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Specific Heat of Dilute Gadolinium in Scandium Alloys*

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The specific heats of scandium and of a series of dilute gadolinium in scandium alloys were measured in the 0.5–4-K range. In alloys with less than 0.1-at.% gadolinium, there is a contribution to the specific heat due to solute-matrix interaction. In higher-concentration alloys, the major contribution to the specific heat is due to long-range solute spin-spin interactions. In a 1.0-at.% alloy, the phase transformation due to magnetic ordering is observed. The electronic specific-heat coefficient increases rapidly with alloying. The spin-spin interaction is shown to be of the Ruderman-Kittel-Kasuya-Yosida type.

The anomalous properties of dilute solutions of magnetic solutes in nonmagnetic hosts are well known.[1] The strongly exchange-enhanced metal, scandium, is readily spin polarized by the magnetic solutes, gadolinium and dysprosium. In scandium gadolinium, the polarization is positive, i.e., an enhancement of the effective moment per gadolinium is observed.[2,3] In alloys containing up to 0.1 at.% of gadolinium, the moment enhancement is inversely proportional to solute concentration. In alloys with solute concentration in the 0.1–5-at.% range, the moment enhancement is independent of solute concentration. This behavior may signal the onset of long-range magnetic order due to solute spin-spin interactions. Specific heats, as a function of solute concentration, were determined in order to elucidate the magnetic-ordering phenomena in scandium-dilute gadolinium alloys.

The properties of scandium are extremely sensitive to impurities. To minimize extraneous impurity effects, the experimental alloy specimens were prepared by successive enrichment of a scandium ingot with gadolinium. Analysis of the starting material, reported previously,[4] revealed a rare-earth impurity content of 100 ppm. The specimens were prepared by levitation melting and casting into a chilled copper mold. The melts were held in the liquid state for a prolonged time to ensure thorough mixing of the components, hence no subsequent homogenizing treatments were applied. Since no weight losses were detected in the preparation procedure, the nominal compositions were accepted as being correct.

The specific heats were measured using a recirculating mode helium-three cryostat and the heat-pulse technique. The calorimetric addendum was measured in a separate experiment. The system performance and the technique was checked for systematic errors by measurement of the specific heat of a standard copper sample.[5] At least two complete experimental runs between 0.5 and 4.2 K were made on each alloy specimen. Since no systematic differences were found from run to run, individual runs on the specimens are not separately indicated in the results presented.

The experimental results are presented in Fig. 1 in the form of specific-heat-versus-temperature plots. Numerical values of the specific heats are given at even intervals of temperature in Table I. The measured specific heat of scandium fitted the expression

$$C_{p,\mathrm{Sc}}(T) = (10.72\pm 0.05)T + (0.042\pm 0.003)T^3 + (0.4\pm 0.2)T^{-2}\ \mathrm{mJ\,mole^{-1}\,K^{-1}}$$

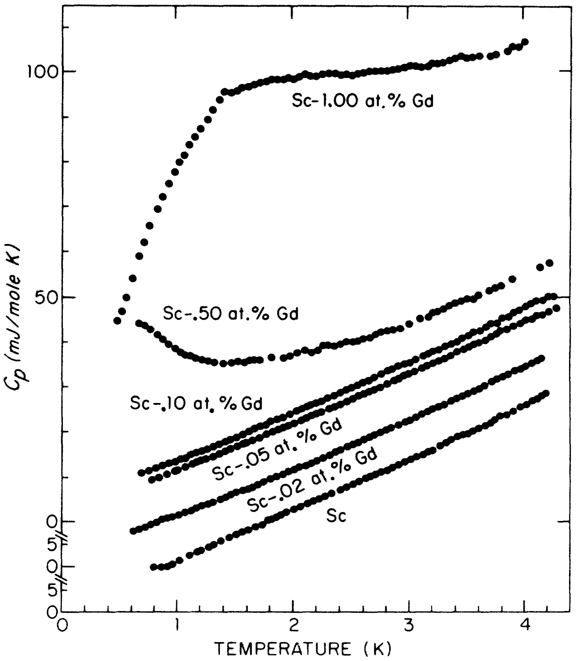

FIG. 1. Specific heat C_p vs temperature for dilute gadolinium in scandium alloys. Note the displacements in the ordinate scale.

TABLE I. Heat-capacity data for scandium-gadolinium alloys. Units are T in K, C_p in mJ mole^{-1} K^{-1} and concentration f in at. % Gd.

f			C_p			
T	0	0.02	0.05	0.10	0.50	1.00
0.5	7.00	7.45	7.70	9.50	41.50	45.50
0.6	7.55	7.90	8.15	10.10	42.30	52.80
0.7	8.35	8.85	8.95	10.85	42.35	61.00
0.8	9.25	9.75	9.80	11.70	42.60	67.00
0.9	10.15	10.65	10.65	12.65	40.55	73.00
1.0	11.15	11.55	11.60	13.60	38.55	78.30
1.1	12.20	12.45	12.50	14.55	37.15	82.90
1.2	13.20	13.35	13.45	15.50	36.25	86.85
1.3	14.30	14.25	14.45	16.50	35.65	90.95
1.4	15.30	15.30	15.50	17.50	35.35	94.00
1.5	16.40	16.35	16.55	18.55	35.45	95.70
1.6	17.50	17.35	17.60	19.65	35.60	96.75
1.7	18.55	18.35	18.70	20.75	35.80	97.55
1.8	19.65	19.40	19.75	21.85	36.10	98.15
1.9	20.75	20.45	20.85	23.00	36.50	98.50
2.0	21.85	21.55	21.90	24.10	36.95	98.75
2.1	23.00	22.55	22.85	25.25	37.45	98.95
2.2	24.10	23.60	23.90	26.30	38.00	99.15
2.3	25.25	24.70	25.00	27.40	38.60	99.30
2.4	26.35	25.75	26.05	28.50	39.25	99.50
2.5	27.50	26.85	27.15	29.65	39.95	99.75
2.6	28.65	28.00	28.25	30.75	40.75	99.95
2.7	29.80	29.10	29.40	31.90	41.60	100.15
2.8	31.00	30.25	30.55	33.00	42.45	100.40
2.9	32.15	31.35	31.65	34.10	43.35	100.75
3.0	33.35	32.45	32.75	35.25	44.35	101.05
3.1	34.50	33.60	33.85	36.35	45.30	101.40
3.2	35.70	34.80	34.95	37.45	46.30	101.85
3.3	36.90	35.95	36.15	38.65	47.30	102.35
3.4	38.15	37.15	37.30	39.85	48.35	102.90
3.5	39.35	38.30	38.55	41.05	49.45	103.50
3.6	40.55	39.45	39.40	42.25	50.55	104.20
3.7	41.80	40.65	40.95	43.50	51.65	104.90
3.8	43.05	41.85	42.10	44.75	52.70	105.65
3.9	44.30	43.10	43.35	46.00	53.80	106.35
4.0	45.60	44.35	44.60	47.35	54.90	107.10
4.1	46.85	45.55	45.90	48.70	55.95	107.85
4.2	48.15	46.75	47.15	50.10	57.15	108.65

over the temperature range of 0.6–4.2 K. The linear term in temperature represents the specific heat of the conduction electrons, the cubic term in temperature represents the lattice specific heat, and the term proportional to T^{-2} represents the impurity contributions. The indicated uncertainties in the coefficients are the standard deviations of the least-squares polynomial fit to the data. The results for scandium are in good agreement with previous data.[6,7] The Debye temperature corresponding to this value of the lattice specific heat is 360 K, in excellent agreement with elastic-constant data.

Inspection of the results for the dilute alloys (0.02-, 0.05-, and 0.10-at.% Gd) shows that the specific heats of these are nearly parallel to that of scandium. The raw data for the alloys were corrected for the residual impurity contribution present in the scandium matrix by subtracting an amount equal to $0.4T^{-2}$. The corrected data were then fitted to expressions of the form

$$C_{p,\mathrm{alloy}}(T) = \gamma T + \beta T^3 + \alpha ,$$

where γT and βT^3 represent the electronic and lattice specific heat, respectively, and α represents the specific-heat contribution due to solute-matrix interaction. The numerical values of β were found to be invariant and identical to that of the cubic-term coefficient for scandium within the limits of one standard deviation. Thus the lattice specific heat of scandium does not appear to change upon the addition of small amounts of gadolinium. The values obtained for γ and α in the several alloys are given in Table II.

The results for the 0.5- and 1.0-at.% Gd in scandium alloys clearly indicate that for these alloys the major contribution to the low-temperature specific heat is due to long-range magnetic ordering. The magnetic ordering temperature is a function of solute concentration. The ordering temperature for the 0.5-at.% alloy is near 0.6 K, the lower end of the experimental data, while the ordering temperature for the 1.0-at.% alloy is about 1.45 K.

Since the magnetic contribution to the specific heat is the dominant term, it is difficult to separate, unambiguously, the various contributions to the total specific heat without assuming a particular model for the magnetic interaction. In order to obtain an estimate for the electronic part of the specific heat, the lattice specific heat was assumed to be invariant with solute concentration. This assumption may be justified by noting that the specific-heat curve of the 0.5-at.% alloy becomes nearly parallel to the dilute alloy curves near the upper temperatures of the measurement. Furthermore, any error introduced by this assumption will be small since the lattice specific heat is only a small fraction of the total specific heat over the temperature range of the measurements. Thus the experimental specific heat diminished by the calculated

TABLE II. Calculated values of γ, α, and β for the scandium-gadolinium system. Units are mJ mole^{-1} K^{-2} for γ, mJ mole^{-1} K^{-1} for α, mJ mole^{-1} K^{-4} for β, and at.% Gd for concentration f.

f	γ	α	β
0	10.72 ± 0.05		0.042 ± 0.003
0.02	10.20 ± 0.05	0.7 ± 0.1	0.042
0.05	10.24 ± 0.05	0.9 ± 0.1	0.042
0.10	10.50 ± 0.05	2.6 ± 0.1	0.042
0.50	12.5 ± 0.5		0.042
1.00	20 ± 2		0.042

lattice specific heat is assumed to have the functional form

$$C_{p,\mathrm{alloy}}(T) - \beta T^3 = C_{\mathrm{Mag}}(T) + \gamma T ,$$

where C_{Mag} represents the specific-heat contribution due to solute-matrix interaction and solute-solute interaction. Numerical values for γ were obtained by the asymtotic extrapolation of $(C_p(T) - \beta T^3)/T$ against T. The reliability of these numbers is indicated by the uncertainty shown in Table II.

The decrease in the value of the electronic specific-heat coefficient γ in the dilute alloys relative to the pure scandium is not an experimental or computational artifact. Similar results were observed by Lynam *et al.*[7] The results are reasonable, if one keeps in mind that the experimentally determined γ value reflects not only the density of states of the conduction electrons but also all the enhancement effects due to electron interactions. There is no *a priori* reason why the enhancement effects would not be substantially smaller in the alloys than in the pure scandium. One would expect that there will be an increase in the unenhanced γ values, if the effect of solute addition is to drive the whole system magnetic, thus splitting the energy bands in scandium. Such an increase in the γ values of the alloys is observed.

The excess specific heat α of the dilute alloys is temperature independent. It is tempting, therefore, to postulate the existence of small superparamagnetic clusters[8] in these alloys. However, if this would be the case, then α should be proportional to the solute concentration. This is not the case. It is, therefore, believed that α represents the specific heat due to the interaction between a single magnetic solute and the conduction electrons of the host matrix. Such an effect would be expected to be a weak function of concentration.

The qualitative difference in the specific heats of the 0.5- and 1.0-at.% alloys with respect to the more dilute alloys is very striking. Not only is the excess specific heat of these alloys temperature dependent, but a cooperative-type phase transformation is observed for the 1.0-at.% alloy. This excess specific heat must be due to a long-range interaction between the solute spins. Only a semiquantitative interpretation of these results is warranted.

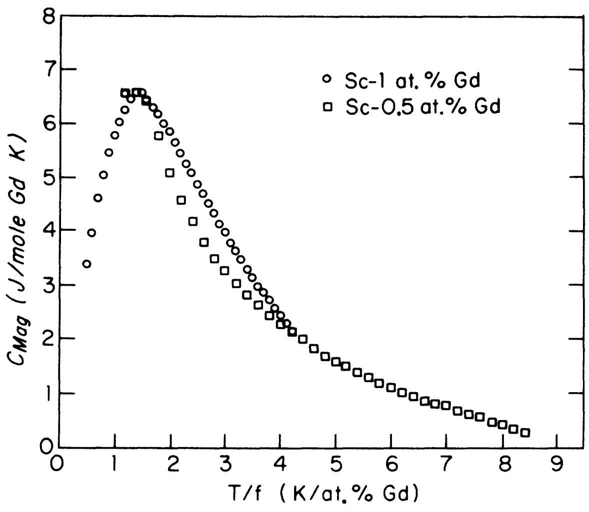

FIG. 2. Magnetic specific heat C_{Mag} vs reduced temperature T/f for the 0.5 and 1.0-at.% Gd alloys.

If an interaction of the Ruderman-Kittel-Kasuya-Yosida (RKKY) type is assumed to exist between the magnetic solutes, then the magnetic specific heat per unit quantity (mole) of solute should be a concentration-independent function of the "reduced temperature" T/f, where f is the solute concentration.[9] In Fig. 2 a plot of the appropriate data for the 0.5 and 1.0 at.% is presented. The agreement with the predictions of the model is reasonable, bearing in mind the arbitrariness of the method used to estimate the γ values, and the fact that no attempt was made to separate the single-solute-matrix-interaction specific heat from the spin-spin interaction specific heat. Thus we conclude that the long-range interaction between the magnetic spins is of the RKKY type.

Finally, the most significant conclusion that one may infer from the experimental results is that in the dilute gadolinium in scandium system, long-range magnetic interactions are operative at concentrations as low as about 0.1-at.% gadolinium. From the data of Nigh *et al*,[10] one would have concluded that to obtain the antiferromagnetic phase one would need at least 7 at.% of gadolinium.

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†Present address.

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