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Interplay of the Kondo effect and ferromagnetism in the $CeNi_xGa_{4-x}$ alloys

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The magnetic susceptibility (4.2–300 K) and heat capacity (C) (0.5–20 K) of the alloys, $CeNi_xGa_{4-x}$ ($x=0.5-1.1$), exhibit features attributable to the interplay of the Kondo effect and ferromagnetism ($T_c \cong 5$ K). The value of C/T (where T is the temperature) shows an upturn below about 10 K for all the compositions; particularly in the case of the $x=1.1$ specimen, which is found to be nonmagnetic above 0.5 K, C/T increases to about 2.2 J/mol K^2 at 0.5 K, as if this alloy is a giant heavy-fermion material. In addition, the full magnetic entropy (R ln2) is attained only above 10 K in all alloys. This finding suggests either the persistence of the Kondo effect even in the ferromagnetically ordered state or some sort of itinerant magnetism.

It was generally believed that the Kondo lattices, if they order magnetically at all, should be antiferromagnetic, and the competition between antiferromagnetism and the Kondo effect has been extensively investigated in the case of Ce systems during the last decade. In the literature, particularly in the recent past, a few ferromagnetic Kondo systems[1–6] have been identified. The ferromagnetic ground state in Ce systems is now theoretically realized[7] and it will be of interest to activate experimental investigations in order to understand the consequences of an interplay of such a ground state with the Kondo effect. Following the report[8] of the synthesis of the new alloys, $CeNi_xGa_{4-x}$ ($x=0.5-1.1$) and $CeCu_yGa_{4-y}$ ($y=0.5-1.5$) crystallizing in the $BaAl_4$-type tetragonal structure, we have demonstrated on the basis of the electrical resistivity measurements[6] that there is a competition between magnetism and Kondo effect as a function of composition in this class of compounds. While the Ni (Cu) -rich compositions tend to become nonmagnetic, the Ga-rich end is presumably weakly ferromagnetic below about ($T_c=$) 4.5 K as evidenced in our hysteresis measurements at 0.5 K. In this paper, we present the results of magnetic susceptibility (χ) and heat-capacity (C) measurements of the alloys $CeNi_xGa_{4-x}$ in order to probe the coexistence of Kondo effect and ferromagnetism.

The samples employed in the present investigation are the same as those of Ref. 6. The compositions outside the x values mentioned above are found to be multiphase.[8] The χ measurements (4.2–300 K) were performed employing a superconducting quantum interference device in a magnetic field of 1 kOe. The C data were taken on selected compositions in the temperature interval 0.5–20 K.

The results of χ measurements are shown in Fig. 1. χ exhibits Curie-Weiss behavior above 50 K and there is a deviation from this behavior at lower temperatures due to the crystal-field effects. The effective magnetic moments ($\pm 0.05\mu_B$) and the paramagnetic Curie temperatures Θ_p obtained from the high-temperature data with the corresponding x values in parentheses are (1.1) $2.6\mu_B$, -24 ± 3 K; (0.875) $2.43\mu_B$, -33 ± 2 K; (0.75) $2.51\mu_B$, -19 ± 2 K; (0.625) $2.68\mu_B$, -10 ± 4 K; and (0.5) $2.48\mu_B$, -7 ± 2 K. The values of the magnetic moments are almost the same as that expected for the tripositive Ce ion. The essential

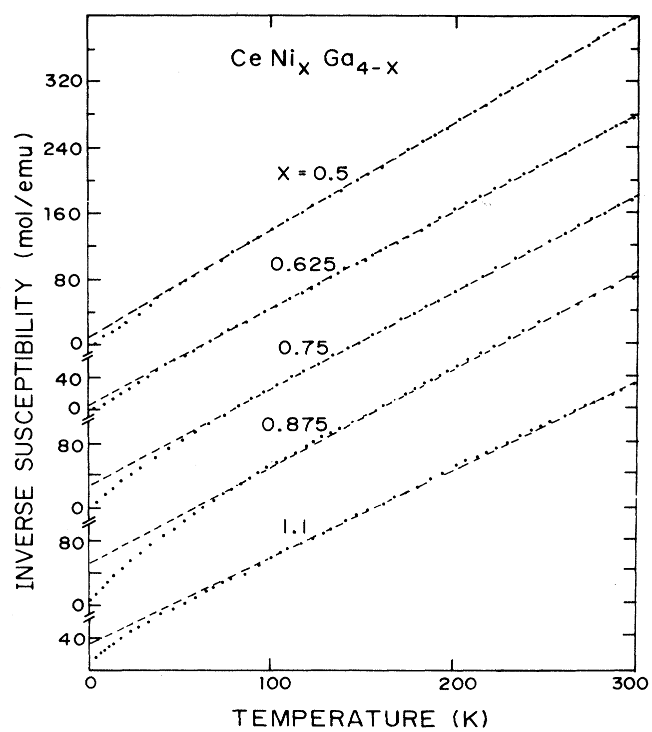

FIG. 1. Inverse susceptibility as a function of temperature for the alloys $CeNi_xGa_{4-x}$. The dashed lines are drawn to show the Curie-Weiss behavior in the high-temperature region.

point is that value of Θ_p tends to become[9] more negative as the Ni composition is increased. This implies increasing contribution of Kondo temperature to Θ_p (Ref. 10). The large negative value, without any evidence for magnetic ordering above 0.5 K for $x=1.1$ (see below) may characterize this composition as a nonmagnetic Kondo lattice. The values of Θ_p estimated from the data below 30 K are relatively small (less than 5 K) in all the alloys indicating very low Kondo temperature (T_K) associated with the crystal-field split ground state. The isothermal magnetization curves at 2 K for the Ga-rich specimens tend to saturate above 2 T; the value of the saturation moment is close to $1\mu_B$ (Ref. 8); in addition, Ga-rich compositions exhibit a weak hysteresis behavior at 0.5 K, though not noticeable at 1.7 K (not shown here). Therefore, we tend to assume that these alloys exhibit ferromagnetism (from the doublet ground state) and this needs confirmation from neutron diffraction studies.

The heat-capacity measurements were performed only on the compositions of interest. The composition chosen among the ferromagnetic alloys at the Ga-rich end is the one ($x=0.75$) in which there is a very well-defined and distinct resistive anomaly at T_c (Ref. 6). The results are shown in different ways in Figs. 2 and 3. The small bump in the C versus temperature data at 6 K for $x=0.875$ (Fig. 2) may arise from small amounts of magnetic Ce oxides. By fitting the data in the temperature region 10–18 K with the Debye formula, we estimate that the linear contribution (γ) to C and the Debye temperature Θ_D are in the range of 60–80 mJ/mol K^2 and of 230–240 K, respectively. These values may not be strictly reliable, as a Schottky peak due to the occupation of higher-lying crystal-field levels can interfere in this temperature range. For $x=0.75$, we see a distinct jump at 4.5 K characteristic of magnetic ordering in the C versus T plot (Fig. 2). For $x=0.875$, a peak appears at 1.5 K, but no prominent peak is observable for 1.1 in the temperature range of investigation. These findings are consistent with the

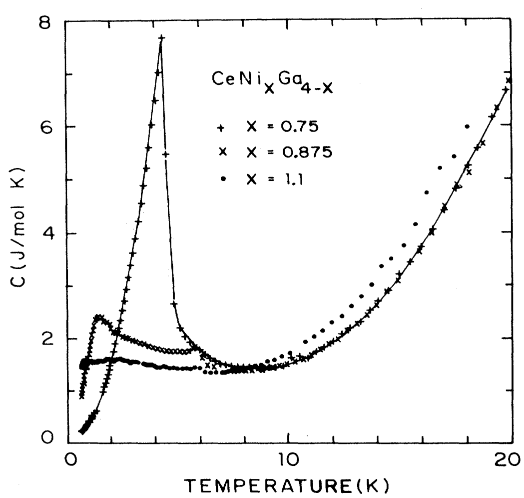

FIG. 2. Heat capacity as a function of temperature (0.5–20 K) for the alloys $CeNi_xGa_{4-x}$. A line through the data points of $x=0.75$ is drawn as a guide to the eye.

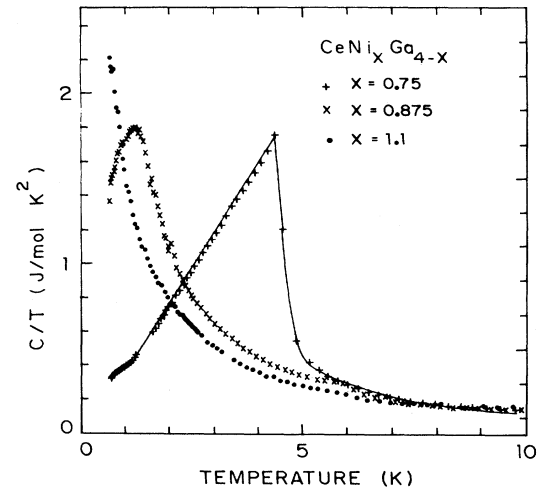

FIG. 3. Heat capacity divided by temperature vs temperature (0.5–10 K) for the alloys $CeNi_xGa_{4-x}$. A line drawn through the data points of $x=0.75$ serves as a guide to the eye.

features in the electrical resistivity data.[6] The shapes of the C versus T curves above T_c is of special interest to the aim of this article and the significance of this finding can be highlighted by plotting C/T versus T. The value of C/T starts increasing below about 10 K; for instance, in the case of $x=0.875$, it reaches a value of more than 1 J/mol K^2 at about 2 K before a rise due to magnetic ordering. It is apparent from Fig. 3 that there is a tendency for this behavior even for $x=0.75$. It may be recalled[11] that similar heat-capacity behavior has been noted in the antiferromagnetic Ce systems and was attributed to the large enhancement of the electronic contribution. For the specimen with $x=1.1$, which is found to be nonmagnetic above 0.5 K, a dramatic increase of C/T to 2.2 J/mol K^2 at 0.5 K is noted.

We now focus our attention on the origin of C/T variation (in the paramagnetic state) mentioned above. In order to see whether possible thermal population of the crystal-field levels in this temperature range[12] is responsible for the observed enhancement of C/T, we tried to fit the data for a Schottky peak, but this analysis yielded unsatisfactory results. This finding is apparent even from the nearly temperature-independent C values below 10 K for $x=1.1$. Therefore, we tend to believe that the Schottky anomalies are not the main source of the C/T enhancement. Alternatively, magnetic precusor effects can also enhance the heat capacity at temperatures well above T_c, as similar observations have been made even in normal systems such as $GdCu_2Si_2$ (Ref. 13). Although we cannot firmly exclude this possibility for the ferromagnetic compositions, it is rather difficult to believe the existence of a dominant contribution from this source until 10 K in the nonmagnetic alloy $CeNi_{1.1}Ga_{2.9}$. It is worth noting that the values of C/T above 6 K are the same for the two compositions, $x=0.75$ and 0.875; the magnetic precursor effects in alloys with such widely varying T_c values are not expected to exhibit this behavior. In addition, for the composition $x=1.1$, the $4f$ contribution (C_m) to C obtained after subtracting the phonon contribution (using the values of γ and Θ_D estimated from the data above 12 K) increases nearly logarithmically with decreasing temperature down to 2 K in accordance with the Kondo behavior as predicted by Rajan.[14] For these reasons, presently, we are in favor of attributing the low-temperature upturn of C/T (in the paramagnetic state) to the enhancement of the effective mass. If this conclusion is proved beyond doubt by other experimental methods, then the alloy with $x=1.1$ is one of the rarest Ce compounds exhibiting a giant heavy-fermion behavior.

An interesting finding is made with respect to the temperature dependence of the $4f$ contribution to entropy (S_m) derived from the knowledge of C_m data (Fig. 4). The choice of the above γ and Θ_D values employed to derive S_m may not be very precise; however, qualitatively, the temperature dependence of S_m below 10 K is not influenced by different reasonable values of these parameters. The magnetic entropy at T_c is much smaller than R ln2 and the full entropy from the doublet ground state is noted only above 10 K. While this finding is consistent with the Kondo screening of the magnetic moments even in the ferromagnetically ordered state, the itinerant nature of the $4f$ magnetism as a possible cause of the reduction of the entropy cannot be ruled out. It will be interesting to explore this aspect further.

To conclude, the depression of magnetism in the Kondo lattice system $CeNi_xGa_{4-x}$ with increasing nickel composition is probed by magnetic susceptibility and heat-capacity methods. The features indicating the persistence of the Kondo effect in the presumably ferromagnetic alloys are observed. The low-temperature heat-capacity variation of the alloy, $CeNi_{1.1}Ga_{2.9}$, is typical of that expected for giant heavy fermions. Since the Kondo temperature as inferred from the low-temperature Θ_p values appears to be rather small, this series of alloys falls in the low coupling limit of Doniach's magnetic phase diagram.[15] In this limit, one would expect that the magnetic ordering alone should prevail thereby destroying the low-temperature heavy mass. Therefore, the low-temperature rise in C/T arising from the electronic contribution is unexpected. These properties, analogous to those encountered in the case of a heavy-fermion antiferromagnet, $CePt_2Sn_2$ (Ref. 11), suggest that these alloys could provide a unique opportunity to understand the interactions in the low coupling limit of a ferromagnetic case.

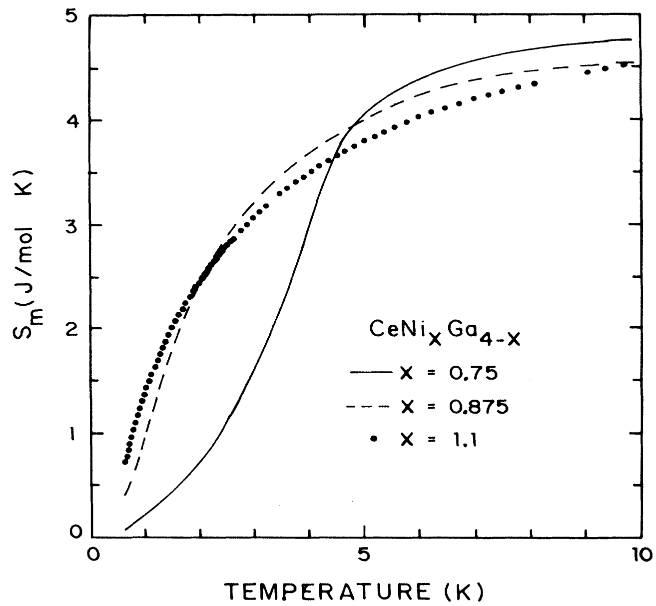

FIG. 4. The magnetic entropy (S_m) obtained as described in the text as a function of temperature (0.5–10 K) for the alloys $CeNi_xGa_{4-x}$.

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on $CeCu_{1.5}Ga_{2.5}$ down to 0.5 K. We see a sharp peak at about 1.0 K, which we believe is due to magnetic ordering. Though the high-temperature tail above 1 K is very close to that expected for a Schottky peak, we could not obtain a satisfactory fit on the basis of this contribution alone.

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