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On the Cobalt-Induced Moments in Ternary Gadolinium–Yttrium Compounds

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The results of magnetic measurements on $(Gd_xY_{1-x})Co_2$ compounds between 4.2 and 1300°K are presented. The experimental data are analyzed assuming that the cobalt atoms present a paramagnetic moment or an exchange-enhanced paramagnetism. Both models showed that the cobalt-ordered moments are linearly dependent on the exchange field acting on these atoms ($H_{ex}/\mathcal{M}^{\circ}_{Co} \approx 3 \cdot 10^6$ Gs/μ_B), being essentially induced by the magnetic interactions. The experimental data seem to be in agreement with the presence of the cobalt paramagnetic contribution. No first-order transition in these systems is observed.

Nous présentons les résultats des mesures magnétiques des composés $(Gd_xY_{1-x})Co_2$ de 4.2 à 1300°K. Les données experimentales sont analysées tant dans une modèle où le cobalt a un moment paramagnétique, que dans le modèle où il présente une paramagnétisme renforcé par l'échange. Les deux modèles montrent que les moments du cobalt varient linéairement avec le champ d'échange sur ces atomes ($H_{ex}/\mathcal{M}^{\circ}_{Co} \approx 3 \cdot 10^6$ Gs/μ_B) et sont essentiellement induits par les interactions magnétiques. Les résultats expérimentaux semblent en accord avec la présence d'un moment paramagnétique du cobalt. Les composés etudiés ne présentent pas des transitions magnétiques du premier ordre.

1. Introduction

Previous studies on the magnetic behavior of gadolinium–cobalt compounds (*1*, *2*) have shown that the cobalt moment is dependent on the rare-earth content, decreasing from 1.71 μ_B in cobalt metal, to 1.02 μ_B in $GdCo_2$ compound. This behavior is attributed to the partial filling of the 3*d* band by the conduction electrons contributed by the rare-earth element.

It is also interesting to study the cobalt behavior in ternary systems where the number of conduction electrons is constant. In a previous article, Lemaire and Schweizer (*3*) described an interesting magnetic behavior of cobalt atoms in $(Gd_xY_{1-x})Co_2$ compounds. The ordered moment is dependent on the gadolinium content and is assumed to be induced by the magnetic interactions. It is our purpose to extend these measurements in the paramagnetic range. By paramagnetic investigations, we intend to obtain complementary information on the cobalt behavior outside the magnetically ordered domain. Furthermore, we want to make a quantitative analysis of the magnetic behavior of these compounds.

The features of the $(Gd_xY_{1-x})Co_2$ system can be summarized as follows:

(a) The compounds crystallize in $MgCu_2$ type structure. The point symmetry of cobalt atoms is trigonal ($\bar{3}m$) and that of gadolinium and yttrium is cubic ($\bar{4}3m$). The Co and Gd(Y) atoms occupy equivalent crystallographic sites in the lattice.

(b) Since gadolinium is in *S*-state, its magnetic moment, unlike the other rare earths, is only slightly influenced by the crystalline field.

(c) If the cobalt atoms carry a magnetic moment, the coupling between the cobalt and gadolinium sublattices is antiparallel oriented.

2. Experimental

The compounds were prepared by a method, previously described, where any contamination due to crucible is avoided (*1*). The samples were annealed for 1 week at various temperatures, depending on the concentration. X-ray analysis showed the crystallographic purity of the compounds. In all cases only one phase is observed. The lattice constants are presented in Table I.

The magnetic measurements were performed between 4.2 and 1300°K. The saturation magnetization was studied in fields up to 30 kG. In Fig. 1, we present the magnetization isotherms at 4.2°K. The spontaneous magnetization is obtained by extrapolation in zero field. The paramagnetic studies were performed by means of translation balances. One of these was previously described by Aléonard (*4*). The samples were sealed in quartz ampoules under vacuum. The measurements were performed at the two values of the magnetic field, both on heating and cooling the samples. The results were the same, indicating absence of ferromagnetic impurities or oxidation phenomena.

The greatest part of the experimental data were analyzed by an IBM-370 computer of the Institute of Atomic Physics, Bucharest.

TABLE I

LATTICE CONSTANTS OF $(Gd_xY_{1-x})Co_2$ COMPOUNDS

Compound (x)	1.0	0.8	0.6	0.4	0.2	0.0
Lattice constants (Å)	7.258	7.249	7.238	7.235	7.220	7.215

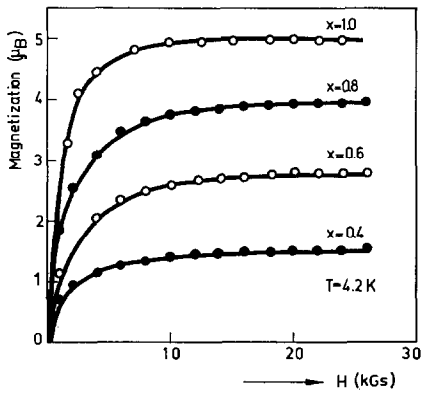

FIG. 1. The magnetization isotherms at 4.2°K.

3. Experimental Results and Discussion

3.1. Molecular Field (MF) Model

In Fig. 2, we present the thermal variation of spontaneous magnetization. The results show the general trend of the previous data (*3*). The cobalt ordered moment $\mathcal{M}^{\circ}_{Co}$ is obtained by assuming a ferrimagnetic coupling between the gadolinium and cobalt sublattices. These values are presented in Table II. A nonlinear variation of the cobalt moment as a

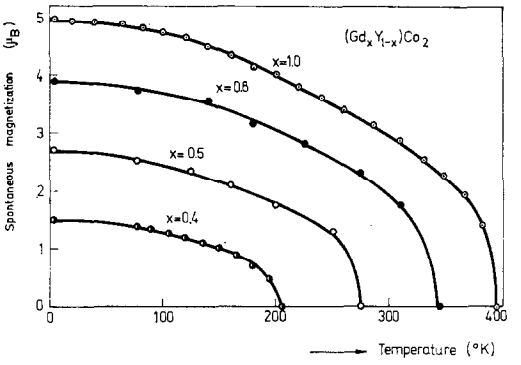

FIG. 2. Thermal variation of spontaneous magnetization.

TABLE II

DATA OBTAINED FROM MAGNETIC MEASUREMENTS BELOW THE CURIE TEMPERATURE

Compound (x)	1	0.8	0.6	0.4
Saturation moment per formula unit at 4.2°K (μ_B)	4.96	3.90	2.76	1.50
Cobalt moments $\mathcal{M}^{\circ}_{Co}$ (μ_B)	1.02	0.85	0.72	0.65
Curie temperature (°K)	395	347	275	203

function of the gadolinium content is observed (Fig. 3).

In Fig. 4, we present the results of paramagnetic measurements. The experimental points were analyzed only up to temperature T_s, where a small, but sudden, decrease of the susceptibility is observed. We attribute this variation to a phase transition.

A good fit with the experimental data was obtained assuming a Néel type variation (5) superimposed on the Pauli paramagnetic term χ_p:

$$(\chi - \chi_p)^{-1} = \chi_0^{-1} + TC^{-1} - \sigma(T-\theta)^{-1} \quad (1)$$

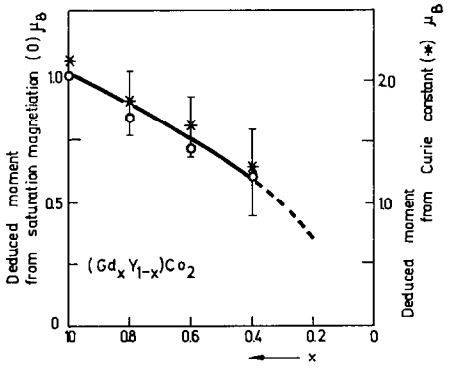

FIG. 3. The ordered and paramagnetic contribution of cobalt atoms.

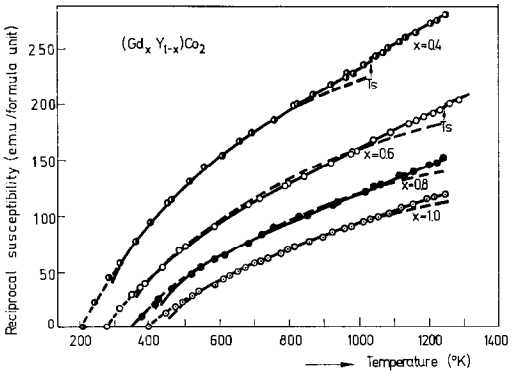

FIG. 4. Thermal variation of reciprocal susceptibility. The solid line gives the theoretical prediction according to (1), using the values from Table III. The broken line gives the prediction of the EEP model using the values from Table IV.

where C is the Curie constant and the parameters χ_0, σ, and θ are related to the values of magnetic interaction J_{AA}, J_{AB}, and J_{BB} (A = Gd and B = Co). These parameters are listed in Table III.

Except in a region near the Curie temperatures, good agreement between theoretical prediction according to (1), (by solid lines) and the experimental data is observed (Fig. 4). One notes a discrepancy around the Curie points, this being ascribed by Néel (5) to the molecular field fluctuations.

The paramagnetic measurements on RNi_2 compounds (where R is a rare-earth element and Ni is nonmagnetic) indicated a behavior similar to that of the rare-earth R^{3+} ions (6, 7). Taking this result into account, in agreement with the addition law of susceptibilities, we determined the contribution of the cobalt atoms to the Curie constant. The paramagnetic cobalt moments $\mathcal{M}^p_{Co}$ are listed in Table III. The variation of these moments with the gadolinium content has the same trend as that determined from saturation data (Fig. 3). The paramagnetic moments are in constant ratio with those deduced from saturation measurements. Their ratio is about 2.

The values of the Pauli paramagnetic terms $\chi_p(x)$ increase with the decrease of the gadolinium content. The $\chi_p(x)$ values scale approximately linearly with the yttrium content

$$\chi_p(x) = (1-x)\,\chi_p(0) \quad (2)$$

TABLE III

DATA OBTAINED FROM PARAMAGNETIC MEASUREMENTS USING THE MOLECULAR FIELD MODEL

Compound (x)	1.0	0.8	0.6	0.4
Curie constant per formula unit C(emu)	9.15	7.16	5.40	3.52
Paramagnetic moments of cobalt atoms, $\mathcal{M}^p_{Co}$ (μ_B)	2.16	1.84	1.65	1.25
$\chi_p \cdot 10^{-4}$ (emu)	$\approx$0.05	4.1	7.6	11.3
$1/\chi_0$	−8.44	−7.20	−2.50	10.4
σ	1653	1455	1280	1115
θ	425	380	315	250

where $\chi_p(0) = 20 \cdot 10^{-7}$ emu/formula unit is the value of the YCo_2 susceptibility at 4.2°K (Fig. 5).

The gadolinium atoms have a well-localized magnetic moment. This cannot be assumed for the cobalt atoms. To analyze the magnetic behavior of cobalt in these pseudobinary compounds quantitatively, the magnetic interactions were evaluated. The J_{AA}, J_{AB}, and J_{BB} values were estimated by two methods:

(a) From the ordered domain. A computing program was elaborated to calculate the magnetic interactions by fitting the saturation data, and assuming a two-sublattice Néel ferromagnet.

(b) From the paramagnetic data. As mentioned, the parameters C, $1/x_0$, σ, and θ are also related to the values J_{ij} $(i, j = A, B)$.

No major differences between these two estimations have been observed, though the values deduced from paramagnetic results are not expected to be so accurate (*8*).

The exchange field H_{ex} on the cobalt and gadolinium atoms was calculated according to:

$$H_{ex}(\mathrm{Co}) = J_{BB} M_B + J_{AB} M_A \qquad (3a)$$

$$H_{ex}(\mathrm{Gd}) = J_{AA} M_A + J_{AB} M_B. \qquad (3b)$$

One observes (Fig. 6) that the H_{ex}(Co) scales linearly with the cobalt magnetic moments. The proportionality constant is $A = 3 \cdot 10^6$ G/μ_B. This fact suggests that the cobalt moment is induced by magnetic interactions in the compounds to which both gadolinium and cobalt atoms contribute.

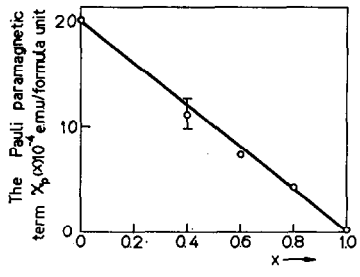

FIG. 5. The composition dependence of $\chi_p(x)$ Pauli paramagnetic term. The solid line gives the prediction according to the relation (2).

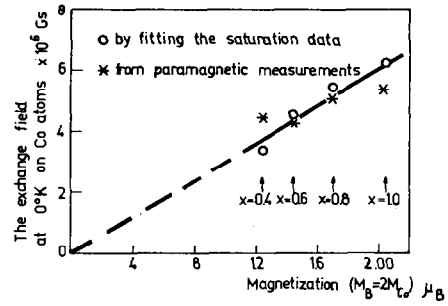

FIG. 6. The relation between the cobalt sublattice magnetization and the exchange field.

The induced cobalt moments also seem to be present in the paramagnetic range, where the magnetic interactions are also present. The variation of the cobalt moment with the gadolinium content in the ordered and paramagnetic range is similar, though the cobalt paramagnetic moment is twice as great as that deduced from saturation data. An explanation for these differences is not clear at the present. The same behavior is observed in cobalt metal (*9*) or in other rare-earth–cobalt compounds (*2*). This difference was among the basic reasons for developing the band model (*10*), but as noted, these moments also present some features which characterize localized behavior. It is interesting to analyze the degree of localization of the cobalt moment. One may test to what extent the Néel model may describe the magnetic behavior of these systems starting from paramagnetic data. As we know, this model was developed for magnetic insulators, where the moments are well-localized.

The thermal variation of the spontaneous magnetization of a two sublattices Néel ferrimagnet is given in (*3*)

$$M = M_A - M_B \qquad (4)$$

where

$$M_A = M_A(0) \cdot B_{S_A}(x_A) \qquad (5)$$

$$x_A = \frac{S_A g_A \mu_B}{k^B T}(J_{AA} M_A + J_{AB} M_B) \qquad (6)$$

and similar expressions for the B sublattice magnetization. B_{S_A} is the Brillouin function.

A computing program was used to calculate the thermal variation of spontaneous magnetization of the sublattices. The agreement with the experimental data is good enough for the compounds with $x = 0.6$ and $x = 0.8$ (Fig. 7) and $x = 1.0$ (*11*). For the compound with $x = 0.4$, the values of the exchange interactions deduced from the paramagnetic range seem to be rather great, the agreement being not so good. Small errors in determining the cobalt contribution to the Curie constant may increase the exchange field rather greatly. These experimental errors can especially affect the compounds with low gadolinium content, where C_{Co} is only a small part of the Curie constant C (Table III).

Our test suggests that the cobalt atoms show also some features of localized behavior.

The cobalt moments are strongly dependent on magnetic interactions in the compounds. These atoms are nearly magnetic in YCo_2. This compound is a strong Pauli paramagnet (*1*, *12*). Replacing yttrium by gadolinium, magnetic interactions determine the appearance of the localized moment on the cobalt atoms. The interactions modify the density of states $\rho_d(E_F)$ as suggested by Blandin and Friedel (*13*), so that the Stoner criterion for magnetism $\rho_d(E_F) \cdot U > 1$ is fulfilled. By increasing the gadolinium content, the exchange field on the cobalt atoms can also be increased, and thus, a continuous increase of their magnetic contribution is observed.

There seems to exist a threshold value for the exchange interaction above which the cobalt atoms possess a localized moment. This is indicated by the fact that the compound with $x = 0.1$ is nonmagnetic up to 2°K (*3*). On the other hand, the analysis of the magnetic properties of $Gd(Co_xNi_{1-x})_2$ compounds (*14*) is also in agreement with this supposition. Only groups of at least three cobalt atoms in interaction carry a magnetic contribution.

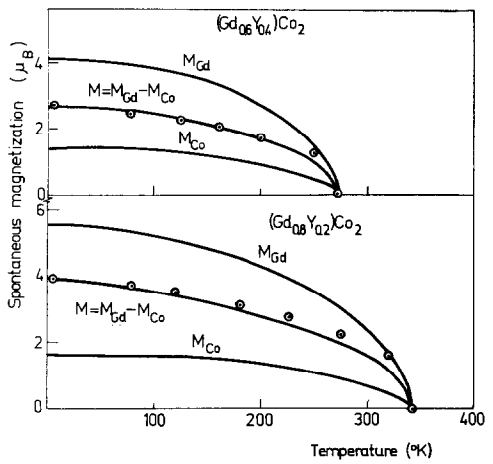

FIG. 7. The calculated magnetization from paramagnetic data and the experimental points for $(Gd_{0.8}Y_{0.2})Co_2$ and $(Gd_{0.6}Y_{0.4})Co_2$ compounds.

3.2. *Model of the Exchange-Enhanced Paramagnetism (EEP)*

This model (*15*) was applied to the ACo_2 compounds and assumes that A atoms possess a well-localized magnetic moment and the B atoms present an exchange enhanced paramagnetic susceptibility. In the high-temperature range, the magnetization of B atoms in an applied magnetic field is

$$M_B = \chi_{B,0}(H + J_{BB} M_B + J_{AB} M_A), \quad (7)$$

where $\chi_{B,0}$ is the paramagnetic susceptibility. When substituting magnetic atom A by a nonmagnetic one, the total susceptibility is the exchange-enhanced susceptibility

$$\chi_y = \frac{M_B}{H} = \frac{\chi_{B,0}}{(1 - J_{BB}\chi_{B,0})}. \quad (8)$$

The magnetic moment of the transition metal induced by the magnetic interactions, in case of gadolinium compounds ($g_A = 2$) is:

$$M_B = J_{AB}\chi_y S_A. \quad (9)$$

Making use of this model, we have calculated the values J_{AA}, J_{AB}, and χ_y. These are listed in Table IV, together with the J_{AA}, J_{AB}, and J_{BB} values deduced from the paramagnetic measurements, using the MF model. No sensible differences between these two evaluations are observed.

The agreement between the calculated curves using the EEP model (with the values listed in Table IV) and the experimental points is also good (Fig. 4).

TABLE IV

COEFFICIENTS CHARACTERIZING THE MAGNETIC INTERACTIONS IN $(Gd_xY_{1-x})Co_2$ COMPOUNDS DEDUCED FROM PARAMAGNETIC DATA

	J_{AA}				J_{AB}				J_{BB}				$\chi_y \cdot 10^4$			
x	1.0	0.8	0.6	0.4	1.0	0.8	0.6	0.4	1.0	0.8	0.6	0.4	1.0	0.8	0.6	0.4
Molecular field model	27	25	24	13	67	79	89	121	235	310	304	400	43.5	38.3	38.2	38.4
Exchange-enhanced model	29	28	28	29	72	85	100	121	—	—	—	—	39.8	36.7	29.6	24.5

Some predictions of this model are very close to those of the MF model, as we shall see below:

(a) Using (3a), relation (7) may be written as:

$$M_B = \chi_{B,0} H_{ex}(\mathrm{Co}) \qquad (10)$$

where we neglected H, compared to $H_{ex}(\mathrm{Co})$. This is justified because $H_{ex}(\mathrm{Co}) \approx 10^6$ G, while $H \approx 5 \cdot 10^3$ G and thus the errors are smaller than 0.5%. This is also confirmed by the experimental results. The values of the susceptibility measured at $2 \cdot 10^3$ G and 10^4 G are the same. According to (10) and (8), we obtain the same proportionality between the exchange field and the magnetic moment: $H_{ex}(\mathrm{Co})/\mathcal{M}^{\circ}_{\mathrm{Co}} \approx (2.8 \pm 0.2)10^6$ G/μ_B as in the case of the MF model.

(b) The χ_y values calculated in the EEP model are close to those obtained using (8) with the parameters J_{ij} as obtained in the MF model (Table IV). As a consequence, the induced moments calculated according to (9) are almost the same, using the interaction values deduced in both models.

4. Conclusions

The magnetic moments of cobalt in $(Gd_xY_{1-x})Co_2$ compounds are essentially induced by the magnetic interactions acting on the form of the exchange field. These induced moments present some features of the localized behavior and may be considered, probably, in the model proposed by Friedel *et al.* (*16*). The good agreement between the prediction of the MF model and the EEP model is probably connected with the common origin of both models.

The cobalt atoms also seem to present a magnetic contribution in the paramagnetic range. No first-order transitions are observed in these systems to suggest the disappearance of cobalt moment (*17*) at temperatures above the Curie points.

Acknowledgments

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