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Field-dependent specific heat in Fe₂VAl and the question of possible 3d heavy fermion behavior

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Specific heat measurements on Fe₂VAl show the previously reported upturn in electronic specific heat coefficient (γ) to be sample dependent, and related to magnetic defects. These measurements, in temperatures as low as 0.6 K and magnetic fields up to 8 T, indicate the presence of Schottky anomalies arising from magnetic clusters having a moment $3.7\mu_B$. This result is in good agreement with theoretical estimates for Fe antisite defects in the material. The inherent $\gamma = 1.5 \pm 0.3$ mJ/mol K² deduced from this work is considerably less than previously reported, and the behavior does not appear consistent with heavy fermion behavior. However, the mass enhancement is significant when compared to nuclear magnetic resonance and band calculations, and we propose a spin-fluctuation mechanism. [S0163-1829(99)51444-6]

The recently discovered compound Fe₂VAl exhibits a rich variety of interesting phenomena, including its anomalous specific heat.¹ Plots of C/T versus T^2 were noted to exhibit an upturn with decreasing temperature, reminiscent of the heavy fermion materials. The electronic specific heat coefficient (γ evaluated as the low-temperature limit for C/T) was found to approach 14 mJ/mol K², relatively large given the low carrier density of this alloy.²⁻⁶ The corresponding effective mass was found to be 20–70 times as large as the band mass deduced from band structure calculations.²⁻⁴ Based on this observation, several authors suggested that Fe₂VAl is a possible candidate for 3d heavy fermion material.^{1,2}

Heavy fermion systems are found among rare-earth compounds, with strong correlations involving localized f electrons.⁷ For 3d intermetallics, the larger radial extent of 3d states produces more highly dispersive electron bands, so that the 3d wave functions play a significant role in the resulting band structure. This tends not to favor heavy fermion formation. Some transition-metal-based materials have exhibited characteristics similar to those of heavy fermion or Kondo insulator systems, the prototype being FeSi.^{8,9} Much experimental and theoretical effort has been devoted to understanding the features of such 3d intermetallics.¹⁰ In

Fe₂VAl, transport and photoemission give contradictory results regarding metallic behavior,¹ a finding reminiscent of the behavior of FeSi. Thus it is important to understand whether this material can be understood on the basis of standard band theory.

Magnetic defects and spin glass behavior can result in specific heat enhancement, leading in some cases to false indications of heavy fermion behavior.^{11,12} Investigation of magnetic changes in the specific heat can help identify these mechanisms. For this reason, we have carried out field-dependent specific heat measurements on Fe₂VAl. The results show convincing evidence that the low- T upturn in specific heat can be attributed to magnetic defects.

The Fe₂VAl sample studied here was prepared from 99.97% Fe, 99.7% V, and 99.9% Al by mixing appropriate amounts of elemental metals. These were melted several times in an Ar arc furnace. The loss of weight upon melting was about 0.1%. The resulting ingot was annealed in a vacuum-sealed (10^{-5} torr) quartz tube at 1000°C for two days, and then annealed for $L2_1$ ordering at 400°C for more than 12 h followed by furnace cooling. This sample preparation is the same as reported by Nishino *et al.*¹ Powder from the same ingot was used for previous nuclear magnetic reso-

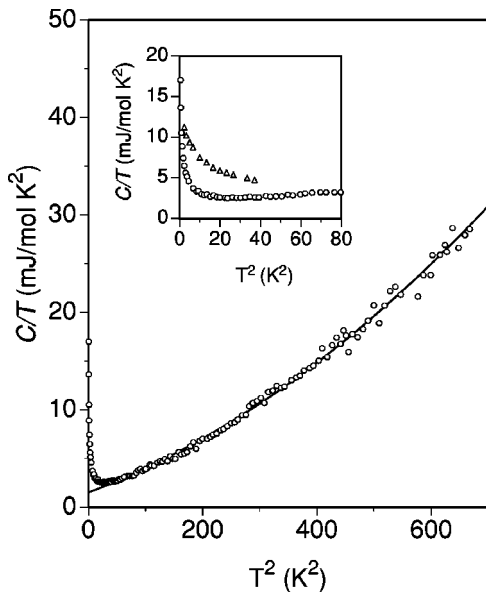


FIG. 1. Plot of C/T vs T^2 for Fe_2VAI below 26 K. The solid curve is the fitted function described in the text. Data of Ref. 1 (triangles) and our low- T data (circles) are shown in the inset.

nance (NMR) measurements.⁶ An x-ray analysis taken with $\text{Cu } K\alpha$ radiation showed two strong reflections which could be indexed to (200) and (220) planes according to the expected $L2_1$ or DO_3 structure. The determined lattice constant $a = 5.756 \text{ \AA}$, a bit below that published in the literature.¹ No other reflections were seen, indicative of a single phase in our sample.

Specific heat was measured in the temperature range 0.6–8 K with a ^3He relaxation calorimeter using the heat-pulse technique in magnetic fields up to $H = 8 \text{ T}$. To examine the accuracy of the field dependent specific heat, $C(T, H)$ of a copper ingot was tested under $H = 0, 1, \text{ and } 8 \text{ T}$. The error of the measurement in this temperature range was less than 1%.

In $H = 0$, we extended our measured temperature to 40 K. The zero-field C/T vs T^2 plot below 26 K is shown in Fig. 1. A low- T upturn in C/T is seen in our sample. For compari-

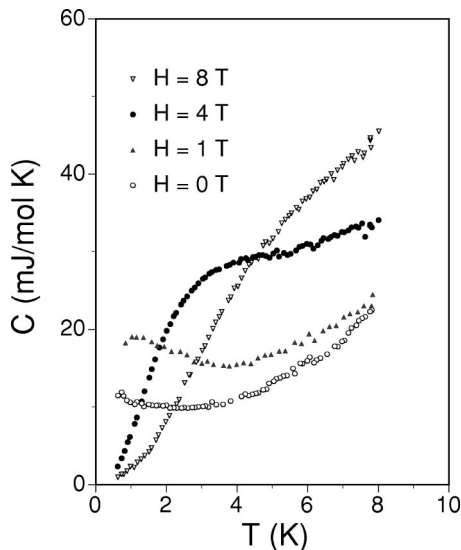


FIG. 2. Plots of C vs T in fields of 0, 1, 4, and 8 T below 8 K.

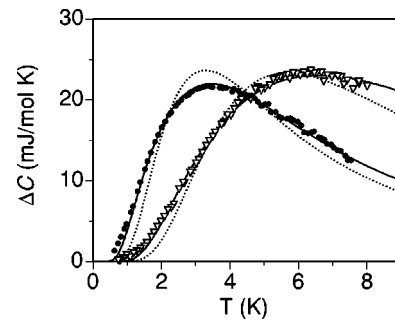


FIG. 3. ΔC vs T in fields of 4 T (circles) and 8 T (triangles). Dotted curves: fits to a single Schottky function; solid curves: fits to a multilevel Schottky function.

son, we include previously reported data from Ref. 1 as triangles in the inset of Fig. 1. As one can see, the low- T upturn in C/T is sample dependent. This implies that effects leading to such an upturn are not intrinsic properties of the Fe_2VAI system.

The high-temperature specific heat is believed to be intrinsic and is a combination of electron and lattice excitations. We have fit the data between 8 K and 25 K to $C(T) = \gamma T + \beta T^3 + \delta T^5$. The first term represents the standard electronic contribution while the remaining two terms are phonon contributions, the last due to anharmonic effects.¹³ (The next term in the anharmonic expansion, T^7 , we found not to be significant.) From a χ^2 minimization we obtained $\gamma = 1.5 \pm 0.3 \text{ mJ/mol K}^2$, $\beta = 0.021 \pm 0.003 \text{ mJ/mol K}^4$, and $\delta = (3.1 \pm 0.5) \times 10^{-5} \text{ mJ/mol K}^6$. This fit is shown in Fig. 1. The $T = 0$ Debye temperature can be obtained from $\Theta_D = (234R/\beta)^{1/3}$,¹³ where R is the ideal gas constant, yielding $\Theta_D = 450 \text{ K}$ in this case. Fits were limited to the range 8 to 25 K because the contribution from the sample holder becomes significant above 30 K, while the low-temperature upturn is due to magnetic defects, as shown below.

To better understand the low-temperature C/T upturn in our sample, we performed field-dependent specific heat measurements. Results are illustrated in Fig. 2. The specific heat at zero field starts to increase when the temperature decreases below 3 K, while a broad maximum appears at about 1.2 K in $H = 1 \text{ T}$. The maximum shifts to higher temperatures with increasing field, resembling a Schottky anomaly due to magnetic defects.¹³ Assuming that the specific heat is a sum, $\Delta C + \gamma T + \beta T^3 + \delta T^5$, and using the three parameters extracted above, we obtained the excess specific heat, ΔC , plotted in Fig. 3. Note that ΔC goes almost to zero below 1 K, in $H = 8 \text{ T}$, indicating that the entire excess specific heat in this field can be attributed to such defects. We fit the data to a two-level Schottky function,

$$C_{Sh} = Nk_B \left(\frac{\epsilon}{k_B T} \right)^2 \frac{e^{\epsilon/k_B T}}{(1 + e^{\epsilon/k_B T})^2}, \quad (1)$$

where k_B is the Boltzmann constant and N the number of Schottky centers. Fits for the high-field data ($H = 4$ and 8 T), shown as the dotted curves in Fig. 3, follow the trend of the data, although the peaks in ΔC are somewhat broader than the fitted curves. The resulting energy splittings correspond to defects with a magnetic moment of approximately $1.1\mu_B$.

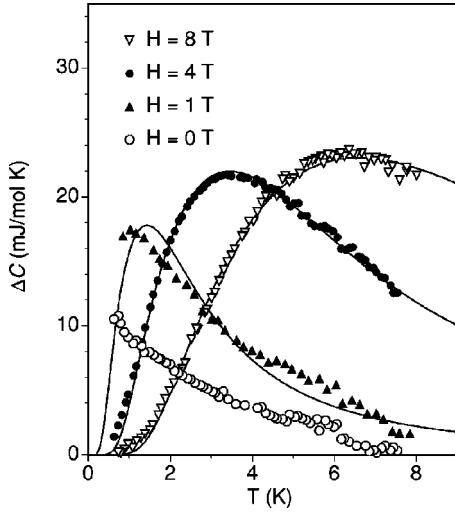


FIG. 4. Temperature dependence of ΔC in fields of 0, 1, 4, and 8 T below 8 K. Curves: fits to the functions described in the text.

While Fe₂VAl is nominally nonmagnetic, magnetism can be induced in the material by wrong-site transition atoms. Fe_{2+x}V_{1-x}Al alloys arise from Fe₃Al, with a cubic DO₃ (BiF₃) structure containing two Fe sites, denoted as Fe-I and Fe-II. The L₂₁ structure (AlCu₂Mn-type Heusler structure) is formed by preferential site occupation: Fe-I is occupied by V in Fe₂VAl, and Fe-II by Fe. In Fe₂VAl, Fe on Fe-II is magnetically inactive. Our sample was shown by NMR to be nonmagnetic,⁶ but with magnetic defects indicated by the NMR linewidth, so we infer the L₂₁ ordering to be substantially complete. Antisites may result from incomplete ordering or from a thermal equilibrium distribution of atoms among sites. The presence of magnetic clusters was also deduced from magnetic measurements in more Fe-rich Fe_{2+x}V_{1-x}Al alloys, and was associated with the observation of giant magnetoresistance.¹⁴ Local spin density approximation calculations³ indicated antisite Fe atoms on the Fe-I site to carry a local moment of $2.1\mu_B$, with further polarization of neighboring atoms. Thus, magnetic defects may be associated with antisite Fe atoms, either alone or as Fe-V antisite pairs.

For independent magnetic clusters with spin $J \neq 1/2$, the magnetization can be described by Langevin theory¹⁵ and the corresponding specific heat should be generalized to the so-called multilevel Schottky function:¹⁶

$$C_m = Nk_B \left[\frac{x^2 e^x}{(e^x - 1)^2} - (2J + 1)^2 \frac{x^2 e^{(2J+1)x}}{(e^{(2J+1)x} - 1)^2} \right], \quad (2)$$

where $x = g\mu_B H/k_B T$, and g is the effective g factor for the cluster. In order to examine whether the cluster picture is applicable, we fit ΔC for each field to Eq. (2) with N , J , and g as parameters.

The high field data (4 and 8 T) agree very well with this picture. The fits are plotted as solid curves in Fig. 3, along with the two-level Schottky fits. The optimum J and g values are $3/2$ and 1.93 for both fields. Using these values, the effective magnetic moment per cluster is determined to be $\mu = g\mu_B \sqrt{J(J+1)} = 3.7\mu_B$. The cluster concentrations are de-

TABLE I. Fermi-level DOS of Fe₂VAl, in states/eV atom. Refs. 2–4 are calculated values.

| Reference | 2 | 3 | 4 | 6 (NMR) | this work (γ) |
|-----------------|------|-----|-----|---------|------------------------|
| $g(\epsilon_f)$ | 0.08 | 0.3 | 0.1 | 0.055 | 0.6 ± 0.1 |

termined to be 0.0037 and 0.0036 per formula unit, for 8 and 4 T, respectively, from these fits. These curves provide an excellent fit to the data.

As shown in Fig. 4, the fit for lower fields is less satisfactory. For $H = 1$ T, the fitted cluster concentration is 0.0026 per formula unit, somewhat smaller than for high fields. This is presumably due to a broadening of the Schottky feature due to a distribution in the orientation or magnitude of magnetic anisotropy. The peak positions for the 1 T, 4 T, and 8 T data scale with field, as expected, with the effect of the anisotropy being a reduction in the peak with no shift. At the higher fields, anisotropy corresponding to an effective field of 1 T or less would be much less noticeable. Isolated Fe antisites should have no crystalline anisotropy due to the octahedral site symmetry, but Fe-V antisite pairs, or other interacting defect configurations, could exhibit such a field.

The zero-field ΔC can be understood in terms of a distribution of magnetic anisotropies. Data at sufficiently low temperatures are not available and only the high-temperature tail falls in the measured temperature range. However, the observed upturn is believed to be the Schottky anomaly tail arising from such a distribution, although we have not fit the data to a specific field distribution. The observation that ΔC decreases nearly to zero in 8 T at low temperatures helps confirm our assignment of the low-temperature specific heat upturn to magnetic defects. A similar result was found for the specific heat in Ni_{0.62}Rh_{0.38}, which was originally fit to spin fluctuation behavior, but found from the field dependence to be due to superparamagnetism.¹⁷

Note that a spin glass also exhibits a specific heat maximum shifted and rounded by increasing applied fields.¹⁸ As suggested by Singh and Mazin, a Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction mediated by low-density carriers could lead to a spin glass state in Fe₂VAl.³ The specific heat upturn could be attributed to a spin glass transition with a freezing temperature close to zero. However, in a magnetic field, the specific heat peak near the spin glass freezing temperature characteristically shifts to higher temperatures and is suppressed and rounded. Our data fail to satisfy such a description because the excess specific heat was observed to increase with increasing fields.

Thus, the specific heat anomaly is found to arise from a distribution of magnetic defects in the sample. The best-fit curves indicate these defects to have a spin of $J = 3/2$. The Schottky anomaly becomes broader as J increases, and very poor agreement is obtained for J greater than about 2. The fit yields a fractional population per formula unit $f = 3.6 \times 10^{-3}$. Further evidence supporting this picture is found in NMR linewidths. A previous report⁶ estimated the defect density from NMR data using a defect moment of $1\mu_B$. Modifying this estimate¹⁹ using $\mu = 3.7\mu_B$ per defect obtained here gives $f = 3.3 \times 10^{-3}$, in excellent agreement with

the value extracted from specific heat. Thus the clusters identified here must be the same, as evidenced from magnetic measurements.

The moment per cluster, $3.7\mu_B$, is very close to the calculated result of Ref.3 for Fe-V antisite pairs in Fe_2VAl , where the Fe antisite was found to carry a local moment of $2.1\mu_B$, with polarization of three of its neighbors giving a cluster moment totaling $3.6\mu_B$, from a simple sum of moments. The total J of $3/2$ which we obtained is reasonable for such a composite cluster. Also, the observed anisotropy effects are consistent with antisites occurring as pairs, although further experimentation would be required to verify this specific cluster configuration.

Returning to γ , our value is considerably less than the previously reported value¹ deduced from the low-temperature upturn in specific heat. We deduced γ from the data above 8 K, but the high-field results indicate little or no additional upturn at temperatures below the Schottky anomaly, down to 0.6 K. The determined $\gamma=1.5 \pm 0.3$ mJ/mol K² corresponds to a Fermi-level density of states $g(\epsilon_f)=0.6 \pm 0.1$ states/eV atom. In Table I, this value is compared to the results of band structure calculations and NMR measurements. The electronic structure calculation of Ref. 4 included the spin-orbit coupling, and gave $g(\epsilon_f)=0.1$ states/eV atom. Similar values were obtained in other calculations.^{2,3} NMR T_1 measurements yielded a slightly smaller result: in Ref. 6, $g(\epsilon_f)=0.04$ states/eV atom was reported, extrapolated from V-site local density of states. Using a more recent hyperfine field value^{19,20} makes this estimate 0.055 states/eV atom, as reported in the table. The NMR T_1 is weakly enhanced by electron-electron interactions in normal metals, in contrast to the susceptibility, so in that case the T_1 can be considered to measure the band density of states. Compared to these results, γ is enhanced by a factor in the range of 6–11. Enhancement of γ can be due to electron-phonon and electron-electron effects. One estimate² of the electron-phonon enhancement factor in Fe_2VAl is $\lambda_{ep}=0.53$. It is unlikely that this term is significantly larger, so we deduce the electron-electron enhancement term to be on order $\lambda_{ee}=5-10$.

Although heavy fermions exhibit effective masses several orders of magnitude larger than the free electron mass, the enhancement is 15–25 when compared to the band mass.⁷ Thus, the mass enhancement evidenced here is somewhat smaller than that of the heavy fermions, though still significant. Heavy fermion materials exhibit several types of specific heat behavior, but generally C/T is temperature dependent, with the low-temperature upturn a ubiquitous feature.^{7,21} Thus it is unlikely that the enhanced γ obtained from the

fit from 8 K to 25 K is due to a heavy fermion effect, since C/T monotonically decreases with the temperature in this range. Another possibility is that an upturn in C/T is obscured beneath the sample-dependent magnetic defect contribution at low temperatures. In this scenario, this upturn must be completely quenched in a field of 8 T, as evidenced by our ΔC returning to zero at low temperatures (Fig. 3). The specific heat in heavy fermions is generally much less sensitive to applied magnetic fields: for instance, in UAl_2 , C/T is reduced by less than 10% in 10 T at low temperatures.²² Thus this behavior is not characteristic of heavy fermion systems.

For the specific heat of Fe_2VAl to be consistent with band theory, the large value of λ_{ee} must be explained. At issue is whether Fe on site Fe-II is fully hybridized by conventional means,⁵ or whether there may be a Kondo or related mechanism giving it its nonmagnetic behavior, as proposed for FeSi.^{8,9} Spin fluctuation behavior can provide a large λ_{ee} , but with a nearly divergent Stoner enhancement factor, since λ_{ee} depends on its logarithm.^{13,23} This would be appropriate, since Fe_2VAl is nearly ferromagnetic, with T_c going to zero in $\text{Fe}_{2+x}\text{V}_{1-x}\text{Al}$ at the Fe_2VAl composition.¹⁴ For a spin fluctuation model, a $T^2 \ln T$ contribution to C/T is also expected²² below the spin-fluctuation temperature, T_{sf} . Our efforts to fit the low-temperature upturn consistently with such a function were not successful. However, T_{sf} should be very small in a semimetal with a small Fermi temperature.²² If $T_{sf} \approx 2$ K, the specific heat anomaly would be obscured by the magnetic defect term. In contrast to the heavy fermion case, the anomaly is much more sensitive to applied fields for weak ferromagnets. For instance, the spin fluctuation term in Sc_3In is almost completely quenched in a field of 10 T.²² It is therefore possible to explain the behavior of Fe_2VAl as a Stoner enhanced paramagnet. Measurements of the Pauli susceptibility would be useful in verifying the spin fluctuation mechanism, although this may be difficult due to the small $g(\epsilon_f)$ and presence of magnetic defects.

Thus, we find that the anomalous specific heat tail in Fe_2VAl is due to a sample-dependent Schottky mechanism. Fits to the magnetic-field dependence indicate the presence of magnetic clusters of moment $3.7\mu_B$, attributed to Fe antisite defects, in excellent agreement with magnetic measurements and calculations. Previous NMR measurements⁶ were in reasonable agreement with theoretically predicted band overlaps, and the inherent γ also points to conventional behavior rather than heavy fermion behavior. The mass enhancement indicates the presence of a large spin-fluctuation term.

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