Semiconductorlike Behavior of Electrical Resistivity in Heusler-type Fe_2VAl Compound

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An anomalous negative temperature dependence of electrical resistivity has been observed in $(Fe_{1-x}V_x)_3Al$ alloys with V compositions up to $x = 0.35$. In particular, the Heusler-type Fe_2VAl compound is found to be on the verge of magnetic ordering and to exhibit a semiconductorlike behavior with the resistivity reaching 3000 $\mu\Omega$ cm at 2 K, in spite of the possession of a clear Fermi cutoff as revealed in photoemission valence-band spectra. A substantial mass enhancement deduced from specific heat measurements suggests that Fe_2VAl is a possible candidate for a $3d$ heavy-fermion system. [S0031-9007(97)03978-1]

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Intermetallic compounds Fe_3Si and Fe_3Al are well-ordered ferromagnets with a $D0_3$ crystal structure. Recently, Nishino *et al.* [1,2] found an anomalous temperature dependence of electrical resistivity in a series of the pseudobinary alloys in which Fe atoms are partly replaced by other $3d$ transition elements. These alloys possess common features characterized by (1) a resistance maximum near the Curie point T_c in contrast to an angular change observed in ordinary ferromagnets, and (2) a negative resistivity slope at higher temperatures up to 1000 K and above. The substitution of $3d$ elements to the left of Fe in the periodic table seems to be responsible for the occurrence of the negative temperature dependence of the resistivity [1,2]. In other words, the elements with less than half-filled d states are more effective for the anomaly than those with more than half-filled ones. Since the substitution of Ti, V, Cr, and Mn always causes a sharp reduction in T_c and in magnetization, the anomalous resistance behavior could be attributed to a weakening of ferromagnetism compelled by the substituents [1].

The most spectacular feature of the resistance anomaly has been found for $(Fe_{1-x}V_x)_3Al$ [2], as well as for $(Fe_{1-x}V_x)_3Si$ [1] and $(Fe_{1-x}V_x)_3Ga$ [3]. Among them, the $(Fe_{1-x}V_x)_3Al$ system is of greater interest because a single phase of the $D0_3$ structure remains stable over a wide V composition range [2,4]. In this Letter, we demonstrate the occurrence of the negative temperature dependence of the electrical resistivity in $(Fe_{1-x}V_x)_3Al$ with V compositions up to $x = 0.35$. In particular, the Heusler-type Fe_2VAl compound ($x = 0.33$) exhibits a strong anomaly in a manner similar to a semiconductor. It may be worthwhile mentioning here that such a semiconductor-like negative resistivity slope can also be found for heavy-fermion compounds [5], all of which are of f-electron systems. Furthermore, as will be discussed later, the present Fe_2VAl compound is proved to be in a marginally magnetic state. In this regard, Fe_2VAl shows an apparent similarity to a nonmagnetic narrow-gap semiconductor, FeSi, which has been classified by Fisk *et al.* [6] as a unique d-electron system among the family of "strongly correlated" or "Kondo" insulators. In addition to the resistivity measurements, the electronic structure of Fe_2VAl has been investigated by means of high-resolution photoemission spectroscopy and electronic specific-heat measurements. We present strong evidence that Fe_2VAl has actually a well-defined Fermi edge and is a possible candidate for a $3d$ heavy-fermion system.

The pseudobinary alloys $(Fe_{1-x}V_x)_3Al$ were prepared by repeated melting of appropriately composed mixtures of 99.99% pure Fe and Al, and 99.7% pure V, in an argon arc furnace. Since the weight loss after melting was less than 0.3%, the nominal composition was accepted as being accurate. The ingots were homogenized at 1273 K for more than 170 ks in vacuum. Samples for resistivity measurements were cut from the ingot with an alumina-blade saw to the size of $1 \times 1 \times 15$ mm^3. Each sample, sealed in an evacuated quartz capsule, was held at 1273 K for 3.6 ks and then annealed for $D0_3$ ordering at 673 K for 14.4 ks followed by furnace cooling.

X-ray diffraction spectra were taken with Cu $K\alpha$ radiation on powder samples prepared as above. The formation of the $D0_3$ single phase has been confirmed in the V composition range $x \leq 0.38$. As shown in Fig. 1, the lattice parameter first decreases with increasing x, although the atomic size of V atoms is larger than that of Fe in bcc Fe solid solutions [7]. This means that the lattice contraction has occurred presumably because of an enhanced cohesion by the $D0_3$-type ordering [2]. However, the lattice parameter turns to increase above $x = 0.33$, where the (111) and (200) superlattice reflections were weakened in intensity. Such an anomalous variation of the lattice parameter was also found for $(Fe_{1-x}V_x)_3Ga$ [8].

In Fe_3Al with the $D0_3$ structure, there are two inequivalent sites for Fe atoms with specific neighbor configurations, which are named Fe_I and Fe_{II} sites. The former has eight Fe nearest neighbors in an octahedral configuration

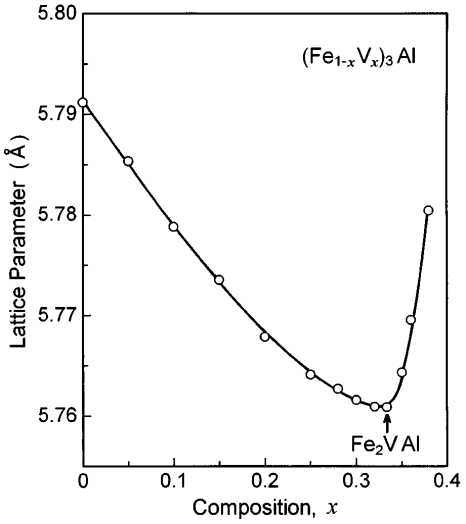

FIG. 1. Lattice parameter of the $D0_3$ phase in $(Fe_{1-x}V_x)_3Al$ as a function of V composition x. The arrow indicates the composition ($x = 0.33$) of the Heusler-type Fe_2VAl compound.

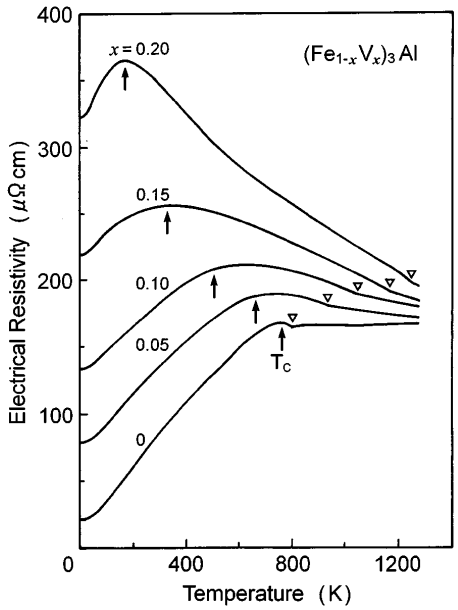

FIG. 2. Temperature dependence of electrical resistivity in $(Fe_{1-x}V_x)_3Al$ with $0 \leq x \leq 0.20$. The arrows indicate the Curie temperatures T_c, and the open triangles indicate the $D0_3$-$B2$ transformation temperatures.

and the latter has four Fe and four Al nearest neighbors in a tetrahedral configuration. It is known in Fe_3Si that $3d$ elements to the left of Fe in the periodic table substitute for the Fe_I site, while those to the right substitute for the Fe_{II} site [9]. The substitution of V for the Fe_I site in Fe_3Al is also supported by the band calculations [10], but the Mössbauer experiment [4] suggested the Fe_{II} site preference. It should be remarked in Fig. 1 that the V composition of $x = 0.33$ at which the lattice parameter reaches a minimum is very close to that for the constitution of the Heusler-type Fe_2VAl compound. This $L2_1$ ordered structure is known to be formed in $[Fe_I][Fe_{II}]_2Al$, where V atoms selectively occupy the Fe_I site alone [2]. Indeed, the formation of the $L2_1$-type Fe_2VAl has been confirmed by neutron diffraction [11]. Thus the data in Fig. 1 are taken as experimental evidence for the Fe_I site selection of V atoms in the composition range up to $x = 0.33$.

The electrical resistivity was measured by a standard dc four-terminal method with a current of 100 mA. The measurements from 2 to 300 K and those from 300 to 1273 K were carried out in a cryostat and in a vacuum furnace, respectively, with a rising rate of 0.05 K/s. Figure 2 shows the temperature dependence of the electrical resistivity in $(Fe_{1-x}V_x)_3Al$ for low V compositions $x = 0$–0.20. These curves were obtained on heating and on cooling, both of which almost coincided with each other. The arrows denoted by T_c indicate the Curie temperatures determined from thermomagnetic measurements. A relatively high residual resistivity of Fe_3Al ($x = 0$) may be simply attributed to the Fe-Al site disorder [12]. When V atoms are substituted for Fe atoms, the electrical resistivity increases rapidly and forms a maximum at or near T_c. The resistance maximum has been discussed in relation to an extremely large spin disorder scattering [1,3]. A negative resistivity slope dominates above T_c for all samples with $x \geq 0.05$. The temperature region having the negative resistivity slope expands markedly, with increasing V composition in parallel with a sharp reduction in T_c.

It is also noted in Fig. 2 that the resistivity curves in the samples with $x = 0$–0.20 show an inflection marked by open triangles at temperatures above 800 K, which has been interpreted as arising from the $D0_3$-$B2$ phase transformation [13,14]. As is clear from Fig. 2, the inflection point shifts to higher temperatures with increasing V composition and, hence, the substitution of V results in a remarkable stabilization of the $D0_3$ structure relative to the $B2$ structure over a wide temperature range up to 1200 K and above [2].

Figure 3 shows the temperature dependence of the electrical resistivity in $(Fe_{1-x}V_x)_3Al$ for high V compositions $x = 0.20$–0.35: the curve for $x = 0.20$ is the same as that in Fig. 2. With increasing V composition, the electrical resistivity increases significantly at low temperatures and becomes strongly dependent on temperature. The resistance maximum can clearly be seen for the samples up to $x = 0.30$, as shown in Fig. 3. Popiel *et al.* [4] suggested that there is no long-range magnetic order in $(Fe_{1-x}V_x)_3Al$ with $x > 0.20$ and that the superparamagnetic state persists down to 4.2 K. However, our magnetic susceptibility measurements made in fields of 0.2 T using a SQUID magnetometer revealed an indication of weak magnetic order in the vicinity of the observed resistance maximum for all samples with $x = 0.20$–0.30.

The resistance maximum has disappeared for Fe_2VAl ($x = 0.33$), and the resistivity continues to increase down to the lowest temperature of at least 2 K. The resistivity

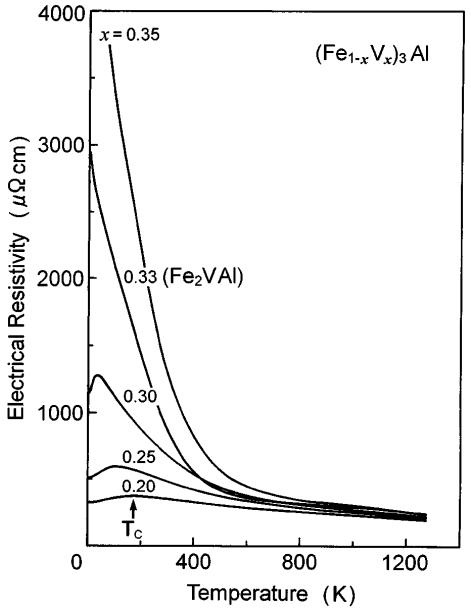

FIG. 3. Temperature dependence of electrical resistivity in $(Fe_{1-x}V_x)_3Al$ with $0.20 \leq x \leq 0.35$. The curve for $x = 0.20$ is the same as that shown in Fig. 2, and the arrow indicates the Curie temperature T_c. Note that Fe_2VAl ($x = 0.33$) exhibits a semiconductorlike behavior.

reaches about 3000 $\mu\Omega$ cm at 2 K and shows a remarkable negative temperature dependence over a whole temperature range examined. Indeed, the magnetic ordering has apparently disappeared for the samples with $x \geq 0.33$. Accordingly, the anomalous increase in the resistivity with decreasing temperature must be a phenomenon which is enhanced prior to the onset of the magnetic ordering and is closely related to spin fluctuations in the $D0_3$ (or $L2_1$) structure. We also find that the absolute value of the residual resistivity in Fe_2VAl is 2 or 3 orders of magnitude higher than those found for ordinary $3d$ transition metal alloys. The $\ln\rho$ versus $1/T$ plots (ρ, resistivity; T, temperature) for the data in the temperature interval 400–800 K become almost linear, and an energy gap of approximately 0.1 eV is deduced from its slope. It is of interest to note that the apparent energy gap thus obtained happens to be of the same order as that of FeSi [6]. Therefore, we consider it to be of crucial importance to investigate the electronic structure, particularly at the very vicinity of the Fermi level, to gain more insight into the mechanism for the occurrence of a seemingly semiconductorlike behavior in Fe_2VAl.

High-resolution photoemission measurements were performed at the beam line (BL-3B) of a 2.5 GeV storage ring, Photon Factory of National Laboratory for High Energy Physics in Tsukuba, Japan. Light from the storage ring was monochromatized with a 24-m spherical grating monochromator [15], and emitted photoelectrons were detected with a hemispherical analyzer (Scienta, SES200) in an analyzing chamber. Clean surfaces were prepared by scraping the Fe_2VAl sample of $5 \times 3 \times 3$ mm^3 in size with a diamond file at 40 K. The Fermi energy, i.e., the origin of the binding energy, was calibrated using the Fermi edge of a photoelectron spectrum of Au evaporated onto the measured Fe_2VAl sample. A total energy resolution was estimated as about 60 meV from the Au photoelectron spectrum. The base pressure of the analyzing chamber was 5×10^{-8} Pa, and no significant change was observed in the photoelectron spectrum during measurements.

Figure 4 shows an energy distribution curve of Fe_2VAl (dots) near the Fermi level in comparison with that of Au (open circles) evaporated onto the Fe_2VAl sample. The spectra are plotted so that intensities coincide with each other at the binding energy of 0.1 eV, because we are mainly interested in the energy spectra at the very onset of the occupied band. A valence-band photoelectron spectrum of Fe_2VAl is also presented in the inset of Fig. 4. All these spectra were measured at 40 K with an exciting photon energy of 63 eV. According to the Fe $3p$-$3d$ resonant photoemission measurement [16], the Fe $3d$ states contribute to the band near the Fermi level. It can be seen that the energy distribution curve of Fe_2VAl agrees well with the Au spectrum within the limit of the energy resolution. This clearly demonstrates the absence of an energy gap, at least, of the order of a few 10 meV at the Fermi level. The presence of a very small energy gap less than 10 meV is also unlikely. Instead, we believe that Fe_2VAl has indeed a metallic band structure with a clear Fermi cutoff, which is fundamentally different from a narrow-gap semiconductor FeSi [6]. A question should be addressed as to why an extremely high resistivity occurs in spite of the possession of a large density of states at the Fermi level in Fe_2VAl.

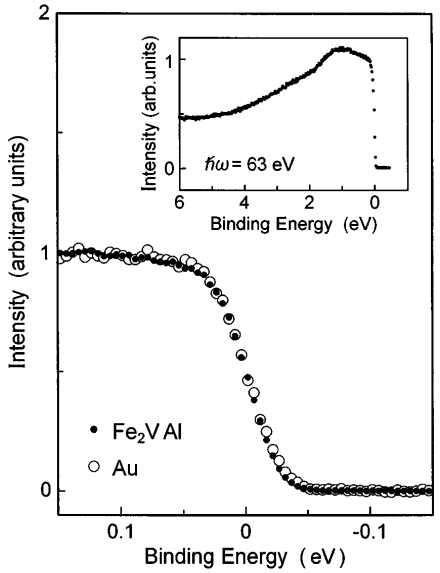

FIG. 4. Energy distribution curve of Fe_2VAl (dots) near the Fermi level in comparison with that of Au (open circles). A valence-band photoelectron spectrum of Fe_2VAl is also shown in the inset. All the spectra were measured at 40 K with an exciting photon energy $\hbar\omega = 63$ eV.

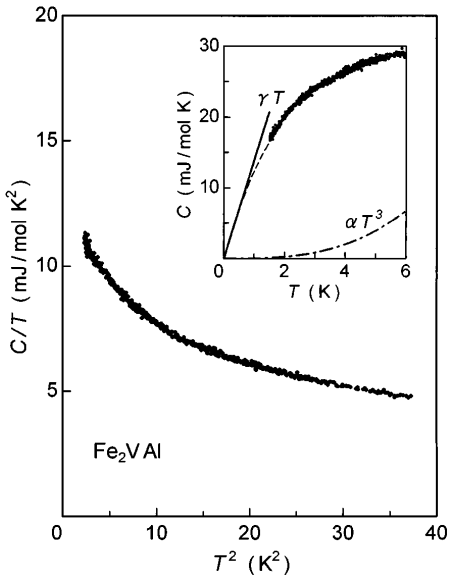

FIG. 5. Specific heat divided by temperature, C/T, versus T^2 measured for Fe_2VAl. The inset shows the C versus T plots, and the dash-dotted line represents the lattice contribution αT^3 ($\alpha = 0.031$ mJ/mol K^4) for Fe_3Al (Ref. [17]). The specific heat is approximately of the form $C = \gamma T$ at sufficiently low temperatures.

The low-temperature specific heat C was measured on Fe_2VAl in the temperature range 1.6–6 K using a dc adiabatic method. The results are shown in Fig. 5 in the ordinary form of C/T versus T^2. An anomalous upturn in C/T can be observed with decreasing temperature, which is known to be characteristic of most heavy-fermion compounds [5]. In the inset, we show the C versus T plots, and, for comparison, the lattice specific-heat contribution αT^3, evaluated from the data on Fe_3Al [17], is also represented by the dash-dotted line. The electronic specific-heat coefficient γ may be evaluated by extrapolating the C versus T data to absolute zero and applying the linear relation $C = \gamma T$ for $T \rightarrow 0$, in the same spirit as employed in heavy-fermion systems [18]. The effective mass is calculated from the resulting γ value of about 14 mJ/mol K^2 and turns out to be almost 20 times as large as the free electron mass. At this stage, we consider the mass enhancement to originate from spin fluctuations and to be most likely responsible for the anomalous electron transport in Fe_2VAl. Unique semiconductorlike behavior with a well-defined Fermi edge certainly deserves further studies, particularly concerning magnetic states at low temperatures in the marginally magnetic Fe_2VAl compound.

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