Transport and magnetic properties of the Heusler-type $Fe_{2-x}V_{1+x}Al$ system $(-0.01 \leqslant x \leqslant 0.08)$

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We report on the temperature dependence of magnetization, electrical resistivity, and specific heat for the Heusler-type $Fe_{2-x}V_{1+x}Al$ alloys with compositions $-0.01 \leqslant x \leqslant 0.08$. The resistivity for a slightly Fe-rich sample with $x=-0.01$ reaches 3000 $\mu\Omega$ cm at 4.2 K, showing a semiconductorlike temperature dependence over the wide temperature range up to 1300 K. In contrast, a slightly V-rich sample with $x=0.02$ possesses a residual resistivity of only 300 $\mu\Omega$ cm with a positive temperature slope below 300 K. The magnetization and specific-heat data on the $x=-0.01$ sample provide ample evidence for the possession of local magnetic moments, whereas the annealed $x=0.02$ sample can be regarded as a nearly nonmagnetic semimetal. When quenched from high temperatures, even the slightly V-rich sample exhibited a steep rise of resistivity at low temperatures in parallel with an enhancement in the magnetization and the electronic specific heat. The low-temperature resistivity substantially enhances with increasing magnetic moment associated with Fe antisite defects, whose concentration is evaluated to be about 0.5% for the slightly Fe-rich annealed sample. The cause for the large resistivity at low temperatures is attributed to strong spin fluctuations of magnetic antisite defects, while the negative resistivity slope at temperatures above 400 K is attributed to the possession of a deep pseudogap at the Fermi level.

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I. INTRODUCTION

The Heusler-type intermetallic compound Fe_2VAl has attracted special attention because of the occurrence of a semiconductorlike temperature dependence of electrical resistivity over a wide temperature range up to 1200 K and above.[1] Band-structure calculations so far reported[2–6] consistently predicted the presence of a deep pseudogap at the Fermi level due to the hybridization effects. Nuclear magnetic resonance (NMR)[7] and Hall-effect[8] measurements strongly support that Fe_2VAl is characterized as a low carrier-density semimetal. Optical conductivity[9,10] and photoemission spectroscopy[11] measurements further confirmed the existence of a pseudogap of 0.1–0.2 eV in width. Nevertheless, the pseudogap scenario itself could not account for a steep rise of resistivity at low temperatures.

The electronic-structure calculations have shown that no magnetic state can be stabilized for the stoichiometric Fe_2VAl compound.[2–6] In fact, thermomagnetic measurements provide no evidence of ferromagnetic transition in the temperature range down to 2 K, although the magnetization enhances significantly at low temperatures.[12] Thus Fe_2VAl is proved to be in a marginally magnetic state and is also found to exhibit an enhancement in the electronic specific heat at low temperatures.[1,12] The observed unusual transport properties have been interpreted as arising from spin fluctuations[2,3] or from excitonic correlations.[4] Singh and Mazin[3] suggested that spin fluctuations are caused by the existence of magnetic antisite defects associated with Fe atoms on the nominally V site in Fe_2VAl. A steep rise of resistivity at low temperatures has been ascribed to the presence of antisite defects with a magnetic moment, as suggested by a variety of experiments including specific heat,[13] NMR,[7,14] and magnetization measurements,[10,12] although their exact nature still remains elusive. These defects unavoidably present in measured Fe_2VAl samples are also considered to be responsible for the observation of a giant magnetoresistance (GMR) effect.[15]

We have recently found that the resistivity for a slightly V-rich sample of $Fe_{2-x}V_{1+x}Al$ with $x=0.02$ is reduced to only 300 $\mu\Omega$ cm at 4.2 K,[16] which is almost an order of magnitude lower than that for a nominally more stoichiometric sample. It has been suggested that the resistivity behavior of Fe_2VAl can be significantly affected by a small deviation of the chemical composition,[17] which would result in the generation of magnetic antisite defects mentioned above. The transport properties of Fe_2VAl appear to be strongly sample-dependent, probably because of the existence of magnetic defects in measured samples. In the present study, we have investigated the magnetization, electrical resistivity, and specific heat for annealed samples of $Fe_{2-x}V_{1+x}Al$ with compositions $-0.01 \leqslant x \leqslant 0.08$, and also for quenched samples of the slightly V-rich $Fe_{1.98}V_{1.02}Al$, where more magnetic defects could be introduced than annealed samples with the same composition. The purpose of this study is to clarify the effect of magnetic antisite defects on the unusual transport and magnetic properties of Fe_2VAl.

II. EXPERIMENTS

Ingots of $Fe_{2-x}V_{1+x}Al$ alloys with compositions $-0.01 \leqslant x \leqslant 0.08$ were prepared by repeating arc melting of appropriate mixtures of 99.99% pure Fe and Al, and 99.9% pure V in a purified argon atmosphere. The chemical composition was determined within the accuracy of ±0.2% by inductively coupled argon plasma atomic-emission spectroscopy. In par-

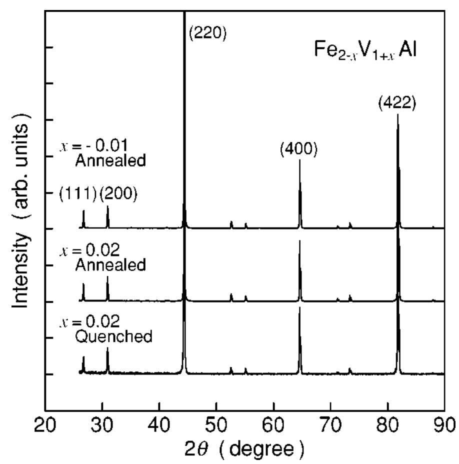

FIG. 1. Powder x-ray diffraction patterns for $Fe_{2-x}V_{1+x}Al$: the annealed $x=-0.01$ sample, and the $x=0.02$ samples annealed and quenched after holding at 1173 K, respectively.

ticular, special care was taken to ensure that the composition thus determined agrees with the nominal one for all samples studied. Since the reproducibility was confirmed for at least three samples with the same composition, we can safely discuss the composition dependence of various physical properties with the accuracy of ±0.1% in the present work. The ingots were homogenized at 1273 K for 48 h in vacuum. Samples were cut from the ingots with a SiC blade saw to the size of $1\times1\times15\ mm^3$ for resistivity measurements, $1\times1\times5\ mm^3$ for magnetization measurements, and $6\times6\times15\ mm^3$ for specific-heat measurements. Each sample was sealed in an evacuated quartz capsule and was annealed at 1273 K for 1 h and then at 673 K for 4 h followed by furnace cooling. The preparation of annealed samples is the same as adopted in Ref. 1. We also prepared quenched samples for $x=0.02$: after annealing at 1273 K for 1 h, they were held at a temperature between 1023 and 1173 K for 4 h followed by quenching into water.

Powder x-ray diffraction (XRD) spectra were measured with the Cu $K\alpha$ radiation for annealed and quenched samples thus prepared. Figure 1 shows powder XRD patterns for the annealed $x=-0.01$ sample, and the $x=0.02$ samples annealed and quenched after holding at 1173 K, respectively: peak heights were normalized with respect to that of the (220) peak. No significant difference was found between annealed and quenched samples with the same composition, all of which were identified as a single phase Heusler-type ($L2_1$) structure. It is important to note that all the diffraction peaks are very sharp, as compared with XRD results reported by Feng *et al.*,[10] and that relative intensities of the diffraction peaks in the present studies are in good agreement with the calculated ones for the stoichiometric $L2_1$ structure free from any antisite defect. As a matter of fact, the Rietveld structure analysis failed to detect reliably if the amount of antisite defects increases with departing x from zero due presumably to the near location of Fe and V in the periodic table. In spite of this difficulty, we convince ourselves that the samples employed in this experiment are of a high quality.

The electrical resistivity was measured by a standard dc four-terminal method with a current of 100 mA over the temperature range 4.2–1300 K and with a rising rate of 0.05 K/s: the measurements at high temperatures were carried out in a vacuum of 6×10^{-4} Pa. The magnetization was measured from 2 to 300 K in a magnetic field of 1 T, and the magnetic-field dependence was measured from 0 to 5 T at 5 K using a superconducting quantum interference device (SQUID) magnetometer. The low-temperature specific heat was measured from 1.6 to 10 K using a dc adiabatic method.

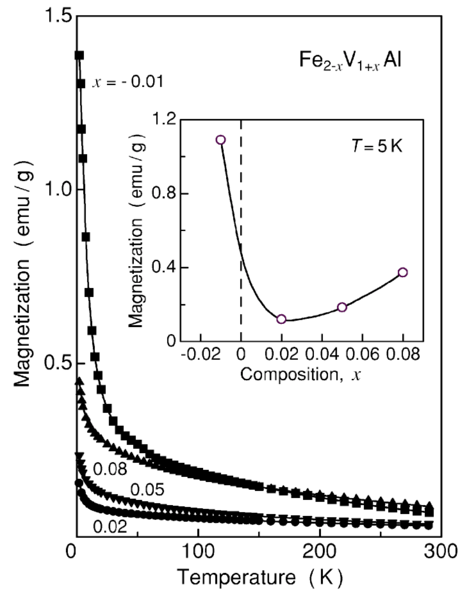

FIG. 2. Temperature dependence of magnetization in $Fe_{2-x}V_{1+x}Al$ with compositions $-0.01\leqslant x\leqslant0.08$. The magnetization was measured under a magnetic field of 1 T. The inset shows the magnetization at 5 K as a function of composition x.

III. RESULTS AND DISCUSSION

A. Effects of nonstoichiometry

In order to lay a foundation for understanding the unusual transport properties of Fe_2VAl, we first measured the temperature dependence of the magnetization under a magnetic field of 1 T for $Fe_{2-x}V_{1+x}Al$ with compositions $-0.01\leqslant x\leqslant0.08$. As shown in Fig. 2, a sharp enhancement in the magnetization can be observed at low temperatures for the slightly Fe-rich sample with $x=-0.01$. It is interesting to note that the magnetization is approximately three orders of magnitude smaller than that for Fe_3Al.[12] The magnetic-field dependence of the magnetization was analyzed using a modified Arrott-plot method,[18] but all of the samples were found to be paramagnetic in the temperature range at least above 2 K. Singh and Mazin[3] suggested that, due to antisite defects associated with nonstoichiometry, Fe atoms on the nominally V site in Fe_2VAl yield local magnetic moments. For the slightly Fe-rich sample with $x=-0.01$, such antisite Fe atoms would naturally arise even from a thermal equilibrium distribution of atoms among sites. These antisite defects most likely cause an enhancement in the magnetization at low temperatures. In contrast, the magnetization for the slightly V-rich sample with $x=0.02$ is almost temperature independent and is an order of magnitude lower than that with $x=-0.01$ at 2 K, suggesting a remarkable reduction in magnetic antisite defects. Rather than relying on the structural data shown in Fig. 1, we have, therefore, employed the magnetization data to draw a decisive conclusion about the possession of magnetic antisite defects. Now we can naturally assume the slightly V-rich sample with $x=0.02$ to best represent the nonmagnetic Fe_2VAl for which the band calculations were made. Recent Hall-effect measurements[17] also identified a similar V-rich sample of $Fe_{1.98}V_{1.02}Al$ to be an exception that does not exhibit an anomalous Hall effect at low temperatures among the family of both stoichiometric and off-stoichiometric Fe_2VAl samples.

As shown in the inset of Fig. 2, the magnetization at 5 K measured under a magnetic field of 1 T increases gradually with increasing x beyond 0.02. This apparently indicates an increase in the number of magnetic antisite defects. We are well aware that the lattice parameter decreases with the partial substitution of V for Fe in Fe_3Al because of an enhanced cohesion due to the site selectivity of V atoms but starts to increase after showing a minimum at the stoichiometric composition of Fe_2VAl. The increase in the lattice parameter has been interpreted as arising from the fact that the $L2_1$ $(D0_3)$ phase becomes less stable.[1] It is important to note that the V site in the Fe_2VAl lattice is quite different from the Fe site in terms of both coordination and size: in particular the V site is larger in volume than the Fe site and has no Al neighbors. Although V atoms, being larger than Fe, certainly prefer to occupy the V site, V atoms in excess of stoichiometry in the V-rich region, i.e., $x>0$ would be forced to enter the smaller Fe site. This site disorder could cause intermixing of Fe and V atoms or partial Fe occupation on the nominally V site in the measured samples with $x>0.02$. The band calculations suggest that intermixing of Fe and V atoms results in a ferromagnetic ordering in Fe_2VAl.[2] In fact, the magnetization data for $x>0.02$ in Fig. 2 provide clear evidence for the presence of local magnetic moments. We conclude from Fig. 2 that the $x=0.02$ sample must contain the least amount of antisite defects for a series of $Fe_{2-x}V_{1+x}Al$ over $-0.01 \leqslant x \leqslant 0.08$.

Figure 3 shows the temperature dependence of the electrical resistivity in $Fe_{2-x}V_{1+x}Al$ with compositions $-0.01 \leqslant x \leqslant 0.08$. The resistivity for $x=-0.01$ reaches 3000 $\mu\Omega$ cm at 4.2 K and shows a negative temperature dependence over the whole temperature range up to 1300 K. The observed semiconductorlike behavior is consistent with the sharp enhancement in the magnetization at low temperatures. In parallel with the significant decrease in the magnetization, however, the resistivity for the slightly V-rich sample with $x=0.02$ is drastically reduced to only 300 $\mu\Omega$ cm at 4.2 K, which is an order of magnitude lower than that for $x=-0.01$. The resistivity for $x=0.02$ shows a positive slope in its temperature dependence below 300 K, forming a broad maximum, and then turns to decrease with a further rise in temperature. A similar resistance maximum has been observed for slightly V-rich Fe_2VAl samples as far as they are well annealed.[16,17] Although the data on $x=0$ are not plotted in Fig. 3, the resistivity for a stoichiometrically prepared sample was found between those for $x=-0.01$ and 0.02, or about 2600 $\mu\Omega$ cm at 4.2 K, as reported previously.[19] The resistivity data shown in Fig. 3 are also consistent with our earlier conclusion that the sample least affected by magnetic antisite defects is obtained at about $x=0.02$.

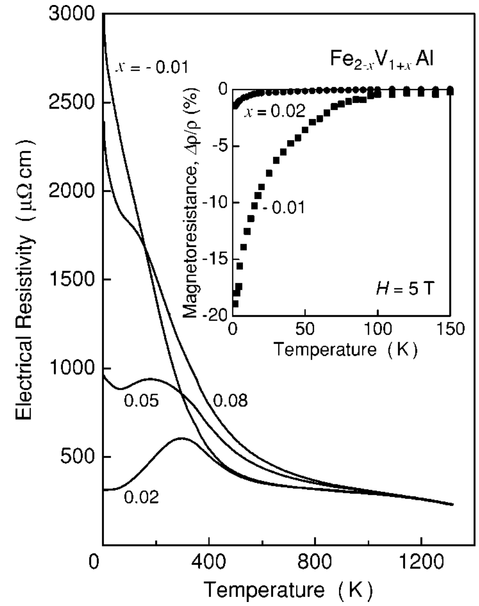

FIG. 3. Temperature dependence of electrical resistivity in $Fe_{2-x}V_{1+x}Al$ with compositions $-0.01 \leqslant x \leqslant 0.08$. The inset shows the temperature dependence of the magnetoresistance $\Delta\rho/\rho$ measured under 5 T magnetic field for $x=-0.01$ and 0.02.

In the inset of Fig. 3, the magnetoresistance $\Delta\rho/\rho$ for $x=-0.01$ and 0.02 is plotted as a function of temperature, where $\Delta\rho$ is defined as a difference in the resistivity in the presence and absence of a magnetic field of 5 T. The magnetoresistance is always negative at low temperatures. This can be taken as evidence for the suppression of magnetic scattering upon the application of 5 T. The magnitude of the negative magnetoresistance is very small for $x=0.02$ but reaches approximately 20% at 2 K for $x=-0.01$. The appearance of a large negative magnetoresistance for $x=-0.01$ resulted in a slightly positive slope at temperatures below 20 K in the temperature dependence of the resistivity under the presence of 5 T magnetic field. The present magnetoresistance data are in good agreement with previously reported ones,[10,15,17] and a consistent behavior between the resistivity and the magnetoresistance strongly lends support to our claim that a steep rise of resistivity at low temperatures is indeed magnetic in origin.

Further increase in the V composition above $x=0.02$ causes a significant increase in the low-temperature resistivity up to 2400 $\mu\Omega$ cm at 4.2 K for $x=0.08$. It is interesting to note that an overall behavior for $x=0.08$ resembles that for $x=-0.01$, suggesting that magnetic antisite defects are the richest in these two samples and that these defects play a key role in the electron-transport properties. Despite the possession of the large resistivity for $x=0.08$, its temperature dependence does not seem to be fitted to an ordinary $\exp(-\Delta/2k_BT)$-type equation expected to hold for a semiconductor with an energy gap Δ. Hence, a steep rise below 100 K may be indicative of the superposition of a temperature-dependent magnetic scattering effect associated

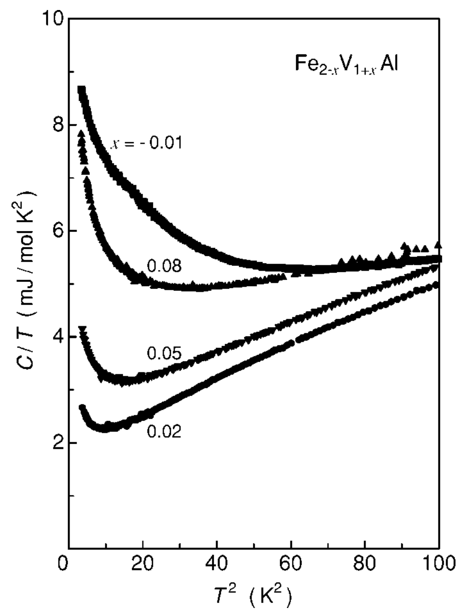

FIG. 4. Specific heat over temperature, C/T, vs T^2 measured for $Fe_{2-x}V_{1+x}Al$ with compositions $-0.01 \leqslant x \leqslant 0.08$.

with spin fluctuations, although the effect of spin fluctuations on the electron transport remains speculative because of the lack of a theoretical model.

In spite of a large difference in the low-temperature resistivity behavior between $x=-0.01$ and 0.02, the resistivity curves almost coincide with each other above 400 K. As we reported previously,[1] plots of ln ρ versus $1/T$ (ρ, resistivity; T, temperature) for the data in the temperature interval 400–800 K become almost linear, and an energy gap Δ of about 0.1 eV is deduced from its slope. A similar thermal excitation behavior has been observed in NMR experiments,[7] which yield an energy gap of about 0.2 eV. We believe that an overall temperature dependence of the resistivity for the $x=0.02$ sample is interpreted by assuming the system to be nonmagnetic while possessing a deep pseudogap at the Fermi level. A positive slope at low temperatures is simply caused by an increasing phonon scattering and, when the temperature is increased beyond 300 K, a negative slope dominates as a result of increasing thermal excitations across the pseudogap of the order of 0.1 eV in width.

The semiconductorlike behavior of electrical resistivity in Fe_2VAl occurs concomitantly with an upturn of the specific heat over temperature, C/T, with decreasing T^2, suggesting also a spin-fluctuation mechanism.[1] Later, Lue *et al.*[13] reported specific-heat measurements in the presence of magnetic fields down to 0.6 K and pointed out that the low-temperature upturn is attributed to a Schottky anomaly arising from local magnetic moments. In Fig. 4, the specific heat C measured for $Fe_{2-x}V_{1+x}Al$ with compositions $-0.01 \leqslant x \leqslant 0.08$ is shown in the conventional form of C/T against T^2 over the temperature range 1.6–10 K. Note here that the present value of C is defined in units of mJ per mole atom K and should be multiplied by a factor of 4 when expressed in terms of "chemical formula" mole. The low-temperature upturn in C/T was clearly observed for the $x=-0.01$ sample in Fig. 4. In contrast, the upturn in C/T is considerably suppressed for the $x=0.02$ sample and, instead, C/T varies almost linearly with T^2 in the temperature range above 3 K. Thus the γ value for $x=0.02$ is determined to be 1.9 mJ/mol K^2. This γ value for the least magnetic sample happens to be quite close to that of 1.5 mJ/mol K^2 reported in Ref. 13, which was obtained by fitting their data between 8 and 25 K to the ordinary equation $C=\gamma T+\alpha T^3+\delta T^5$. This is taken as a strong indication that the $x=0.02$ sample contains the least amount of magnetic defects in $Fe_{2-x}V_{1+x}Al$ with compositions $-0.01 \leqslant x \leqslant 0.08$. Further increase in the V composition x beyond 0.02 again introduces the C/T upturn, lending support to an increase in magnetic antisite defects discussed above. Thus, we consider the present specific-heat data to be well consistent with the data of resistivity and magnetization at low temperatures.

B. Effects of heat treatment

The influence of heat treatment on the transport and magnetic properties of Fe_2VAl was investigated by Matsushita and Yamada,[20] who observed the semiconductorlike behavior of electrical resistivity only when quenched into water after high-temperature annealing. This is apparently contrasted with the steep rise of resistivity observed for the well-annealed sample.[1] Thus the question arises whether the number of antisite Fe defects depends on either being well annealed or quenched from high temperatures. All the data shown in Figs. 2–4 in the present work were taken for samples subjected to annealing at 1273 K for 1 h and then at 673 K for 4 h in vacuum with subsequent slow cooling to room temperature. As emphasized in the preceding section, the $x=0.02$ sample was the least contaminated with magnetic antisite defects and exhibited a semimetallic electron-transport behavior with a substantially low residual resistivity.

We consider the antisite disorder to be very sensitive to the heat-treatment conditions under which samples are prepared and naturally expect that such forms of crystallographic disorder could be frozen in upon quenching from high temperatures. The concentration of such magnetic defects is, therefore, considered to increase with increasing quenching temperature. In order to gain further insight into the effect of magnetic antisite defects, we studied the temperature dependence of the electrical resistivity, specific heat, and magnetization by selecting different quenching conditions for the slightly V-rich $Fe_{1.98}V_{1.02}Al$ ($x=0.02$) sample, which has been identified to be almost nonmagnetic in the annealed state.

Figure 5 shows the temperature dependence of the electrical resistivity for the $x=0.02$ samples quenched after holding at 1023, 1073, 1123, and 1173 K for 4 h, respectively. The dotted curve for the annealed sample is reproduced from that in Fig. 3. As the quenching temperature increases, the low-temperature resistivity increases rapidly and the negative temperature dependence appears on the resistivity curves whose slope becomes steeper with increasing quenching temperature. In particular, when quenched from 1173 K, the resistivity reaches 2600 $\mu\Omega$ cm at 4.2 K, which is almost an order of magnitude higher than that for the annealed sample,

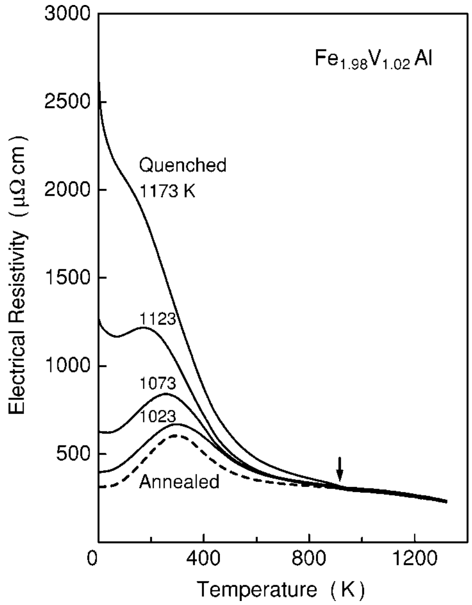

FIG. 5. Temperature dependence of electrical resistivity in $Fe_{1.98}V_{1.02}Al$ ($x=0.02$) quenched after holding at 1173, 1123, 1073, and 1023 K: the dotted curve is for the annealed sample. The arrow shows the inflection of the resistivity curves.

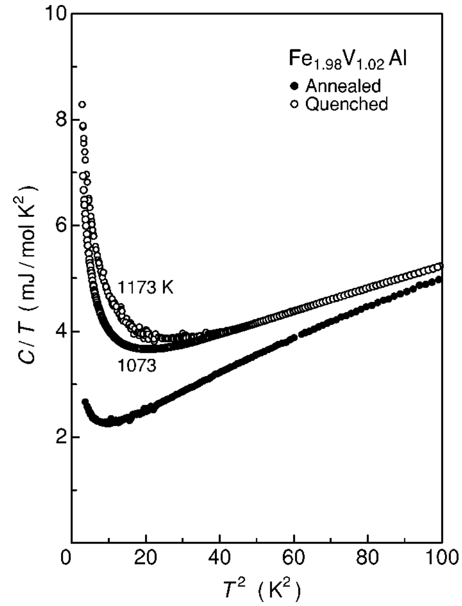

FIG. 6. The specific heat over temperature, C/T, vs T^2 measured for $Fe_{1.98}V_{1.02}Al$ ($x=0.02$) quenched after holding at 1173 and 1073 K (open circles): the solid circles show the data on the annealed sample.

and shows a negative resistivity slope over the whole temperature range. This is actually very similar to that for the annealed sample with $x=0.08$ in Fig. 3. It is interesting to note that the resistivity for quenched samples with $x=-0.01$ exhibited a much steeper rise at low temperatures than those shown in Fig. 5, reaching approximately 10 000 $\mu\Omega$ cm at 4.2 K when quenched from 1173 K.

In the temperature range higher than 400 K, the electrical resistivity for the quenched samples decreases exponentially with increasing temperature in the same manner as that for the annealed sample. It is worthwhile noting that the resistivity curves for the quenched samples exhibit an inflection at about 920 K, as shown by the arrow in Fig. 5, which is hardly observed for the annealed sample. A change in resistivity at the inflection point is only less than 50 $\mu\Omega$ cm. Since the temperature at the inflection is about half the melting point of approximately 1750 K for Fe_2VAl, it might be caused by a recovery and recrystallization process, during which crystallographic disorders, such as vacancies introduced in the quenched samples, disappear. Above the inflection point, all the resistivity curves fall on a master curve, irrespective of the quenching temperature.

In order to confirm the effect of antisite defects, we further measured the low-temperature specific heat and the magnetization for the quenched samples. In Fig. 6, the C/T versus T^2 data are shown for the $x=0.02$ samples quenched after holding at 1073 and 1173 K for 4 h: the solid circles are reproduced from Fig. 4 for the annealed sample. In contrast to an almost linear behavior for the annealed sample, the low-temperature upturn in C/T is found to be substantially enhanced for the quenched samples. Therefore the sharp rise of resistivity at low temperatures is always accompanied by the enhancement in the electronic specific heat, as in the case for the annealed sample with $x=-0.01$.

Figure 7 shows the temperature dependence of the magnetization measured under a magnetic field of 1 T for the $x=0.02$ samples quenched after holding at 1073 and 1173 K for 4 h: the solid circles are reproduced from Fig. 2 for the annealed sample. All the samples are identified as paramagnets in the temperature range above 2 K as confirmed from

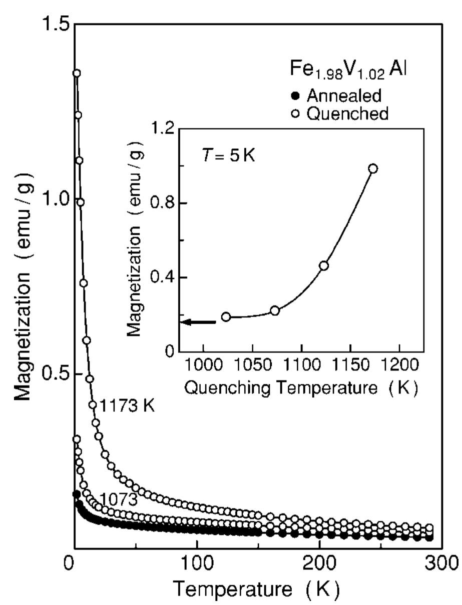

FIG. 7. Temperature dependence of magnetization in $Fe_{1.98}V_{1.02}Al$ ($x=0.02$) quenched after holding at 1173 and 1073 K (open circles): the solid circles show the data on the annealed sample. The magnetization was measured under a magnetic field of 1 T. The inset shows the magnetization at 5 K as a function of quenching temperature: the arrow indicates the value for the annealed sample.

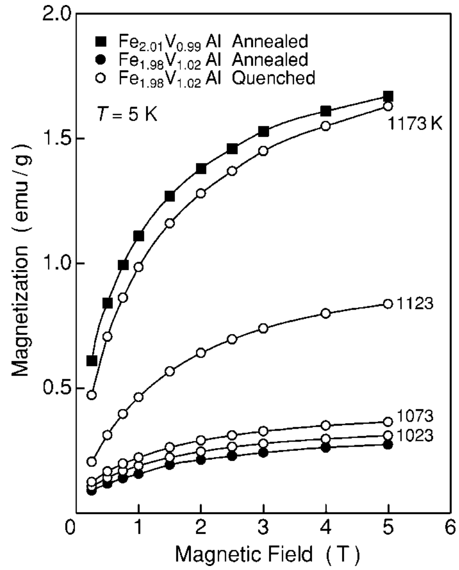

FIG. 8. Magnetic-field dependence of magnetization measured at 5 K in $Fe_{2.01}V_{0.99}Al$ ($x=-0.01$) and $Fe_{1.98}V_{1.02}Al$ ($x=0.02$). The solid and open symbols show the data on annealed and quenched samples, respectively.

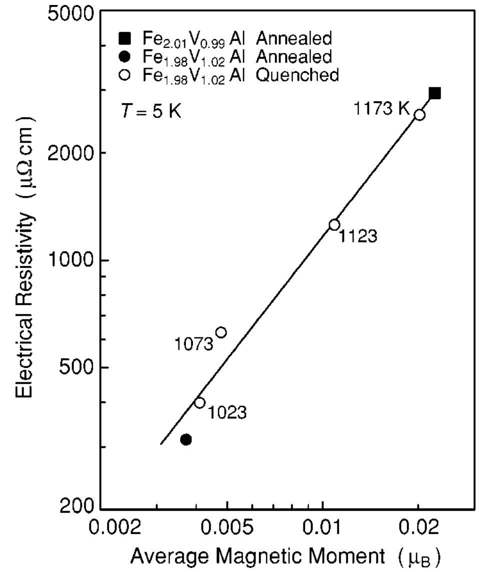

FIG. 9. Relation between the electrical resistivity at 5 K and the average magnetic moment of Fe atoms in $Fe_{2.01}V_{0.99}Al$ ($x=-0.01$) and $Fe_{1.98}V_{1.02}Al$ ($x=0.02$). The solid and open symbols show the data on annealed and quenched samples, respectively.

the Arrott plots for the data on magnetic-field dependence of the magnetization. The magnetization increases rapidly with increasing quenching temperature and shows an upturn at low temperatures, suggesting an increase in the defect concentration due to quenching. It must be remembered at this stage that such a remarkable change in the magnetic behavior between the annealed and quenched samples was never reflected in the peak intensities of XRD data, such as that shown in Fig. 1, though a slight suppression of the (111) peak can be observed due to structural disorder caused by quenching. In the inset of Fig. 7, the magnetization at 5 K is plotted as a function of the quenching temperature: the value for the annealed sample is shown by the arrow. Remarkably, the magnetization for the sample quenched from 1173 K is found to be comparable to that for the annealed $x=-0.01$ sample shown in the inset of Fig. 2. We are, therefore, led to conclude that the transport and magnetic properties of $Fe_{2-x}V_{1+x}Al$ are very sensitive to the number of magnetic antisite defects that heavily depends on the heat-treatment conditions to which samples are subjected.

C. Relation between resistivity and magnetic moment

While most of the theoretical works point to the importance of spin fluctuations as a primary cause for the unusual transport properties of Fe_2VAl, no quantitative discussion has been made in the past because of the lack of experimental data on the number of magnetic antisite defects. We consider it to be of crucial importance to evaluate quantitatively the concentration of magnetic defects, to gain more insight into the mechanism for the steep rise of resistivity at low temperatures. The magnetic-field dependence of magnetization was measured at 5 K for the annealed sample of $Fe_{2.01}V_{0.99}Al$ ($x=-0.01$) and also for the annealed and quenched samples of $Fe_{1.98}V_{1.02}Al$ ($x=0.02$). As shown in Fig. 8, the magnetization for $Fe_{1.98}V_{1.02}Al$ increases with raising quenching temperature, so that the curve for the sample quenched from 1173 K closely resembles that for the annealed sample of $Fe_{2.01}V_{0.99}Al$. The magnetization is found to increase with increasing magnetic field in a manner similar to that for soft ferromagnets. Feng *et al.*[10] also reported similar magnetic-field dependence for nearly stoichiometric samples prepared under different annealing conditions. The present result strongly suggests that antisite defects produced by distributing Fe atoms on the nominally V site are responsible for the generation of local magnetic moments. Hence, the observed large resistivity at low temperatures is ascribed to the interaction of conduction electrons with spin fluctuations arising from dynamical motions of such local magnetic moments.[3]

The local magnetic moments associated with antisite Fe atoms may be obtained from the magnetic-field dependence of the magnetization shown in Fig. 8. The magnetization, M, at high fields is expressed in the following form:

$$M = M_0 + \chi H, \tag{1}$$

where χ is the susceptibility at high fields, H is the magnetic field, and M_0 is the intercept obtained by extrapolating the magnetization curves to $H=0$. The average magnetic moment of Fe atoms, μ_{av}, is obtained in units of the Bohr magneton (μ_B) as follows:

$$\mu_{av} = M_0 W / 2 N_A \mu_B, \tag{2}$$

where W is in g mol per formula unit, N_A denotes Avogadro's number, and the factor of 2 in the denominator arises because of two Fe atoms per formula unit.

Figure 9 shows the electrical resistivity at 5 K as a function of the average magnetic moment of Fe atoms estimated as discussed above. The data are found to fall on a universal line on the log-log scale, whose slope is approximately equal to 1. This means that the electrical resistivity is directly proportional to the average magnetic moment of Fe atoms. It is interesting to note that the data on the annealed $Fe_{2.01}V_{0.99}Al$ is also in line with those for the annealed and quenched $Fe_{1.98}V_{1.02}Al$. The supercell band calculations[3] and the Korringa-Kohn-Rostoker coherent-potential approximation (KKR-CPA) calculations[6] showed that Fe atoms on the V site carry local magnetic moments of 2.1–2.4 μ_B and 3.2 μ_B, respectively. Of course, Fe atoms on the original Fe site could also possess a magnetic moment when the surrounding V atoms are replaced by Fe atoms. On the assumption that the magnetic moment of antisite Fe atoms is 2.2 μ_B and other atoms carry no moments, the concentration of antisite Fe atoms is estimated to be 0.52% and 0.46% for the annealed $Fe_{2.01}V_{0.99}Al$ and the quenched $Fe_{1.98}V_{1.02}Al$ after holding at 1173 K, respectively. The antisite defect concentration is extremely large as compared with the value of less than 0.1% for the annealed $Fe_{1.98}V_{1.02}Al$. All of the analysis above led us to conclude that local magnetic moments associated with these antisite defects, in combination with a very low carrier density originating from the pseudogap at the Fermi level, must be a crucial factor responsible for the steep rise of resistivity at low temperatures.

In our recent report on the effects of off stoichiometry on the electrical resistivity and the Seebeck coefficient,[19] the pseudogap system Fe_2VAl has been shown to be an intriguing candidate for low- and intermediate-temperature thermoelectric application. In particular, a small deviation of the Al content from stoichiometry causes a significant decrease in the low-temperature resistivity and a large enhancement in the Seebeck coefficient with a change in its sign depending on the Al-rich or Al-poor sample. Similarly, a large Seebeck coefficient with a negative sign has been found for V-rich $Fe_{2-x}V_{1+x}Al$ samples,[21,22] although the resistivity is much higher than those with off stoichiometry for the Al content. Substantial enhancements for the Seebeck coefficient can be explained by using the electronic structure, in which the Fermi level shifts slightly from the center of the pseudogap due to off stoichiometry.[19] Further studies are in progress to clarify the role of spin fluctuations on the thermoelectric properties in the marginally magnetic Fe_2VAl system.

IV. CONCLUSIONS

After the discovery of the semiconductorlike temperature dependence of electrical resistivity in Fe_2VAl (Ref. 1), a vast amount of resistivity data has been reported from different groups but they were, unfortunately, not necessarily consistent with each other. In order to show how the transport properties of Fe_2VAl are affected by the presence of magnetic defects, we have systematically measured the magnetization, electrical resistivity, and specific heat for $Fe_{2-x}V_{1+x}Al$ with $-0.01 \leqslant x \leqslant 0.08$. The slightly V-rich $x=0.02$ sample exhibited the smallest magnetization over the range 2–300 K coupled with the lowest residual resistivity with a positive temperature slope below 300 K. This shows that the $x=0.02$ sample contains a very small concentration of antisite defects, the lowest concentration among those samples that we prepared. Other data including magnetoresistance, the specific heat over the range 1.6–10 K, plus the annealing effect on these properties are also consistently explained along this line. Therefore, we conclude that the annealed $x=0.02$ sample contains the least amount of magnetic defects and best represents a nonmagnetic semimetal as predicted by the band calculations. Indeed, a shift in x from 0.02, regardless of either positive or negative direction including $x=0$, always leads to a sharp rise of resistivity at low temperatures along with an enhancement in the magnetization and the electronic specific heat.

When quenched from high temperatures, even the $x=0.02$ sample exhibits a steeper rise of resistivity at low temperatures because of the introduction of a larger number of magnetic defects. Based on a linear relation between the electrical resistivity and the magnetic moment carried by antisite Fe atoms, we can reliably estimate the defect concentration to be about 0.5% for the $x=-0.01$ sample but to be less than 0.1% for the annealed $x=0.02$ sample. A substantial increase in the low-temperature resistivity is attributed to spin fluctuations of magnetic antisite defects in combination with a very low carrier density originating from the pseudogap at the Fermi level.

[1] Y. Nishino, M. Kato, S. Asano, K. Soda, M. Hayasaki, and U. Mizutani, Phys. Rev. Lett. **79**, 1909 (1997).

[2] G. Y. Guo, G. A. Botton, and Y. Nishino, J. Phys.: Condens. Matter **10**, L119 (1998).

[3] D. J. Singh and I. I. Mazin, Phys. Rev. B **57**, 14 352 (1998).

[4] R. Weht and W. E. Pickett, Phys. Rev. B **58**, 6855 (1998).

[5] M. Weinert and R. E. Watson, Phys. Rev. B **58**, 9732 (1998).

[6] A. Bansil, S. Kaprzyk, P. E. Mijnarends, and J. Tobola, Phys. Rev. B **60**, 13 396 (1999).

[7] C. S. Lue and J. H. Ross, Jr., Phys. Rev. B **58**, 9763 (1998); *ibid.* **61**, 9863 (2000).

[8] M. Kato, Y. Nishino, S. Asano, and S. Ohara, J. Jpn. Inst. Met., **62**, 669 (1998).

[9] H. Okamura, J. Kawahara, T. Nanba, S. Kimura, K. Soda, U. Mizutani, Y. Nishino, M. Kato, I. Shimoyama, H. Miura, K. Fukui, K. Nakagawa, H. Nakagawa, and T. Kinoshita, Phys. Rev. Lett. **84**, 3674 (2000).

[10] Ye Feng, J. Y. Rhee, T. A. Wiener, D. W. Lynch, B. E. Hubbard, A. J. Sievers, D. L. Schlagel, T. A. Lograsso, and L. L. Miller, Phys. Rev. B **63**, 165109 (2001).

[11] K. Soda, T. Mizutani, O. Yoshimoto, S. Yagi, U. Mizutani, H. Sumi, Y. Nishino, Y. Yamada, T. Yokoya, S. Shin, A. Sekiyama, and S. Suga, J. Synchrotron Radiat. **9**, 2333 (2002).

[12] M. Kato, Y. Nishino, U. Mizutani, and S. Asano, J. Phys.: Con-

dens. Matter **12**, 1769 (2000).

[13] C. S. Lue, J. H. Ross, Jr., C. F. Chang, and H. D. Yang, Phys. Rev. B **60**, R13 941 (1999).

[14] C. S. Lue, J. H. Ross, Jr., K. D. D. Rathnayaka, D. G. Naugle, S. Y. Wu, and W.-H. Li, J. Phys.: Condens. Matter **13**, 1585 (2001).

[15] H. Matsuda, K. Endo, K. Ooiwa, M. Iijima, Y. Takano, H. Mitamura, T. Goto, M. Tokiyama, and J. Arai, J. Phys. Soc. Jpn. **69**, 1004 (2000).

[16] H. Sumi, M. Kato, Y. Nishino, S. Asano, and U. Mizutani, J. Jpn. Inst. Met. **65**, 771 (2001).

[17] A. Matsushita, T. Naka, Y. Takano, T. Takeuchi, T. Shishido, and Y. Yamada, Phys. Rev. B **65**, 075204 (2002).

[18] A. Arrott and H. Sato, Phys. Rev. **114**, 1420 (1959).

[19] Y. Nishino, H. Kato, M. Kato, and U. Mizutani, Phys. Rev. B **63**, 233303 (2001).

[20] A. Matsushita and Y. Yamada, J. Magn. Magn. Mater. **196–197**, 669 (1999).

[21] C. S. Lue and Y.-K. Kuo, Phys. Rev. B **66**, 085121 (2002).

[22] Y. Hanada, R. O. Suzuki, and K. Ono, J. Alloys Compd. **329**, 63 (2001).