

Variable pressure-temperature neutron diffraction of wüstite (Fe_{1-x}O): Absence of long-range magnetic order to 20 GPa

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Neutron diffraction measurements have been performed on polycrystalline Fe_{1-x}O (wüstite) up to 20.3 GPa using a large-volume moissanite anvil cell at room temperature to examine the existence of long-range magnetic ordering in the high-pressure rhombohedral phase of the material. This investigation is crucial for understanding the nature of high-pressure phase transitions in Fe_{1-x}O . Low temperature ambient pressure neutron diffraction measurements on the same sample were also conducted at 190, 180, and 85 K to compare with the high-pressure results. Magnetic peaks are expected to be observed under pressure similar to those at 180 K at ambient pressure. However, no magnetic peaks were evident in the high-pressure diffraction patterns (to 20.3 GPa at 300 K). The absence of magnetic peaks indicates the absence of long-range magnetic order in Fe_{1-x}O under these conditions. This result indicates the need to reconsider the interpretation of high-pressure Mössbauer studies and the mechanism of the high-pressure phase transitions in Fe_{1-x}O . © 2005 American Institute of Physics. [DOI: 10.1063/1.1852075]

The study of highly correlated transition-metal oxides is a fundamentally important topic in diverse fields ranging from condensed-matter physics and chemistry to earth science.^{1,2} The properties of these compounds are complicated by the interactions of charge, spin, lattice, orbital moment, and defects in the system. A combination of many techniques is required to investigate the interactions. With the availability of new high-pressure techniques³⁻⁵ and third-generation high-intensity neutron scattering facilities, large-volume high-pressure neutron scattering provides a way to study how the interactions evolve with pressure, information crucial for understanding transition-metal oxide systems. Nonstoichiometric Fe_{1-x}O (wüstite), a rocksalt-structured, antiferromagnetic, charge-transfer type insulator with T_N at 198 K, is usually considered to be a prototype compound in this group. The magnetic structure of Fe_{1-x}O below T_N determined by neutron powder diffraction indicates that the Fe spins align ferromagnetically with a given $\{111\}$ plane, but the planes are stacked antiferromagnetically along the $\langle 111 \rangle$ direction. The magnetic spin lattice is twice that of the Fe nuclear lattice, and the two observed magnetic peaks are indexed by cubic symmetry as superlattice reflections $3/2$, $1/2$,

$1/2$ and $3/2$, $3/2$, $1/2$, respectively, in the low-temperature ambient pressure neutron powder experiments. Accompanied by magnetic ordering below T_N , the cubic cell distorts on cooling into a rhombohedral cell due to magnetostriction⁶ (see the structural models in Fig. 1). On the other hand, under pressure, the material transforms from a cubic cell into a rhombohedral cell at 15 GPa.

Okamoto *et al.*⁸ reported the pressure dependence of the Néel temperature of Fe_{1-x}O to be $dT_N/dP=6.5$ K/GPa, and Vaughan and Drickamer⁹ observed magnetic dipole splitting in their high-pressure Mössbauer experiments near 14 GPa at 300 K. Later, Yagi *et al.*¹⁰ proposed that the transition at 15 GPa (300 K) that was found in their experiments was also a magnetic ordering transition, based not only on the similarity of cell distortion between the high-pressure, room-temperature, and ambient pressure, low-temperature transitions, but also because the pressure dependence of the Néel temperature gives T_N 300 K at 15 GPa. Later, high-pressure Mössbauer studies¹¹ confirmed the magnetic splitting of FeO above 15 GPa, which was also attributed to magnetic ordering. Consequently, the conjecture of Ref. 10 has been generally accepted as correct.^{12,13} Despite this agreement, the long-range magnetic subsystem of Fe_{1-x}O at low-temperature ambient pressure has been determined by the neutron diffraction method,^{2,14} whereas the magnetic lattice predicted at high-pressure 300 K has never been confirmed.

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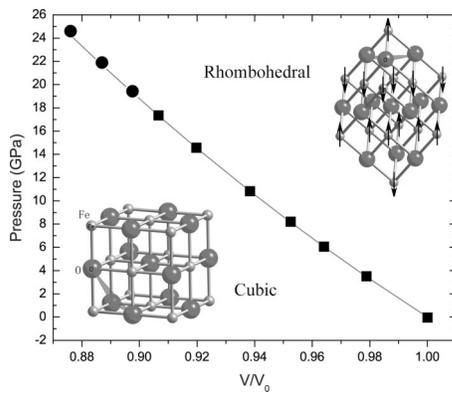


FIG. 1. P - V data and fit below 19.6 GPa and corresponding structural models (solid square: cubic phase; solid circle: rhombohedral phase).

Since Mössbauer spectroscopy probes the average local structure in the vicinity of the Fe ion, it cannot be used to unambiguously prove the existence of a long-range magnetic lattice if the sample contains ferric ion clusters and impurities (e.g., a magnetite component).^{15–17} We have carried out neutron powder diffraction with a moissanite anvil cell (MAC) to investigate Fe_{1-x}O to 20.3 GPa to investigate the predicted long-range magnetic ordering at 15 GPa, which is crucial for understanding the nature of the transition in Fe_{1-x}O at room temperature. The measurements represent the highest pressure achieved on a $>2 \text{ mm}^3$ sample volume for high-pressure neutron experiments with a MAC. In contrast to spectroscopic techniques, diffraction can provide direct information on the periodicity of the nuclei and magnetic lattice.

The Fe_{1-x}O sample was prepared by cold-pressing reagent-grade hematite (Fe_2O_3) into centimeter-sized pellets. The hematite pellets were held for $\sim 24 \text{ h}$ at 1200°C and 10–11 bars f_{O_2} in a CO/CO_2 gas-mixing furnace. The formation of magnetite on cooling was avoided by drop quenching the sample into a separate container with the same gas mixture. The cell parameter a of the FeO was measured by x-ray diffraction to be $4.30269(22) \text{ \AA}$, corresponding to $\text{Fe}_{0.93}\text{O}$.¹⁸ The details of MAC and experimental setup are reported elsewhere.⁵ Pressures were generated between two gem-quality single crystal moissanite anvils with 6 mm cutlets. A 2 mm hole was drilled in a 2 mm thick Ti/Zr composite gasket into which about 12 mm^3 of polycrystalline wüstite $\text{Fe}_{0.93}\text{O}$ was placed (the final sample volume was about 4.4 mm^3 after compression to 20.3 GPa).

The high-pressure neutron experiments were performed at the High Pressure Preferred Orientation Diffractometer (HIPPO) beam-line of Los Alamos Neutron Science Center (LANSCE), Los Alamos National Laboratory. The incident unpolarized thermal neutrons pass into the press and through one of the single-crystal moissanite anvils to the sample along the unique axis of the cell. At each pressure, the data were collected for 8 h and the diffraction patterns were obtained by integrating the intensities from detectors mounted at diffraction angles of 90° . Though great effort was made to shield the diffraction from the MAC and press, Fe diffraction from the cell and press was still recorded in experiment when the pressures were applied. The collected intensity versus converted to intensity vs. d -spacing for GSAS refinement.¹⁹ In order to simplify the experiments and be able to clearly record any peaks that may appear under pressure, no pressure sensor was used in the sample chamber and the pressure of

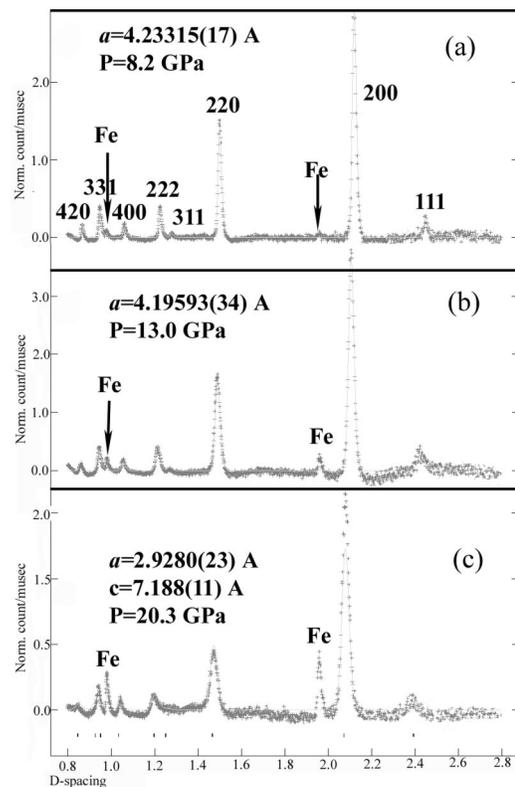


FIG. 2. Neutron diffraction patterns (with background removed) collected at different pressures: (a) 8.2 GPa; (b) 13.0 GPa; and (c) 20.3 GPa. The solid lines are the calculated patterns from Ref. 19.

the sample was determined from its equation of state (EOS) by using the measured lattice parameters. The EOS of the powder sample was determined separately under hydrostatic conditions (using helium as a pressure medium) with a diamond anvil cell using synchrotron radiation at HPCAT Sector 16, Advanced Photon Source (APS), Argonne National Laboratory. The low-temperature ambient pressure powder diffraction was measured at high intensity powder diffraction (HIPD) at Intensive Pulse Neutron Source (IPNS), Argonne National Laboratory to compare with the high-pressure results, and a small amount of Fe was added to the sample in order to simulate the diffraction patterns of Fe from the MAC and press. The data were collected at temperatures of 190, 180, and 85 K using detectors at a diffraction angle of 90° ; the exposure time at each temperature was about 3 h.

A fit of a third order Birch–Murnaghan EOS to the pressure-volume data is shown in Fig. 1. The peak splitting of 111 and 220 are observed after 19.6 GPa, but noticeable peak broadening of 220 can be observed after 14.5 GPa. The initial broadening of the 220 peak is regarded as the onset of the phase transition, and the transition appears nearly complete by 19.6 GPa. The isothermal bulk modulus K_0 and its pressure derivative K'_0 that were obtained from the fit are $158.2(2.7) \text{ GPa}$ and $2.4(0.4)$, respectively.

The measured neutron diffraction patterns collected at different pressures and different temperatures, together with the calculated patterns are displayed in Figs. 2 and 3. Since the pressure was estimated for nonhydrostatic conditions by using EOS from hydrostatic conditions, the pressure might be underestimated.²⁰ Notably, the 111, 311, and 420 peaks are broadened dramatically in the pattern collected at 20.3 GPa, similar to the synchrotron data at 19.6 GPa. The neutron patterns at 8.2 GPa and 13.0 GPa can be indexed

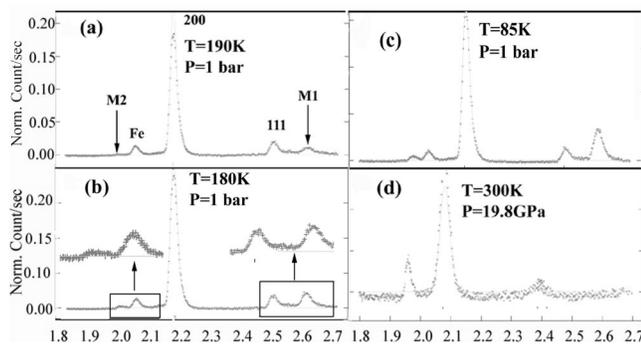


FIG. 3. Comparison of neutron diffraction patterns (from 1.8 to 2.7 Å) collected at (a) 190 K ambient pressure; (b) 180 K ambient pressure; (c) 85 K ambient pressure; and (d) from 20.3 GPa 300 K. The solid lines represent that calculated patterns from GSAS without magnetic ordering. M1: magnetic peak which has half d -spacing of nuclear peak of (311) and can be indexed as $3/2, 1/2, 1/2$; M2: magnetic peak which has half d spacing of nuclear peak of (331) and can be indexed as $3/2, 3/2, 1/2$. The observation of magnetic superlattice peaks is compatible with previous experiments.

with a cubic cell, whereas the pattern at 20.3 GPa is best indexed as rhombohedral ($c/a=2.455$), though it is close to cubic symmetry ($c/a=2.450$). The R_{wp} and R_p values for using rhombohedral and cubic symmetries fitted to the experimental diffraction patterns are 3.6%, 2.6%, and 4.0%, 3.2%, respectively. The refined cell parameters, peak indexing, and the calculated pressures are also shown in Fig. 2.

The most important diffraction pattern at 20.3 GPa does not show the splitting of 111. This is because the splitting is very sensitive to hydrostaticity and is not easily observed under nonhydrostatic condition.^{21,22} X-ray diffraction studies, show that the cubic to rhombohedral phase transformation occurs around 8–15 GPa by the sign of the broadening of the diffraction 111 and 220,^{7,21,22} which occurs much earlier than the appearance of splitting. Based on the previously reported dT_N/dP ,⁸ T_N at 20.3 GPa should be equal to 330.0 K (198 K+20.3 GPa*6.5), resulting in T/T_N close to $300/330.0=0.91$. According to experiments on powdered FeO at 180 K and ambient pressure, the intensity ratio of the $3/2, 1/2, 1/2$ magnetic peak to the 200 nuclear peak with the similar T/T_N ratio (180/198 K=0.91) is around 10% (Fig. 3). No magnetic superlattice reflections, roughly corresponding to peaks at 1.903 and 2.500 Å at 20.3 GPa, were observed in the high-pressure room temperature experiment, however. Though the background of spectra at 20.3 GPa is about 4–6 times that of spectra at low temperature, the 111 peak at 20.3 GPa still can be resolved. The M1 magnetic peak shown in Fig. 3 with half d -spacing of nuclear peak 311, has a similar intensity to that of nuclear peak 111 at 180 K ambient pressure, therefore, it is expected that this magnetic peak would be observed if the pressure dependence of T_N had been predicted correctly.

That no magnetic peaks were observed in this neutron diffraction experiment indicates that no long-range magnetic ordering of $Fe_{1-x}O$ occurs below 20.3 GPa at 300 K. Thus, this conclusion contradicts the interpretation of Mössbauer studies. Measurement carried out at ambient condition have demonstrated that^{15–17,23} non-stoichiometric $Fe_{1-x}O$ has complex defect clusters formed from ferric Fe (located in tetrahedral site of oxygen) and the surrounding vacancies (in octahedral sites of oxygen), which have their own magnetic ordering schemes that couple with the FeO lattice.²⁴ With compression, the distribution and the geometry of defect

clusters change. Since Mössbauer spectroscopy probes the averaged local electric and magnetic environment of Fe nuclei, the results cannot be used to infer the existence of a uniform, long-range magnetic order if the structure contains magnetic defect clusters and impurities. The magnetic dipole splitting observed in the high-pressure Mössbauer results therefore do not necessarily provide information on long-range magnetic ordering but instead may probe magnetic and quadrupole interaction originating from defect clusters or impurities. The absence of the long-range magnetic lattice in $Fe_{1-x}O$ at these high pressures should suggest the need to modify previously reported P - T phase diagrams of the material, as well as a reconsideration of magnetoelastic coupling between phonons and the magnetic subsystem of FeO as the driving force for the 15 GPa phase transition.¹³ The contribution to the softening of the elastic modulus element C_{44} of $Fe_{1-x}O$ under pressure from the changing geometry and distribution of the defect clusters should be considered along with the magnetic coupling between the defect clusters and FeO lattice at high pressure. Thus, how the magnetic defect clusters affect the high-pressure phase transition is an interesting and continuing problem to be investigated with the new technique presented here.

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