

***Ab initio* study of the composition dependence of the pressure-induced spin transition in the (Mg_{1-x},Fe_x)O system**

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[1] We present *ab initio* calculations of the zero-temperature composition dependent spin transition pressures in rocksalt (B1) (Mg_{1-x},Fe_x)O. We predict that the spin transition pressure decreases with increasing Mg content, consistent with experimental results. At high-pressure, we find that the effective size of Mg is smaller than high-spin Fe but quite close to low-spin Fe, consistent with a simple compression argument for how Mg reduces the spin transition pressure. We also show that the spin transition is primarily driven by the volume difference between the high-spin and low-spin phases, rather than changes in the electronic structure with pressure. The volume contraction at the transition is found to depend non-monotonically on Fe content. For FeO we predict a B1 → iB8 transition at 63 GPa, consistent with previous results. However, we also predict an unexpected reverse transition of high-spin iB8 → low-spin B1 at approximately 400 GPa. **Citation:** Persson, K., G. Ceder, A. Bengtson, and D. Morgan (2006), *Ab initio* study of the composition dependence of the pressure-induced spin transition in the (Mg_{1-x},Fe_x)O system, *Geophys. Res. Lett.*, 33, L16306, doi:10.1029/2006GL026621.

1. Introduction

[2] Magnesiowüstite (Mg_{1-x},Fe_x)O is a major component in the Earth's lower mantle (660–2900 km depth). At ambient conditions, wüstite (FeO) is a high-spin (HS) paramagnetic Mott insulator. The HS electronic configuration of the Fe²⁺ ion (3t_{2g}↑2e_g↑t_{2g}↓, S = 2) is a result of the competition between the inter-atomic crystal field, which favors low-spin (LS) states, and the intra-atomic Hund exchange energy, which is minimized in the HS state. External pressure is expected to drive a HS → LS transition through three mechanisms: increase in crystal field energy (due to decreasing transition metal-ligand distances), decrease in Hund coupling strength (due to electron delocalization associated with increasing wave function overlap), and stabilization of the smaller LS phase and stabilization of the smaller LS phase. There is considerable experimental evidence that the Fe²⁺ ion in (Mg_{1-x},Fe_x)O undergoes a HS → LS transition at pressures occurring in the lower mantle [Pasternak *et al.*, 1997; Badro *et al.*, 2003; Lin *et al.*, 2005b; Speziale *et al.*, 2005; Fei *et al.*, 2005; Lin *et al.*, 2006; Goncharov *et al.*, 2006]. The magnetic collapse in FeO [Cohen *et al.*, 1997; Sherman and Jansen, 1995] and

Mg-rich (Mg_{1-x},Fe_x)O [Sturhahn *et al.*, 2005; Tsuchiya *et al.*, 2006] have also been theoretically investigated. Furthermore, experiments show that the spin transition pressure, P_t , decreases with increasing Mg content [Speziale *et al.*, 2005; Lin *et al.*, 2006], which was suggested by Cohen *et al.* [1997] but has so far not been seen in calculations [Tsuchiya *et al.*, 2006].

[3] Both wüstite (FeO) and periclase (MgO) have the rocksalt (B1) crystal structure at ambient conditions and form a solid solution at higher temperatures. It has been shown experimentally that MgO remains in the B1 structure up to 227 GPa [Duffy *et al.*, 1995] while FeO and Fe-rich (Mg_{1-x},Fe_x) undergo structural transformations around 16–20 GPa and low temperature [see Ding *et al.*, 2005, and references therein]. At high temperature and 70–90 GPa, the HS B1 FeO transforms to the inverse-NiAs (iB8) AF phase [Fei and Mao, 1994; Mazin *et al.*, 1998; Fang *et al.*, 1998].

[4] Fe spin transitions can potentially impact nearly every aspect of lower mantle properties. In particular, the compositional dependence of the spin state will couple strongly to equations-of-state, element partitioning, and phase stability. Therefore, in order to better understand spin transition trends with composition, this Letter presents a study of the pressure-induced spin transitions in B1 (Mg_{1-x},Fe_x)O as a function of iron content. Although no entropy effects are included, we consider the system in a state appropriate to geophysical conditions by modeling the magnetic as well as compositional configurations as quasirandom.

2. Calculations

[5] Our calculations are based on density functional theory (DFT) within the generalized gradient approximation (GGA) method [Perdew *et al.*, 1996], using the projector-augmented plane-wave (PAW) method [Blöchl, 1994; Kresse and Joubert, 1999] as implemented in the Vienna Ab-initio Simulation Package (VASP) [Kresse and Furthmüller, 1996]. For oxygen we have chosen the standard 2s²2p⁴ pseudopotential, but to ensure accuracy when pressure is applied the pseudopotentials for Fe and Mg include p⁶ semi-core states in addition to the 3d⁶4s² and 3s² configurations, respectively. Additionally, we model the electron correlation by using the GGA + *U* method, implemented in the Liechtenstein scheme [Liechtenstein *et al.*, 1995]. The DFT + *U* approach has had great success in predicting the ground state and some pressure-induced properties of the Mott insulator FeO and recently for Mg-rich (Mg_{1-x},Fe_x)O [Fang *et al.*, 1999; Gramsch *et al.*, 2003; Cococcioni and de Gironcoli, 2005; Tsuchiya *et al.*, 2006], for which traditional DFT fails. We have chosen two different *U* values for our calculations; *U* = 5 eV which gives a good agreement with ground state properties for FeO at *P* =

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Table 1. Least-Square Fitted Birch-Murnaghan [Birch, 1986] EOS Parameters Fitted for $-20 < P < 200$ GPa for Paramagnetic HS and LS B1 (Mg_{1-x},Fe_x)O and HS AF iB8 FeO Phases, Obtained by GGA + U Calculation, Compared to Experimental Results

Phase	x	$U = 5$ eV				$U = 3$ eV				Exp.		
		K_0 , GPa	$\frac{\partial K_0}{\partial P}$	V_0 , Å ³ /f.u.	E_0 , meV/f.u.	K_0 , GPa	$\frac{\partial K_0}{\partial P}$	V_0 , Å ³ /f.u.	E_0 , eV/f.u.	K_0 , GP	$\frac{\partial K_0}{\partial P}$	V_0 , Å ³ /f.u.
HS B1	0.17	-	-	-	-	-	-	-	-	160.7 ^a	3.28 ^a	19.03 ^a
HS B1	0.25	153	4.1	19.78	-12.391	154	4.0	19.76	-12.524	-	-	-
HS B1	0.27	-	-	-	-	-	-	-	-	158.4 ^b	5.49 ^b	19.08 ^b
HS B1	0.36	-	-	-	-	-	-	-	-	155 ^c	3.8 ^c	19.36 ^c
HS B1	0.50	163	4.0	20.15	-12.823	156	4.0	20.03	-13.101	-	-	-
HS B1	0.56	-	-	-	-	-	-	-	-	155.8 ^b	5.53 ^b	19.36 ^b
HS B1	0.75	148	4.4	20.70	-13.246	141	4.4	20.47	-13.669	151.3 ^b	5.55 ^b	19.52 ^b
HS B1	1.0	157	4.0	21.23	-13.676	145	4.0	21.01	-14.276	175 ^d , 180 ^e	4.9 ^c	19.97 ^b
AF iB8	1.0	133	4.5	20.64	-13.386	190	4.1	19.39	-14.266	172 ^f	4.3 ^f	19.78 ^f
B1	0.0	153	4.1	19.26	-11.987	153	4.1	19.26	-11.987	160 ^g	4 ^g	18.67 ^b
LS B1	0.17	-	-	-	-	-	-	-	-	250 ^a	4 ^a	17.22 ^a
LS B1	0.25	170	4.1	18.74	-11.969	172	4.1	18.66	-12.204	-	-	-
LS B1	0.50	186	4.2	18.38	-11.921	191	4.2	18.20	-12.382	-	-	-
LS B1	0.75	203	4.2	18.13	-11.824	208	4.3	17.89	-12.497	-	-	-
LS B1	1.0	220	4.2	17.98	-11.692	220	4.4	17.70	-12.560	-	-	-

^aLin et al. [2005b].^bJacobsen et al. [2002].^cvan Westrenen et al. [2005].^dZhang [2000].^eJackson et al. [1990].^fFei and Mao [1994].^gSpeziale et al. [2001].

0 [Fang et al., 1999; Cococcioni and de Gironcoli, 2005; Gramsch et al., 2003] and $U = 3$ eV. The smaller U is chosen to accommodate possible pressure-induced broadening of the d electron states and is the smallest U which will still result in semiconducting ($E_{\text{gap}} > 0$ eV) states for the Mg rich side of the (Mg_{1-x},Fe_x)O system, where resistivity measurements at high pressure show evidence of a band gap [Dobson et al., 1997]. All calculations are performed with exchange parameter $J = 1$ eV. Only states calculated with the same Hubbard U are compared energetically with each other. A plane wave basis set with a kinetic cutoff energy of 400 eV is used and the Brillouin zone is sampled by a Monkhorst-Pack [Monkhorst and Pack, 1976] k -point grid with 8 kpoints/atom. The relative energies are converged with respect to k -points and cutoff to better than 5 meV/f.u.

[6] To model the solid solution behavior of the (Mg_{1-x},Fe_x)O system consistent with quenched materials (or elevated temperatures) and intermediate compositions, all phases are calculated employing so-called Special Quasirandom Structures (SQS), which mimic the chemical correlations in a completely random alloy [Lu et al., 1992]. The HS B1 phase is modeled as a disordered collinear paramagnet to simulate room- to high-temperature behavior. However, we assume a [001] antiferromagnetic (AF) ordering of the iB8 FeO phase, which is supported by its anomalously strong AF coupling [Fang et al., 1998]. We restrict the SQS cell form to cubic, consistent with experimental findings at higher temperatures. Further information and discussion about the calculational details are given in the auxiliary material.¹

3. Results

[7] Table 1 lists the fitted third order Birch-Murnaghan equation-of-state (EOS) parameters for calculated HS and LS B1 and AF iB8 phases, for $U = 5$ and 3 eV. The LS

phases generally exhibit larger bulk moduli (K_0) than the HS phases, although the difference decreases with increasing Mg content. By comparing the K_0 to experimentally obtained K_0 at ambient conditions (see Refs in Table 1) we find that the $U = 5$ eV results compare better in the HS Fe-rich B1 (Mg_{1-x},Fe_x)O. However, the $U = 3$ eV calculations generally give a better volume agreement with experiments. It should also be noted that the experimentally obtained bulk modulus and equilibrium volume of LS B1 (Mg_{0.83},Fe_{0.17})O [Lin et al., 2005b] conflict with our calculated values for (Mg_{0.75},Fe_{0.25})O (see Table 1) as well as other recent experimental results for LS B1 [e.g., Fei et al., 2005]. The possible causes of this discrepancy are under investigation. Based on the EOS we predict a structural transition from paramagnetic HS FeO B1 → AF FeO iB8 at 63 GPa for $U = 5$ eV (which compares well to previous calculations of AF FeO B1 → AF FeO iB8 [Fang et al., 1999]) and 1 GPa for $U = 3$ eV, to be compared with the experimental FeO B1 → iB8 transition pressures of 70–90 GPa at high temperatures.

[8] From the EOS we obtain the HS → LS spin transition pressure P_t and volume changes at P_t . Figure 1 shows the calculated and experimental P_t for B1 and the calculated data is summarized in Table 2 for both B1 and iB8. Somewhat surprisingly, we find that the LS iB8 phase is mechanically unstable and will transform spontaneously to the LS B1 phase. This unusual reversion to the low pressure structure under higher pressures is due to the coupling of the structure and spin state. In Table 2 we therefore present results for a coupled spin and structural transition: AF iB8 → LS B1. The results indicate that AF iB8 → LS B1 FeO will only occur at very high pressures. We find that P_t decreases with decreasing Fe content, which is consistent with the experimental trend. Figure 2 shows the HS and LS (Mg_{1-x},Fe_x)O volumes as a function of Fe content for different pressures. From Figure 2 it can be shown that the volume difference $\Delta V_{\text{HS-LS}}(P)$ increases with increasing Fe content at constant P , and that $\Delta V_{\text{HS-LS}}(P)$ decreases with

¹Auxiliary materials are available in the HTML. doi:10.1029/2006GL026621.

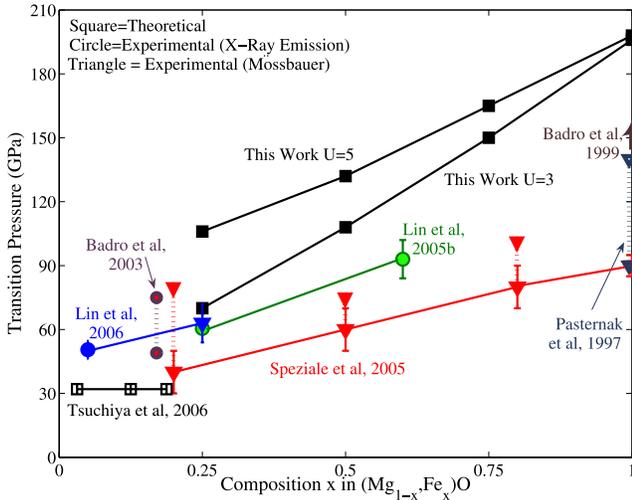


Figure 1. Calculated HS \rightarrow LS spin transition pressures, P_t , in B1 $(\text{Mg}_{1-x},\text{Fe}_x)\text{O}$, as a function of composition, compared with experiments. Error bars are given in solid vertical lines and ranges (where available), indicating the onset and range of the transition, are represented by broken lines. The transition pressures are measured at room temperature except for [Speziale *et al.*, 2005], which are measured at $T = 6\text{--}300$ K.

increasing P . Thus, the non-monotonic trend in $\Delta V(P_t)$ with Fe content is a result of these two competing factors. Experiments have recorded a 1.6% volume change in $(\text{Mg}_{0.4},\text{Fe}_{0.6})\text{O}$ [Lin *et al.*, 2005a] and an estimated 4.6% volume change for $(\text{Mg}_{0.8},\text{Fe}_{0.2})\text{O}$ [Speziale *et al.*, 2005]. [Tsuchiya *et al.*, 2006] obtained 4.2% for $(\text{Mg}_{0.8125},\text{Fe}_{0.1875})\text{O}$ by methods similar to ours. These latter two values compare qualitatively with our volume change for $(\text{Mg}_{0.75},\text{Fe}_{0.25})\text{O}$ of $0.46\text{--}0.54 \text{ \AA}^3/\text{f.u.}$ (corresponding to 3.4–3.5%) for $U = 5$ and 3 eV, respectively.

4. Discussion and Conclusion

[9] The trend in the calculated spin transition pressures P_t agrees with experiments. However, the predicted pressures are higher than expected from experimental results. The closest agreement with experiments is found in the Mg-rich region of the system. Moreover, we find that the HS \rightarrow LS transition pressures in B1 $(\text{Mg}_{1-x},\text{Fe}_x)\text{O}$ agree better with experiments for $U = 3$ eV compared to $U = 5$ eV, which

Table 2. Calculated Spin Transition Properties for HS \rightarrow LS B1 and AF iB8 \rightarrow LS B1 $(\text{Mg}_{1-x},\text{Fe}_x)\text{O}$ Phases Obtained by GGA + U Calculation, $U = 5$ and 3 eV

Transition	x	$U = 5$ eV		$U = 3$ eV	
		P_t , GPa	$\Delta V(P_t)$, $\text{\AA}^3/\text{f.u.}$	P_t , GPa	$\Delta V(P_t)$, $\text{\AA}^3/\text{f.u.}$
HS \rightarrow LS B1	0.25	106	0.46	69	0.54
HS \rightarrow LS B1	0.50	132	0.77	108	0.69
HS \rightarrow LS B1	0.75	165	0.97	150	0.78
HS \rightarrow LS B1	1.0	198	0.97	196	0.68
AF iB8 \rightarrow LS B1	1.0	382	0.36	438	0.28

suggests that the lower U provides a better description of the high-pressure electronic structure in the $(\text{Mg}_{1-x},\text{Fe}_x)\text{O}$ system. The quantitative disagreement between calculations and experiments could be due to deficiencies in the GGA + U approach which still only offers an approximation of the real correlation effects. In addition, our model does not include off-stoichiometry effects or Fe^{3+} , which are both known to increase with Fe content in $(\text{Mg}_{1-x},\text{Fe}_x)\text{O}$. Another possible source of error could be the presence of intermediate spin states [e.g., Li *et al.*, 2004]. Our results are also somewhat higher, and show more concentration dependence, than those calculated by Tsuchiya *et al.* [2006]. This discrepancy is likely due to their use of the local density approximation (LDA) together with distinct self-consistent U values for the HS and LS phases, as opposed to the GGA and the fixed U values used across all phases in this work.

[10] When calculating P_t , the important quantity is the enthalpy difference between the HS and LS phases: $\Delta H_{\text{HS-LS}}(P) = \Delta E_{\text{HS-LS}}(P) + P\Delta V_{\text{HS-LS}}(P)$. It is interesting to compare the relative importance of the bare energy difference $\Delta E_{\text{HS-LS}}(P)$, and the $P\Delta V_{\text{HS-LS}}(P)$ term in determining P_t . The bare energy difference is the energy required to change the spin state without allowing the volumes to adjust to the new electronic state, whereas the $P\Delta V_{\text{HS-LS}}(P)$ term constitutes the effect of the volume change between the HS and LS ions. In Figure 3 we plot $\Delta E_{\text{HS-LS}}(P)$ and $P\Delta V_{\text{HS-LS}}(P)$ in units of eV/Fe, as a function of Fe content, for different pressures. First, we find that $\Delta E_{\text{HS-LS}}(P)$ is *not* close to zero at P_t (as is sometimes assumed [Hofmeister, 2006]) and that the transition occurs, despite the increase in internal energy, because the $P\Delta V_{\text{HS-LS}}(P)$ term balances the non-zero energy difference. From Figure 3 we also note that, as a function of pressure, the change in $P\Delta V_{\text{HS-LS}}(P)$ is generally larger than the change in $\Delta E_{\text{HS-LS}}(P)$. For example, for $x = 0.25$, $P\Delta V_{\text{HS-LS}}(P)$ increases by 1.1 eV/Fe^{2+} , while the magnitude of $\Delta E_{\text{HS-LS}}(P)$ only decreases by 0.5 eV/Fe ion for $P = 0 \rightarrow 100$ GPa. This suggests that the dominant driving force for the pressure-induced spin transition resides in the volume difference between the HS and LS phases, rather than in the change of the fixed volume spin energy.

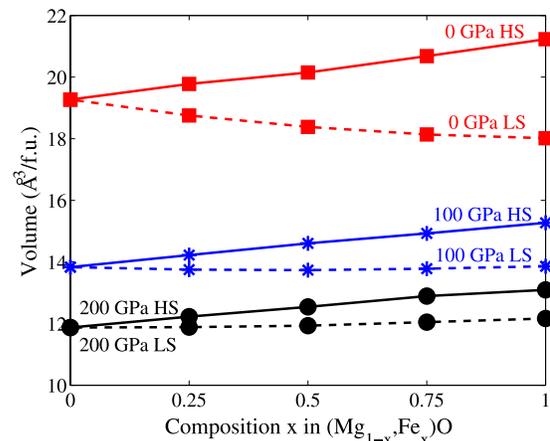


Figure 2. Calculated HS and LS B1 $(\text{Mg}_{1-x},\text{Fe}_x)\text{O}$ volumes for $U = 5$ eV, at $P = 0, 100$ and 200 GPa, as a function of composition.

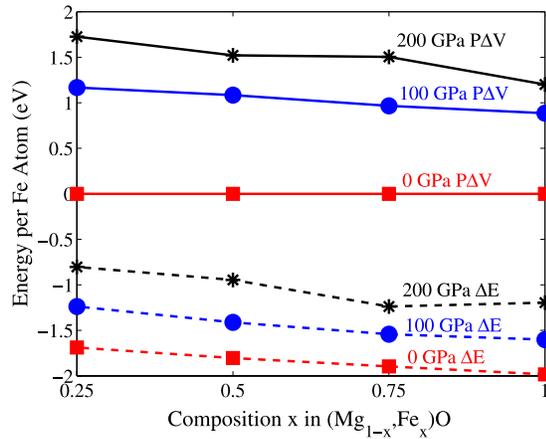


Figure 3. Calculated $\Delta E_{\text{HS-LS}}(P)$ and $P\Delta V_{\text{HS-LS}}(P)$ terms for $U = 5$ eV, as a function of composition, at $P = 0, 100,$ and 200 GPa.

[11] It is generally assumed that the decrease in P_t with increasing Mg content is driven by the small size of the Mg ion, which puts an effective chemical pressure on the HS Fe^{2+} ion [Cohen et al., 1997; Speziale et al., 2005]. We have established that the dominant driving force for the spin transition is due to $P\Delta V_{\text{HS-LS}}(P)$ and therefore we need to carefully consider the effect of the Mg ion on the HS and LS FeO volume. The $P = 0$ sizes of the ions can be estimated as HS Fe^{2+} : 78 pm, LS Fe^{2+} : 61 pm and Mg^{2+} : 72 pm, respectively [Shannon, 1976]. Thus, at $P = 0$, the Mg ion compresses the HS FeO B1 matrix and expands the LS FeO B1 matrix about equally, and it is not clear whether the compression/expansion effect is more destabilizing for the HS or the LS phase. From Figure 2, it is evident that the expansion of the LS FeO phase, due to the larger Mg^{2+} ion, largely vanishes at high pressures. This suggest LS Fe^{2+} and Mg^{2+} have similar ionic radii at high pressure, consistent with the recent results of [Fei et al., 2005]. However, a compression of the HS phase, due to the relatively smaller Mg^{2+} ion, remains even at 200 GPa. Thus we find that the compression of the HS $(\text{Mg}_{1-x},\text{Fe}_x)\text{O}$ is a likely driving force for the decrease in P_t with increasing Mg content.

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