Crystal/chemical structures and magnetic properties of naturally occurring $Mn_{1.7}Fe_{1.3}O_4$

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An unusually pure $Mn_xFe_{3-x}O_4$ sample ($x \cong 1.3$) from a regionally metamorphosed ore body is expected to exhibit an approach to thermodynamic equilibrium unattainable in synthetic materials. This expectation is confirmed by the observation of (1) a small tetragonal distortion and (2) a complete ordering of Fe on the B sublattice. ^{57}Fe Mössbauer spectra, obtained at 298, 175, 125, and 92 K and in an external field of 30 kG at 92 K, exhibit magnetic hyperfine splitting requiring the fitting of two subspectra, I and II. At 298 K, $H_{eff} = 418$ kOe, $\alpha = 0.36$ mm s^{-1}, and $\epsilon \approx 0$ for the more intense subspectrum I, whereas for II $H_{eff} = 403$ kOe, $\delta = 0.34$ mm s^{-1}, and $\epsilon \cong -0.15$ mm s^{-1}. The two subspectra are not split by a 30 kG external field. Subspectra I and II correspond to Fe^{3+} ions located on a single magnetic sublattice. Subspectrum II is assigned to Fe^{3+} ions in regions with locally, large tetragonal distortions as a consequence of Mn^{3+} clustering, which has often been invoked to explain the crystal chemistry and physical properties of $Mn_xFe_{3-x}O_4$.

INTRODUCTION

Among the spinel ferrites, the $Mn_xFe_{3-x}O_4$ system, for $1 < x \leqslant 3$, is perhaps equaled only by Fe_3O_4 (Ref. 1) in the challenges it has presented to the development of a comprehensive description of its structure, properties, and their interrelationships.[2] Thus, notwithstanding the large body of previous works, the crystal chemistry, and electrical and magnetic properties of $Mn_xFe_{3-x}O_4$ are of current interest.[3] The principal obstacle in and between investigations of this system is the difficulty in achieving equilibrium among a number of interrelated processes. For example, the occurrence of the tetragonal distortion is determined not only by the achievement of equilibrium in the cation distribution of the Mn and Fe ions but also by the approach to equilibrium of redox processes among the +3 and +2 oxidation states of Fe and Mn and by electron transfer processes which can occur at temperatures too low for the concomitant changes in atomic positions necessary for thermodynamic equilibrium. Therefore, the availability of a naturally occurring $Mn_xFe_{3-x}O_4$ sample from a setting suggesting a high degree of thermal equilibration has generated this study as the investigation of this sample might provide a unique opportunity to further our understanding of the $Mn_xFe_{3-x}O_4$ system. This is a report of some of our studies of this mineral which is known as iwakiite.[4]

The close approach of the crystal/chemical structures in this sample to thermodynamic equilibrium is indeed demonstrated by (1) the observation of a tetragonal distortion at a manganese content lower than that for any tetragonally distorted synthetic sample, (2) an ordering of Fe^{3+} exclusively on the B sites, and (3) compelling evidence for Mn^{3+} clustering.

EXPERIMENT

The iwakiite specimen used in this study comes from the Type locality, Gozaisho Mine, near the city of Iwaki, Japan.[4]

The iwakiite occurs in a regionally metamorphosed ore deposit in which the mineral assemblage indicates formation temperatures between 675 and 975 K and pressures between 0.4 and 0.8 GPa, conditions appropriate to the medium pressure epidote-amphibolite metamorphic facies.[5] The regional basis of the metamorphism leading to this occurrence of iwakiite indicates heating and cooling rates much lower than those obtainable in a laboratory synthesis, a more facile mass exchange between solid and vapor phases,[4,6] and hence, greater opportunities for attaining equilibrium crystal/chemical structures.

Chemical analysis of iwakiite from the Gozaisho Mine was performed by earlier investigators and the composition was found to be $Mn_{1.644}Fe_{1.278}Mg_{0.035}Al_{0.014}Ti_{0.009}O_4$. As ions other than Fe and Mn are present at less than 0.1 atoms per AB_2O_4 formula unit, the composition of this specimen may be given to a good approximation as $Mn_{1.7}Fe_{1.3}O_4$.

X-ray powder diffraction was performed using Cu$K\alpha$ radiation and a powder diffractometer. After repeated grinding with an agate motor and pestle, ultrasonic dispersal and separation with a hand magnet, a pure iwakiite specimen with a particle size less than 50 μm was mixed with a silicon internal standard and the following lattice constants were determined from the (404) and (440) lines: $a_0 = 0.8514$ nm and $c_0 = 0.8552$ nm ($c/a = 1.004$), in good agreement with previous values.[4]

The techniques for obtaining[7,8] and analyzing the Mössbauer spectra have been reported in detail elsewhere. The only aspect worthy of note here is the higher resolution of the room-temperature spectra (512 data points) relative to the low-temperature spectra (256 data points).

RESULTS AND DISCUSSION

The ^{57}Fe Mössbauer spectra are shown in Figs. 1 and 2. In Fig. 1 the data (points) are shown with the results of a single hyperfine pattern fit (solid line). The inadequacy of
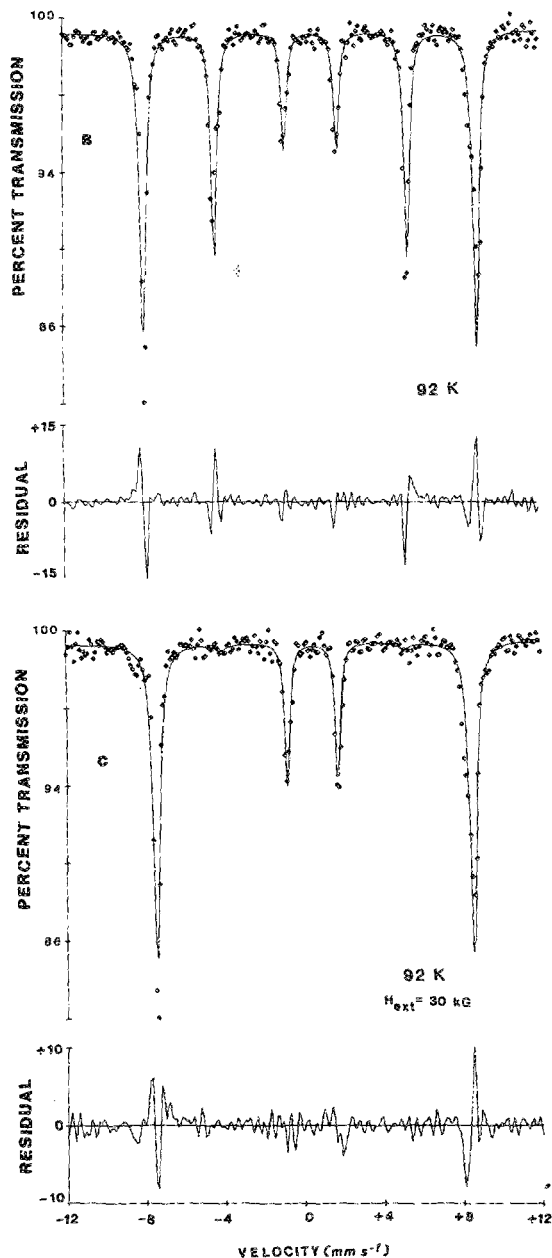
FIG. 1. ^{57}Fe Mössbauer spectra of iwakiite at (a) 92 K and (b) 92 K, and in an externally applied field of 30 kG. The points are the experimental data and the solid line is the fit of a *single* hyperfine pattern to the data. The RESIDUAL is the difference between the data and the fitted pattern. The large amplitude of and considerable structure in the RESIDUAL are to be noted.
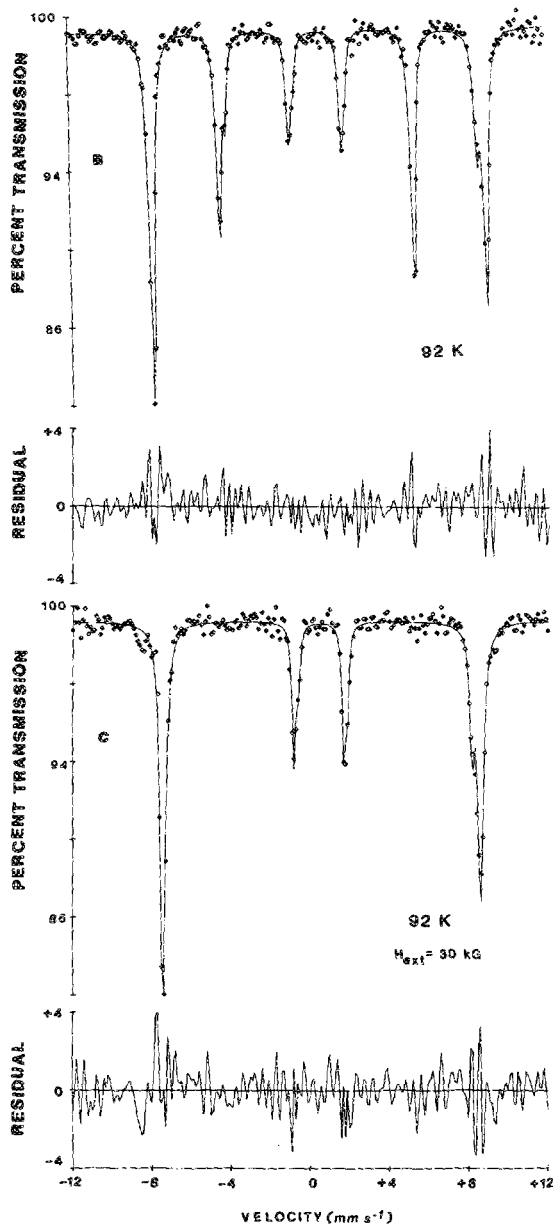
FIG. 2. Same as Fig. 1 except that the solid line now represents a fit of *two* hyperfine patterns to the data. Comparison with Fig. 1 shows a considerable reduction in the amplitudes of the RESIDUAL and a randomization of the structure in the RESIDUAL.

this fitting scheme is clearly evidenced in the pronounced structure in the plots of the difference between the data and the fitted pattern, e.g., the RESIDUAL, and in the maximum excursions in magnitude of the RESIDUAL at individual points which is 4–5 times that expected. Further, the structure in the RESIDUAL indicates the presence of another hyperfine pattern. Therefore, the spectra were fitted to two hyperfine patterns and the results are shown in Fig. 2. The improvement in the fits is clearly evidenced in the close correspondence between the data and fits, especially for the line near + 8 mm s^{-1}, in the reduction of the magnitude of the RESIDUAL, and in the randomization in the structure

of the RESIDUAL. The hyperfine parameters resulting from the two pattern fits are given in Table I.

Irrespective of how the data are fitted, it is clear that the applied, longitudinal magnetic field of 30 kG occasions no additional splitting of the spectrum even though the sample is magnetically saturated [see Figs. 1(c) and 2(c)]. If Fe occupied the A and B sites of the spinel structure, a splitting of the spectrum into two distinct components would be expected.[9] The application of the external field leads to a reduction of H_{eff} for subspectra I and II, and the Fe^{3+} ions are, therefore, located on the B sites.[9] Thus, with respect to the iron cation distribution, this manganese ferrite is highly ordered.

The observation of a bulk tetragonal distortion provides further evidence of the high degree of thermal equilibration

TABLE I. ^{57}Fe Mössbauer parameters of iwakiite at several temperatures and in an applied magnetic field.

Temperature	Subspectrum	H_{eff} (kOe)	ϵ (mm s^{-1})	$\Delta(\delta)^{a}$ (mm s^{-1})	Integrated intensity
298 K	I	418 (4)^{b}	0.03 (2)		85
	II	403 (3)	− 0.15 (3)	003 (1)^{c}	15
175 K	I	480 (1)	0.07 (1)		67
	II	467 (1)	− 0.13 (2)	0.018 (6)	33
125 K	I	498 (1)	0.06 (1)		67
	II	486 (1)	− 0.12 (1)	− 0.004 (4)	33
92 K	I	507 (1)	0.05 (1)		75
	II	495 (1)	− 0.15 (1)	0.005 (5)	25
92 K	I	481 (1)	0.05 (1)		75
$H_{ext} = 30\,kG$	II	469 (1)	− 0.15 (1)	− 0.002 (3)	25

$^{a}\Delta(\delta) = \delta_{IS}(I) - \delta_{IS}(II)$.
^{b}Number in parentheses indicates error in last digit of reported values.
^{c}Relative to an iron metal absorber, $\delta(I) = 0.365(1)$ and $\delta(II) = 0.339(8)$ at 298 K.

in this sample. The cubic-tetragonal phase boundary at 300 K had been placed previously at $x \approx 1.9$ in $Mn_xFe_{3-x}O_4$ (Ref. 10) and only noncooperative local distortions were proposed for a synthetic sample with an x value of 1.66.[11] In contrast, the tetragonally distorted iwakiite indicates that the equilibrium, cubic-tetragonal phase boundary is closer to an x value of ~ 1.7.

It now remains to provide some insights into the nature of the iron sites giving rise to subspectra I and II. The difference in δ is not statistically significant and is in all likelihood an artifact of the fitting scheme that treats δ as a free variable. The quadrupole interaction is significant and indicates that the iron species of subspectrum II is subject to a much larger field gradient and presumably larger site distortion than that of subspectrum I. It is proposed that the greater local site distortion results from a clustering of Mn^{3+} ions in the vicinity of the Fe^{3+} species of subspectrum II. The occurrence of an Fe^{3+} ion in a cluster of Mn^{3+} ions would lead to a decrease in the magnitude of H_{eff}[12,13] in good accord with the relative magnitudes of H_{eff} (I) and H_{eff} (II).

CONCLUSION

In comparison with synthetic samples, the expectation of a closer approach to thermodynamic equilibrium of the crystal/chemical structures of a manganese ferrite (iwa-kiite) occurring under the pressure, temperature, and time conditions of regional metamorphism has been confirmed. The Fe^{3+} ions occur exclusively on the octahedral (B) site. The x value in $Mn_xFe_{3-x}O_4$ at the cubic-tetragonal phase boundary is also lowered to ~ 1.7 in this naturally occurring sample. Convincing evidence for Mn^{3+} clustering is also provided by ^{57}Fe Mössbauer spectroscopy.

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