

# Phase Transition and Effect of Defects on Thermal Expansion in $\text{Fe}_x\text{O}$

J. Zhang,<sup>1,2</sup> Y. Zhao,<sup>1</sup> Y. Wang,<sup>3</sup> T. Uchida<sup>3</sup>

<sup>1</sup>Los Alamos National Laboratory, Los Alamos, NM, U.S.A.

<sup>2</sup>Consortium for Materials Properties Research in Earth Sciences (COMPRES), Mineral Physics Institute (MIP), State University of New York (SUNY) at Stony Brook, NY, U.S.A.

<sup>3</sup>Consortium for Advanced Radiation Sources, The University of Chicago, Chicago, IL, U.S.A.

## Introduction

Transition-metal monoxides, such as NiO, CoO, FeO, and MnO, have been receiving considerable attention as model materials for elucidating defect structures, the nature of interaction between defects, and effect of nonstoichiometry on physical properties. Wüstite is an iron oxide that possesses rock-salt structure and exhibits a wide range of nonstoichiometry ( $0.88 < x < 1$  in  $\text{Fe}_x\text{O}$ ). At atmospheric pressure, the stoichiometry of wüstite is defined by two univariants; one is for wüstite in equilibrium with iron, and the other is for wüstite in equilibrium with magnetite. The eutectoid point is located at 849K and  $x \approx 0.945$  in the temperature-composition space.

The precise values of the eutectoidal temperature and composition at high pressure, however, have not been determined by any previous experiment. While several studies have aimed at determining the wüstite/iron phase boundary, the effect of pressure on the wüstite/magnetite (i.e., oxygen-rich) phase boundary is entirely not known, even though some insights can be inferred from the only available experimental study of Shen et al. [1].

Another important issue deals with the effect of defect concentration on the thermal expansion of wüstite. Overall, only a few attempts have been made to address this issue at atmospheric pressure [2]. This limited effort is primarily due to the fact that such a volume-related thermal property is more difficult to study in wüstite than in most defect-free materials because the arrangement of defect clusters and the extent of magnetite exsolution may adjust to changes in temperature [3, 4]. Thus, an experimentally difficult challenge is to separate the volume changes contributed by metal-oxygen bond expansion from those possibly contributed by continuous stoichiometry variation with temperature. Nevertheless, from available experimental data [2], it is generally concluded that thermal expansion of wüstite does not appear to vary with stoichiometry.

## Methods and Materials

$\text{Fe}_x\text{O}$  with  $x = 0.945$  was used as a starting material. The experiments were carried out using both DIA-type and T-cup multi-anvil apparatus, interfaced with synchrotron x-ray diffraction at the 13-BM beamline at

the APS. In one group of DIA experiments, the data were collected at a constant pressure of 1.93 GPa and at temperature intervals of 50 to 100K up to 1073K upon both heating and cooling. In the other group, three quench-type experiments were conducted at  $2.0 \pm 0.2$  GPa at 673, 773, and 1073K. In the T-cup experiment, the data were obtained at conditions up to 14.0 GPa and 1073K. Only room-temperature data are presented in this report.

## Results

The variation of full width at half-maximum (FWHM) as a function of pressure at ambient temperature is plotted in Fig. 1 for (111) and (200) peaks of wüstite. As expected, the wüstite sample behaves elastically with increasing pressure up to 4-4.5 GPa and yields at higher pressures. At pressures near 11 GPa, however, the width of the (111) peak increases dramatically, and the width of the (200) peak decreases. The increase in the peak width is most likely due to the phase transition to rhombohedral structure, which is characterized by a splitting of the (111) diffraction line. The decrease in the peak width may be due to the phase-transformation-induced stress relaxation. Our observation is in agreement with a previous finding that the cubic-rhombohedral transition under

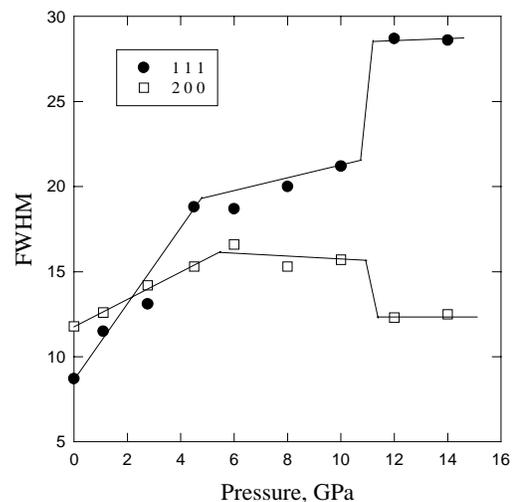


FIG. 1. Variation of peak width of polycrystalline  $\text{Fe}_{0.945}\text{O}$  as a function of pressure at ambient temperature.

nonhydrostatic conditions in wüstite may occur at much lower pressures than the pressure for its equilibrium boundary [5].

For the experiments performed at 1.93 GPa, exsolution of magnetite was first observed upon heating to 523-573K (Fig. 2). Magnetite was found to coexist with wüstite up to 823K; above this, wüstite was the only stable phase. During cooling from 1073K, the process was reversible, and magnetite exsolution reoccurred at 673-723K. The relative intensity of magnetite increased dramatically from 723 to 673K, whereas at lower temperatures, it remained constant. The wüstite + magnetite assemblage returned to room temperature upon further cooling and was recovered at ambient conditions. From these observations, the eutectoid temperature at 1.93 GPa is estimated to be 673K, which is substantially lower than it is at atmospheric pressure.

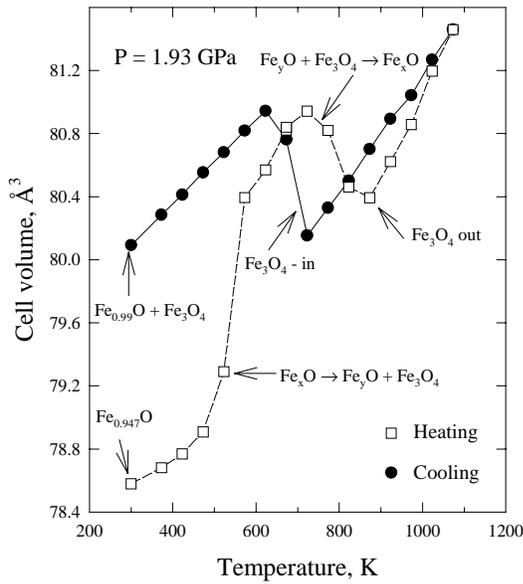


FIG. 2. Variation of unit-cell volume of  $Fe_xO$  as a function of temperature at a constant pressure of 1.93 GPa.

Magnetite exsolution causes the lattice parameters of the coexisting wüstite to show large discontinuous variations with temperature upon either heating or cooling, as shown in Fig. 2. Since no iron metal (bcc or fcc phase) was observed in the diffraction patterns upon either heating or cooling, the observed processes must follow a kinetically controlled reaction  $Fe_xO \rightarrow Fe_yO + Fe_3O_4$ , with  $y$  that is  $>x$  [6]. In the presence of magnetite, the compositions of the recovered wüstite approach  $Fe_{0.99}O$ , even though the starting wüstite sample was significantly more depleted in iron. Such a change in

stoichiometry is similar to earlier observations at atmospheric and high pressures [1, 6, 7].

Because of the magnetite exsolution, two volume-temperature data sets were obtained in the experiment at 1.93 GPa, with a break at the temperatures between 673 and 773K (Fig. 3). These experiments are thus capable of yielding the thermal expansion for wüstite of two different compositions, which, based on the experimental results presented below, are  $Fe_{0.99}O$  and  $Fe_{0.945}O$ .

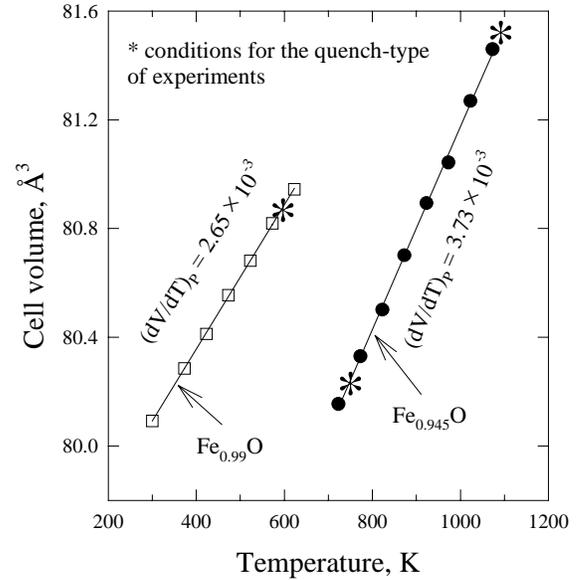


FIG. 3. Effect of defect on thermal expansivity of  $Fe_xO$ .

To explore the possibility that the observed volume changes in  $Fe_xO$  (Fig. 3) may be partly due to continuous stoichiometry variation, three quench-type in situ experiments were conducted at  $2.0 \pm 0.2$  GPa and at temperature conditions indicated in Fig. 3. For a wüstite + magnetite assemblage, the composition of the coexisting wüstite quenched from 673K was similar to the compositions of those recovered via slow cooling to room temperature (Fig. 2), with the lattice parameters approaching  $4.328 \pm 0.001$  Å (i.e.,  $Fe_{0.99}O$ ). These results are thus in agreement with previous findings. At the temperatures where magnetite was unstable ( $T > 723K$ ), the wüstite samples were recovered with lattice parameters similar to those of the starting wüstite. The composition variation of wüstite in the 773-1073K temperature range was negligibly small, within errors of the refinements. These results suggest that the observed volume changes in Fig. 3 reflect the bond expansion in  $Fe_xO$ . As revealed by Fig. 3,  $Fe_{0.945}O$  shows a slope of  $(\partial V/\partial T)_P$  that is about 30% larger than that of  $Fe_{0.99}O$ , which provides the first experimental evidence of a

substantial difference in thermal expansivity between iron-rich and more iron-deficient wüstite.

## Discussion

Our observation that the composition of  $\text{Fe}_x\text{O}$  does not vary in a temperature range of 773 to 1073K differs from the general trend established by previous studies that the stoichiometry of  $\text{Fe}_x\text{O}$  in equilibrium with iron metal tends to increase with pressure but decrease with increasing temperature [8-11]. Katura et al. [9], however, observed that in the absence of iron metal, the wüstite sample was significantly more iron-depleted than samples recovered at similar pressures and temperatures conditions but in equilibrium with iron, even though in the former case, the sample may have reacted with the iron of the capsule. This and the present observations thus suggest that the dependence of wüstite's composition on pressure is affected by the presence of iron and hence by the oxygen buffers. In addition, some scatters were found in previous studies. The data of Simons and Seifert [11], for example, show little dependence of the wüstite composition on temperature in the range of 873 to 1073K, which is similar to the present observations. It is thus concluded that below 1073K, the contribution of the defect structure variations to the volume changes or thermal expansion of wüstite is small, and the determined values of thermal expansion of this study primarily reflect metal-oxygen bond expansion.

## Acknowledgments

This work was performed under the auspices of the U.S. Department of Energy (DOE) under Contract No. W-7405-ENG-36 with the University of California. COMPRES is supported by the National Science Foundation. Use of the APS was supported by the DOE Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-ENG-38.

## References

- [1] P. Shen, W.A. Bassett, and L. Liu, *Geochim. Cosmochim. Acta* **47**, 773-778 (1983).
- [2] M. Hayakawa, J.B. Cohen, and T.B. Reed, *J. Am. Ceram. Soc. Bull.* **55**, 160-164 (1972).
- [3] R.M. Hazen and R. Jeanloz, *Reviews of Geophysics and Space Physics* **22**, 37-46 (1984).
- [4] W. Schweika, A. Hoser, M. Martin, and A.E. Carlsson, *Phys. Rev. B* **51**, 15771-15788 (1995).
- [5] Mao et al., *Phys. Earth Planet. Int.* **96**, 135-145 (1996).
- [6] N.N. Greenwood and A.T. Howe, *J. Chem. Soc. Dalton* **1**, 116-121 (1972).
- [7] S. Stolen, R. Glockner, F. Gronvold, T. Atake, and S. Izumisawa, *Am. Mineral.* **81**, 973-981 (1996).
- [8] Y. Fei, in *Mineral Spectroscopy: A Tribute to Roger G. Burns*, edited by M.D. Dyar, C. McCammon, and M.W. Schaefer (1996), pp. 243-254.
- [9] T. Katsura, B. Iwasaki, S. Kimura, and A.J. Akimoto, *Chem. Phys.* **47**, 4559-4560 (1967).
- [10] C.A. McCammon, *Science* **259**, 66-68 (1993).
- [11] B. Simons and F. Seifert, *Carnegie I. Wash.* **78**, 625-626 (1979).