

# Hyperfine interactions in rare-earth orthoferrites during hydrostatic compression

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The effect of large hydrostatic pressures on hyperfine interactions in rare-earth orthoferrites at  $T = 4.2$  K has been studied by a  $^{57}\text{Fe}$  NMR method. A new result is found: The baric coefficient of the hyperfine field depends strongly (to the point of changing sign) on the bond angle in the chain  $\text{Fe}^{3+\uparrow} - \text{O}^{2-} - \text{Fe}^{3+\downarrow}$ .

No experimental data are available on the effect of hydrostatic compression on the hyperfine fields at nuclei in magnetically ordered oxides (orthoferrites, iron garnets, spinels, etc.) at low (liquid-helium) temperatures. The studies which have been reported (see the review by Nikolaev, for example<sup>1</sup>) have been carried out at room temperature—at temperatures comparable to the magnetic ordering temperature  $T_N$  of the compounds studied. For this reason, the published results reflect the trivial fact that the sublattice magnetization changes because of a change in  $T_N$  under pressure. In order to obtain data directly on hyperfine interactions, i.e., on the changes in the spin density at the nucleus as a result of the application of pressure, one should carry out measurements at  $T \ll T_N$ , which usually means in the liquid-helium range.

To some extent the study which we are reporting here bridges this gap. We have carried out the first study of the hyperfine interactions in the rare-earth orthoferrites  $\text{RFeO}_3$  ( $\text{R} = \text{Pr}, \text{Gd}, \text{Er}, \text{Tm}, \text{Yb}$ ) by a  $^{57}\text{Fe}$  NMR method at  $T = 4.2$  K, during the imposition of hydrostatic pressures up to 17 kbar. There are good reasons for choosing

RFeO<sub>3</sub> compounds for this study: It is in this series of model crystals, with well-studied magnetic properties and a well-studied crystal structure, that the greatest success has been achieved in the theoretical explanation of hyperfine interactions for Fe<sup>3+</sup> S ions at standard pressure.<sup>2-4</sup> In addition, there are experimental Mössbauer data<sup>5</sup> at  $T = 300$  K and at pressures up to 150 kbar.

The hyperfine fields at the <sup>57</sup>Fe nuclei are measured by the Hahn spin-echo method. For improved accuracy, we integrate the echo signal and subject the spectra to statistical analysis. High pressures are produced in a piston-cylinder container with a low-capacitance high-voltage shutter. The pressure is measured directly at 4.2 K by a digital NMR pressure gauge.<sup>6</sup>

Figure 1 shows the measured values of the baric coefficient of the modulus of the hyperfine field,  $d|H_n|/dP$ , as a function of the atomic number of the rare earth. An unexpected result which emerges from these data is the strong dependence of the baric coefficient on the atomic number (to the point that the coefficient changes sign). For the orthoferrites of the light rare earths we observe a large positive baric coefficient, while for the orthoferrites of the heavy elements we observe a small negative coefficient. The sign changes at  $Z = 68-69$ . It is interesting to compare these results with results<sup>5</sup> from measurements of  $d|H_n|/dP$  at 300 K by a Mössbauer method. Approximately the same value,  $+9 \times 10^{-2}$  kOe/kbar, was found for orthoferrites of La, Pr, Gd, and Tm in Ref. 5. This value is four to six times the values which we find at 4.2 K for PrFeO<sub>3</sub> and GdFeO<sub>3</sub> and does not agree in sign with the result for TmFeO<sub>3</sub>. Consequently, the data reported by Halasa *et al.*<sup>5</sup> (as they themselves conclude) reflect primarily an increase in  $T_N$  under pressure, rather than a change in the constant of the hyperfine interaction.

We will show that this result is not a consequence of the individual properties of the rare-earth ions or of a difference in the magnetic structures at 4.2 K ( $G_z F_x$  or  $G_x F_z$ ); it can be explained by the existing theory of the hyperfine interaction in magnetic oxides,<sup>2,4,7</sup> when allowance is made for the way in which the crystal structure varies in several orthoferrites.<sup>8</sup>

When the method of linear combinations of atomic orbitals is used to describe the wave functions of valence electrons, it becomes possible to write the hyperfine field as the sum of three terms with a clear physical meaning:

$$H_n = H_{\text{free}} \frac{S}{S_0} + H_{\text{cov}} + H_{\text{inhf}} \quad (1)$$

The first (and dominant) term is the negative contact field modified as a result of the change (decrease) in the spin ( $S$ ) of the central Fe<sup>3+</sup> ion in the Fe<sup>3+</sup> - 6O<sup>2-</sup> octahedral complex (for a free ion with  $S_0 = 5/2$ , we have  $H_{\text{free}} = -630$  kOe). The second term is the positive covalent component of the hyperfine field, which is determined primarily by charge transfer to the normally empty 4s shell of the Fe<sup>3+</sup> ion. Since the covalency increases with decreasing cation-anion distance  $r_{\text{Fe-O}}$  (with increasing pressure), the spin  $S$  decreases, while  $H_{\text{cov}}$  increases. These components, which depend on only  $r_{\text{Fe-O}}$ , thus act in a consistent way, leading to a decrease in  $|H_n|$ . An interesting feature of the crystal structure of RFeO<sub>3</sub> is a very weak dependence of  $r_{\text{Fe-O}}$  on the ionic radius of the rare-earth ion.<sup>8</sup> It is thus highly accurate to

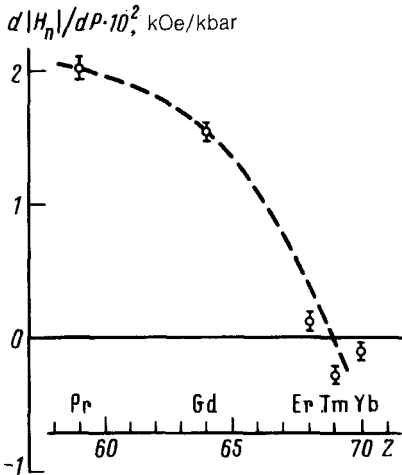


FIG. 1. The baric coefficient of the modulus of the hyperfine field at  $^{57}\text{Fe}$  nuclei in rare-earth orthoferrites versus the atomic number of the rare earth ( $T = 4.2$  K).

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write  $d(H_{\text{free}}S/S_0 + H_{\text{cov}})/dr = \text{const}$ . Numerical calculations<sup>7</sup> of the radial profile of  $H_n$  lead to the value

$$d(H_{\text{free}}S/S_0 + H_{\text{cov}})/dr \approx -215 \text{ kOe}/\text{\AA} \quad (2)$$

for all orthoferrites at  $r_{\text{Fe-O}} \approx 2 \text{ \AA}$ .

The third term is the indirect hyperfine field which arises as a result of the transport (delocalization) of the spin density away from the surrounding ions  $\text{Fe}^{3+\downarrow}$  to the central ion  $\text{Fe}^{3+\uparrow}$  in the expanded complex  $\text{Fe}^{3+\uparrow}-6\text{O}^{2-}-6\text{Fe}^{3+\downarrow}$ . In the case of an antiferromagnetic order,  $H_{\text{inhf}}$  has the same sign as  $H_{\text{free}}$ , leading to an increase in  $|H_n|$  with increasing pressure. In addition to the "normal" dependence of the modulus of  $H_{\text{inhf}}$  or  $r_{\text{Fe-O}}$ , this component is characterized by a dependence on the bond angle  $\theta$  in the chain  $\text{Fe}^{3+\uparrow}-\text{O}^{2-}-\text{Fe}^{3+\downarrow}$ . According to Ref. 7, we thus have

$$dH_{\text{inhf}}/dr \approx +315 \{ (1 - \kappa) \cos^3 \theta + \kappa \} \text{ kOe}/\text{\AA}. \quad (3)$$

Here  $\kappa = A_\pi/A_\sigma$ ,  $A_\sigma$  and  $A_\pi$  are covalent parameters,  $A_\sigma = B_\sigma + S_\sigma$ ,  $A_\pi = B_\pi + S_\pi$ ,  $S_\sigma$  is an overlap integral,  $\langle d_z^2 | p_z \rangle$ ,  $S_\pi$  is the integral  $\langle d_{xz} | p_x \rangle$ ,  $B_\sigma$  and  $B_\pi$  are the  $p_z \rightarrow d_z^2$  and  $p_x \rightarrow d_{xz}$ , respectively, transport parameters.

For  $\text{RFeO}_3$ , it has been found that the angle  $\theta$  depends strongly on the ionic radius of the rare-earth ion.<sup>2,9</sup> As we go from  $\text{R} = \text{La}$  to  $\text{Lu}$ , for example,  $\theta$  changes from  $157^\circ$  to  $142^\circ$ . This aspect of the crystal structure is the primary reason for the changes in the values of  $T_N$  (Ref. 2),  $H_n$  at  $P = 0$  (Refs. 2-4), and (as we will show here)  $dH_n/dP$  in the series of  $\text{RFeO}_3$  compounds. Assuming that  $\kappa$  varies only slightly with the pressure, assigning it the value  $\kappa = 0.19$ , found<sup>2</sup> from the  $T_N(\overline{\cos^2 \theta})$  dependence at standard pressure, and summing (2) and (3), we find the resultant relation

$$dH_n/dr \approx (-155 + 255 \cos^2 \theta) \text{ kOe}/\text{\AA}. \quad (4)$$

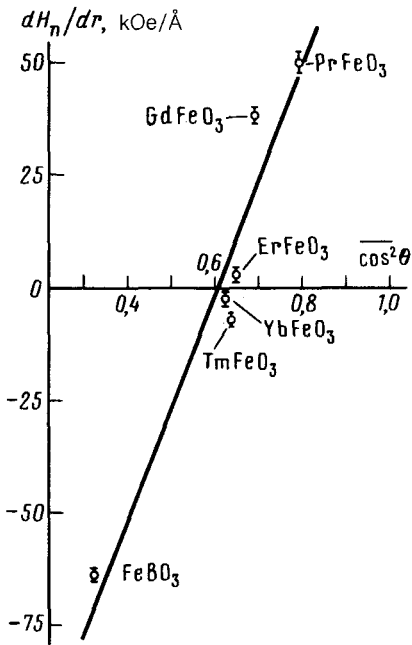


FIG. 2.  $dH_n/dr_{\text{Fe-O}}$  versus the mean square cosine of the angle of the  $\text{Fe}^{3+\uparrow} - \text{O}^{2-} - \text{Fe}^{3+\downarrow}$  bond. Line—calculated in the approximation of linear combinations of atomic orbitals with  $r_{\text{Fe-O}} \approx 2 \text{ \AA}$ ; points—experimental data on  $\text{RFeO}_3$  and  $\text{FeBO}_3$  at  $T = 4.2 \text{ K}$ .

Figure 2 shows the experimental data, plotted versus  $\overline{\cos^2\theta}$ , along with theoretical result (4). Here we have used the estimate<sup>9</sup>  $dr/dP = -4 \times 10^{-4} \text{ \AA/kbar}$ . We see that there is a good correspondence in the data both with regard to the angle at which components (2) and (3) cancel out  $\theta_c \approx 141^\circ$  and with regard to the slope of the lines.

To test the universality of this behavior, we have plotted in Fig. 2 data for the rhombohedral weak ferromagnet  $\text{FeBO}_3$ , for which the distance  $r_{\text{Fe-O}}$  is essentially the same as that for  $\text{RFeO}_3$ , but for which the bond angle is substantially smaller:  $\theta = 125^\circ$ . The large negative baric coefficient of the NMR frequency<sup>6</sup> in  $\text{FeBO}_3$  is also explained satisfactorily by (4).

In summary, these results show that in magnetically ordered oxides the pressure dependence of the hyperfine field which is determined by radial effects also depends substantially on the angular geometry of the exchange bonds. For this reason, the interpretation offered in Ref. 10 of the experimental data of Ref. 5 should be judged incorrect: The angular dependence of the indirect hyperfine field was totally ignored in Ref. 10.

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