# Characteristics of magnetic ordering in $Y_2(Ni_{1-x}Co_x)_7$ and $Y(Ni_{1-x}Co_x)_3$ systems

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Static fields up to 60 kOe and pulsed fields up to 270 kOe were used in measurements of the magnetization of the intermetallics $Y(Ni_{1-x}Co_x)_3$ and $Y_2(Ni_{1-x}Co_x)_7$. The Curie temperature $T_C$ and the saturation magnetization $M_s$ were found to depend nonmonotonically on the cobalt concentration. In both systems the terminal compositions were ferromagnetic, while compositions in the range $0.2 \leqslant x \leqslant 0.5$ of the $Y(Ni_{1-x}Co_x)_3$ system and near $x = 0.2$ of the $Y_2(Ni_{1-x}Co_x)_7$ system were Pauli paramagnets. The values of $T_C$ and $M_s$ of the $Y(Ni_{1-x}Co_x)_3$ system passed through a maximum at $x = 0.05$. The results were explained qualitatively by the characteristic features of the density of states near the Fermi level after allowing for the shift of this level as a result of substitutions.

## INTRODUCTION

In most of the published investigations the magnetic properties of the *d* electron system responsible for the magnetism of the intermetallic compounds of yttrium with transition metals belonging to the iron group are considered using the band theory of magnetism.[1] It is necessary to allow for the fact that the bands of the 3*d* electrons of the transition metal and of the 4*d* electrons of yttrium become hybridized and the dependence of the density of states on the energy $N(\varepsilon)$ in such a hybridized band differs considerably from the corresponding dependences exhibited by the component metals.[2,3]

The theory of band magnetism[1] predicts that the magnetic properties of the *d*-electron subsystem should be governed by the position of the Fermi level $\varepsilon_F$ and by the behavior of $N(\varepsilon)$ near $\varepsilon_F$. In particular, it is shown in Ref. 2 that it is the low density of states at the Fermi level $N(\varepsilon_F)$ which is responsible for the paramagnetic properties of the intermetallic $YNi_5$ (with the hexagonal crystal structure of the $CaCu_5$ type): this compound does not satisfy the Stoner criterion of band ferromagnetism

$$IN(\varepsilon_F) > 1, \tag{1}$$

where $I$ is the exchange integral. The intermetallic compounds $Y_2Ni_7$ (rhombohedral structure of the $Gd_2Co_7$ type) and $YNi_3$ (rhombohedral structure of the $PuNi_3$ type) have low Curie temperatures (58 and 30 K, respectively) and low magnetizations, which are considerably less than in the case of metallic nickel (0.15 and $0.41\mu_B$ per formula unit, respectively).[4–6]

These last two compounds are good model objects for the investigation of the characteristics of the band magnetism of intermetallics. The exchange splitting of the subbands of these compounds in much less than the width of the subbands, so that they can be considered using a simple model of very weak band of ferromagnets.[1,2] Moreover, the Fermi level of $YNi_3$ and $Y_2Ni_7$ is located near a local density-of-states maximum,[2] which gives rise to an unusual behavior of the magnetic properties when nickel is replaced with other elements.

It was reported in Ref. 7 that replacement of nickel with cobalt in the $Y_2(Ni_{1-x}Co_x)_7$ and $Y(Ni_{1-x}Co_x)_3$ systems gives rise to intermediate compositions with no magnetic ordering. This is unexpected, because $YCo_3$ and $Y_2Co_7$ are both strong ferromagnets,[8,9] have high Curie temperatures (301 and 639 K, respectively), and large magnetic moments (1.4 and $7.4\mu_B$ per formula unit, respectively). However, only a few of the substituted compositions of these systems were investigated,[7] so that the authors were unable to analyze the composition dependences of the magnetic properties and, in particular, to determine the range of concentrations where the mixed compounds were paramagnetic. Therefore, we carried out a more thorough investigation of the magnetic properties of the compounds $Y_2(Ni_{1-x}Co_x)_7$ and $Y(Ni_{1-x}Co_x)_3$ in order to determine details of their magnetic phase diagram and to compare the magnetic behavior of the two systems with the theoretical calculations reported in Ref. 10.

## SAMPLES AND EXPERIMENTAL METHODS

Samples of $Y_2(Ni_{1-x}Co_x)_7$ and $Y(Ni_{1-x}Co_x)_3$ (prepared with compositions in steps of 0.01 in the case of $0 \leqslant x \leqslant 0.1$ and 0.05 in the range $0.1 < x < 1$) were melted from the component elements using an argon-filled arc furnace with a cold hearth or in an induction furnace under quasilevitation conditions. The samples were remelted two or three times. The resultant ingots were subjected to a homogenizing anneal at 960–1060 °C for a week in a dynamically maintained vacuum. In preparation of the $Y(Ni_{1-x}Co_x)_3$ samples the elements were taken in the ratio 1:2.8, whereas in the case of $Y_2(Ni_{1-x}Co_x)_7$ they were taken in the stoichiometric ratio 2:7 when the cobalt content was less than 50% and in the ratio 2:6.9 for $x \geqslant 0.5$. The quality of the samples was checked by x-ray diffraction and thermomagnetic analysis methods. All the samples used in our measurements consisted of a single phase and had the $PuNi_3$ [$Y(Ni_{1-x}Co_x)_3$] or $Gd_2Co_7$ [$Y_2(Ni_{1-x}Co_x)_7$] structures.

We measured the magnetization in static magnetic fields up to 60 kOe using a vibrating-sample magnetometer and in pulsed magnetic fields up to 270 kOe by an induction method; this was done in the temperature range 4.2–300 K. The Curie temperatures were determined from the magnetic susceptibility $\chi_0$ in weak ($\sim$0.3 Oe) alternating fields.

## EXPERIMENTAL RESULTS

Figure 1 shows the magnetization curves of some compositions belonging to the $Y_2(Ni_{1-x}Co_x)_7$ (a) and

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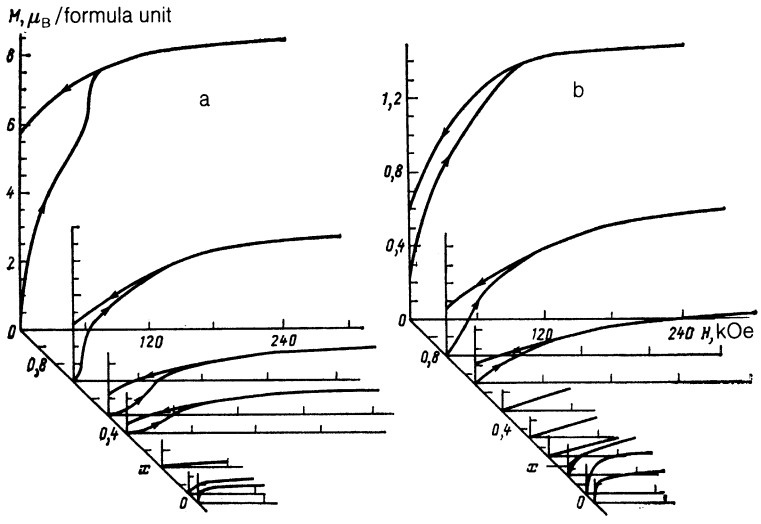


FIG. 1. Magnetization isotherms at 4.2 K plotted for some compositions of the $Y_2(Ni_{1-x}Co_x)_7$ (a) and $Y(Ni_{1-x}Co_x)_3$ (b) systems.

$Y(Ni_{1-x}Co_x)_3$ (b) systems; these curves were recorded at 4.2 K. Some general features of the behavior of the magnetization of both systems at helium temperature should be noted. The majority of the compositions had the magnetization curves typical of ferromagnets, but in the case of some of the intermediate compositions the spontaneous moment was absent and the magnetization varied linearly with the field. The magnetization curves of the compounds with low cobalt concentrations became saturated in the weak fields and exhibited a narrow hysteresis loop, while compositions with a large amount of cobalt had a much wider hysteresis loop and the magnetic saturation occurred in strong fields. This was evidence of an increase in the magnetic anisotropy when nickel was replaced with cobalt.

Figure 2 shows how the saturation magnetization $M_s$ depended on the cobalt concentration at 4.2 K. It was worth noting the following important features of our dependences $M_s(x)$. Firstly, the magnetization of both systems depended nonmonotonically on $x$. It was low, but different from zero for the compositions with small amounts of cobalt replacing nickel; there was a range of intermediate compositions with the saturation magnetization equal to zero (this range was considerably wider for the 1:3 system) and a further increase in the cobalt concentration increased the magnetization considerably. A qualitative difference was observed between the magnetizations of the 2:7 and 1:3 systems: in the former case the saturation magnetization decreased monotonically with $x$ for samples with small amounts of cobalt, whereas in the case of the second system it passed through a maximum at $x = 0.05$.

The temperature dependence of the saturation magnetization of some of the investigated compositions of the two systems is plotted in Fig. 3. It is clear from this figure that all the ferromagnetic compositions had basically similar behav-

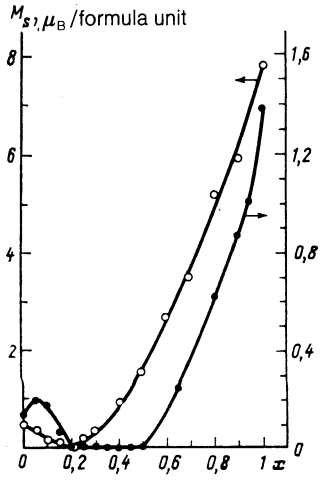


FIG. 2. Composition dependences of the saturation magnetization at 4.2 K for the $Y_2(Ni_{1-x}Co_x)_7$ (○) and $Y(Ni_{1-x}Co_x)_3$ (●) systems.

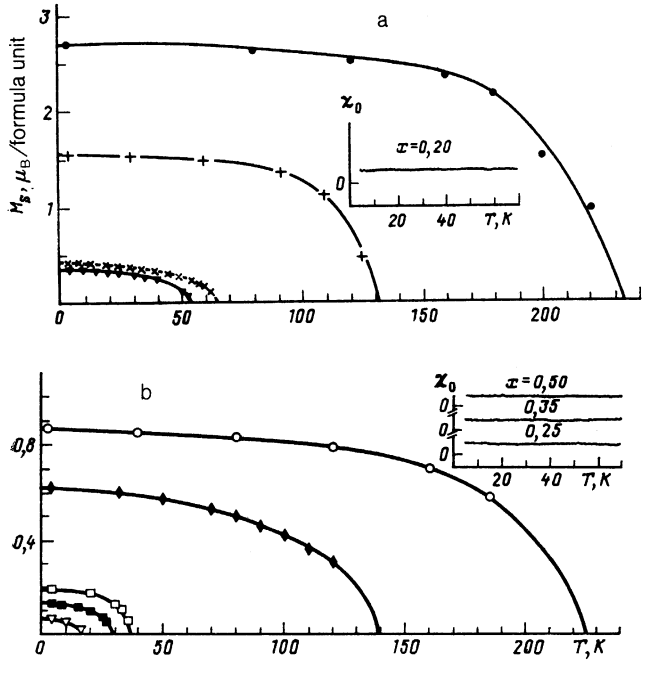


FIG. 3. Temperature dependences of the saturation magnetization of some compositions: a) $Y_2(Ni_{1-x}Co_x)_7$ system with $x = 0.0$ (×), 0.05 (▼), 0.50 (+), 0.60 (●); b) $Y(Ni_{1-x}Co_x)_3$ with $x = 0.0$ (■), 0.05 (□), 0.15 (▽), 0.80 (◆), 0.90 (○). The insets show the temperature dependence of the initial susceptibility of the paramagnetic composition (in relative units).

ior: the saturation magnetization fell smoothly with increasing temperature and vanished at the Curie point $T_C$. [As in the case of the compound $Y_2Ni_7$, we found that the substituted samples of the $Y_2(Ni_{1-x}Co_x)_7$ system showed no thermally induced ferromagnetism, reported earlier for $Y_2Ni_7$ in Ref. 11. A more detailed discussion of this aspect can be found in Refs. 5 and 12.]

The susceptibility of the mixed compositions showing no spontaneous magnetization depended weakly on temperature (insets in Fig. 3). Consequently, these compositions were band Pauli paramagnets.

Figure 4 shows the magnetic $x$–$T_C$ phase diagrams of the $Y_2(Ni_{1-x}Co_x)_7$ and $Y(Ni_{1-x}Co_x)_3$ systems. Clearly, the range of the paramagnetic compounds with the intermediate compositions was much wider in the case of the second system. A qualitative difference in the behavior of the 2:7 and 1:3 systems should be noted. In the former case when the amount of cobalt was small, the Curie temperature fell monotonically, whereas in the latter system the value of $T_C$ passed through a maximum at $x = 0.05$ (i.e., at the same cobalt composition as in the case of the magnetization).

Our $x$–$T_C$ phase diagrams differed from those reported in Ref. 7, according to which the Curie temperatures of some of the compositions rich in cobalt were considerably higher. A comparison of these diagrams and also of the $x$–$T_C$ diagram for the $Y(Ni_{1-x}Co_x)_5$ system reported in Refs. 13 and 14 demonstrated that samples of the $Y(Ni_{1-x}Co_x)_3$ system investigated earlier[7] clearly contained phases of the $Y_2(Ni, Co)_7$ type as admixtures, whereas samples of the $Y_2(Ni_{1-x}Co_x)_7$ system had admixtures of phases of the $Y(Ni, Co)_5$ type. These admixtures gave rise to additional peaks in $\chi_0(T)$ at temperatures above $T_C$, as observed also for some of the our samples consisting of several phases.

## DISCUSSION OF RESULTS

As pointed out already, both $Y_2Ni_7$ and $YNi_3$ are very weak band ferromagnets. In the case of these ferromagnets the temperature dependence of the magnetization can be described (ignoring spin fluctuations) by[1]

$$M_s(T)/M_s(0) = [1-(T/T_C)^2]^{1/2}. \qquad (2)$$

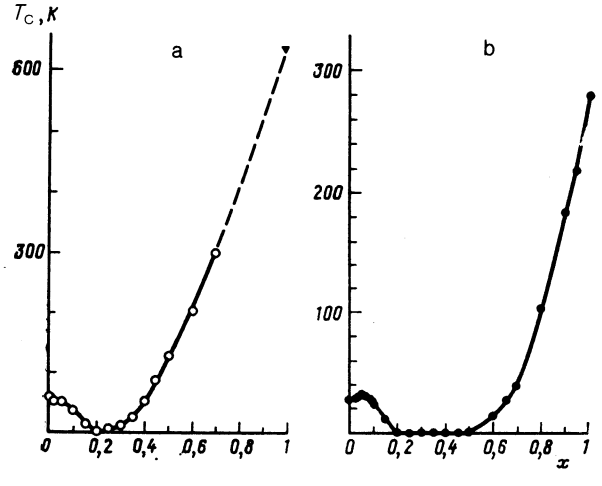


FIG. 4. Composition dependences of the Curie temperature of the $Y_2(Ni_{1-x}Co_x)$ (a, ●, data from Ref. 8) and $Y(Ni_{1-x}Co_x)_3$ (b) systems.

Figure 5 shows how the square of the reduced saturation magnetization $M_s(T)/M_s(0)$ of different compositions in the $Y_2(Ni_{1-x}Co_x)_7$ and $Y(Ni_{1-x}Co_x)_3$ systems depends on the square of the reduced temperature $T/T_C$. Clearly, in the case of the compositions with low cobalt concentration this dependence was a straight line, i.e., such materials obeyed the relationship (2). In the case of the system $Y(Ni_{1-x}Co_x)_3$ the deviation of $M_s(T)$ from Eq. (2) began at $M_s(0) \gtrsim 0.6\mu_B$, whereas for the $Y_2(Ni_{1-x}Co_x)_7$ system it began at $M_s(0) \gtrsim 1.5\mu_B$ per formula unit. Our estimates indicated that in the case of these two systems such results indicated that the magnetic moment was approximately $0.2\mu_B$ per one $3d$ atom.

When the fluctuations were strong, the temperature dependence of the magnetization changed, becoming[15]

$$M_s(T)/M_s(0) = [1-(T/T_C)^2]^{3/4}. \qquad (3)$$

Our calculations showed that Eq. (3) did not describe the temperature dependence of the magnetization of the samples of these systems for any value of $x$, which was in agreement with the theoretical conclusions[2] that fluctuations had little influence on the magnetic properties of $Y_2Ni_7$ and $YNi_3$, and indicated that their role was not dominant either in the case of the magnetic properties of the samples with higher cobalt concentrations. The temperature dependence of the saturation magnetization of such compositions was close to the Brillouin type for spin $\frac{1}{2}$ or 1.

All this demonstrated that cobalt-rich compositions could no longer be regarded as weak band ferromagnets. This was to be expected, because the Curie temperatures were fairly high and we could not assume that the exchange splitting of the subbands with different spin directions was small. This was supported also by the strong magnetization of these compositions (per $3d$ atom), comparable with the magnetization of pure cobalt.

We now consider the composition dependence of the magnetic properties of the investigated systems. The theoretical energy dependence of the densities of states of the $d$ electrons in $Y_2Ni_7$ and $YNi_3$ was calculated in Ref. 2. In these compounds the Fermi level is typically located near a local maximum of the energy dependence of the density of states: in the case of $Y_2Ni_7$ the Fermi level $\varepsilon_F$ is located at the left of the maximum, whereas in the case of $YNi_3$ it lies to the right of the maximum. Introduction of cobalt (electron configuration $3d^7$) in place of nickel (configuration $3d^8$) reduces the $d$ electron density and shifts the Fermi level to the left on the energy scale.

At low cobalt concentrations an increase in $x$ lowers the density of states $N(\varepsilon_F)$ in the $Y_2(Ni_{1-x}Co_x)_7$ system and this reduces the Curie temperature and the magnetization, whereas at high cobalt concentrations when the density of states at the Fermi level decreases so much that the Stoner band ferromagnetism criterion is no longer satisfied, the $d$-electron system becomes paramagnetic.

Replacement of nickel with cobalt in the $Y(Ni_{1-x}Co_x)_3$ system increases both $T_C$ and $M_s$ [when $\varepsilon_F$ approaches the maximum of the dependence $N(\varepsilon)$]; a further increase in $x$ causes $T_C$ and $M_s$ to fall, and ultimately the paramagnetic state is induced. The increase in $N(\varepsilon_F)$ at low cobalt concentrations in the $Y(Ni_{1-x}Co_x)_3$ system is supported by the specific heat data. According to Ref. 16 the

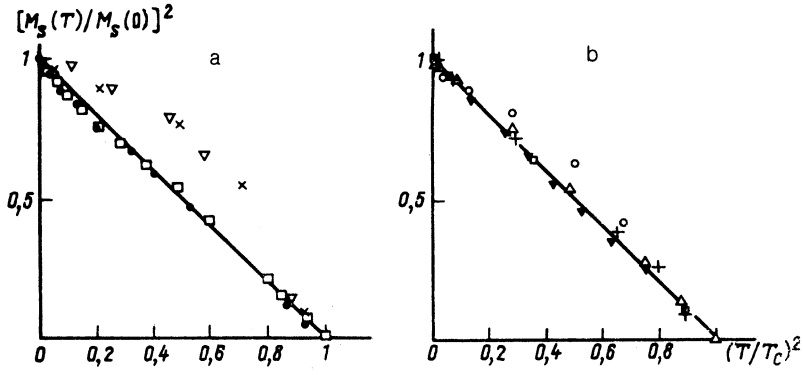


FIG. 5. Dependences of $[M_s(T)/M_s(0)]^2$ on $(T/T_C)^2$ for some compositions: a) $Y_2(Ni_{1-x}Co_x)_7$ system with $x = 0.0$ (□), 0.05 (●), 0.50 (×), 0.60 (▽); b) $Y(Ni_{1-x}Co_x)_3$ system with $x = 0.0$ (△), 0.05 ( + ), 0.15 (■), 0.80 (▼), 0.90 (○).

density of states at the Fermi level passes through a maximum at $x \lesssim 0.15$ and is lowest for $x = 0.2$.

A further reduction in the $d$-electron density as a function of the cobalt concentration should result, according to Ref. 2, in a considerable increase in the density of states at the Fermi level and should give rise to a strong ferromagnetism of the cobalt-rich samples.

The qualitative ideas deduced from the theoretical representations of the band structure of $Y_2Ni_7$ and $YNi_3$ thus allow us to explain the nonmonotonic dependences of the magnetic characteristics of these systems using a simple band model.

A similar approach was used in theoretical calculations of these parameters of the $Y(Ni, Co)_3$ and $Y_2(Ni, Co)_7$ systems carried out quite recently[10] and satisfactory qualitative agreement with the experimental data was found.

However, a comparison of our results with the data for other isostructural systems where nickel was replaced indicated that the real physical situation was more complex. For example, the above simple analysis would suggest that the $Y_2(Ni_{1-x}Al_x)_7$ and $Y(Ni_{1-x}Al_x)_3$ systems should behave qualitatively similarly to systems with cobalt, except that the evolution of the magnetic properties due to the substitution should occur much faster since the replacement with aluminum ($3d^0$ configuration) emptied the $d$ band much faster than the rate of replacement with cobalt ($3d^7$ configuration). However, this was not confirmed. Although the experimental data of Ref. 17 indicated that an increase in the aluminum content in $Y_2(Ni_{1-x}Al_x)_7$ and $Y(Ni_{1-x}Al_x)_3$ resulted in very rapid suppression ("poisoning") of ferromagnetism and the compositions with $x \geqslant 0.015$ and $x \geqslant 0.04$ were consequently paramagnetic, there

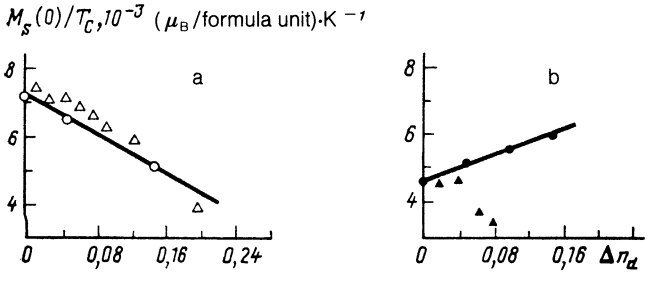


FIG. 6. Dependences of $M_s(0)/T_C$ on $\Delta n_d$ per one $3d$ atom for the following systems: a) $Y_2(Ni_{1-x}Co_x)_7$ (○), and $Y_2(Ni_{1-x}Al_x)_7$ (△, Ref. 17); b) $Y(Ni_{1-x}Co_x)_3$ (●), $Y(Ni_{1-x}Al_x)_3$ (▲, Ref. 17).

was no rise of the Curie temperature and the magnetic moment in the $Y(Ni_{1-x}Al_x)_3$ system at low aluminum concentrations, similar to that observed by us for the $Y(Ni_{1-x}Co_x)_3$ compounds. In our opinion this was because in the case of the $Y(Ni_{1-x}Al_x)_3$ system we could not use the rigid band approximation, i.e., we could not assume that the $d$ energy bands of nickel and aluminum were identical and the replacement of nickel with aluminum simply emptied the $d$ band without deforming it. Moreover, here and in Ref. 10 it was assumed that the exchange interaction was not affected by the substitution, which is again only a rough approximation.

We can identify the main cause of the difference between the magnetic properties of the systems with cobalt and aluminum by plotting the dependence of the ratio $M_s(0)/T_C$ for these systems on the change in the $d$-electron density $\Delta n_d$ (Ref. 6). According to the theory of weak band ferromagnetism,[1] this ratio should be independent of the exchange and should be governed solely by the characteristics of the energy band in question:

$$\frac{M_s(0)}{T_C} = \pi k g \mu_B N(\varepsilon_F) \left( \frac{[N'(\varepsilon_F)]^2 - N(\varepsilon_F) N''(\varepsilon_F)}{3[N'(\varepsilon_F)]^2 - N(\varepsilon_F) N''(\varepsilon_F)} \right)^{1/2}, \quad (4)$$

where $N'(\varepsilon_F)$ and $N''(\varepsilon_F)$ are the corresponding derivatives of the density of states at the Fermi level and $g$ denotes the $g$ factor. It is clear from Fig. 6 that in the case of the 2:7 systems with cobalt and aluminum the ratio $M_s(0)/T_C$ varies with the $d$-electron density in approximately the same way. Hence, in the case of these systems the characteristics of the $d$-electron band varies with $\Delta n_d$ in a similar manner and in comparing them we can use the rigid band approximation. On the other hand, the ratio $M_s(0)/T_C$ for the 1:3 systems in cobalt and aluminum varies in a different way with the $d$-electron density. Consequently, in the case of these systems the dependences of the $d$-band parameters on $\Delta n_d$ are different and in comparing the properties of systems of the 1:3 type with cobalt and aluminum we cannot use the rigid band approximation.

We conclude by noting that we also investigated the composition dependences of $T_C$ for the $Y_2(Ni_{1-x}Cu_x)_7$ and $Y(Ni_{1-x}Cu_x)_3$ systems. We found that $T_C$ in this case fell steeply with $x$ and the compositions with $x = 0.1$ and 0.04 for these two systems were paramagnets. Since, according to Ref. 10, introduction of copper into $Y_2Ni_7$ should ensure that the $T_C(x)$ curve passed through a maximum, this result demonstrated that the rigid $d$-band approximation

was also invalid at least in the case of the $Y_2(Ni_{1-x}Cu_x)_7$ system.


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