

Synchrotron Moessbauer Spectroscopy and Resistivity Studies of Iron Oxide Under High Pressure

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ABSTRACT

The strong electron correlations play a crucial role in the formation of a variety of electronic and magnetic properties of the transition metal oxides. In strongly correlated electronic materials many theoretical predictions exist on pressure-induced insulator-metal transitions, which are followed by a collapse of localized magnetic moments and by structural phase transitions [1]. The high-pressure studies provide additional degree of freedom to control the structural, electronic, optical, and magnetic properties of transition metal oxides. With the development of the high-pressure diamond-anvil-cell technique the experimental studies of such transitions are now possible with the advanced synchrotron techniques. In our studies, the iron monooxide $\text{Fe}_{0.94}\text{O}$ was studied under high pressures up to 200 GPa in diamond anvil cells. The single crystals enriched with Fe^{57} isotopes have been prepared for nuclear resonance measurements. The results of synchrotron Mössbauer spectroscopy (nuclear forward scattering - NFS), and electro-resistivity measurements suggest a complicated scenario of magnetic interactions governed by band-broadening effects.

INTRODUCTION

The active topic of current research in systems with strong electron correlations is high-pressure-induced insulator-metal transition (I-M), which is accompanied by the collapse of the magnetic moments [1]. The oxides of transition metals present a very large class of materials, which are important for both fundamental science and practical applications. They include high temperature superconductors, manganites with colossal magneto resistance, heavy fermion and Kondo systems. A variety of different electronic, magnetic, transport and optical properties in these materials provides the basis for a new type of applications in electronics and optoelectronics. The studies of oxides and perovskites doped with iron are very important for understanding the deep Earth's interior composition and properties [1].

Compression of a solid presents a natural means to tune interatomic distances and induce a variety of transitions (e. g. insulator-metal transitions, spin-crossover transitions) in correlated materials. The most widely used technique for this purpose - diamond anvil cell (DAC) technology - has developed rapidly over the past few years [2,3]. A number of techniques, which were previously limited to ambient pressure (because of the requirement of a large sample

volume) may now be used at high and even ultrahigh pressures [4-8] and can be applied to studies of materials with strong electronic correlations.

The electronic structure of correlated materials is usually described in terms of two major parameters governing the *d*-electrons repulsion on metal ions (Hubbard *U*) and *p-d* energy separation (charge transfer *Δ*) from the metal *d*-states to the ligand ion *p*-states [9]. Such simplified model completely neglects the crystal field effects, which split *d* states into multiplets with varying spin and orbital properties. The nature of the ground state is determined by the competition of the crystal-field effects and electronic correlations within the *d*-orbitals [10]. Thus, the high-spin or low-spin configurations are usually realized in many correlated materials, and pressure variable is a natural way to change the high-spin ground state to the low-spin state. The orbital *d*-states have received a lot of attention recently due to their dramatic manifestation in manganates and other *d*-metal compounds [11].

The pressure-induced high-spin to low-spin transition has been suggested in FeO at 140 GPa from conventional Mössbauer studies to 120 GPa [12]. Several x-ray emission studies [13-15], synchrotron Mössbauer experiments [16], and optical absorption studies [17] have unambiguously identified high-spin to low-spin transition in diluted $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ (ferropericlasite) system at 50 -70 GPa. The x-ray emission study on FeO [13] has provided a probe of the high-spin state of Fe^{2+} to 140 GPa (close to pressure conditions at the Earth's core-mantle boundary). We will present below the recent progress in complimentary techniques (synchrotron Mössbauer and resistive studies in DAC). It will be shown that the theoretically suggested band-broadening mechanism [1] does have a stabilizing effect on the high-spin state in FeO to at least 200 GPa.

EXPERIMENT

The cubic crystals of the iron monoxide $\text{Fe}_{0.94}\text{O}$, were studied under high pressures in diamond anvil cells. The single crystals enriched with ^{57}Fe isotope were prepared for nuclear resonance measurements. The Mössbauer synchrotron (or Nuclear resonance Forward Scattering -NFS) spectroscopy, and the direct resistivity measurements were performed. The experiments were done in a Mao-Bell type diamond anvil cell. The resistivity measurements in the wide P-T range were similar to previous studies of superconductivity in boron [18]. Two experiments with different diamond anvil sizes and sample arrangements were conducted. In the first experiment we have used diamonds with flat culets 200 μm in diameter, no pressure medium was used, and the sample was embedded into a composite BN-epoxy gasket. In the second experiment beveled diamonds with a 50 μm flat culet and 300 μm bevel were used. The sample was placed in a pit made by laser in the BN-epoxy gasket and filled with NaCl pressure medium, to ensure more hydrostatic pressure environment. Due to large pressure gradients, two-probe measurements were used in these two experiments. Two additional experiments without and with NaCl pressure medium were done by four probe technique using Van der Pauw method. These experiments gave similar results and extended the pressure range to 180 GPa. The temperature dependence of the resistivity is shown in Fig. 1b; the activation energies (resulting from linear fits as indicated in Fig. 1b) are shown in Fig. 1a. The activation energy extrapolates to zero at pressure above 140 GPa for the sample compressed without pressure medium. However, slightly different temperature behavior of resistivity is found for the sample embedded in NaCl (Fig. 1a, red circles). The stress effects are certainly involved in this complicated behavior.

The samples used in the NFS study were synthesized from starting materials enriched in Fe^{57} (95%) and the stoichiometry of the samples was $\text{Fe}_{0.94}\text{O}$, established based on the measured

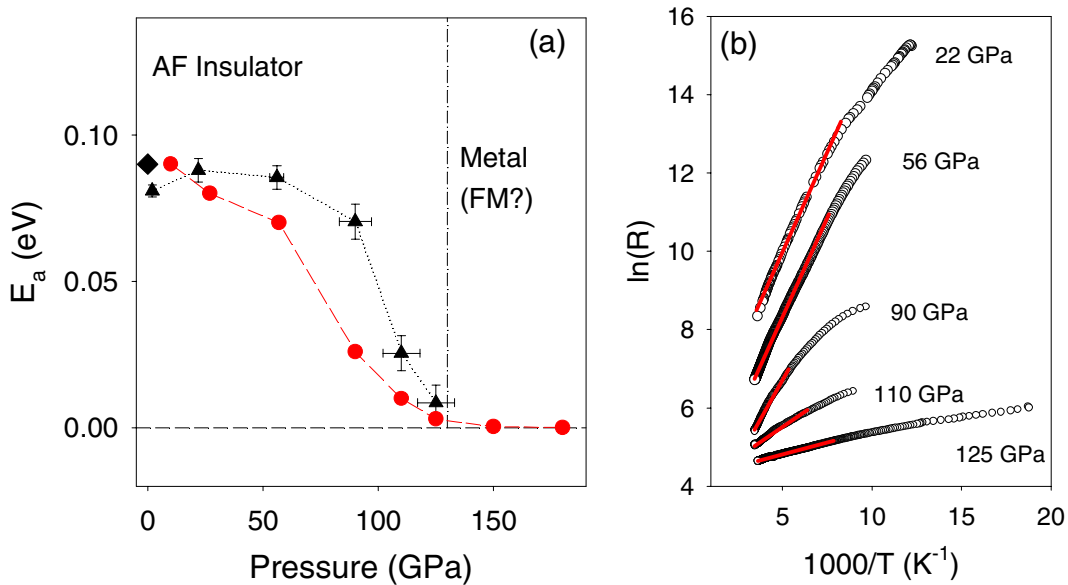


Figure 1. (a) The pressure dependence of the activation energies for conductivity in FeO. The activation energies are shown for nonhydrostatic (no pressure medium -triangles) and quasihydrostatic (NaCl pressure medium – circles) experiments. The black diamond is a literature value for $\text{Fe}_{0.99}\text{O}$. The stress effects are certainly involved in this complicated behavior. No superconductivity was found at 180 GPa down to 4 K. (b) The corresponding representative $\ln(R)$ versus $1/T$ plots are shown in the right panel (the data are offset vertically, to avoid overlap near the room temperature; room temperature pressure effect is negligible in the logarithmic scale).

lattice parameter. The NFS measurements in the lower P-T range were performed in a Bassett-type [19] externally-heated DAC. We have used diamonds with flat culets 400 μm and 300 μm in diameter, and the sample in NaCl pressure medium was enclosed in rhenium gasket. At each pressure, the externally heated cell was cycled several times to the highest temperature of the experiment and pressure was measured at high P-T conditions using high temperature ruby pressure scale proposed in [20]. The megabar experiments were performed in a Mao-Bell type DAC; diamonds with a 70 μm flat culet and 300 μm bevel were used. The sample (25-30 μm in diameter) was placed in a drilled hole in a Re gasket without pressure medium. Pressure was measured using ruby and diamond Raman signal [21]. Details of the NFS technique can be found elsewhere [22].

The hyperfine splitting (H), quadrupole splitting (QS), and isomer shifts (IS) are responsible for the oscillations of the observed NFS signal in the time-domain. The hyperfine magnetic fields of the order of 30-50 Tesla are usually responsible for fast temporal variation of the NFS signal with a periods ranging from 5-10 to 30 nsec. In the case of vanishing hyperfine field the quadrupole splitting QS and the isomer shifts IS between the different species become important and introduce large-period oscillations (50-100 nsec) in the NFS signal. Thus, the magnetic and nonmagnetic materials produce very different NFS spectra, and high-frequency beats are unambiguous indication of the macroscopic magnetic order in the material. However, the detailed information (H, QS, IS, relative weights of different magnetic species) could be obtained only from the complicated nonlinear fitting with the application of the detailed models of the magnetic structure and the geometry of the experiment [22].

The NFS spectra of the iron oxide sample pressurized to 200 GPa do show high-frequency beats characteristic for magnetically-ordered material – Figure 2a. We have not attempted to fit these spectra above 80 GPa (the detailed fitting requires a knowledge of the magnetic structure, which is not available at the moment). The fits below 80 GPa give reasonable

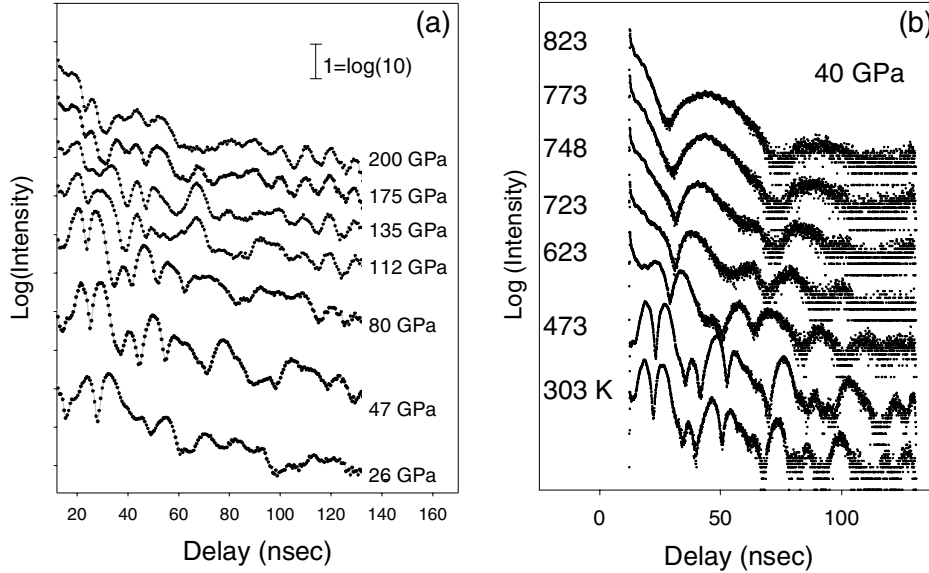


Figure 2. (a) The pressure dependence of the NFS signal from iron oxide sample in the DAC at room temperature. (b) The temperature dependence of the NFS signal in the DAC at 40 GPa. The characteristic high-frequency beats corresponding to the hyperfine magnetic splitting disappear above ~ 750 K, which is a signature of the transition to the paramagnetic state. The time spectra are offset vertically for clarity in (a) and (b).

agreement with previously reported Mössbauer measurements [12]. However, the character of the NFS beats in the time spectra changes above 80 GPa, which is consistent with the observation of the central non-magnetic peak developing with pressure in conventional Mössbauer measurements [12]. Contrary to the suggested in Ref.12 extrapolation, we do see magnetic beats up to the highest pressure in this experiment (200 GPa). The character of the magnetic NFS spectra changes very little above 140-150 GPa, possibly indicating a new magnetic structure which occurs concomitantly with the emergence of nearly metallic conductivity. We suggest that this magnetic structure may be ferromagnetic, since it will have a reduced scattering rate of charge carriers due to the parallel alignment of spins, similar to spin-controlled conductivity in manganates [23].

DISCUSSION

The sluggish transition in the 80 to 140 GPa range both in resistivity and synchrotron Mössbauer studies is not compatible with the spin collapse scenario, since the magnetic order is preserved up to 200 GPa. The transition is also very different from that observed in MnO (see e. g. [24] and references therein), since we do not observe discontinuous drop in resistivity up to 180 GPa, and magnetic ordering is preserved to 200 GPa. At 180 GPa iron oxide sample behaves like semimetal with very small activation energy (about 0.1 meV) down to 40 K [25]. The theoretical predictions of the phase transitions and magnetic properties of FeO [1,26-30] vary depending on the calculation method used and various assumptions regarding structural distortions. Isaak et al. [26] predict decrease of local magnetic moments in cubic and rhombohedrally strained FeO to zero when pressure is increased to 150-180 GPa. Cohen et al. [1] have calculated pressures as high as 200 GPa for the collapse of magnetic moments in FeO. They further argue that non-stoichiometry of the real samples should not matter for the calculation of local moments, since the predicted collapse is not related to the cooperative effects

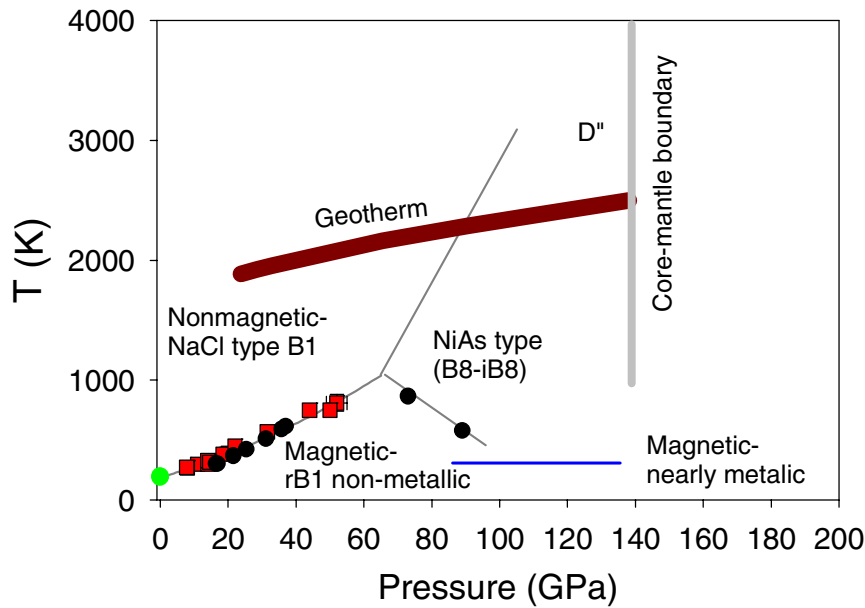


Figure 3. The phase diagram of FeO constructed from x-ray diffraction data taken by Fei et. al. [30] (black diamonds) and our synchrotron Mössbauer data (red squares). The broad transition to semi-metallic state from resistivity studies is shown by a blue line). The green circle indicates the Néel point at ambient pressure.

and magnetic ordering. The studies by Fang et al. [27,28] have predicted high-spin state in both antiferromagnetic rhombohedral strained rB1 and inverse B8 (iB8) phases to 150-180 GPa. Our measurements of the NFS spectra do provide evidence of the magnetic order at room temperature, and should correspond to substantial local magnetic moments at the iron sites at 200 GPa. However, since we do not know the details of the magnetic and crystalline structure at these high pressures, further structural and magnetic studies are required to establish the reason for the stabilization of magnetic moments in FeO at such high pressures. Our observed transition to nearly metallic behavior matches nicely the predictions by Gramsch et. al. [29] from LDA+U calculations for monoclinic structure and Hubbard parameter $U=6$.

The tentative phase diagram of FeO is presented in Fig. 3. The continuation of the rhombohedral to NiAs-type phase transition line into higher pressures matches our observed “transitions” in magnetic signal and in resistivity at room temperature and below. While relatively little is known about the structure of the FeO above 120 GPa, it would be natural to suggest some degree of correspondence between the magnetic low-temperature phase and higher-temperature NiAs-type phase [31]. This may have major implications for our understanding of the magnetic properties of the deep-mantle phases of iron-rich oxides.

CONCLUSIONS

Both synchrotron Mössbauer and resistance measurements are compatible with a transition to a semimetallic magnetic state in the range from 80 to 140 GPa, which does not favor Mott-type transition scenario [24] in FeO to at least 200 GPa. Magnetic properties of the high-pressure modification of FeO are not yet established, however, the high-spin state of Fe^{2+} is preserved at pressures up to 200 GPa. Further experimental and theoretical studies are needed to establish the nature of the high-pressure magnetic phase of the iron oxide.

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