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

CAMILLA HAAVIK,1 SVEIN STØLEN,1,* HELMER FJELLYVÅG,1 MICHAEL HANFLAND,2 AND DANIEL HÄUSERMANN2

1Department of Chemistry, University of Oslo, Postbox 1033, N-0315 Oslo, Norway
2European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble, France

ABSTRACT

Fe3O4 has been studied by high-pressure diffraction to 43 GPa. No major changes in the spinel-type structure of magnetite is 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, Km = 217 (2) GPa, and h-Fe3O4, Km = 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 Fe3+ and the octahedral sites contain equal amounts of Fe2+ and Fe3+ (Fleet 1981). Three transformations are observed 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 Fe3+ is octahedrally coordinated and Fe2+ 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 (Ramasetha et al. 1994). For pressures up to 66 GPa, Mössbauer spectra characteristic of divalent iron were not detected (Pasternak et al. 1994). Hence,