Weak itinerant ferromagnetism in Heusler-type Fe2VAl0.95


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Weak itinerant ferromagnetism in Heusler-type Fe₂VAl₀.₉₅

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We report measurements of the magnetic, transport, and thermal properties of the Heusler-type compound Fe₂VAl₀.₉₅. We show that while stoichiometric Fe₂VAl is a nonmagnetic semimetal a 5% substitution on the Al site with the 3d elements Fe and V atoms leads to a ferromagnetic ground state with a Curie temperature $T_C=33 \pm 3$ K and a small ordered moment $\mu_s=0.12 \mu_B$/Fe in Fe₂VAl₀.₉₅. The reduced value of the ratio $\mu_s/\mu_B=0.08$, where $\mu_B=1.4 \mu_B$/Fe is the effective Curie-Weiss moment, together with the analysis of the magnetization data $M(H,T)$, show magnetism is of itinerant nature. The specific heat shows an unusual temperature variation at low temperatures with an enhanced Sommerfeld coefficient, $\gamma=12$ mJ K⁻² mol⁻¹. The resistivity, $\rho(T)$, is metallic and follows a power law behavior $\rho=\rho_0+AT^n$ with $n=1.5$ below $T_C$. With applying pressure, $T_C$ decreases with the rate of $(1/T_C)(dT_C/dP)=-0.061$ GPa⁻¹. We conclude substitution on the Al site with Fe and V atoms results in itinerant ferromagnetism with a low carrier density.

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I. INTRODUCTION

Weak ferromagnetic (or antiferromagnetic) transition metal and rare earth or actinide metallic compounds are intensively investigated, since novel ground states, such as heavy fermion behavior, non-Fermi-liquid states and unconventional superconductivity, may emerge at low temperatures. These exotic phases are located at the boundary of magnetically ordered states, and may be reached by tuning the ground state by chemical pressure (alloying), mechanical pressure and/or applying an external magnetic field. Heusler- and semi-Heusler-type of compounds composed of transition metals form an attractive materials family to investigate novel emerging phenomena, the more because these are candidates for half metallic states, in which the band electrons are fully spin polarized.² In the magnetically ordered state of half metals, the exchange gap is quite large and the minority spin band is fully occupied. This might be of practical use in spin sensitive devices,¹ which provides a second reason why Heusler-type compounds are investigated intensively. Since applications demand both a high spin polarization and stable ferromagnetism above room temperature, this is an exigent and challenging mission.

Although the concept of the half-metal comes truly from an itinerant electron picture, one can address the question how much local moment character strongly spin-polarized metals possess.⁵ In fact, it is well known that in nearly and weak ferromagnetic itinerant electron systems, such as ZrZn₂ and MnSi, the conduction electrons are responsible for both the itinerant and localized electron nature (i.e., the Curie-Weiss behavior in magnetic susceptibility). For a few candidate materials only the low-temperature magnetic and thermal properties could be analyzed satisfactorily in the framework of itinerant electron magnetism. We mention the semi-Heusler-type ferromagnet NiMnSb (Ref. 4) and antiferromagnet CuMnSb,⁵ which were examined under magnetic field and high pressure.

In this paper we focus on the magnetic transition and the low-temperature properties of the Heusler-type iron-vanadium compound, Fe₂VAl₀.₉₅. Fe₂VAl and related alloys have attracted considerable attention since it was claimed that these 3d-electron systems with small carrier concentration, $n\approx 0.01$ per unit formula,⁶ exhibit a significant carrier mass enhancement and non-Fermi-liquid behavior.⁶ Stoichiometric Fe₂VAl is nonmagnetic and related alloys, such as Fe₂⁺ₓV₁−ₓAl and Fe₂VAl₁−ₓSb exhibit ferromagnetic transitions.⁷,¹⁰,¹⁴ Consequently, the samples at $x=0$ and $\delta=0$ are located at the brink of ferromagnetic order, close to the ferromagnetic quantum critical point, i.e., $T_C\to0$.⁸ Stimulated by these findings, theoretical work claimed Fe₂VAl is a nonmagnetic semimetal with the pseudogap at the Fermi level.¹⁵ The considerable mass enhancement of the conduction carriers was attributed to excitonic correlations⁶ or spin fluctuations.¹⁷ However, subsequent specific heat, $C(T)$, measurements in applied magnetic fields showed that the upturn in $C/T$ at low temperatures results from a Schottky contribution of magnetic clusters in Fe₂VAl.⁸ The effects of off-stoichiometry have not been investigated quantitatively in the framework of nearly and weak ferromagnetism at $x=0$ and $\delta=0$ yet. Another interesting aspect of Fe₂VAl is its potential for application in thermoelectric devices, since off-stoichiometry and heat-treatment procedures may result in an enhancement of the Seebeck coefficient.⁶,¹¹,¹² In Fe₂⁺ₓV₁−ₓAl (Refs. 11 and 12) and Fe₂VAl₁−ₓSb¹² the thermoelectric power is enhanced for $x\approx 0$ and $\delta=0$: with a negative sign for $x<0$ and $\delta>0$, and positive sign for $x>0$ and $\delta<0$. In the case of stoichiometric Fe₂VAl the negative temperature coefficient in the electrical resistivity observed up to 1300 K and the constant value of the Hall coefficient at low temperatures⁶,¹² suggest it is a low carrier-density semimetal with a pseudogap at the
Fermi level. Antisite defects and magnetic nanoclusters induced by heat treatment and nominal off-stoichiometry bring about ferromagnetism and superparamagnetism. With increasing x in Fe$_{2+x}$V$_{1-x}$Al, the excess of Fe atoms occupy the nominal V site and, consequently, Fe$_3$Al (Fe$_2$FeAl) clusters are formed [notice bulk Fe$_3$Al is ferromagnetic with $T_C=803$ K (Refs. 6 and 13)]. The presence of antisite Fe atoms on the nominal V site in the FeV$_2$Al system brings about a simultaneous enhancement of the magnetization and resistivity at low temperatures. This led to the claim that localized magnetic moments must be a crucial factor in the strong magnetic scattering of the conduction electrons responsible for the steep rise of the resistivity, the negative temperature coefficient of the resistivity, $d\rho/dT<0$ and a giant magnetoresistance at $x>0$. Thus it is proposed that the steep rise of the electrical resistivity at lower temperature is not due to the energy gap but due to strong magnetic scattering.

Al poor Fe$_2$VAI$_{1.5}$ ($\delta>0$), seems to undergo a ferromagnetic transition and shows metallic conduction below room temperature. The Fe$_2$VAI$_{1.5}$ system at $\delta>0$ yields the opportunity to examine quantitatively not only the magnetic but also the transport and thermal properties within the framework of itinerant electron ferromagnetism, as established for intermetallic compounds, such MnSi and ZrZn$_2$. In this paper we report a comprehensive study of the low temperature bulk properties of Fe$_2$VAI$_{0.95}$, notably magnetization, electrical resistivity, and specific-heat measurements. Whereas, as pointed out above, the magnetism in Fe$_2$VAI$_{1.5}$ is considered to be due to magnetic clusters having a semilocalized nature, our results on Fe$_2$VAI$_{0.95}$ show it is a weak ferromagnet, with a bulk magnetic transition at $T_C=33$ K and a low carrier concentration $n=0.06$.

II. EXPERIMENTAL

Polycrystalline samples of Fe$_2$VAI$_{0.95}$, Fe$_2$VAI, and Fe$_2$VAI$_{1.05}$ were prepared by arc melting the proper amounts of elements into the nominal chemical composition. The samples were subjected to a heat treatment at 1000 °C for 15 h for homogenization purposes, and next annealed at 400 °C for 15 h. For all samples the crystal structure was identified as the Heusler-type. No secondary phases were detected in the powder x-ray diffraction (XRD) profiles. Since after annealing the grain size (i.e., the individual crystallite size) in the polycrystalline samples is quite large (>several hundredths μm), we expect that the volume fraction of impurity phases located at the grain boundaries is quite low. The samples we report on in this work are the same as those previously characterized by XRD, scanning electron microscopy (SEM), and energy dispersive x-ray spectroscopy (EDS).

dc-magnetization, four-probe ac electrical resistivity and specific-heat measurements down to $T=2$ K were carried out using a conventional superconducting quantum interference device magnetometer and a physical property measurement system (Quantum Design), respectively. Resistivity measurements down to $T=0.23$ K were carried out in a $^3$He refrigerator (Heliox VL, Oxford Instruments) with a sensitive

![Graph](image-url)

FIG. 1. (a) X-ray diffraction patterns of Fe$_2$VAI$_{1-\delta}$ at $\delta=-0.05, 0.00, 0.05$ and a simulated one for Fe$_2$VAI with the Heusler structure. The top XRD pattern of $\delta=-0.05$ is magnified ten times vertically. Ticks and numbers being along the simulated pattern indicate the position of the Bragg reflections and corresponding Miller indices, respectively, for the Heusler structure. (b) Lattice parameters obtained in this work as a function of $\delta$ (open circle). Solid line is a guide for eyes. Solid circles at $\delta=0$ represent reported values in Refs. 18 and 20.

LR700 (Linear Research) ac resistance bridge at the Van der Waals-Zeeman Institute of the University of Amsterdam. In the high-pressure measurement, a handmade measurement system specialized for high-pressure measurement with a glass Dewar vessel was used. To generate high pressure a hybrid clamp cell made from nonmagnetic NiCrAl and CuBe alloys was used. The sample was mounted on a specially designed plug and put inside a Teflon cell with the pressure-transmitting medium Daphne 7373 (Idemitsu).

III. RESULTS AND DISCUSSION

A. Crystallographic

X-ray diffraction patterns of Fe$_2$VAI$_{1-\delta}$ at $\delta=-0.05, 0,$ and $0.05$ are apparently identified to be of the single phase Heusler-type (Cu$_2$MnAl) structure in the space group $Fm\overline{3}m$. A as shown in Fig. 1(a), no impurity phases were detected, except for small amounts of Al and Al oxide inclusions indicated by SEM and EDS measurements. Therefore, we expect, the actual Al composition, $\delta$, is slightly smaller than the
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nominal one. Figure 1(b) shows the δ dependence of lattice constant, a, estimated in this work with those reported in previous works for comparison. The lattice constant at δ=0 measured in this work corresponds well with those for annealed samples. The linear dependence of a versus δ supported that the excess Fe and V atoms occupy the Al site for δ>0 and the excess Al atom locates at the Fe and/or V site(s) for δ<0, since Al has smaller ionic radius than those of Fe and V.

As shown below (see Sec. III C), the resistivity versus temperature curve obtained for δ=0.05 is quite similar to those reported by Nishino et al.12 Rounded maxima in the resistivity were observed at $T_{\text{low}}=40 \text{ K}$ and $T_{\text{high}}=250 \text{ K}$ in a sample with composition (Fe$_{2.3}$V$_{1.3}$)75.7Al$_{24.3}$,12 which corresponds to δ=0.035 in the notation Fe$_2$VAl$_{1-\delta}$ used here. The maximum at $T=40 \text{ K}$ in the resistivity for δ=0.035 locates the Curie temperature slightly lower than $T_{\text{low}}=50 \text{ K}$ of δ=0.05 observed in this work [Fig. 5(a)]. Following the argument of the effect of off-stoichiometry based on the rigid band model12,21 which is consistent with the Al content variations of the sign in Seebeck and Hall coefficients,7,12 we are convinced that the excess Fe and V atoms in Fe$_2$VAl$_{1-\delta}$ occupy the Al site for δ>0, and vice-versa. Actually, it was shown recently by comprehensive magnetic and transport studies in the vicinity of δ=0 that not only the Curie point, $T_C$, but also the saturation moment, $\mu_s$, shows a continuous variation as a function of δ.22

B. Magnetization

In Fig. 2(a) we show the magnetization of Fe$_2$VAl$_{0.95}$ as a function of magnetic field, $M(H)$, measured at various fixed temperatures. A spontaneous moment appears in the temperature range $T=30–40 \text{ K}$, which indicates ferromagnetic order [see Fig. 4(a)]. In Fig. 2(b) we have traced the temperature variation in the magnetic susceptibility, $\chi(T)$, measured in a field of 20 kOe. As indicated by the straight line in the plot of 1/$\chi(T)$ versus $T$ the susceptibility follows a Curie-Weiss law, $\chi(T)=C/(T−\Theta)$, for $T>100 \text{ K}$, from which we extract the Curie constant C=0.243 emu K /g and a Curie-Weiss temperature $\Theta=51 \text{ K}$. By using $C=\gamma\mu_B^2\mu_B^2/3k_B$, an effective magnetic moment $\mu_B=1.4\mu_B/\text{Fe}$ is obtained, where $\gamma$, $\mu_B$, and $k_B$ are the number of magnetic (Fe) atoms, the Bohr magneton and Boltzmann’s constant, respectively. This value of $\mu_B$ is considerably larger than that of heat-treated Fe$_2$VAl ($\mu_B=0.2\mu_B/\text{Fe}$).23 The saturation moment at $T=2 \text{ K}$ is $\mu_s=0.12\mu_B/\text{Fe}$, which is much smaller than the paramagnetic moment, $\mu_B=1.4\mu_B/\text{Fe}$. The small value of the ratio $\mu_s/\mu_B=0.083$ corroborates the itinerant electron nature of ferromagnetism in Fe$_2$VAl$_{0.95}$. It is noteworthy that an Al-site substitution of only 5% (δ=0.05) modifies the magnetic properties strongly: the appearance of a spontaneous moment and low magnetic transition temperature and a strong enhancement of the paramagnetic moment. We stress that these changes cannot be due to an impurity phase, like for instance Fe$_{1-x}$V$_x$(x=1/3), for which the estimated values of $\mu_B$ and $\mu_s$ are one order of magnitude larger than those observed and $T_C$ is above room temperature.24 In contrast with the observations concerning magnetism in annealed Fe$_2$VAl (Ref. 18) and Fe$_2$V$_{1-x}$Cr$_x$Al,25 the ferromagnetic transition in Fe$_2$VAl$_{0.95}$ is also signaled: (i) in the temperature derivative of the resistivity, (1/ρ)(dρ/dT), shown in Fig. 5(b), (ii) by the temperature variation of the specific heat divided by temperature, $C/T$, showing a $\lambda$-peaklike shape [Fig. 9(b)], (iii) by the $M^2$-$M$/$H$ plot [Fig. 3(a)], and (iv) by the $M^2$-$M$/$H$ plot [Fig. 4(a)]. Notably, the transition temperatures $T_C=33±3 \text{ K}$ determined by the different techniques agree within the uncertainty of 3 K. Correspondingly, both coercive force, $H_C$, and remanent magnetization, $M_r$, emerge around $T_C$ [Fig. 2(b)].

As mentioned in Sec. I, it is interesting to examine whether magnetism in Fe$_2$VAl$_{0.95}$ has an itinerant or localized character. In the latter case it is expected that the induced spin is localized at the Fe or V substituted on the Al site. In Figs. 3(a) and 3(b) we analyze the magnetization data around $T_C$ in terms of $M^2$-$H/M$ and $M^2$-$H/M$ (Arrott) plots, respectively. For weak ferromagnetic systems the $M^2$ versus $H/M$ curve at $T=\text{fixed}$ is predicted to be linear with an intercept zero.26 Inspecting Fig. 2(a) we conclude $T_C=33 \text{ K}$. Notice, in the Arrott plot the $M^2$ versus $H/M$ curves all exhibit a strong curvature toward the $H/M$ axis.

FIG. 2. (a) Magnetization versus field (M-H) of Fe$_2$VAl$_{0.95}$ at fixed temperatures as indicated. (b) Coercive force, $H_C$, and remanent magnetization, $M_r$, as a function of temperature. (c) Magnetic susceptibility, $\chi(T)=M/H$, and reciprocal susceptibility, 1/$\chi(T)$, as a function of temperature measured in a fixed field $H=20 \text{ kOe}$. The susceptibility is expressed in units per gram.

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magnetization data provide strong evidence for itinerant ferromagnetism. By using the mean-field model, this feature is quite similar to those found in prototypical itinerant ferromagnets, such as MnSi22 and Ni3Al.23 The magnetization data provide strong evidence for itinerant ferromagnetism with \( T_C = 33 \) K in Fe2VAl0.05. Based on the generalized Rhodes-Wohlfarth plot,23 we obtain the characteristic temperature \( T_0 = 895 \) K for Fe2VAl0.05. The ratio \( T_C/T_0 \) is an important parameter as it characterizes the degree of localization or itineracy of the spin moment.20 For \( T_C/T_0 \ll 1 \) the magnetic material has a strong itinerant character while at \( T_C \approx T_0 \) local moment magnetism results. The estimated value \( T_C/T_0 = 0.038 \) is comparable to the values reported for MnSi (0.13), Ni3Al (0.0116), ZrZn2 (0.053), and Sc3In (0.0097) which all exhibit weak ferromagnetism.21 With help of \( T_0 \), one may calculate the temperature dependence of the magnetization below \( T_C \). With decreasing \( T_C/T_0 \) the \( M(T) \) curve deviates more and more from the mean-field behavior, \( M = M(0)[1 - (T/T_C)^2]^{1/2} \), and has a tendency to follow \( M = M(0)[1 - (T/T_C)^4]^{1/2} \). In fact, as shown in Fig. 4(b), \( M^2(T) \) of Fe2VAl0.05 obeys the \( T^{4/3} \) dependence for a weak itinerant ferromagnet rather than the \( T^2 \) dependence of the mean-field model.22 By using \( M(T) = M(0)[1 - (T/T_C)^4]^{1/2} \), the zero-temperature magnetization and Curie point are estimated to be \( M(0) = 5.7 \) emu/g and \( T_C = 36 \) K at \( H = 200 \) Oe, respectively.

**C. Electrical resistivity**

In Fig. 5(a) we show the temperature dependence of the resistivity, \( \rho(T) \). The resistivity, \( \rho(T) \), exhibits rounded maxima at \( T_{\text{low}} = 52 \) K and \( T_{\text{high}} = 260 \) K. A comparison with Fe2+xV1−xAl at \( x \approx 0 \) (Refs. 7, 10, and 14) reveals that the resistivity above \( T > 260 \) K is dominated by scattering due to thermal excitations in the pseudogap. Below \( T \sim 260 \) K...
$\rho(T)$ exhibits metallic behavior, with a low carrier number.\textsuperscript{7} On the other hand, the maximum at $T_{\text{low}}^\text{max}=52$ K is caused by the para-to-ferromagnetic phase transition, as was also observed in the Fe-rich composition of Fe$_{2+x}$V$_{1-x}$Al.\textsuperscript{7,10,14} In Fe$_2$VAl$_{0.95}$, $\rho(T)$ remains metallic down to $T\sim 1$ K, while in the case of Fe$_{2+x}$V$_{1-x}$Al, especially for $x\approx 0.05$, a semiconductor behavior is reported. The latter was corroborated by weak localization effects of the carriers in a random potential.\textsuperscript{8} As shown in Fig. 5(b), the sharp anomaly in $(1/\rho)(d\rho/dT)$ is indicative of a bulk ferromagnetic transition at $T=33$ K. In the ferromagnetic phase the resistivity follows a power law behavior $\rho(T)\sim T^n$ with $n=3/2$ [see inset to Fig. 5(a)]. Notice, it was derived by the self-consistent renormalization (SCR) theory that the temperature dependence of $\rho$ should follow a power law $\sim AT^2$ at $T<T_C$.\textsuperscript{19}

D. Magnetoresistance and low-temperature electrical resistivity

The itinerant ferromagnetic character of Fe$_2$VAl$_{0.95}$ is also reflected in the transverse magnetoresistance (TMR), $[\rho(H) - \rho(0)]/\rho(0)$, especially around $T=T_C$, as shown in Fig. 6(a). The TMR is negative below 100 K and has a minimum at a temperature slightly above $T_C$. The TMR reaches a maximum size of $-11\%$ at $T=33$ K in the ferromagnetic phase the resistivity follows a power law behavior $\rho(T)\sim T^n$ with $n=3/2$ [see inset to Fig. 5(a)]. Notice, it was derived by the self-consistent renormalization (SCR) theory that the temperature dependence of $\rho$ should follow a power law $\sim AT^2$ at $T<T_C$.\textsuperscript{19}

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E. Pressure effects on resistivity

As mentioned above, crystallographic and chemical defects affect strongly on the magnetic grand state of Fe$_2$VAl and related alloys.\textsuperscript{7} Remarkably, lattice constant of Fe$_2$VAl reflects sensitively these structural deviations from the Heusler structure.\textsuperscript{18} Plausibly, Curie temperature, $T_C$, is a function of not only carrier number but also the variation of lattice constant, $\Delta a/a$. To distinguish those effects on the ferromagnetic transition in Fe$_2$VAl$_{0.95}$, it is expected that resistivity measurement under high pressure provides crucial information. The lattice expansion, $\Delta a/a=0.10\%$ at $\delta=0.05$, can be compensated by applying an experimentally accessible pressure, $\Delta P=3\Delta a(a)\delta a_{0.05}/k_T\approx 0.5$ GPa, where $k_T$ is volume compressibility estimated to be $6.81 \times 10^{-3}$ GPa$^{-1}$ for $\delta=0.20$. As shown in the inset of Fig. 7, $T_{\text{high}}^\text{max}$ increases while $T_{\text{low}}^\text{low}$ decreases with pressure. The increment of $T_{\text{high}}^\text{high}$ with applying pressure can be responsible for that the pseudo gap locating at the Fermi level increases. On the other hand, the decrement of $T_{\text{low}}^\text{low}$ seems to be related to that of $T_C$. Pressure dependence of $T_C$ obtained from the temperature variation of $(1/\rho)(d\rho/dT)$ is shown in Figs. 8(a) and 8(b). With increasing pressure the anomalous point shifts toward lower temperature with the pressure coefficient of $(1/T_C)(dT_C/dP)=-0.061$ GPa$^{-1}$ [Fig. 8(b)], which corresponds well with $(1/T_{\text{low}}^\text{low})(dT_{\text{low}}^\text{low}/dP)=-0.074$ GPa$^{-1}$. The volume effect on $T_C$ is comparable with those for itinerant ferromagnets, such as Ni$_2$Al $[-0.10$ GPa$^{-1}$ (Refs. 30 and 31)]. Therefore, the emergence of the ferromagnetism at $\delta > 0$ can result from mainly the carrier doping in Fe$_2$VAl$_{1-\delta}$ while the volume expansion seems to be a minor effect. At $T\ll T_C$, it is noteworthy that $\rho_0$ increases with the pressure coefficient of $(1/\rho_0)(d\rho_0/dP)=0.038$ GPa$^{-1}$ while the exponent of temperature, $n$, decreases from $n=1.42$ at 0.11 GPa to...
F. Specific heat

In Fig. 9(a) we show the specific heat divided by temperature, $C/T$, as a function of $T^2$ measured on Fe$_2$VAl$_{1-x}$ samples with $x=0.05$, 0, and +0.05. A low-temperature upturn as present for Fe$_2$VAl$_{0.95}$ and Fe$_2$VAl was also observed previously in Fe$_2$VAl (Refs. 6 and 8) and in Fe$_{2-x}$V$_{1-x}$Al. Remarkably, for Fe$_2$VAl$_{0.95}$ $C/T$ has a strong curvature toward the $T^2$ axis. Assuming that this curvature in $C/T$ is due to a ferromagnetic spin-wave contribution, $C_{sw} \sim a T^{3/2} + \beta T^2$, below 20 K (not shown in Fig. 9(a)). The fitting parameters are $a=12.6$ mJ K$^{-2}$ mol$^{-1}$, $a_{sw} = 1.38$ mJ K$^{-5/2}$ mol$^{-1}$, and $\beta=0.025$ mJ K$^{-4}$ mol$^{-1}$. However, the presence of the spin-wave contribution in the low-temperature specific heat is not supported by measurements in magnetic field. In field the curvature in $C/T$ enhances significantly. At $H=80$ kOe our fitting procedure results in a larger value for $a_{sw}$, whereas the spin-wave contribution should be suppressed under magnetic field, as for instance in Ni (Ref. 32) and CeRu$_2$Ge$_2$. This strongly suggests that the low-temperature variation in $C(T)/T$ is not due to a ferromagnetic spin-wave contribution.

As indicated in Fig. 9(a), the difference in specific heat between $\delta=0$ and $-0.05$ is quite small except in the low-temperature region where $C/T$ showing an upturn. We fitted the high temperature specific heat, $C_{HT}$, in the temperature range 8–30 K to $C_{HT} = \gamma T + \beta T^3 + \eta T^5$ and estimated $\gamma=3.10 \pm 0.02$ mJ mol$^{-1}$ K$^{-2}$, $\beta=0.0265 \pm 0.0001$ mJ mol$^{-1}$ K$^{-4}$, and $\eta=(1.82 \pm 0.02) \times 10^{-5}$ mJ mol$^{-1}$ K$^{-6}$ for $\delta=-0.05$, and $\gamma=2.19 \pm 0.02$ mJ mol$^{-1}$ K$^{-2}$, $\beta=0.0283 \pm 0.0001$ mJ mol$^{-1}$ K$^{-4}$, and $\eta=(1.75 \pm 0.01) \times 10^{-5}$ mJ mol$^{-1}$ K$^{-6}$ for $\delta=0$. These estimated parameters correspond well to those of Fe$_2$VAl obtained previously in the temperature range 8–25 K.

G. Comparison with paramagnetic Fe$_2$VAl in the specific heat

Contrasted to the case of $\delta=-0.05$, $C/T$ of $\delta=0.05$ is enhanced obviously compared with that of $\delta=0$. Employing paramagnetic Fe$_2$VAl as a reference material in the specific heat, the compositional change in $C(T)$, $\Delta C \equiv C(Fe_2VAl) - C_{HT}(Fe_2VAl)$ is obtained as shown in Fig. 9(b). Obviously, at zero field a pronounced anomaly is present at $T=34$ K, i.e., at the same temperature where $C(\rho)$ exhibits a maximum. This anomaly is superposed on the background which has a broad maximum around $T=30$ K [see inset Fig. 9(b)]. The magnetic entropy is obtained by integrating $C_{PM}/T$ versus $T$ and is estimated at 0.7% of $R \ln 2$, where $R$ and $C_{PM}$ are the gas constant and the ferromagnetic component in the specific heat, respectively. Such a small value is expected for a weak itinerant ferromagnet. Below the phase transition point the $\Delta C/T$ curve decreases further with decreasing temperature. Below $T \sim 10$ K the specific heat can be expressed by the sum of linear ($T$) and quadratic ($T^2$) terms. The magnetic field wipes out the magnetic transition anomaly in $\Delta C/T$ and
causes $\Delta C/T$ to decrease, as shown in Fig. 9(b). An anomalous $T^2$ temperature dependence in the specific heat was observed also in Pd$_2$MnIn, GdCu, CuMnSb, and CeNiSn. It seems to be due to a sharp density of state (DOS) shape around $E_F$, such as the V-shape density of states with small residual component at the Fermi level, as observed in the Kondo insulator CeNiSn. In CeNiSn, at lower temperature the temperature variation in the specific heat shows a deviation from the $T$-linear dependence, which can be fitted by the sum of a $T$ linear and a $T^2$ terms. Additionally, the band structure below $T_C$ in Fe$_2$VAl$_{0.95}$ is more complicated because the ferromagnetic ordering seems to modify considerably the DOS structure due to the exchange splitting, $\Delta_e$, between the spin-up and spin-down bands, which increases effectively with applying external field below $T_C$. In fact, the low-temperature specific heat $\Delta C \sim \gamma T + \delta T^2$ changes, that is, the ratio of $\gamma/\delta$ decreases upon application of a magnetic field [Fig. 9(b)].

Next, let us discuss quantitatively the comparison between the magnetic moment, $\mu_p r$, and carrier concentration, $n$, modified by the off-stoichiometry in Fe$_2$VAl$_{0.95}$. As shown in Fig. 6(b), the resistivity follows a quadratic temperature dependence below $T = T^*$, with $T^*$ increasing with magnetic field. The larger value of the coefficient of the $T^2$ term, $A = 10^{-7} - 10^{-5}$ $\Omega$ cm K$^{-2}$, estimated in Fe$_2$VAl$_{0.95}$ reminds one of the mass enhancement in the stoichiometric samples. To compare with the Kadowaki-Woods law, we should consider the small carrier concentration, $n$, in Fe$_2$VAl and related alloys. In the Fermi-liquid theory, $A/\gamma^2$ is proportional to $1/k_F^2$, where $\gamma$ and $k_F$ are the Sommerfeld constant in the specific heat and the Fermi wave vector, respectively. Compared with heavy fermion systems with $n = 1$ (per rare earth or actinide element), it is expected that $A/\gamma^2$ is enhanced by a factor of $1/n^3 = 2300 - 360$ in the case of Fe$_2$VAl since $n = 0.003 - 0.012$. In this estimate, we assumed $k_F \sim n^{1/3}$ given by the Drude model (the free electron model). Therefore, $A/\gamma^2$ can be a measure of $n$, or in other words, the Fermi surface volume. In Fe$_2$VAl$_{0.95}$, $A/\gamma^2$ is $2 \times 10^{-3}$ $\Omega$ cm K$^{-2}/(JK^{-2} \text{mol}^{-1})^2$ being a factor of 40 larger than that established as the Kadowaki-Woods ratio $\sim 1 \times 10^{-2}$ $\Omega$ cm K$^{-2}/(JK^{-2} \text{mol}^{-1})^2$. Therefore, $n \sim 40 - 3/4 = 0.063$ per unit formula in Fe$_2$VAl$_{0.95}$. This value of $n$ is one order of magnitude larger than in Fe$_2$VAl (Ref. 7) and seems to be consistent with the value of the Hall coefficient of Fe$_2$VAl$_{0.95}$. The observed value $\gamma = 12$ mJ mol$^{-1}$ K$^{-2}$ at $H = 0$ is rather large when we consider the carrier concentration, $n = 0.06$, and the value of normal metals, $\gamma = 1$ mJ mol$^{-1}$ K$^{-2}$. Consequently, the enhancement factor $m^*/m_e$ is $\sim 30$, where $m_e$ is the bare electron mass. Compared with the values $\gamma = 1.5 - 2.2$ mJ mol$^{-1}$ K$^{-2}$ and $n = 0.003 - 0.012$ (Ref. 7) in nonmagnetic Fe$_2$VAl, this large enhancement of $\gamma$ in ferromagnet Fe$_2$VAl$_{0.95}$ is surprising because Fe$_2$VAl is located closer to the magnetic quantum critical point, $T_C \rightarrow 0$, where the magnetic fluctuations should be more strongly enhanced. As $C/T$ below $T_C$ has an anomalous temperature and magnetic field dependence, we speculate that the enhancement mechanism of $\gamma$ distinctly differs from the electron-electron correlation mechanism realized in the heavy fermion systems. Stoichiometric Fe$_2$VAl is located at the vicinity of a ferromagnetic threshold composition, $\delta_0$. However, not only the Curie temperature, $T_C$, but also the paramagnetic moment, $\mu_p$, which is strongly dependent on the number of conduction carriers, seems to disappear at $\delta = \delta_0$ in Fe$_2$VAl$_{1-x}$. In contrast, heavy fermion systems show only the magnetic transition temperature, $T_M$, going to zero while keeping a magnetic moment which has both a localized and an itinerant nature. In other words, the paramagnetic moment does not vanish around the critical point in heavy fermion systems.

IV. SUMMARY

Magnetic, transport, and specific-heat measurements have been carried out on the Heusler-type compound Fe$_2$VAl$_{0.95}$. The data reveal a ferromagnetic transition takes place at $T_C = 33$ K with the characteristics of an itinerant electron ferromagnet. With applying pressure, $T_C$ decreases with the pressure coefficient of $(1/T_C)(dT_C/dP) = -0.061$ GPa$^{-1}$. The Sommerfeld coefficient in the specific heat is enhanced, $\gamma \approx 12$ mJ mol$^{-1}$ K$^{-2}$, compared to $3$ mJ mol$^{-1}$ K$^{-2}$.
The temperature dependence of resistivity deviates from the characteristics of a Fermi liquid, $\Delta T^2$, while under magnetic field the quadratic temperature dependence, $\rho(T) \sim T^2$, appears below a certain temperature, $T_c$, which increases with increasing magnetic field. At lower temperature the temperature variation in the specific heat shows a deviation from the $T$-linear dependence, especially, under magnetic field, which can be fitted by the sum of a $T$-linear and a $T^2$ terms. While the magnetism has a typical characteristics of a weak itinerant ferromagnet, the deviations from the Fermi-liquid characteristics are quite different from those (i.e., non-Fermi-liquid behavior) in a heavy fermion system and a nearly or a weak itinerant ferromagnet.

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