JOURNAL OF SOLID STATE CHEMISTRY 37, 1–5 (1981)

Magnetic Resonance Study of $(Gd_xY_{1-x})Co_2$ Compounds

E. BURZO, MAGDA BĂLĂNESCU, AND M. CHIPARĂ

National Center of Physics, P.O. Box 5206, Bucharest, Romania

Received January 24, 1980; in revised form March 31, 1980

The results of magnetic resonance studies on ferrimagnetic $(Gd_xY_{1-x})Co_2$ compounds, both below and above the Curie points, are presented. The ferrimagnetic resonance measurements show that the effective g values can be described by using the Wangsness relation. The spectroscopic splitting factors of cobalt atoms are not composition dependent. In the paramagnetic range the thermal variation of the linewidth is not linear and the g values are a function of temperature. This behavior is analyzed in correlation with the magnetic data.

1. Introduction

In a previous paper (*1*) we reported the magnetic behavior of $(Gd_xY_{1-x})Co_2$ compounds. They crystallize in $MgCu_2$-type structure. In this structure cobalt occupies $\bar{3}m$ sites, while gadolinium and yttrium are distributed in $\bar{4}3m$ positions. The compounds are ferrimagnetic; the magnetization of gadolinium is antiparallel oriented to that of cobalt (*1, 2*). The mean cobalt moment depends on the gadolinium content and seems to be essentially induced by the magnetic interactions. A linear variation of the cobalt moment with the exchange field is observed. The transition from the ordered to the paramagnetic state is of second order. In the paramagnetic range a nonlinear temperature dependence of reciprocal susceptibility is observed. The data were analyzed both in a model which supposes that above the Curie points, cobalt has an exchange-enhanced paramagnetic susceptibility (*3*) and in a model which supposes an intrinsic magnetic moment (*4*). Both models describe the experimental data rather well.

In order to obtain further data on the cobalt magnetic behavior we studied the $(Gd_xY_{1-x})Co_2$ compounds by ferrimagnetic and electron paramagnetic resonance measurements.

2. Experimental

The preparation and control of $(Gd_xY_{1-x})Co_2$ samples with $x = 0.4$, 0.6, 0.8, and 1.0 were previously reported (*1*). We extended the investigated concentration range for $0.30 \leq x \leq 0.46$. These samples were obtained by melting the constituents in an arc furnace, in helium atmosphere. The samples were thermally treated for 1 week at ~850°C. The X-ray analysis showed the presence of one phase only.

Magnetic measurements for the samples with $0.30 \leq x \leq 0.46$ were made in an extended temperature range as previously related (*1*). The ferrimagnetic and electron paramagnetic resonance (EPR) measurements were performed with a JEOL equipment using X band (9.4 GHz) and K band (23.4 GHz). Some data were also obtained

0022-4596/81/040001-05$02.00/0

in Q band (35 GHz). The samples were studied in the temperature range 78–400 K.

3. Ferrimagnetic Resonance Measurements

For ferrimagnetic resonance measurements the samples were in the form of small spheres. The g_{eff} value, for metallic spherical samples with diameters greater than the skin depth, is given by (5)

$$(\omega_i/\gamma)^2 = \left(H_i + H_A - \frac{4\pi M}{3}\right)\left(H_i + H_A + 4\pi M - \frac{4\pi M}{3}\right). \quad (1)$$

We denoted by ω_i the resonance frequency, H_i the resonance field, and M the magnetization of the sample; $\gamma = eg_{eff}/2m$ and H_A includes the contributions from the anisotropy and strain field. We assumed that H_A is not dependent on the external field.

The magnetization M was obtained from measurements performed on the same samples. Then, we determined to what extent the resonance field H_i represents the field necessary to saturate the magnetization. As previously stated (6) for K- and Q-band measurements the saturation is fully attained in the resonance field. For X-band measurements the true saturation is not completely attained in the resonance field. The magnetization is, however, close to this value.

By solving simultaneously the system of Eqs. (1) we obtained g_{eff} and H_A values. The composition dependence of the effective spectroscopic splitting factors, g_{eff}, at 78 K is shown in Fig. 1. In order to analyze the experimental data we considered a two-sublattice ferrimagnet. In this case, the g_{eff} values are given by the Wangsness relation (7)

$$g_{eff} = \frac{M_{Gd} - M_{Co}}{M_{Gd}/g_{Gd} - M_{Co}/g_{Co}}. \quad (2)$$

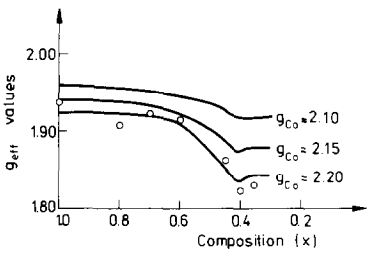

FIG. 1. The composition dependence of the effective splitting factors, at 78 K. Solid lines are plots of the calculated values with $g_{Gd} = 2.00$ and $g_{Co} = 2.10$, 2.15, and 2.20.

The magnetization of gadolinium (M_{Gd}) and cobalt (M_{Co}) sublattices, at 78 K, was determined by using the molecular field approximation (8), as previously stated (1). Assuming that $g_{Gd} = 2.00$ and using the magnetization data, we calculated the composition dependence of g_{eff}, for $g_{Co} = 2.10$, 2.15, and 2.20. These values are plotted in Fig. 1 by solid lines. The form of these curves shows both the changes in composition and the changes due to the thermal variation of sublattice magnetizations. The last effect is important for compounds with small Curie points.

The analysis of experimental data shows that g_{Co} does not seem to be dependent on composition, the determined values lying between $g_{Co} = 2.15$ and $g_{Co} = 2.20$.

4. Electron Paramagnetic Resonance Measurements

For EPR measurements, the samples were powdered, shifted by a 325-mesh sieve, and incorporated in silicon grease. The g values and the linewidth, DH, were determined by computer analysis of the derivatives of the lines, considering an admixture of dispersive component to the absorption signal. Corrections for demagnetizing effects were made.

In Fig. 2 we plotted the temperature dependence of the linewidth for samples

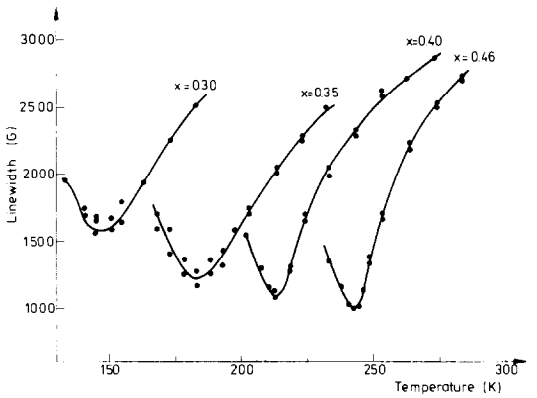

FIG. 2. Thermal variation of the linewidths for the samples with $x = 0.30, 0.35, 0.40, 0.46$.

with $0.30 \leq x \leq 0.46$. The thermal variations of g values for these cases are shown in Fig. 3. Inspection of the data shows that the slopes of the linewidth, $b = DH/T$, are not constants and the g values are temperature dependent. The above results are similar to those previously reported in ferrimagnetic $Gd(Co_xNi_{1-x})_2$ compounds (*9*). The EPR measurements were performed in a relatively restrained temperature range. At higher temperatures as compared to T_c, a resonance line centered at lower fields is observed. This line, which can be attributed to the presence of a small quantity of an ordered phase, disturbs the main line. The intensity of the main line decreases rapidly with temperature.

For gadolinium ions, in nonmagnetic metallic hosts, the interactions are described by an RKKY model (*10*). The slope of the linewidths and the g values are not temperature dependent. This behavior is also observed if the Gd ions are introduced in a metallic host which has an exchange-enhanced paramagnetic susceptibility, such as, for example, palladium (*11*). The forms of temperature dependences of the b and g values, as shown in Figs. 2 and 3, indicate a more complex behavior than that described by the RKKY model. The present data suggest that at $T > T_c$ cobalt seems to have an intrinsic magnetic moment rather than an exchange-enhanced paramagnetic susceptibility.

Inspection of Fig. 2 shows that the thermal variation of the linewidth is not linear as a function of temperature. The "mean" slopes of the linewidth seem to increase with increasing gadolinium content. The rather large increase of the linewidth with temperature shows that no bottleneck effects are present. The cobalt atoms break the bottleneck between the conduction electrons and the lattice, providing a path whereby the conduction electron magnetization can relax to the lattice. A narrowing of resonance lines is observed when the gadolinium content and exchange interactions, respectively, are increased. The increase of the linewidth by approaching the Curie points is due to the appearance of magnetic order (*11, 12*).

In order to analyze the temperature and composition dependence of the g values we start with relation (2), supposing thus a two-sublattice ferrimagnet at $T > T_c$. We admit that at the Curie points there are no changes in the electronic structure of cobalt as suggested by the second-order transition, from the order to paramagnetic state (*1*). In this case, the g values are given by

$$g = \frac{r - 1}{r/g_{Gd} - 1/g_{Co}} \tag{3}$$

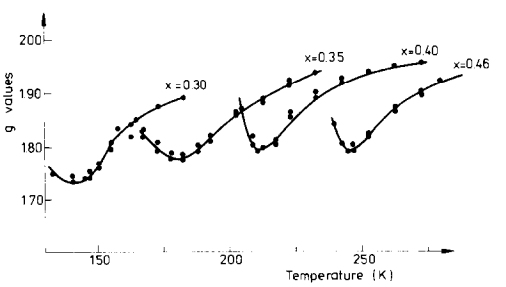

FIG. 3. The temperature dependence of the g values for the samples with $x = 0.30, 0.35, 0.40$, and 0.46.

We denoted by r the ratio of the susceptibilities of the two sublattices $r = x_{Gd}/\chi_{Co}$. The r values were obtained from the thermal variation of magnetic susceptibilities determined on the same samples. In the molecular field model we have (*8*)

$$r = \frac{C_{Gd}(T - C_{Co}J_{CoCo}) - C_{Gd}C_{Co}J_{GdCo}}{C_{Co}(T - C_{Gd}J_{GdGd}) - C_{Gd}C_{Co}J_{GdCo}} \quad (4)$$

We denoted by J_{GdCo}, J_{GdGd}, and J_{CoCo} the molecular field coefficients characterizing the interactions between and inside the magnetic sublattices. C_{Gd} and C_{Co} are the contributions of the gadolinium and cobalt sublattices, respectively, to the Curie constants. The parameters involved in relations (4), determined from magnetic measurements, are listed in Table I.

The molecular field model describes correctly the experimental data only at temperatures greater by ~40 K than the Curie points (*1, 8*). This discrepancy between the predictions of the model and the experimental data is ascribed by Néel (*8*) to the molecular field fluctuations. We expect that the EPR data will be also correctly described in the temperature range $T > (T_c + 40)$ K.

By fitting the experimental data according to relations (3) and (4) we determined g_{Co} and g_{Gd}. These values are plotted in Fig. 4. Because of the relatively restrained temperature range investigated, g_{Co} and g_{Gd} were not determined with high accuracy. We note that if g values determined by EPR are attributed only to gadolinium, the data can be interpreted by consideration of a negative polarization. The g shift is negative as compared with the g value characteristic of the gadolinium ion in a diamagnetic insolating environment (g = 1.992) (*13*). By considering a two-sublattice system, according to relations (3) and (4) we obtain $g_{Co} = 2.18 \pm 0.03$ and $g_{Gd} = 2.04 \pm 0.03$. The g_{Co} values are similar to those obtained from resonance measurements below the Curie points. The g_{Gd} values reflect a positive polarization, as expected in a system where no bottleneck effects are apparent.

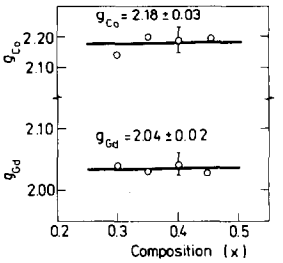

FIG. 4. The composition dependence of g_{Co} and g_{Gd} determined according to relations (3) and (4).

The minimum of the g values obtained by measurements at $T > T_c$ has the same composition dependence as the g_{eff} values obtained at 78 K. The apparent increase of the g values by approaching T_c is due to the appearance of magnetic order as previously

TABLE I

THE MOLECULAR FIELD COEFFICIENTS AND THE CONTRIBUTION OF COBALT AND GADOLINIUM SUBLATTICES TO THE CURIE CONSTANTS

Composition (x) (mole%)	J_{Gd-Gd} (emu/mole)	$-J_{Gd-Co}$ (emu/mole)	J_{Co-Co} (emu/mole)	C_{Gd} (emu/mole)	C_{Co} (emu/mole)
0.30	12.0	119	440	2.270	0.290
0.35	12.5	115	425	2.765	0.305
0.40	13.0	121	400	3.160	0.360
0.46	15.6	105	381	3.634	0.402

stated (*11, 12*). The real g values can be obtained, in this temperature range, only by considering the demagnetizing effects and also the anisotropic field. This is difficult to estimate since the form of the powdered samples is not spherical for all particles. The above magnetic model can justify the constancy of g_{Co} values.

The EPR measurements at $T > T_c$ can be analyzed well in a model which supposes that cobalt has an intrinsic magnetic moment.

5. Conclusions

The ferrimagnetic resonance measurements on $(Gd_xY_{1-x})Co_2$ compounds show that the g_{Co} values are nearly constant, ranging between 2.15 and 2.20. A similar behavior was observed for g_{Fe} and g_{Co} in $(Gd_xY_{1-x})Fe_2$ and $Gd(Co_xNi_{1-x})_2$ compounds (*6, 9, 14*). The electron concentration of the $(Gd_xY_{1-x})Co_2$ system is not dependent on composition and consequently a partial filling of the cobalt $3d$ band cannot be responsible for the diminution of its magnetic contribution. The decrease of the mean cobalt moment by increasing the Y content seems to be due to a reduced exchange splitting of the Co $3d$ states (*1*). This mechanism has recently been confirmed in Gd–Fe system by the analysis of the valence band spectra (*15*), or in the $(Gd_xY_{1-x})Co_2$ compounds by nuclear magnetic resonance measurements (*16*). In this last case, the coexistence of magnetic and nonmagnetic cobalt atoms in the whole concentration range is also shown. The presence of cobalt magnetic atoms is related to a critical value of exchange interactions as in the case of $Gd(Co_xNi_{1-x})_2$ compounds (*17*).

References

1. E. Burzo and D. P. Lazăr, *J. Solid State Chem.* **16,** 257 (1976).
2. R. Lemaire and J. Svhweizer, *Phys. Lett.* **21,** 366 (1966).
3. D. Bloch and R. Lemaire, *Phys. Rev. B* **2,** 2648 (1970).
4. E. Burzo, *Phys. Rev. B* **6,** 2882 (1972).
5. J. O. Artman, *Phys. Rev.* **105,** 74 (1957).
6. E. Burzo and I. Ursu, *J. Appl. Phys.* **50,** 1471 (1979).
7. R. K. Wangsness, *Amer. J. Phys.* **24,** 60 (1956).
8. L. Néel, *Ann. Phys. (Paris)* **3,** 137 (1948).
9. E. Burzo and M. Bălănescu, *Solid State Commun.* **28,** 693 (1978).
10. M. A. Ruderman and C. Kittel, *Phys. Rev.* **96, 99** (1954); T. Kasuya, *Progr. Theor. Phys.* **16,** 45 (1956); K. Yoshida, *Phys. Rev.* **106,** 893 (1957).
11. R. H. Taylor, *Advan. Phys.* **24,** 681 (1975).
12. E. Burzo, I. Ursu, and J. Pierre, *Phys. Status. Solidi B* **51,** 463 (1972).
13. M. Peter, J. Dupraz, and H. Cottet, *Helv. Phys. Acta* **40,** 301 (1967).
14. E. Burzo, *J. Phys. (Paris)* **40,** C5–184 (1979).
15. J. Azoulay and L. Ley, *Solid State Commun.* **31,** 131 (1979).
16. S. Hirosawa, T. Tsuchida, and Y. Nakamura, *J. Phys. Soc. Japan* **47,** 804 (1979).
17. E. Burzo, D. P. Lazăr, and M. Ciorăscu, *Phys. Status. Solidi B* **65,** K145 (1974).