Modified scaling of thermopower to heat capacity observed with low-temperature measurements in $FeSi_{1-x}Al_x$

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Low-temperature thermopower S and heat-capacity C measurements are reported for Al-doped correlated semiconductor FeSi. Scaling proposed by Behnia *et al.* [J. Phys.: Condens. Matter **16**, 5187 (2004)] for metals is shown to be invalid for metals derived by metal-insulator transition in FeSi due to low carrier density n. We invoke the entropy of the free carriers to show that $\epsilon+\mu=1$ where $C/T=\gamma\propto n^{\epsilon}$,$S/T\propto n^{-\mu}$ in the zero-temperature limit for all the systems. We define a modified scaling by taking carrier concentration into consideration. We show that universality of the scaling relies on electronic entropy of the free carriers.

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I. INTRODUCTION

Thermopower S in a generalized form is given by Mott formula:[1]

$$S=-(\pi^2/3)(k_B^2T/e)(d\ln\sigma/dE)_{E=E_F}, \quad (1)$$

where k_B is the Boltzmann constant, e is the electronic charge, E_F is Fermi energy, and σ is the electrical conductivity. S depends not only on the conductivity but also on its energy derivative.

In metals conductivity arises due to electron diffusion and hence the above expression leads to[1]

$$S=(\pi^2k_B^2/2e)(T/T_F)=\gamma T/ne. \quad (2)$$

Here γ is the Sommerfeld coefficient and is given by

$$\gamma=C_{\mathrm{el}}/T=(\pi^2/2)(1/T_F)nk_B, \quad (3)$$

where C_{el} is the electronic specific heat and n is the carrier density.

Recently Behnia *et al.*[2] noticed the importance of correlation between S/T and γ in the zero-temperature limit. This leads to a scaling in metals as

$$q=(S/T)N_{\mathrm{av}}e/\gamma=\pm 1, \quad (4)$$

where N_{av} is the Avogadro's number. Compilation of heat-capacity C and S at low temperatures on various systems is done by Behnia *et al.*[2] In real systems different scattering mechanisms/interactions will contribute differently to the thermopower. In such cases it is difficult to separate out the contributions from different mechanisms. Hence, the validity that q should be constant and equal to unity is questionable. However, most of the metals show remarkable validity of $|q|\simeq 1$, irrespective of whether the system is a simple metal or a heavy fermion. Exception was observed for low carrier density system CeNiSn.[2] We expect this to be true for other low carrier density systems too like metals near metal-insulator (MI) transition. Hence, we choose metals derived by MI transition in correlated semiconductor FeSi through Al substitution. FeSi has a narrow activation gap of about 50 meV. For more than three decades, FeSi has been attractive due to its unusual magnetic properties.[3–7] Metals derived by Al doping in FeSi are heavy Fermi liquids.[8,9] Similarities in MI transitions between Si:P and $FeSi_{1-x}Al_x$ suggest that this is an ideal system to check the universality of the S/T to γ scaling.

In this paper, invalidity of $|q|\simeq 1$ is shown for metals derived by Al substitution in FeSi. Such an invalidity is discussed by considering low carrier density of metals near MI transition. We invoke the entropy of the free carriers to show that $\epsilon+\mu=1$ where $\gamma\propto n^{\epsilon}$, $S/T\propto n^{-\mu}$ in the zero-temperature limit for all the systems. A modified scaling is thus defined by taking into consideration the carrier concentration to have a universality.

II. EXPERIMENTAL DETAILS

Polycrystalline samples were prepared by taking elements of purity better than 99.95%. The ingredients in stoichiometric proportions were melted in an argon arc furnace. The samples were then vacuum sealed and annealed at 1000 °C for one week. Thermopower measurements were carried out using a closed cycle refrigerator in the temperature range of 4–300 K. Conventional differential sandwich method with an in-house developed measurement platform has been employed. Heat-capacity measurements were carried out down to 2 K using a Quantum Design PPMS.

III. RESULTS

Thermopower measurements down to $\simeq$4 K for the parent FeSi and Al-doped samples are shown in Fig. 1. At 300 K, S is positive and has a value of about 1 μV/K for all samples. In FeSi, S becomes negative when temperature is decreased below 290 K. It reaches to a negative peak of value 25 μV/K at 150 K. Manifestation of a gap in the density of states below 200 K results in a large positive peak of 900 μV/K at 35 K. In literature,[9–12] the peak values vary from 300 μV/K to 900 μV/K.[12] It has been shown that the maximum peak value appears for the exact stoichiometric samples while it reduces drastically for off-stoichiometric samples.[11] One can also see in the literature[9–12] that for all these samples, resistivity has an increase of 4 orders of magnitude when cooled from 300 K to 4 K which is similar to the present case.[13] Since S is very sensitive to carrier density, for semiconductor, it is expected that the higher the S values, the higher the quality of the samples. In FeSi, S approaches

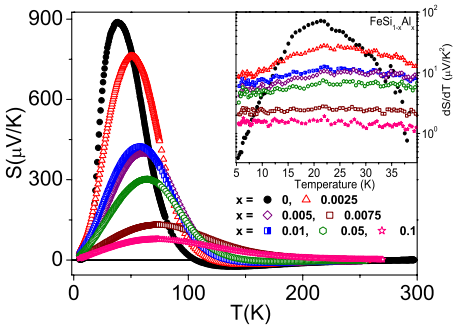

FIG. 1. (Color online) Thermopower of Al-doped FeSi up to $x=0.1$. Introduction of carriers decreases the absolute thermopower at low temperatures. High-temperature negative thermopower becomes positive as Al concentration increases due to hole doping. (Inset) dS/dT showing linear S below 40 K for doped samples.

rapidly to zero below 35 K. The origin of this low-temperature peak may root either from the phonon drag mechanism[10] or to the hybridization out of strong correlations.[14] There is a decrease in absolute value of S due to carrier doping through Al substitution. Large variation of S in the region 30–200 K is observed across the MI transition. The S values of our 5% and 10% doped samples match well with that reported in the literature.[9,10] dS/dT as a function of temperature in the range of 4–40 K is plotted in the inset of Fig. 1. One sees clearly that dS/dT shows a tendency to become constant as Al concentration increases. This shows that there is a linear variation of S with T at low temperatures for FeSi with large aluminum concentrations.

At low temperatures, heat capacity of a metal may be expressed as $C=\gamma T+\beta T^3$. In Fig. 2, C/T is plotted as a function of T^2. Below 10 K, lattice contribution to C may be neglected as there is a large enhancement of γ for doped samples. For $x=0.1$, we observe an upturn in C/T at low temperatures. The possible reason may either be due to excess heat capacity for metals near MI transition due to local moments[15] or due to non-Fermi liquid state.[16] However, measurements below 2 K are required to understand this behavior. More measurements are underway in this regard. Effective mass is estimated from S and C measurements (inset of Fig. 3) by taking nominal Al concentration as carrier concentration n and a band degeneracy of $\nu=8$. The results are

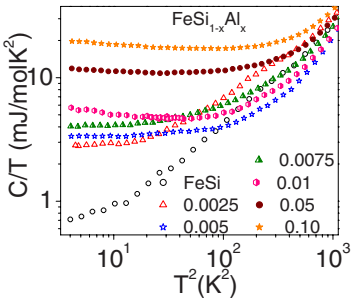

FIG. 2. (Color online) The C/T as a function of T^2 for $FeSi_{1-x}Al_x$. Below 10 K, the lattice contribution to heat capacity is very small as compared to electronic contribution for doped samples. Hence, the enhancement in C/T itself can be taken as an enhancement in γ.

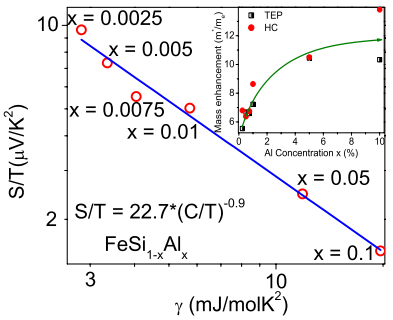

FIG. 3. (Color online) Power-law dependence of S/T on γ for $FeSi_{1-x}Al_x$. The solid line is the power-law fit to the data using an exponent −0.9. This is in contradiction to the observed behavior for other metals as proposed by Behnia *et al.* (Ref. 2). The inset shows mass enhancement (m^*/m_e) estimated from S and C using Eqs. (2) and (3) and relations $k_BT_F=h^2k_F^2/8\pi^2m^*$ and $k_F^3=3\pi^2n/\nu$. The solid line is a guide for the eye.

in good agreement with the literatures values of $(14\pm2)m_e$.[8,9] In Fig. 3, we show a power-law dependence of S/T on γ. The solid line is the fit using an exponent −0.9. The exponent is estimated to be about -0.89 ± 0.06 using least-squares fit. This is in clear contradiction to that proposed by Behnia *et al.*[2]

IV. DISCUSSION

In metals, with $n=N_{\rm av}$, S/T and C/T in the zero-temperature limit are expected to behave as $n^{-\mu}$ and n^{ε}, respectively. The exponents μ and ε depend on the band structure near the Fermi level. For a simple parabolic band $\mu=2/3$ and $\varepsilon=1/3$. However, for metals near MI transition, when approached from metallic side, a divergent S/T is predicted[17–20] as $S/T=(n-n_c)^{-\mu}$. Without loss of generality, we can approximate it to the form $n^{-\mu}$ for metals far from MI transition, but μ will be renormalized depending upon the interactions involved. In case of γ, a deviation from $n^{1/3}$ has been observed,[15,21] but an exact functional form is not known. In Fig. 4, a log-log plot of S/T is shown as a function of Al concentration. The solid line is the power-law fit using

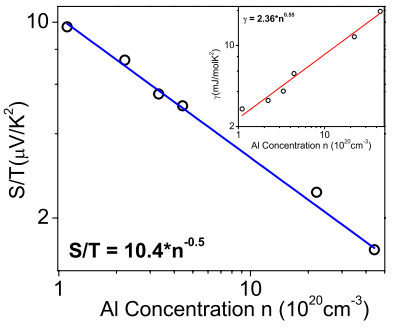

FIG. 4. (Color online) Power-law dependence of S/T as a function of Al concentration. The solid line is the power-law fit to the data using an exponent $\mu=0.5$. The inset shows the Sommerfeld coefficient γ as a function of Al concentration. The solid line is the power-law fit to the data using an exponent $\varepsilon=0.55$. The exponents are far from that of a simple metal.

an exponent $\mu=0.5$. A least-squares fit to the data gives an estimate of the exponent μ to be about 0.52 ± 0.02. This is very close to 0.44 of Si:P.[22] The inset shows the power-law dependence of γ on carrier concentration. The solid line is the fit using $\varepsilon=0.55$. The value of ε is estimated to be about 0.54 ± 0.04 using the least-squares fit. In case of Si:P, $\varepsilon=0.33$ is recovered for metals far from MI transition.[15]

For a metal, $\gamma\propto N_{\mathrm{av}}^{\epsilon}$, $S/T\propto N_{\mathrm{av}}^{-\mu}$, $S/T=\gamma/eN_{\mathrm{av}}$, and hence $\epsilon+\mu=1$. Hence, entropy of free carriers scales S/T as well as γ leading to the validity of S/T to γ scaling for most of the metals.[2] However, for metals near MI transition, n is orders of magnitude less as compared to metals like Cu. Then, the above relations hold if N_{av} is replaced by n as $\gamma\propto n^{\epsilon}$ and $S/T\propto n^{-\mu}$, but ϵ and μ will be renormalized. For cases where $n\neq N_{\mathrm{av}}$, the entropy of the free carriers $\Delta E\propto\gamma\propto n^{\epsilon}$ is still valid [Eq. (3)]. Then from Eq. (2), ΔE will now be proportional to nS/T rather than S/T, leading to $\epsilon+\mu=1$. This appears to be supported from the values of μ and ϵ obtained by plotting S/T and γ as a function of Al concentration (Fig. 4). By taking these entropy relations,[23] the scaling defined in Ref. 2 has been modified. In Fig. 5, nS/T is plotted as a function of γ. The data for samples of Al-doped FeSi are included along with those of $CeCu_2Si_2$ for the field of 4 T,[24,25] $CeCu_6$,[26,27] $CeAl_3$,[28] $CeRu_2Si_2$,[29,30] $CeCoIn_5$ at 6 T,[31,32] $CePt_2Si_2$,[33,34] and $CeSn_3$.[35,36] The data on Si:P (Refs. 15 and 20) with $n=7.3\times10^{18}$ cm^{-3} which is a metal very close to the MI transition are also included. One can see all the systems fall over a universal line.

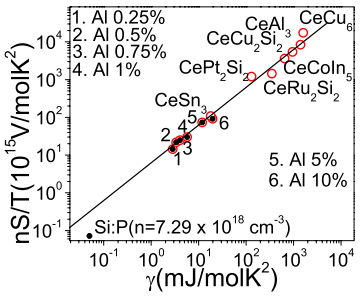

FIG. 5. (Color online) Modified nS/T to γ scaling to account for low carrier systems $FeSi_{1-x}Al_x$ and Si:P also. The solid line represents reference line with a slope of unity in the log-log scale. In linear scale it is the reference line with the slope $1/e$ [Eq. (4)]. Universality of this scaling relies on the entropy of the free carriers. For metals other than $FeSi_{1-x}Al_x$ and Si:P, $n=N_{\mathrm{av}}$ is considered.

V. CONCLUSIONS

In conclusion, we have shown invalidity of scaling proposed by Behnia *et al.*[2] for metals near MI transition. We have also shown that the invalidity arises due to low carrier density of the systems. We invoked the entropy of the free carriers to show that the relation $\epsilon+\mu=1$, where $\gamma\propto n^{\epsilon}$, $S/T\propto n^{-\mu}$ is valid for any system. By considering carrier concentration, a modification is introduced to have universality in scaling.

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