

## Magnetic ordering transition in $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{SiO}_3$ orthopyroxene

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### ABSTRACT

Mössbauer spectroscopy of polycrystalline synthetic orthopyroxene of composition  $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{SiO}_3$  demonstrates that magnetic ordering sets in at temperatures below 5 ( $\pm 2$ ) K. The low Fe concentration of the sample implies that spin correlations must extend over unit-cell dimensions ( $\sim 0.5$  nm or more), and that magnetic ordering can contribute to the third-law entropies of Fe-poor minerals.

### INTRODUCTION

Magnetic properties of minerals containing small concentrations of transition elements are poorly documented (e.g., Coey and Ghose, 1988). Although the spin-spin interactions are expected to be weak, the fact that most of the Earth's minerals contain relatively small concentrations of Fe and other paramagnetic ions motivates us to study the properties of such magnetically dilute minerals. Such an investigation is of interest both because it can give us a more complete understanding of the microscopic interactions within common rock-forming silicates and because magnetic ordering can contribute to the thermodynamic properties of minerals (e.g., Ulbrich and Waldbaum, 1976). In particular, we investigate a composition of 10% (molar) Fe in magnesium silicate that is typical of the Earth's upper mantle and is therefore of considerable interest in petrology and geophysics (e.g., Jeanloz and Thompson, 1983; Akaogi et al., 1989).

### METHODS AND RESULTS

We have used Mössbauer spectroscopy to examine orthopyroxene containing  $^{57}\text{Fe}$ . Approximately 50 mg of the polycrystalline sample was synthesized hydrothermally in  $\text{Ag}_{80}\text{Pd}_{20}$  capsules by means of standard piston-cylinder techniques. The synthesis was carried out from oxide components, and metallic Fe containing over 90%  $^{57}\text{Fe}$  was the ultimate source of the isotopic enrichment. The pressure and temperature of synthesis was 1.5 GPa and 900 °C, respectively, and the  $f_{\text{O}_2}$  was defined by the Fe-wüstite buffer. X-ray diffraction and electron microprobe analyses, along with Mössbauer spectroscopy, show that the sample is an orthopyroxene with a composition of  $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{SiO}_3$ , and that it contains no  $\text{Fe}^{3+}$  within our

limits of resolution (estimated to be  $\sim 1\%$  for  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ; cf. Hafner, 1975). This pyroxene was used as starting material in the study of Jeanloz et al. (1991).

Mössbauer spectra were obtained from room temperature to less than 2 K using a  $\text{Rh}^{57}\text{Co}$  source at the same temperature as the sample. The results are in good agreement with the spectra that have been published for orthopyroxenes, although most of the samples examined previously have significantly higher Fe concentrations than the one studied here (Bancroft et al., 1967; Evans et al., 1967; Marzolf et al., 1967; Shenoy et al., 1969; Virgo and Hafner, 1970; Annersten et al., 1978; Srivistava, 1986, 1987; Wiedenmann et al., 1986; Rossman, 1980; Hawthorne, 1988; Dyar et al., 1989; Straub et al., 1991). The spectra can be analyzed in terms of two doublets, corresponding to Fe in the M1 and M2 sites of the structure with space group *Pbca* (Fig. 1; Table 1). The doublets have similar isomer shifts and widths but unequal quadrupole splitting and amplitude, reflecting the differing amounts of distortion of the two sites and the preferential occupancy of Fe in the M2 site.

The Mössbauer spectrum of  $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{SiO}_3$  orthopyroxene at 4 ( $\pm 1$ ) K clearly shows the onset of magnetic ordering (Fig. 2). We interpret the spectrum in terms of three sites: one with a magnetic hyperfine relaxation combined with a static quadrupole interaction and two with pure quadrupole interactions. The fitting was done assuming a random  $\gamma$ -ray orientation and three sites for the powder sample, along with the following spin Hamiltonian:

$$\begin{aligned} H = & -\mu H_{\text{hyp}}[I_z \cos \theta + (I_x \cos \phi + I_y \sin \phi) \sin \theta] \\ & + eQV_{zz}I[4I(2I - 1) \\ & \cdot [3I_z^2 - I(I + 1) + \eta(I_x^2 - I_y^2)]. \end{aligned}$$

Here,  $eQV_{zz}$  is the quadrupole coupling,  $H_{\text{hyp}}$  the hyperfine field,  $I$  the nuclear spin and its respective operators,  $\eta$  the asymmetry parameter of the electric field gradient

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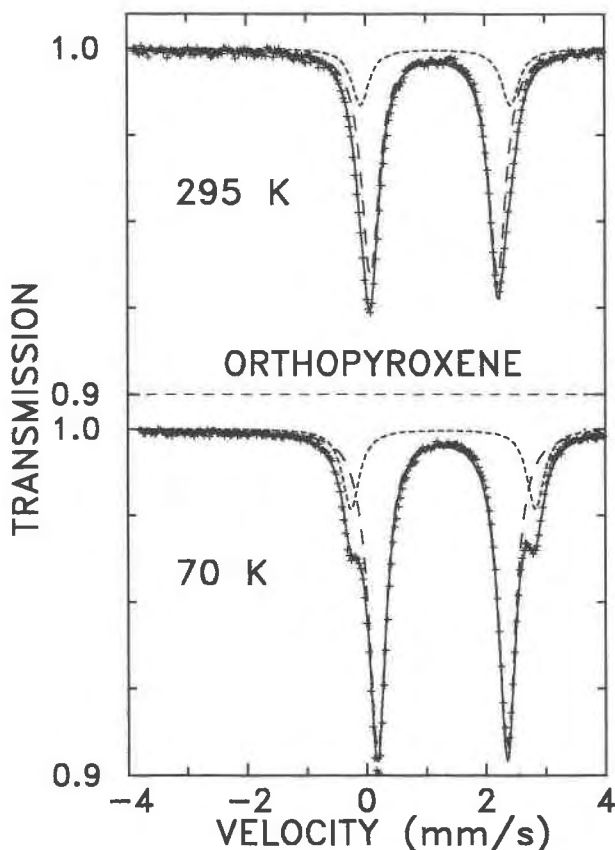


Fig. 1. Mössbauer spectra of polycrystalline  $\text{Mg}_{0.957}\text{Fe}_{0.1}\text{SiO}_3$  orthopyroxene at 295 and 70 K are shown relative to Fe metal and corrected to a room-temperature source. Fits to the M1 and M2 doublets and the total spectrum are indicated by short- and long-dashed curves and by a solid curve, respectively.

(efg) tensor, and  $\theta$  and  $\phi$  are the angles specifying the directions of  $H_{\text{hyp}}$  with respect to the efg (Abragam, 1964).

The spectral parameters derived for the two nonmagnetic sites are the same as those obtained from the spec-

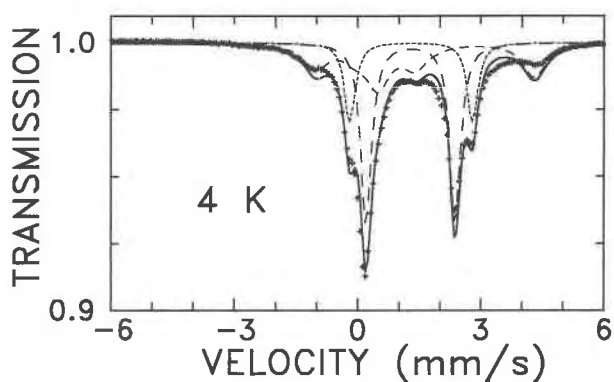


Fig. 2. Mössbauer spectrum of polycrystalline  $\text{Mg}_{0.957}\text{Fe}_{0.1}\text{SiO}_3$  orthopyroxene at 4 K showing the onset of magnetic ordering. The solid line through the experimental points is a least-squares fit to the data, with the model including the full spin Hamiltonian described in the text. Three spectral sites are assumed present, one magnetic and two nonmagnetic. The computed sub-spectra correspond to nonmagnetic M1, nonmagnetic M2, and magnetic M2 sites, respectively (cf. Fig. 1). The magnetic interaction is due to spin-spin relaxation, but the fitting was performed assuming a static field with artificially broad lines.

trum at 70 K. As for the magnetic component, we assumed a static field with a broad absorption line in order to circumvent the effects of magnetic relaxation. The results are as follows:  $H_{\text{hyp}} = 121 (\pm 7)$  kOe, isomer shift =  $1.49 (\pm 0.02)$  mm/s, quadrupole splitting =  $2.1 (\pm 0.1)$  mm/s, line width =  $1.2 \text{ mm/s}$ ,  $\eta = 0.1 (\pm 0.1)$ ,  $\theta = 12 (\pm 5)^\circ$ , and  $\phi = 0 (\pm 10)^\circ$ . That the quadrupole splitting is indistinguishable, within the experimental uncertainties, from that of the nonmagnetic M2 site (Table 1) strongly suggests that the magnetic (spin-spin) interaction emanates from Fe in the M2 site. The fact that the asymmetry parameter  $\eta \sim 0$  (and consequently  $\phi \sim 0^\circ$ ) implies a quasi threefold symmetry around the magnetically split  $\text{Fe}^{2+}$ , with moments tilted by  $12 \pm 7^\circ$  relative to the symmetry axis. We note that similar results have previously been obtained on more Fe-rich samples (e.g., Srivistava, 1986, 1987).

## DISCUSSION

Our fit indicates that 25% of the  $\text{Fe}^{2+}$  in M2 are magnetically ordered in our sample at 4 K. It may well be that Fe in M1 orders at temperatures lower than those we studied. We anticipate, by analogy with data from the literature on pyroxenes and other silicates (e.g., Coey and Ghose, 1988), that the ordering is antiferromagnetic in nature. However, this cannot be proved from the Mössbauer data alone and will require independent documentation. In particular, we do not have sufficient information to interpret our results in terms of the detailed model presented by Wiedenmann et al. (1986).

There are eight M2 sites in the unit cell of orthopyroxene [ $Z = 8 M_2\text{Si}_2\text{O}_6$  ( $M = \text{Mg, Fe}$ )]. Hence, for our composition, only  $\sim 1.3$  M2 sites on average contain Fe in each unit cell, the remaining Fe being fractionally distributed in one of the eight M1 sites of the unit cell. The

TABLE 1. Mössbauer parameters for  $\text{Mg}_{0.957}\text{Fe}_{0.1}\text{SiO}_3$  orthopyroxene\*

Temperature	295 K	70 K
<b>M1 site</b>		
Isomer shift	1.179(2)	1.295(4)
Quadrupole splitting	2.51(1)	3.08(1)
Line width	0.38(1)	0.35(1)
Amplitude (normalized)	0.20(1)	0.20(1)
<b>M2 site</b>		
Isomer shift	1.147(2)	1.270(1)
Quadrupole splitting	2.22(2)	2.17(1)
Line width	0.38(1)	0.35(1)
Amplitude (normalized)	0.80(1)	0.80(1)

\* All values except the nondimensional relative amplitudes are in millimeters per second, with the isomer shift being relative to Fe metal and corrected to a room-temperature source and the line width being the full width at half maximum of the absorption peak. The relative amplitudes for the M1 and M2 peaks were determined at 70 K and are assumed unchanged in fitting the 295 K spectrum (e.g., Virgo and Hafner, 1968). Uncertainties in the last digit are given in parentheses.

magnetic ordering of approximately one out of four occupied M2 sites at 4 K consequently suggests spin correlations extending over unit-cell dimensions of at least 0.5 nm. Such correlation lengths are reasonable, with pressure-amorphized  $\text{Fe}_2\text{SiO}_4$  offering an example in which antiferromagnetic correlations probably extend some 1–2 nm (Kruger et al., 1992). Therefore, although it may be surprising to observe magnetic ordering in a sample with a 90% enstatite component, we actually infer that compositions with as little as 3–5% ferrosilite component could exhibit ordering at low temperatures. For comparison, we note that  $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$  olivine and  $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{SiO}_3$  in the high-pressure perovskite structure also order magnetically at  $\sim 5$  K (Rao et al., 1979; Jeanloz et al., 1991).

Magnetic ordering contributes to the thermodynamic properties of crystals and must be considered in evaluating the third-law entropies of transition metal-bearing minerals (Ulbrich and Waldbaum, 1976; Robie et al., 1982a, 1982b). From the present work, it is evident that magnetic ordering must even be considered for the common minerals that contain relatively little Fe. For  $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{SiO}_3$  pyroxene, the ideal magnetic contribution to the entropy is 1.3 J/mol·K, according to Ulbrich and Waldbaum (1976). This is small when compared with the value, but not the uncertainty, of the entropy at 298 K: 67.9 ( $\pm 0.4$ ) J/mol·K for  $\text{MgSiO}_3$  enstatite (Robie et al., 1978).

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