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## Hyperfine Interactions of Fe<sup>2+</sup> in Ilmenite

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Hyperfine interactions at the Fe<sup>2+</sup> sites in ilmenite have been determined by Mössbauer spectroscopy. At 5°K the internal magnetic field is  $(-43 \pm 3)$  kOe and the quadrupole-coupling constant  $\frac{1}{2}e^2qQ$  is  $(+1.44 \pm 0.01)$  mm/sec. Theoretical interpretation of the internal magnetic field in terms of dipolar-, orbital-, and core-polarization contributions is shown to depend critically upon the lattice contribution to  $\frac{1}{2}e^2qQ$ , which is still unknown.

### I. INTRODUCTION

The hyperfine structure of Fe<sup>2+</sup> in ilmenite (FeTiO<sub>3</sub>) was studied by low-temperature Mössbauer spectroscopy several years ago.<sup>1</sup> A relatively small internal magnetic field  $H_{int}$  was observed in the antiferromagnetic state and only partial resolu-

tion of the hyperfine spectrum was obtained. Theoretical calculations suggested that the sign of  $H_{int}$  was negative and that the core-polarization contribution to  $H_{int}$  was low.<sup>2</sup>

In conjunction with an investigation of the Fe<sub>2-x</sub>Ti<sub>x</sub>O<sub>3</sub> system<sup>3</sup> with compositions similar to lunar ilmenite specimens, we have synthesized stoichio-

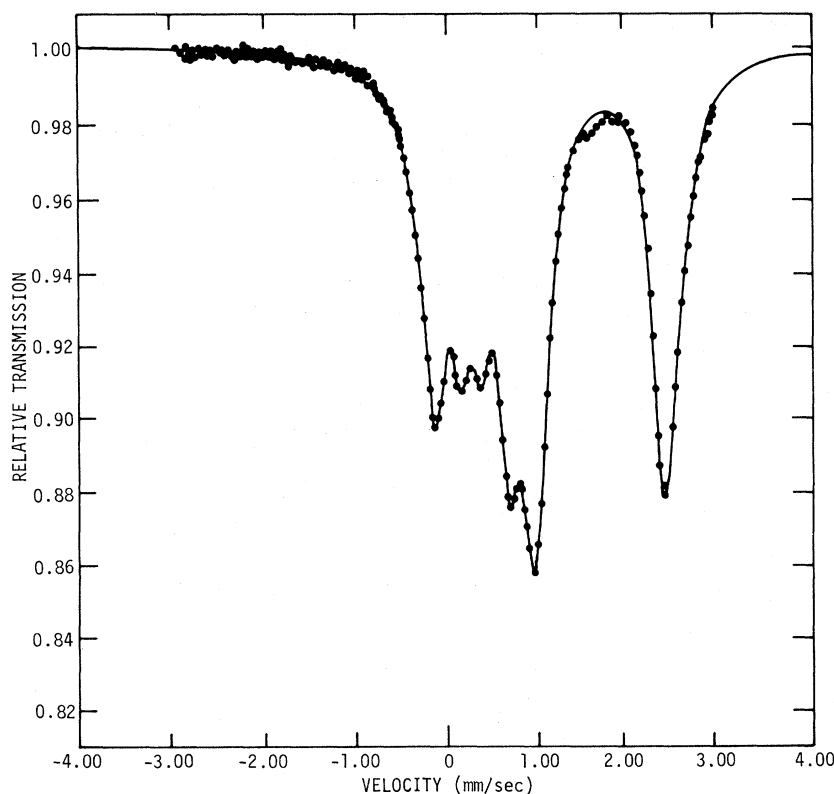


FIG. 1. Mössbauer spectrum of synthetic polycrystalline ilmenite ( $\text{FeTiO}_3$ ) at 5°K. Source was  $\text{Co}^{57}$  in Cu ( $\approx 22^\circ\text{C}$ ).

metric  $\text{FeTiO}_3$ . The liquid-helium-temperature Mössbauer spectrum of this material had narrow linewidths and hence showed a well-resolved hyperfine structure. An analysis of this spectrum and data on a single-crystal mineral sample is presented.

## II. EXPERIMENTAL

Synthetic ilmenite was prepared by solid-state reaction of appropriate amounts of high-purity Fe,  $\text{Fe}_2\text{O}_3$ , and  $\text{TiO}_2$ ; the iron powder was prepared from Johnson, Matthey and Co. iron sponge by reduction in  $\text{H}_2$  for 1 h at  $1175^\circ\text{C}$  followed by rapid cooling. The starting material was finely ground, compressed, and fired at  $850^\circ\text{C}$  (2 h) and  $1200^\circ\text{C}$  (2 h) in high vacuum ( $\approx 10^{-8}$  mm of Hg). Powder-diffraction x-ray photography was used to establish that the material was single phase. The lattice constants measured for this material based on a hexagonal unit cell are  $a = 5.085 \text{ \AA}$  and  $c = 14.087 \text{ \AA}$ .

Mössbauer measurements were made with an automated mechanical constant-velocity spectrometer operating in the transmission mode; the spectrometer is described briefly elsewhere.<sup>4</sup> The source used was  $\text{Co}^{57}$  in Cu at room temperature ( $\approx 22^\circ\text{C}$ ).

The single-crystal mineral specimen of ilmenite (from Quebec) contained a considerable amount of exsolved hematite  $\alpha\text{-Fe}_2\text{O}_3$  and also about 10%  $\text{Fe}^{3+}$

in solution. Nonetheless the  $\text{Fe}^{2+}$  spectrum was sufficiently sharp and well resolved from the  $\text{Fe}^{3+}$  absorption lines to be clearly interpretable. The sample was oriented by back-reflection Laue x-ray-diffraction photography and mechanically polished  $\perp$  to the  $c$  axis to  $\approx 1.8$ -mil thickness.

## III. RESULTS AND DISCUSSION

Ilmenite crystallizes in the trigonal space group  $R\bar{3}$ .<sup>5</sup> The structure is derived from the  $\alpha\text{-Fe}_2\text{O}_3$  structure by replacing layers of  $\text{Fe}^{3+}$  which are perpendicular to the  $c$  axis by alternating layers of  $\text{Fe}^{2+}$  and  $\text{Ti}^{4+}$ . All  $\text{Fe}^{2+}$  sites are crystallographically equivalent and have point symmetry 3. Neutron-diffraction,<sup>6</sup> magnetic,<sup>7</sup> and specific-heat measurements<sup>8</sup> establish that the material orders antiferromagnetically below about  $57^\circ\text{K}$  with spin directions  $\parallel c$ . The  $\text{Fe}^{2+}$  moments are ferromagnetically coupled within layers  $\perp c$  and antiferromagnetically coupled between adjacent layers. The magnetic space group can be derived from this information and is  $R_R\bar{3}$ .

The Mössbauer spectrum of synthetic polycrystalline ilmenite at  $5^\circ\text{K}$  is shown in Fig. 1. A least-squares computer fit to six unconstrained Lorentz line shapes is shown through the data. The point symmetry of the  $\text{Fe}^{2+}$  site requires the nuclear electric field gradient to be axially symmetric with the principal axis  $z$  of the largest diagonalized ele-

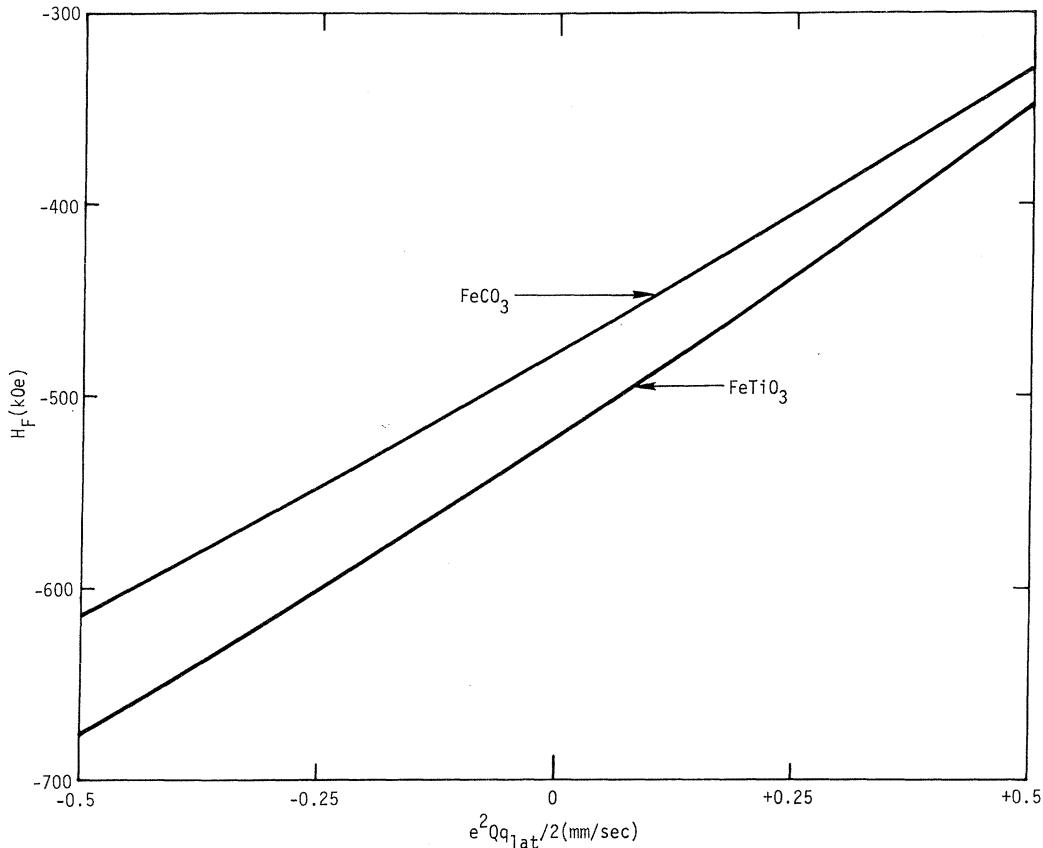


FIG. 2. Dependence of core-polarization contribution to the internal magnetic field  $H_F$  in  $\text{FeCO}_3$  and  $\text{FeTiO}_3$  (calculated as described in text) on lattice contributions to the nuclear electric field gradient.

ment  $V_{zz}$  parallel to  $c$ . Thus  $H_{\text{int}}$  and  $z$  are  $\parallel$  and simple analytical expressions<sup>9</sup> can be obtained for the transition energies in terms of  $|H_{\text{int}}|$ ,  $e^2qQ$ , and  $\delta$ , where  $e$  is the proton charge,  $q = V_{zz}/e$ ,  $Q$  is the nuclear quadrupole moment, and  $\delta$  is the isomer shift. The typical six-line hyperfine pattern observed for nonmagnetized randomly oriented powders of magnetically ordered  $\text{Fe}^{57}$  containing materials has relative absorption intensities 3:2:1:1:2:3 in order of ascending energy. The small  $H_{\text{int}}$  and large  $e^2qQ$  observed in ilmenite at 5°K shifts the  $|-\frac{3}{2}\rangle \rightarrow |-\frac{1}{2}\rangle$  transition to higher energy than the  $|+\frac{1}{2}\rangle \rightarrow |+\frac{3}{2}\rangle$  transition and leads to relative intensities 2:1:1:2:3:3 in order of ascending energy. The experimental values of  $H_{\text{int}}$ ,  $\frac{1}{2}e^2qQ$ , and  $\delta$  observed in the 5°K spectrum of ilmenite are given in Table I.

To determine the sign of  $H_{\text{int}}$ , an external magnetic field  $H_{\text{ext}}$  of 55 kOe was applied to the single-crystal mineral specimen of ilmenite. The absorber was at 87°K (in the paramagnetic state) and  $\vec{H}_{\text{ext}} \parallel c$ . The internal field observed at the  $\text{Fe}^{2+}$  nuclei was  $(41 \pm 3)$  kOe, which experimentally established the negative sign of  $H_{\text{int}}$  predicted by theoretical

arguments.<sup>2</sup> At 87°K and  $H_{\text{ext}} = 55$  kOe, the magnetization is far from saturated which accounts for the small reduction in  $H_{\text{int}}$ .

Okiji and Kanamori<sup>2</sup> have calculated the orbital  $H_{\text{orb}}$  and dipolar  $H_{\text{dip}}$  contributions to  $H_{\text{int}}$  for the  $\text{Fe}^{2+}$  sites in the trigonal crystals  $\text{FeTiO}_3$  and  $\text{FeCO}_3$  (ferrous carbonate crystallizes in space group  $R\bar{3}c$  and the  $\text{Fe}^{2+}$  site has 3 point symmetry). They express both  $H_{\text{orb}}$  and  $H_{\text{dip}}$  in terms of the valence contribution to the nuclear electric field gradient and calculate the core-polarization term  $H_F$  in conjunction with the experimental values of  $H_{\text{int}}$ . Based on previously reported  $\text{FeTiO}_3$  results ( $|H_{\text{int}}| = 70$  kOe and  $\frac{1}{2}e^2qQ = +1.14$  mm/sec)<sup>1</sup> they obtained  $H_F = -455$  kOe. This rather low value of

TABLE I. Hyperfine parameters of  $\text{Fe}^{2+}$  in  $\text{FeTiO}_3$  at 5°K.

$H_{\text{int}}$ (kOe)	$-43 \pm 3$
$\frac{1}{2}e^2qQ$ (mm/sec)	$+1.44 \pm 0.01$
$\delta$ (mm/sec) <sup>a</sup>	$+1.22 \pm 0.01$

<sup>a</sup>Relative to  $\alpha$ -Fe at room temperature.

$H_F$  compared with the expected free-ion value<sup>2,10</sup> was attributed by Okiji and Kanamori,<sup>2</sup> and more recently by Hazony,<sup>11</sup> to the covalent nature of  $\text{Fe}^{2+}$  in  $\text{FeTiO}_3$ . Our present low-temperature  $\text{FeTiO}_3$  results (Table I) differ considerably from previous ones; in addition, improved liquid-helium-temperature data for  $\text{FeCO}_3$  are now available [ $H_{\text{int}} = (+185 \pm 3)$  kOe,  $\frac{1}{2}e^2qQ = (+2.05 \pm 0.03)$  mm/sec].<sup>12-14</sup> Thus we have recalculated the internal-field contributions in both  $\text{FeTiO}_3$  and  $\text{FeCO}_3$  making the same assumptions as were made by Okiji and Kanamori. The recalculated values for  $\text{FeTiO}_3$  are  $H_{\text{orb}} = +420$ ,  $H_{\text{dip}} = +59$ , and  $H_F = -522$  kOe; for  $\text{FeCO}_3$ ,  $H_{\text{orb}} = +579$ ,  $H_{\text{dip}} = +85$ , and  $H_F = -479$  kOe.

In general, the quadrupole-coupling constant in ionic  $\text{Fe}^{2+}$  compounds will have both lattice and valence contributions. Usually neglect of lattice contributions to  $q$  is a major source of error in relating  $H_F$ , as calculated above, to the degree of covalency. Because of the axial symmetry present at the  $\text{Fe}^{2+}$  sites in both  $\text{FeTiO}_3$  and  $\text{FeCO}_3$ , the valence and lattice contributions to  $q$  may be ex-

pressed simply as  $q = q_{\text{val}} + q_{\text{lat}}$ . The extreme sensitivity  $H_F$  to  $q_{\text{lat}}$  is shown in Fig. 2 where we have evaluated  $H_F$  by the method of Okiji and Kanamori but have considered the possible presence of a small  $q_{\text{lat}}$  term. In ionic  $\text{Fe}^{3+}$  compounds where only  $q_{\text{lat}}$  is present,  $\frac{1}{2}e^2qQ$  values  $> 1$  mm/sec are observed. In  $\alpha\text{-Fe}_2\text{O}_3$ , which is structurally similar to  $\text{FeTiO}_3$ , the quadrupole splitting is  $\frac{1}{2}e^2qQ = (+0.440 \pm 0.012)$  mm/sec.<sup>15</sup> If a  $q_{\text{lat}}$  term of this magnitude were present in  $\text{FeTiO}_3$ , the derived value of  $H_F$  would change by 150 kOe (Fig. 2). Thus, until lattice contributions to  $q$  can be determined with confidence, correlations of covalency and calculated  $H_F$  values must be rather uncertain.

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