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Thermal and electrical transport properties of ordered $FeAl_2$

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Abstract

The thermal and electrical transport properties of the ordered intermetallic $FeAl_2$ have been measured as a function of temperature between 10 and 300 K. The electrical resistivity (ρ) is about 400 $\mu\Omega$ cm over a broad temperature range. In character, it resembles those of semimetals, in spite of its anomalous low-temperature upturn. The thermal conductivity (κ) at room temperature is high, approximately 7 W m^{-1} K^{-1}. The measured thermoelectric power is negative at low temperatures where there is also a positive phonon-drag effect, but changes to positive values above 220 K. This observation is ascribed to the positive carriers thermally excited across the pseudogap at higher temperatures. The electronic characteristics of $FeAl_2$ are compared to those of other semimetallic materials.

1. Introduction

Materials with complex band structures have been of considerable interest due to their unusual magnetic behaviour and transport properties. Phenomena such as heavy-fermion behaviour, a Kondo insulating state, and unconventional superconductivity are generally found in these materials, and the effect of hybridization has been considered as an important mechanism responsible for these observations [1–4]. These unusual features are commonly seen in rare-earth-based compounds, as the localized f electrons of the rare-earth element have a tendency to hybridize with the s and/or p electrons of other elements. Such a hybridization effect may lead to the formation of narrow electronic gaps or pseudogaps in the Fermi-level density of states (DOS). For transition-metal-based materials, the relatively dispersive d-electronic wavefunctions usually have a weaker hybridization effect but form d bands instead [2]. Hence, it is of particular importance to study the hybridization scenario for unconventional transition-metal-based alloys to shed light on these issues. For example, the semiconducting behaviour observed previously in FeSi and $RuAl_2$ has been attributed to such hybridization-induced (pseudo)gaps in their Fermi-level DOS [5, 6].

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Recent electronic structure calculations predict that $FeAl_2$, crystallized in the tetragonal $MoSi_2$ structure, is also a hybridization-gap semiconductor [7]. However, there is no evidence of such a phase for the reported preparation conditions [8, 9]. Crystallographically, ordered $FeAl_2$ has a triclinic unit cell with $a = 4.878$ Å, $b = 6.461$ Å, and $c = 8.800$ Å; $\alpha = 91.75°$, $\beta = 73.27°$, and $\gamma = 96.89°$. With such a crystal structure, each Fe site is surrounded by a cage of 10–11 nearest neighbours consisting mostly of Al, with an average 1.6 neighbouring Fe sites and 1.8 neighbouring mixing sites [8]. The Fe–Al distances are the shortest for each Fe site in $FeAl_2$, indicating the importance of Fe–Al hybridization. Accordingly, the strong mixing of the d and sp electrons in this material may give rise to unusual band features. To achieve further understanding of the nature of the electronic states in $FeAl_2$, we thus performed thermoelectric power (TEP) measurements, a sensitive probe of energy relative to the Fermi surface, on the title material, $FeAl_2$. In addition, we measured the electrical resistivity (ρ) and thermal conductivity (κ) to complete a full investigation of the transport properties of $FeAl_2$.

2. Experiments and results

The samples studied here were prepared in an induction furnace under a partial argon atmosphere, homogenized by annealing at 850 °C for four days. A Cu Kα x-ray analysis of powdered $FeAl_2$ shows the ordered structure—the same as that reported in the literature [8, 9]. For the present transport measurements, the samples were obtained from the same ingot as was used for the magnetic measurements [10]. The electrical resistivity was measured during a warming process by a standard four-terminal method. The thermal conductivity study was carried out in a closed-cycle refrigerator over the temperature range from 10 to 300 K, using a direct heat-pulse technique. The $FeAl_2$ ingot was cut to a rectangular parallelepiped shape of typical size $1.5 \times 1.5 \times 5.0$ mm^3, and one end glued (with thermal epoxy) to a copper block that served as a heat sink, while a calibrated chip resistor serving as a heat source was glued to the other end. The temperature difference was measured by using an E-type differential thermocouple with junctions thermally attached to two well-separated positions along the longest axis of the sample. The temperature difference was controlled to be less than 1 K to minimize the heat loss through radiation. During measurements the sample space was maintained as a good vacuum (better than 10^{-4} Torr). For the TEP measurements, Seebeck voltages were detected using a pair of thin Cu wires electrically connected to the sample with sliver paint at the same positions as the junctions of the differential thermocouple. The stray thermal emfs are eliminated by applying long current pulses ($\sim$100 s) to the chip resistor, where the pulses appear in an off–on–off sequence. All experiments were performed while warming, at a rate slower than 20 K h^{-1}. The reproducibility of the measurements of κ and the TEP is better than 2%, while the absolute accuracy of the κ-measurements is approximately 15%, mainly as a result of the error in measuring the geometrical factor of the samples and the heat loss.

As shown in the inset of figure 1, ρ observed for $FeAl_2$ is approximately 400 $\mu\Omega$ cm over a wide temperature range—similar to those of semimetals such as the half-Heusler compounds ZrCoSb and HfCoSb [11]. Around 50 K, an upturn in ρ was observed, consistent with the previously reported result [10]. While such a feature is reminiscent of those Kondo effects arising from the strong magnetic impurity scattering, it was found that the low-T ρ-upturn in $FeAl_2$ does not follow the logarithmic dependence on temperature, ρ increasing as $-\ln T$, expected from the theory of a Kondo state [2–4]. Instead, the behaviour of the low-temperature resistivity in $FeAl_2$ was presumably associated with the manifestation of spin glass effects, in agreement with the magnetic measurements [10].

The T-dependent thermal conductivity of $FeAl_2$ is displayed in figure 1. At low temperatures, κ increases with temperature and a maximum appears at around 30 K. This

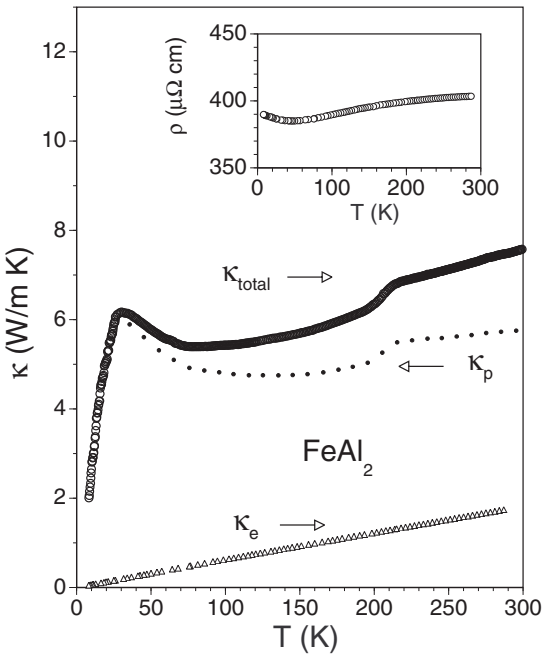

Figure 1. The temperature dependence of the thermal conductivity of $FeAl_2$. Open triangles and closed dots represent the electronic and lattice thermal conductivity respectively. Inset: the temperature dependence of the electrical resistivity of $FeAl_2$.

is a typical feature for reduction of thermal scattering at lower temperatures. The maximum appears at the temperature where the phonon mean free path is approximately equal to the crystal site distance. After passing through the maximum, κ drops with increasing temperature. As the temperature is raised further, κ keeps increasing with temperature, and an abrupt slope change in κ was observed near 220 K.

The temperature variation of the TEP for $FeAl_2$ is plotted in figure 2. At high temperature, the data show quasilinear behaviour with positive values, signifying that hole-type carriers dominate the high-temperature TEP. With decreasing temperature, the TEP changes sign from positive values to negative values at around 220 K, indicating a change of conduction mechanism or dominant carrier at this temperature. It is noted that this temperature happens to coincide with the temperature of the abrupt slope change in κ. At about 100 K, a broad minimum in the TEP develops. Upon further cooling, the TEP increases again and a maximum appears at around 30 K. The coincidence of the maxima in the TEP and κ suggests that the low-temperature variation of the TEP is essentially due to the phonon-drag effect [12].

To further examine whether the slope change in κ and the sign change in TEP are associated with any phase transitions, we carried out specific heat measurements at temperatures between 77 and 300 K using a high-resolution (0.1%) ac calorimeter, with chopped light as a heat source [13]. Photoabsorbing lead sulfide films were evaporated on the front surface of samples, which were sanded to a thickness of about 0.2 mm to ensure one-dimensional heat flow. Such a technique has been applied to the charge-density-wave (CDW) material $Lu_5Ir_4Si_{10}$, for which a spike-shaped specific heat jump was discovered near the CDW transition [14]. In contrast, the relative heat capacity of $FeAl_2$ (not shown here) exhibits a monotonically Debye-like variation with no anomaly in this temperature range. This result excludes a possible phase transition manifesting the observed features of κ and the TEP.

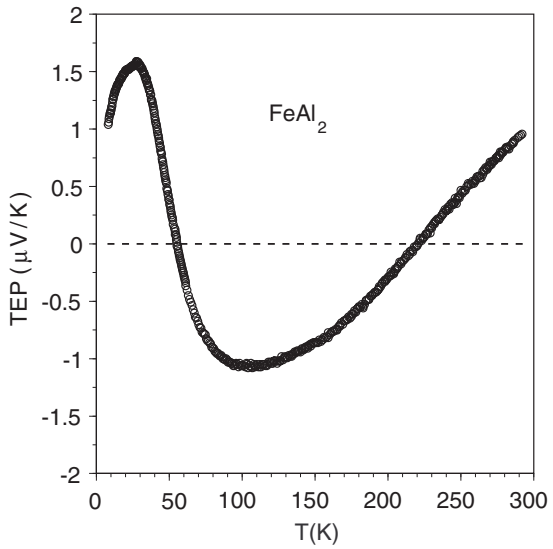

Figure 2. TEP as a function of temperature for $FeAl_2$.

3. Discussion

For conventional metals and semimetals, the total thermal conductivity can be expressed as a sum of lattice (κ_P) and electronic (κ_e) terms: $\kappa = \kappa_P + \kappa_e$. The electronic contribution can be estimated by means of the Wiedemann–Franz law: $\kappa_e \rho / T = L_0$. Here ρ is the dc electric resistivity and the Lorentz number $L_0 = 2.45 \times 10^{-8}$ W Ω K^{-2}. We thus calculated κ_e using the Wiedemann–Franz law and measured resistivity data. The lattice thermal conductivity is taken as the difference between κ and κ_e. This estimate indicates that the measured thermal conductivity shown in figure 1 is essentially dominated by the lattice thermal conductivity. Such a characteristic is consistent with those of ordinary semimetals [15]. Also it appears that the observed abrupt increase near 220 K is associated with additional lattice contributions, although the origin of this anomaly is not yet understood at this moment.

It is known that the TEP measurement could yield information about the Fermi-level band structure. In this study, the most remarkable feature for $FeAl_2$ is the sign change in the TEP near 220 K. It is worth pointing out that measurements of the TEP in $RuAl_2$ also reveal a similar temperature variation at higher T, in spite of the larger absolute values of the TEP [16]. This comparison suggests that the origins of such behaviour in the two systems may be the same mechanism. It could be understood as the positive carriers being thermally excited across the pseudogap, due to a slight overlap between electron and hole pockets in the DOS spectrum of $FeAl_2$.

For the present case of $FeAl_2$, the small absolute value of the TEP <2 μV K^{-1} over the entire temperature range of the measurements implies that the electrons and holes involved in the thermal conduction processes are 'nearly compensated'. However, the carriers are still predominantly electrons and hence the TEP is negative regardless of the positive phonon-drag effect. As the temperature is raised further, the intrinsic electrons and holes are thermally excited. If the holes have a slightly higher mobility than the electrons in $FeAl_2$, the hole carriers will eventually govern the TEP, and the TEP will once again become positive. For the

measured data, the slope of the TEP changes sign for $FeAl_2$ at around 100 K—much lower than for $RuAl_2$ (∼370 K). This thus indicates that $FeAl_2$ has a narrower pseudogap of about 0.1–0.2 eV, as compared to the value of 0.6 eV in $RuAl_2$ [16].

The recent TEP measurements for semimetallic $Fe_{1.98}V_{1.02}Ga$ also exhibited a broad minimum near 100 K and a sign change close to 200 K [15]. The pseudogap of this compound has been estimated to be about 0.2 eV or less, unlike that of the stoichiometric compound Fe_2VGa. The pseudogap value of about 0.22 eV in Fe_2VGa was extracted by means of nuclear magnetic resonance (NMR) relaxation rates [17]. Hence the value of the pseudogap deduced from the TEP result for $FeAl_2$ seems quite reasonable. It is worth mentioning the differences between κ in the present case $FeAl_2$ and that for $Fe_{1.98}V_{1.02}Ga$ [15]—in spite of the similarity in TEP of the two systems. At higher temperatures, κ for $FeAl_2$ increases with temperature, due to an additional contribution from κ_e. For $Fe_{1.98}V_{1.02}Ga$, κ decreases monotonically with temperature above 50 K, a feature commonly seen in solids because the total thermal conductivity is dominated by κ_P. Also, the values of κ for $Fe_{1.98}V_{1.02}Ga$ are 2–3 times larger than those for $FeAl_2$ in the temperature range between 100 and 300 K, even though the electrical conductivities of the two samples are comparable. This would lead to an insignificant contribution from κ_e to the total thermal conductivity of $Fe_{1.98}V_{1.02}Ga$, further suggesting that the lattice thermal conductivity dominates in the high-T value of κ for $Fe_{1.98}V_{1.02}Ga$.

4. Conclusions

We have performed detailed thermal and electrical transport measurements on the ordered intermetallic $FeAl_2$. The observed resistivity of $FeAl_2$ is nearly temperature independent over a broad temperature range, resembling those of semimetals. Analysis on the thermal conductivity suggests that the measured κ arises essentially from the lattice contribution. The features of the temperature-dependent TEP could be understood as a typical response for a compensated semimetal. In addition, a pseudogap size of 0.1–0.2 eV in the DOS spectrum of $FeAl_2$ was estimated. Future studies, such as optical conductivity measurements, are needed to provide further confirmation of the pseudogap characteristics.

Acknowledgments

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