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Specific heat of magnetic glass system $LaAl_2$:Gd between 0.55 and 10 K*

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Specific-heat measurements between 0.55 and 10 K are reported for the alloy system $LaAl_2$:Gd for Gd concentrations of 0, 1.0, 2.0, and 3.0 at.%. Broad peaks associated with magnetic ordering between solute spins are observed and are consistent with models based on a Ruderman-Kittel-Kasuya-Yosida-like interaction. A concentration-independent linear term is observed at low temperatures and when compared with a molecular-field model yields $|J_{sf}| = 0.08$ eV. An anomalous enhancement of the electronic-specific-heat term is also observed, but is smaller than expected from previous measurements on samples with lower concentrations.

I. INTRODUCTION

Low-temperature specific-heat measurements have been made on the alloy system $LaAl_2$: Gd in order to determine how well the interactions between the Gd solute ions can be described by existing magnetic-glass theories. Magnetic-glass behavior is expected when a nonmagnetic metal contains randomly distributed magnetic moments in such low concentration that they are coupled only by a long-range oscillatory Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction. Because the $4f$ states in Gd are well localized and because the exchange coupling between the Gd solute in $LaAl_2$: Gd and the conduction electrons is positive,[1] those contributions to the specific heat from direct exchange effects between solute ions and from single-impurity effects should be negligible. For these reasons it is believed that at low temperatures the $LaAl_2$: Gd system approaches the ideal magnetic-glass state.

Articles and discussions on the properties of magnetic glasses are contained in a recent book.[2] One of the striking features of these systems is a broad specific-heat anomaly associated with ordering of the solute spins and characterized by a large concentration-independent term which varies linearly with temperature. Such anomalies have been observed in a number of systems, and a review of previous specific-heat work is contained in an article by Phillips.[3] For the most part, rigorous efforts to derive the thermal properties of magnetic glasses have been based on the concept of a distribution of molecular fields, as suggested by Blandin and Friedel.[4] Marshall[5] showed that, when calculated for an Ising model, the linear term in the specific heat was due to those spins sitting in near-zero molecular fields. Extensions of Marshall's theory have been made by others.[6–8] The validity of an Ising-model approach has been questioned because it does not allow for spin-wave excitations, which should be important at low temperatures. On the other hand, while a Heisenberg model admits spin waves, it yields $P(H=0)=0$ and hence no linear term. For these reasons it is interesting to learn how well the molecular-field theories describe a material like $LaAl_2$: Gd. While the theoretical approach appropriate to this problem may be uncertain at present, a number of the basic features of magnetic glasses, including the linear term and the concentration dependence of the height of the anomaly, can be attributed directly to the form of the RKKY Hamiltonian, as has been demonstrated by Souletie and Tournier.[9]

Additional motivation for the present work stems from recent specific-heat measurements by Luengo and Maple[10] on $LaAl_2$: Gd with Gd concentrations of 0.21 and 0.41 at.%. While their data show evidence of magnetic-glass behavior at the lowest temperatures, the most surprising result was the observation of a large concentration-dependent enhancement of γ, the coefficient of the electronic specific heat, which is not understood in terms of present theory. It was hoped that the measurements reported here might provide additional information as to the dependence of this enhancement on Gd concentration.

II. EXPERIMENTAL

Four samples with Gd concentrations of 0, 1.0, 2.0, and 3.0 at.% were prepared in the following way. First, La : Gd alloys were prepared by melting together appropriate quantities of La and Gd, both of 99.9% nominal purity (obtained from Research Chemicals, Inc.), in an arc furnace with a Zr-gettered Ar atmosphere. Each alloy was turned over and remelted eight or more times to promote homogeneity. The proper amount of 99.999% Al was then melted together with each La : Gd alloy to produce ingots weighing about 5 g. Finally, to make larger samples for specific-heat measurements, several ingots of the same Gd concentration were placed in a Mo crucible and melted together by induction heating in an Ar atomsphere.

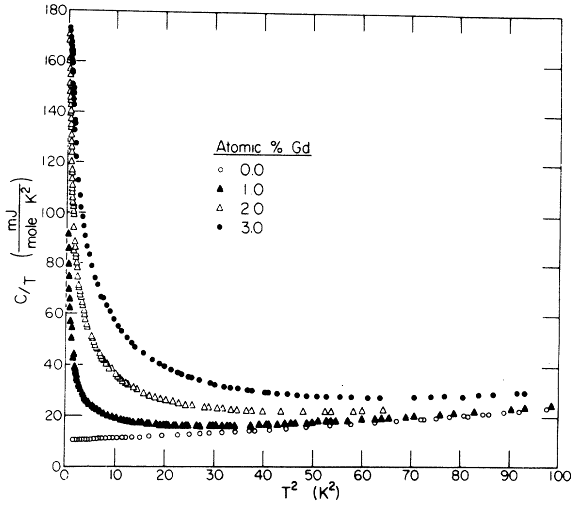

FIG. 1. C/T vs T^2 for $LaAl_2$: Gd alloys. Data for pure $LaAl_2$ taken in an external field of 2 kG.

The resulting ingots weighed 25–40 g, and the weight changes during fabrication were so small (always less than 0.01%) that the final Gd concentrations were assumed to be those calculated from the weights of the starting materials.

Specific-heat measurements were made in a ^3He calorimeter using standard techniques described elsewhere.[11] Temperatures below 1.2 K were measured with a Cryo-Cal CR-50 germanium thermometer which had been calibrated against the vapor pressure of ^3He. A polynomial of the form $\ln R = \sum A_n \ln^n T$ with n running from 0 to 9, fit the calibration data to within 1 mK. As a check, the specific heat of a 5.8-mole Cu sample (99.999% purity Cominco Products, Inc.) was measured. Smoothing corrections of 2.5 mK or less were made to the calibration so that the deviation from the reference equation[12] was less than 1%. Above 1.2 K a Honeywell germanium thermometer was used; its calibration in zero applied field has been discussed previously.[13] Measurements on Cu were repeated in magnetic fields up to 2 kG, and the data were found to change by less than 0.2%. Therefore, the zero-field calibration was used for all data.

III. RESULTS AND DISCUSSION

A plot of C/T versus T^2 for pure $LaAl_2$ and the three alloys is shown in Fig. 1. Representative data are presented in Table I. In pure $LaAl_2$ a superconducting transition is observed at 3.29 K, in agreement with previous results.[10,14] In an external field of 2 kG the sample was normal at the lowest temperatures measured, and a least-squares fit to the data below 4.2 K yields $C = (0.61 \pm 0.1)/T^2 + (10.08 \pm 0.05)T + (0.124 \pm 0.001)T^3$ mJ/mole K. The term proportional to $1/T^2$ was chosen following the work of Isaacs,[15] who observed a similar term in Sc : Gd and attributes it to magnetic impurities in the starting materials. The value of the coefficient of the linear term (γ) is in reasonable agreement with that obtained by other workers,[10,14,16] although the spread of values found in the literature is considerable. This spread is believed to be due to magnetic impurities in the starting materials, which have been shown to affect γ anomalously.[10] The coefficient of the cubic term corresponds to a Debye temperature of 362 K, which falls between the values obtained by Hungsberg and Gschneidner[14] and Luengo and Maple.[10] At temperatures above about 7.5 K the T^3 law is inadequate for a repre-

TABLE I. Representative values of specific heat C in mJ/mole K for $LaAl_2$: Gd with Gd concentrations of 0, 1.0, 2.0, and 3.0 at.%. Data for pure $LaAl_2$ below 4.2 K taken in an external field of 2 kG.

$c=0$		$c=1.0$ at.%		$c=2.0$ at.%		$c=3.0$ at.%	
T (K)	C	T (K)	C	T (K)	C	T (K)	C
		0.590	54.04	0.562	95.80	0.594	102.1
		0.682	54.09	0.674	102.2	0.691	115.3
		0.775	54.99	0.770	107.7	0.809	133.8
		0.876	54.37	0.889	112.0	0.913	142.7
		1.040	52.49	1.068	112.9	1.068	152.5
		1.202	51.37	1.176	114.5	1.196	157.3
1.308	13.77	1.330	51.90	1.320	113.7	1.330	162.4
1.421	15.04	1.425	52.50	1.445	115.6	1.495	168.7
1.508	15.98	1.554	52.25	1.546	115.1	1.595	170.3
1.617	17.07	1.662	52.63	1.635	115.0	1.689	172.4
1.690	17.89	1.829	53.28	1.714	115.7	1.774	174.8
1.843	19.69	1.988	53.10	1.801	116.2	1.853	175.7
1.937	20.56	2.094	53.68	1.986	114.6	2.030	176.0
2.122	22.68	2.211	54.04	2.092	115.1	2.135	177.7
2.229	23.73	2.336	55.31	2.309	116.4	2.246	177.4
2.337	25.28	2.419	55.47	2.410	115.1	2.420	179.7
2.465	26.93	2.526	56.59	2.643	115.7	2.636	181.0
2.587	28.46	2.648	57.02	2.763	115.6	2.738	181.3
2.723	30.06	2.778	57.78	2.885	115.7	2.846	180.6
2.854	31.77	2.919	58.79	2.983	115.4	2.965	181.4
2.980	33.56	3.122	60.33	3.170	115.1	3.116	181.0
3.088	35.03	3.275	61.34	3.243	114.9	3.243	179.8
3.244	36.98	3.423	62.47	3.390	114.5	3.353	179.3
3.395	39.03	3.584	63.95	3.487	114.8	3.510	178.8
3.515	40.77	3.680	64.90	3.550	114.7	3.723	178.0
3.681	43.24	3.842	66.65	3.806	115.3	3.866	177.6
3.887	46.41	4.068	68.78	4.093	116.2	4.107	177.5
4.116	50.20	4.283	72.26	4.370	117.1	4.352	177.4
4.774	60.82	4.454	73.71	4.650	119.3	4.613	177.3
5.006	65.08	4.684	76.79	4.782	120.4	4.844	177.3
5.227	69.33	5.180	84.56	5.056	122.9	5.039	178.7
5.404	73.00	5.408	88.50	5.301	125.5	5.490	179.7
5.633	77.93	5.625	92.46	5.547	128.9	5.768	182.5
5.864	83.05	5.862	97.10	5.784	132.2	5.909	184.4
6.093	88.61	6.119	102.6	6.046	136.1	6.129	187.5
6.437	97.04	6.541	112.9	6.310	141.2	6.541	192.3
6.990	112.8	7.064	126.9	6.607	147.2	6.979	199.3
7.614	133.2	7.748	148.5	6.938	154.9	7.602	214.6
7.907	143.8	8.090	160.7	7.642	173.3	7.973	225.2
8.493	168.4	8.461	175.7	8.026	186.3	8.399	240.9
8.988	190.5	9.103	204.6			8.973	256.3
9.433	213.1	9.507	225.7			9.318	277.0
9.877	238.5	10.13	263.1			9.567	290.3

TABLE II. Values of some parameters found from our work for different concentrations of Gd.

c (at.% Gd)	T_m (K)	$\Delta\gamma$ (mJ/mole K^2)	A (mJ K/mole)	A' [(mJ K/mole) (1/at.% Gd)^2]	$S/R\ \ln 8$
1.00	<0.6	0.6±0.2	350±50	350	0.89
2.00	1.15±0.1	2.0±0.5	1450±100	360	0.92
3.02	1.9±0.1	2.8±0.5	3500±300	385	0.89

sentation of the lattice specific heat; accordingly, a fit of the high-temperature data was made to an equation of the form $(C - \alpha/T^2) = \alpha T + \beta T^3 + \delta T^5$. Such an equation describes the data to within 1%, but γ is changed by 2%, β by 19%, and the standard deviations of the coefficients are several times larger than those found at lower temperatures. Inclusion of a T^7 term makes matters worse. Similar behavior has been reported previously.[14]

Because the excess specific heat of the alloys C_E, defined as the specific heat of the alloy minus that of pure $LaAl_2$, is relatively large, it is difficult to determine whether or not the lattice term is altered by alloying. We have assumed that it is not, based on the observation that in the 1-at.%-Gd sample the quantity C/T becomes parallel to that of pure $LaAl_2$ above 7 K, implying only an enhancement of the linear term. Furthermore, measurements on samples with Gd concentrations up to 0.41 at.% show no change in the lattice contributions.[10]

C_E is composed of two parts: an enhancement of the linear term, $(\Delta\gamma)\,T$, and a broad maximum C_m due to ordering between Gd spins. Since $C_m \rightarrow 0$ at high temperatures, $C_E \rightarrow (\Delta\gamma)\,T$. Figure 1 shows this for the 1-at.%-Gd alloy, for which $\Delta\gamma \approx 1$ mJ/mole K^2. In the 2- and 3-at.% samples Fig. 1 indicates that C_m is still significant at the highest temperatures measured. In order to extract $\Delta\gamma$ for these samples it was assumed, based on the reported behavior of La : Gd,[17] that $C_m \approx A/T^2$ at temperatures well above the temperature for which C_m is maximum. Thus at high temperatures $C_E = A/T^2 + (\Delta\gamma)\,T$, and a plot of $C_E T^2$ versus T^3 should yield a straight line. Such plots do indicate an approach to $1/T^2$ behavior for C_m, although the scatter in the data is considerable because C_E is only a few percent of the total specific heat near 10 K. Values of A and $\Delta\gamma$ obtained from these plots are listed in Table II, along with their estimated errors. It is observed that A is roughly proportional to c^2, where c is the solute concentration, and the quantity $A' = A/c^2$ is also listed in Table II. Enhancements of the linear term of $LaAl_2$: Gd have been reported for samples with Gd concentrations of 0.21 and 0.41 at.%.[10] It was found that $\Delta\gamma \approx 5.7$ mJ/mole K^2 at.%Gd for these samples. Our values fall substantially below an extrapolation of this result to the higher concentrations reported here. It appears that further measurements are needed to establish the concentration dependence of $\Delta\gamma$. The mechanism responsible for this enhancement is not understood, but similar effects have been observed in other systems including Sc : Gd,[15] La : Gd,[17] and $LaAl_2$: Ce.[18]

The magnetic specific heat C_m of the three alloys is plotted in Fig. 2. The temperature T_m corresponding to the maximum height of each peak is listed in Table II. The maximum for the 1-at.% sample lies below the temperature range investigated.

Souletie and Tournier[9] have shown that if the ordering between moments is due to a RKKY-like interaction which oscillates as $\cos(2k_F r)$, where k_F is the Fermi wave vector, and falls off as $1/r^3$, then the reduced specific heat, defined as C_m/c, is related to the reduced temperature T/c by a unique function which is independent of the solute concentration c. A plot of C_m/c versus T/c, shown in Fig. 3, is in reasonable agreement with this result, especially at low temperatures. One implication of such behavior is that T_m varies linearly with c if the magnitude of C_m at T_m varies linearly with c. This is a well-known experimental result[9] and is consistent with our data. Magnetic measurements by Maple,[19] however, yield paramagnetic Curie-Weiss temperatures for $LaAl_2$: Gd which decrease faster than linearly with decreasing c and vanish at finite c. These results are supported by

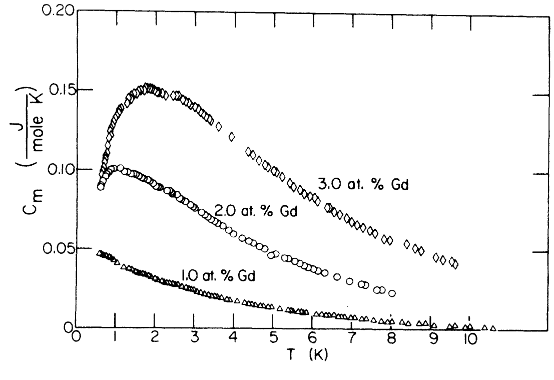

FIG. 2. Magnetic specific heat C_m vs T for $LaAl_2$: Gd.

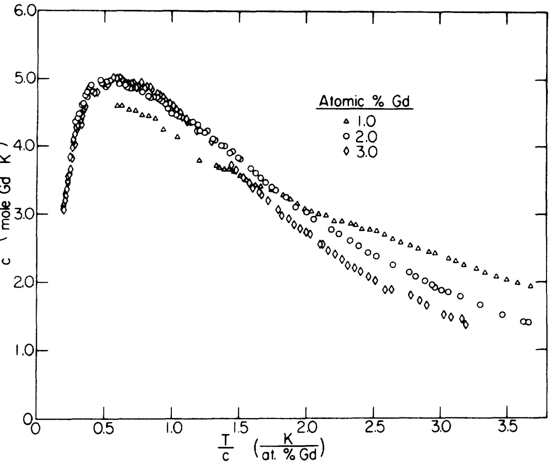

FIG. 3. Reduced magnetic specific heat C_m/c vs reduced temperature T/c, where c is the Gd concentration in at.%.

the nuclear-quadrupole-resonance measurements of MacLaughlin and Daugherty,[20] who obtained nuclear Curie-Weiss temperatures from observed maxima in the spin-echo amplitude. Such apparent discrepancies between specific-heat and paramagnetic-susceptibility results are not unusual in magnetic glasslike materials. Wohlleben and Coles[21] point out that for sufficiently dilute alloys the characteristic energy $k_B T_m$ due to the RKKY interaction is no longer reliably found from the Curie-Weiss temperatures θ_p measured above T_m. Only when the temperature is lowered does the interaction fully manifest itself as a susceptibility maximum at T_m. T_m turns out to be larger than θ_p and varies linearly with concentration. The data presented here give $T_m \approx 0.55c$, when c is expressed in at.%, and are consistent with the previous measurements on samples of 0.41 at.% and less, which showed upturns in the specific heat in zero field at 0.5 K.[10]

At higher temperatures Fig. 3 indicates a deviation from the scaling law of Souletie and Tournier. In the region where $C_m \approx A/T^2$ the scaling law would predict $A \propto c^3$ instead of $A \propto c^2$, as observed. This may be due to an interaction that is not of the RKKY type, but at present there is no explanation.

Figure 3 shows that below T_m there is an apparent approach of C_m to linear concentration-independent behavior. Extrapolating C_m to zero temperature results in a limiting value of $C_m/T \approx 0.17$ J/mole K^2. Comparison of this result with a molecular-field theory makes possible an extraction of $|J_{sf}|$, the magnitude of the exchange coupling between the solute spins and the conduction electrons. Here we shall use the mean-random-field theory of Klein,[7] which is based on an Ising model and the assumption that the RKKY interaction can be approximated by $v = \pm a/r^3$, where v may take on positive or negative values with equal probability. This assumption should be valid as long as the distance between the solute ions is large compared to the wavelength of the cosine term in the RKKY Hamiltonian. The validity of the Ising-model approach, however, is questionable and therefore makes our comparison with this theory interesting. Klein obtains the result

$$\lim_{T\to 0} \frac{C_m}{T} = \frac{N_0 \pi k_B^2}{12\,\Delta(\infty)/c}\ , \tag{1}$$

where N_0 is Avogadro's number, k_B is Boltzmann's constant, and $\Delta(\infty) = \frac{2}{3}\pi^2 |a| n_0 c$ is the width of the distribution of molecular fields at zero temperature. n_0 is the number of sites per unit cube and $|a|$ is the magnitude of the RKKY interaction between two ions separated by a distance of one lattice constant. We take $n_0 = 8$ and

$$a = |S|^2 \left(\frac{3n}{N}\right)^2 2\pi J_{sf}^2 \frac{\cos(2k_F d)}{(2k_F d)^3 E_F}\ ,$$

where $S = \frac{7}{2}$ for Gd, $n/N = 3$ is the number of conduction electrons per atom, and $d = 8.145$ Å[22] is one lattice constant. $E_F = 1.52\times 10^{-11}$ erg and $k_F = 1.58$ Å^{-1} are taken in the free-electron approximation. Setting $\cos(2k_F r)$ equal to its rms value we get $|a| = 1.56\times 10^9$ (J_{sf}^2 erg) and $\Delta(\infty)/c = 8.24\times 10^{10}$ (J_{sf}^2 erg). Putting this into Eq. (1) along with our measured value of C_m/T we get $|J_{sf}| \approx 0.08$ eV. This is very close to the value of J_{sf} obtained by NMR[23] (0.09 eV), ESR[1] (0.13 eV), and measurement of T_c depression on alloys in the superconducting state[24] (0.07 eV). This result must be interpreted with some reservation since these calculations are largely based on a free-electron model. Furthermore, Klein's extension of this theory to higher temperatures predicts $T_m \approx \Delta(\infty)/k_B\pi$, which yields T_m values substantially below those actually observed; for example, in the 3-at.%-Gd sample it predicts $T_m \approx 0.2$ K.

Assuming that C_m goes to zero temperature linearly, it is possible to calculate the entropy associated with C_m. For a complete magnetic transition one expects $S = R\ln(2S+1) = R\ln 8$ per mole Gd. The ratios of the measured entropy to $R\ln 8$ are listed in Table II. The entropy of the 1% sample was calculated assuming that the maximum occurs at 0.55 K. The fact that the measured values are less than expected may mean that the assumption that C_m approaches zero linearly is not valid. It is not believed that errors in determining $\Delta\gamma$ or in extrapolating C_m to high temperatures can account for such large discrepancies.

IV. CONCLUSION

The experimental results presented here indicate that present magnetic-glass theories based on the RKKY interaction describe quite well the specific heat of $LaAl_2$: Gd at sufficiently low temperatures. A molecular-field model for an Ising system yields a quantitatively acceptable result for the strength of the s-f exchange interaction, but fails to predict the correct specific heat at temperatures comparable to T_m. Above T_m deviations from Souletie and Tournier's scaling law may be evidence of a mechanism not of the RKKY type.

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