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^{59}Co nuclear magnetic resonance in the metamagnetic system $Y_{1-x}Gd_xCo_3$

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A detailed nuclear magnetic resonance (NMR) study of some intermetallic compounds of the series $Y_{1-x}Gd_xCo_3$ is presented. These are results where the NMR lines corresponding to the four magnetic sites of these compounds appear clearly resolved in the NMR spectra. We found, however, that the number of lines and their widths are strongly dependent on the radio frequency (rf) power level, which may help to explain some of the discrepancies found in NMR literature on these compounds. From the dependence of the NMR spectra with rf power we concluded that the site labeled 18*h* presents the largest local magnetic anisotropy. No significant changes are observed in the value of the hyperfine fields at any site as a function of the Gd concentration, *x*. *© 2000 American Institute of Physics.* [S0021-8979(00)30008-1]

I. INTRODUCTION

The RCo_3 intermetallic compounds exhibit a *d*-band structure formed from the hybridization of the Co 3*d* electrons with Y 4*d* or rare earth (R) 5*d* electrons. The characteristics of the band structure of these compounds result in magnetic instability of the itinerant subsystem,[1] which is related to the fact that the Fermi level lies in a very special position with respect to the density of state (DOS) curve.[2]

This Co instability is the origin of the two successive metamagnetic transitions observed in the YCo_3 magnetization curve under ultrahigh magnetic field (60 and 82 T). In the first transition, the ground state of the Co subsystem goes from a low magnetic state (LMS), to an intermediate one (IMS), and then, in the second transition, to a strong magnetic state (SMS).[2] These transitions can also be driven by the molecular field from the R subsystem when Y is replaced by a magnetic rare earth ion. Therefore, in the $Y_{1-x}Gd_xCo_3$ series it is observed that, in the low Gd concentration range, $x<0.10$, the Co subsystem ground state is in the LMS ($M_{Co}=2.0\,\mu_B$/f.u.), in the $0.10<x<0.25$ range in the IMS ($M_{Co}=2.2\,\mu_B$/f.u.), and for $x>0.25$ in the SMS ($M_{Co}=3.7\,\mu_B$/f.u.).[1] Magnetization studies[3] of YCo_3 showed that this compound is a ferromagnet whose critical temperature is close to 305 K. On the other hand, $GdCo_3$ is ferrimagnetic[4] with $T_C=612$ K and presents a compensation temperature (T_{com}), where $M=M_{Co}+M_{Gd}=0$, below (above) which M_{Gd} is larger (smaller) than M_{Co}. T_{com} decreases as *x* decreases, and at a compensation concentration (x_{com}) becomes zero; in this series[1] $x_{com}=0.52$ at 4.2 K.

The crystal structure of the RCo_3 compounds belongs to the R 3*m* space group ($PuNi_3$ type rhombohedral). In this structure the Co ions occupy three different crystallographic Co sites, called 3*b*, 6*c*, and 18*h*, with 6, 3 and 5 R ions nearest neighbors, respectively,[3] and are populated according to the ratio 1:2:6, respectively. The 18*h* site can be magnetically further divided into the $18h_1$ and $18h_2$ sites,[5] although in special cases the magnetization component exists perpendicular to the *c* axis. The R ions are located at two crystallographic sites, R 3*a* and R 6*c*. Whereas the local symmetry of the R 3*a* site is hexagonal, with the RCo_5 structure, the R 6*c* site exhibits the symmetry of the R site in a cubic RCo_2,[5] and has a population ratio of 1:2.[3,5]

Streever[6] showed that the Co atoms at the 3*b* and 6*c* sites are expected to make a large spin–orbit contribution to the magnetic anisotropy, whereas those at the 18*h* site produce only a small contribution.

In the present work we describe a nuclear magnetic resonance (NMR) spectroscopy study of ^{59}Co in $Y_{1-x}Gd_xCo_3$ in the concentration range of $0\leqslant x\leqslant 1$. Four well-resolved lines are observed in the spectra. Both this number and the linewidths depend on the rf power level. From the dependence of the intensity of these lines upon the power level, one can identify the sites by their local anisotropy. Very little change is observed in the line positions with the *x* concentration.

II. EXPERIMENTAL DETAILS

Polycrystalline samples were prepared by arc melting the constituent metals in argon atmosphere, followed by annealing at 1050 °C under dynamic vacuum for 24 h in order to minimize lattice defects. X-ray diffraction analysis indicated that all the samples were single phase with the $PuNi_3$-type structure. The spin-echo amplitude was measured in an automated homemade coherent pulse NMR spectrometer[7] at 4.2 K and zero external static magnetic field. The samples were powdered and soaked in silicon oil in a cylindrically shaped plastic sample holder. The repeti-

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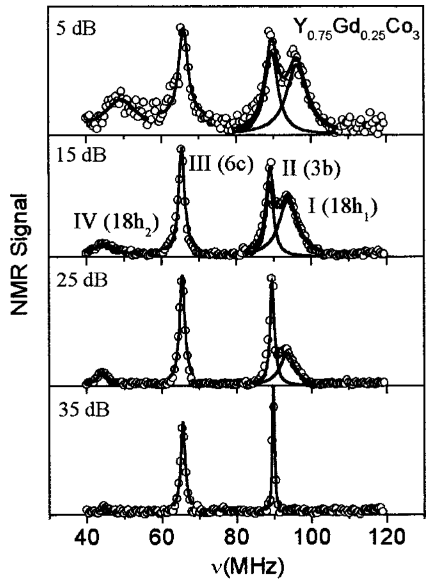

FIG. 1. ^{59}Co zero field spin-echo NMR spectra of $Y_{0.75}Gd_{0.25}Co_3$ with 5, 15, 25, and 35 dB rf power attenuation, starting from above, at 4.2 K.

tion rate was typically 0.1–0.2 kHz. The rf power was controlled by a variable 63 dB Wavetek attenuator. The value of $B_1/B_{1\,\max}=1(0)$ corresponds to 0 (63) dB of attenuation, with $B_{1\,\max}\sim 10$ G.

III. RESULTS AND DISCUSSION

Figure 1 displays measured ^{59}Co spin-echo spectra in $Y_{0.75}Gd_{0.25}Co_3$ at 4.2 K for several values of rf power intensity. The most remarkable aspect of these spectra is their strong dependence on the rf power. For larger values of rf power one can observe four well-defined peaks, whereas only three (the lowest frequency peak nearly vanishes) narrow peaks appear at lower values of the rf amplitude. The same behavior is observed for all other concentrations. Note that, at first glance, this effect cannot be attributed simply to domains versus domain wall signals, as observed in other compounds, since for high rf power the signal arises from the domains, whereas for low rf power the line comes from the domain walls.[8] We have also observed contributions from both the domain and the domain walls at high rf power, and only domain walls contribution at low rf power, as shown in Fig. 2, for the spin–spin relaxation rate.

There are other two important aspects to be noticed in the spectra: first, the line positions practically do not change along the series up to $x\sim 0.25$, as shown in Fig. 3 for the spectra obtained with an attenuation of 20 dB. Above this, lines II and III remain unaltered, whereas lines I and IV change by about 12%, in opposite directions. To the best of our knowledge, such spectral features in these compounds have not been reported in the literature on NMR.

The four NMR peaks in the spectra are associated to four magnetically inequivalent sites in these compounds. The amplitude of the lines labeled I and IV diminishes with rf power. Lines II and III, on the other hand, remain unaltered. We also observe that line III narrows from a halfwidth of 3.76 MHz to 1.15 MHz as the rf power decreases in $GdCo_3$, whereas the width of line II, on the contrary, remains unchanged (1.08 MHz at 45 dB and 1.02 MHz at 20 dB). The same behavior is observed for all other concentrations. Keeping in mind that the spin-echo amplification factor is inversely proportional to the anisotropy field,[9,10] one concludes that these lines belong to the same crystal site, the one with larger local magnetic anisotropy. Based on this and on the results in Ref. 5, we identify this site as 18*h*. According to Yoshie and Nakamura[4] and Yoshie *et al.*,[3] substituted nickel atoms in $GdCo_3$ and YCo_3 tend to preferentially occupy the 6*c* site in these compounds. These authors observe a vanishing line near 60 MHz which is attributed to signals from this site. Therefore, the peak labeled III in our spectra can be assigned to the site 6*c*, and, consequently, the remaining peak (II) comes from the contribution of the site 3*b*.

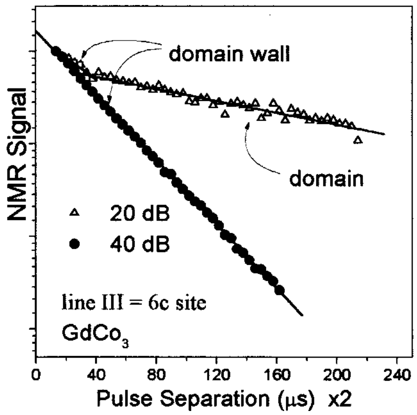

FIG. 2. Comparison of the $GdCo_3$ spin–spin relaxation rate $(1/T_2)$ with 20 and 40 dB rf power attenuation obtained at 4.2 K.

The small changes observed in the hyperfine fields of the site 18*h* (lines I and IV) (Fig. 3) cannot be attributed to the changes of the magnitude of the Co ions since the shift occurs above $x=0.25$, the concentration at which the Co moments undergo a magnetic transition. Besides, lines II and III do not change their position at all throughout the series. The shifts of lines I and IV is another clear indication that these

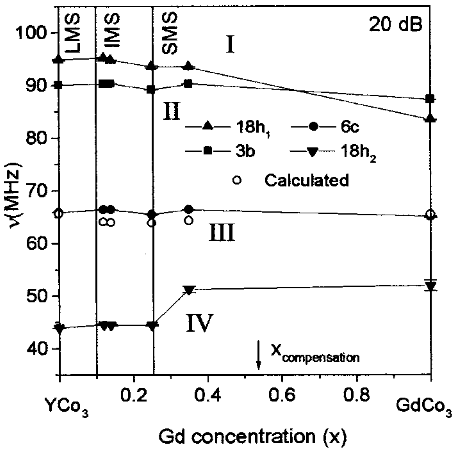

FIG. 3. Gd concentration *x* dependence of the ^{59}Co resonance frequency of $Y_{1-x}Gd_xCo_3$ at 4.2 K for the four different sites at 20 dB rf power attenuation. The open circles are values computed with the procedure that we used.

peaks are contributions from the same crystal site, and they are probably caused by a small change in the easy direction of magnetization upon alloying.

One can attempt to understand these features by approximating the total hyperfine field as a sum of contributions appearing from three different sources: one from the parent ion moment (B_p), another coming from the polarization of conduction electrons by first neighbor Gd ions (transferred field, B_{tr}), and a dipolar contribution (B_d), this one being responsible for the magnetic splitting in other compounds.[5,11] The following analysis will be carried out for the $6c$ site, because of the availability of other NMR results for this site in the literature.

The total hyperfine (hf) field is written as

$$B_{\mathrm{hf}}^{6c}(x)=B_p^{6c}(x)+B_{\mathrm{tr}}^{6c}+B_d^{6c}(x)=\alpha M_{\mathrm{Co}}(x)+\beta M_{\mathrm{Gd}}(x)+\beta' M_{\mathrm{Gd}}(x)=\alpha M_{\mathrm{Co}}(x)+\gamma M_{\mathrm{Gd}}(x). \qquad (1)$$

Replacing the experimental values for $B_{\mathrm{hf}}^{6c}(0)=65.6\,\mathrm{kG}$, $M_{\mathrm{Co}}^{6c}(0)=0.94\,\mu_B$ (Ref. 12) and $M_{\mathrm{Gd}}(0)=0\,\mu_B$, we obtain $\alpha=+69.8\,\mathrm{kG}/\mu_B$. Now, from the condition $B_{\mathrm{hf}}^{6c}(0)=B_{\mathrm{hf}}^{6c}(1)$, one obtains the parameter γ as

$$\gamma=\beta+\beta'=\alpha\left(\frac{M_{\mathrm{Co}}^{6c}(0)-M_{\mathrm{Co}}^{6c}(1)}{M_{\mathrm{Gd}}(1)}\right)=-2.6\mathrm{kG}/\mu_B, \qquad (2)$$

where $M_{\mathrm{Co}}^{6c}(1)=1.2\,\mu_B$ (Ref. 12) and $M_{\mathrm{Gd}}(1)=7\,\mu_B$.[1]

From the value $B_{\mathrm{tr}}^{6c}=6.5\,\mathrm{kG}$, reported in Ref. 12 for one Gd ion neighbor, one evaluates the total transferred field as $B_{\mathrm{tr}}^{6c}(1)=3\times 6.5\,\mathrm{kG}=19.6\,\mathrm{kG}=\beta M_{\mathrm{Gd}}(1)$. Therefore, $\beta=-2.8\,\mathrm{kG}/\mu_B$ and, using Eq. (2), $\beta=+0.2\,\mathrm{kG}/\mu_B$.

From these considerations, let us evaluate the total hyperfine field as a function of Gd concentration (x).

Taking into account the fact that Gd ions are distributed according to the probabilities[9]

$$P_n(x)=\frac{N!x^n(1-x)^{N-n}}{n!(N-n)!}, \qquad (3)$$

and that the Co moment is a function of the rare earth subsystem moment (for the $6c$ site $N=3$), one writes the cobalt moment for a concentration x as

$$M_{\mathrm{Co}}^{6c}(x)=0.94(P_0+P_1)+1.2(P_2+P_3). \qquad (4)$$

Substituting this expression into Eq. (1), along with the values obtained for α, β, and β', and assuming that $M_{\mathrm{Gd}}(x)=7x\,\mu_B$, as in Ref. 1, we obtained the points shown in Fig. 3 (open circles). These are within 2% of the measured values.

IV. CONCLUSIONS

In this article we presented a NMR study of the series $Y_{1-x}Gd_xCo_3$ using ^{59}Co as the nuclear probe. Throughout the series the NMR spectra are composed of four well-resolved lines which are attributed to four inequivalent magnetic sites. The spin-echo amplitude of two of these lines, however, is strongly dependent on the rf power. In spite of two metamagnetic transitions, one at $x=0.10$ and the other at $x=0.25$, followed by changes in the magnitude of the magnetic moment of the Co ions, no major line shift is observed in the NMR spectra. This result disagrees with those of Ref. 4 and 12. One must emphasize, however, that in the present results the NMR lines attributed to the four sites appear clearly resolved in the spectra.

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