High-pressure ^{57}Fe Mössbauer study of Fe_3O_4 at 298 K

B. J. Evans and Lu-San Pan
Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 49109

At 298 K, ^{57}Fe Mössbauer spectra of Fe_3O_4 exhibit an increase in complexity with increasing pressure in the range 1×10^5 to 5×10^9 Pa. There is an incipient splitting of the B-site pattern into two components with relative intensities of 3 : 1. For the more intense pattern, H_n is 462 kOe and 470 kOe at 1×10^5 and 5×10^9 Pa, respectively; the corresponding values for the less intense patterns are 454 and 448 kOe. The B-site electric quadrupole interactions also exhibit appreciable changes. The A-site pattern exhibits no qualitative changes in line profiles and only modest changes in the hyperfine interaction parameters are observed. For example, at 1×10^5 and 5×10^9 Pa, H_n is 492 and 490 kOe, respectively; the corresponding isomer-shift values are 0.258 and 0.233 mm s^{-1}. These results are consistent with the broadening of the lines of the B-site patterns at ambient temperature and pressure arising from the different relative orientations of the direction of magnetization and of the axes of the electric field gradient tensor.

INTRODUCTION

High-pressure investigations of low-mobility conducting oxides can provide critical data for pheonomenological descriptions of their electronic structures.[1] Such investigations would be expected to be particularly useful for Fe_3O_4 inasmuch as no simple model of conducting oxide provides an adequate description of its electrical and magnetic properties even at 300 K. Thus, the earlier report of diminishing fine structure with increasing pressure of the B-site component in the ^{57}Fe Mössbauer spectrum of Fe_3O_4 would support a marginally delocalized state for the conduction electrons.[2] These results occasion some concern, however, inasmuch as two B-site components with different isomer shifts were also reported to have been observed at 295 K and a pressure of 10^5 Pa, in contrast to reported results on stoichiometric or nearly stoichiometric magnetite specimens.[3]

This investigation has been undertaken to determine the influence of pressure on the Mössbauer spectrum of a nearly stoichiometric sample of Fe_3O_4 that exhibits no isomer shift induced splitting of the B-site patterns of the spectrum at 300 K and a pressure of 10^5 Pa.[4] In contrast to the earlier report, the complexity of the ^{57}Fe Mössbauer spectrum of Fe_3O_4 has been observed to increase with increasing pressure in the range 1×10^5 to 5×10^9 Pa. This increase in complexity is not due to differences in isomer shifts at the B site. An interpretation of the data indicates that the electronic structure of Fe_3O_4 at 300 K undergoes no qualitative changes at these moderate increases in pressure.

EXPERIMENT

The sample employed in this investigation has been characterized in a number of earlier investigations.[5,6] The lattice constant is 8.936×10^{-1} nm. Wet chemical analysis of the iron content led to a value of 72.40 ± 0.03 wt. % (ideal Fe_3O_4 value is 72.36 wt. %). The temperature of 119 K for the Verwey transition indicates a deviation x from ideal stoichiometry, in the formula $Fe_{3-x}O_4$, that does not exceed 0.0075.

The high-pressure Mössbauer technique, employing boron carbide anvils and a strain gauge controlled feedback loop for maintaining the pressure constant within $\pm1\times10^8$ Pa during the long periods required to obtain a spectrum, has been described before.[7] A typical spectrum was obtained in 24 h. Spectra were obtained at ambient pressure (1×10^5 Pa), 2.8×10^9 and 5.0×10^9 Pa.

A constant acceleration spectrometer, with a symmetric, triangular velocity waveform and a 1024 channel multichannel analyzer, was used to obtain the spectra. A single spectrum consisted of 512 data points, which correspond to a twofold increase in resolution over that usually employed in studies of Fe_3O_4. The source was a 50-mCi ^{57}Co/Pd source and both source and absorber were held at 298 K. Iron metal was used to calibrate the spectrometer.

The general scheme for fitting the spectra has been described previously.[8] The fitted variables for each pattern are the magnetic hyperfine field H_n, the isomer shift δ, the electric quadrupole interaction ϵ, one-intensity parameter I_1, and three linewidths Γ_i ($i=1,2,3$). The widths and intensities are assumed to be symmetric relative to the center of gravity of the patterns. However, because of the important role played by the relative intensities of the patterns, in the interpretation of the spectra, fittings were also performed in which the intensities of all of the lines in each pattern were free variables. The adequacy of the fits were based on the MISFIT parameter and the absence of any structure in the plots of the residuals. The MISFIT values were between 0.4% and 0.6% for the fits involving constrained intensities and between 0.01% and 0.09% for the fits with widths and intensities as free variables.

RESULTS

^{57}Mössbauer spectra of Fe_3O_4 at three different pressures are shown in Fig. 1. The points are the experimental data and the solid lines are results of fitting the spectrum.

Despite some initial concern,[9] it is now well established

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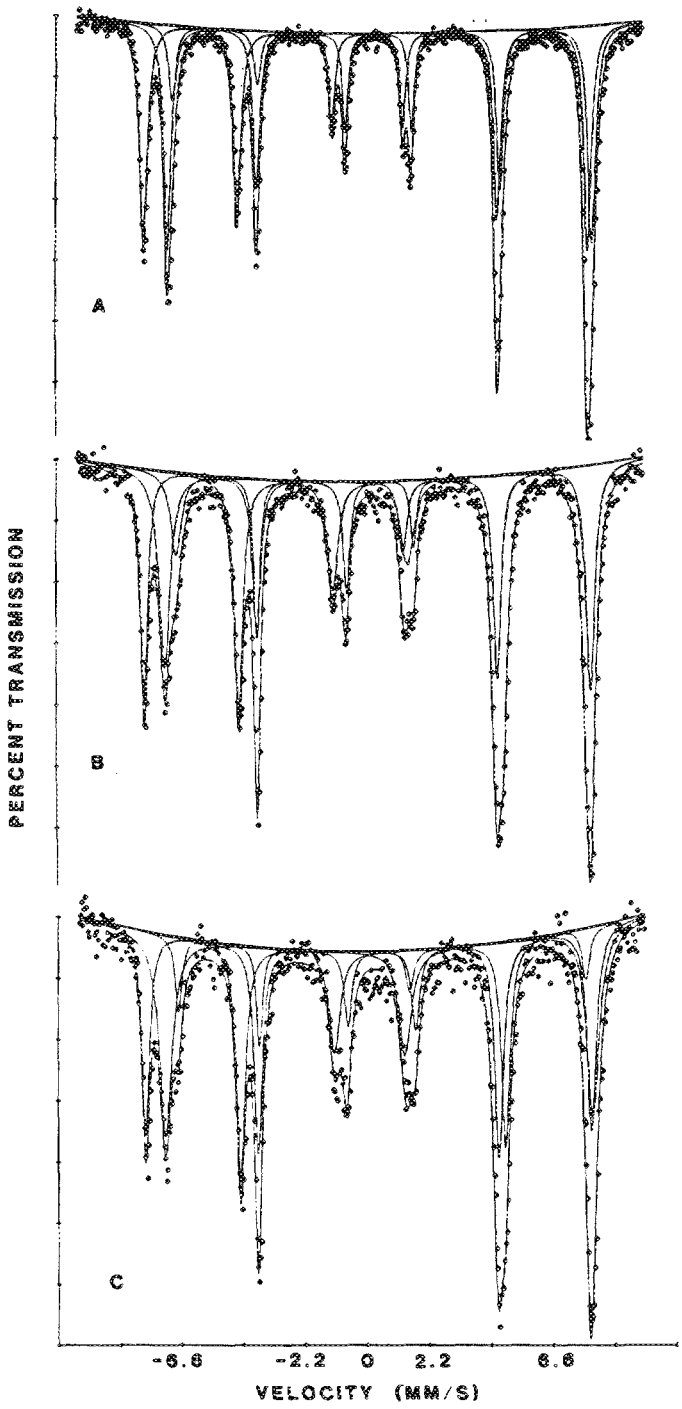

FIG. 1. ^{57}Fe Mössbauer spectra of Fe_3O_4 at 298 K and different pressures. (a) 1×10^5 Pa (ambient pressure). (b) 2.8×10^9 Pa. (c) 5.0×10^9 Pa. The solid lines show the deconvolution of the fitted spectrum into the two B-site and one A-site component.

that there are two components in the B-site pattern and only one component in the A-site pattern. The two B-site patterns arise from differences in the combined magnetic hyperfine the electric quadrupole interactions as a consequence of differences in the orientation of the magnetization and of the principal axis of the electric field gradient.[10,11] Magnetic dipolar fields have also been shown to contribute to the splitting of the B-site pattern.[11] Therefore, each of the spectra have been fitted to three components. The parameters of the fit are shown in Table I.

DISCUSSION

The fits of two components to the B-site pattern and one to the A-site pattern adequately account for the spectra in the pressure range investigated. Thus, it is clear that at ambient pressure the two components of the B-site pattern differ only in the algebraic values of ϵ and in the magnitudes of H_n. The isomer shifts are indistinguishable within experimental error, contrary to the earlier report.[2]

The splitting of the low-velocity line in the B-site pattern increases with increasing pressure and the analysis of the data shows this to be due primarily to increasing differences in H_n and ϵ. These results can be understood in terms of the following considerations: For combined magnetic hyperfine H_n and electric quadrupole ϵ interactions, the lines are shifted according to the following relationship when $H_n > \epsilon$:

$$\epsilon = 1/4eQV_{zz}(3\cos^2\theta - 1),$$

where θ is the angle between the z direction of the electric field gradient tensor and the magnetization direction. [111] is the easy magnetization axis for Fe_3O_4 and it is also the principal axis of the field gradient tensor. The four equivalent [111] directions are indistinguishable, however, in the case of the electric field gradient. Consequently, only for one of the [111] directions is θ equal to 0°; for the remaining three directions θ is 70.5°. There are, therefore, two values for ϵ at the B site. One has a magnitude 1/3 of the other, is opposite in sign, and occurs three times more frequently than the other. A calculation of the magnetic dipolar fields at the B site has also been made and these dipolar fields make an additional contribution to the splitting of the B site patterns as shown in Fig. 2.[4]

As shown in Fig. 1, lines 2 and 3 and the line at the highest positive velocity position show no tendency to broaden as the pressure is increased. This result indicates that both the magnetic dipolar and electric quadrupole interaction are increasing with increasing pressure. For, as seen in Fig. 2, an increase in the splitting of the B-site pattern at line

TABLE I. ^{57}Fe Mössbauer parameters of Fe_3O_4 at several different pressures and for three component fits.

Pressure	H_n(A)[a]	H_n(B1)[a]	H_n(B2)[a]	δ(A)[b]	δ(B1)[b]	δ(B2)[b]	ϵ(A)[c]	ϵ(B1)[c]	ϵ(B2)[c]
1×10^5 Pa	493	462	454	0.26	0.63	0.63	0.01	−0.01	0.03
2.8×10^9 Pa	490	468	448	0.23	0.64	0.61	−0.01	−0.04	0.09
5.0×10^9 Pa	491	470	448	0.23	0.64	0.60	−0.02	−0.05	0.10

[a] In units of kOe. Typical errors for H_n were ± 3 kOe.
[b] In units of mm s^{-1} and measured relative to an Fe metal absorber. Typical errors were ± 0.01 mm s^{-1}.
[c] In units of mm s^{-1}. Typical errors were ± 0.01 mm s^{-1}.

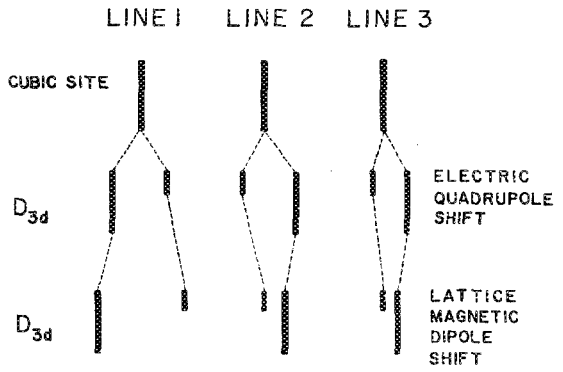

FIG. 2. A schematic representation of the shifts in the line positions of the B-site spectrum as a consequence of the electric quadrupole interactions and magnetic dipolar fields.

1 would not be accompanied by an increase in the width of line 2 for pressures that are not high enough to cause a crossing of the two B-site components.

There is some ambiguity regarding the difference in δ of the two B-site components when the sample is under pressure. If the δ(B1) and δ(B2) are treated as independent and free variables, the results presented in Table I are obtained. On the other hand, if δ(B1) and δ(B2) are constrained to be equal, the value of MISFIT remains virtually unchanged and no pronounced structure is observed in the plot of the residual. The difference in isomer shifts at high pressure is probably an artifact of attempting to fit the strongly overlapping lines.

CONCLUSION

The influence of pressure on the ^{57}Mössbauer spectrum of Fe_3O_4 at 298 K requires that the B sites be treated as crystallographically equivalent; the two components in the B site are shown to be due to differences in magnetic dipolar fields and in the combined electric quadrupole and magnetic hyperfine interactions of the B site. With increasing pressure these differences are amplified and the B-site pattern exhibits an increased broadening and incipient splitting of some lines while other lines exhibit no tendency to either split or broaden.

These results are entirely consistent with those expected for a well-defined electronic state for the B-site Fe ion. Within the range investigated, high pressures appear to bring about no qualitative changes in the electronic structure of Fe_3O_4 as the high-pressure data can be understood by means of the same model developed to explain the ^{57}Fe Mössbauer spectrum at 1×10^5 Pa.

ACKNOWLEDGMENT

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[1]H. G. Drickamer and C. W. Frank, *Electronic Transitions and the High Pressure Chemistry and Physics of Solids* (Chapman and Hall, London, 1973).
[2]N. A. Halasa, G. DePasquali, and H. G. Drickamer, Phys. Rev. B **10**, 154 (1974).
[3]B. J. Evans, AIP Conf. Proc. **24**, 73 (1975).
[4]B. G. Falk, L.-S. Pan, B. J. Evans, and E. F. Westrum, Jr., J. Chem. Thermodynamics **11**, 367 (1979).
[5]E. F. Westrum, Jr. and F. Gronvold, J. Chem. Thermodynamics **1**, 543 (1969).
[6]R. Argon, D. J. Buttrey, J. P. Shepherd, and J. M. Honig, Phys. Rev. B **31**, 430 (1985).
[7]B. J. Evans and G. Amthauer, J. Phys. Chem. Solids **41**, 985 (1980).
[8]R. Vogel and B. J. Evans, J. Magn. Magn. Mater. **13**, 294 (1979).
[9]B. J. Evans, AIP Conf. Proc. **5**, 296 (1973).
[10]L. Haggstrom, H. Annersten, T. Ericsson, R. Wapplin, W. Karner, and S. Bjarman, Hyperfine Interactions **5**, 201 (1978).
[11]A. M. van Diepen, Phys. Lett. **57A**, 354 (1976).