Electrical and thermoelectric properties of the intermetallic FeGa₃

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Abstract
The transport properties including electrical resistivity (ρ), thermal conductivity (κ), as well as Seebeck coefficient (S) of intermetallic FeGa₃ have been measured as a function of temperature between 10 and 300 K. The electrical resistivity exhibits metallic behavior in the temperature range we investigated. The thermal conductivity is approximately 6 W/m K at room temperature, and is mainly governed by the lattice thermal conductivity. The observed Seebeck coefficient is positive, indicating p-type carriers dominating the thermoelectric transport for FeGa₃. In addition, the Fermi level of 0.14 eV measured from the top of valence band was estimated. These observations are in contrast with the reported semiconducting behavior for this compound, presumably attributed to the off-stoichiometric effect on the electronic band structure of FeGa₃.

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1. Introduction
Materials with complex band structures have been of considerable interest due to their unusually magnetic and transport properties. Phenomena such as heavy fermion behavior, a Kondo insulating state, and unconventional superconductivity are frequently found in these materials. It has been argued that the effect of hybridization plays an important role for these observations [1–6]. The peculiar features are commonly seen in rare-earth-based compounds, as the localized f electrons of the rare-earth element have the 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 at the Fermi level density of states (DOS). For transition-metal-based materials, the relatively dispersive d-electronic wave functions normally have a weaker hybridization effect but form d-bands instead [2]. Hence, it is of particular importance to examine the physical properties on the unconventional transition-metal-based alloys in order to shed light on such a hybridization scenario. For examples, the semiconducting and semimetallic behavior observed previously in RuGa₂ and Fe₂VGa, respectively, have been attributed to such hybridization-induced gap and pseudogap at their Fermi level DOS [7,8].

Intermetallic FeGa₃ crystallizes in the tetragonal CoGa₃-type structure with the space group symmetry P4₂/mnm. A recent electronic structure calculation predicted that FeGa₃ is also a hybridization-gap semiconductor with a bandgap of about 0.3 eV [9]. Accordingly, the strong hybridization of the Fe-d and Ga-p electrons in this material is responsible for the unusual band feature. To further understand the nature of electronic states in FeGa₃, we thus performed the Seebeck coefficient (S) measurement, a sensitive probe of energy relative to the Fermi surface, of the titled compound. Since S is not influenced by intergrain transport, it should reflect more intrinsic properties of the studied material. In addition, we reported the electrical resistivity (ρ) and thermal conductivity (κ) to provide a full investigation of the transport properties of FeGa₃.

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2. Experiments and results

The polycrystalline FeGa$_3$ sample studied here was prepared in an induction furnace under partial argon. To promote homogeneity, the resulting ingot was annealed in a vacuum-sealed quartz tube at 800 °C for 2 days; this was followed by furnace cooling. The same preparation technique has been reported in the literature[10]. An X-ray analysis taken with Cu Kα radiation on the powder specimen shows a single phase. All reflection peaks in the diffraction spectra could be indexed according to the expected structure, as demonstrated in Fig. 1. The determined lattice parameters are $a = 0.6251$ and $c = 0.6543$ nm, respectively, consistent with previously reported values[9].

The electrical resistivity was measured during warming process by a standard four-terminal method. The thermal conductivity was carried out in a close-cycle refrigerator over temperatures from 10 to 300 K, using a direct heat-pulse technique. The FeGa$_3$ ingot was cut to a rectangular parallelepiped shape of typical size of 1.5 mm x 1.5 mm x 5.0 mm with one end glued (with thermal epoxy) to a copper block that served as a heat sink, while a calibrated chip resistor 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 is maintained in a good vacuum (better than $10^{-2}$ Pa). For the Seebeck coefficient measurements, Seebeck voltages were detected using a pair of thin Cu wire electrically connected to the sample with silver paint at the same positions as the junctions of 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 during warming with a rate slower than 20 K/h. The reproducibility of $\kappa$ and $S$ measurements is better than 2%, while the absolute accuracy of $\kappa$ is approximately 15%, which mainly arises from the error in measuring the geometrical factor of the samples.

As shown in Fig. 2, the observed $\rho$ of FeGa$_3$ exhibits a metallic character (positive temperature coefficient), in contrast to the semiconducting behavior reported by Haussermann et al.[9]. The rather large $\rho$ values in the entire temperature range we measured may be attributed in part to the grain boundaries. However, the magnitude of measured $\rho$ is similar to those of semimetals such as FeAl$_2$[11]. Possible reasons for the inconsistency between the reported result and our data will be addressed in Section 3.

The $T$-dependent thermal conductivity of FeGa$_3$ is displayed in Fig. 3. At low temperatures, $\kappa$ increases with temperature and a maximum appears at around 40 K. This is a typical feature for the reduction of thermal scattering at lower temperatures. The maximum takes place at the temperature where the phonon mean free path is approximately equal to the crystal site distance. After passing through the maximum, $\kappa$ drops with increasing temperature. For conventional metals and semimetals, the total thermal conductivity ($\kappa_{\text{tot}}$) can be expressed as a sum of lattice ($\kappa_{\text{lat}}$) and electronic ($\kappa_{\text{e}}$) terms: $\kappa_{\text{tot}} = \kappa_{\text{lat}} + \kappa_{\text{e}}$. The electronic contribution can be estimated by means of the Wiedemann-Franz law: $\kappa_{\text{e}}T = L_0$. Here $\rho$ is the dc electric resistivity and $L_0 = 2.45 \times 10^{-8}$ W K$^{-2}$ is the Lorentz number. We thus
calculated $\kappa_e$ using the Wiedemann–Franz law and measured resistivity data. The lattice thermal conductivity is taken as the difference between $\kappa_{\text{tot}}$ and $\kappa_e$. This estimate indicates that $\kappa_e$ is about two orders of magnitude smaller than $\kappa_L$ in FeGa$_3$.

The temperature variation of Seebeck coefficient for FeGa$_3$ is plotted in Fig. 4. The positive $S$ values signify that hole-type carriers dominate the thermoelectric transport in this material. The observed $S$ consists of two contributions: diffusion thermoelectric power $S_d$ and phonon-drag part $S_g$ \cite{12}. The diffusion thermoelectric power of metals is expected to be a linear function of temperature, as we did observe in our sample for temperature above 200 K. Upon cooling, $S$ decreases and a maximum appears at around 40 K. The coincidence of the maxima in $\kappa$ and $S$ suggests that the low temperature peak in $S$ is essentially due to phonon-drag effect.

It is known that the Seebeck coefficient measurement could yield information about the Fermi level band structure. Since the $S$ data vary rather linearly with temperature above 200 K for FeGa$_3$, one can try to extract the value of Fermi energy $E_F$ through the classical formula $S = \frac{\pi^2}{3} k_B^2 T/2eE_F$ assuming a one-band model with an energy-independent relaxation time. With this fit, $S = 0$ can be obtained by extrapolating the linear behavior to $T \rightarrow 0$, consistent with the free-electron scenario. A value of $E_F = 0.14$ eV was extracted for FeGa$_3$, indicative of the metallic nature for this alloy. Note that this value represents a measure from the top of valence band to the Fermi level.

3. Discussion

In this investigation, all measured quantities indicate a metallic or semimetallic character for FeGa$_3$. These observations are in contrast to the reported semiconducting behavior by Hausermann et al. \cite{9}. The origin of the inconsistency could be interpreted as below. Although the calculated DOS also revealed a bandgap for FeGa$_3$, the Fermi level $E_F$ (indicated by an arrow in Fig. 5) locates near the top of valence pocket instead of the midpoint of the energy gap \cite{9}. Based on such an electronic structure, $E_F$ is sensitive to structural defects such as vacancies and off-stoichiometry. We thus suspect that if a more accurate DOS calculation is performed by considering the effects of structural defects, the Fermi level may fall into the valence band as $E_F$ (see Fig. 5). As a consequence, it would lead to a p-type metal for FeGa$_3$, as we indeed observed by Seebeck coefficient measurement ($E'_F = 0.14$ eV away from the top of valence band). In this regard, the reported non-metallic transport behavior might be attributed to the off-stoichiometric effect. If there is a little amount of Ga that substitutes for Fe (leading to the formula of Fe$_{1-x}$Ga$_x$) in their samples, the excess gallium acting as an n-type dopant would cause a shift of the Fermi level toward the energy gap, which in turn results in the semiconducting behavior in their electrical resistivity data. The above arguments are illustrated as a schematic picture in Fig. 5.

Alternatively, FeGa$_3$ is truly an intrinsic semiconductor. Our sample may contain a bit less Ga content from the stoichiometry, causing $E_F$ a downward shift to the valence band, so our sample exhibits metallic nature as we observed. It is also possible that there is antisite disorder between Fe and Ga sites in the given compound, leading to a change of band feature in the vicinity of Fermi surface. In most cases, the prime effect of disorder on the band structure is to broaden the electronic bands, resulting in closing of the bandgap. It is worthwhile mentioning that similar off-stoichiometric effects on the transport properties have been seen in the semimetallic Fe$_2$VAl and Fe$_2$VGa systems \cite{13–15}.

4. Conclusions

We have performed detailed electrical and thermal transport measurements on the intermetallic FeGa$_3$. Our exper-
Results indicate that FeGa$_3$ is a p-type metal, in spite of the rather high electrical resistivity values. Analysis of the thermal conductivity suggests that the measured $\kappa$ is essentially from the lattice contribution. The features of the temperature-dependent Seebeck coefficient could be understood as a typical response for a metal. In addition, the Fermi level of 0.14 eV measured from the top of valence band in the DOS spectrum of FeGa$_3$ was estimated. In contrast to the semiconducting behavior reported previously, the metallic character of FeGa$_3$ found in the present study is presumably due to the off-stoichiometric effect.

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