Coexistence of localized and (induced) itinerant magnetism and heat-capacity anomalies in $Gd_{1-x}Y_xNi$ alloys

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The results of magnetization (M), electrical resistivity (ρ), and heat-capacity (C) measurements for the alloys, $Gd_{1-x}Y_xNi$, are reported. The x-ray-diffraction patterns indicate that there is a change in the crystal structure from CrB-type to FeB-type orthorhombic structure for increasing x near $x=0.4$. GdNi has been known to order ferromagnetically at 70 K and the observed x dependence of T_C and θ_p proves that the strength of Gd-Gd exchange interaction is enhanced by a factor of about 1.5 in the FeB structure. The M data suggest that there is an excess moment for the Gd-rich alloys. The observed magnetization behavior is taken as an evidence to show that there is coexistence of localized magnetism (from Gd) and itinerant ferromagnetism of induced-type, presumably from Ni $3d$ band. There is an enhancement of C with decreasing temperature above T_C over a wide temperature range presumably due to short-range order effects in these alloys. [S0163-1829(97)02513-7]

I. INTRODUCTION

Our recent investigations on some of the rare-earth (R) systems not containing Ce have been very informative[1] and the conclusions drawn are of significant relevance to the field of strongly correlated electron systems. As a part of our program to probe such *normal R* systems, we have subjected the compound GdNi and its yttrium substituted alloys to careful bulk measurements like magnetization (M), electrical resistivity (ρ), and heat capacity (C). The results of our preliminary measurements on these alloys have been reported elsewhere.[2] Subsequently, we have made further interesting observations, which we report in this article. We have chosen the compound GdNi in the present investigation based on certain crystallographic and magnetic features found in RNi ($R=$ rare earth) series.[3–7] While La, Ce, Pr, Nd, Gd, and Tb compounds of this series have been reported to crystallize in the CrB-type orthorhombic structure (space group, Cmcm), the heavy rare-earth compounds (Dy to Tm as well as Y) appear to form in the FeB-type orthorhombic structure (space group, Pnma). The ratio of the volume of the transition-metal atoms to that of R atoms appears to decide the stability of these structures for a given R.[8] With respect to magnetism, the R sublattice (for $R=$ Pr to Er) has been known to order ferromagnetically, for instance, at a rather high temperature ($T_C=70$ K) for GdNi. Though it has been believed that Ni is nonmagnetic in this class of compounds, some of the publications report an excess effective moment ($\mu_{\rm eff}$) of the order of $0.5\mu_\beta$ for GdNi in the paramagnetic state which has been attributed to polarization cloud of the conduction electrons around Gd ion, while some others do not find evidence for such a moment.[3–7] The present investigation on the pseudobinary series, $Gd_{1-x}Y_xNi$, has been undertaken to probe carefully the presence of this excess moment and associated magnetic behavior. The crystal structure change resulting from the positive chemical pressure exerted by Y on Gd helps us to understand the relative strength of the exchange interaction in the CrB and FeB structures.

II. EXPERIMENT

Polycrystalline samples of $Gd_{1-x}Y_xNi$ ($x=$ 0.0, 0.15, 0.25, 0.35, 0.4, 0.5, 0.6, 0.75, 0.8, 0.9, and 1.0) were prepared by arc melting stoichiometric amounts of constituents. The alloys, $Gd_{0.95}Y_{1.05}$ and $Gd_{1.05}Y_{0.95}$, were also synthesized. We did not find any weight loss during arc melting and thus our samples appear to be perfectly stoichiometric. Unless otherwise stated, all the data reported here are on as-cast specimens; a portion of GdNi was of course homogenized at 600 °C for one week and in addition isothermal M behavior on this alloy was probed. The x-ray-diffraction patterns were obtained employing Cu K_α radiation. These patterns show that there is a transformation from the CrB- to the FeB-type structure with increasing x at $x\approx 0.4$, and it appears that $0.35 \leqslant x \leqslant 0.4$ represents a two-phase region. There are indications from our ac χ data (not presented here) that the $x=0.35$ composition may contain only small amounts of FeB phase, as this phase could not be detected by x-ray diffraction. The ρ on all these alloys by a conventional four-probe method, dc magnetic susceptibility χ [in the presence of a magnetic field (H) of 2 kOe in the temperature interval 2–300 K] and M (at 2 K or 5 K up to about 55 kOe) by a superconducting quantum interference device were also measured. We have not attached much significance to the absolute values of ρ due to microcracks in the samples. The isothermal magnetization data at several additional temperatures were also carefully measured on the annealed specimen of GdNi. The C measurements on select compositions were performed over a wide temperature range employing a setup fabricated by us.[9]

III. RESULTS AND DISCUSSION

Typical temperature-dependent χ behavior is shown in Fig. 1 for select compositions in the form of a plot of inverse χ versus temperature below 150 K; isothermal magnetization data at 5 K for select compositions (2 K data for $x=0.75$ and 0.9) are shown in Fig. 2. As known earlier,[5] for GdNi, χ

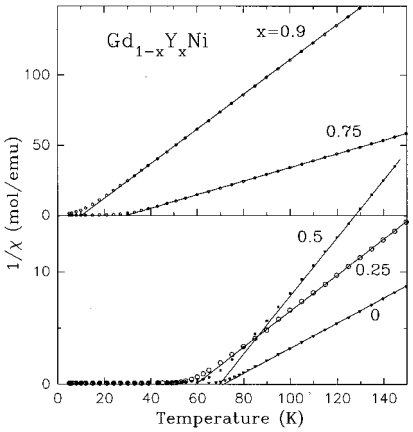

FIG. 1. Inverse susceptibility as a function of temperature (2-150 K) for the alloys, $Gd_{1-x}Y_xNi$. The continuous lines represent the least-squares fit of the data to Curie-Weiss behavior in the paramagnetic state.

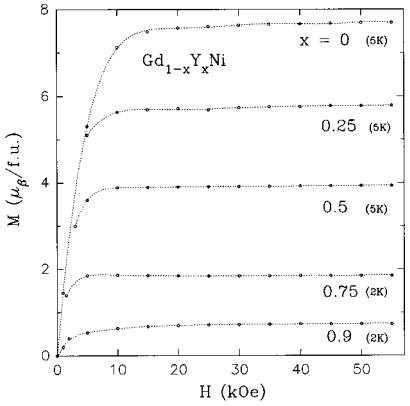

FIG. 2. Isothermal magnetization behavior of the alloys, $Gd_{1-x}Y_xNi$ ($x=0.0$, 0.25, 0.5, 0.75, 0.9). A smooth line is drawn through the data points.

diverges at about 70 K and tends to saturate at lower temperatures; in addition the plot of M versus H tends towards saturation from about 10 kOe. These features confirm that GdNi orders ferromagnetically at about 70 K. The plot of inverse χ versus T is linear above 80 K. The value of the effective moment (μ_{eff}) is larger than that expected for the Gd^{3+} ion[10] ($7.94\mu_\beta$), though a small difference was found in the values for the as-cast ($8.53\mu_\beta$) and annealed ($8.25\mu_\beta$) specimens. This excess effective moment was earlier attributed[5] to the formation of a polarization cloud of the conduction electrons around Gd ions. We propose here that this excess moment arises from the Ni $3d$ orbital and is induced by Gd. Under this assumption, the value of μ_{eff} on Ni(μ_{Ni}) is calculated from the formula, $\mu_{\text{eff}}=(\mu_{\text{Ni}}^2+\mu_{\text{Gd}}^2)^{1/2}$, assuming the free-ion value for Gd^{3+}, and it turns out to be $3.1\mu_\beta$ for the as-cast sample and $2.2\mu_\beta$ for the annealed specimen. These values are very close to spin-only moment[10] on Ni^{2+}. This moment on Ni is ferromagnetically coupled to that of Gd at low temperatures, as the moment at 5 K (μ_S) in the presence of 50 kOe is larger (by 0.6 and $0.4\mu_\beta$, respectively, see column 5, Table I and Fig. 2) than that expected for the free Gd^{3+} ion. At this point, we would like to mention that, in some of the earlier reports[5,7] on GdNi, the authors find negligible enhancement of μ_S. In order to find out whether this discrepancy is due to deviations from perfect stoichiometry, we have measured M as a function of H at 5 K on two alloys, $Gd_{1.05}Ni_{0.95}$ and $Gd_{0.95}Ni_{1.05}$. We have noticed that the excess moment in both these alloys is reduced to $0.2\mu_\beta$, thereby indicating that significant deviations from perfect stoichiometry or site exchange can reduce this excess saturation moment. The excess moment in the ordered state is about five times smaller than the value of μ_{Ni} derived from the paramagnetic χ data. This behavior is similar to that noted for Ni metal and it appears to be consistent with the predictions of theories on itinerant magnetism.[11] *Thus GdNi presents a situation in which there is coexistence of localized magnetism (due to Gd) and induced itinerant ferromagnetism (presumably from Ni 3d band).* Generally speaking, in rare earth compounds containing moment bearing transition-metal (TM) ions, the R-TM coupling is usually antiferromagnetic.

We have carefully measured the isothermal magnetization at several temperatures (Fig. 3) below T_C for the annealed specimen of GdNi, to gain further insight into the nature of magnetism in GdNi. It is to be noted that there is a weak field dependence of M at all temperatures, even at 5 K, and suggests the existence of a field-dependent component superimposed over the Gd^{3+} moment (saturated at low fields). The Arrott plots (M^2 vs H/M) are shown in Fig. 4. These plots are parallel over a wide temperature range. The spontaneous magnetization (M_S) can be deduced from above by linear extrapolation of the high-field slope to zero field, and plot of M_S^2 versus T^2 (Fig. 5) is found to be linear. All these features are consistent with the existence of some component of very weak itinerant ferromagnetism.[11–13] On the basis of such magnetization characteristics, very weak itinerant magnetism in $Lu_3Co_{8-x}Sn_4$ has recently been established,[14] though the major contribution to the absolute values of M in GdNi comes from localized Gd magnetism.

We have also obtained the composition dependence (see Table I) of the excess moment and the paramagnetic Curie temperature (θ_p) from the M data as well as of T_C both from M and ρ data for the series, $Gd_{1-x}Y_xNi$. There is a fairly

TABLE I. The values of the paramagnetic Curie temperature (θ_p) from the χ data above 100 K, Curie temperature (T_C), the magnetic moment (μ_S) at 50 kOe in the magnetically ordered state, excess moment in the ordered state (μ_{excess}), observed effective moment (μ_{eff}), and the effective moment (μ_{Ni}, derived) on Ni in the as-cast alloys, $Gd_{1-x}Y_xNi$. The values in column 5 are obtained after subtracting the moment on Gd^{3+} in the ordered state ($=7\mu_\beta$) from column 4. For column 7, see text.

x	θ_p (K)	T_C (K)	μ_S (μ_β)	μ_{excess} (μ_β)	μ_{eff} (μ_β)	μ_{Ni} (μ_β)
0	71	70	7.60	0.60	8.53	3.1
0.15	67	62	6.28	0.33	8.32	2.3
0.25	59	55	5.79	0.54	7.07	1.6
0.35	72	65	5.00	0.55	6.70	2.0
0.40	68	65	4.50	0.30	6.32	1.5
0.50	69	65	3.93	0.43	5.54	≈ 0
0.60	52	50	2.83	0.03	5.00	≈ 0
0.75	29	27	1.78	0.03	4.06	≈ 0
0.90	10	6	0.70	0	2.64	≈ 0

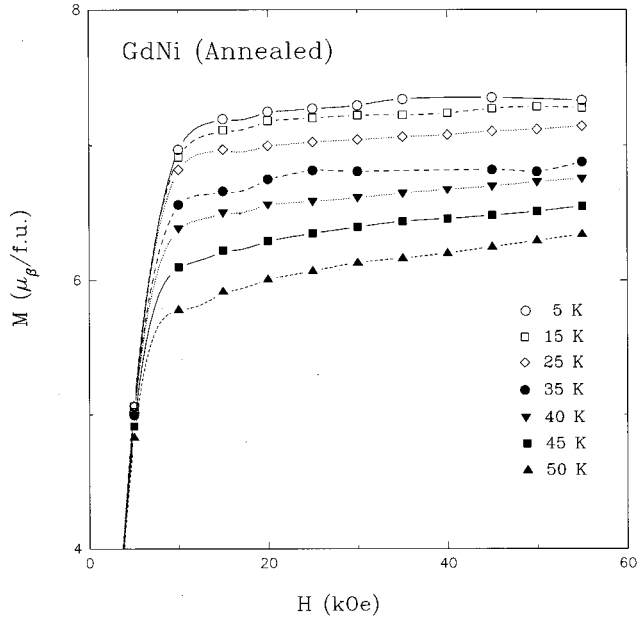

FIG. 3. Isothermal magnetization at several temperatures for the annealed specimen of GdNi. A line drawn through the data points for each temperature serves as a guide to the eyes.

good qualitative agreement in the composition dependence of T_C obtained from ρ (shown for select compositions in Fig. 6) and χ data. The values of θ_p closely follow those of T_C as a function of composition and this suggests insignificant antiferromagnetic component in any of these alloys. ρ varies quadratically with temperature at low temperatures in GdNi as found by other workers,[5,7,15] consistent with spin waves in ferromagnets.[16] This tendency persists at least up to $x=0.5$, though for higher values of x the quadratic dependence apparently diminishes; similar behaviour has been noted in the series, $Gd_{1-x}La_xNi$.[7] The values of χ obtained in a magnetic field of 100 Oe for both the field-cooled and zero-field-cooled specimens are found to be the same down to 2 K for

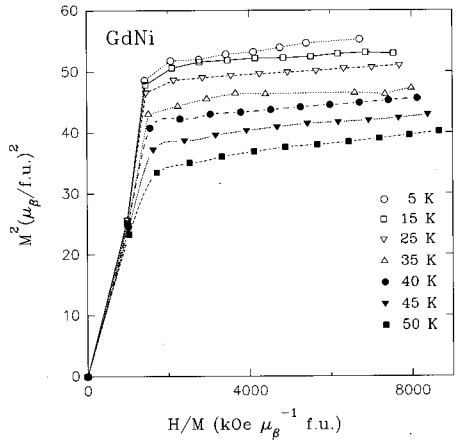

FIG. 4. Arrott plots for GdNi. The lines drawn through the data points are guides to the eye.

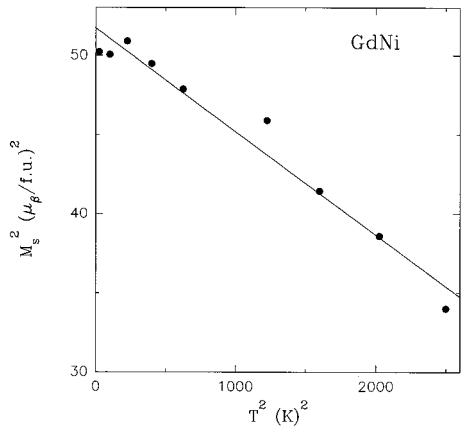

FIG. 5. Square of spontaneous magnetization as a function of square of temperature for GdNi. The continuous line is a linear fit to the data points.

all the selected compositions, particularly at the Gd-rich and Y-rich ends. This finding suggests the absence of spin-glass ordering even in the dilute limit ($x=0.9$). The point of note here is that both T_C and θ_p initially decrease with increasing x, and at $x=0.4$ there is clear evidence for a sharp rise. As mentioned earlier, there is a change in the crystal structure from CrB to FeB type at x= 0.4 and therefore these results imply that the exchange interaction strength is enhanced in the FeB structure following the compression of the lattice. For $x=0.35$, the apparently large value of T_C at 65 K is due to the presence of a small amount of FeB type of phase. A comparison of the θ_p and T_C values for $x=0.5$ proves that the enhancement factor is about 1.5. With respect to μ_S and μ_{eff} moments, clearly there is a decrease in the excess moment as well as in the (proposed) paramagnetic moment on Ni with the dilution of Gd lattice for $x<0.5$ (see columns

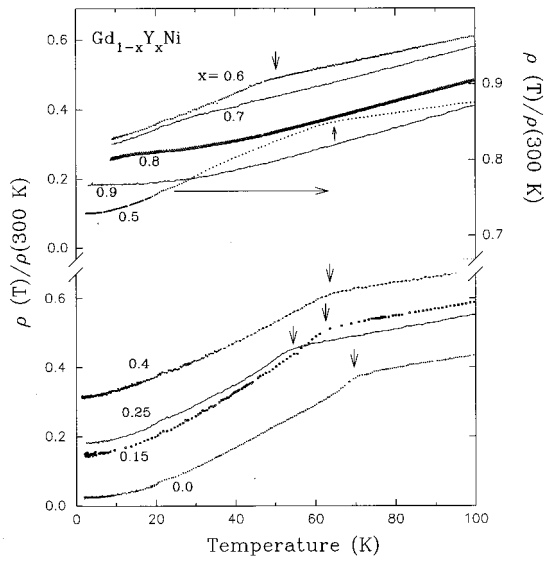

FIG. 6. Electrical resistivity as a function of temperature below 100 K for the alloys, $Gd_{1-x}Y_xNi$ ($x=0.0$, 0.15, 0.25, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9). The arrows indicate the values of T_C as mentioned in Table I.

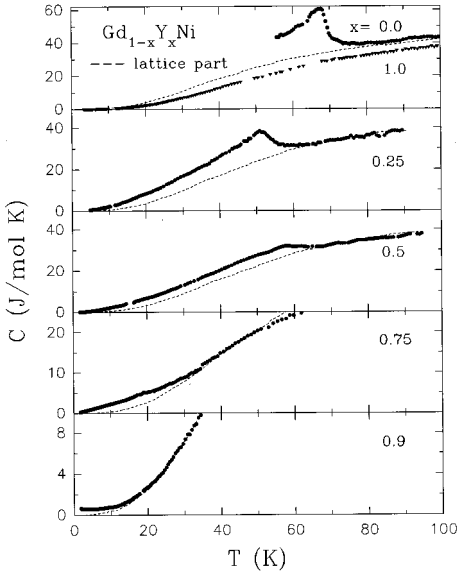

FIG. 7. Heat-capacity (C) as a function of temperature in the alloys, $Gd_{1-x}Y_xNi$ ($x=0.0$, 0.25, 0.5, 0.75, 0.9, and 1.0). The lattice part is obtained as described in Ref. 17.

5 and 7 in Table I). This proves that the excess moment is actually Gd-induced. The excess effective moment, if attributed to Ni, can be clearly seen for $x \leqslant 0.5$, and is negligibly small for the Y-rich compositions. It is difficult to obtain precise values of μ_{Ni} for $x \geqslant 0.75$ due to errors introduced by possible nonuniform distribution of Gd ions.

The heat-capacity (C) behavior for GdNi has been discussed at length by Blanco *et al.*[17] We now discuss the behavior of heat capacity (Fig. 7) on select compositions ($x=0.0$, 0.25, 0.5, 0.75, 0.9, and 1.0) of the series, $Gd_{1-x}Y_xNi$. The features observed for GdNi are in good agreement with those reported in Ref. 17. A well-defined anomaly can be observed at T_C for $x=0.0$, 0.25, 0.5, and 0.75. Though the estimation of the magnetic contribution (C_m) to C is generally difficult due to lack of proper reference for lattice contribution, we have followed the procedure suggested in Ref. 17 employing the C values of YNi for lattice contribution. The corresponding C_m values are presented in Fig. 8. The maximum values of C_m (per Gd mol) at the peak position decreases from about 27 J/Gd mol for GdNi to about 19 J/Gd mol, 10 J/Gd mol, and 10 J/Gd mol for $x=0.25$, 0.5, and 0.75, respectively. It may be recalled[18] that a correlation between the peak value in C_m and the type of magnetic structure in Gd compounds has been established. For an equal moment magnetic structure, the C_m at the peak is about 27 J/Gd mol and for a modulated or any complicated structure, the value should be reduced. In light of this correlation, the observed peak values of C_m in our alloys may be taken as an evidence to suggest that there may be deviations for $x \geqslant 0.25$ from equal-moment ferromagnetic structure known in GdNi. The humps at temperatures below T_C have been known to arise from the Schottky-like anomaly in the ordered state involving the $(2J+1)$-fold degenerate multiplet.[19] Above T_C, C_m does not vanish over a wide temperature range, for instance, till 95 K for GdNi, and the theoretical entropy, R ln 8, is not reached even at 100 K. These

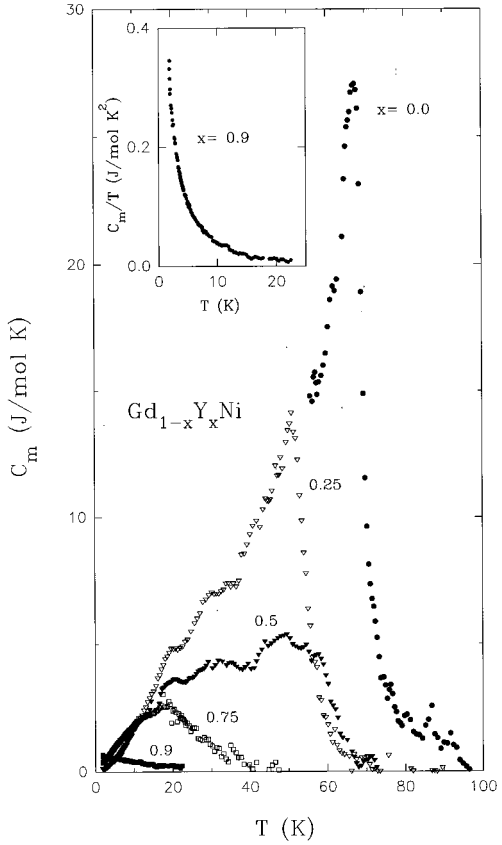

FIG. 8. The $4f$ contribution (C_m) to heat capacity (C) as a function of temperature for the alloys, $Gd_{1-x}Y_xNi$. The plot of C_m/T versus T for $x=0.9$ is also shown in the inset.

observations suggest that the magnetic fluctuations persist well above T_C. For $x=0.75$, the short-range magnetic correlation effects are noted till about 50 K, though T_C is close to 20 K. It is to be noted that, for $x=0.9$, C_m/T increases from 20 K reaching a value of about 800 mJ/Gd mol K^2 at 6 K (at which long-range magnetic order sets in) mimicking the behavior in many magnetically ordering ''heavy-fermions'' of Ce. These results support our earlier proposal[20] that the enhancement of C can occur beyond twice the magnetic ordering temperatures, in contrast to the belief in the literature,[21] mimicking heavy-fermion behavior.

We would like to add that the magnetoresistance measurements performed by us on GdNi show, at T_C, a large value of magnetoresistance similar to the well known behavior in giant magnetoresistance systems. In addition, the magnetoresistance changes sign below 20 K. These interesting findings will be reported in a future communication.

IV. CONCLUSION

We have identified a Gd alloy, viz. GdNi, in which there is apparently coexistence of localized and induced itinerant ferromagnetism. Magnetic fluctuations persist well above T_C resulting in C anomalies. In short, compounds like GdNi, which have been believed to exhibit relatively simple magnetic properties, in fact show interesting features.

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