Effect of Defects on the Elastic Properties of Wüstite

Jianzhong Zhang
Center for High-Pressure Research and Mineral Physics Institute, State University of New York at Stony Brook, Stony Brook, New York 11794

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Wüstite (Fe_xO) has been studied under static high pressure in the composition range $x = 0.95-0.99$. $Fe_{0.99}O$ is substantially less compressible than Fe_xO with $x < 0.98$. Such observations provide the only direct evidence of a significant effect of defect concentration on the elastic properties and support the results of crystal-field modeling for ideal stoichiometric wüstite. The bulk moduli of Fe_xO show a discontinuous variation at compositions that are within the predicted range for the defect clusters to form, a behavior that may be caused by an order-disorder transition of the defect structure.

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The variation of elastic properties with defect concentration or stoichiometry, a fundamental problem in the study of defect materials, has generally not been well understood by either experiments or theories. The experimental constraints on this issue have, until now, mainly come from studies of wüstite, an iron oxide that possesses rocksalt structure and exhibits a wide range of nonstoichiometry ($0.88 < x < 1$ in Fe_xO) [1]. The elastic moduli of these compounds have been extensively studied by dynamic [2–4] and static [5–10] measurements and found to be insensitive to the degree of nonstoichiometry over a composition range $x = 0.90-0.98$. Such observations seem to be in accord with existing continuum and atomistic theories that predict a minor change in bulk modulus with stoichiometry of wüstite [8]. However, the bulk moduli of ideal stoichiometric FeO, predicted from crystal field contributions to the elastic moduli for the $3d$ transition-metal monoxides [4,8,11], are (15–20)% larger than the experimentally determined values for Fe_xO. This difference, inferring a possible effect of defect concentration on the elastic properties of wüstite has so far not been demonstrated by direct experimental evidence.

The present study is further motivated by theoretical predictions of a presumably order-disorder transition of the defect microstructure at deviations greater than 0.01 from ideal stoichiometry in $3d$ transition-metal monoxides of $B1$ structure [12]. Neither direct structure information nor indirect experimental proof, however, is yet given for this predicted behavior for Fe_xO. In this regard, studies of the physical properties near ideal stoichiometric composition may provide some indications of the defect structure present in Fe_xO.

Wüstite is thermodynamically stable only at temperatures above 849 K at atmospheric pressure, with compositions of rapidly quenched Fe_xO samples limited to $x \leq 0.95$ [1]. The iron content of Fe_xO in equilibrium with metallic iron increases with pressure but reaches a plateau near $Fe_{0.98}O$ at pressures greater than 10 GPa [10,13]. At both atmospheric and high pressures, however, wüstite tends to exsolve magnetite (Fe_3O_4) on slow cooling when the temperature is below 849 K [14,15]. In the presence of magnetite, the composition of the coexisting wüstite approaches ideal or near-ideal stoichiometry, even though the starting wüstite sample is significantly more depleted in iron. In the present study, I have made use of this phenomenon to measure the elastic property for a near-stoichiometric wüstite at ambient temperature. In addition, comparative studies were carried out on MgO, $Fe_{0.95}O$, and $Fe_{0.96}O$, which eliminate pressure and deviatoric stress as variables in the present measurements, and allow detection of subtle difference in compressibilities.

The starting wüstite was prepared by heating Fe_2O_3 to 1473 K under controlled oxygen fugacity ($f_{O_2} = 10^{-11.9}$ atm) in a CO-CO_2 gas-mixing furnace. The lattice parameter of this synthesized sample is $a_0 = 4.309(1)$ Å, corresponding to composition $Fe_{0.945}O$ [16]. Five series of experiments (Table I) were carried out to measure variation of the unit-cell parameters as functions of pressure and temperature, using a large-volume, DIA-type apparatus interfaced with synchrotron x-ray diffraction [17]. Samples were loaded in boron-nitride (BN) capsules; when $Fe_{0.945}O$ and MgO were studied in the same experiments, they were separated by NaCl that also served as a pressure standard. Pressure was determined using the Decker equation of state for NaCl [18], and temperature was measured with a W/Re24%-W/Re6% thermocouple. In each experiment, the samples were first compressed at ambient temperature to the targeted pressure, followed by heating to the temperature of 1073 K. Energy dispersive x-ray spectra were collected on heating and cooling cycles, and on decompression in the experiments 2, 3, and 5 (Table I), immediately after the high temperature cycle (i.e., without first releasing the pressure to ambient). This paper, however, reports the volume measurements obtained at ambient temperature only. The full width half maxima of the diffraction peaks of near-stoichiometric wüstite at high pressures and ambient temperature are identical to those of the starting wüstite and NaCl, indicating a relaxation of deviatoric stress after the heating-cooling cycle [17].

The near stoichiometric wüstite (Table I) was obtained by exsolving magnetite (Fe_3O_4) from $Fe_{0.945}O$

TABLE I. Ambient unit-cell parameters and compositions of Fe_xO recovered from various temperature and pressure conditions.

Run	Starting material	P,[a] GPa	T,[a] °C	Run product	Lattice parameter,[b] Å	x[c] in Fe_xO
1	$Fe_{0.945}O$, MgO	2.65	800	$Fe_xO + Fe_3O_4$	4.3275(9)	0.987(3)
2	$Fe_{0.945}O$, MgO	5.44	800	$Fe_xO + Fe_3O_4$	4.3260(11)	0.985(3)
3	$Fe_{0.945}O$, MgO	8.20	1000	Fe_xO_4	4.3113(11)	0.950(3)
4	$Fe_{0.945}O$	1.93	800	$Fe_xO + Fe_3O_4$	4.3273(10)	0.987(3)
5	$Fe_{0.945}O$ + Fe	8	1000	Fe_xO + Fe	4.3149(6)	0.958(2)

Numbers in parentheses refer to the standard deviation of the last digit(s).

[a] Conditions at which slow cooling or quenching took place.

[b] The lattice parameters throughout this work were calculated by least-squares fitting using five diffraction lines; the relative standard deviations (σ) in unit-cell volumes are typically less than 0.08%. The values listed here are averages of two or three measurements; the lattice parameters measured at different positions of recovered samples are identical within 1σ of the refinements, indicating a homogeneous sample.

[c] Calculated on the basis of the composition-lattice parameter relationship of Simons [16]; a detailed discussion of this issue was given by Hazen and Jeanloz [1].

via slow heating and cooling in the temperature range 300–1073 K at 1.93, 2.65, and 5.44 GPa, following a kinematically controlled reaction $Fe_xO \longrightarrow Fe_yO + Fe_3O_4$, with $y > x$ [15]. The compositions of the recovered Fe_xO samples from this process are independent of pressure up to 5.44 GPa (Table I) and are similar to earlier results obtained at atmospheric and high pressures [14,15]. These observations indicate that stoichiometry and, hence, defect structure of Fe_xO are unlikely to show continuous variation with pressure at ambient temperature. Magnetite exsolution, however, was not observed in the experiment at 8.2 GPa on heating and cooling in the range 300–1073 K. In the absence of magnetite, the composition of the recovered wüstite sample ($Fe_{0.95}O$) is only marginally different from that of the starting wüstite; this is consistent with the observation that the lattice parameters show a small discontinuous variation near 573 K during heating. The $Fe_{0.96}O$ sample was synthesized from a mixture of $Fe_{0.945}O$ and metallic iron at 8 GPa and 1273 K. This wüstite is more iron depleted than those previously synthesized [10,13], approaching $Fe_{0.98}O$ at similar pressure and temperature conditions. This is probably due to the difference in the oxygen fugacity, which was not controlled in the present experiments. Since MgO and NaCl in all experiments were recovered with their initial unit-cell parameters, the observed change in the wüstite compositions cannot result from a change in system calibration.

The room-temperature compression data of Fe_xO and MgO from five experiments are plotted in Fig. 1 in the form of V/V_0. It is evident that, for all three experiments where near-stoichiometric wüstite (Fe_xO with $x =$ 0.985–0.987, denoted thereafter as $Fe_{0.99}O$) was recovered from pressures up to 5.44 GPa, the compression data form a smooth trend, with $Fe_{0.99}O$ being less compressible than MgO. On the other hand, $Fe_{0.95}O$ and $Fe_{0.96}O$, which show similar compressibilities within uncertainties of the experiments, are more compressible than MgO and therefore substantially more compressible than $Fe_{0.99}O$. Not only do these results demonstrate reproducibility of the present measurements but they provide the sole experimental evidence of a substantial difference in compressibilities between iron-rich and more iron-deficient wüstite.

The pressure-volume data are fitted to a Eulerian finite-strain equation of state [19]. The pressure P is given to third order in strain f by

$$P = 3f(1 + 2f)^{5/2}K_0[1 - 2\xi f + \ldots], \qquad (1)$$

with $\xi = 3/4(4 - K_0')$ and $f = 1/2[(V/V_0)^{-2/3} - 1]$, where K_0 and K_0' are isothermal bulk modulus and its

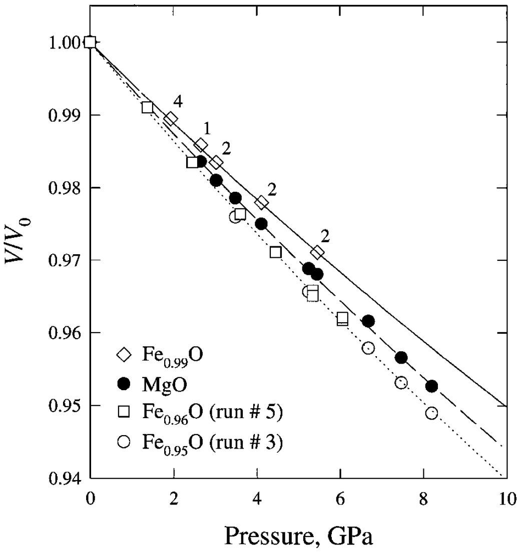

FIG. 1. Compression data of MgO, $Fe_{0.95}O$, $Fe_{0.96}O$, and $Fe_{0.99}O$ at room temperature. The numbers next to the diamond symbols indicate the experiments from which the data were collected. Measurements with MgO and wüstite in the same experiments can be identified by the data points at identical pressures. The solid, dashed, and dotted curves represent results of calculation using Eq. (1), with the K_0 values of 175, 155, and 142 GPa, respectively. Errors in the volume measurements are less than or equal to symbol size. The uncertainty in pressure is about 0.1 GPa.

pressure derivative, respectively. Because of the limited pressure range of the present study that inhibits an accurate constraint on K_0', a second-order equation of state is employed, with $\xi = 0$ in Eq. (1). The resulting least-squares fits for the bulk modulus are 141, 143, 155, and 175 GPa for $Fe_{0.95}O$, $Fe_{0.96}O$, MgO, and $Fe_{0.99}O$, respectively. Note here that the bulk modulus of 175 GPa was obtained from the data set of Fe_xO having $x = 0.985–0.987$ (Fig. 1). The uncertainties in K_0 values for Fe_xO are estimated to be approximately 5 GPa, associated with errors as well as reproducibilities in the lattice parameter measurements (Table I). For MgO, the K_0 value is in agreement with previously determined values using a variety of experimental techniques ([20] and references therein). For Fe_xO, the discrepancies exist among some of the earlier studies for compositions $x = 0.90–0.98$ (Fig. 2). The spread of K_0 values in Fig. 2 is in part due to the fact that this is a compilation of measurements of different reliability; errors may arise, for example, from influence of deviatoric stress [4,10]. On the other hand, because all measurements, including the present study, were conducted on Fe_xO samples that are outside their stability field and because *in situ* neutron diffraction studies have revealed that types of the defect structures are a function of temperature [21], it is possible that the elastic properties would be affected by different defect microstructures associated with thermal histories of the samples studied. The isothermal bulk moduli of Fe_xO from previous studies for compositions $0.90 < x < 0.98$, however, lie in the range 144–152 GPa and are insensitive to the degree of nonstoichiometry (Fig. 2). The K_0 values of $Fe_{0.95}O$ and $Fe_{0.96}O$ of this study are thus in agreement with previous findings.

The bulk moduli of Fe_xO with $x > 0.98$ have not previously been determined; the values found in this investigation for $Fe_{0.99}O$, however, are supported by the results of theoretical and empirical predictions for ideal stoichiometric wüstite. The crystal-field modelings among the essentially stoichiometric 3*d* transition-metal monoxides [4,8,11,22] have predicted that the bulk modulus should increase through the sequence MnO, FeO, CoO, and NiO, with the bulk modulus of FeO being in the range 176–180 GPa (Fig. 2). Additional confidence in the present measurements on $Fe_{0.99}O$ and in the crystal-field models derives from the observations of a linear increase of the bulk modulus with unit-cell volume among MnO, CoO, and NiO (Fig. 3), with the predicted bulk modulus of stoichiometric FeO being in accord with the present finding for $Fe_{0.99}O$. Further evidence on this matter lies in the fact that the difference in the bulk modulus between $Fe_{0.99}O$ and MgO (175 versus 155 GPa) is in accord with the trend established by other ferromagnesian materials, in that the complete substitution of Fe for Mg in various structure types results in increases of the bulk modulus that range from a few to more than ten percent ([23] and references therein). The significant difference in the elastic moduli between $Fe_{0.99}O$ and more iron-depleted

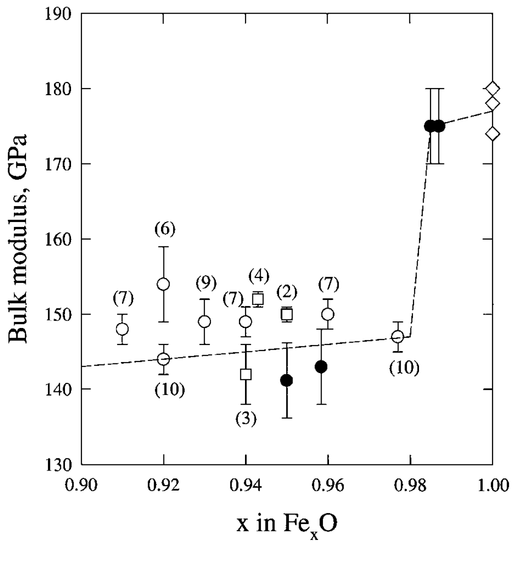

FIG. 2. Variation of isothermal bulk modulus of Fe_xO as a function of nonstoichiometry. Solid circles represent data of the present study. Open squares and circles indicate results obtained from earlier dynamic and compression experiments, respectively; numbers in parentheses refer to the source of studies in the reference list. The bulk modulus data with large errors [5,8] are not included in this compilation. Compression data are all reduced based on $K_0' = 4$, and adiabatic moduli have been corrected to isothermal values. Open diamonds correspond to the values predicted from crystal-field models [4,8,11]. The dashed lines schematically show a possible $K_{0,T}$-x relation over the indicated composition range.

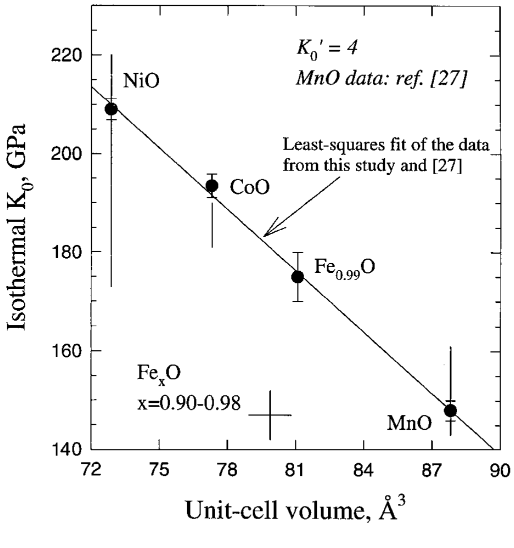

FIG. 3. The bulk modulus-volume systematics for the 3*d* transition-metal monoxides of rocksalt structure. The bulk moduli of NiO and CoO were obtained from eight volume measurements up to 8.2 GPa at ambient temperature, with all the data being collected upon quench from 1073 K to minimize errors resulting from deviatoric stress. These two oxides were studied in a single experiment, separated by NaCl, using the same technique as employed for Fe_xO and in the study of MnO [27]. Equation (1) was used, with $\xi = 0$, to determine the K_0 values. Vertical lines represent the ranges of previous experimental data for NiO, CoO, and MnO, with references already given in [27].

Fe_xO demonstrates that there exists a large discontinuity near $x = 0.98$ in the variation of the bulk modulus with composition (Fig. 2). Outside this critical region, the effect of nonstoichiometry on the bulk moduli seems to be small, within uncertainty of the experiments.

Two types of theories, continuum [24] and atomistic [25], have been proposed to model the changes in elastic properties with defect concentration. Both approaches provide no clue with regard to the presence of a discontinuity in the K_0-x relationship for Fe_xO [8], because the change in elastic modulus in these models is dominated by the leading, structure-independent terms that involve the elastic constants, c_{ij}, and because both theories require input of the c_{ij} values for ideal FeO which are not known. On the other hand, there are indications that the discontinuity in Fig. 2 may be associated with a radical change in the defect structure near the composition $x = 0.98$. It has been well known that the defect structure of Fe_xO with $x \leq 0.95$ is characterized by the presence of octahedral cation vacancies as well as interstitial cations. The defects in Fe_xO do not remain isolated but tend to cluster in periodic arrangements, with each interstitial Fe^{3+} surrounded by four cation vacancies (namely, 4:1 cluster). There is substantial experimental and theoretical evidence that by edge or corner sharing the 4:1 clusters can associate to form larger and more stable 6:2, 8:3, 13:4, etc., defect clusters [26], even though the exact defect structure, i.e., the size, shape, and distribution of these clusters in Fe_xO, and its dependence on temperature are still a matter of much debate. At small deviations from the ideal stoichiometric composition, however, thermodynamic calculations of the defect formation and interaction [12] have suggested that the aggregated defect clusters in wüstite and other rocksalt transition-metal monoxides must dissociate into isolated and randomly distributed point defects. The composition range over which the defects clusters would dominate is model dependent but is generally at deviations of 0.01–0.025 from ideal stoichiometry. In this regard, the discontinuity in Fig. 2, which falls within this predicted composition range, provides a possible new experimental evidence for the presumably order-disorder transition of the defect structure in wüstite.

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