Synchrotron X-ray and Mössbauer Spectroscopy of Some Compound Iron Oxides Under High Pressures

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Introduction

The high-pressure studies provide additional degree of freedom to control the structural, electronic, optical, and magnetic properties of transition metal oxides, which are the most interesting classes of solids from both fundamental and applied points of view. The strong electron correlations play the crucial role in the formation of variety of electronic and magnetic properties of the transition metal oxides, and by high pressure it is possible to influence the electron correlations. In the systems with strong electron correlations, many theories predict the high-pressure-induced dielectric-metal transition, which is followed by collapse of localized magnetic moment and structural phase transition [1]. With the development of the high-pressure diamond-anvil-cell tecnique, the experimental investigations of such transitions are now possible especially due to the synchrotron radiation fasilities.

Methods and Materials

A variety of different electronic, magnetic, and optical properties that are known for the transition metal oxides provides the basis for a new type of electronics. In these studies, several synchrotron radiation techniques have been applied to perform the high-pressure experiments with compound iron oxides having different crystal structures. The cubic yttrium iron garnet $Y_3Fe_5O_{12}$, the perovskite-like rare-earth orthoferrites $RFeO_3$ (R = Nd, Lu, Y) and multiferroic $BiFeO_3$ crystals, the hematite Fe_2O_3 with corundum structure, the rhombohedral iron borates $FeBO_3$ and trigonal rare-earth borate $GdFe_3(BO_3)_4$, were studied under high pressures up to 150 GPa created in diamond anvil cells. The single crystals enriched with Fe-57 isotopes have been prepared for nuclear resonance measurements. The Mössbauer transmission and Mössbauer synchrotron (NFS) spectroscopy (including low-temperature NFS measurements down to 4.2 K), X-ray diffraction and the synchrotron high-resolution Kβ X-ray emission spectroscopy (XES), optical absorption spectroscopy, Raman scattering, electron microscopy, and electro-resistivity measurements have been applied.

Results and Discussion

The sharp transition from the magnetic to a nonmagnetic state was discovered in all investigated crystals at pressures of about 40-50 GPa. For example evolution of the synchrotron Mössbauer spectra in $^{57}FeBO_3$ demonstrates disappearance of the quantum beats in the spectra at about 50 GPa which indicates the magnetic collapse. The Mössbauer, XES, and optical spectra in selected materials [$FeBO_3$, $GdFe_3(BO_3)_4$, $BiFeO_3$] indicate that the magnetic collapse is accompanied by transformations in electronic and spin structures of iron ions. In most cases, this is explained by spin crossover in *3d* electron system with the transition of Fe^{3+} ions from the high-spin S = 5/2 ($^6A_{1g}$) state to a low-spin S = 1/2 ($^2T_{2g}$) state. It was established from the behavior of the optical absorption edge and from direct electro-resistivity measurements that in the $FeBO_3$, $RFeO_3$ and $GdFe_3(BO_3)_4$ crystals, the transition from the insulating to a semiconducting state takes place at the critical pressures. In the $Y_3Fe_5O_{12}$ and $BiFeO_3$ crystals the decrease of optical gap almost to zero value was measured indicating a possibility of the insulator-metal transition. In addition to magnetic and electronic transformations, the X-ray spectra indicate that structural phase transitions of first-order type with a sharp drop of the unit cell volume take also place near the critical pressure. We have found that unambiguous detection of the nature of the transition requires combined application of multiple probes under high pressure: Mössbauer, optical, XES spectra, and direct resistivity measurements in DAC. As to magnetic behavior, the low-spin state of Fe^{3+} in the high-pressure phase is not diamagnetic, and the low-temperatures synchrotron Mössbauer measurements of $FeBO_3$ indicate the magnetic correlations related to magnetic ordering of Fe^{3+} ions in the low-spin system. The magnetic ordering temperature of the low-spin Fe^{3+} ions was evaluated, and P – T magnetic phase diagrams were plotted. Several theoretical approaches for explanation of the observed transitions are discussed in connection with the breakdown of strong *d-d* electronic correlations. The proposed theoretical consideration explains some details of the high-pressure magnetic properties.

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