Equation of state of magnetite and its high-pressure modification:
Thermodynamics of the Fe-O system at high pressure

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ABSTRACT
Fe3O4 has been studied by high-pressure diffraction to 43 GPa. No major changes in the spinel-type structure of magnetite are observed below 21.8 GPa. At higher pressure a sluggish transition to a high-pressure modification, h-Fe3O4, is observed. The X-ray diffraction pattern of the high-pressure modification is consistent with the orthorhombic unit cell (CaMn2O4-type structure, space group Pbcm) recently proposed for h-Fe3O4 by Fei et al. (1999), however, it is also consistent with a more symmetric CaTi2O4-type structure (space group Bbmm). Bulk modulus values for magnetite, K0 = 217 (2) GPa, and h-Fe3O4, K0 = 202 (7) GPa, are calculated from the pressure-volume data using a third-order Birch-Murnaghan equation of state. A thermodynamic analysis of the Fe-O system at high pressure is presented. The proposed equation of state of h-Fe3O4 gives an increased stability of wüstite relatively to a two-phase mixture of iron and h-Fe3O4 compared to earlier equations of state and removes an inconsistency in the thermodynamic description of the Fe-O system at high pressure.

INTRODUCTION
Magnetite is, at ambient pressure and low temperature, a ferrimagnetic inverse spinel where the tetrahedral positions are occupied by Fe2+ and the octahedral sites contain equal amounts of Fe2+ and Fe3+. With increasing temperature the Verwey transition at 119 K is related to a change in the degree of electron localization of the iron atoms (Verwey 1939) and fast electron exchange between the octahedral Fe2+ and Fe3+ is observed above the transition temperature. Transport-property measurements indicate that the charge distribution depends on temperature and a gradual disordering of the inverse spinel toward a random one is observed with increasing temperature (Wu and Mason 1981). Magnetite becomes paramagnetic at Tc = 848.5 K (Grønvold and Sveen 1974).

The high-pressure modification of magnetite, h-Fe3O4, which slowly appears at pressures above ≈25 GPa (Mao et al. 1974), is paramagnetic at ambient temperature (Pasternak et al. 1994). The density of h-Fe3O4 was first estimated from the tentative unit-cell assignment by Mao et al. (1974), based on an insufficient number of diffraction lines for monoclinic symmetry. It was argued that the calculated density indicates that all iron atoms are in sixfold coordination (Mao et al. 1974). This would require a massive reconstructive transition from the low-pressure spinel-type structure where iron is partly fourfold and partly sixfold coordinated. A recent Mössbauer spectroscopy study (Pasternak et al. 1994) on the other hand indicates that the Fe atoms remain in their original coordination environments in the high-pressure modification, and suggests that the transition involves a distortion of the tetrahedra and octahedra of the low pressure structure only. A smaller volume decrement connected with the magnetite to h-Fe3O4 transition than suggested by Mao et al. (1974) is, hence, indicated. Recently Fei et al. (1999) proposed that h-Fe3O4 takes the CaMn2O4-type structure (Pbcm) where Fe2+ is octahedrally coordinated and Fe3+ is eightfold coordinated (bicapped trigonal prismatic). With this structure assignment h-Fe3O4 is about 6.5% more dense than magnetite at 24 GPa. In earlier thermodynamic evaluations of the Fe-O system (Saxena et al. 1993; Fabrichnaya and Sundman 1997) a large volume decrement for the transformation from magnetite to h-Fe3O4 is used which implies a considerable increase in the stability of magnetite at high pressure compared to that obtained by extrapolation using the volume of the low-pressure structure. A large volume decrement for the transformation results in a disproportion of wüstite, Fe1–yO, to iron and magnetite at high pressure (Huang and Bassett 1986; Stølen and Grønvold 1996). This conclusion contradicts phase diagram studies which show that NaCl-type wüstite is stable to pressures near 70 GPa at 1000 K where after the NaCl-type structure transforms to a NiAs-type structure (Fei and Mao 1994).

The mechanism of the transformation is not clear. Magnetite and h-Fe3O4 are reported to coexist as a two-phase mixture over several GPa (Mao et al. 1974; Huang and Bassett 1986; Pasternak et al. 1994) and the transition, hence, appears to be of first order. The transition is not related to the Verwey transition because Tc decreases with P (Ramasesha et al. 1994). For pressures up to 66 GPa, Mössbauer spectra characteristic of divalent iron were not detected (Pasternak et al. 1994). Hence,
the fast electron exchange between Fe$^{2+}$ and Fe$^{3+}$, characteristic of magnetite above the Verwey transition, is still present. The small change in magnitude of the resistivity connected with the pressure induced transition supports this conclusion (Morris and Williams 1997). High pressure single-crystal diffraction data up to 4.5 GPa at ambient temperature (Finger et al. 1986) show no evidence of any valence disordering between tetrahedral and octahedral sites. Furthermore, in that pressure range both the tetrahedra and the octahedra display the bulk modulus characteristic for the unit-cell volume. The oxygen x-coordinate, the only variable atomic position coordinate for the spinel structure, does not vary with pressure for $P < 4.5$ GPa (Finger et al. 1986; Nakagiri et al. 1986).

The present investigation reports an improved equation of state for magnetite and proposes an equation of state for h-Fe$_3$O$_4$ based on the CaMn$_2$O$_4$-type structure (Fei et al. 1999). Alternative descriptions of the crystal structure of h-Fe$_3$O$_4$ are discussed. The calculated phase relations in the Fe-O system at high pressure are in better agreement with experiments than earlier evaluations (Huang and Bassett 1986; Saxena et al. 1993; Fabrichnaya and Sundman 1997).

**EXPERIMENTAL METHODS**

Sample preparation and characterization

The sample was prepared from Fe$^{3+}$ oxide (pro analysi, E. Merck No. 3924) and iron. Prior to use Fe$_3$O$_4$ was heated in a furnace at 1273 K until a constant mass was attained. A small part of the sample was reduced to Fe in dry hydrogen gas at 1073 K for 6 h and afterward crushed to a fine powder. Stoichiometric amounts of the resulting iron and Fe$_3$O$_4$ were heated in evacuated and sealed vitreous silica tubes at 1273 K for 2 days and cooled with the furnace. X-ray powder diffraction showed only reflections from Fe$_3$O$_4$. The resulting unit-cell constant, $a = 839.65$ (7) pm, is in good agreement with Fleet (1981).

High-pressure technique

The high-pressure measurements were performed at room temperature in a membrane-type diamond anvil cell with the sample loaded in a hole in a stainless steel gasket with a diameter of 125 μm and an initial thickness of 40 μm. N$_2$ was used as pressure transmitting medium. It solidifies at 2.3 GPa at ambient temperature. Weak reflections from solid N$_2$ were thus observed in several sets of data. Three crystalline modifications of N$_2$ are reported at high pressure. The disordered hexagonal low-pressure structure (Streib et al. 1962) transforms to a disordered cubic structure between 4 and 5 GPa (Cromer et al. 1981) which again transforms to an ordered rhombohedral modification near 16 GPa (Mills et al. 1986). The rhombohedral modification is stable at least to 44 GPa (Olijnyk 1990). Pressure was measured by the ruby fluorescence technique using the non-linear hydrostatic pressure scale (Mao et al. 1986).

The powder X-ray diffraction data were collected on beamline ID9 at the European Synchrotron Radiation Facility (ESRF). The diffractograms were collected on an image plate, scanned and thereafter integrated with the computer program FIT2D (Hammersley et al. 1996) and thereby transformed to a one-dimensional data set. The monochromator was a single reflection Si (111) monochromator with wavelength $\lambda = 47.60$ (4) pm. The 2D-image plate distance and the wavelength were calibrated using Si (Deslattes and Henins 1973) as an external calibration source. The conical opening of the pressure cell allowed the observation of the full diffraction rings for $d > 95$ pm.

Rietveld refinement of the crystal structure of magnetite at the different pressures was done by means of the GSAS (Larson and von Dreule 1986) package. The background was described by means of 9-term cosine Fourier series polynomials and the peak shape by a Gaussian-Lorentzian function (5 parameters). In addition the zero point, one unit-cell dimension, one atomic coordinate parameter and isotropic displacement factors were refined, altogether 17 to 19 variables. The 20 range $\approx 5$ to $\approx 25^\circ$ was used, containing $\approx 1100$ data points and 14 contributing Bragg reflections. The diffraction data for h-Fe$_3$O$_4$ were analyzed assuming a two-phase mixture with magnetite. Different structural models were considered. Soft distance restraints were introduced for the Fe-O separations in the CaTi$_2$O$_4$-type structure model, see below.

**RESULTS AND DISCUSSION**

A three-dimensional representation of the X-ray diffractograms recorded on increasing pressure ($P_{\text{max}} = 40$ GPa) is given in Figure 1. Weak reflections from solid N$_2$ (cubic) are present in the diagrams at pressure above 3.4 GPa, see e.g., the small peak at around $20 = 10^\circ$ for $P = 3.4$ to 13.5 GPa. At higher pressure this peak overlaps with the magnetite 311 line. No major changes in the spinel-type structure are observed below 21.8 GPa. At higher pressure the intensities of the char-
acteristic magnetite reflections are reduced and those of the high-pressure modification evolve gradually. Reflections that can be ascribed to magnetite appear to be present at least up to 30.3 GPa and the slow kinetics of the transformation (e.g., Mao et al. 1974) is confirmed. The slow kinetics is also seen during decompression for diffractograms recorded at 30, 24, 19, 12, and 6 GPa. Hysteresis is observed and h-Fe$_3$O$_4$ does not revert completely to magnetite even at 6 GPa.

The structural transformation is apparently accompanied by a gradual increase in non-coherent scattering and the quality of the diffractograms deteriorates. The change in the diffractograms may in part relate to the fact that the transformation involves atomic motion and/or large strain which reduces the long-range order. Alternatively, this effect may be related to a deformation of the gasket. Even though the non-coherent scattering increases with increasing pressure, the peak shape seems to develop reasonably. The full peak width at half maximum (FWHM) intensity for the magnetite 111 line increases with a constant slope with increasing pressure (Fig. 2a). A similar observation is made for the magnetite 311 line (Fig. 2a) for $P < 25$ GPa. At higher pressure a change in slope of the FWHM for what appears to be magnetite 311 is observed. In this pressure range, the FWHM shows a pressure dependence similar to that for the $d = 257$ pm reflection (open squares) which for certain can be assigned to h-Fe$_3$O$_4$. Above 25 GPa the apparent magnetite 311 seems therefore to contain a major component from the high-pressure modification. An apparent jump in the $d$-value of magnetite 311 at around 30 GPa substantiates this argument, see Figure 2b. The $d$-value for the apparent magnetite 311 on decompression suggests that this reflection contains major components from the high-pressure modification.

Crystal structure and equation of state of magnetite

Magnetite is an inverse spinel at ambient pressure and low temperature (Fleet 1981). The ideal spinel structure is cubic with space group Fd$ar{3}$m and $Z = 8$. Using the centrosymmetric description of the space group the tetrahedral cations are located at $(1/8,1/8,1/8)$, the octahedral cations at $(1/2,1/2,1/2)$, and the oxygen atoms at $(x, x, x)$, where $x = 0.25$. According to Fleet (1981), $x = 0.2549 (1)$ at room temperature. Refined structural parameters are in Table 1. A representative diffractogram is in Figure 3.

The oxygen position parameter ($x$) does not vary with pressure within two standard deviations. No change in the cation distribution is indicated, and the inverse spinel modification seems to be stable in the pressure range covered. The reduced volumes presently obtained for magnetite are compared with earlier reported values in Figures 4 and 5.

The different determinations are in reasonable agreement at pressures below 25 GPa, although the values by Mao et al. (1974) show a larger spread than the others. The reduced molar volumes reported at high pressure by Mao et al. (1974), and also the value presently deduced from the 30.3 GPa diagram are low compared with the extrapolated curve from the lower pressure determinations. This discrepancy is probably related to wrong peak assignment in the indexing of the two-phase mixture diagrams, and these determinations are, therefore, not included in the equation of state analysis which follows.

The bulk modulus of magnetite was calculated by least-

![Figure 2](image-url)

**Figure 2.** (a) Full peak width at half maximum intensity (FWHM) as a function of pressure. Circles = magnetite 111; triangles = magnetite 311; squares = the $d = 258$ pm reflection for h-Fe$_3$O$_4$. (b) The $d$-value of magnetite 311. Circles = magnetite 311 on compression; triangles = magnetite 311 on decompression.

| Table 1. Refined structural parameters, selected bond-distances and cation polyhedra volumes |
|---|---|---|---|---|---|
| $P$ (GPa) | $d$ (pm) | $x$ | A-O (pm) | $V_{BO} \times 10^{-4}$ (pm$^3$) | $B$-O (pm) | $V_{BO} \times 10^{-4}$ (pm$^3$) |
| 0 | 839.65 (7) | 0.2549 (3)† | 188.9 (1)‡ | 3.460 (8)‡ | 205.9 (1)‡ | 11.61 (2)‡ |
| 1.4 | 838.37 (5) | 0.2554 (4) | 189.4 (6) | 3.48 (3) | 205.3 (3) | 11.48 (6) |
| 2.3 | 836.85 (6) | 0.2550 (4) | 188.4 (6) | 3.43 (3) | 204.9 (3) | 11.44 (5) |
| 3.4 | 835.17 (6) | 0.2548 (3) | 186.7 (5) | 3.34 (2) | 203.8 (3) | 11.19 (5) |
| 6.6 | 831.22 (8) | 0.2549 (3) | 186.7 (5) | 3.30 (2) | 202.6 (3) | 11.06 (5) |
| 8.3 | 829.66 (8) | 0.2549 (3) | 185.9 (4) | 3.30 (2) | 202.6 (3) | 11.06 (5) |
| 11.3 | 826.26 (9) | 0.2549 (3) | 185.9 (4) | 3.30 (2) | 202.6 (3) | 11.06 (5) |
| 12.5 | 825.47 (11) | 0.2547 (3) | 185.9 (4) | 3.30 (2) | 202.6 (3) | 11.06 (5) |
| 13.5 | 823.96 (12) | 0.2543 (4) | 185.9 (4) | 3.30 (2) | 202.6 (3) | 11.06 (5) |
| 15.7 | 823.21 (19) | 0.2548 (3) | 185.9 (4) | 3.30 (2) | 202.6 (3) | 11.06 (5) |
| 17.5 | 821.40 (16) | 0.2552 (4) | 185.9 (4) | 3.30 (2) | 202.6 (3) | 11.06 (5) |
| 19.4 | 818.91 (18) | 0.2555 (4) | 185.9 (4) | 3.30 (2) | 202.6 (3) | 11.06 (5) |
| 21.8 | 817.10 (4) | 0.2553 (5) | 184.7 (4) | 3.32 (4) | 200.1 (4) | 10.64 (7) |
| 24.2 | 815.09 (21) | 0.2554 (5) | 184.7 (4) | 3.32 (4) | 200.1 (4) | 10.64 (7) |
| 26.9 | 811.77 (30) | 0.2552 (4) | 183.7 (4) | 3.32 (4) | 199.0 (4) | 10.49 (7) |
| 30.3 | 806.36 (80) | 0.2527 (9) | 177.9 (1.3) | 2.89 (6) | 199.0 (8) | 10.50 (12) |

*For $P > 21.8$ GPa, two-phase sample.
†Fleet (1981).
‡Calculated using the x-parameter from Fleet (1981).
squares fit of the pressure-volume data to a third order Birch-Murnaghan equation of state:

\[ P = \frac{3}{2} K_0 \left\{ \frac{V_o}{V} \right\}^{7/3} - \left( \frac{V_o}{V} \right)^{5/3} \left\{ 1 - \frac{3}{4} K_0' \left( \frac{V_o}{V} \right)^{2/3} - 1 \right\} \]

(1)

The resulting bulk modulus and its pressure derivative are 222 (8) GPa and 4.1 (9), where the stated inaccuracy refers to the standard deviation of the fit. The bulk moduli of the cation tetrahedra and octahedra are equal to the bulk modulus characteristic of the entire crystal in agreement with the lower pressure data by Finger et al. (1986), see Figure 6. Nakagiri et al. (1986) report that tetrahedra and octahedra have different polyhedral bulk moduli values for \( P < 4.5 \) GPa; 170 (10) and 200 (8) GPa, respectively.

Nine independent studies give bulk modulus values in the range from 155 to 215 GPa (Table 2). Both the pressure range covered and the pressure derivative obtained vary. The determinations by Gerward and Staun-Olsen (1995) and by Staun-Olsen et al. (1994) appear to be in agreement with the presently obtained value. A much lower value was obtained by Wilburn and Bassett (1977), whereas intermediate values are reported by Mao et al. (1974), Hazen et al. (1981), Finger et al. (1986), and Nakagiri et al. (1986).

The reason for the discrepancy between the bulk modulus presently obtained and that reported by Mao et al. (1974) is obviously related to the fact that Mao et al. (1974) included the higher-pressure determinations in their analysis. A re-evaluation based on the data by Mao et al. (1974) using data for \( P < 20 \) GPa only, gives a higher bulk modulus value, \( K_0 = 209 \) (9) GPa (for \( K_0' = 4 \)), in good agreement with the present result. After this correction, the four studies covering \( P > 10 \) GPa are in good agreement.

The bulk modulus values obtained by other techniques are in general lower than the present value. No obvious explanation is found. The pressure range of most of the earlier determinations is limited. We assume the X-ray diffraction determinations to be more reliable and the best estimate of the bulk modulus value is considered to result from an analysis taking into consideration most of the reported reduced volumes.
The present data below 27 GPa is combined with those by Mao et al. (1974) below 20 GPa, and those by Nakagiri et al. (1986), by Finger et al. (1986) and by Staun-Olsen et al. (1994). Numeric data are not reported by Gerward and Staun-Olsen (1995) or by Hazen et al. (1981). The data set of Wilburn and Bassett (1977) gives an anomalous low bulk modulus value and is, hence, disregarded in the analysis. The resulting bulk modulus, given by solid lines in Figure 4 and 5, is \((K'_T = 4) 217\) GPa, in agreement with the value obtained using the presently reported determinations only. An improved fit is obtained for the low-pressure region if \(K'_T = 6.7 (8)\) and \(K = 198 (5)\) GPa, see dotted line in Figures 4 and 5. The solid line, representing \(K'_T = 4\), is considered to best describe the reduced volume against pressure curve and is used in the following discussions.

Unit cell and equation of state of the high-pressure modification of magnetite

The observed h-Fe₃O₄ pattern and the available data for hematite and wüstite at around 40 GPa (Table 3; Fig. 7) suggest that the transition relates to structural rearrangements of Fe₂O₃ and not to decomposition of Fe₃O₄ to FeO + Fe₂O₃. Magnetite and h-Fe₃O₄ coexist over a large pressure range and the transition shows a considerable hysteresis. The phase transition is probably reconstructive and of first order.

A requirement for correct determination of the molar volume of the high-pressure modification is that the h-Fe₂O₃ reflections are properly distinguished from reflections from untransformed magnetite. Even at the highest pressures a reflection coincident with the strongest magnetite reflection at 2\(\theta = 10^\circ\) is present (magnetite 311 line). The same reflection was observed by Fei et al. (1999), e.g., at 34 GPa and 300 K. However, their reflection disappeared on heating and it was no longer observed at 26 GPa and 723 K. This may indicate that the present sample is a two-phase mixture of magnetite and h-Fe₂O₃ even at the highest pressures. Still, both the increase in the FWHM and the discontinuous shift in the position for the apparent magnetite 311 above 25 GPa (Fig. 2) suggest that this reflection contains major contributions from h-Fe₂O₃. Furthermore, the intensity ratio between the magnetite 220 and the h-Fe₂O₃ reflection at \(d = 257\) pm decreases from (1/2) to (1/90) between 30.3 and 40.0 GPa, whereas the apparent magnetite 311 reflection remains strong. In conclusion one should not neglect the possibility that there is a structural distinction between h-Fe₂O₃ transformed at 300 K and h-Fe₂O₃ subjected to subsequent annealing.

The present high-pressure diffractograms and those obtained on decompression were indexed assuming the sample to consist of two phases; Fe₂O₃ and CaMn₂O₄-type h-Fe₂O₃. At 24 GPa, the unit-cell dimensions for h-Fe₂O₃ are, \(a = 278.4 (2.4)\), \(b = 950.6 (5.7)\), and \(c = 954.6 (7.9)\) pm. At 23.96 GPa and 823 K, Fei et al. (1999) report the following unit-cell dimensions; \(a = 279.92 (3)\), \(b = 940.97 (15)\), and \(c = 948.32 (9)\) pm.

![Figure 7. Observed XRD pattern of h-Fe₂O₃ at P = 40 GPa. λ = 47.60 pm.](image)

**Table 2. Reported values of the bulk modulus of magnetite**

<table>
<thead>
<tr>
<th>Reference</th>
<th>(K'_0) GPa</th>
<th>(K''_0) GPa</th>
<th>(P_{max}) GPa</th>
<th>Sample</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Madelung and Fuchs (1921)</td>
<td>185 (3)</td>
<td>–</td>
<td>0.02</td>
<td>bulk mineral</td>
<td>static compr.</td>
</tr>
<tr>
<td>Bridgman (1925)</td>
<td>175 (3)</td>
<td>–</td>
<td>0.02</td>
<td>bulk mineral</td>
<td>static compr.</td>
</tr>
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<td>Doraiswami (1947)</td>
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<td>–</td>
<td>1.2</td>
<td>natural single cryst.</td>
<td>static compr.</td>
</tr>
<tr>
<td>Bridgman (1949)</td>
<td>162</td>
<td>–</td>
<td>–</td>
<td>natural single cryst.</td>
<td>sonic</td>
</tr>
<tr>
<td>Bhagavantam (1955)</td>
<td>161</td>
<td>–</td>
<td>–</td>
<td>natural single cryst.</td>
<td>sonic</td>
</tr>
<tr>
<td>Waldron (1955)</td>
<td>170 (5)</td>
<td>–</td>
<td>2.9</td>
<td>single crystal</td>
<td>static compr.</td>
</tr>
<tr>
<td>Simons and England (1969)</td>
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<td>–</td>
<td>–</td>
<td>single crystal</td>
<td>sonic</td>
</tr>
<tr>
<td>Mao et al. (1974)</td>
<td>177</td>
<td>–</td>
<td>–</td>
<td>powder</td>
<td>IR</td>
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<tr>
<td>Mao et al. (1974)*</td>
<td>183 (10)</td>
<td>4</td>
<td>(0.4)</td>
<td>32</td>
<td>powder XRD</td>
</tr>
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<td>4</td>
<td>20</td>
<td>powder</td>
<td>XRD</td>
</tr>
<tr>
<td>Hazen et al. (1981)</td>
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<td>4</td>
<td>6.5</td>
<td>powder</td>
<td>XRD</td>
</tr>
<tr>
<td>Finger et al. (1986)</td>
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<td>4</td>
<td>4.5</td>
<td>single crystal</td>
<td>XRD</td>
</tr>
<tr>
<td>Nakagiri et al. (1986)</td>
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<td>4</td>
<td>4.5</td>
<td>single crystal</td>
<td>XRD</td>
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<tr>
<td>Staun-Olsen et al. (1994)</td>
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<td>5.5(15)</td>
<td>4.5</td>
<td>single crystal</td>
<td>XRD</td>
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<td>Gerward and Staun Olsen (1995)</td>
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<tr>
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<td>powder</td>
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<td>This work</td>
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<tr>
<td>This work</td>
<td>217(2)</td>
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<td>27</td>
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</table>

* Note: \(K'_0\) values of “4” are assumed.

* Subset of the dataset of Mao et al. (1974) evaluated by us.
at ambient conditions the true inaccuracy of the bulk modulus data for h-Fe₃O₄ (see Table 4) and the fictive unit-cell volume deviation of the fit. Considering the quality of the experimental inaccuracy of the bulk modulus is related to the standard de-
is expected to have a higher bulk modulus. Again the stated than the one found for magnetite. In general the denser phase
ambient pressure is extrapolated to 41.89 (14) cm³/mol whereas
The pressure-volume data are in Table 4 and in Figure 8. From these data the bulk modulus (for
K’₀ = 202 (7) GPa). The molar volume at ambient pressure is extrapolated to 41.89 (14) cm³/mol whereas the volume decrement for the Fe₃O₄ to h-Fe₃O₄ transition at 25 GPa is 6.1%. The bulk modulus of h-Fe₃O₄ is slightly smaller than the one found for magnetite. In general the denser phase is expected to have a higher bulk modulus. Again the stated inaccuracy of the bulk modulus is related to the standard deviation of the fit. Considering the quality of the experimental data for h-Fe₃O₄ (see Table 4) and the fictive unit-cell volume at ambient conditions the true inaccuracy of the bulk modulus for h-Fe₃O₄ is higher.

Much higher bulk-modulus values, 340 GPa (Ahrens et al. 1969) and 450 GPa (Anderson and Kanamori 1968), have been deduced from shock-wave experiments at pressures from 65 to 130 GPa. Extrapolation to ambient pressure gave low molar volumes 38.27 cm³/mol (Ahrens et al. 1969) and 39.21 cm³/mol (Anderson and Kanamori 1968).

Crystal structure of the high-pressure modification of magnetite

There are indications that the crystal structure of h-Fe₃O₄ is not a CaMn₂O₄-type. In CaMn₂O₄ the local environment around Mn³⁺ is irregular due to Jahn-Teller deformation of the MnO₆-octahedra (Couffon et al. 1964). The high pressure of the spinel related MnO₆ also takes this structure type (Paris et al. 1992). In h-MnO₃ at 39 GPa, the Mn³⁺-O²⁻ bond lengths for the octahedral site and the Mn³⁺-O²⁻ bond lengths for the eight-fold-coordinated site range from 177.2 to 223.6 pm and from 210.0 to 249.7 pm, respectively (Paris et al. 1992). In h-Fe₃O₄ of orthorhombic CaMn₂O₄-type, Fei et al. (1999) report large distortions of the cation environments. The Fe³⁺-O²⁻ bond lengths for the octahedral sites and the Fe²⁺-O²⁻ bond lengths for the eight coordinated sites at 24 GPa range from 171.5 to 258.9 pm and from 177.5 to 271.9 pm, respectively (Fei et al. 1999). Considering the 3d⁰ count for Fe³⁺ and Fe⁰, no Jahn-Teller deformation is expected for Fe and the driving force for the large distortions is not easily understood. For CaMn₂O₄ (Couffon et al. 1964) and h-MnO₃ (Paris et al. 1992) the variance in the Mn-O distances are modest compared with those reported for h-Fe₃O₄ (Fei et al. 1999). Furthermore, on the basis of bond valence considerations the crystal data for h-Fe₃O₄ clearly indicate charge ordering with Fe²⁺ occupying a strongly deformed eight coordinated site. This appears to contradict reported Fe Mössbauer data (Pasternak et al. 1994).

Despite the inferior quality of the present diffraction data, Rietveld analysis was attempted to clarify the possibility of a different structural description of h-Fe₃O₄. The CaMn₂O₄-type structure is a deformed variant of the CaTi₂O₄-type (Bertaut and Blum 1956) and is related to the CaFe₂O₄-type (Decker and Kasper 1957). These three, quite dense, structure types are compared in Figure 9. The diffraction data were clearly not consistent with the CaFe₂O₄-type. On turning from the deformed CaMn₂O₄-type to the more symmetric CaTi₂O₄-type, the space group symmetry is changed from Pbcm to Bbmm, however, no major changes are introduced in the unit-cell dimensions, and the volume decrement is still of the order of 6% for the magnetite to h-Fe₃O₄ transition. In the Rietveld refinements, the two non-equivalent iron atoms in the CaTi₂O₄-type description were subjected to soft distance restraints in order to secure rather
symmetric Fe-O coordinations. The simulated pattern (assuming 1% strain in all directions) derived on the basis of the refined model (Fig. 10) has strong similarities with that observed by Fei et al. (1999). Proposed atomic coordinates are in Table 5. Calculated interatomic Fe-O distances are for Fe1 183 pm ($\times 2$) and 209 pm ($\times 4$), for Fe2 191 pm, 193 pm, 197 pm ($\times 2$) and 202 pm ($\times 2$). Further experiments are required in order to settle the structural ambiguity for h-Fe$_3$O$_4$.

**Thermodynamics of the Fe-O system at high pressure**

The main motivation for the present study was the inconsistency in the thermodynamics of the Fe-O system at high pressure, which was considered to relate to the large volume decrement proposed for the magnetite to h-Fe$_3$O$_4$ transition (Saxena et al. 1993; Fabrichnaya and Sundman 1997). An analysis of the Fe-O system at high pressure based on the presently obtained equations of state is, hence, considered to be of interest.

The stability of Fe$_{1-y}$O, and Fe$_3$O$_4$ at high pressure is evaluated by assuming the phases to be stoichiometric. Inclusion of non-stoichiometry in the calculations does not affect the phase stability significantly. Our analysis is based on earlier published thermodynamic descriptions of wüstite, magnetite, and hematite at ambient pressure (Grønvold et al. 1993; Stølen et al. 1996; Stølen and Grønvold 1996). Key parameters are in Table 6. The temperature derivatives of the bulk modulus values are not known and the average value for six minerals (Anderson et al. 1991) is used. Thermodynamic descriptions of iron metal and oxygen are taken from Guillermet and Gustafson (1985).

**TABLE 5. Atomic coordinates for the proposed crystal structure of h-Fe$_3$O$_4$ of CaTi$_2$O$_4$-type at 40 GPa**

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe1</td>
<td>4c</td>
<td>0.375</td>
<td>0.25</td>
<td>0.00</td>
</tr>
<tr>
<td>Fe2</td>
<td>8f</td>
<td>0.135</td>
<td>0.087</td>
<td>0.00</td>
</tr>
<tr>
<td>O1</td>
<td>4c</td>
<td>0.005</td>
<td>0.25</td>
<td>0.00</td>
</tr>
<tr>
<td>O2</td>
<td>8f</td>
<td>0.214</td>
<td>0.605</td>
<td>0.00</td>
</tr>
<tr>
<td>O3</td>
<td>4a</td>
<td>0.5</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Space group $Bbmm$, $a = 927.3(7)$ pm, $b = 923.9(4)$ pm, and $c = 274.6(2)$ pm.

**FIGURE 9.** Comparison of the three related structure types CaFe$_2$O$_4$ (upper), CaMn$_2$O$_4$ (middle) and CaTi$_2$O$_4$ (bottom). Ca-atoms are shown as spheres, transition metal as coordination polyhedra. Projections along the short z-axis. Note that octahedra are shown for CaMn$_2$O$_4$ where the Jahn-Teller deformed Mn-coordination actually is 4 + 2.

**FIGURE 10.** Simulated diffraction pattern for (a) h-Fe$_3$O$_4$ of CaTi$_2$O$_4$-type structure and (b) h-Fe$_3$O$_4$ of CaMn$_2$O$_4$-type structure according to Fei et al. (1999). $\lambda = 47.60$ pm.
and from Belanoshko et al. (1992).

The molar volume of h-Fe₃O₄ is obtained from the structure proposed by Fei et al. (1999) and the presently proposed equation of state. The Gibbs energy of formation at ambient pressure but at different temperatures is obtained by shifting the Gibbs energies of formation of h-Fe₃O₄ reported earlier (Saxena et al. 1993) by a temperature-independent factor in order to force magnetite and h-Fe₃O₄ to co-exist at 25 GPa at 300 K. The resulting difference in magnetite and h-Fe₃O₄ to co-exist at 25 GPa at 300 K. The resulting difference in the Gibbs energy of formation of wüstite from iron and magnetite at 16.5 GPa is that the difference in Gibbs energy of formation at ambient pressure and 300 K is 67 kJ/mol. Much larger ΔGₘₐ₉-differences at 300 K have been reported earlier; 161 kJ/mol (Saxena et al. 1993) and 137 kJ/mol (Fabrichnaya and Sundman 1997), see Figure 11. The equations of state proposed in the two latter studies are, hence, quite different from the present one. The molar volumes for magnetite and h-Fe₃O₄ are compared in Figure 8. The volume decrement of the transition at ambient pressure is presently estimated to 2.63 cm³/mol, whereas 8.08 cm³/mol results from the earlier evaluations (Saxena et al. 1993; Fabrichnaya and Sundman 1997). The present thermodynamic description gives a destabilization of h-Fe₃O₄ compared to earlier thermodynamic analyses, which significantly influence the calculated phase relations in the Fe-O system at high pressure.

The temperature of the eutectoid formation of wüstite from bcc-iron and magnetite decreases from 843 K at ambient pressure (Knacke 1988) to near 430 K at 430 K at ambient pressure, 15 J/(K·mol). The experiments performed by Shen et al. (1983) of −13.5 K/GPa (Fig. 12a), but it is in good agreement with the pressure variation of the transition temperature calculated from the Clausius-Clapeyron equation, dT/dP = −43 K/GPa (using the molar volumes and entropies of the different phases at T = 298.15 K as a first approximation). Huang and Bassett (1986) calculated the entropy of formation of wüstite from iron and magnetite at 16.5 GPa and 628 K by using the experimental d²T/dP² and ΔV₀ obtained by Shen et al. (1983). The resulting value of 44 J/(K·mol) is much larger than that obtained from experimental data at 300 K and ambient pressure, 15 J/(K·mol). An estimate of the entropy of formation of wüstite from iron and magnetite at the temperature-pressure conditions in the study by Shen et al. (1983), evaluated from the present thermodynamic description, give ΔSₘₐ = 20 J/(K·mol). The experiments performed by Shen et al. (1983) must be considered in some detail.

According to Shen et al. (1983) wüstite forms eutectoidally from iron and magnetite when P is increased to 20 GPa at 573 K. However, at 11, 14, and 20 GPa wüstite dominates the X-ray diffraction pattern and only small amounts of iron and magnetite are observed. On the other hand, at 6.5 GPa, iron and magnetite dominates the X-ray photographs, and only a small amount of wüstite is observed. Shen et al. (1983) suggests that the reason for the small amounts of iron and magnetite observed e.g., at 11 GPa in comparison with the much larger amounts observed at 6.5 GPa is that the difference in Gibbs energy of formation between wüstite and the stable two-phase mixture of iron and magnetite, i.e., the driving force, becomes small when the phase boundary is approached. It is tempting to suggest an alternative explanation. The presence of small amounts of iron and magne-

### TABLE 6. Thermodynamic parameters for wüstite and magnetite

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔHₘ(298)</th>
<th>ΔSₘ(298)</th>
<th>ΔGₘ(298)</th>
<th>Vₘ(298)</th>
<th>Kₘ0</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO</td>
<td>−264.06</td>
<td>60.45</td>
<td>−243.52</td>
<td>12.25</td>
<td>150</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>−1115.73</td>
<td>146.15</td>
<td>−1012.53</td>
<td>44.56</td>
<td>217</td>
</tr>
<tr>
<td>h-Fe₃O₄</td>
<td>−826.23</td>
<td>87.40</td>
<td>−744.25</td>
<td>30.30</td>
<td>222</td>
</tr>
</tbody>
</table>

Note: All phases are treated as stoichiometric line compounds. Kₘ is assumed to equal 4.

* Stolen and Granvoid (1996).
† Stolen et al. (1996).
‡ Haas and Hemingway (1992).
§ Fei (1996).
‖ Granvoid et al. (1993).
# Morris et al. (1981).
The volume decrement and the \(-68\) K/GPa, when relevant kinetic effects were considered. From increasing pressure and tentatively determined the equilibrium slope as K/GPa on increasing pressure and 170 (10) K/GPa on decreases in the thermodynamics of magnetite to h-FeO transition, the entropy of the magnetite to h-FeO transition is calculated through the Clausius-Clapeyron equation. This large entropy of transition 34 J/(K.mol) relates to the increased vibrational density of states toward lower frequencies. The earlier reported equations of state for high-magnetite based on the high bulk-modulus values deduced from shock-wave experiments and/or the structure suggested by Mao et al. (1974) give a weaker variation of the transition pressure with temperature.

The present thermodynamic description removes an earlier inconsistency in the thermodynamics of the Fe-O system at high pressure; decomposition of wüstite and the formation of (h-FeO + iron) at high pressure. Both the recently published thermodynamic descriptions by Saxena et al. (1993) and by Fabrichnaya and Sundman (1997) result in decomposition of FeO at high pressure. This is mainly due to the much higher density used for h-FeO by Saxena et al. (1993) and by Fabrichnaya and Sundman (1997).

In the preceding discussion, the relative stability of wüstite and iron (iron + magnetite) was considered without taking the trivalent iron oxide, hematite, into consideration. The volume decrement for the disproportion of magnetite to wüstite and hematite at ambient pressure is negative and indicates that magnetite must decompose at these conditions although a decomposition should not occur in a reducing atmosphere in the diamond anvil cell or by disproportion of magnetite to wüstite and hematite into consideration. The volume decrement and the AO + B2O3 mixtures. The spinels are believed to be stable in the Fe-O system only for pressures below 12 GPa at ambient temperature and h-FeO appears to be metastable. High-temperature‒high-pressure annealing of 15 A3+SiO4 type spinels at 12 GPa at 1273 K (Ringwood and Reid 1969) resulted in four different types of behavior, MnAlO4, FeAlO4, NiAlO4, and CoAlO4 decomposed into AO (rock salt) + B2O3 (corundum) mixtures. The driving force for the decomposition is the increased density when the spinels transform to the two-phase mixtures. ZnAlO4, MgAlO4, MgCrO4, CoGaO4, NiGaO4, and ZrGaO4 did not decompose at these conditions although a decomposition should be expected from the density difference between the spinels and the AO + B2O3 mixtures. The spinels are believed to be kinetically stable only and to decompose under higher pressure where the driving force for the reaction is larger (Ringwood and Reid 1969). CdCrO4 and CdFeO4 transform into denser AB2O4 structures, whereas the results for Fe3O4, ZnFe2O4, and MgFe2O4 were inconclusive due to partial reduction of Fe3+ to Fe2+ during the experiments. Further experiments are needed.

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HAAVIK ET AL.: EQUATION OF STATE OF MAGNETITE


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