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Magnetic and electrical properties of $Fe_{2+x}V_{1-x}Al$

T. Kanomata[a,*], T. Sasaki[a], T. Hoshi[a], T. Narita[a], T. Harada[a], H. Nishihara[b], T. Yoshida[b], R. Note[c], K. Koyama[c], H. Nojiri[c], T. Kaneko[c], M. Motokawa[c]

[a]*Department of Applied Physics, Faculty of Engineering, Tohoku Gakuin University, 1-13-1 Chuo, Tagajo, 985-8537, Japan*
[b]*Faculty of Science and Technology, Ryukoku University, Otsu, 520-2123, Japan*
[c]*Institute for Materials Research, Tohoku University, Sendai, 980-8577, Japan*

Abstract

Magnetization, electrical resistivity, thermoelectric power and magnetoresistance were measured for the ordered alloys $Fe_{2+x}V_{1-x}Al$ ($0 \leq x \leq 0.4$). The magnetization measurement shows that the phases are ferromagnetic. Both the Curie temperature and the spontaneous magnetization increase with increasing x. The samples with $x \leq 0.1$ exhibit a semiconductor-like behavior. Energy gap E_G decreases with increasing x. The electrical resistivity versus temperature curves make a broad maximum near T_C for the samples with $x=0.18$, 0.20 and 0.40. For $Fe_{2.18}V_{0.82}Al$, negative large magnetoresistance is observed.

Keywords: $Fe_{2+x}V_{1-x}Al$; Spontaneous magnetization; Curie temperature; Electrical resistivity; Magnetoresistance; Thermoelectric power

1. Introduction

Webster and Ziebeck reported that Fe_2VAl forms a single-phase intermetallic compound with the Heusler $L2_1$ structure [1]. The crystal structure of Fe_2VAl is shown in Fig. 1. According to their experimental results of the magnetic measurement, Fe_2VAl remains weakly paramagnetic in the temperature range from 5 to 300 K. This paramagnetic property of Fe_2VAl was shown to be non-Curie–Weiss. Recently, Fe_2VAl has attracted the interest because of the intriguing behavior of its transport, photoelectric and thermodynamic properties [2–7]. The resistivity shows semiconducting behavior with a negative temperature coefficient suggesting an energy gap of ~0.1 eV [2]. The photoemission spectrum, on the other hand, shows a clear Fermi edge characterizing the metallic properties of Fe_2VAl [2]. Low-temperature specific heat measurements revealed an unusual upturn in C/T with decreasing temperature, commonly observed in most heavy-fermion systems [2,7]. From band structure calculations, Fe_2VAl is a semimetal with a pseudogap at the Fermi level [8–11].

Intermetallic compound Fe_3Al is a ferromagnet with a DO_3 crystal structure. The Curie temperature T_C and the saturation magnetic moment at 4.2 K of Fe_3Al are ~770 K [12] and ~5.2 μ_B/f.u. [13], respectively. The mixed crystals $Fe_{2+x}V_{1-x}Al$ ($0 \leq x \leq 1$) of Fe_2VAl and Fe_3Al form

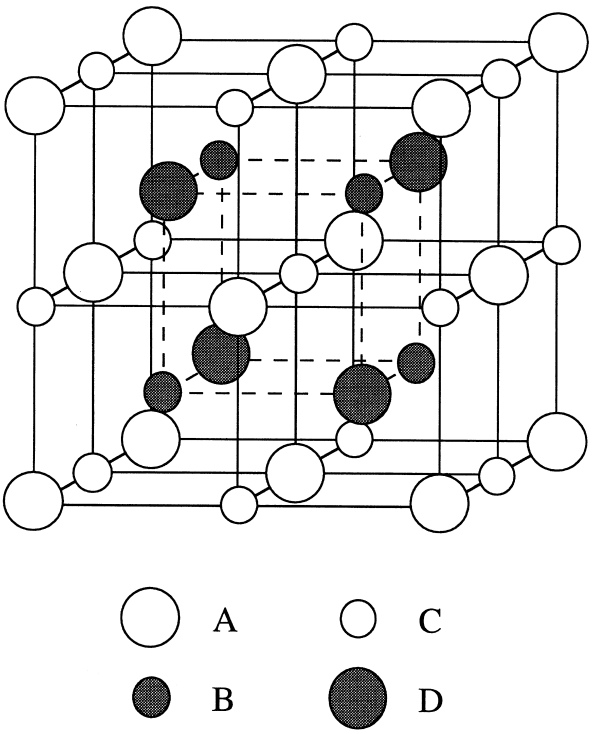

Fig. 1. Unit cell of the cubic Heusler-type compound Fe_2VAl. The sites are represented by A, B, C and D. The A and C sites are equivalent and are occupied by Fe atoms, the B site is occupied by V, and the D site by Al.

*Corresponding author. Fax: +81-22-368-7070.
E-mail address: kanomata@tjcc.tohoku-gakuin.ac.jp (T. Kanomata).

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a complete solid solution [14]. Nishino et al. [2] and Endo et al. [3] found that $Fe_{2+x}V_{1-x}Al$ with $1 \geq x > 0$ shows ferromagnetism, and a curious 'resistance maximum' near T_C in the electrical resistivity ρ versus temperature curves. At temperatures above T_C, the temperature gradient of ρ was negative, similar to that of semiconductor. Moreover, Endo et al. found that the absolute value of the transverse magnetoresistance represented by $\Delta\rho/\rho(0)$ takes maximum near T_C for $Fe_{2.2}V_{0.8}Al$, where $\Delta\rho$ is $\rho(H) - \rho(0)$, and $\rho(0)$ is zero field resistivity at the measured temperature. The value of $\Delta\rho/\rho(0)$ for $Fe_{2.2}V_{0.8}$ Al is negative and ~5% at 13 kOe near T_C. Such resistance phenomena have not yet been explained. To make clear the origin of these transport properties, we have studied systematically the magnetic and electrical properties of Heusler-type pseudobinary alloys $Fe_{2+x}V_{1-x}Al$ ($0 \leq x \leq 0.4$).

2. Experimental

The pseudobinary alloys $Fe_{2+x}V_{1-x}Al$ ($0 \leq x \leq 0.4$) were prepared by repeated melting of appropriately composed mixtures of 99.95% pure Fe, 99.9% pure V and 99.9999% pure Al, in an argon arc furnace. Since the weight loss after melting was negligible, the nominal composition was accepted as being accurate. To get the homogenized samples, the reaction products were sealed in evacuated silica tubes, heated at 1000°C for 3 days and then quenched in water. X-ray diffraction spectra were taken with Cu Kα radiation on powder samples prepared as above. All X-ray lines of the prepared samples were indexed with the cubic structure. The lattice parameters were determined from the X-ray diffraction patterns using the Nelson and Rily method [15]. The lattice parameter was found to be $a = 5.7629$ Å for Fe_2VAl ($x = 0$). The value of a for Fe_2VAl is consistent with those previously reported by Webster and Ziebeck [1], Buschow et al. [16], and Buschow and van Engen [17]. The concentration dependence of the lattice parameter a at room temperature for $Fe_{2+x}V_{1-x}Al$ ($0 \leq x \leq 0.4$) is shown in Fig. 2. The lattice parameter increases with increasing Fe concentration. The V atom in Fe_2VAl has eight Fe nearest neighbors and the Fe atom has four V and four Al nearest neighbors. For $Fe_{2+x}V_{1-x}Al$, the selective substitution of Fe atoms for the V site in Fe_2VAl was supported by X-ray analysis [14] and band calculation [8]. We have confirmed the atomic ordering for all samples from the appearance of the superlattice lines in X-ray diffraction spectra.

Magnetization data were taken using a commercial superconducting quantum interference device (SQUID) magnetometer. The DC electrical resistivity (ρ) was measured by a four-probe technique using mechanical positional point contacts, where tungsten wires (0.3 mm Ø) are used as spring for pressure contact and platinum is soldered on the end of the tungsten wires to ensure the electric contact. The thermoelectric power S was measured by the same method as that of Nagy and Toth [18]. The transverse magnetoresistance measurement, using the standard four-probe DC technique, was performed in the magnetic fields up to 220 kOe using a pulse magnet.

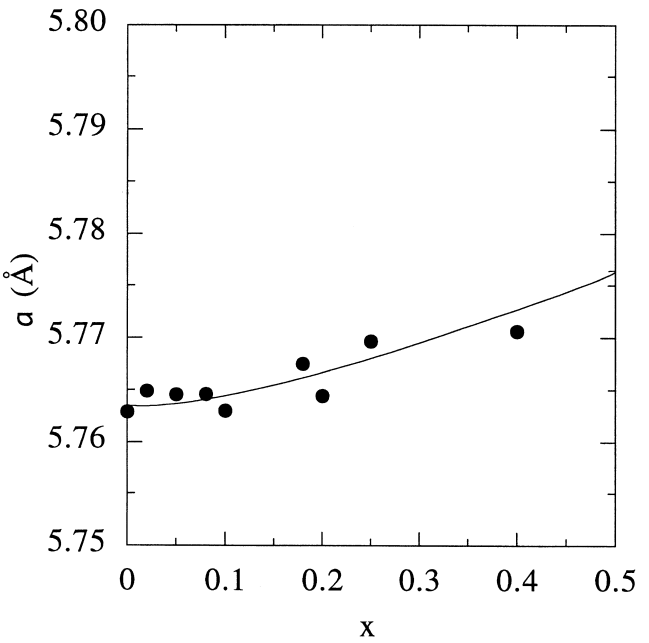

Fig. 2. Lattice parameter versus concentration x curve for $Fe_{2+x}V_{1-x}Al$ at room temperature. Solid line in the figure is a guide for the eye.

3. Results and discussions

Fig. 3 shows the magnetization curves at 5 K of $Fe_{2+x}V_{1-x}Al$ ($x = 0.05$, 0.18, 0.25 and 0.40) in magnetic fields up to 50 kOe. As seen in Fig. 3, the magnetization σ of samples is saturated in the magnetic field of about 10 kOe. The magnetization increases with increasing x. The spontaneous magnetization σ_s at 5 K was determined by the linear extrapolation to $H/\sigma = 0$ of the σ^2 versus H/σ curves (Arrott plot) at high fields. The concentration dependence of σ_s at 5 K is shown in Fig. 4 with the data reported by Endo et al. [3]. The spontaneous magnetization of $Fe_{2+x}V_{1-x}Al$ increases linearly with increasing x. The magnetic moment at 5 K of $Fe_{2.05}$ $V_{0.95}Al$ is found to be 0.26 μ_B per formula unit. Assuming that excess Fe atoms at the V sites in $Fe_{2.05}V_{0.95}$ Al form 9Fe atom clusters and carry magnetic moments, the magnetic moment per cluster is found to be 5.2 μ_B. Recently, Bansil et al. [11] have carried out the band calculation for $Fe_{2+x}V_{1-x}Al$ ($x = 0.25$, 0.50 and 0.75), together with the end compounds Fe_3Al and Fe_2VAl, and the limiting cases of a single V impurity in Fe_3Al and a single Fe impurity at the V sites in Fe_2VAl using the methodology based on the Korringer–Kohn–Rostoker formalism and the coherent-potential approximation [11]. In the $x = 0$ limit (the dilute Fe impurity

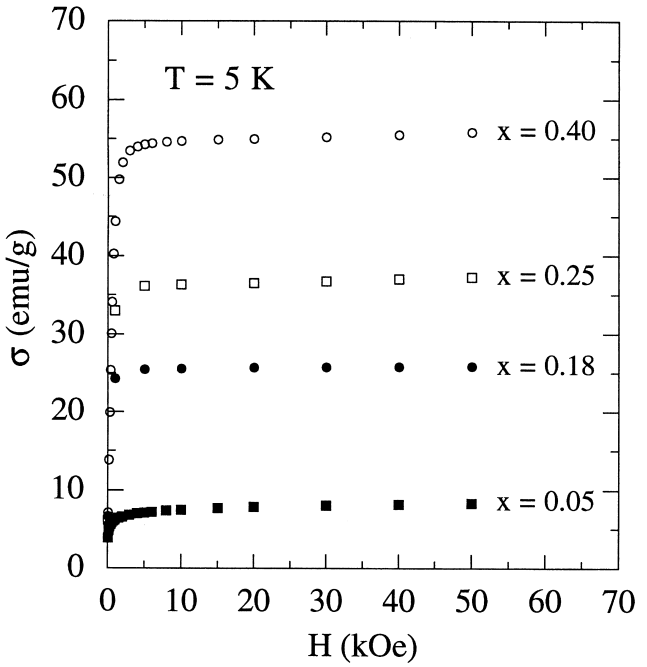

Fig. 3. Magnetization curves at 5 K of $Fe_{2+x}V_{1-x}Al$ at various concentrations.

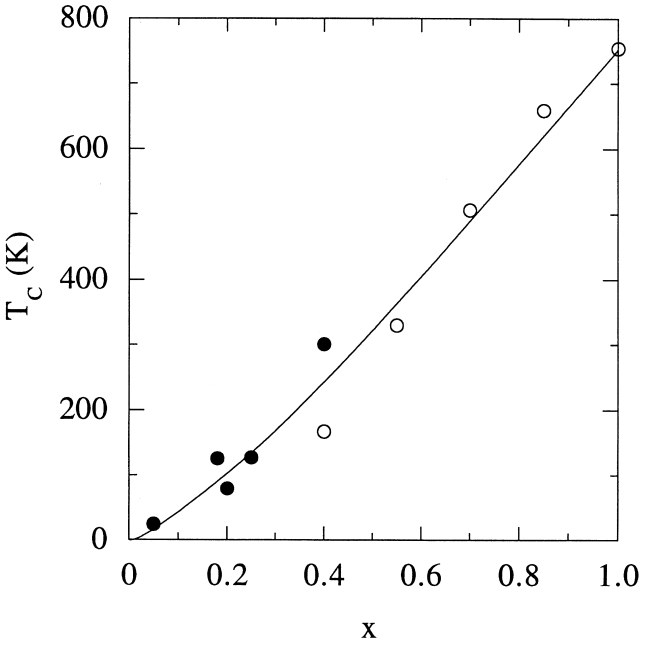

Fig. 5. Concentration dependence of the Curie temperature T_C for $Fe_{2+x}V_{1-x}Al$. The closed and open circles are the present results and the data from Ref. [2], respectively. The solid line in the figure is a guide for the eye.

limit), the magnetic moment on Fe atom at the V sites was found to be 3.2 μ_B. Therefore, 8Fe atoms surrounding the center atom in a cluster may be expected to carry a small magnetic moment for $Fe_{2.05}V_{0.95}Al$.

Fig. 5 shows the concentration dependence of T_C for $Fe_{2+x}V_{1-x}Al$ together with the results obtained by Nishino et al. [2]. In this figure our results, represented by the closed circles, are on the curve extended from the results obtained by Nishino et al. [2], suggesting that Fe_2VAl is paramagnetic.

Fig. 6 shows the temperature dependence of the electri-

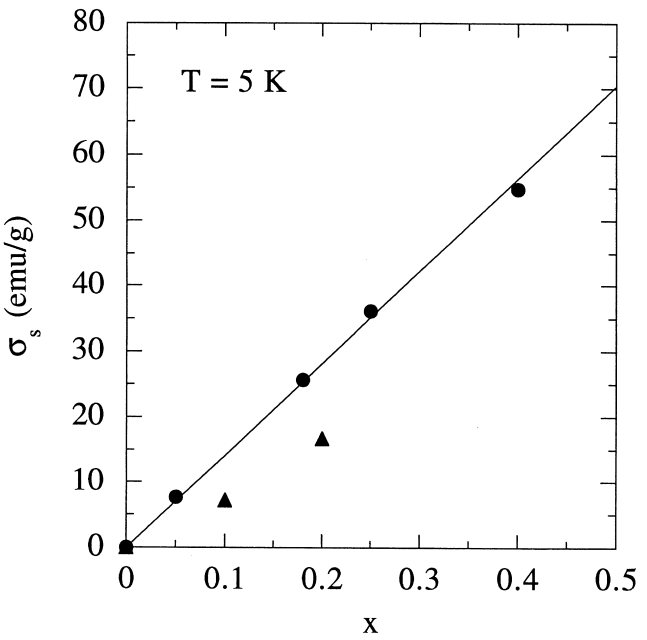

Fig. 4. Concentration dependence of spontaneous magnetization σ_s at 5 K for $Fe_{2+x}V_{1-x}Al$. The closed circles and closed triangles are the present results and the data from Ref. [3], respectively.

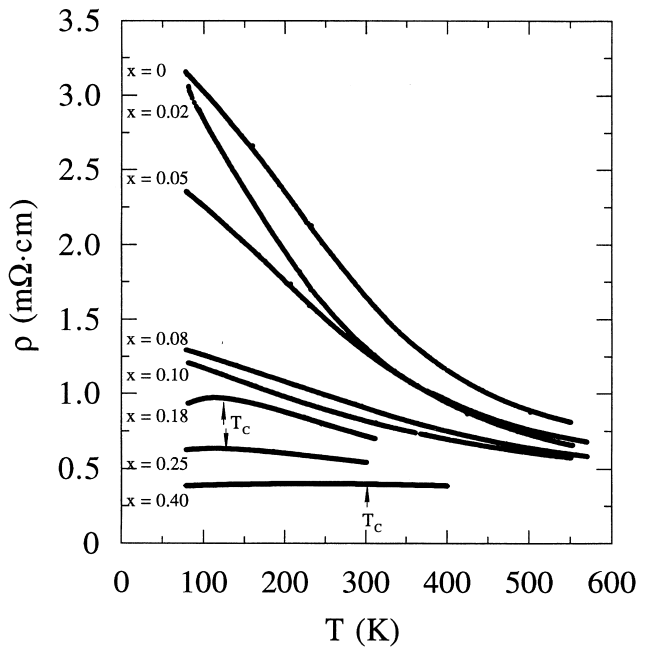

Fig. 6. Temperature dependence of the electrical resistivity ρ for $Fe_{2+x}V_{1-x}Al$ for various concentrations. The arrows indicate the Curie temperature T_C.

cal resistivity ρ in $Fe_{2+x}V_{1-x}Al$ with various concentrations. As seen in the figure, ρ increases with increasing V concentration. The samples with $x \leq 0.10$ exhibit a semiconductor-like behavior in the temperature range investigated. We can estimate the energy gap E_G of Fe_2VAl to be 0.0847 eV from the slope of ln ρ versus $1/T$ curve between 300 and 550 K. This value is somewhat smaller than that ($E_G \sim 0.1$ eV) reported by Nishino et al. [2]. Endo et al. [3] reported the value of $E_G = 0.07$ eV for Fe_2VAl. For the data of $Fe_{2+x}V_{1-x}Al$ ($x = 0$, 0.02, 0.05, 0.08 and 0.10), the ln ρ versus $1/T$ plots are linear in the temperature range from ~350 to ~570 K. The concentration dependence of the energy gap deduced from ln ρ versus $1/T$ is shown in Fig. 7. The energy gap decreases linearly with increasing the concentration x. For $x = 0.18$, 0.25 and 0.40, ρ makes a broad maximum at T_C or near T_C as shown in Fig. 6. The arrows in Fig. 6 indicate T_C determined from the thermomagnetic measurements.

Fig. 8 shows the temperature dependence of the thermoelectric power S for $Fe_{2.18}V_{0.82}Al$. As shown in the figure, S decreases with decreasing temperature and makes a minimum at 400 K, and then increases. The small negative dip is observed at T_C. This behavior of the S versus T curve suggests that the Fermi surface is very sensitive to temperature.

The high-field transverse magnetoresistance $\Delta\rho/\rho(0)$ for $Fe_{2.18}V_{0.82}Al$ is shown in Fig. 9. $\Delta\rho/\rho(0)$ for $Fe_{2.18}V_{0.82}Al$ is always negative and reaches 20.5% at 220 kOe, while it is not yet saturated. The temperature dependence of $\Delta\rho/\rho(0)$ with various fields is shown in Fig. 10. The absolute values of $\Delta\rho/\rho(0)$ are maximum near T_C as indicated by arrows.

A theoretical treatment applicable to our experimental results was done by de Gennes and Friedel [19]. By using the Born approximation and assuming an exchange interaction of the form $V = G \Sigma \delta(\boldsymbol{r} - \boldsymbol{R}_j)\boldsymbol{S}_j \cdot \boldsymbol{s}$ between the spin of the atom $\boldsymbol{S}_j$ at position $\boldsymbol{R}_j$ and the spin of the conduction electron $\boldsymbol{s}$, they showed that at temperatures well above T_C the magnetic part of the resistivity ρ_o^{mag} is temperature-independent and at T_C decreases with decreasing temperature. The temperature dependence of ρ at $T < T_C$ is given

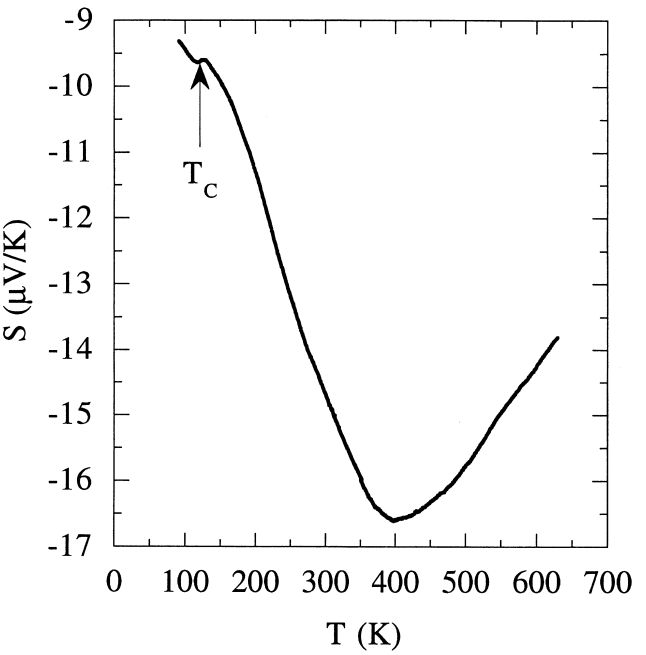

Fig. 8. Temperature dependence of the thermoelectric power S for $Fe_{2.18}V_{0.82}Al$.

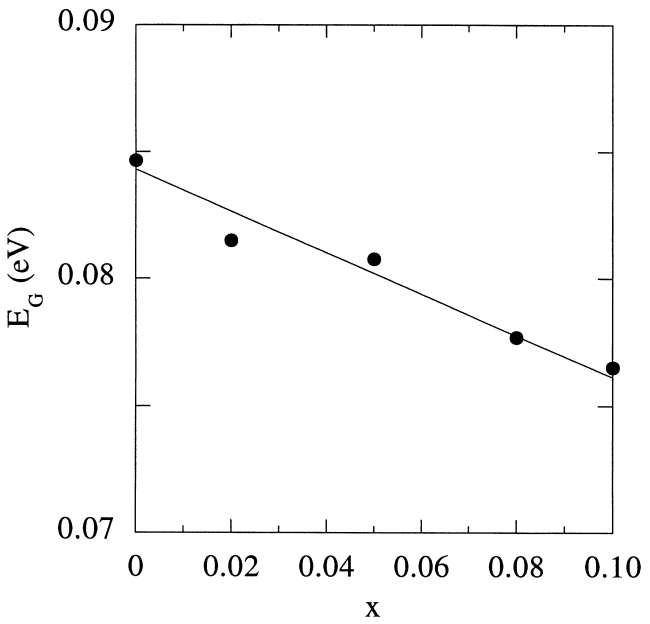

Fig. 7. Energy gap E_G versus concentration x curve for $Fe_{2+x}V_{1-x}Al$.

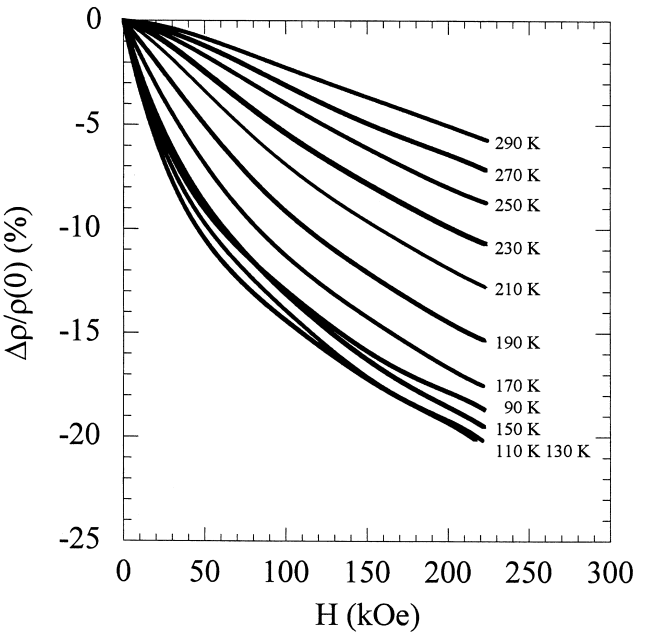

Fig. 9. Field dependence of the transverse magnetoresistance $\Delta\rho/\rho(0)$ for $Fe_{2.18}V_{0.82}Al$ at various temperatures.

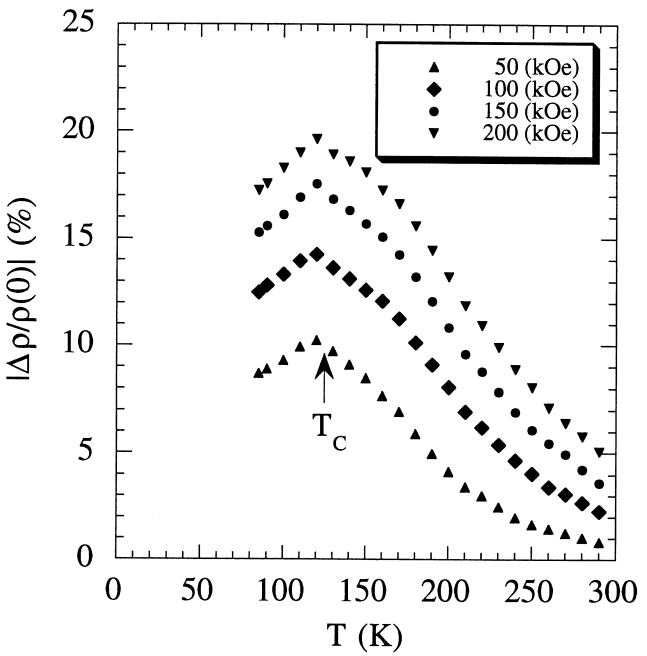

Fig. 10. Temperature dependence of the transverse magnetoresistance $|\Delta\rho/\rho(0)|$ for $Fe_{2.18}V_{0.82}Al$ at various fields. The arrow indicates the Curie temperature T_C determined from the thermomagnetic measurement.

by $\rho_o^{mag}\{1-\langle \boldsymbol{S}\rangle^2/S(S+1)\}$, where S is the spin of the magnetic atom. Furthermore, they showed that when there exists the short range order in the spin lattice just above T_C, ρ versus T curve makes a cusp near T_C. This idea was derived by taking account of the scattering of the conduction electrons due to the spin fluctuations. It should be noted that ρ versus T curves of $Fe_{2+x}V_{1-x}Al$ ($x=0.18$, 0.25 and 0.40) obtained in this study show small maximum though the sharp cusp as proposed by de Gennes and Friedel was not observed in ρ versus T curves. The negative giant magnetoresistance near T_C of $Fe_{2.18}V_{0.82}Al$ may be due to the suppression of the large spin fluctuations by external magnetic fields.

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