Magnetism in FeO at Megabar Pressures from X-Ray Emission Spectroscopy

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We report evidence for a preserved magnetic state in FeO up to 143 GPa at room temperature using high-resolution x-ray emission spectroscopy. This observation is based on the spectral line shape of the Fe $K\beta$ emission line. Up to the highest pressure, FeO remains a magnetic insulator. Combining our results with previous Mössbauer data, we present a new magnetic phase diagram of FeO. Features like a closed-loop P-T antiferromagnetic domain confirm that high-pressure investigations can reveal new physical properties and unexpected phenomena.

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Transition metal (TM) monoxides are prototypical examples of strongly correlated electron systems. The strength of electron correlation in these systems is characterized by the ratio between the on-site d-d Coulomb interaction energy U and $3d$ bandwidth W [1]. Since pressure can be used to directly control the bandwidth of the TM $3d$ band, high-pressure studies are considered an important tool in the understanding of these systems. This is particularly true if the pressure is high enough to induce structural, metal-insulator, high-spin to low-spin, or superconducting transitions. The transition pressures, stable structures, electronic structures, and transport and magnetic properties of the high pressure phases together provide stringent tests for theory.

Possible magnetic collapse in TM monoxides has been predicted by first-principles calculations [2,3] at pressures within the reach of current diamond anvil cell techniques. This has motivated the experimental search for the high-spin to low-spin (HS to LS) transitions in these systems. So far, the only HS to LS transition in TM monoxides reported was a high-pressure Mössbauer spectroscopy (MS) study of FeO [4]. A new quadrupole-split component appears in the Mössbauer spectrum between 60 and 90 GPa, which has been assigned to a diamagnetic (nonmagnetic) LS state of Fe^{2+}. Measurements up to 120 GPa show that the relative intensity of this component increases with pressure at the expense of that from the magnetic component. On the basis of these measurements, and extrapolating their trends to higher pressures, Pasternak *et al.* [4] argued that Fe in FeO would be entirely in the low-spin state at 140 GPa. The authors also base their interpretation on the eventual transformation from the rhombohedral phase to the NiAs phase at pressures in the 70–90 GPa range [5], where Fe is presumably in the LS state.

However, recent state-of-the-art *ab initio* calculation predicts that the ground states of the high-pressure phases of both FeO [6–8] and MnO [7,8] are antiferromagnetic band insulators with the unusual inverse NiAs ($iB8$) structure. Moreover, no collapse of the magnetic moment of Fe in FeO is predicted [8], but only a reduction of the magnetic moment with increasing pressure. These results were obtained either by LAPW implementation of GGA [6] or by full structure optimization using the generalized gradient approximation (GGA) for the high-pressure phase and supplemented by LDA + U calculations in the low-pressure regime where electron correlations are too strong to be handled by GGA [7,8].

This apparent contradiction between theory and experiment has led us to reinvestigate the magnetic state of Fe in FeO at high pressure using high resolution x-ray emission spectroscopy (XES). The sensitivity of this technique to local magnetic moment has been well established by many XES studies of TM elements and their compounds [9–12], and has been recently applied to the study of pressure-induced HS to LS transitions [13]. In this case, the emission spectrum of HS Fe is characterized by a main peak $K\beta_{1,3}$ with an energy of 7058 eV, and a satellite peak $K\beta'$ located at lower energy appearing as a result of the $3p$ core-hole $3d$ exchange interaction in the final state of the emission process. Since the LS state of Fe^{2+} (d^6 configuration) is characterized by a total magnetic moment equal to zero, the eventual collapse of the $3d$ magnetic moment as a consequence of pressure increase should lead to the disappearance of the low energy satellite, a very clear spectral signature.

In this Letter, we report a study of the spin state of FeO up to 143 GPa using high-resolution x-ray emission spectroscopy (Fe $K\beta$). Up to the highest pressure, we

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find that Fe possesses a constant finite magnetic moment, indicating no HS to LS transition.

The experiments were conducted on the undulator beam line at Sector 13, Consortium for Advanced Radiation Sources of the Advanced Photon Source at Argonne National Laboratory. X-ray emission spectra were obtained using white undulator radiation. The undulator gap was set so that the first harmonic energy is slightly above the Fe K absorption edge to optimize the absorption cross section. The x-ray beam size was focused down to $10 \times 5\ \mu$m using a pair of rhodium-coated Kirkpatrick-Baez (KB) mirrors [14,15]. This focusing stage is crucial in such high-pressure experiments. It allows only a small region of the sample to be probed, thus limiting the effect of nonhydrostatic stresses. Furthermore, it reduces the contribution from iron-bearing surroundings of the sample (e.g., impurities in the gasket). The measurements were made using a 870 mm diameter Rowland circle spectrometer arranged in the horizontal plane. A spherically bent Si(440) single crystal analyzer was used. At the $K\beta$ emission line energy, the associated Bragg angle is equal to 66.20°. The angle between the incident x-ray beam and the sample-analyzer direction was set to 90° to reduce elastic scattering background.

X-rays are strongly attenuated by diamond below 10 keV, the spectral range that covers the K edges of all $3d$ TM elements. The use of low-Z element gaskets (Be) provides a way to overcome this problem, if both the incident and emitted photons pass through the gasket. In this study, we used a high-strength beryllium gasket [16], and the experimental geometry was configured so that both incident and emitted beams passed through the gasket.

High purity $Fe_{0.92}O$ powder was used in the experiment; the sample preparation and characterization are reported elsewhere [17]. A 4:1 mixture of methanol-ethanol was used as pressure medium. The gasket was a high-strength beryllium disk 5 mm in diameter and 1 mm initial thickness. The pressure was measured using the ruby fluorescence technique with variable Ar^+ laser line excitation. We also used x-ray diffraction data to obtain a rough estimate of the pressure gradient across the sample (e.g., 10 at 135 GPa [18]).

Figure 1 shows the Fe $K\beta$ x-ray emission spectra of FeO for pressures between 0 and 143 GPa. All spectra are normalized to transmitted intensity, and also shifted so that the peak of the Fe $K\beta$ main emission line (also known as the $K\beta_{1,3}$ line) is set to 7058 eV. The most important feature is a well-defined satellite located at 7045 eV and denoted $K\beta'$, present up to the highest pressure measured, though the spectral region between the main line and the satellite is gradually filled up with increasing pressure, due to a broadening of the $K\beta$ main line with increasing pressure (Fig. 1). To our knowledge, this is the first report of resolved XES above 100 GPa.

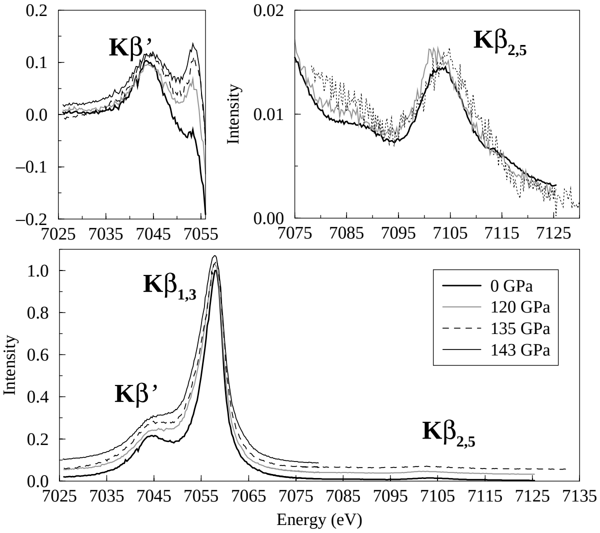

FIG. 1. Room-temperature Fe x-ray emission spectra in FeO as a function of pressure (bottom). At all pressures, the $K\beta'$ satellite at 7045 eV indicates that spin exchange still occurs and that Fe is in the HS state. The top right figure shows a detail of the high-energy region, and is characteristic of emission from the valence band ($K\beta_{2,5}$). These two spectral features are mostly unaffected by pressure up to 143 GPa. The top left figure shows the difference spectra between FeO and FeS_2 as a function of pressure, characteristic of the emission line from the minority spins. It shows that hybridization increases with pressure, characterized by a broadening of the $K\beta_{1,3}$ and $K\beta'$ lines, and suggests a bandwidth increase of the $3d$ orbitals in Fe. On the other hand, there is no relative shift in the position of the $K\beta'$ line or change in its relative intensity, indicating that neither the total spin nor the exchange integral J seem to be modified up to 143 GPa.

As pointed out previously, the $K\beta'$ satellite should disappear if a HS to LS transition were to occur in the studied pressure range. To further illustrate this point, we also measured the $K\beta$ emission spectra of Fe_2O_3 as a function of pressure for comparison since Fe_2O_3 has a well-known transition from the low-pressure HS state to a high-pressure phase with lower spin at 50 GPa [19,20]. Figure 2 shows the $K\beta$ spectra of HS Fe_2O_3 and LS Fe_2O_3, as well as that of FeS_2, a Fe^{2+} reference LS system. The sensitivity of this technique is clearly demonstrated as one can see a pronounced satellite peak in the $K\beta$ spectrum of the HS Fe^{3+}, a weak satellite for LS Fe^{3+} and no satellite for LS Fe^{2+}.

In addition, a subtle difference between compounds with different oxidation states is evident. In the case of Fe^{2+} (e.g., FeO, FeS_2, and FeS [13]), the electronic configuration is $(\mathrm{Ar})3d^6$ and the d levels consist of two sets of orbitals t_{2g} and e_g which are split according to the octahedral (all of these compounds have iron in sixfold coordination) ligand field $10Dq$. In the HS state, the electrons occupy the orbitals according to Hund's rule, and therefore the final electronic configuration of the $3d^6$ orbitals is $t_{2g\uparrow}^3 e_{g\uparrow}^2 t_{2g\downarrow}^1$. In the LS state, this configuration

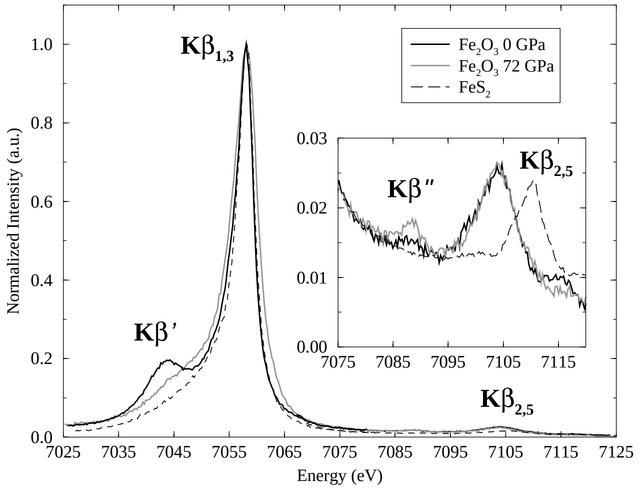

FIG. 2. XES spectra of FeS_2 in the LS state (room pressure and temperature) and Fe_2O_3 in the low-pressure HS and high-pressure LS states. The inset shows a magnification of the high-energy region of the spectra. The line shape of the $K\beta$ line is characteristic of the spin state of the system. The case of Fe_2O_3 is slightly different from FeO and FeS_2, because the total $3d$ magnetic moment of Fe is not equal to zero in the LS state. Therefore, spin exchange still occurs in the LS state and a weak $K\beta'$ line is still present. At higher energy, we note that the intensity of a weak band at 7088 eV increases. It is the $K\beta''$ line, assigned to the projection of the oxygen $2s$ band on the iron site. The intensity of this band is directly linked to the Fe-O distance [22].

becomes $t_{2g\uparrow}^3 t_{2g\downarrow}^3$. In this case, the total $3d$ magnetic moment is zero, and the $K\beta'$ satellite in the emission line vanishes. In the case of Fe^{3+} bearing compounds (Fe_2O_3), the electronic configuration is $(\mathrm{Ar})3d^5$ and the configuration of the $3d$ orbitals is $t_{2g\uparrow}^3 e_{g\uparrow}^2$ in the HS state and $t_{2g\uparrow}^3 t_{2g\downarrow}^2$ in the LS state to a first approximation. The exact electronic configuration and magnitude of magnetic moment would depend on the nature of the ligand field, crystal structure, and $3d$ band structure. However, a finite moment is expected in the case of lower-spin Fe_2O_3, and a weak $K\beta'$ satellite should exist, as is confirmed by the high-pressure spectrum of Fe_2O_3.

We conclude that Fe in FeO has a finite moment for pressures up to 143 GPa (e.g., Figs. 1 and 2). Moreover, the magnitude of the moment is most likely constant from ambient to 143 GPa, though detailed calculation is necessary to quantify the moment. In the following, we will address the apparent discrepancy between the MS report [4] and our results. First, it is important to note that MS and XES have very different probing time scales. The lifetime of the ^{57}Fe nuclear resonance is on the order of 100 nanoseconds, while the Fe K shell core-hole lifetime is on the order of a femtosecond. Hence, MS is sensitive to magnetic order of the sample, but cannot distinguish a paramagnetic state from a diamagnetic state. On the other hand, XES exploits the exchange interaction between the $3p$-core hole and the $3d$ moment, which is insensitive to the magnetic order of the sample, but very sensitive to the local moment. We now reexamine the MS data. The quadrupole-split component, that first appeared at room temperature between 60 and 90 GPa, was assigned to the diamagnetic LS state of Fe^{2+}. The possibility that it could be paramagnetic was not discussed. At 120 GPa, a temperature-dependent measurement showed that the transition temperature is between 77 and 100 K. Combined with our observation of a preserved magnetic moment on the Fe ion, we assign this high-pressure phase to a paramagnetic state, and attribute the MS observations to a Néel transition instead of the proposed HS to LS transition. This immediately implies a *decrease* of the Néel temperature with increasing pressure between 60 and 120 GPa. Such an effect is surprising, as one expects an increase of the antiferromagnetic effective exchange coupling parameter J with increasing pressure (decreasing Fe-Fe distance). The compressional behavior of FeO at very high pressure is peculiar, however, in the sense that volume reduction is not only accounted for by a compression of the unit cell, but also by distortion of the rhombohedral structure, as a result of which the total volume decreases while the distance between antiferromagnetically coupled Fe ions increases (111 direction). This also explains the large pressure range on which the MS transformations are observed, as this is due to the fairly large distribution of the rhombohedral distortion angle at high pressure, spanning a very large range of the order of 10% distortion [21]. This reinterpretation of the data places the Néel temperature of FeO at 300 K between 60 and 90 GPa and between 77 and 100 K at 120 GPa. The observations are summarized on the magnetic phase diagram in Fig. 3. The figure shows an unusual closed-loop P-T antiferromagnetic existence domain for FeO, and predicts a maximum Néel temperature $T_N^{\max}$ around 50 GPa.

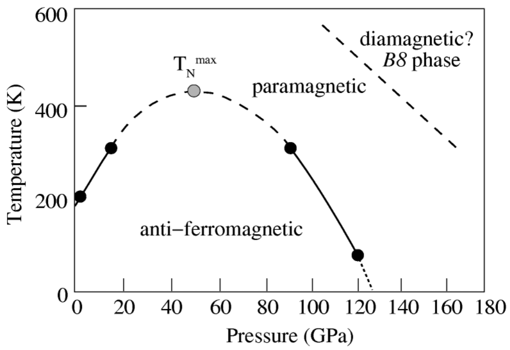

FIG. 3. Magnetic phase diagram of FeO. The room pressure point is from McCammon [25], the room temperature point at 15 GPa is from Nasu *et al.* [20], and the very high pressure points are from Pasternak *et al.* [4] and this study. A maximum Néel temperature $T_N^{\max}$ is therefore expected in the 50 GPa range, and is denoted by the gray point. At very high pressure, one can expect the destruction of the antiferromagnetic order ($T_N \longrightarrow 0$), and the phase diagram shows a closed-loop P-T antiferromagnetic domain of stability. At high pressure and higher temperature, the total magnetic moment of iron may vanish.

Finally, we note that valence band emission (VBE) is clearly observed ($K\beta_{2,5}$), as shown in the inset of both Figs. 1 and 2. The intensities of these lines are about 30 times smaller than those of the $K\beta_{1,3}$ emission lines. VBE provides a direct measurement of the symmetry-projected valence band density of states. We find no change of the $K\beta_{2,5}$ line shape with increasing pressure from 7090 eV up to the top of valence band in both FeO (Fig. 1) and Fe_2O_3 (Fig. 2). On the other hand, there is a significant increase in intensity for the spectral feature located between 7085 and 7090 eV in the high-pressure Fe_2O_3 spectrum. This is the $K\beta''$ line, which corresponds to the transition from the O $2s$ band into the Fe K-shell core hole. It has recently been suggested that the intensity of this line increases with decreasing Fe-O bond length [22], which is consistent with our observation. Perhaps this part of the VBE spectrum can be developed into a new source of information on local structure.

In conclusion, we report the observation of a preserved high-spin state in FeO to 143 GPa using XES. The results contrast with the interpretation of a recent MS study [4]. Our observations suggest that the transition observed by MS at 90 GPa and room temperature arises from a decrease in the Néel temperature with pressure, and a maximum Néel temperature $T_N^{\max}$ is expected around 50 GPa. Study of the stable high-pressure phase by XES is underway. We also demonstrate that the technique can be extended to measure both the symmetry-projected local electronic density of states of the valence band and information on local structure.

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