Orbital-selective pressure-driven metal to insulator transition in FeO from dynamical mean-field theory

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In this work we report the LDA+DMFT (method combining local-density approximation with dynamical mean-field theory) results of magnetic and spectral properties calculation for paramagnetic phases of FeO at ambient and high pressures (HPs). At ambient-pressure (AP) calculation gave FeO as a Mott insulator with Fe 3d shell in high-spin state. Calculated spectral functions are in a good agreement with experimental photoemission spectroscopy and IPES data. Experimentally observed metal-insulator transition at high pressure is successfully reproduced in calculations. In contrast to MnO and Fe_2O_3 (d^5 configuration) where metal-insulator transition is accompanied by high-spin to low-spin transition, in FeO (d^6 configuration) average value of magnetic moment $\sqrt{\langle\mu_z^2\rangle}$ is nearly the same in the insulating phase at AP and metallic phase at HP in agreement with x-ray spectroscopy data [J. Badro, V. V. Struzhkin, J. Shu, R. J. Hemley, H.-k. Mao, C.-c. Kao, J.-P. Rueff, and G. Shen, Phys. Rev. Lett. **83**, 4101 (1999)]. The metal-insulator transition is orbital selective with only t_{2g} orbitals demonstrating spectral function typical for strongly correlated metal (well pronounced Hubbard bands and narrow quasiparticle peak) while e_g states remain insulating.

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I. INTRODUCTION

For many years one of the central issues of condensed-matter physics is the metal-insulator transition (MIT) in d- or f-elements compounds.[1] The most spectacular examples are pressure-driven transitions from wide gap Mott insulators to metallic state for transition-metal oxides. For MnO and Fe_2O_3 (d^5 configuration) metal-insulator transition is accompanied by high-spin to low-spin transition (HS-LS). Recently MIT in those materials was successfully described theoretically by LDA+DMFT (method combining local-density approximation with dynamical mean-field theory) (Ref. 2) calculations.[3,4]

Iron oxide also exhibits MIT under high pressure. Resistivity measurements showed that FeO becomes metallic at pressures exceeding 72 GPa.[5] Correct description of MIT under pressure in wüstite ($Fe_{1-x}O$) is crucial in Earth science because iron oxides are believed to be major constituents of Earth mantle.

At ambient pressure (AP) and room temperature FeO has cubic rocksalt B1 structure.[6] Below Néel temperature $T_N = 198$ K FeO transforms into rhombohedral structure that could be viewed as a slight elongation along cube diagonal of the original cubic structure. Under pressure at room temperature rhombohedral distortion is observed at ≈ 15 GPa and this structure is preserved up to at least 140 GPa.[7,8] This transformation to rhombohedral structure was believed to accompany long-range magnetic ordering due to increasing of Néel temperature with pressure.[9] However recent neutron-diffraction study of wüstite at room temperature under pressure[10] showed the absence of magnetic peaks corresponding to antiferromagnetism. At high pressures and temperatures ($P > 120$ GPa and $T > 1000$ K) FeO transforms into NiAs B8 phase.[11]

In contrast to MnO and Fe_2O_3 there are controversial experimental evidences if FeO undergoes HS–LS transition with increase in pressure. Mössbauer spectroscopy[12] shows that quadrupole splitting appears between 60 and 90 GPa at room temperature. The authors interpreted that as LS diamagnetic state. On the other hand high-pressure x-ray emission spectroscopy[13] demonstrates that the satellite feature in Fe Kβ line associated with HS Fe^{2+} state does not disappear up to 143 GPa. Note, that accurate treatment of Mössbauer data[13] confirms the absence of HS-LS transition.

Electronic-structure calculations in standard density-functional-theory (DFT) methods predict an antiferromagnetic metallic ground state[14] in contrast to experimentally observed insulator with an optical band gap of 2.4 eV.[15] The LDA+U method[16] has been successfully applied to investigate strongly correlated transition-metal oxides and predicted an insulating ground state in FeO at ambient pressure.[17] Further investigation done by Gramsch *et al.*[18] for stoichiometric wüstite has showed that using the value of Coulomb parameter U that reproduces experimentally observed energy gap at ambient pressure one can obtain metal-insulator transition in LDA+U calculations for unrealistically high pressures only.

MIT in transition-metal oxides with pressure can be successfully described using LDA+DMFT calculations.[3,4] In the present work we demonstrate that LDA+DMFT method reproduces MIT for FeO with pressure. However in contrast to MnO and Fe_2O_3 MIT is not accompanied by high-spin to low-spin transition and metallic spectral function is observed only for t_{2g} orbitals while e_g states remain insulating.

II. METHOD

The LDA+DMFT method[2] calculation scheme is constructed in the following way: first, a Hamiltonian $\hat{H}_{\mathrm{LDA}}$ is produced using converged LDA results for the system under investigation, then the many-body Hamiltonian is setup, and finally the corresponding self-consistent DMFT equations are solved. The calculations presented below have been done for crystal volumes corresponding to values of pressure up to 140 GPa and room temperature. Since no structure transition has been observed at low temperatures[8] and NiAs phase appears above 1000 K only all calculation were performed for simple NaCl (B1) cubic crystal structure with lattice constant scaled to give a volume corresponding to applied pressure.[5] *Ab initio* calculations of electronic structure were obtained within the pseudopotential plane-wave method PWSCF, as implemented in the QUANTUM ESPRESSO package.[19] Hamiltonians $\hat{H}_{\mathrm{LDA}}$ in Wannier function (WF) basis[20,21] were produced using projection procedure that is described in details in Ref. 22.

The WFs are defined by the choice of Bloch functions Hilbert space and by a set of trial localized orbitals that will be projected on these Bloch functions. The basis set includes all bands that are formed by O 2*p* and Fe 3*d* states and correspondingly full set of O 2*p* and Fe 3*d* atomic orbitals to be projected on Bloch functions for these bands. That would correspond to the extended model where in addition to *d* orbitals all *p* orbitals are included too.

The resulting 8×8 *p*-*d* Hamiltonian to be solved by DMFT has the form

$$\hat{H} = \hat{H}_{\mathrm{LDA}} - \hat{H}_{\mathrm{dc}} + \frac{1}{2}\sum_{i,\alpha,\beta,\sigma,\sigma'} U_{\alpha\beta}^{\sigma\sigma'} \hat{n}_{i\alpha\sigma}^{d}\hat{n}_{i\beta\sigma'}^{d}, \quad (1)$$

where $U_{\alpha\beta}^{\sigma\sigma'}$ is the Coulomb interaction matrix, $\hat{n}_{i\alpha\sigma}^{d}$ is the occupation number operator for the *d* electrons with orbitals α or β, and spin indices σ or σ' on the *i*th site. The term $\hat{H}_{\mathrm{dc}}$ stands for the *d*-*d* interaction already accounted for in LDA, so-called double-counting correction. In the present calculation the double counting was chosen in the following form $\hat{H}_{\mathrm{dc}}=\bar{U}(n_{\mathrm{DMFT}}-\frac{1}{2})\hat{I}$. Here n_{DMFT} is the self-consistent total number of *d* electrons obtained within the LDA+DMFT, $\bar{U}$ is the average Coulomb parameter for the *d* shell and $\hat{I}$ is unit operator.

The elements of $U_{\alpha\beta}^{\sigma\sigma'}$ matrix are parametrized by *U* and J_H according to procedure described in Ref. 23. The values of Coulomb repulsion parameter *U* and Hund exchange parameter J_H were calculated by the constrained LDA method[24] on Wannier functions.[22] Obtained values J_H=0.89 eV, U =5 eV are close to previous estimations.[18] The effective impurity problem for the DMFT was solved by the hybridization expansion continuous-time quantum Monte Carlo method (CT-QMC).[25] Calculations for all volumes were performed in the paramagnetic state at the inverse temperature $\beta=1/T=40$ eV^{-1} corresponding to 290 K. Spectral functions on real energies were calculated by maximum entropy method (MEM).[26]

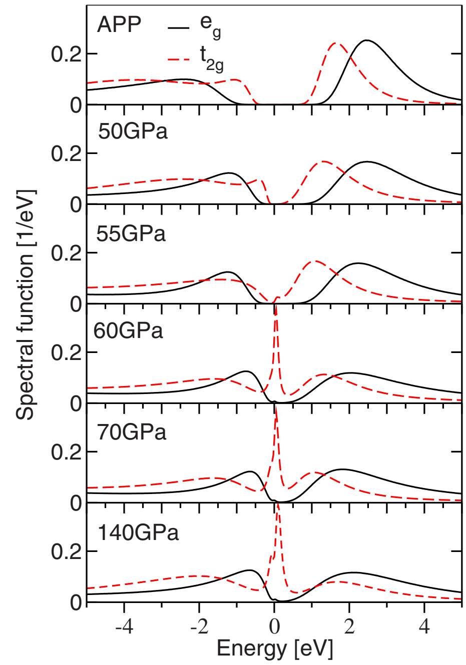

FIG. 1. (Color online) Spectral function of Fe *d* states vs pressure obtained in LDA+DMFT (CT-QMC) calculations at room temperature.

III. RESULTS AND DISCUSSION

The Fe *d* band is split by crystal field in triply degenerated t_{2g} and doubly degenerated e_g subbands. LDA fails to describe insulating ground state of FeO at AP and for all volumes FeO is metallic.

Including Coulomb correlation effects in frames of LDA+DMFT method results in high-spin state wide gap Mott insulator for AP phase (APP) of FeO in agreement with experimental data. The calculated energy gap value of about 2 eV agrees well with IPES measurement[27] value 2.5 eV and optical spectrum[15] value 2.4 eV. The occupation numbers for Fe *d* orbitals are $n(e_g)$=0.54 and $n(t_{2g})$=0.68. The average value of local magnetic moment $\sqrt{<\mu_z^2>}$ is 3.8 μ_B. Those numbers agree very well with high-spin state of Fe^{+2} ion (d^6 configuration) in cubic crystal field: two electrons in e_g states $[n(e_g)=1/2]$ and four electrons in t_{2g} states $[n(t_{2g})=2/3]$ with magnetic moment value 4 μ_B. Spectral functions $A(\omega)$ for all pressure values calculated by MEM using Green's function $G(\tau)$ from CT-QMC calculations are presented in the Fig. 1. The spectral function for APP shows well defined insulating behavior for all *d* orbitals. However the energy gap for e_g states is nearly two times larger than for t_{2g} states indicating that the latter orbitals are closer to MIT than the former ones. Figure 2 contains calculated total spectral function compared with spectrum combined from photoemission spectroscopy (PES) and inverse photoemission spectroscopy (IPES) experiments.[28,29] The theoretical and experimental curves are in a good agreement.

LDA+DMFT calculation made for small volume values corresponding to high pressures gave metallic state for FeO (see Fig. 3) starting from 60 GPa in agreement with experiment.[5] One can see that t_{2g} orbitals become metallic

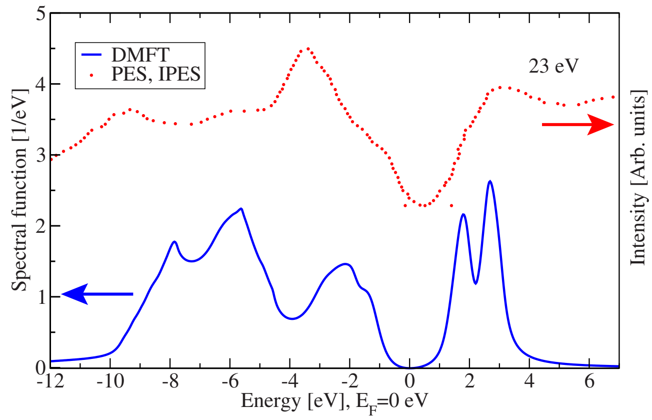

FIG. 2. (Color online) Total spectral function of FeO in ambient–pressure phase calculated within LDA+DMFT (CT-QMC) (β=40 eV^{-1})(solid blue line) in comparison with combined PES and IPES experimental data (red dots) from Refs. 28 and 29.

whereas e_g ones remain insulating. This behavior reminds the orbital-selective Mott transition in ruthenates.[30] Occupation number values in Fe d shell are practically not changed comparing with APP and are $n(e_g)$=0.55 $n(t_{2g})$=0.68 at 140 GPa. The magnetic moment value decreases on a few percent only and is 3.5 μ_B at 140 GPa. The only interpretation for those values is that an iron d shell in high-pressure metallic phase of FeO still corresponds to high-spin state of Fe^{+2} ion. This conclusion agrees well with analysis of high-pressure x-ray emission spectroscopy experiment made in Ref. 13. The occupation numbers and magnetic moment vs pressure are presented in the Fig. 3. One can see that all curves exhibit the kink at 60 GPa. We argue that this feature is due to MIT and corresponding reconstruction of spectral function at Fermi level. Spectral functions $A(\omega)$ for t_{2g} in the Fig. 1 for pressure values larger then 60 GPa become typical for strongly correlated metal close to MIT: well pronounced Hubbard bands and narrow quasiparticle peak. $A(\omega)$ for e_g is still insulating with Hubbard bands only but energy gap value is strongly decreased comparing with APP (see Fig. 1). The crystal-field splitting obtained as the difference between gravity centers of e_g and t_{2g} bands is 1.07 eV in APP and

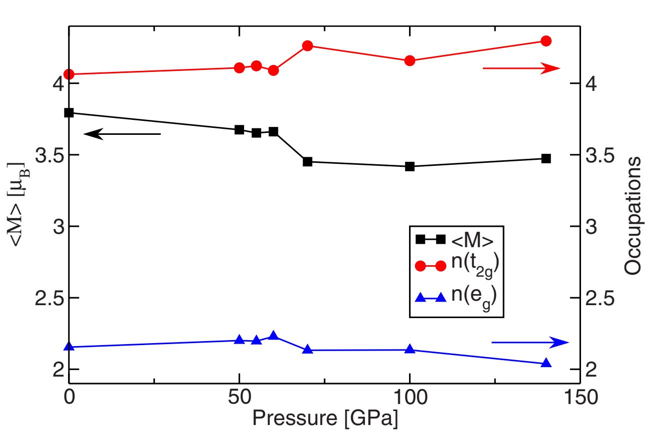

FIG. 3. (Color online) Magnetic moments (black squares) and occupancies of t_{2g} (red circles) and e_g (blue triangles) shells vs pressure obtained in LDA+DMFT (CT-QMC) calculations.

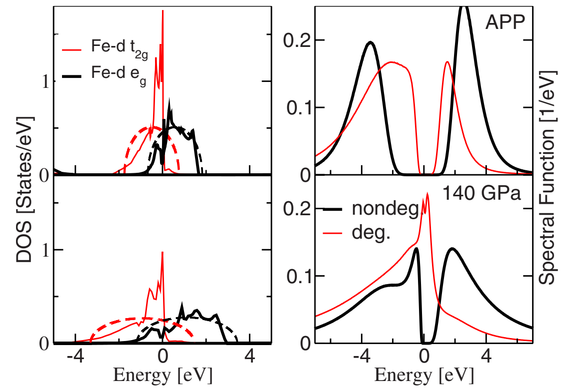

FIG. 4. (Color online) Left panels-LDA DOS (e_g thin solid lines, t_{2g} bold solid lines) and corresponding model semicircle DOS (dashed lines). Right panels—spectral functions from model DMFT (CT-QMC) calculations for two values of pressure. Nondegenerate orbital (bold black lines) reproduces e_g orbitals and two times degenerate one reproduces t_{2g} orbitals (thin red line).

2.05 eV at 140 GPa. Note that it is smaller than in MnO case where the crystal-field splitting is about 2 eV at AP and 2.7–3.0 eV at transition pressure.[3] This could be the reason why magnetic collapse is absent in FeO.

To understand these results the following simple model was used. The model has two semicircle density of states (DOS) of the same width with three orbital and four electrons. One orbital is nondegenerate and two other orbitals are degenerate. The centers of gravity and DOS widths were taken from *ab initio* LDA calculations. In this model nondegenerate orbital stands for e_g orbital in FeO and two others for t_{2g}. Occupations in model in HS state are 1/2 for nondegenerate orbital (the same as in realistic LDA+DMFT calculation for FeO) and 3/4 for degenerate orbitals comparing with 2/3 in the case of t_{2g} orbitals in FeO. The Kanamori parametrization of Coulomb repulsion (with the same U =5 eV and J=0.89 eV) was used. Note, that corresponding matrix elements $U^{\sigma,\sigma'}_{\alpha,\beta}$ [Eq. (1)] are set to be the same for all orbitals. The model was solved using DMFT (CT-QMC) method and obtained spectral functions for two values of pressure (APP and 140 GPa) are presented in the Fig. 4.

The orbital-selective metal-insulated transition (OSMT) was reproduced in these calculations. Similar results have been previously obtained for similar model in Ref. 31. Since DOSs for all three orbitals have the same width [in contrast to OSMT (Ref. 30) in ruthenates where two bands have very different widths] and actual structure of DOS is neglected we can conclude that effects of different degeneracy of orbitals and deviation from half filling are the driving force of this separate transition. It is known that critical value of Coulomb interaction parameter U_c needed for metal-insulator transition in half-filled degenerate Hubbard model is $U_c \approx \sqrt{N}U_c^{N=1} - NJ$ (Ref. 32) (N is degeneracy and $U_c^{N=1}$ is critical U value for nondegenerate case). That means that for more degenerate t_{2g} orbitals one needs larger effective U value to become insulating than for less degenerate e_g orbitals. In addition to that for half-filled states an estimation for effective U_{eff} value is $U+(N-1)J$ while for the occupancy one electron more then half filling an estimation is U_{eff}=U

$-J$. Then for 2/3 filled t_{2g} orbitals one needs much larger U value to drive them into insulating state than for half-filled e_g states.

IV. CONCLUSION

We have performed LDA+DMFT calculation for FeO at room temperature and values of pressure from the ambient one till 140 GPa. In the agreement with experiment spectral function for FeO at AP demonstrates an energy gap of about 2 eV. At the pressures higher then 60 GPa FeO is metallic but only for t_{2g} orbitals while e_g states remain insulating that corresponds to orbital selective Mott transition scenario. The MIT obtained in our calculations is not accompanied by change in spin state and FeO has HS with large local moment in APP and all HPP. This result agrees with high-pressure x-ray emission spectroscopy data.

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