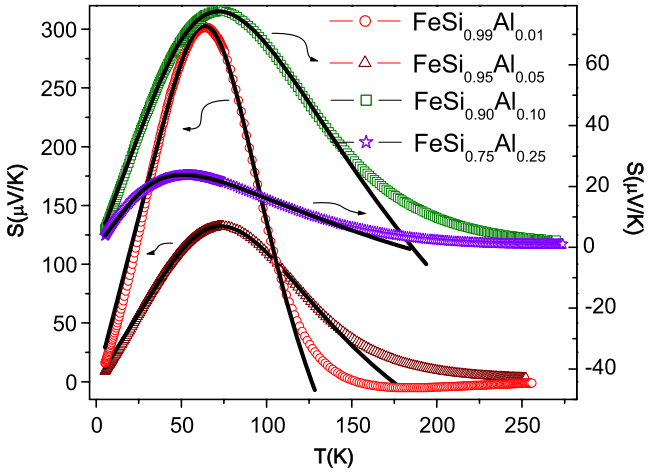

Figure 5. Two-band model of thermopower of Al concentration $x = 0.01$, 0.05 and 0.1 and 0.25. The open circles are the experimental data points and the solid line represents the fit using equation (2).

where $S_1 = AT = \pi^2 k_B^2 T/2eE_F$ is the diffusion thermopower for metals and S_2 is the thermopower for semiconductors. $S_2 = C + 8.61E_g/T$ is for the present case [16]. For metals far from the MI transition, one can use the simplified version of this equation [14].

At low temperatures, as activated carriers freeze out, the conductivity is dominated by the impurity band, leading to a positive coefficient of resistivity and a linear thermopower. At high temperatures, electrons at the valence band will gain sufficient energy to jump into the conduction band and these activated carries dominate the conductivity. Hence, an exponential decrease in resistivity and an inverse temperature dependence of thermopower are the expected outcomes.

4.2. Two-band description for $FeSi_{1-x}Al_x$

Doping of Al in FeSi introduces holes at the Fermi level. In the semiconducting regime, i.e. for $x < x_c$, the electronic states will be localized and the hopping conduction will dominate. In such cases, it is not possible to fit the resistivity by equation (1). However, for $x > x_c$ the electronic states will form into a band. Then the conductivity at low temperature is dominated by this band leading to a metallic behavior. The resistivity for samples with $x = 0.01$–0.25 is plotted in figure 4. The solid line represents the fit using equation (1). The parameters of the fit are given in table 1. At low concentration of Al, the temperature dependence of metallic conductivity is negligibly small. The scattering from this band acts as a background resistivity $\rho_{01} = 1/\sigma_{01}$ over which semiconducting behavior is seen. However, below 20 K there is a drop in resistivity for $x = 0.01$ which cannot be accounted for by this model. This is due to the assumption of linear resistivity for the metallic band. The resistivity of metals close to MI transition has a different temperature dependence than that assumed, and hence deviations are observed for this composition. Again, at high temperatures, the fit deviates from the parallel-resistor model due to the closure of the activation gap. As concentration of Al increases, the coefficient a of the metallic contribution increases and the gap value decreases. Hence, the fitting is applicable below 200 K for $x \leqslant 0.1$. However, at $x = 0.25$, metallic contribution dominates with resistivity similar to metals like Cu, hence our assumption of σ_{01} is true over the entire temperature range.

In the case of heavily doped semiconductors or metals near the metal insulator transition, the temperature dependence of S is described by equation (2) [19]. Figure 5 shows the two-band model fits for thermopower using equation (2). The parameters $1/\sigma_{01}$, a and $1/\sigma_{02}$ are taken from table 1. The activation gap E_{gS} is taken as a variable while fitting. The values A, CE_{gS} are tabulated in table 1. The term A decreases as Al concentration increases due to an increase in the carrier concentration. The values reach dS/dT in the zero temperature limit for metals far from the MI transition. The activation gaps estimated from resistivity and thermopower are in good agreement with each other. However, the values are higher

than those estimated from simple activation behavior alone at high temperatures [11, 12]. This is due to the removal of electronic states at the band edges and the appearance of states at the Fermi level when carriers are doped. Hence, at low concentration of Al, where the states at the Fermi level are localized, the effective gap estimated from the two-band model has a larger value.

5. Conclusion

The conductivity in metals near MI transitions has two contributions. At low temperatures, the conductivity is dominated by the impurity band leading to a positive coefficient of resistivity and a linear temperature dependence of thermopower. At high temperatures, the activated carriers dominate the conductivity with an exponential and inverse temperature dependence of resistivity and thermopower respectively. A parallel-resistor model can be used to describe the temperature dependence of resistivity and thermopower of such systems.

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