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Phase transitions in $FeBO_3$ under pressure: DFT+DMFT study

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The iron borate $FeBO_3$ is one of a few materials that are transparent in the visible range and have a spontaneous magnetization at room temperature. The iron borate crystallizes in the rhombohedral calcite structure with the space group $R\bar{3}c$. Under normal conditions $FeBO_3$ is an antiferromagnet with weak ferromagnetism [1] and Néel temperature of 348 K, and is an insulator with the optical gap of 2.9 eV [2, 3].

Recent experimental studies show an abrupt magnetic collapse in $FeBO_3$ in vicinity of 46 GPa [4], accompanied with the high-spin (HS) to low-spin (LS) transition. Optical and resonant inelastic X-ray spectroscopy (RIXS) studies show an insulator-semiconductor transition with a decrease of the optical gap to 0.8 eV [5–7] occurring at the same pressure as the magnetic collapse, and an increase of Néel temperature with pressure [5]. Previous X-ray diffraction studies show an isostructural transition at 53 GPa with a volume collapse of 9 % [8].

Local spin density approximation studies predicted the antiferromagnetic solution to be metal [9] instead of insulator. Another study in frames of density functional theory (DFT) with the generalized gradient approximation (GGA) predicted the isostructural transition to occur in $FeBO_3$ at 22 GPa with a 12 % volume collapse [10]. Further first-principle studies by means of GGA+U [11] method predicted an antiferromagnetic, high-spin, insulating electronic structure at ambient pressure (AP), using the Coulomb repulsion parameter $U = 7$ eV [12]. An empirical multielectron model suggested strong hybridization between s–p electrons in BO_3 group, and obtained effective Coulomb repulsion value parameter $U_{\text{eff}} = 2.97$ eV.

In this work we employ the DFT+DMFT approach to investigate the electronic structure and magnetic properties of the iron borate $FeBO_3$ and probe for possible phase transitions under high pressure. We find that the Fe ions in $FeBO_3$ undergo a high-spin to low-spin (HS-LS) transition under pressure with the change from antiferromagnetic to paramagnetic state, and demonstrate that the spin and magnetic transitions are accompanied by the isostructural transition with the volume collapse of 13 %.

We calculated the electronic structure and magnetic properties of $FeBO_3$ for experimentally observed low-pressure (LP) phase up to 60 GPa. For high-pressure (HP) phase we performed calculations for structures corresponding to pressures 40–70 GPa. Results of our calculations indicate that $FeBO_3$ is an antiferromagnet in the LP phase with the highest spin polarization at 40 GPa and higher. Our calculations resulted in insulating state at AP with the gap of ~ 2 eV, the gap widens to ~ 3 eV at 40 GPa, where as for HP phase at 46 GPa our spectral functions show the gap of ~ 0.5 eV. The DFT densities of states along with the respective DFT+DMFT spectral functions are presented in Fig. 1. The densities of states obtained in DFT as expected exhibit metallic behavior and are in qualitative agreement with the previous LSDA calculations [9].

Calculations of local magnetic moment $\sqrt{\langle \mu_z^2 \rangle}$ performed for the LP phase resulted in a HS state with the value of local magnetic moment of $4.6\mu_{\text{B}}$ for pressures up to 46 GPa, beyond it the value of local magnetic moment decreases slowly and becomes $4.5\,\mu_{\text{B}}$ at 60 GPa. On the other hand, calculations performed for the HP phase indicate a finished transition into the paramagnetic LS state with the value of local magnetic moment of 1.5 μ_{B}.

To investigate the experimentally observable phase transition to the same structure with a 9 % collapse of volume, we have carried out the DFT+DMFT calculations of total energy and enthalpy of the system as implemented in the AMULET package [13]. The values of the total energy of $FeBO_3$ obtained in DFT+DMFT were fitted using the third order Birch–Murnaghan [14] equation of state. Using the obtained in the fit values of pressure $P(V)$ we calculated enthalpy $H = E_{\text{total}} + PV$ of the system. The calculated enthalpy curves show that the high-pressure LS regime becomes more energetically profitable than the intermediate pressure HS regime at pressure 50.4 GPa, where the volume difference of two regimes is ~ 13 %. The obtained value of critical pressure $P_{\text{c}} = 50.4$ GPa confirms the suggestion [8] that the

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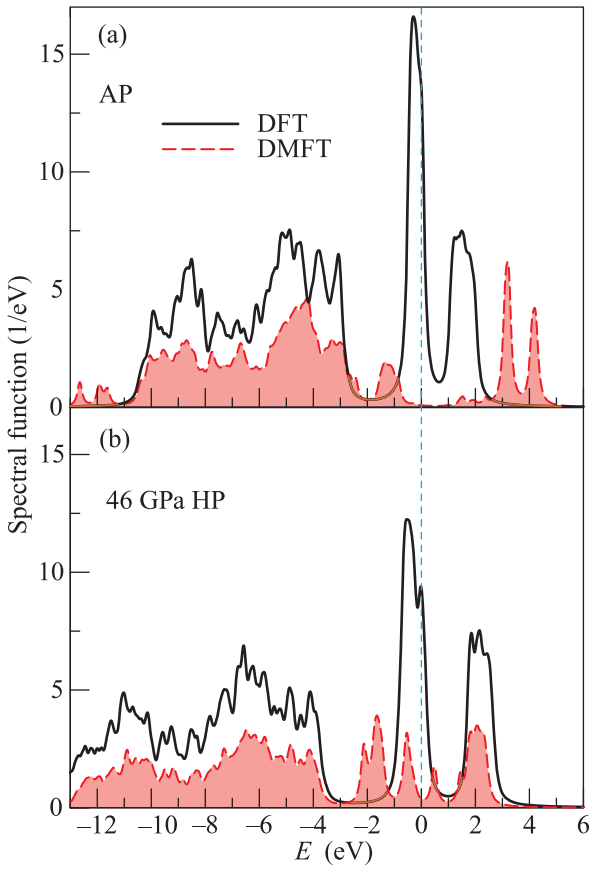

Fig. 1. (Color online) Cumulative Fe-3d and O-2p spectral functions and densities of states of $FeBO_3$ at ambient pressure (low pressure phase) and at 46 GPa (high pressure phase), calculated by DFT+DMFT at 300 K (dashed outline, filled) and by DFT (solid line), respectively. The DFT densities of states are shown at double scale for clarity

isostructural transition with a volume collapse of 9 %, experimentally observed at 52 GPa, and the magnetic transition, observed at 46–48 GPa, indeed both occur simultaneously and the discrepancy in the experimental values can be attributed to the difference in experimental samples.

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