^{59}Co NMR Studies of Rare Earth Cobaltites

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^{59}Co NMR studies of rare earth cobaltites, $LnCoO_3$ (Ln = La, Pr, Nd, Ho, Er, Yb, Y) have shown evidence for quadrupolar and hyperfine interaction effects in these systems.

Among the transition metal oxide systems of perovskite structure, the rare earth cobaltites, $LnCoO_3$ (Ln = rare earth), have been found to be particularly interesting with regard to their electronic and magnetic properties [1]. Mössbauer and other studies [2 – 5] show that the trivalent cobalt ions in these compounds are in the diamagnetic low-spin state (t_{2g}^6) at low temperature and transform to the paramagnetic high-spin state ($t_{2g}^4\ e_g^2$) with increase in temperature. The nature of the spin state transition in the lighter rare earth cobaltites like $LaCoO_3$ or $NdCoO_3$ is quite different from that in the heavier rare earth cobaltites like $HoCoO_3$ or $ErCoO_3$. Thus, in the lighter rare earth cobaltites, there is evidence for electron transfer between the high spin and the low-spin cobalt ions shortly above the spin state transition temperature. In the heavier rare earth cobaltites, however, the ratio of the low and the high spin ions after spin state transition remains constant (1:1) upto high temperature. The crystal structure of the first three members of the $LnCoO_3$ family is also different from others. $LaCoO_3$ and $PrCoO_3$ show rhombohedral distortion while $NdCoO_3$ shows tetragonal distortion; all the other cobaltites are orthorhombic [6]. We have initiated a programme to investigate the electronic and magnetic properties of rare earth cobaltites by employing ^{59}Co ($I = 7/2$) NMR spectroscopy. In the course of these investigations, we have for the first time observed quadrupolar interaction effects in the cobaltites, which are too small to be discerned in Mössbauer spectra. We have also been able to observe transferred hyperfine interaction effects in these oxide systems.

The ^{59}Co NMR powder pattern of $LnCoO_3$ samples recorded in the frequency range of 2 – 12 MHz, belongs to the diamagnetic low spin Co^{III},

Table 1. Magnetic and quadrupolar hyperfine interaction parameters of ^{59}Co NMR in $LnCoO_3$ at 300 K.

Ln^{3+}	ν_Q in MHz	K_i^{exp} %	$K_i(T)$ %
La	0.30 [a]	+2.550	+1.100 [c]
Pr	—	+1.320	−0.130 [c]
Nd	0.43 [b]	+1.376 [b]	−0.074 [c]
Ho	—	+1.890	+0.440
Er	0.082 [a]	+1.880	+0.430
Yb	0.081 [a]	+1.874	+0.424
Y	0.071 [a]	+1.864	+0.414

Data taken on Varian WL Spectrometer. All resonances are measured w.r.t. diamagnetic reference $K_3Co(CN)_6$ in solution.

[a] From satellite pair separation.
[b] Determined from splitting of the central component.
[c] Estimated as described in the text.

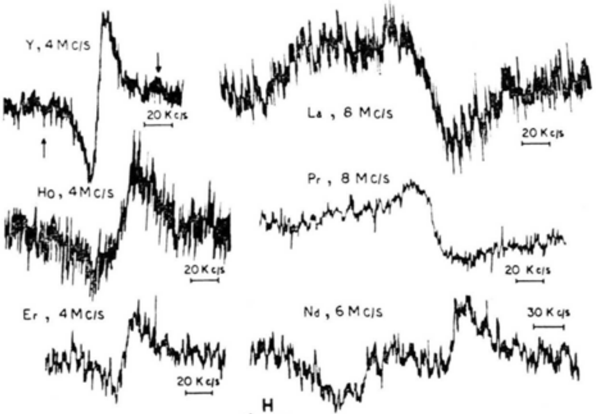

Fig. 1 a. Some typical ^{59}Co NMR powder spectra of $LnCoO_3$ samples recorded at 300 K. The "arrows" (↑ and ↓) indicate the first pair of satellite in case of $YCoO_3$. The direction of increasing magnetic field is shown by the symbol $\overset{H}{\leftarrow}$.

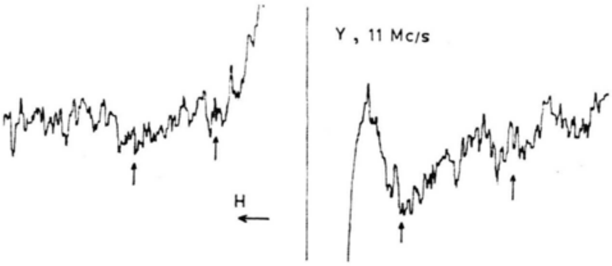

Fig. 1 b. Amplified ^{59}Co NMR signal of $YCoO_3$ showing the satellites (↑) just resolved from the central line.

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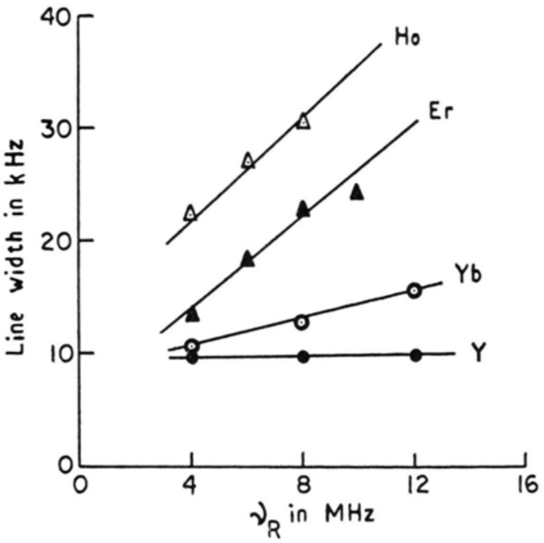

Fig. 2. Plots of linewidth versus resonance frequency (ν_R) for the $LnCoO_3$ system.

which however is linked to a paramagnetic high spin Co^{3+} ion as also to the rare earth ion through oxygen. Thus magnetic hyperfine effects are interwoven with quadrupolar effects in this system. In the present work the relevant NMR parameters viz., quadrupolar coupling constant ν_Q and shift K_i^{exp} have been measured following the method of Jones et al. [7]. The results are presented in Table 1. Typical NMR spectra of some of the members are shown in Figure 1. In general three types of spectra are obtained corresponding to the three different types of crystal structure in rare earth cobaltites. The central transition ($+1/2 \longleftrightarrow -1/2$) in La and Pr (rhombohedral distortion) cobaltites exhibits a single asymmetric line at high frequencies (Figure 1 a). At low frequencies however, La shows a characteristic second-order splitting and the ν_Q value estimated from the central line is in agreement with that obtained from satellite separation. Though indications of second-order splittings have been obtained at lower frequencies in case of Pr also, a quantitative estimation of ν_Q could not be made due to poor signal to noise ratio. Consequently satellites could not be detected in this system. In $NdCoO_3$ (tetragonal distortion), a quadrupolar split central line (Fig. 1 a) is obtained at all frequencies, the quadrupolar splitting varying inversely as the field. The heavier rare-earth cobaltites $YCoO_3$, $HoCoO_3$, $ErCoO_3$ and $YbCoO_3$ (orthorhombic distortion), on the other hand, show a single unsplit central line at all frequencies (Y, Er and Ho, Figure 1 a). A pair of weak satellites have also been detected in case of Y (Fig. 1 b), Er and Yb. Further the satellite separations indicate a first-order interaction. The line width, which depends on the magnetic moment, is largest in the case of Ho as expected and as such no satellite could be detected in this case. It is indeed interesting that less distorted $NdCoO_3$ shows a larger (second-order) quadrupolar interaction (Table 1) as compared to that (first-order) in the more distorted orthorhombic cobaltites studied in the present paper. This can not be explained from considerations of simple crystal symmetry alone. Bonding may be an important factor in determining the strength of the quadrupolar interaction parameter in this system.

For the heavier rare earths (Er, Ho and Yb), though the anisotropic magnetic hyperfine interaction is not manifest in the almost symmetric single central line, frequency variation studies (Fig. 2) reveal the characteristic broadening [8] arising from such an interaction. In $YCoO_3$ the line width is frequency independent, but it shows a definite temperature dependence of the shift indicating the presence of an isotropic hyperfine interaction from the paramagnetic cobalt ions.

The observed isotropic shift K_i^{exp} (Table 1) consists of two parts viz. (i) dominating temperature independent Van Vleck's contribution [9] and (ii) temperature dependent paramagnetic shift $K_i(T)$. From the linearity of the K_i^{exp} versus susceptibility χ_g plot of Y and Er (Fig. 3), the resonance shift can be written as

$$K_i^{\mathrm{exp}} = A\,\chi_g(T) + K_i = A'(1/T) + K_i\,,$$

where A' gives the hyperfine field at the ^{59}Co nuclei and K_i is a measure of the Van Vleck term. Since Van Vleck's contribution for the Co^{III} ion to the total susceptibility is not found readily, the relation $K_i^{\mathrm{exp}}.\ T = K_i T + A'$ has been used to estimate the temperature-independent shift K_i. The slope of the curve $K_i^{\mathrm{exp}}\,T$ versus T (Fig. 4) gives the temperature independent part K_i, and $K_i(T)$ can then be separated. The estimated values of the Van Vleck term in these three cobaltites (Y, Er and Yb) are very nearly the same ($\sim 1.4\%$). A similar value of the Van Vleck term is reported in ^{59}Co NMR of Co_3O_4 [10].

Assuming Van Vleck's contribution to be the same throughout the $LnCoO_3$ series, $K_i(T)$ may be evaluated (Table 1). It is to be noted that even in

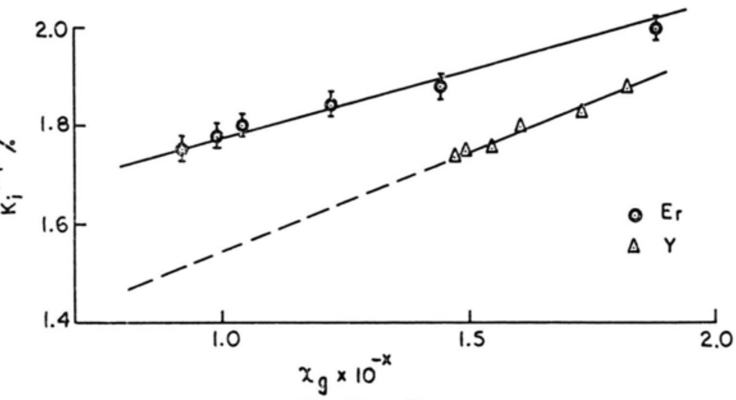

Fig. 3. Plot of ^{59}Co resonance shift (K_i^{exp} %) as a function of susceptibility [3–5] expressed in emu/g ($\chi_g \times {}^{-x}$). [$x = 4$ and 5 for Er and Y, respectively.]

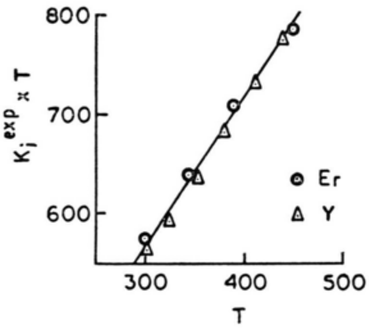

Fig. 4.
Plot of $K_i^{\text{exp}}\,T$
against T for Y and Er.

$YCoO_3$, where the ratio of the low spin to the high spin state is rather small (1 : 0.4) in comparison to other cobaltites, the transferred hyperfine interaction of the type $Co^{3+} - O - Co^{III}$ is not inconsiderable [$K_i(T) \sim 0.4\%$]. Interestingly, the rare earth contribution, though small ($\sim 0.02\%$), is nevertheless revealed in the expected sign reversal [11] of the shift across the rare-earth series as measured with respect to $YCoO_3$. $LaCoO_3$ shows a much larger shift compared to other cobaltites, probably because of the occurrence of electron transfer between the low-spin and high spin state of cobalt ion at low temperature giving rise to divalent and tetravalent cobalt ions [2, 3].

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