Inverse versus Normal NiAs Structures as High-Pressure Phases of FeO and MnO

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The phase stability of FeO and MnO under high pressure was studied with the first-principles calculations. Our results predict that the high-pressure phase of MnO is a metallic normal NiAs (B8) structure, while that of FeO is the inverse B8 structure (iB8). No materials have ever been known to take the iB8 structure. The novel feature of the iB8 FeO is that the system should be a band insulator in the antiferromagnetic state. Analysis of x-ray diffraction experiments provides further support to the present theoretical prediction for both FeO and MnO. [S0031-9007(98)06813-6]

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FeO and MnO have occupied a special position in condensed-matter physics for decades as prototypical examples of the Mott insulator [1]. Their basic properties are governed by electron correlation, whose strength is measured by U/W with U the effective Coulomb interaction integral between d electrons, and W the d-band width. As the d-band width is directly controlled by pressure, high-pressure studies have been regarded as a useful way to understand the basic properties of Mott insulators.

Under normal pressure, when temperature is decreased below the Néel temperature, FeO and MnO both take the rock-salt (B1) structure with a rhombohedral distortion along the ⟨111⟩ direction of cubic cell. This distorted B1 structure is called rB1 hereafter. Intensive high-pressure experiments on the transition-metal monoxides have revealed that FeO [2–6] and MnO [7–9] undergo a pressure-induced first-order phase transition at around 70 and 90 GPa, respectively. The high-pressure phase of FeO was identified as the NiAs (B8) type [5,6]. Based upon all the known examples of the B8 (NiAs) structure compounds, one expects Fe to occupy the Ni site and O the As site. This structure is named nB8. However, another structure, which is named inverse B8 (iB8), is possible by exchanging the Fe and O positions [10]. The high-pressure phase of MnO is yet unclear [8,9]. An empirical analysis suggested that its high-pressure phase would be the B2 structure [8]. However, a recent x-ray diffraction experiment [9] is inconsistent with this suggestion, although this experiment cannot give us an unambiguous answer because of multiphase coexistence.

In the present work, we have performed first-principles density functional calculations to analyze the high-pressure phases of FeO and MnO. The plane-wave basis pseudopotential method is used to perform the structural optimization. The $2p$ states of oxygen and $3d$ states of Mn and Fe are treated by the Vanderbilt ultrasoft pseudopotential [11,12]. The electron-electron interaction is treated by the generalized gradient approximation (GGA) [13] as employed in similar calculations [10,14].

The GGA calculation is supplemented by the LDA + U method [15], particularly in the low-pressure regime where MnO and FeO are regarded as Mott insulators.

Highly converged total energy calculations were performed for different crystal structures (B1, B2, nB8, iB8) and spin structures [ferromagnetic(FM) and antiferromagnetic(AF)] for different volumes (shown in Fig. 1). The equation-of-state parameters obtained in the present calculations [16] agree well with those obtained in similar calculations [14,17]. First we pay attention to the compressed volume range, over which the GGA calculation will be reliable because of the reduced U/W. Surprisingly for FeO [Fig. 1(a)], the AF-iB8 structure is the most stable high-pressure phase rather than the nB8 structure. At this stage, two fundamental questions are to be answered: (1) Why is the nB8 structure realized rather than iB8 for most of the transition-metal compounds with the B8 structure? (2) What is special about FeO, leading to such a strong stability of iB8?

Anions around a transition metal ion form an octahedron in nB8, and a trigonal prism in iB8. In the latter case, absence of the local inversion symmetry not only about the transition metal site but also about the oxygen site in the AF state reduces the strength of the hybridization of the $3d$ orbitals with the oxygen $2p$ orbitals [18]. As the p-d hybridization contributes to the stability of the structure, this aspect favors the nB8 structure and will explain the general feature that the nB8 structure is actually realized in most cases. However, the calculated electronic density of states (DOS) (shown in Fig. 2) clearly demonstrates the existence of a well defined band gap for the AF-iB8 structure of FeO in the whole volume range shown in Fig. 1(a), which contributes to special stability of this structure. It should be noted that the AF-iB8 FeO is a *band insulator* rather than a Mott insulator because it is insulating even in the high-pressure range where the Mott insulating condition breaks down [10,19]. The calculated band gap even increases slightly with pressure: 0.7 eV at normal pressure and 1.0 eV at 96 GPa.
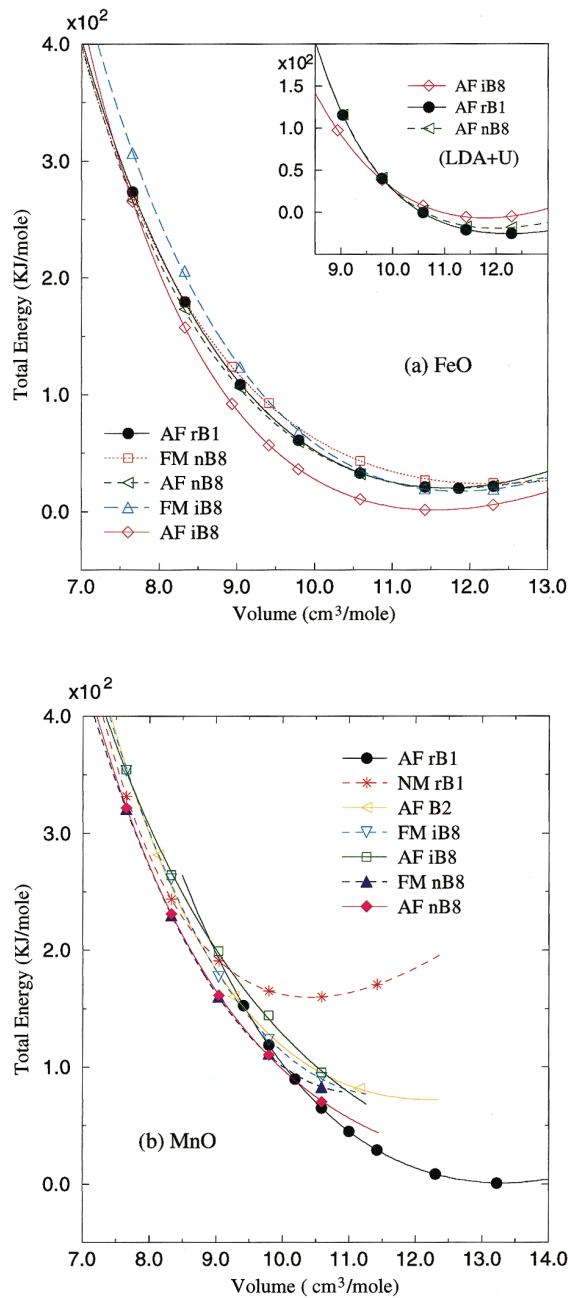
FIG. 1(color). The total energies of FeO (a) and MnO (b) as a function of the volume. The least-squares-fitted curves to Murnaghan's equation of state [26] are shown. For FeO, the results based on the LDA + U calculation with $U_{eff} = 4$ eV are shown as an inset.
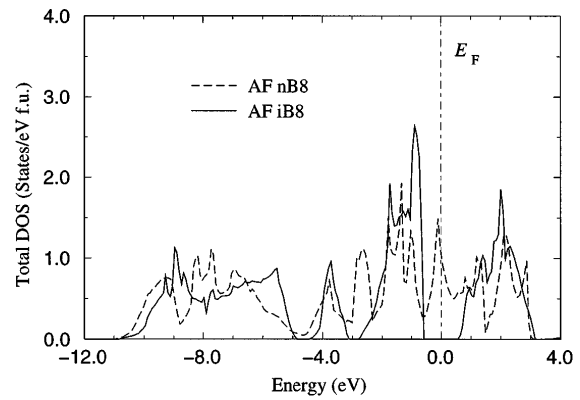

FIG. 2. The calculated electronic density of states (DOS) for AF-iB8 and AF-nB8 FeO with the use of experimentally determined lattice parameters at 96 GPa and 800 K [6].

Puzzling features are that the iB8 structure is predicted to be significantly more stable than the rB1 structure, even at zero pressure, and that the nB8 structure is nearly degenerate in energy with the rB1 structure in a wide volume range. These reflect the fact that the GGA cannot describe the electronic structure of Mott insulators properly: the GGA incorrectly predicts that FeO is metallic at normal pressure. In order to reproduce the correct ground state of FeO, we have to take account of the local electron correlation and the spin-orbit interaction as well. We adopt the LDA + U method with the LMTO (linear-muffin-tin orbital) basis [20] to estimate the corrections caused by these ingredients [21]. This method, with the effective Coulomb interaction parameter U_{eff} of 4 eV, can reproduce a band gap of AF-rB1 FeO in good agreement with the result of an elaborate theoretical analysis [22], and at the same time predicts that the AF-rB1 structure is more stable than the AF-iB8 and AF-nB8 structures at normal pressure. On the other hand, for a compressed volume [6], the same calculation still predicts that the AF-iB8 structure is most stable. After including the U_{eff} correction, the total energies of the AF-rB1 and AF-nB8 phases relative to those of the AF-iB8 phase are shown as an inset of Fig. 1(a).

According to the present calculation, the high-pressure phase of FeO with the iB8 structure should be insulating in contrast to the experimental observation of metallic behavior [23,24]. There are two possible origins of this disagreement. Our calculation assumes stoichiometric FeO, while real samples contain about 5% Fe deficiency. As the AF-iB8 FeO is a band insulator, itinerant carriers will be introduced via Fe deficiency. Another possibility is the mixture of other NiAs type metallic phases in the temperature range of the observed metallic behavior (above 1000 K). According to the present calculation, even if the crystal structure is the iB8 type, FM order makes the system metallic, and moreover, the AF- and FM-nB8 phases are also metallic. Nevertheless, the more than 19 kJ/mole enthalpy gain of the AF-iB8 phase relative to other phases at 100 GPa is large enough to make the AF-iB8 phase dominant even at 1000 K. This statement is based on the following analysis. As the AF and FM states are energetically very close in the nB8 structure [Fig. 1(a)], magnetic order around 1000 K may be totally random, while in the iB8 structure the large energy difference of about 50 kJ/mole between the AF and FM states suggests the existence of at least strong short range AF order. Therefore as an extreme case the magnetic entropy is taken into account only for the

nB8 structure. This contributes about -9 kJ/mole to the Gibbs free energy at 1000 K. Another contribution of -5 kJ/mole at 1000 K from the electronic entropy through the metallic behavior of the AF- and FM-nB8 phases has to be added. Note that the above estimation of the entropy contribution to the Gibbs free energy was made so as to be favorable to the nB8 structure, and yet the estimated enthalpy gains still support the stability of the AF-iB8 phase.

There are other pieces of strong evidence for the iB8 structure as the high-pressure phase of FeO. First, the intensity profile of the observed x-ray diffraction pattern [6] can be reproduced only by the iB8 type, but not by the nB8 type. We consider the relative intensity between (100) and (101) peaks as an example. Experimentally, the latter is stronger than the former. This feature is correctly reproduced only by the iB8 structure. Second, the experimental pressure-volume (P-V) relation for FeO agree best with the theoretical curve for the AF-iB8 structure as shown in Fig. 3(a).

To the best of our knowledge, no materials have ever been known to take the iB8 structure. The uniqueness of FeO in this sense may become even clearer by comparing FeO with FeS which, at normal pressure, takes a structure whose basic building block is the nB8 structure rather than the iB8 structure. The present calculation correctly predicts stronger stability of nB8 compared with iB8 for FeS. This is because the AF-iB8 phase of FeS has a band gap of only 0.18 eV, which is too small to stabilize the iB8 structure.

As for MnO, the present calculation shown in Fig. 1(b) suggests that the most stable high-pressure phase will be the nB8 structure rather than the B2 [8] or iB8 structure. Detailed comparison of the total energies predicts that the FM-nB8 structure has the lowest energy rather than the AF-nB8 structure, though the energy difference is rather marginal.

This theoretical prediction can explain a recent experiment [9] on MnO in a high-pressure range ($>$120 GPa) very well. The consistency of the assignment of the experimental x-ray diffraction peaks at 137 GPa by the nB8 structure is demonstrated in Table I. Almost an exact fit of peak position and good agreement of the intensity profile can be obtained, with the exception of one peak for $d_{\exp} = 1.844$ Å, which is explained as originating from the metastable nonmagnetic (NM) rB1 phase. This NM-rB1 phase will take a "stretched" rather than "compressed" rB1 structure [25]. The intensity of this peak is actually reduced after annealing. The volume ($= 7.89$ cm^3/mole) and the c/a ($= 2.08$) estimated by fitting the peak positions are in good agreement with the present calculated results, which give a volume $= 7.92$ cm^3/mole and $c/a = 2.2$ for the FM-nB8 state, and volume $= 7.94$ cm^3/mole and $c/a = 2.1$ for the AF-nB8 state (at 137 GPa).

The P-V relation for MnO [shown in Fig. 3(b)] is clearly consistent with the AF-rB1 phase in the
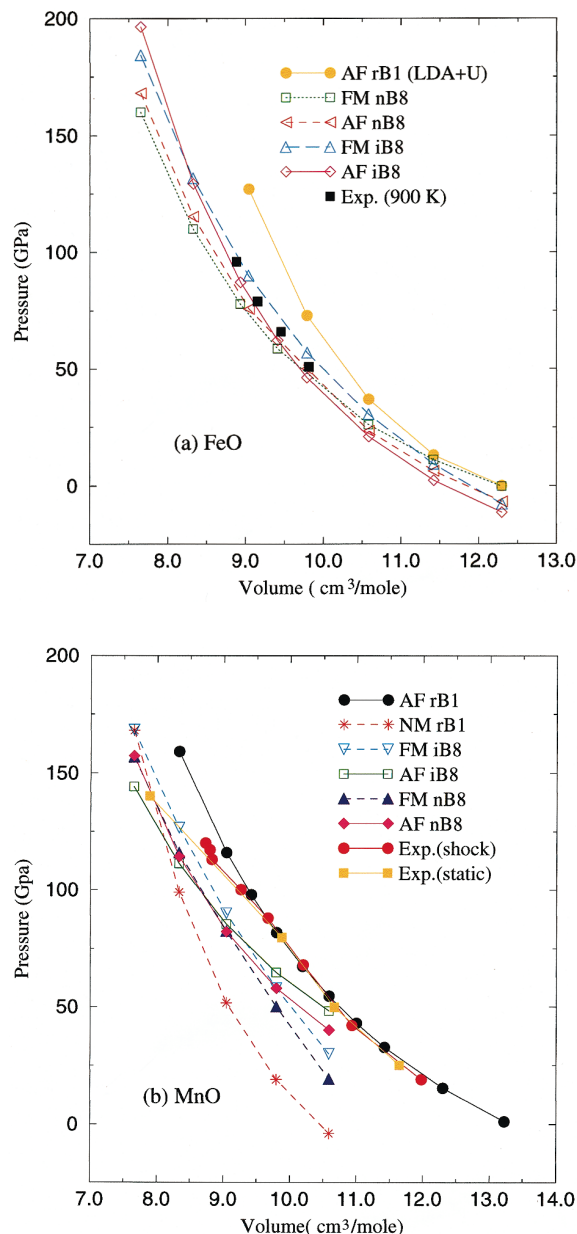

FIG. 3(color). The pressure-volume curves for different phases of FeO (a) and MnO (b). For FeO, the data from Ref. [6] on the isothermally (900 K) decompressed high-pressure phase of FeO are shown for comparison to the present theoretical calculations. For MnO, two experimental results with shock compression [8] and static compression [9] (at room temperature) are shown.

low-pressure range. The experimental data point near 120 GPa by shock compression is located just in between the curves corresponding to the rB1 and nB8 structures, suggesting that the sample is in a mixed phase. On the other hand, the highest pressure data point obtained by the static compression followed by laser annealing is just on the line of the P-V curve for the nB8 structure.

For both of the iB8 FeO and nB8 MnO under high-pressure, the c/a values exceed 2.0, being unusually large

TABLE I.   Observed [9] and fitted x-ray diffraction pattern of MnO at 137 GPa after laser annealing.

d_{exp}[a]	I_{exp}[b]	I_{fit}[b]	d_{fit}[a] (nB8)	h	k	l	d_{exp}-d_{fit}
2.534	w	m	2.538	0	0	2	−0.004
2.110	s	s	2.114	1	0	0	−0.004
1.955	w	w	1.952	1	0	1	0.003
1.844	s		Coming from NM rB1				
1.628	s	s	1.624	1	0	2	0.004
1.218	m	m	1.220	1	1	0	−0.002
1.099	m	w	1.100	1	1	2	−0.001

[a]d_{exp} and d_{fit} are experimental and fitted d spacings, respectively, in units of Å.
[b]The relative intensities of the peaks are described as strong (s), medium (m) and weak (w).

compared with the values for most other related systems. However, we have found that c/a is an increasing function of r_c/r_a with r_c (r_a) denoting the cation (anion) ionic radius, and that the c/a values of the MnO and FeO are on the extrapolated line of this general trend. As anions are more compressible than cations, r_c/r_a becomes larger, and c/a increases under pressure.

In conclusion, iB8 versus nB8 structures have been predicted as the high-pressure phases of FeO and MnO by the present first-principles calculations. Analysis of x-ray diffraction experiments provides a further support to the present theoretical prediction for both FeO and MnO. The predicted high-pressure phase of FeO will be the first example of a transition-metal compound with the iB8 structure. It has a unique insulating state, i.e., a band insulator rather than a Mott insulator.

[1] N. F. Mott, *Metal-Insulator Transitions* (Taylor & Francis Ltd., London, 1974).
[2] R. Jeanloz and T. J. Ahrens, Geophys. J. R. Astron. Soc. **62**, 505 (1980).
[3] T. Yagi, K. Fukuoka, H. Takei, and Y. Syono, Geophys. Res. Lett. **15**, 816 (1988).
[4] T. Yagi, T. Suzuki, and S. Akimoto, J. Geophys. Res. **90**, 8784 (1985).
[5] H. K. Mao *et al.,* Phys. Earth Planet. Inter. **96**, 135 (1996).
[6] Y. W. Fei and H. K. Mao, Science **266**, 1678 (1994).
[7] R. Jeanloz and A. Rudy, J. Geophys. Res. **92**, 11433 (1987).
[8] Y. Noguchi, K. Kusaba, K. Fukuoka, and Y. Syono, Geophys. Res. Lett. **23**, 1469 (1996).
[9] T. Kondo, T. Yagi, and Y. Syono, T. Kikegawa, and O. Shimomura, Rev. High Pressure Sci. Technol. **7**, 148 (1998).
[10] R. E. Cohen, I. I. Mazin, and D. G. Isaak, Science **275**, 654 (1997).
[11] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[12] The cutoff energy for the plane-wave expansion is 36.0 Ry, and sampling of k points gives absolute total energy convergence to better than 1.0 mRy/fomular unit ($\sim$1.3 KJ/mole). Note that the convergence in the relative energy between different structures is generally order of magnitude much better than that in the absolute total energy.
[13] J. P. Perdew, in *Electronic Structure of Solids,* edited by P. Ziesche and H. Eschrig (Akademie-Verlag, Berlin, 1991).
[14] D. M. Sherman and H. J. F. Jansen, Geophys. Res. Lett. **22**, 1001 (1995).
[15] In this method, the interaction between localized d electrons is explicitly taken into account through the screened effective Coulomb interaction parameter U_{eff}. See I. V. Solovyev, P. H. Dederichs, and V. I. Anisimov, Phys. Rev. B **50**, 16861 (1994).
[16] The actual values by the present calculations with GGA for the bulk modulus B, its pressure derivative B' and the equilibrium lattice constant a are 180 GPa, 3.55 and 4.28 Å for AF-rB1 FeO and 157 GPa, 3.23 and 4.46 Å for AF-rB1 MnO. The corresponding values after including the U_{eff} ($=$ 4 eV) correction for FeO are 196 GPa for B, 4.90 for B' and 4.33 Å for a.
[17] D. G. Isaak, R. E. Cohen, M. J. Mehl, and D. J. Singh, Phys. Rev. B **47**, 7720 (1993).
[18] The reduction in the p-d hybridization in the iB8 structure compared with that in the nB8 structure was confirmed in the present calculation by estimating the energy separation between the centers of the p and d bands.
[19] O. Gunnarsson, E. Koch, and R. M. Martin, Phys. Rev. B **54**, R11026 (1996).
[20] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).
[21] The total energy in the LDA + U scheme including the spin-orbit interaction (SOI) was estimated in the following way. As the LMTO method in the atomic sphere approximation cannot predict the structural energy difference accurately, this method is used only to estimate the energy change $\Delta E_A(U_{\mathrm{eff}}, \mathrm{SOI})$ caused by the effective Coulomb interaction U_{eff} and SOI for a given system A. Then, $\Delta E_A(U_{\mathrm{eff}}, \mathrm{SOI})$ is added to the total energy E_A^{pp}(LSDA) obtained by the pseudopotential method within the local-spin-density approximation (LSDA).
[22] M. Takahashi and J. Igarashi, Phys. Rev. B **54**, 13566 (1996).
[23] E. Knittle and R. Jeanloz, Geophys. Res. Lett. **13**, 1541 (1986).
[24] E. Knittle, R. Jeanloz, A. C. Mitchell, and W. J. Nellis, Solid State Commun. **59**, 513 (1986).
[25] See our detailed paper, Z. Fang *et al.* (to be published).
[26] F. D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. **30**, 244 (1944).