Enhancement of heat capacity above the Néel temperature in $Gd_{1-x}Y_xNi_2Si_2$ alloys, and its implications

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(Received 7 September 1994)

The results of heat-capacity (C) measurements on the alloys $Gd_{1-x}Y_xNi_2Si_2$ in the temperature interval 2–30 K are reported. The Gd contribution to the heat capacity (C_m) shows a strong increase with decreasing temperature before the Gd sublattice orders magnetically, resembling the behavior in Ce-based heavy-fermion antiferromagnets. For instance, in the case of the alloy $Gd_{0.4}Y_{0.6}Ni_2Si_2$, for which the Néel temperature is about 5 K, C_m varies as T^{-2} (where T is the temperature) below 25 K. There is a tendency of isothermal magnetization data in the paramagnetic state to saturate with the application of the magnetic field. The existence of short-range ferromagnetic correlations over an unusually wide temperature range so as to cause a heavy-fermion-like C_m anomaly is clearly brought out through these observations. The findings emphasize the need to consider such magnetic precursor effects while interpreting the C data of f-electron materials.

In several Ce- and U-based intermetallic compounds ordering magnetically, it is often observed that there is an upturn of the heat capacity (C) from far above the magnetic ordering temperatures (T_C or T_N) with decreasing temperature (T). The C/T attains value which is as high as a few joules per mol per kelvin before the onset of magnetic ordering, characteristic of alloys (heavy fermions) exhibiting many-body enhancement of the density of states.[1] Though magnetic fluctuations can also contribute to such an upturn of C before magnetism sets in, it has been generally believed that such effects, if present, dominate the heat capacity only at temperatures well below $2T_N$.[2–4] Most of these Ce compounds usually order below 4 K, and the enhancement of C from below 10 K naturally led to arguments in favor of heavy-fermion behavior. However, consistent interpretation of the magnetic ground state in the presence of heavy mass is found to be difficult within the theoretical framework, particularly in the low f-electron conduction-band coupling limit characterizing these compounds.[3] In view of this, there is a need to completely rule out the role of other factors, particularly magnetic precursor effects, in enhancing C. This question can be unambiguously settled only in such cases where there are no complications due to crystal-field or Kondo effects, unlike in the case of Ce or U. In this sense, the alloys of Gd are ideally suited as the Gd $4f$ orbitals are deeply localized and the crystal-field effects are negligible.

With this motivation, we report here the results of heat-capacity measurements in the temperature range 2–30 K on the alloys $Gd_{1-x}Y_xNi_2Si_2$ ($x=0.0$, 0.2, 0.4, 0.6, 0.8, and 1.0), crystallizing in a $ThCr_2Si_2$-type structure. The present pseudoternary series is chosen following a report that the C values of $GdNi_2Si_2$ over a decade of temperature above T_N ($=14$ K) are larger[2,5] compared with those of YNi_2Si_2. The investigation of this series of alloys enables us to compare the origin of the low-temperature rise in C with that of Ce systems.[3]

The polycrystalline specimens were prepared by arc melting stoichiometric amounts of constituent elements and characterized by x-ray diffraction. The heat-capacity measurements were performed by a semiadiabatic heat-pulse method in the temperature interval 2–100 K; the data presented here are restricted only up to 30 K, as there is no meaningful feature in the data above 30 K. Magnetic susceptibility (χ) (2–30 K) and isothermal magnetization (M) measurements at various temperatures in the paramagnetic state were also performed employing a superconducting quantum interference device (SQUID) for $x=0.6$ and 0.8.

The results of the C measurements are shown in Fig. 1(a). The data for $x=0.0$ and 1.0 are in excellent agreement with those reported earlier.[2] There is a peak in the plot of C versus T for all the Gd-containing compositions, except for $x=0.8$, signaling the onset of long-range magnetic order. This is apparent from the near agreement of the temperatures at which the minimum of the plot of $d\chi/dT$ versus T (obtained in magnetic field of $H=100$ Oe) and the peak in C occur for $x=0.6$ [see Fig. 1(b)]. The values of the Néel temperatures (T_N) obtained from the C data (approximately denoted by the peak) scales with the concentration of Gd ions. There is no clear-cut anomaly for magnetic ordering for $x=0.8$ in the temperature range of investigation. This scaling of T_N is consistent with the indirect exchange interaction, and this may also indicate the homogeneous nature of the magnetic ordering. Even if there is a slight error in this value of T_N, the conclusions of this paper are not affected. It may be remarked at this juncture that Ni is known not to possess any magnetic moment in this class of compounds. At this juncture, it may be mentioned that the values of χ turn out to be the same irrespective of whether the samples are cooled in the presence or absence of H, thereby ruling out the existence of a spin-glass transition in these alloys.

The most intriguing feature, which is the central point

0163-1829/95/51(13)/8178(4)/$06.00

of emphasis, is that the plot of C versus T gets more and more rounded with increasing x as the long-range magnetic ordering temperature is approached; see, for instance, the plot for $x = 0.6$ above 5 K, which is similar to that noted in $CePd_2Sn_2$.[3] Clearly, a spin-glass transition as a possible cause of this rounding is excluded.

In order to understand the origin of this rise of C before the onset of magnetic ordering, it is necessary to evaluate the $4f$ contribution (C_m) to C. For this purpose, the C values of YNi_2Si_2 [Fig. 1(a)] can be employed[2] to estimate the lattice contribution. This requires the multiplication of the temperature values in the C versus T plot of YNi_2Si_2 by a factor (e.g., 0.935 for $x = 0.6$), following Bouvier, Lethuillier, and Schmitt,[2] in order to account for the different Debye temperature values. The lattice contribution thus obtained after this normalization is shown by a solid line in Fig. 1(b) for this composition. The values of C_m, obtained by subtracting the normalized lattice contribution, are shown in Figs. 2 and 3 in various ways for all the compositions. It is quite evident that there is a pronounced increase in C_m with decreasing

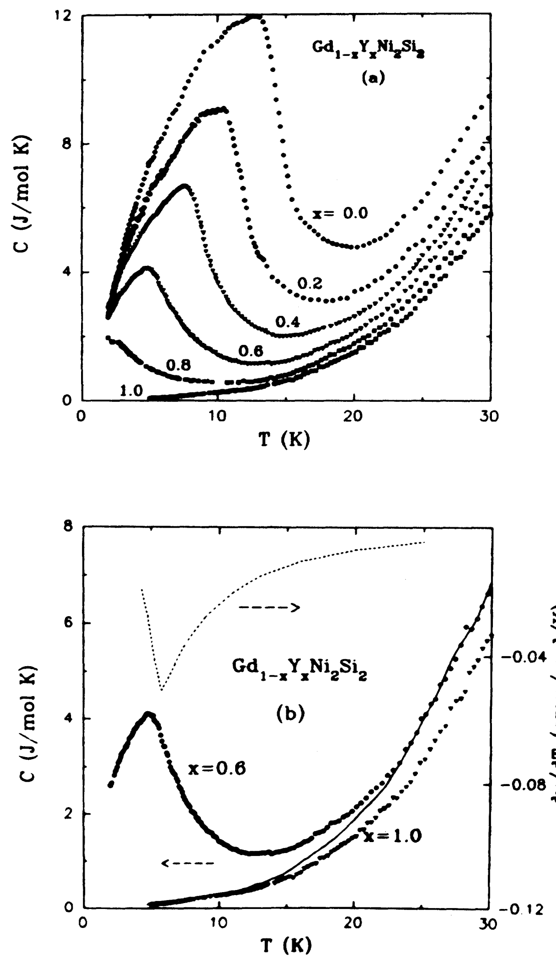

FIG. 1. (a) Heat capacity (C) as a function of temperature (T) for the alloys $Gd_{1-x}Y_xNi_2Si_2$. (b) Heat capacity of the alloys $Gd_{0.4}Y_{0.6}Ni_2Si_2$ and YNi_2Si_2. The heat-capacity values of YNi_2Si_2, after multiplying by a factor to account for the differences in the Debye temperature values of these two compounds, are plotted by a solid line. The dashed line represents the plot of the temperature derivative of magnetic susceptibility as a function of T.

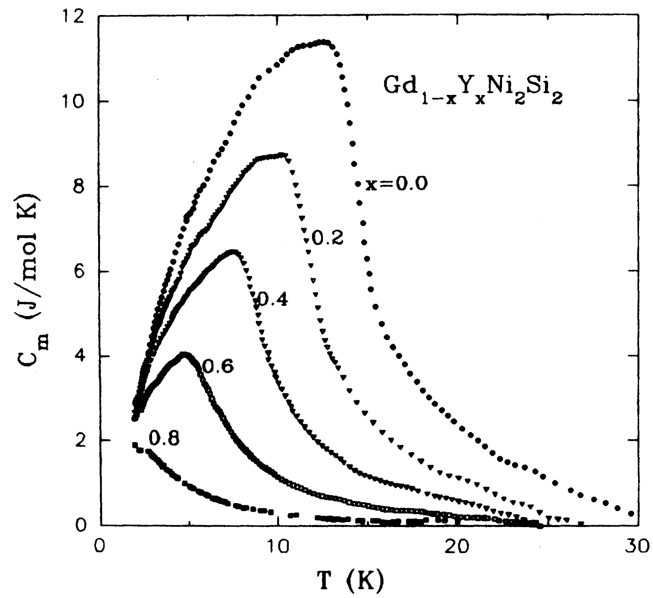

FIG. 2. The Gd $4f$ contribution (C_m) to C as a function of temperature (T) for the alloys $Gd_{1-x}Y_xNi_2Si_2$.

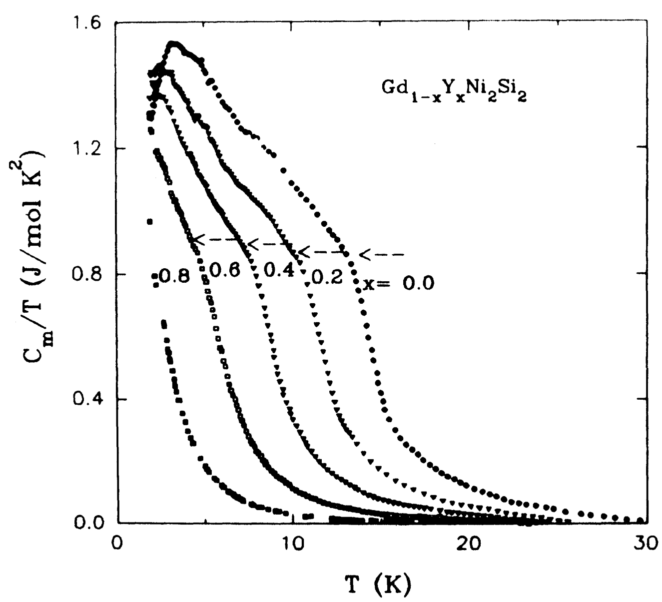

FIG. 3. The Gd $4f$ contribution (C_m) to C divided by temperature as a function of temperature (T) for the alloys $Gd_{1-x}Y_xNi_2Si_2$.

temperature above T_N, for instance, below 25 K for $x=0.6$. The value of C_m/T reaches as much as about 0.8 J/mol K^2 (in other words, 2 J/Gd mol K^2) before the onset of long-range magnetic ordering at 5 K for $x=0.6$ and about 5 J/Gd mol K^2 at 2 K for $x=0.8$. These values are comparable to that noted in any other "heavy-fermion" antiferromagnetic Ce systems before the onset of magnetic order. Since the $4f$ orbitals of Gd are well localized, the heavy-fermion phenomenon cannot be the origin of this enhancement. Therefore short-range magnetic correlations must be the only factor that can account for this C anomaly. Consistent with this, only about 80% of the full entropy is released at T_N. Such magnetic precursor effects have been encountered in some other Gd alloys as well[2,6] for $T<2T_N$.

In order to arrive at the conclusions quantitatively, the data for $x=0.6$ above 5 K are analyzed using a mean-field model[7] where $C_m T^2$ should be almost constant above T_N. For this purpose, we have plotted C_m as a function of T^{-2} in Fig. 4(a). This plot is a straight line in the paramagnetic state, thereby supporting our view that the rise in C could be attributed to magnetic fluctuations. The heat-capacity data of this Gd alloy is also plotted in Fig. 4(b) as a function of ln$t$ (where $t=T/T_N-1$). It is apparent that the shape of this plot in the Gd alloy looks similar to that reported for $CePt_2Sn_2$ (see Fig. 6 of Ref. 3). It is interesting to see that there is a nearly logarithmic variation of C_m with t in the temperature interval 5.5–20 K, as though the data are consistent with the single-impurity Kondo model of Rajan.[8]

The isothermal magnetization data (Fig. 5) indeed render evidence for the existence of short-range fer-

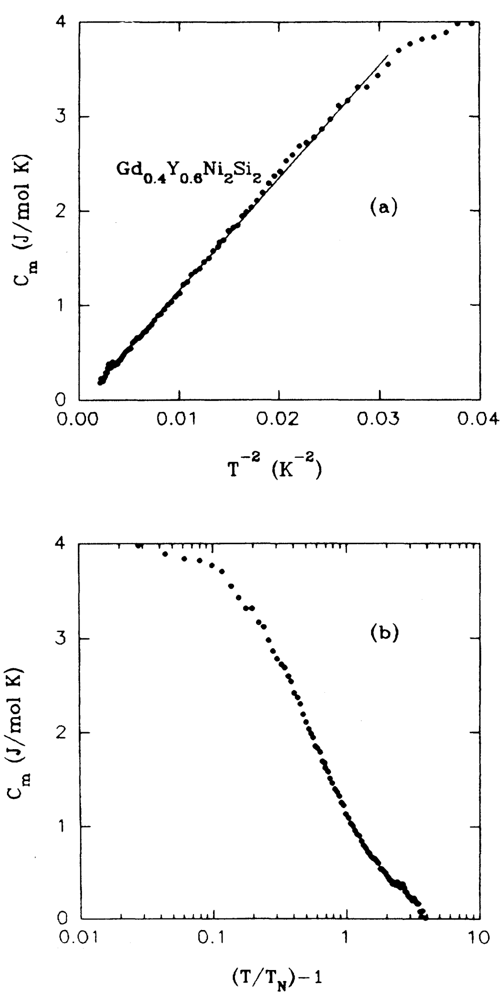

FIG. 4. (a) The plot of C_m vs T^{-2} and (b) the plot of C_m vs ln$t$, where $t=(T/T_N)-1$, for the alloy $Gd_{0.4}Y_{0.6}Ni_2Si_2$. A line is drawn through the data points in the temperature interval 5.6–22 K in (a). The logarithmic dependence of C_m on t in the temperature interval 5.6–12 K can also be seen in (b).

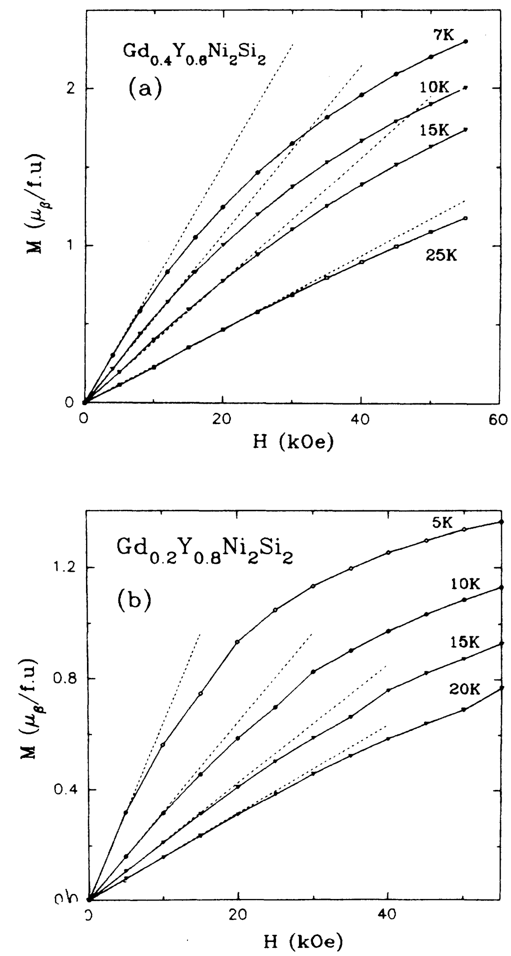

FIG. 5. Isothermal magnetization up to ($H=$) 55 kOe for the alloys (a) $Gd_{0.4}Y_{0.6}Ni_2Si_2$ at 7, 10, 15, and 25 K and (b) $Gd_{0.2}Y_{0.8}Ni_2Si_2$ at 5, 10, 15, and 20 K. A solid line is drawn through the data points at each temperature to serve as a guide to the eyes. A dashed line drawn through the data points for each temperature represents the linear isothermal magnetization behavior extrapolated from the low-field data.

romagnetic correlations at temperatures exceeding $2T_N$. It is apparent that, for $x=0.6$, M is not a linear function of H at 7, 10, and *even at 15 K*, and it tends to saturate with the application of H. It is interesting to see that, even for $x=0.8$, this ferromagnetic tendency persists well above 2 K (even at 20 K).

The observation of ferromagnetic correlations over such a wide temperature range (exceeding $T>5T_N$) is interesting. Possibly, some degree of crystallographic disorder and/or the layered nature of the crystal structure (which are incidentally characteristic of most of the "heavy-fermion" Ce antiferromagnets) trigger such magnetic precursor effects. Lawrence *et al.*[9] stressed on the basis of the observation of a large Wilson ratio that ferromagnetic correlations build as $T \rightarrow T_N$ even in the case of Ce-based layered antiferromagnets. Therefore, whatever may be its origin, one should anticipate and consider ferromagnetic correlation effects in the event C/T exhibits an enhancement.

The results imply that an alloy ordering magnetically in the millikelvin range can result in an upturn in the heat capacity with decreasing temperature, *say, from 10 K*, due to magnetic precursor effects. For such reasons, we were hesitant to attribute the observation of a large low-temperature rise in C/T in the ternary systems Ce-Ni(Cu)-Ga (Ref. 10) to heavy-fermion behavior; in fact, the T^{-2} dependence of C_m can be noticed until 10 K in some of these Ce alloys ordering magnetically below 1 K.

Finally, we wish to state that the present results may bear some relevance to another exotic phenomenon being pursued actively in the current literature, viz., non-Fermi-liquid behavior. For instance, C/T has been found to diverge logarithmically with decreasing T in some Ce and U systems.[11–13] While several groups tend to attribute this non-Fermi liquid behavior to a two-channel Kondo or quadrupolar Kondo effect,[14] some authors suggest that the apparent non-Fermi-liquid behavior may be magnetic in origin.[15–17] The divergence of C_m/T (apparently varying logarithmically in the temperature interval 5–10 K, for instance, in $x=0.6$) with decreasing temperature above T_N even in Gd alloys may emphasize the need to exclude such magnetic correlations as a possible cause of non-Fermi-liquid behavior in a compound.

To conclude, the results firmly establish that the enhancement of the heat capacity can occur over a wide temperature range exceeding $2T_N$ (mimicking heavy-fermion behavior) due to short-range magnetic correlations as the compound under study approaches long-range magnetic order. This paper emphasizes the need to critically analyze the heat-capacity data of the f-electron systems to exclude contributions from such magnetic effects before the low-temperature upturn of the heat capacity can be attributed to any other exotic phenomenon.

We thank K. V. Gopalakrishnan for the magnetization measurements.

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[1]F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Frank, and H. Schafer, Phys. Rev. Lett. **43**, 1892 (1979).

[2]M. Bouvier, P. Lethuillier, and D. Schmitt, Phys. Rev. B **43**, 13 137 (1991).

[3]W. P. Beyermann, M. F. Hundley, P. C. Canfield, J. D. Thompson, Z. Fisk, J. L. Smith, M. Selsane, C. Godart, and M. Latroche, Phys. Rev. Lett. **66**, 3289 (1991); see, for Fig. 6, W. P. Beyermann, M. F. Hundley, P. C. Canfield, J. D. Thompson, M. Latroche, C. Godart, M. Selsane, Z. Fisk, and J. L. Smith, Phys. Rev. B **43**, 13 130 (1991).

[4]S.-K. Ma, *Modern Theory of Critical Phenomena* (Benjamin, London, 1976).

[5]J. A. Blanco, D. Gignoux, P. Morin, and D. Scmitt, Europhys. Lett. **15**, 671 (1991).

[6]S. Tanoue, K. A. Gschneidner, Jr., and R. W. McCallum, J. Magn. Magn. Mater. **103**, 129 (1992).

[7]J. Souletie, J. Phys. (Paris) **49**, 1211 (1988).

[8]V. T. Rajan, Phys. Rev. Lett. **51**, 308 (1983).

[9]J. M. Lawrence, Y.-Y. Chen, J. D. Thompson, and J. O. Willis, Physica B **163**, 56 (1990).

[10]E. V. Sampathkumaran, K. Hirota, I. Das, and M. Ishikawa, Phys. Rev. B **47**, 8349 (1993).

[11]C. L. Seaman, M. B. Maple, B. W. Lee, S. Ghamaty, M. S. Torikachvili, J.-S. Kang, L. Z. Liu, J. W. Allen, and D. L. Cox, Phys. Rev. Lett. **67**, 2882 (1991).

[12]B. Andraka and A. M. Tsvelik, Phys. Rev. Lett. **67**, 2882 (1991).

[13]See Physica B **199&200**, (1994).

[14]D. L. Cox, Phys. Rev. Lett. **59**, 1240 (1987); D. L. Cox and M. Makivic, Physica B **199&200**, 391 (1994).

[15]W. W. Kim, J. S. Kim, B. Andraka, and G. R. Stewart, Phys. Rev. B **47**, 12 403 (1993).

[16]H. V. Lohneyson, T. Pietrus, G. Portisch, H. G. Schlager, A. Schroder, M. Sieck, and T. Trappmann, Phys. Rev. Lett. **72**, 3262 (1994).

[17]B. Andraka, Physica B **199&200**, 239 (1994).