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Pressure-Induced Electronic Spin Transition of Iron in Magnesiowüstite-(Mg,Fe)O

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ABSTRACT

An electronic transition of iron in magnesiowüstite has been studied with synchrotron Mössbauer and X-ray emission spectroscopies under high pressures. Synchrotron Mössbauer studies show that the quadrupole splitting disappears and the isomer shift drops significantly across the spin-paring transition of iron in $(\text{Mg}_{0.75},\text{Fe}_{0.25})\text{O}$ between 62 and 70 GPa, whereas X-ray emission spectroscopy of the Fe-K_β fluorescence lines in dilute $(\text{Mg}_{0.95},\text{Fe}_{0.05})\text{O}$ also confirms that a high-spin to low-spin transition occurs between 46 GPa and 55 GPa. Based upon current results and percolation theory, we re-examine the high-pressure phase diagram of $(\text{Mg,Fe})\text{O}$ and find that iron-iron exchange interaction plays an important role in stabilizing the high-spin state of iron in FeO-rich $(\text{Mg,Fe})\text{O}$.

Magnesiowüstite [(Mg,Fe)O] with the cubic rock-salt (*B1*) structure forms a solid solution between periclase (MgO) and wüstite (Fe_{1-x}O) [1-9]. Periclase is a wide band gap insulator and prototype simple monoxide, whereas wüstite, a classical Mott insulator, is an important member of the highly correlated transition metal monoxide (TMO) group including NiO, CoO, and MnO [10-17]. The Mott insulator-metal transition results from the closure of the Mott-Hubbard *d-d* band gap or of the Charge-Transfer *p-d* gap, and the strength of electron correlation in the TMO systems is characterized by the ratio between the on-site *d-d* Coulomb interaction energy (*U*) and 3*d* bandwidth (*W*) [10]. In TMO compounds, a high-spin to low-spin (spin-pairing) transition occurs when the crystal field splitting exceeds the Hund's-rule exchange energy and the material becomes diamagnetic, resulting in the collapse of magnetic state [10]. Although Mott insulator-metal transitions in TMO have been predicted to occur under high pressures [10,12], it is only very recently that such transition has been experimentally observed in MnO [15,17]. On the other hand, high-pressure X-ray emission spectroscopy (XES) studies indicated that FeO remains a magnetic insulator up to at least 143 GPa [13,14]. (Mg,Fe)O contains partially occupied Fe²⁺ in 3*d* orbitals situated in the band gap [1,2,9]. Hence, the local environment of iron, the 3*d* band width, and iron-iron interaction play important role in the electronic, structural, and physical properties of magnesiowüstite under high pressures. Studies of the complete solid solution MgO-FeO system should thus shed light on the questions regarding the magnetic collapse in highly correlated TMO systems such as FeO at high pressure.

Pressure-induced electronic spin transitions of iron have been described theoretically [1,2,9] and experimentally reported to occur in MgO-rich magnesiowüstite (also called ferropericlase) based on high-pressure XES observation of the Fe-K_β fluorescence lines

in the sample [5,8]; the presence of the satellite peak ($K_{\beta'}$) is typically interpreted as the existence of a high-spin state of iron whereas the sudden change of the satellite peak at high pressures indicates the collapse of the local spins in $3d$ orbitals [18]. Since magnesiowüstite is the second most abundant mineral in the Earth's lower mantle, the electronic spin transition of iron in magnesiowüstite in the Earth's lower mantle may have major geophysical and geochemical consequences [1,2,5,8,9]. However, recent traditional Mössbauer studies suggested that high-spin and low-spin states of iron could co-exist in magnesiowüstite over a very wide range of pressures, leading to a spin crossover at high pressures [19,20]. The apparent discrepancy has led us to investigate the magnetic states of the system using both synchrotron Mössbauer spectroscopy (SMS) [21] and XES under high pressures. SMS spectra, for Fe^{2+} systems in particular, offer a direct way of obtaining the relative concentrations of the spin states since each is associated with its own characteristic set of Mössbauer spectral parameters, isomer shift (IS) and quadrupole splitting (QS) [22]. Based on previous traditional Mössbauer studies on oxides and silicates under ambient conditions, a decrease in IS and the significant decrease or absence of the QS are expected for the transition from the high-spin state to the low-spin state [3,22,23].

Polycrystalline ^{57}Fe -enriched ($\text{Mg}_{0.75}\text{Fe}_{0.25}\text{O}$) sample was synthesized by sintering stoichiometric mixtures of MgO and ^{57}Fe (>95% enrichment) powder at 1378 K to 1478 K for eight hours under a controlled CO_2 - CO atmosphere near the iron-wüstite buffer [3]. After three cycles of grinding and sintering, the final product was compositionally homogeneous in electron microprobe analyses and its ferric iron (Fe^{3+}) content was below the detection limit of Mössbauer spectroscopy. X-ray diffraction data showed that the sample was in the B1 structure with a cell parameter of 4.2411 (± 0.0004) Å [4] and

magnetite (Fe_3O_4) was not detected. To prevent the effects of a large sample thickness on the SMS data and to reduce potential pressure gradient in the sample in the axial direction of the sample chamber, the sample was flattened down between two flat diamonds (5 μm in thickness in Run#1 and 1 μm in thickness in Run#2); the effective thickness in this composition was estimated to be between two to three [21]. Such sample preparation also ensured the homogeneous thickness of the sample. A rhenium gasket was pre-indented to a thickness of 20 μm and a hole of 80 μm was drilled in it. A small flake of the sample with ~ 60 μm in diameter was loaded into the sample chamber of a diamond anvil cell (DAC) with flat diamonds of a culet size of 200 μm . Subsequently, KCl was loaded into the sample chamber as the pressure medium and a few small ruby balls were placed close to the sample for pressure measurements using the ruby R_1 luminescence peak [24].

SMS experiments were carried out at the undulator beamline 3-IDB and 16-IDD of the Advanced Photon Source (APS), Argonne National Laboratory (ANL) [21]. A monochromatic X-ray beam of ~ 14.4125 keV with 1 meV resolution at 3-ID and 2 meV resolution at 16-IDD was used to excite the nuclear resonance of the ^{57}Fe nuclei in the sample. The focused X-ray beam was approximately 7 μm in diameter at 3-IDB and 20 μm in diameter at 16-IDD, where a cleanup slit of 20 μm in diameter was used to get rid of unwanted tail of the focused X-ray beam. The very small X-ray beamsize significantly reduced the influence of the pressure gradients in the radial direction across the sample chamber. The time delayed spectra were recorded by an avalanche photodiode detector in the forward direction. After the SMS spectrum of the sample had been collected, thin stainless steel foil ($\text{Fe}_{55}\text{Cr}_{20}\text{Ni}_{25}$) of 1.4 μm (Run#1) or 0.5 μm (Run#2) in thickness was placed outside of the DAC to serve as a reference for the IS measurements [21-23]. The

data collection time for each SMS spectrum was between one to four hours. The SMS spectra were evaluated with the MOTIF [25] and CONUSS [21] programs to derive the hyperfine parameters, QS and IS.

SMS spectra of the sample only and of the sample with stainless steel reference were collected up to 92 GPa at 300 K (Fig. 1). The derived QS and IS parameters under ambient conditions are consistent with high-spin Fe^{2+} in octahedral coordination in oxides and silicates (Fig. 2) [3,22,23]. The QS increases with increasing pressure up to about 30 GPa, plateaus at further pressure increase to about 62 GPa, and disappears at above 62 GPa. The IS of the high-spin state decreases with increasing pressure and a noticeable drop of the IS occurs at above 62 GPa. The simultaneous disappearance of the QS and the drop of the IS at above 62 GPa are consistent with a high-spin to low-spin electronic transition of iron in the sample between 62 and 70 GPa [5,8], although the width of the transition remains to be further investigated. The QS arises from the interaction between the nuclear quadrupole moment and the nonspherical component of the electronic charge distribution described by its effective electric-field gradient (Δ) in a simplified model. In general, the electric-field gradient in the vicinity of the ^{57}Fe nucleus can be attributed to a lattice contribution from the crystal field produced by the surrounding ions (Δ_{lat}) and an electronic contribution from the nonspherical charge distribution of the electron shell surrounding the nucleus (Δ_{el}) [22]. Since the electronic spin transition of iron in ferropericlase is isosymmetric (without change of the space group) with a very small volume decrease from X-ray diffraction studies [8], a significant change in the Δ_{lat} is not expected across the transition. Therefore, Δ_{el} is most likely the main contribution to the sudden change of the QS and the significant decrease in the IS at above 62 GPa. That is, the effective electric field gradient is dramatically reduced due to

the spin-pairing transition; the electron shell of Fe^{2+} ions in the octahedral coordination of the high-spin state is spherically asymmetric with $S=2$ and $t_{2g\uparrow}^3 e_g^2 t_{2g\downarrow}^1$ (only two electrons are paired and four are unpaired) and Fe^{2+} ions in the low-spin state are more spherically symmetric with $S=0$ and $t_{2g\uparrow}^3 t_{2g\downarrow}^3$ (all six electrons are paired). On the other hand, at pressures below the electronic spin transition the increase of the QS as pressure increases may be attributed to the crystal field contribution (Δ_c) (Fig. 2a).

Furthermore, the IS is proportional to $\delta R/R$ and $\Psi(0)$ where $\delta R/R$ is the difference in the nuclear radii between the ground and excited states (δR in the case of ^{57}Fe is negative) and $\Psi(0)$ is the electron density at the nucleus (also called the contact density) [22]. The $\Psi(0)$ consists of the s -electron density at the nucleus including the perturbing effect of the outer electrons. Therefore, the negative slope in IS as a function of pressure reflects the increase in density with pressure in the high-spin state and low-spin state, respectively, whereas the spin-pairing process in the $3d$ electrons causes a jump in the total s -electron density at the nucleus and hence a drop in the IS. The $d(\text{IS})/dP$ for the low-spin state is lower than that of the high-spin state, suggesting an increase in the incompressibility across the transition (Fig. 2b). It has been observed in X-ray diffraction experiments that the high-spin to low-spin transition of iron in magnesiowüstite results in a much higher bulk modulus (K_T) and bulk sound velocity (V_ϕ) for the high-pressure low-spin state; K_T jumps by $\sim 35\%$ and V_ϕ increases by $\sim 15\%$ across the transition in $(\text{Mg}_{0.83}, \text{Fe}_{0.17})\text{O}$ [8].

To understand the compositional effect on the spin transition in the system, we also carried out *in situ* XES experiments on $(\text{Mg}_{0.95}, \text{Fe}_{0.05})\text{O}$ in a DAC. The very dilute concentration of 5 atom% of Fe^{2+} in the sample allows the average iron-iron distance to

become large enough to result in negligible effects from the iron-iron exchange interactions between neighboring iron atoms [9]. High-pressure XES measurements of the Fe-K $_{\beta}$ were carried out at the HPCAT sector of the APS, ANL. The details of the XES experimental setup and interpretations of the XES spectra of the Fe-K $_{\beta}$ lines are reported elsewhere [8]. XES spectra of the Fe-K $_{\beta}$ fluorescence lines in dilute (Mg $_{0.95}$,Fe $_{0.05}$)O showed that a high-spin to low-spin transition occurs between 46 GPa and 55 GPa (Fig. 3).

In light of the observed electronic transition in magnesiowüstite at high pressures and room temperature, we re-examined the high-pressure phase diagram of MgO-FeO system (Fig. 4). Based on high-pressure X-ray diffraction, XES, and SMS studies, a B1-rhombohedral structural transition occurs in the FeO-rich region and addition of MgO stabilizes the B1 structure to much higher pressures [6,7], whereas an isosymmetric electronic transition from the paramagnetic state (PM) to the diamagnetic state (DM) occurs in MgO-rich region and addition of FeO into MgO stabilizes the high-spin state to much higher pressures [5,8]. The isosymmetric electronic transition is a first-order transition at room temperature because of the volume collapse involved [8,26], but may terminate at a critical point of temperature [9,26]. Here we further assess the effect of iron-iron exchange interaction on the electronic transition using percolation theory [27]. If one neglects the iron-iron exchange interactions between neighboring iron atoms in the system (i.e. at very low iron concentration in the system), the slope of the electronic spin transition as a function of FeO concentration (x) can be evaluated from the lattice expansion due to the substitution of the Mg $^{2+}$ ions with the larger Fe $^{2+}$ which creates an internal pressure on the local Fe $^{2+}$ ions in addition to the external pressure in a DAC. The

transition pressure as a function of FeO concentration (dP/dx) can thus be calculated from the assumption that the spin transition occurs at the same Fe-O bond length; the same internal pressure. Since the addition of 50 atom% of FeO into MgO expands the MgO lattice by approximately 1.4% [4], an additional pressure of about 15 GPa is needed to reach the electronic transition in $(\text{Mg}_{0.50},\text{Fe}_{0.50})\text{O}$ (Fig. 4). However, it is clear from Fig. 4 that this simple argument can only explain the electronic transition in the lower FeO concentration region of the phase diagram; the transition in FeO-rich region occurs at much higher pressure than what the simple calculation predicted. This discrepancy occurs due to the contribution of the Fe-Fe exchange interaction which further stabilizes the high-spin state to much higher pressures. Based on percolation theory, for the face-centered cubic (fcc) lattice the random impurity has a percolation threshold, a continuous percolation path through the 3-dimensional fcc structure, at about 12% concentration [27]. When iron concentration in the $(\text{Mg},\text{Fe})\text{O}$ system is above the percolation threshold, Fe^{2+} atoms form infinitely connected percolation path through the whole structure, where each Fe^{2+} atom has at least two Fe^{2+} neighbors. That is, the $3d$ outer electrons of an Fe^{2+} atom interact with the neighboring $3d$ electrons of the d_{xy} , d_{xz} , and d_{zy} orbitals, which correspond to the t_{2g} states (split down from the e_{2g} orbitals by the octahedral crystal field). This iron-iron interaction would increase the effective crystal field by further splitting mostly t_{2g} orbitals and lowering them with respect to the e_{2g} orbitals and thus would stabilize the high-spin state in the system. In particular, the FeO end member of the magnesiowüstite system is well known for its strength of electron correlation which is characterized by the ratio between the on-site d - d Coulomb interaction energy (U) and $3d$ bandwidth (W) [10]. Although earlier theoretical and experimental studies on FeO had suggested a high-spin to low-spin transition occurring at high pressures [12,13], no

collapse of the magnetic moment was predicted in recent theoretical calculations [28] and FeO preserved high-spin state up to 143 GPa in high-pressure XES studies [14]. Based on the extrapolated electronic transition boundary from our studies, the high-spin to low-spin transition may occur at a pressure above 160 GPa, though the effects of the B1-rhombohedral and the B1-NiAs (or anti-NiAs) structural transition in the very FeO-rich end on the electronic transition should be further considered; the potential magnetic collapse and metallization in FeO under high pressures is suggested to be associated with a structural phase transformation to NiAs or anti-NiAs [11,29].

In summary, we have studied the pressure-induced electronic spin transition in magnesiowüstite by high-pressure SMS and XES. Our SMS studies of $(\text{Mg}_{0.75}\text{Fe}_{0.25})\text{O}$ have shown the disappearance of the quadrupole splitting and the significant drop of the isomer shift between 62 and 70 GPa, consistent with a high-spin to low-spin transition of iron in the sample. Based on current results and percolation theory, we re-examined the high-pressure phase diagram of MgO-FeO system and found that iron-iron exchange interaction in the system plays an important role in stabilizing the high-spin state of iron in FeO-rich region of the system. Our results indicate that the same iron-iron correlation effect is also responsible for stabilizing of the high-spin of iron in FeO to much higher pressures and the magnetic collapse in FeO may occur at a pressure above 160 GPa.

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Figure Captions:

FIG. 1. Representative SMS spectra of (a) $(\text{Mg}_{0.75}, \text{Fe}_{0.25})\text{O}$ and (b) $(\text{Mg}_{0.75}, \text{Fe}_{0.25})\text{O}$ with stainless steel (SS) as a function of pressure at room temperature. Black line, modeled spectrum with the MOTIF program [25]. The sample thickness was approximately $1 \mu\text{m}$, and the thickness of the stainless steel foil was about $0.5 \mu\text{m}$. Evolution of the SMS spectra of $(\text{Mg}_{0.75}, \text{Fe}_{0.25})\text{O}$ with the stainless steel as a reference enables derivation of the IS of the sample as a function of pressure (see FIG. 2). The quantum bits at 0, 13, and 45 GPa are generated from the QS of the high-spin state of iron in the sample, whereas the flat feature of the spectra at 70, 79, and 92 GPa indicates disappearance of the QS.

FIG. 2. Pressure dependence of (a) QS and (b) IS (with respect to (w.r.t.) stainless steel standard) in $(\text{Mg}_{0.75}, \text{Fe}_{0.25})\text{O}$ as revealed from the modeling of the SMS spectra. Open triangle: this study from sample of $\sim 1 \mu\text{m}$ in thickness and SS of $\sim 0.5 \mu\text{m}$ (Run#2); open circles: this study from sample of $\sim 5 \mu\text{m}$ and SS of $\sim 1.4 \mu\text{m}$ (Run#1); vertical bars: error bars for the IS and QS. The error bars for the IS in Run#2 and for the QS (except at 63 GPa) are smaller than the symbol; the relatively larger errors in the IS in Run#1 were due to the dynamic effects (larger sample thickness). A least squares fit to the IS (short dash lines) gives $d(\text{IS})/dP$ of $-0.0037 (\pm 0.0007)$ mm/s·GPa for the high-spin state and $d(\text{IS})/dP$ of $-0.0021 (\pm 0.0010)$ mm/s·GPa for the low-spin state, respectively. Based on the modeling of the SMS spectra, the ratio of the high-spin to low-spin states of iron in $(\text{Mg}_{0.75}, \text{Fe}_{0.25})\text{O}$ as a function of pressure are also consistent with the changes in the QS and IS. The spectrum at 63 GPa is modeled with two states, a low-spin state of Fe^{2+} (20% in ratio) and an intermediate state with a QS of $0.56 (\pm 0.10)$ mm/s. The nature of the intermediate state remains to be further investigated in the future.

FIG. 3. X-ray emission study of the Fe- K_{β} fluorescence lines in $(\text{Mg}_{0.95}\text{Fe}_{0.05})\text{O}$ under high pressures. (a) Integrated and normalized intensity of the satellite peak of iron in $(\text{Mg}_{0.95}\text{Fe}_{0.05})\text{O}$ as a function of pressure. The errors in integrated intensity were propagated from statistical errors in original spectra. (b) Energy shift of the main emission peak ($K_{\beta 1,3}$) as a function of pressure with respect to 7058 eV. An energy decrease of ~ 1.6 eV was observed across the spin transition. These results confirmed a high-spin to low-spin transition of iron in $(\text{Mg}_{0.95}\text{Fe}_{0.05})\text{O}$ between 46 GPa and 55 GPa.

FIG. 4. Phase diagram of the magnesiowüstite- $(\text{Mg,Fe})\text{O}$ system under high pressures and room temperature. Open circle, XES results [8]; solid circle, SMS results. An isosymmetric transition from the paramagnetic state (PM) to the diamagnetic state (DM) occurs in MgO-rich magnesiowüstite (ferropericlase) [5,8], and addition of FeO in MgO stabilizes the high-spin state to much higher pressures [8]. On the other hand, addition of MgO in FeO stabilizes the B1 structure relative to the antiferromagnetic (AFM) rhomboheral phase (R) to much higher pressures [6]. Potential electronic and structural transitions in FeO-rich region remain to be further understood. Dotted line represents the calculated high-spin to low-spin transition boundary based on the assumption that the spin transition occurs at the same Fe-O bond length and the iron-iron exchange interaction could be neglected.

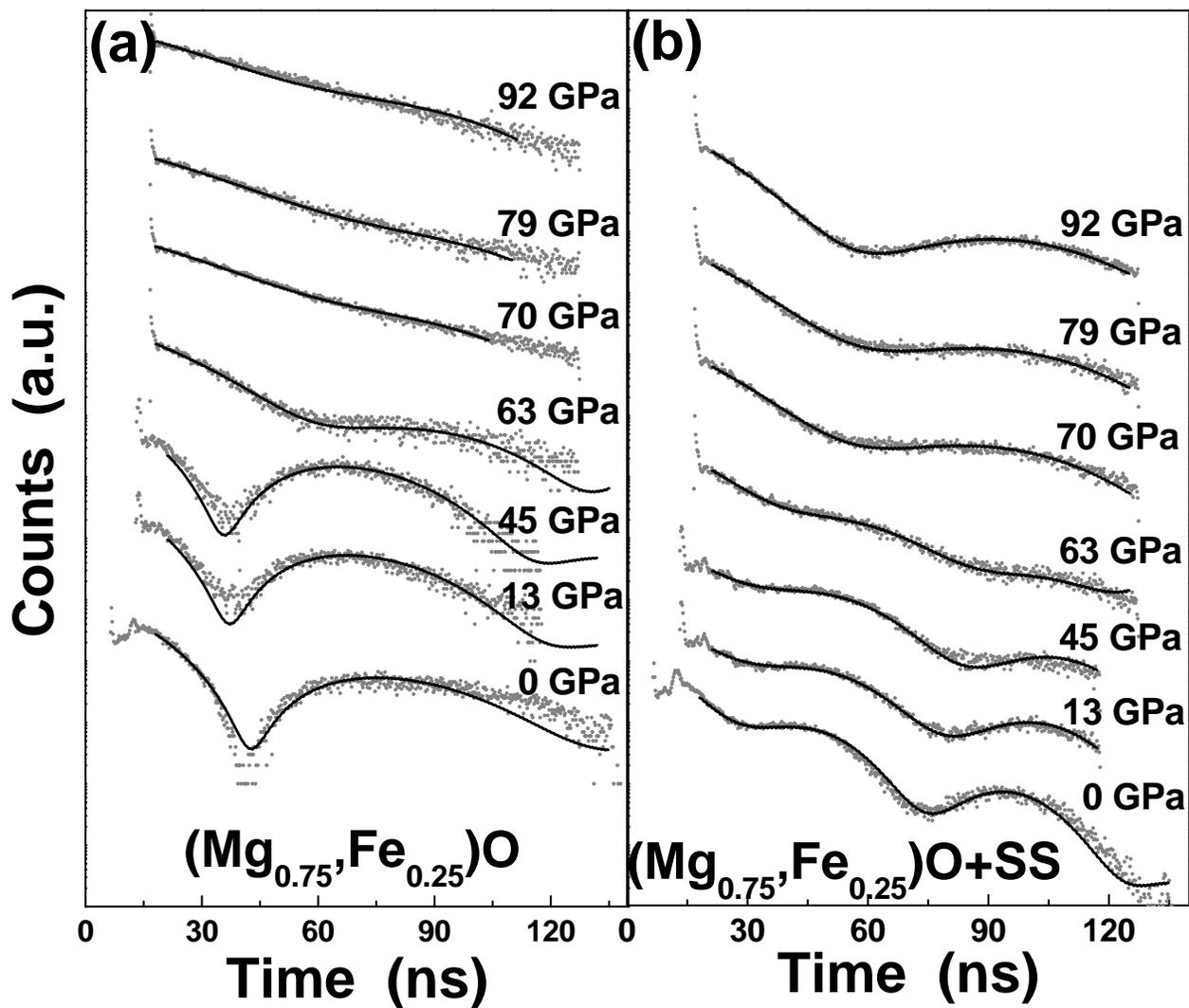


FIG. 1

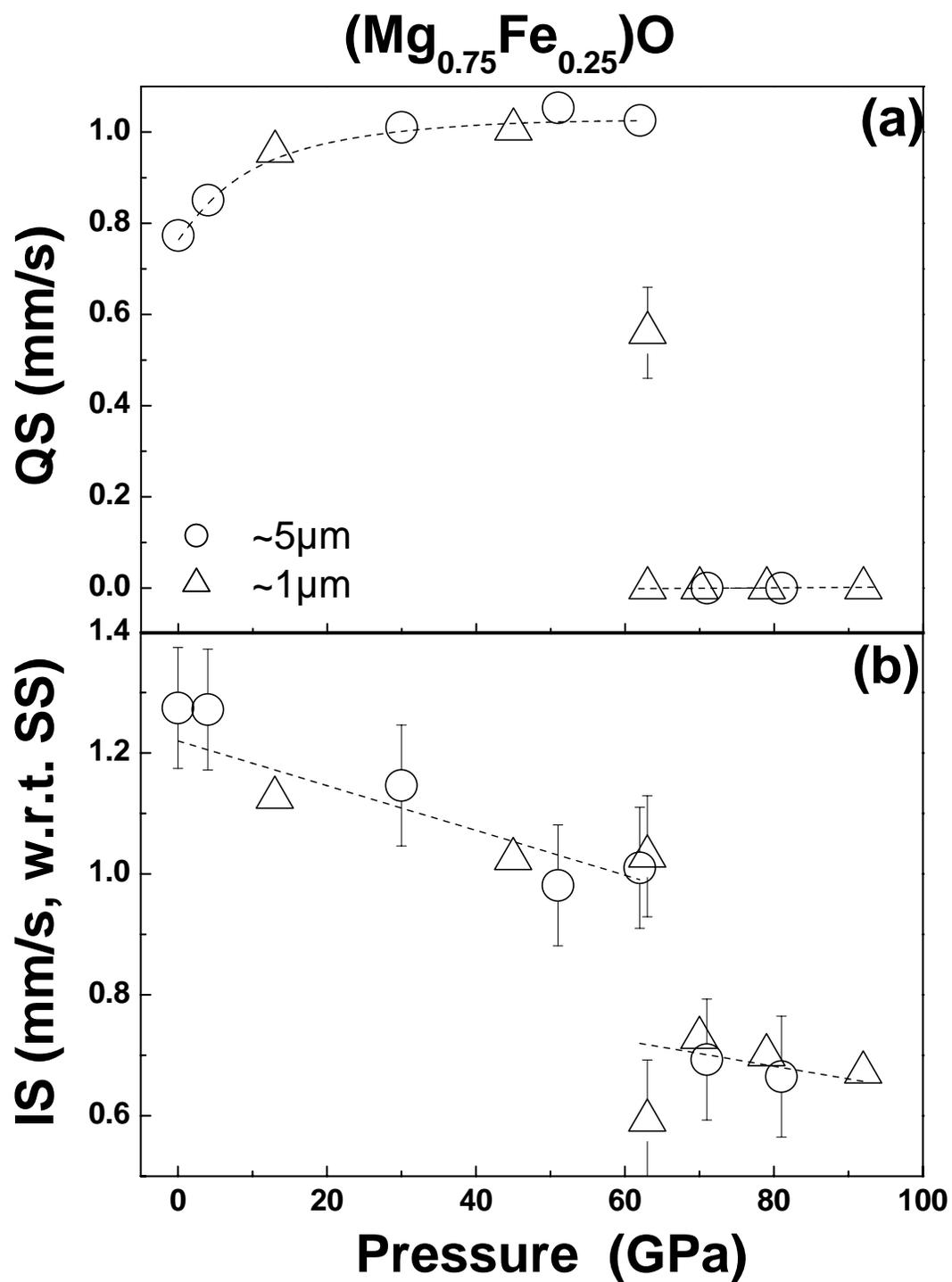


FIG. 2

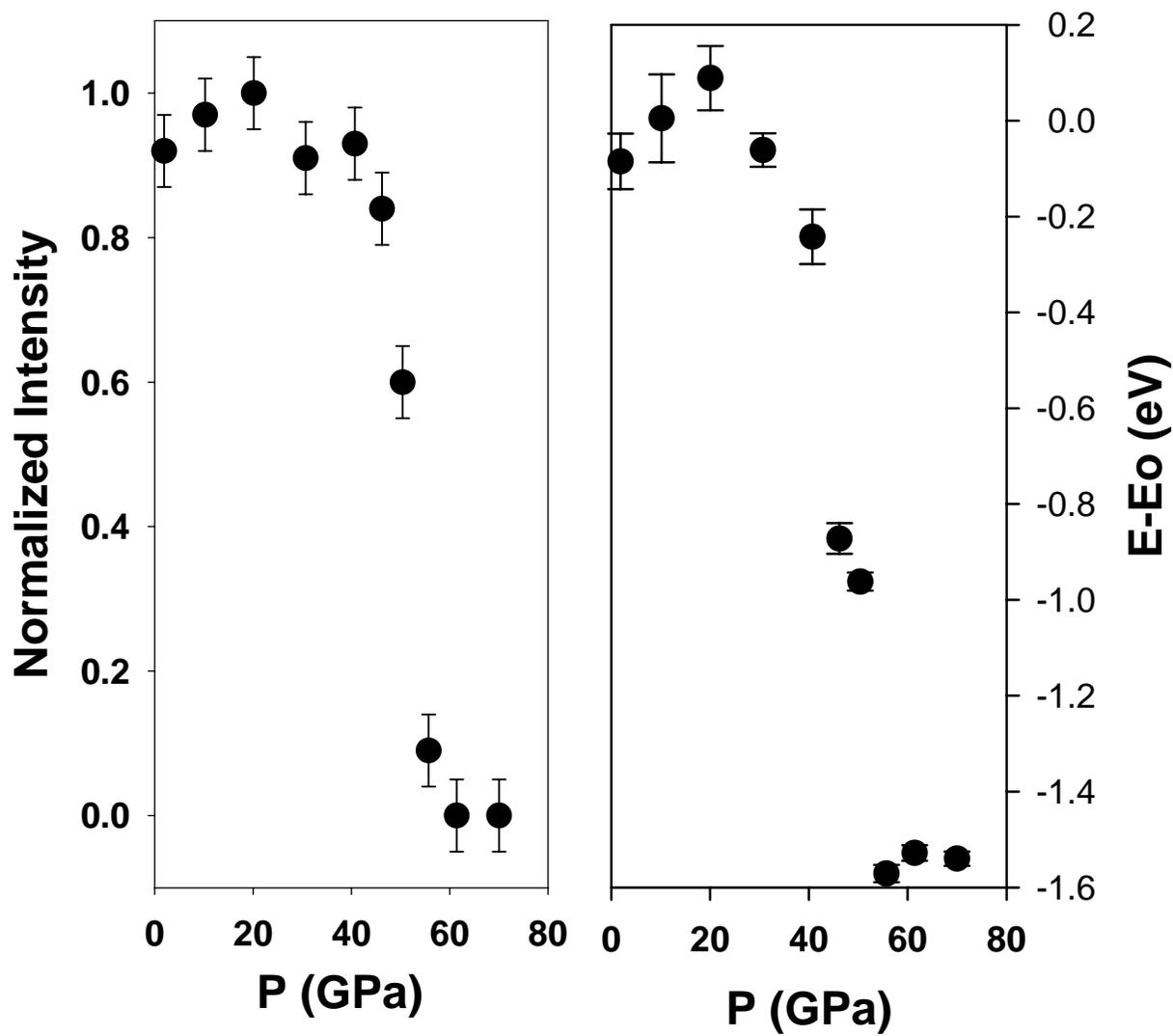


FIG. 3

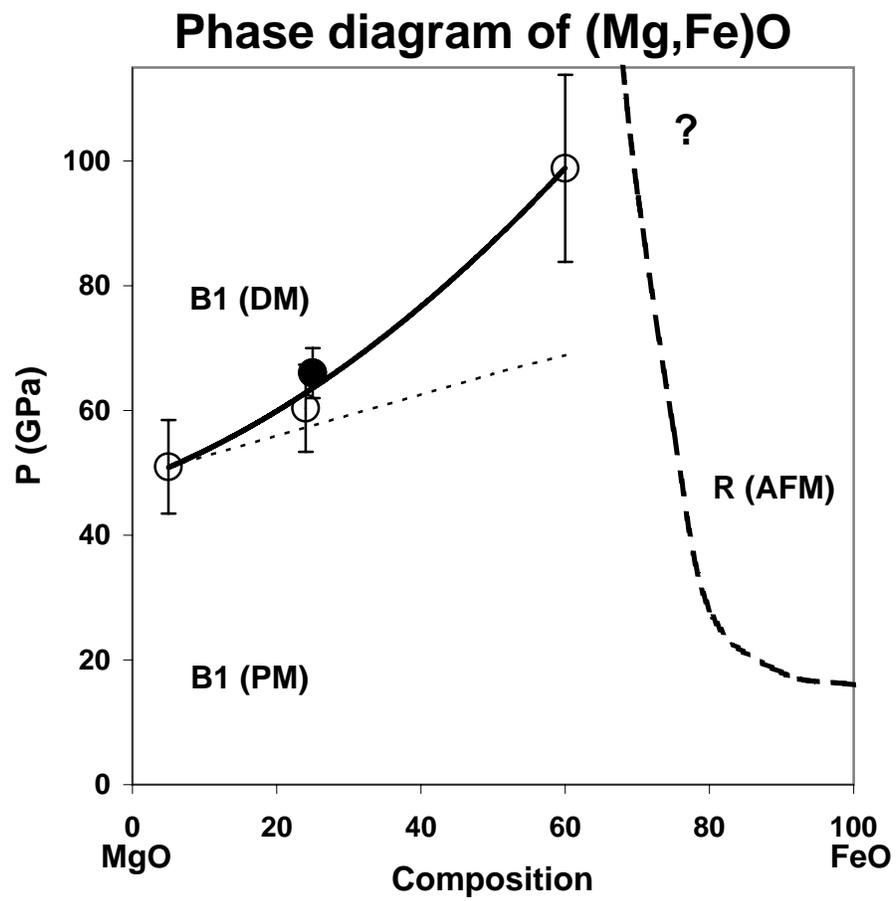


FIG. 4