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Off-stoichiometric effect on the transport and pseudogap characteristics of Fe_2VGa

C S Lue[1], W J Lai[1], C C Chen[1] and Y-K Kuo[2]

[1] Department of Physics, National Cheng Kung University, Tainan 70101, Taiwan
[2] Department of Physics, National Dong Hwa University, Hualien 97401, Taiwan

E-mail: cslue@mail.ncku.edu.tw and ykkuo@mail.ndhu.edu.tw

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Abstract

We report the investigations of transport and thermoelectric measurements on the Heusler compounds Fe_2VGa_{1+x} over the temperature range from 10 to 300 K. It is found that the electrical resistivity and Seebeck coefficient are very sensitive to the off-stoichiometry, while the thermal conductivity is relatively little affected with the composition change. With a removal of Ga content from the stoichiometric Fe_2VGa, a sign change in the Seebeck coefficient accompanied by a broad minimum at around 130 K is observed. The latter feature can be interpreted as thermal excitation of carriers across band edges, in accord with band-structure calculations. Furthermore, an analysis of lattice thermal conductivity indicates that the off-stoichiometric effect on both electrical resistivity and Seebeck coefficient is not influenced by chemical disorder.

1. Introduction

Transition metal–metalloid compounds with unconventional transport and magnetic properties have attracted a great deal of attention in recent years. For instance, the Heusler-type intermetallic Fe_2VAl shows semiconducting behaviour in spite of a clear Fermi edge characterizing the metallic properties [1]. The absence of magnetic ordering and the enhancement of low-temperature specific heat are reminiscent of the heavy-fermion systems [1, 2]. The isostructural Fe_2VGa also exhibits similar physical properties: semiconducting-like behaviour along with a disappearance of ferromagnetic ordering [3, 4]. According to the band-structure calculations [5, 6], hybridization between d and s–p states plays a significant role in the observed unusual behaviour in Fe_2VGa. An NMR study on this material has revealed a small Fermi-level density of states (DOS) within the pseudogap [7], consistent with the semimetallic nature predicted from the theoretical calculations [5, 6]. There have been considerable advances in understanding how a gap or pseudogap may form in the region of the Fermi level in this class of materials. With the aim of learning more about

the pseudogap features of Fe_2VGa, we examine the electronic states in the pseudogap region of Fe_2VGa_{1+x} to understand how the pseudogap and the band feature vary with excess and deficiency of Ga content in Fe_2VGa.[3]

In this investigation, we performed a systematic study of the electrical and thermal transport properties including electrical resistivity (ρ) and Seebeck coefficient (S), as well as thermal conductivity (κ), on Fe_2VGa_{1+x} between 10 and 300 K. It is found that ρ and S are very sensitive to the off-stoichiometric effect. The observed tendency in ρ and S can be qualitatively understood by means of the Fermi energy (E_F) shift in a rigid-band scenario. The variations with composition change in both quantities are found to be little affected by chemical disorder, as revealed from the analysis of lattice thermal conductivity.

2. Experimental details and results

Polycrystalline Fe_2VGa_{1+x} samples studied here were prepared by mixing appropriate amounts of elemental metals. Briefly, mixtures of high-purity elements were placed in a water-cooled copper crucible and then melted several times in an Ar arc-melting furnace. Due to the volatility of Ga at high temperatures, we started with excess Ga for each sample and determined the x values in Fe_2VGa_{1+x} after preparing the ingots, assuming that the weight loss during melting arose entirely from the Ga element. To promote homogeneity, these ingots were annealed in a vacuum-sealed quartz tube at 600 °C for two days, and then further annealed at 400 °C for more than 12 h; this was followed by furnace cooling. The same preparation technique has been used in other studies of similar materials [3, 4, 8, 9], and is known to form a single-phase $L2_1$ (Heusler-type) structure. An x-ray analysis performed with Cu Kα radiation on powder specimens was consistent with the expected $L2_1$ structure, with no other phases evident in the diffraction spectra, as demonstrated in figure 1.

The electrical resistivity data were obtained by a standard dc four-terminal method. In figure 2 we display the temperature variation of electrical resistivity for Fe_2VGa_{1+x} measured during the warming process. These materials exhibit metallic behaviour with an excess of gallium content, but show semiconducting-like characteristics with a reduction of gallium content. This observation is associated with a change of Fermi-level DOS by the off-stoichiometric effect, as will be discussed in the next section. It is worthwhile mentioning that broad maxima in ρ have been found at around 40 and 150 K in Fe_2VGa and $Fe_2VGa_{0.98}$, respectively. These features are not attributed to the ferromagnetic ordering because no such transitions have been observed in magnetization measurements. The development of a broad peak in ρ was also observed in the isostructural $Fe_{2-x}V_{1+x}Ga$ and $Fe_{2-x}V_{1+x}Al$ alloys [3, 10, 11]. The metallic-like resistivity below the maximum in both Fe_2VAl and Fe_2VGa systems could be ascribed to the suppression of magnetic scattering between charge carriers and magnetic impurities and/or clusters [11].

Seebeck coefficients for the Fe_2VGa_{1+x} series were measured with a dc pulse technique. Seebeck voltages were detected using a pair of thin Cu wires electrically connected to the sample with silver paint at the same positions as the junction of a differential thermocouple. The stray thermal emfs are eliminated by applying long current pulses ($\sim$100 s) to a chip resistor which serves as a heater, where the pulses appear in an off–on–off sequence.

In figure 3, we show the observed Seebeck coefficient for all studied samples. Since the Seebeck coefficient is a sensitive probe of energy relative to the Fermi level, the measured Seebeck coefficient can be used to characterize the electronic structure in the region of the semimetallic pseudogap. The positive values of Seebeck coefficient for the stoichiometric

[3] The alloy with excess Ga content in Fe_2VGa corresponds to the deficiency of Fe and V contents in the sample. Therefore $Fe_2VGa_{1.02}$ and $Fe_2VGa_{1.04}$ represent the compounds of $Fe_{1.96}V_{0.98}Ga$ and $Fe_{1.92}V_{0.96}Ga$, respectively.

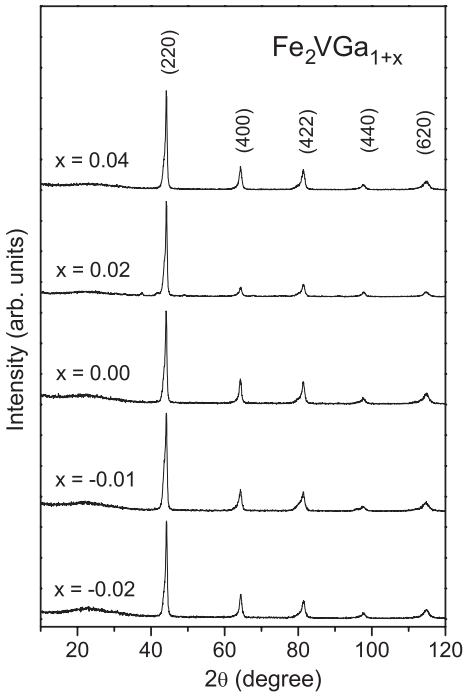

Figure 1. X-ray diffraction patterns in Fe_2VGa_{1+x}.

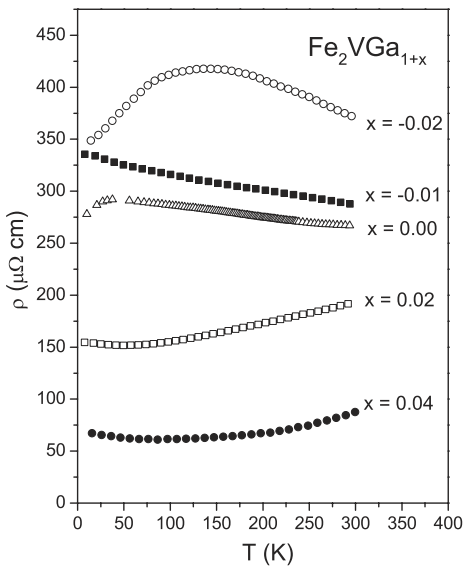

Figure 2. Electrical resistivity as a function of temperature for Fe_2VGa_{1+x}.

compound Fe_2VGa indicate that hole-type carriers dominate the heat transport. The S values remain positive for the non-stoichiometric samples with $x > 0$ in Fe_2VGa_{1+x}. On the other hand, the sign of S changes to negative with $x < 0$, suggesting that the thermal transport is governed by electron-type carriers for these materials. Broad minima in S were found at around 130 K for the $x < 0$ samples, and we connect this feature with the thermally excited

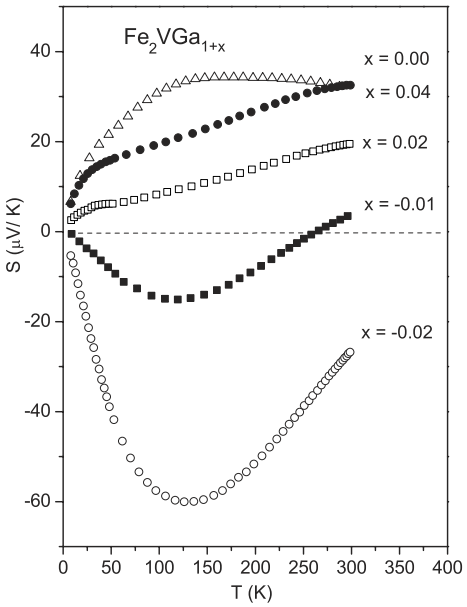

Figure 3. Seebeck coefficient versus temperature in Fe_2VGa_{1+x}.

opposite carriers across the band edges near the Fermi surface. Notice that the minimum in S is not likely to be due to the phonon drag effect, since it occurs at a different temperature compared to the thermal conductivity peaks (∼50 K). The observed Seebeck coefficients can be understood within the framework of two-carrier electrical conduction. Accordingly, the total S can be expressed as [12]

$$S = \left(\frac{\sigma_p S_p + \sigma_n S_n}{\sigma_p + \sigma_n} \right), \tag{1}$$

where $S_{p,n}$ and $\sigma_{p,n}$ represent the Seebeck coefficients and electrical conductivities for the p- and n-type carriers, respectively. Since the signs of S_p and S_n are opposite, tuning these quantities could result in a sign change in S, as we observed in the present study.

Thermal conductivity measurements were carried out in a close-cycle refrigerator, using a direct heat-pulse technique. Samples were cut to a rectangular parallelepiped shape of typical size of $1.5 \times 1.5 \times 5.0$ mm^3 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 sample. The temperature difference was controlled to be less than 1 K to minimize the heat loss through radiation, and the sample space is maintained in a good vacuum (better than 10^{-4} Torr) during measurements. All experiments were performed on warming with a rate slower than 20 K h^{-1}. The absolute accuracy of our thermal conductivity measurements is approximately 20%, mainly due to the error on the determination of sample dimensions.

The T-dependent thermal conductivity of Fe_2VGa_{1+x} is plotted in figure 4. The room-temperature κ values are quite large, 17–22 W m^{-1} K^{-1}, for all samples we investigated. It is noted that κ in Fe_2VGa_{1+x} is relatively little affected with respect to the composition change. At low temperatures, κ increases with temperature and a maximum appears between 50 and 60 K, close to those of the isostructural Heusler compounds [13]. This is a typical feature for the reduction of thermal scattering in metals at low temperatures. In general, the

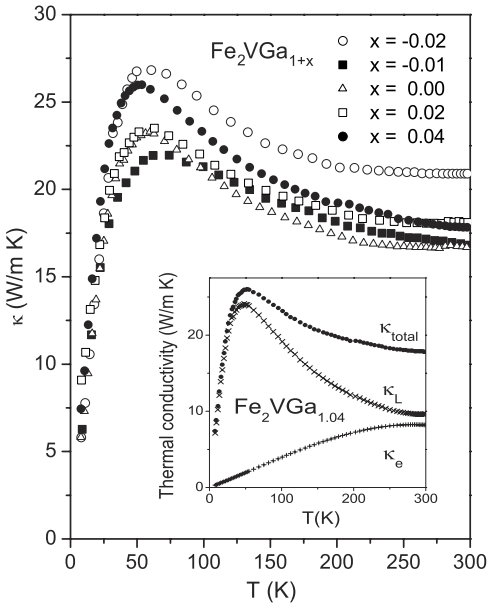

Figure 4. Temperature dependence of the observed thermal conductivity in Fe_2VGa_{1+x}. Inset: the estimated electronic (κ_e) and lattice (κ_L) contributions to the total thermal conductivity in $Fe_2VGa_{1.04}$.

total thermal conductivity for ordinary metals and semimetals is a sum of electronic (κ_e) and lattice (κ_L) terms. The electronic thermal conductivity can be computed by means of the Wiedemann–Franz law: $\kappa_e\rho/T = L_0$. Here ρ is the total dc electrical resistivity, T is the absolute temperature, and $L_0 = 2.45\times10^{-8}\,\mathrm{W\,\Omega\,K^{-2}}$ is the Lorentz number. We thus estimate κ_e using the Wiedemann–Franz law with the measured resistivity data. As demonstrated in the inset of figure 4, the calculated κ_e for $Fe_2VGa_{1.04}$ (the largest κ_e value among all studied samples) is still smaller than κ_L in the temperature range we investigated. This estimate indicates that the total thermal conductivity in these alloys is mainly due to lattice phonons rather than charge carriers, especially at low temperatures.

Previous studies indicated that antisite disorder in the Heusler-type alloys would play a significant role in their anomalous magnetic and transport properties [3, 10, 11, 13, 16]. In order to examine whether disorder correlates with the off-stoichiometric effect in Fe_2VGa_{1+x}, we performed a fit on the lattice thermal conductivity using the Debye approximation. Such an analysis has been successfully applied to the p-type skutterudites and other materials [17–19]. The obtained fitting parameters would provide information about the phonon scattering mechanisms, especially on the lattice imperfection residing in the samples. In the Debye approximation model, κ_L is written as [20, 21]

$$\kappa_L = \frac{k_B}{2\pi^2 v}\left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{\tau_P^{-1}(e^x-1)^2}\,dx, \tag{2}$$

where $x = \hbar\omega/k_B T$ is dimensionless, ω is the phonon frequency, $\hbar$ is the reduced Planck constant, k_B is the Boltzmann constant, θ_D is the Debye temperature, v is the average phonon velocity, and τ_P^{-1} is the phonon scattering relaxation rate. Here τ_P^{-1} is the combination of three scattering mechanisms and can be expressed as

$$\tau_P^{-1} = \frac{v}{L} + A\omega^4 + B\omega^2 T e^{-\theta_D/3T}, \tag{3}$$

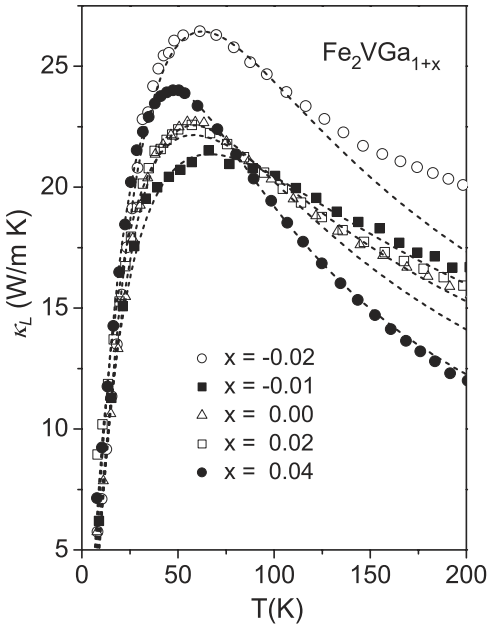

Figure 5. Lattice thermal conductivity for Fe_2VGa_{1+x} versus temperature. The dotted curves represent the fits calculated from equations (2) and (3).

where the grain size L and the coefficients A and B are the fitting parameters. The terms in equation (3) are the scattering rates for the grain boundary, point defect, and phonon–phonon Umklapp scattering, respectively. In general, the grain boundary scattering is a dominant mechanism for the low-temperature κ_L, while the Umklapp procedure is important at high temperatures. The point defect scattering, on the other hand, determines the appearance of the shape and position of the phonon peak occurring in the intermediate-temperature regime. Taking $v = 5000$ m s^{-1} and $\theta_D = 310$ K given from the specific heat measurement for Fe_2VGa [22], the experimental data of all studied samples can be fitted very well for $T < 120$ K, drawn as dotted curves in figure 5. However, the fitting curves deviate from the data points for $T > 120$ K. We attempted to include electron–phonon interaction in the calculations, but such an effort yielded no significant improvement to the overall fit. It thus indicates that electron–phonon scattering has a minor influence on the lattice thermal conductivity in Fe_2VGa_{1+x}. The discrepancy between the measured data and the fit at high temperatures may be attributed to radiation losses during experiments, temperature dependence of the Lorentz number, and the undetermined Debye temperatures for the off-stoichiometric compounds. This discrepancy, however, has little effect on the following discussion.

In table 1, we tabulate the fitting parameters for all samples studied. As seen from this table, the grain size for the studied materials varies from 4 to 13 μm with no obvious tendency among the samples. Also, the Umklapp coefficient B scatters around in these samples, presumably due to the unknown Debye temperature for these materials (except Fe_2VGa). It should be noted that even though the Debye temperature is a significant factor for the Umklapp scattering rate, it only affects the fitting result at high temperatures. According to the model proposed by Klemens [23], the prefactor A increases with the concentration of point defects in the low defect level. As seen form this fit, the parameter A does not follow a consistent variation with x. Based on this result, we concluded that vacancies in the Fe_2VGa_{1+x} compounds have a relatively minor contribution to the point defect scattering. Instead, antisite disorder in the

Table 1. Lattice thermal conductivity fitting parameters determined from equations (2) and (3).

x	L (μm)	A (10^{-42} s^3)	B (10^{-18} s K^{-1})
−0.02	4.06	1.23	1.48
−0.01	7.38	2.42	0.91
0.00	4.94	1.69	1.77
0.02	12.96	2.86	0.97
0.04	8.04	1.81	2.40

studied materials should be a main origin for the point defect scattering which appears to have no consistent variation with x.

3. Discussion

There is general agreement from band theoretical calculations in Fe_2VGa that the electronic states at Fermi level arise from V-dominated electron pockets at X, with the others from Fe-dominated hole pockets at Γ [6]. The hole pockets are larger than the electron ones, leading to a dominant hole carrier for the transport. This is consistent with the positive Seebeck coefficient in Fe_2VGa. The slightly indirect overlap between electron and hole pockets leads to a small but nonzero DOS at the Fermi surface. Outside the pockets, further band edges appear in the conduction and valence bands within 0.2–0.3 eV of the Fermi energy (E_F) for Fe_2VGa, as measured from figure 11 in [6]. A conduction-band edge having little dispersion between X and Γ points is predicted to be approximately 0.1–0.2 eV above E_F, while a valence band maximum appears at X, about 0.1 below E_F. With such a band structure, the transport and thermoelectric properties of these alloys would behave in a manner similar to that of the bipolar semiconductors at high temperatures, as proposed by Gurevich *et al* [24, 25]. As a result, the observed activated behaviour in ρ and S could be connected to the thermal excitation of carriers across these band edges.

With a removal of Ga content from stoichiometric Fe_2VGa, the ρ values increase and the sign of S changes. Such results can be understood by means of an upward shift of E_F within a simple rigid-band scenario. This shift reduces the hole pockets but enlarges the electron pockets, making the electron-type carriers dominate the transport properties. On the other hand, with an excess of Ga, the ρ values decrease and the sign of S remains positive, corresponding to a downward shift of E_F. We thus conclude that, at least in this regard, the off-stoichiometric effect on the transport and thermoelectric properties can be interpreted by the E_F shift in a rigid band of Fe_2VGa.

From the above description, thermal excitation of carriers across band edges near E_F would account for the observed exotic feature in S. For the Ga-poor samples, thermal transport is mainly dominated by electrons at low temperatures. Upon heating, the intrinsic electrons and holes are thermally excited. If the holes have a higher mobility than the electrons in these compounds, the hole carriers will eventually govern the thermoelectric power, leading to positive S values again at high temperatures. From the measured data, the S minima occur at around 130 K, indicative of a small band splitting of about 0.1 eV involved in the excitation, in good agreement with the calculations [6]. Nishino *et al* [26] have similarly seen these features near 250 K in Fe_2VAl_{1+x}. This comparison implies a larger band splitting in Fe_2VAl_{1+x} (∼0.2 eV), consistent with the predicted value given by the band calculations [5, 6, 14, 15]. Thus, the occurrence of a minimum in the Seebeck coefficient can be quantitatively understood with the picture of carrier excitation across band edges in this class of materials, in accordance with the band calculations.

As mentioned above, disorder in the studied samples may affect the tendency of the electrical resistivity and thermoelectric power. An analysis of the lattice thermal conductivity indicated that the effect of disorder is sample dependent with no systematic influence on the transport and pseudogap properties in these materials. We thus conclude that the observed trends in ρ and S are not significantly influenced by disorder introduced during sample preparation.

4. Conclusions

In summary, transport and thermoelectric properties including electrical resistivity (ρ) and Seebeck coefficient (S), as well as thermal conductivity (κ), in the Heusler-type compounds Fe_2VGa_{1+x} were studied in detail. We found that the electrical resistivity and Seebeck coefficient are very sensitive to the off-stoichiometric effect. Within the rigid-band framework, the shift of the Fermi energy with respect to x in Fe_2VGa_{1+x} is responsible for the observations. For the Ga-poor samples, the upturns in S at higher temperatures are presumably due to the contribution of thermally excited quasiparticles across their band edges. These features are consistent with the band signatures identified by the band-structure calculations.

Acknowledgments

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