Specific Heat of the Spin-Fluctuation System UAl_2 †

R. J. Trainor, M. B. Brodsky, and H. V. Culbert
Argonne National Laboratory, Argonne, Illinois 60439
(Received 18 February 1975)

We report measurements of the specific heat of paramagnetic UAl_2 between 0.8 and 25 K in magnetic fields up to 43 kOe. A nearly field-independent $T^3 \ln T$ term dominates the temperature region below 10 K. The susceptibility was measured between 3 and 10 K and varies as $1 - AT^2$. These results, and earlier resistivity measurements, are consistent with the predictions of the spin-fluctuation model. This is the first unambiguous observation of the specific heat predicted by the spin-fluctuation model for an atomically ordered paramagnet.

Experimental verification of the existence of persistent spin fluctuations in exchange-enhanced paramagnets has been unsuccessful for the most part. In particular, the theoretically predicted contributions to the specific heat and magnetic susceptibility had never been unambiguously observed in any uniform metal prior to this work.[1] In this Letter we report low-temperature measurements of the specific heat and susceptibility of the narrow-band intermetallic compound UAl_2 which strongly support the theoretical calculations and indicate the presence of spin fluctuations associated with a narrow $5f$ band. The existence of a low-temperature resistivity proportional to T^2 previously led to the proposal of spin-fluctuation scattering in UAl_2.[2]

The spin-fluctuation modification of the electronic specific heat has been considered by a number of authors. Doniach and Engelsberg[3] and Berk and Schrieffer[4] have shown that the absorption and re-emission of spin fluctuations renormalizes the electronic self-energy, leading to an enhanced effective mass at low temperatures. This effect manifests itself as a low-temperature enhancement of the electronic specific-heat coefficient, γ, which falls off with increasing temperature as $T^3 \ln(T/T_{SF})$ for $T \ll T_{SF}$. Here $T_{SF} = T_F/S$ is the characteristic spin-fluctuation temperature, and T_F and S are the degeneracy temperature of the band and the Stoner exchange-enhancement factor. Brinkman and Engelsberg[5] and Béal-Monod, Ma, and Fredkin[6] showed that this effect will be nearly insensitive to the presence of an external field.

Exchange-enhanced pure metals, notably Pd, exhibit enhanced low-temperature values of γ, but a spin-fluctuation contribution to the enhancement is difficult to separate from that due to the electron-phonon interaction, and quantitative comparisons with spin-fluctuation theory have been largely unsuccessful. The known spin-fluctuation system He^3 exhibits a $T^3 \ln T$ term in the specific heat at very low temperatures,[7] but such terms have not been observed in any metal prior to this work.[8] Very large exchange enhancements are found in some alloys near the critical concentration for ferromagnetism. Upturns in C/T for *Cu*Ni and *Rh*Ni have been fitted by $T^3 \ln T$ terms and attributed to spin fluctuations.[9,10] However, these effects are now known to be due to magnetic clustering (superparamagnetism).[1,11] In the case of *Rh*Ni this was demonstrated by the observation that the upturn in C/T is suppressed by applied fields much smaller than those needed to affect a spin-fluctuation contribution of similar magnitude.[12]

The susceptibility of a spin-fluctuation system has been calculated by Béal-Monod, Ma, and Fredkin.[6] For $T \ll T_{SF}/S^{1/2}$, $\chi(T)$ is expected to decrease from the Stoner-enhanced Pauli maximum as $1 - (3.2\pi^2/24)(T/T_{SF})^2$. A contribution of this form has been observed in He^3 below 50 mK.[13]

The specific heat, C, of UAl_2 was measured between 0.8 and 25 K in applied magnetic fields up to 43 kOe using dc techniques. Preliminary data in zero field down to 1.8 K have been reported previously.[14] The susceptibility, χ, was measured in the temperature range 3–20 K using a Faraday method with applied fields of 3–14.5 kOe. The sample was arc melted from high-purity materials and x-ray patterns indicated only the presence of the cubic Laves-phase structure. Previous NMR[15,16] and resistivity[2] measurements show no indication of magnetic ordering down to 1.5 K.

The specific heat in zero field is shown in Fig. 1, plotted as C/T versus T^2. The striking features of the data are the magnitude and nonlinearity of C/T at the lowest temperatures. The data were analyzed assuming that the Debye T^3 approx-

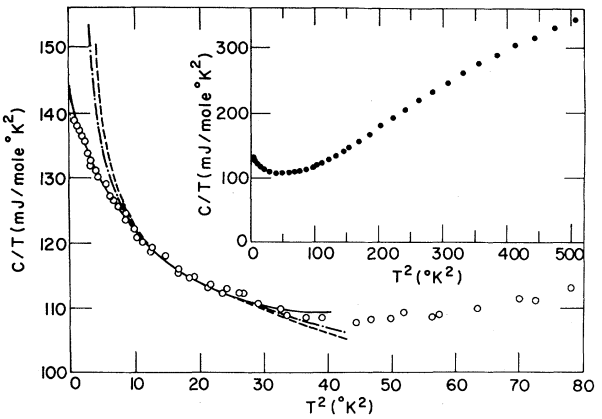

FIG. 1. C/T versus T^2 for UAl_2. Fits using data above 3 K were made with $C=AT+BT^3+Df(T)$, where $f(T)=1/T^2$ (dashed curve), $1/T$ (dash-dotted curve), and $T^3\ln T$ (solid curve). Inset shows the same data over a larger temperature range.

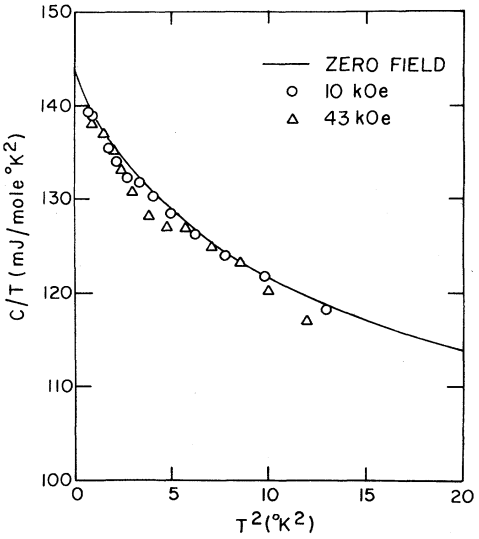

FIG. 2. C/T versus T^2 for UAl_2 in different applied magnetic fields. The solid line represents the best fit to the zero-field data.

imation describes the lattice below about 6 K, so that the total specific heat can be written as

$$C=AT+BT^3+Df(T), \quad (1)$$

where the last term represents the contribution responsible for the deviation from simple metallic behavior. A computer fit using $f(T)=T^3\ln T$ describes the data very well for all temperatures below 6 K (see Fig. 1).[17] Figure 1 also shows that fits using $f(T)=1/T^2$ and $1/T$, which would characterize the high-temperature forms of Schottky and spin-glass anomalies, are clearly incompatible with the data. The specific heat below 4.2 K in applied fields of 10 and 43 kOe is shown in Fig. 2. C/T is depressed by less than 2% even with the larger field.

The specific heat exhibits the temperature dependence expected for a spin-fluctuation system well below T_{SF} and may be compared with the theory,[3,4] which predicts

$$C=\gamma T[m^*m+\alpha(T/T_{SF})^2\ln(T/T_{SF})]+\beta T^3. \quad (2)$$

Here m^*/m is the zero-temperature many-body mass enhancement, which includes spin-fluctuation and electron-phonon contributions, γ is the electronic specific-heat coefficient determined from the band-structure density of states, α is proportional to $S(1-S^{-1})^2$, and βT^3 is the lattice contribution. The spin-fluctuation contribution to the mass enhancement is given by[5]

$$(m^*/m)_{SF}=1+\tfrac{9}{2}\ln(S/3). \quad (3)$$

Comparison of Eq. (2) to the least-squares fit to Eq. (1) gives $A=(m^*/m)\gamma=143$, $B=\beta-(\alpha\gamma/T_{SF}^2)\times\ln T_{SF}=-4.38$, and $D=\alpha\gamma/T_{SF}^2=1.94$ when C is expressed in millijoule/mole-kelvin. Combining the coefficients B and D yields $T_{SF}=12$ K if a Debye temperature $\Theta=250$ K is assumed.[18] Thus, the characteristic temperature, T_{SF}, for specific heat is close to the value obtained from the T^2 region of the resistivity ($T_{SF}=12$–16 K) using Doniach's model.[19]

If a value for the electron-phonon enhancement factor λ is assumed, then $(m^*/m)_{SF}$ and γ can easily be calculated by combining Eq. (3) with the numerical value found for the coefficient A. To do this, the measured susceptibility (corrected for a known orbital contribution[15]) is used to express S in terms of γ, since $S\propto(\chi-\chi_{orb})/\gamma$. Values of $(m^*/m)_{SF}=1.3$–1.6 and $\gamma=74$–79 mJ/mole-K^2 (corresponding to $S\approx 3.5$) are obtained for plausible values of $\lambda=0.3$–0.5.[20] An analysis of the data above 10 K, using a model for the lattice specific heat based on the relative temperature variation of Θ for isostructural $LaAl_2$,[21] yields $(1+\lambda)\gamma\approx 100$ mJ/mole-K^2 for UAl_2. This is in good agreement with the value obtained from Eq. (3) and demonstrates that the magnitude of the upturn in C/T is fully consistent with the spin-fluctuation model.

The spin-fluctuation contribution to C is expected to be sensitive to applied magnetic fields only of order T_{SF} or greater; this corresponds to $H>100$ kOe for UAl_2. Béal-Monod, Ma, and Fred-

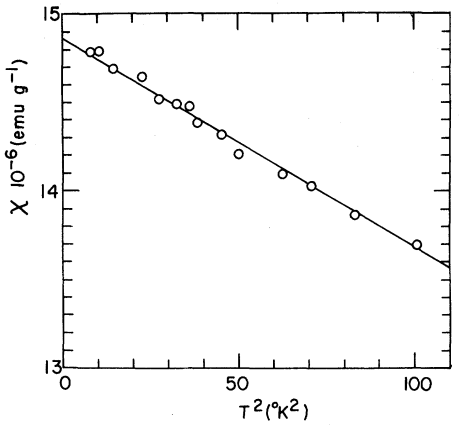

FIG. 3. Susceptibility χ versus T^2 for UAl_2. The solid line corresponds to $\chi = 14.86\times10^{-6}(1-7.94\times10^{-4}T^2)$ emu/g.

kin[6] estimated the shift $\delta C/T$ caused by an applied field H to be

$$\delta C/T \approx 0.1\left(\frac{\mu H}{k_B T_{SF}}\right)^2 \frac{S}{\ln S}\frac{C}{T} \qquad (4)$$

at zero temperature. For $H = 43$ kOe and $S = 3.5$, $\delta C/T \approx 1.5\%$, in good agreement with the data (see Fig. 2).

The susceptibility data up to 10 K are plotted in Fig. 3, versus T^2. Between 3 and 10 K the data are fitted to better than 1% by $\chi = 14.86\times10^{-6}(1 - 7.94\times10^{-4}T^2)$ emu/g. Above 10 K, χ begins to level off with increasing temperature. As reported previously,[16,22] above about 60 K, χ decreases again and follows a Curie-Weiss law above 100 K. The low-temperature variation of χ satisfies the temperature dependence required for a spin-fluctuation contribution[6] and yields a susceptibility characteristic temperature, $T_{SF} \approx 40$ K. However, as pointed out in Ref. 1, the similar temperature dependences of contributions to $\chi(T)$ due either to spin fluctuations or to the narrow band required for their existence make it difficult to separate the two effects. If the existence of a narrow or sharp feature in the density of states $N(E)$ is assumed (presumably associated with the $5f$ band), then the observed $\chi(T)$ might be explained by band-structure effects alone. To first order, the Stoner-enhanced susceptibility varies as $1-AT^2$, where A is proportional to the second energy derivative of $\ln N(E)$, evaluated at $E = E_F$. For a parabolic band a degeneracy temperature $T_F = 64$ K would yield the observed temperature dependence of χ. Although this would be an extremely narrow feature in $N(E)$ it is just what is required to give $T_{SF} = 12$–16 K for $S \approx 4$. Such a band structure would also contribute a negative T^3 term to the specific heat, but, in the parabolic-band approximation, could only account for a 1.5-mJ/mole-K^2 change in γ at 5 K. This term would be combined with the lattice contribution, leading to an underestimate of Θ of about 3% if it is ignored. A model density of states[23] which describes the temperature variation of χ over an extended temperature range predicts a variation of γ of about 2% between 0 and 5 K, which is negligible compared to the magnitude of the observed upturn in C/T.

The specific heat, susceptibility, and resistivity measurements provide a unified picture of UAl_2. The large value of γ found verifies a very high density of states at the Fermi level, consistent with the susceptibility data which indicate an extremely narrow band feature near E_F.[24] This leads to a low spin-fluctuation temperature, as evidenced by the T^2 resistivity and the large logarithmic term in the specific heat. The small sensitivity of the $T^3 \ln T$ term to applied fields makes highly unlikely other explanations of its presence based on magnetic interactions, such as a superparamagnetism caused by atomic disorder.

Finally, we point out that a wide variety of magnetic and nearly magnetic behavior is found in actinide intermetallic compounds, primarily because the degree of localization of the $5f$ electrons is intermediate between that of the $3d$ and $4f$ electrons in transition and rare-earth metals.[25] In particular, a number of paramagnetic actinide intermetallics (e.g., $NpRh_3$, $PuZn_2$, $PuRh_2$, and $PuAl_2$) exhibit large low-temperature T^2 resistivities,[2,26] and these materials are obvious candidates for further study of systems with low spin-fluctuation temperatures.

The authors wish to thank A. J. Arko, S. D. Bader, S. Doniach, F. Y. Fradin, A. J. Freeman, L. L. Isaacs, and G. S. Knapp for stimulating discussions concerning this work. The experimental assistance of R. J. Friddle and G. J. Pokorny is appreciated.

†Work performed under the auspices of the U. S. Energy Research and Development Administration.

[1]E. P. Wohlfarth and P. F. deChatel, Comments Solid State Phys. 5, 133 (1973).

[2]A. J. Arko, M. B. Brodsky, and W. J. Nellis, Phys. Rev. B 5, 4564 (1972).

[3]S. Doniach and S. Engelsberg, Phys. Rev. Lett. 17, 750 (1966).

[4]N. F. Berk and J. R. Schrieffer, Phys. Rev. Lett. 17,

433 (1966).
[5]W. F. Brinkman and S. Englesberg, Phys. Rev. 169, 417 (1968).
[6]M. T. Béal-Monod, S. K. Ma, and D. R. Fredkin, Phys. Rev. Lett. 20, 929 (1968).
[7]W. R. Abel, A. C. Anderson, W. C. Black, and J. C. Wheatley, Phys. Rev. 147, 111 (1966).
[8]Because the pure metals have such high spin-fluctuation temperatures ($T_{SF} \approx 250$ K for Pd), the $T^3 \ln(T/T_{SF})$ variation is spread out over a large temperature region and connot be experimentally separated from the much larger lattice contribution. Spin-fluctuation effects have been observed in the specific heats of some dilute alloys, *Pd*Ni, for example, where a model based on local enhancement effects has been shown to be appropriate. [For a review see D. L. Mills, M. T. Béal-Monod, and P. Lederer, in *Magnetism V*, edited by H. Suhl (Academic, New York, 1973), Chap. 3].
[9]K. H. Bennemann, Phys. Rev. 167, 564 (1968).
[10]E. Bucher, W. F. Brinkman, J. P. Maita, and H. J. Williams, Phys. Rev. Lett. 18, 1125 (1967).
[11]Since the $T^3 \ln T$ term due to spin fluctuations is expected to be strongly modified by the presence of atomic disorder [P. Fulde and A. Luther, Phys. Rev. 170, 570 (1968)], it is not clear that such a term can be observed in any concentrated disordered system. In UAl_2 we estimate the electronic mean free path to be sufficiently long such that appreciable effects due to disorder are expected only well below 1 K.
[12]B. B. Triplett and N. E. Phillips, Phys. Lett. 37A, 443 (1971).
[13]A. C. Anderson, W. Reese, and J. C. Wheatley, Phys. Rev. 127, 671 (1972).
[14]R. J. Trainor, M. B. Brodsky, and L. L. Isaacs, in "Magnetism and Magnetic Materials—1974," AIP Conference Proceedings No. 24, edited by C. D. Graham, Jr., J. J. Rhyne, and G. H. Lander (American Institute of Physics, New York, to be published).
[15]A. C. Gossard, V. Jaccarino, and J. H. Wernick, Phys. Rev. 128, 1038 (1962).
[16]A. J. Arko, F. Y. Fradin, and M. B. Brodsky, Phys. Rev. B 8, 4104 (1973).
[17]The computer-generated curves in Fig. 1 were obtained using data between 3 and 6 K only. The validity of the $T^3 \ln T$ contribution is demonstrated by the fact that the data lie upon an extrapolation of this curve down to 0.8 K.
[18]The assumption of $\Theta = 250$ K is based on an analysis of the higher-temperature specific heat data reported elsewhere (see Ref. 13). The value of T_{SF} obtained is insensitive to the Θ assumed; changing Θ by 50 K changes the calculated T_{SF} by ≈ 1.5 K.
[19]S. Doniach, in *The Actinides*, edited by A. J. Freeman and J. B. Darby (Academic, New York, 1974), Vol. 2, Chap. 2.
[20]We neglect the temperature dependence of λ, since it varies only by about 10% between $T = 0$ and about $\Theta/9 \approx 30$ K for UAl_2.
[21]S. D. Bader, Ph.D. thesis, University of California, 1973 (unpublished).
[22]K. H. J. Buschow and H. J. van Daal, in *Magnetism and Magnetic Materials—1971*, AIP Conference Proceedings No. 5, edited by C. D. Graham, Jr., and J. J. Rhyne (American Institute of Physics, New York, 1972), p. 1464.
[23]F. Y. Fradin, private communication.
[24]The existence of a narrow 5*f* band in UAl_2 was first proposed in the NMR study of Ref. 14.
[25]A. J. Freeman and D. D. Koelling, in *The Actinides*, edited by A. J. Freeman and J. B. Darby (Academic, New York, 1974), Vol. 1, Chap. 2.
[26]M. B. Brodsky, Phys. Rev. B 9, 1381 (1974).

Magnetic Annealing and Directional Ordering of an Amorphous Ferromagnetic Alloy

B. S. Berry and W. C. Pritchet
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598
(Received 3 February 1975)

The amorphous ferromagnetic alloy $Fe_{75}P_{15}C_{10}$ has been found to respond reversibly to magnetic annealing treatments. The response has been studied (a) by measurements of the ΔE effect, which is unusually large, (b) by measurements of the magnetostriction, and (c) by torque curves which yield a value of 550 erg/cm^3 for the uniaxial anisotropy parameter K_u. Internal-friction measurements reveal that the alloy is also susceptible to stress-induced ordering, with an activation energy of 2.2 eV.

It is well known that the structure-sensitive ferromagnetic properties of certain crystalline solid-solution alloys can be significantly modified and made uniaxially anisotropic by annealing in a magnetic field.[1,2] This behavior has been successfully explained in terms of a directionality induced in the state of short-range order of the alloy by the magnetization $\vec{M}$, a process which necessitates local atom motion below the Curie point, T_C. Although developed to explain the behavior of crystalline alloys, this mechanism is actually of wide generality and should also apply to amorphous alloys, since only *short-range* directional order is involved. In confirma-