PHYSICAL REVIEW B VOLUME 50, NUMBER 9 1 SEPTEMBER 1994-I

High-pressure phase of magnetite

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(Received 27 April 1994)

Mössbauer spectroscopy and x-ray diffraction were employed to investigate the magnetic and structural properties of the high-pressure monoclinic phase of magnetite. Measurements were performed to 66 GPa at 300 K using diamond anvil cells. Based primarily upon the Mössbauer parameters, the following features of the high-pressure phase were deduced. With increasing pressure the high-pressure phase evolves at $P \geq 25$ GPa and its abundance increases monotonically at the expense of the low-pressure cubic phase. The high-pressure phase is not magnetic at 300 K and its monoclinic structural features resemble that of the low-pressure phase. The tetrahedral and octahedral sites characteristic of the inverse spinel structure, albeit distorted, remain the building blocks of the high-pressure phase. The fast electron hopping between Fe^{3+} and Fe^{2+} at the octahedral sites prevails to the highest pressure. It is suggested that the cubic→monoclinic→cubic hysteretic cycle involves a mild displacive phase transition not affecting the coordination number of any of the iron cations.

I. INTRODUCTION

Magnetite (Fe_3O_4) is the oldest known magnetic material, the original substance for which Néel ferrimagnetism was described ($T_N = 851$ K), and one of the first materials subjected to high-pressure studies. As early as the mid 1920s, Bridgman[1] carried out a series of studies to determine its equation of state. In the mid-1970s Mao *et al.*,[2] in order to improve the bulk modulus data determined earlier by Bridgman, performed extensive high-pressure x-ray diffaction studies, using diamond anvil cells (DAC's). In the course of those studies, near 25 GPa, a new crystallographic phase was discovered, coexisting with the ambient-pressure phase. Upon decompression close to ambient pressure, magnetite reverted completely to its original phase. The new phase, which we designate as Fe_3O_4(II), was indexed as monoclinic and suggestive of a configuration containing two molecules per unit cell with all cations in a sixfold coordination.

This work was stimulated by the interest in the nature of magnetic compounds, the Mott insulators,[3,4] at high pressures. Fine tuning of electron bands by external pressure provides a unique method for elucidating, in general, the nature of magnetism with decreasing interatomic distances. In particular, it is expected that structural and magnetic information in the high-pressure regime will be extremely valuable, bearing in mind the unusual physical properties of magnetite and their geophysical implications.

It is now well established that Mössbauer spectroscopy (MS) is the only method available for studies of magnetism at very high pressures.[5,6] Concurrently with information on magnetic ordering via the hyperfine interaction, Mössbauer spectroscopy also provides details on local structure and symmetry. In this work we carried out ^{57}Fe Mössbauer spectroscopy in conjunction with x-ray diffraction (XRD) to pressures of 66 GPa using DAC's. High-pressure Mössbauer spectroscopy studies of Fe_3O_4 have been previously[7] reported by Halasa, De Pasquali, and Drickamer. Using high-pressure Bridgman cells to 15 GPa, the influence of pressure on the MS hyperfine parameters was the main subject investigated. In this paper we shall not deal with the high-pressure properties of the cubic spinel Fe_3O_4(I) but rather we shall concentrate on the monoclinic phase Fe_3O_4(II) which is prevalent at $P > 25$ GPa.

II. EXPERIMENTAL

Samples for Mössbauer spectroscopy and x-ray diffraction measurements were synthesized by using the solid-solid reaction of Fe and Fe_2O_3. Stoichiometric quantities of the constituents were thoroughly mixed and the reaction took place in an evacuated quartz tube at 1100 °C. For MS studies, samples were prepared of ^{57}Fe-enriched Fe_2O_3 and natural iron metal. Because of the milligram amounts involved in the former, the mixture placed in a Pt boat was surrounded by gram amounts of chemically well-defined magnetite. The sample quality was checked with x-ray diffraction and Mössbauer spectroscopy. The high-pressure cells were of the Mao-Bell type[8] and the ruby-fluorescence method was used for manometry. Measurements were conducted at room temperature.

III. RESULTS AND DISCUSSION

Typical MS and XRD spectra at various pressures are shown in Fig. 1. The XRD data are in accordance with Mao *et al.*[2] As can be seen, the Mössbauer spectrum at 26 GPa clearly shows a "dip" near zero velocity, a first indication of the onset of the new phase. With increasing pressure the absorption intensity of the Fe_3O_4(II) component increases and at 66 GPa, the highest pressure applied, it surpasses the Zeeman-split component of

0163-1829/94/50(9)/6446(4)/$06.00

TABLE I. Room-temperature values of IS, QS, and hyperfine field H_i for Fe_3O_4(I) and Fe_3O_4(II) at 0.1 MPa and 66 GPa. The IS is relative to α-Fe at 300 K. Numbers in parentheses are errors in last figure. Values for Fe_3O_4(I) are from Ref. 9.

	Fe_3O_4(I) at 0.1 MPa		Fe_3O_4(II) at 66 GPa	
	A	B	A'	B'
QS (mm/s)	0.00(1)	0.00(1)	1.16(1)	0.81(1)
IS (mm/s)	0.26(2)	0.67(2)	0.43(1)	0.33(1)
H_i (T)	49(2)	46(2)	0	0

Fe_3O_4(I).

Magnetite at ambient pressure is an inverse-spinel-type ferrite with a unit cell containing 32 close-packed oxygen atoms in which eight Fe^{3+} occupy the tetrahedral (A) sites. The octahedral (B) sites are occupied by eight Fe^{3+} and eight Fe^{2+}. At room temperature (RT) and down to the Verwey transition temperature ($T_V = 118$ K), due to the fast electron exchange between the Fe^{3+} and Fe^{2+} (at the B site), their Mössbauer parameters are practically identical. Yet there is a distinct difference between the parameters of the A and B sites as can be seen in Table I.

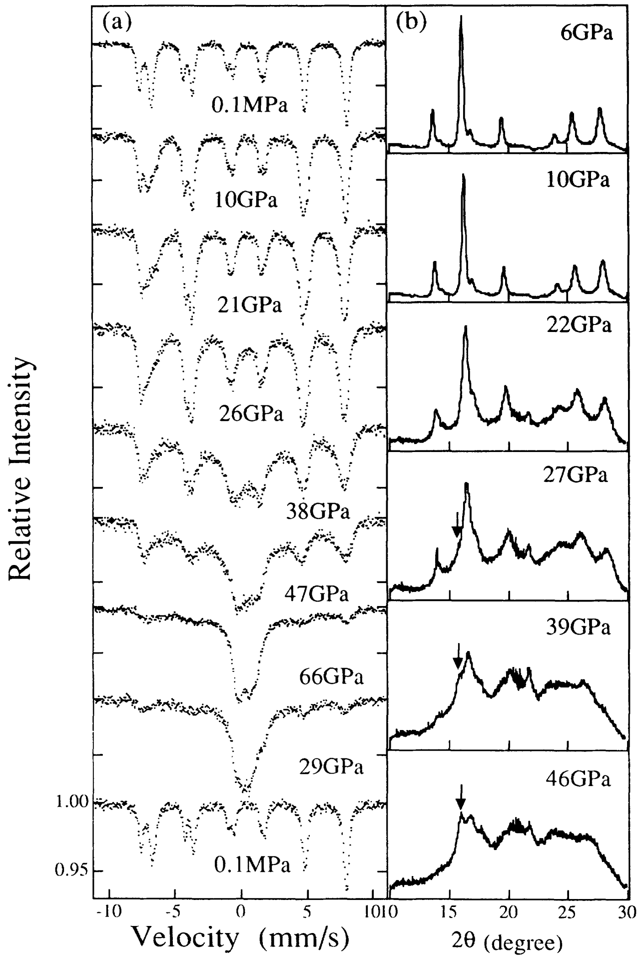

FIG. 1. Room-temperature Mössbauer spectra (a) and x-ray diffraction pattern (b) of magnetite at various pressures. The source used was ^{57}Co(Rh). The two lower spectra were recorded during decompression. Note the onset of the high-pressure phase at $P = 26$ GPa.

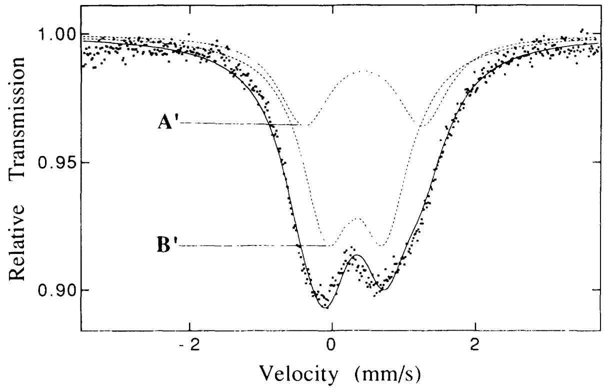

FIG. 2. Mössbauer spectrum of magnetite at 66 GPa on a reduced velocity scale. The solid line is a theoretical spectrum composed of two quadrupole doublets. The deduced values of the QS, IS, and the relative areas under the two components are noted. Values of the IS are with respect to α-Fe at 300 K.

By careful spectral analysis we were able to deduce the pressure dependence of the isomer shift (IS) and the quadrupole splitting (QS) of sites A and B in Fe_3O_4(I) in the 0–25 GPa pressure range.[9] Due to the high symmetry of the A and B sites, the QS values are close to 0 at all pressures. The IS for both sites decreases with increasing pressure.

A typical spectrum of Fe_3O_4(II) recorded at 66 GPa on a reduced velocity scale is shown in Fig. 2. The solid line is a theoretical fit to the experimental points. The fitting was restricted to (a) pure quadrupole interaction, (b) two spectral components, (c) identical linewidth, and (d) variable intensities for each component. Components A' and B' correspond to the lower- and higher-intensity subspectra. The derived values of the QS and IS are given in Table I. As can be seen there is a dramatic change in the QS. A plot of QS and IS vs pressure for each site in the 38–66 GPa pressure range is shown in Fig. 3.

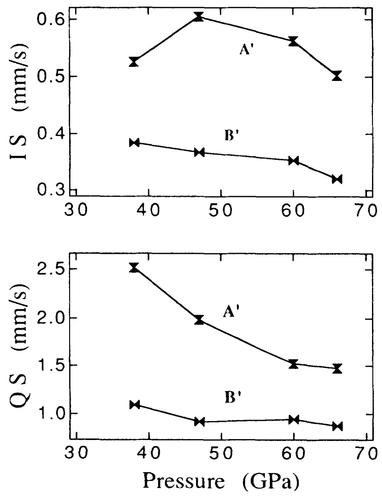

FIG. 3. Pressure dependence of QS and IS of sites A' and B' in Fe_3O_4(II).

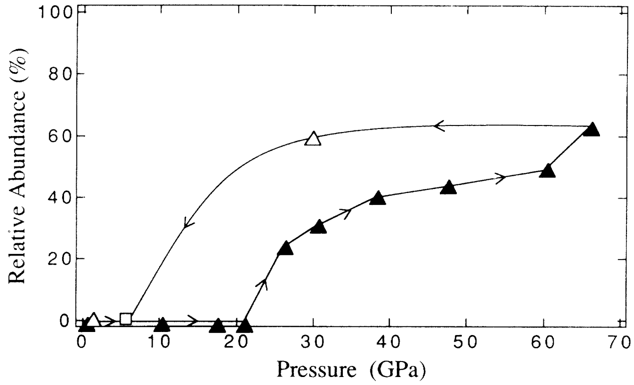

FIG. 4. Relative abundance of Fe_3O_4(II) as a function of pressure. Note the large pressure hysteresis.

Relative abundance of Fe_3O_4(II)

To a fair degree of accuracy, Mössbauer parameters allows determination of the abundance ratio of two or more components. The area A_i of the absorption lines corresponding to the ith component is proportional to its relative abundance a_i,

$$A_i = kf_i a_i \sum_j L_{ij} , \tag{1}$$

where k is a constant accounting for geometry, absorber thickness, etc.,[10] f_i is the recoil-free fraction of component i, and the sum is over the areas under the Lorentzian absorption lines of the ith component derived from the least-squares fit to the experimental data. Assuming equal values (at each pressure) of f_i for Fe_3O_4(I) and Fe_3O_4(II), the relative abundance $a(\mathrm{II})/a(\mathrm{I})$ as a function of pressure can be derived. The pressure dependence of the ratio of the two phases is shown in Fig. 4. Due to the fact that the pressure at which Fe_3O_4(II) is first observed coincides with that found by x-ray diffraction, one may safely assign this Mössbauer component to the monoclinic phase. For site-population analysis in one phase containing Mössbauer probe atoms, the same relation as (1) can hold and the relative abundance a_i indicates the relative occupancy of different sites. One notes the impressive hysteretic curve and the full recovery of Fe_3O_4(I) at 5 GPa. An important and crucial finding relates to the ratio of the area under the absorption peaks of components A' and B' (and therefore their respective abundance). Up to the highest pressure applied and independent of P it was found to be 0.5(1).

Characterization of Fe_3O_4(II)

From x-ray diffraction data it has been established that at the reduced volume of $V/V_0=0.90$ ($P \approx 25$ GPa) an energetically stable phase Fe_3O_4(II) with a monoclinic structure evolves and this phase coexists with the cubic spinel Fe_3O_4(I). The present Mössbauer study definitely shows that this monoclinic high-pressure phase is not magnetically ordered at RT. The vanishing of the hyperfine magnetic interaction may be explained by two possible mechanisms, namely, the onset of a paramagnetic phase with ordering temperature below 300 K or the onset of a nonmagnetic metallic phase due to a Mott transition. This transition in which the charge-transfer or Mott-Hubbard gap closes results in metallization concurrently with the loss of the cation magnetic moment.[3]

The x-ray diffraction of this work and the well-resolved data by Mao *et al.*[2] could not unambiguously determine the number of molecules per unit cell. It has been suggested[2] that, in case of two molecules per unit cell, the density of Fe_3O_4(II) would be consistent with having all cations in sixfold coordination, which is not the case for Fe_3O_4(I). In the ambient-pressure phase, out of 24 cations per unit cell, eight (A site) are fourfold and 16 (B site) are sixfold coordinated, resulting in the Fe abundance ratio $a(A){:}a(B)$ of 0.5. As mentioned before, the Mössbauer spectra analysis of Fe_3O_4(II) (see Fig. 2) invokes the presence of two sites, A' and B', also with abundance ratio of 0.5(1). Mössbauer data cannot quantify cation coordination numbers. However, the conservation of the Fe abundance and the relatively small changes in the IS values for both sites in Fe_3O_4(II) strongly suggest a topology in which the cubic→monoclinic →cubic pressure cycle undergoes a relatively mild displacive phase transition. The unit of the monoclinic inverse spinel, containing 32 close-packed oxygens in the distorted $A'$and B' sites with their original coordination numbers, remains the building block of the high-pressure phase of magnetite. Thus, we suggest a model where Fe_3O_4(II) directly derives from the highly symmetric Fe_3O_4(I) where A and B transform into A' and B' with distorted tetrahedral and octahedral symmetries, respectively. The pressure-induced distortion of the A and B sites leads to the monoclinic phase and is consistent with the onset of an electric-field gradient at the Fe sites.

Finally, it is noteworthy that, to 66 GPa, Mössbauer spectra characteristic of divalent iron were not detected, namely, the fast electron exchange between the Fe^{2+} and Fe^{3+} within the B' site is still present. This may not be surprising. With pressure increase one would expect the wave function responsible for the electron exchange to be further delocalized. In fact, pressure studies to 2.5 GPa by Kakudate *et al.*[11] clearly demonstrated the downward trend of T_V with increasing pressure.

IV. CONCLUSION

The present x-ray diffraction and Mössbauer spectroscopy data confirm the onset of a new phase of magnetite at $P > 25$ GPa. The Mössbauer data show unequivocally that this new phase does not order magnetically at 300 K and that by decompression, following a hysteresis, it reverts to the original magnetite phase. The absence of magnetic order can be accounted for either by a Mott transition into a nonmagnetic metallic state or by the formation of a paramagnetic phase with T_N below 300 K. Low-temperature high-pressure Mössbauer spectroscopy and/or conductivity measurements might resolve between these two points. The high-pressure magnetite is characterized by two Fe sites, A' and B', with an Fe abundance ratio of 0.5(1), the same as in the low-pressure phase. We conclude that A' and B' evolve from A and B with a lower symmetry as manifested by the rather large QS values. The fast electron exchange in the B' site prevails to the highest pressure applied.

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