

In situ structure determination of the high-pressure phase of Fe₃O₄

YINGWEI FEI,^{1,*} DANIEL J. FROST,^{1,†} HO-KWANG MAO,¹ CHARLES T. PREWITT,¹ AND DANIEL HÄUSERMANN²

¹Geophysical Laboratory and Center for High Pressure Research, Carnegie Institution of Washington, 5251 Branch Road, N.W., Washington, D.C. 20015, U.S.A.

²European Synchrotron Radiation Facility, BP220, F38043 Grenoble Cedex, France

ABSTRACT

The crystal structure of a high-pressure Fe₃O₄ phase was determined by in situ X-ray diffraction measurements at high pressure and temperature, using an imaging plate detector and monochromatic synchrotron X-radiation. The high-pressure phase has the *Pbcm* space group (CaMn₂O₄-type structure) with cell parameters $a = 2.7992(3)$ Å, $b = 9.4097(15)$ Å, and $c = 9.4832(9)$ Å at 23.96 GPa and 823 K. Fe³⁺ occupies an octahedral site and Fe²⁺ is in an eightfold-coordinated site described as a bicapped trigonal prism. The high-pressure CaMn₂O₄-type Fe₃O₄ phase is about 6.5% more dense than the spinel form at 24 GPa.

INTRODUCTION

Magnetite (Fe₃O₄) is a mixed valence iron oxide with some Fe³⁺ ions occupying the tetrahedral sites and the Fe²⁺ and the remaining Fe³⁺ ions occupying the octahedral sites in the spinel structure (space group *Fd* $\bar{3}m$) (e.g., Fleet 1981). Its high-pressure behavior has been extensively studied by X-ray diffraction (Mao et al. 1974; Huang and Bassett 1986; Nakagiri et al. 1986; Finger et al. 1986; Pasternak et al. 1994), Mössbauer spectroscopy (Mao et al. 1977; Pasternak et al. 1994), and electrical resistivity measurements (Samara 1968; Ramasesha et al. 1994; Rozenberg et al. 1996; Morris and Williams 1997) because of its geophysical importance and its interesting magnetic properties at high pressure. Mao et al. (1974) demonstrated that magnetite transforms to a high-pressure phase at about 25 GPa. The X-ray diffraction pattern for the high-pressure phase, collected using a diamond cell diffraction camera (Bassett et al. 1967) and conventional X-ray source, was indexed on a monoclinic cell. Because relatively few diffraction lines were observed, the structure assignment was tentative. The high-pressure phase transition was confirmed by Huang and Bassett (1986) who determined its temperature dependence. The structural transition is also accompanied with changes in magnetic properties (Mao et al. 1977; Pasternak et al. 1994) and electrical resistivity (Morris and Williams 1997). Without knowledge of the crystal structure of the high-pressure phase, ambiguity exists in interpreting the Mössbauer spectra of Fe₃O₄ at high pressures.

X-ray diffraction data for the high-pressure phase of Fe₃O₄ collected in previous studies suffer from either low resolution or broad diffraction peaks that sometimes overlap those of magnetite due to the sluggish transition at room temperature. This study presents new diffraction data for the high-pressure phase collected on an imaging plate using monochromatic synchro-

tron X-ray radiation. The diffraction data contain accurate structural information with high resolution. The high quality data allow us to solve the crystal structure of the high-pressure phase of Fe₃O₄.

EXPERIMENTAL PROCEDURE

The starting material used in this study is synthetic magnetite with enriched ⁵⁷Fe, the same starting material used in the Mössbauer spectroscopic study by Mao et al. (1977). High-pressure–high-temperature experiments were conducted using an externally heated high-temperature diamond-anvil cell. The high-temperature cell is capable of achieving pressures greater than 125 GPa at temperatures up to 900 °C (Fei and Mao 1994; Fei 1996). A detailed description of this cell was given by Fei (1996). Here, we used 500 μm flat diamond anvils. The powdered magnetite sample was compacted in a sample chamber, 200 μm in diameter by 49 μm in thickness, drilled in a preindented rhenium gasket. A layer of NaCl powder was placed on the top of the magnetite sample to serve as a pressure-transmitting medium (especially at high temperatures) and as a pressure calibrant. A small piece (<10 μm) of thin gold foil was placed in only one quarter of the sample chamber as a pressure calibrant to obtain diffraction data with or without gold diffraction peaks. One small ruby grain (~5 μm) was also placed in the sample chamber for initial pressure determination at room temperature. At high *T*, sample temperature was measured by a Pt/Pt-10%Rh thermocouple placed near the sample chamber, whereas pressure was determined by measuring the lattice parameters of an internal standard (Au or NaCl), based on its *P*-*V*-*T* equation of state (Anderson et al. 1989; Birch 1978).

We initially compressed the sample to *P* = 34.45 GPa at room temperature, based on the ruby pressure scale (Mao et al. 1978). At this pressure, magnetite should have transformed to the high-pressure phase completely (Huang and Bassett 1986). We then took the diamond cell to the European Synchrotron Radiation Facility (ESRF) for in situ X-ray diffraction measurements. The experimental setup at ESRF (beamline ID30) was described by

*E-mail: fei@gl.ciw.edu

†Present address: Nowat Bayerisches Geoinstitut Universitaet Bayreuth, D-95440 Bayreuth, Germany.

