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Structural phase transition in FeBO$_3$ under pressure

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Abstract. Using the density functional theory the structural and magnetic properties of iron borate under high pressure have been studied. At about $P = 22.7$ GPa a first order phase transition to the phase described by the same space group R$\bar{3}$c has been found. The phase transition is accompanied by a 9% volume change of the unit cell, a four times decrease of the magnetic moment on Fe, an increase of the charge density at Fe, and a disappearance of the energy gap in the electronic density of states.

PACS. 75.50.Ee Antiferromagnetics – 71.15.Nc Total energy and cohesive energy calculations – 75.20.Hr Local moment in compounds and alloys; Kondo effect, valence fluctuations, heavy fermions

Iron borate is an antiferromagnet with weak ferromagnetism and with a Néel temperature of $T = 348$ K. It exists in a rhombohedral phase with the space group R$\bar{3}$c (D$^6_{3d}$) ($Z = 2$). The lattice parameters are $a_r = 5.520$ Å and $\alpha = 49.54°$ [1–4]. The magnetic moments of both Fe atoms reside in the basal symmetry plane (perpendicular to the three-fold symmetry axis), and are almost antiparallel to each other, with a small canting angle of about 1°. The FeBO$_3$ shows the magneto-optic effect [5,4]. At ambient pressure no structural phase transition has been reported. Recently, the nuclear forward scattering measurements [6] show that the hyperfine magnetic field on ^{57}Fe nuclei in ^{57}FeBO$_3$ exhibits, in the process of increasing pressure, an abrupt decrease in the vicinity of 46 GPa and $T = 294$ K, indicating the existence of a phase transition. Moreover, at the same point the transparent white-green color of the sample observed at ambient pressure changes to black color and not transparent form [6]. Recently, the isostructural phase transition [7] with reduction of 8.6% of the unit cell volume, and at 53 ± 2 GPa was found by the X-ray diffraction technique. In this note we report the *ab initio* calculation of the structure, the magnetic moments and the local charge density of the FeBO$_3$ under pressure.

The *ab initio* calculations of FeBO$_3$ were performed within density functional theory, using the ultrasoft pseudopotential method [8] with the generalized gradient approximation (GGA) implemented in the VASP package [9,10]. Vanderbilt-type ultrasoft pseudopotentials, provided with the package, were used for the Fe, B and O atoms. These pseudopotentials represent $3d^74s^1$, $2s^22p^1$ and $2s^22p^4$ valence electron configurations, respectively. We have used the primitive rhombohedral supercells containing 10 atoms. The Brillouin zone integration was confined to 4 symmetry independent special points. Tests with 65 wave vectors showed very little changes of the total energy (of order of 0.03 eV) per unit cell, and only 5% of changes of the magnetic moment.

The calculations of the $1 \times 1 \times 1$ supercell, and within R$\bar{3}$c space group symmetry have been carried out using the following procedure. First, the ground state energy of the supercell was minimized at zero pressure $P = 0$. We found the antiferromagnetic (AFM) state. Next the pressure was gradually increased, and the optimization was repeated. For each next run we used the equilibrium atomic configuration obtained in the previous run. In this way we could preserve the AFM phase till the pressure of $P_{\mathrm{AFM}} = 57.5$ GPa. At higher pressure the system spontaneously transformed to the low magnetic (LM) state with the same R$\bar{3}$c space group and structure but with different lattice parameters. The LM supercell was than optimized at pressure of $P = 80$ GPa. The subsequent runs were carried out releasing the pressure. Below $P_{\mathrm{LM}} = 10$ GPa the LM phase could not be kept metastable anymore, because the supercell transformed spontaneously to the AFM state.

The possibility of phase transitions to other phases were also checked. For that we calculated the phonon dispersion relations at $P = 0, 40$ GPa for AFM and $P = 60$ GPa for LM phases. We found that the frequencies of all modes increase with pressure. Therefore, there is no candidate for a soft mode which could lead to another phase transition.

The results of the pressure-up and pressure-down runs are shown in Figure 1. Figure 1a represents the enthalpies $E = E_{in} + PV$, which at $T = 0$ are equal to the Gibbs free energy. We draw $\Delta E = E_{in}(P) - E_{in}(P = 0) + PV(P) - PV(P = 0)$, where $E_{in}(P = 0) = -75.3608$ eV and $V(P = 0) = 91.65\,\text{Å}^3$ are the internal energy and unit cell volume of the AFM supercell at $P = 0$, respectively.

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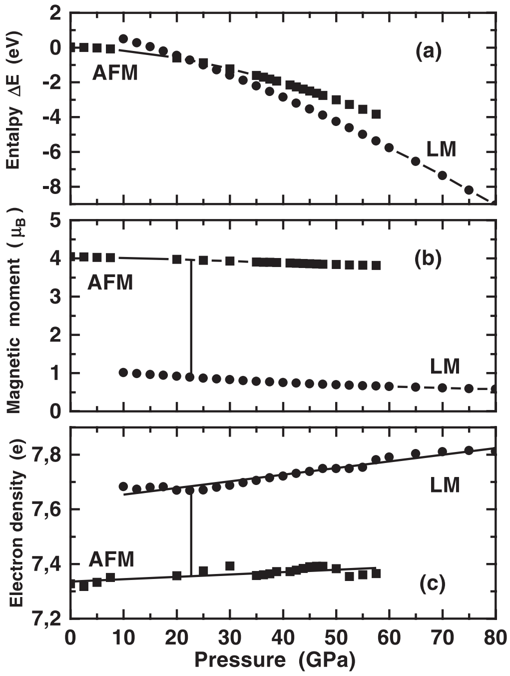

Fig. 1. Enthalpy, magnetic moment on Fe ions and local electron density on Fe ions as a function of pressure for AFM and LM phases of $FeBO_3$.

This representation of data allows us to show the details of the pressure dependence in one figure. The enthalpies of the AFM and LM states cross at the coexistence pressure $P_c = 22.7$ GPa. This is the first order phase transition point. The AFM and LM states could be easy over- and under-pressured, respectively, and in these regions these phases are metastable.

Figure 1b shows the amplitude of the magnetic moment located on the Fe ions. It was estimated as a difference of the local electron densities of spin-up and spin-down integrated over spheres with radii of 1.44, 1.20 and 1.20 Å (at $P = 20$ GPa) for Fe, B and O atoms, respectively. Total volume of spheres of these radii is equal to the unit cell volume. When the pressure changed the unit cell volume, the radii were modified accordingly. The barium and oxygens carry zero magnetic moments. The Fe magnetic moment diminishes more then four times going from AFM to LM state. We found, that the LM phase remains still antiferromagnetic, but with rather small magnetic moment. The changes of the magnetic moment are correlated with the change of the local charge density around Fe ions, Figure 1c. The local charges have been calculated in the same way as the magnetic moments. The charge density gives only an estimate of the number of electrons above the number of core electrons. The elevation of charge density by about 0.4 electron going from AFM to LM state can be roughly attributed to the homogeneous change of the valency of iron from Fe^{3+} to Fe^{2+}. To conserve the unit cell charge, the local charge densities of B and O ions decreased by −0.12 and −0.09 electrons, when going from AFM to LM states.

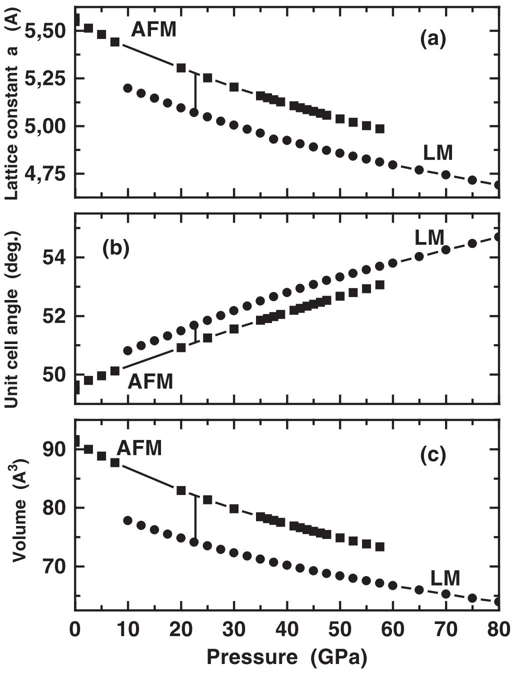

Fig. 2. Lattice constant a, lattice angle α and unit cell volume of rhombohedral $R\bar{3}c$ AFM and LM phases of $FeBO_3$ as a function of pressure.

The lattice constant a and the lattice angle α of the rhombohedral unit cell are different in the AFM and LM phases, Figures 2a and 2b, respectively. The phase transition involves discontinuities of a and α. Figure 2c shows that the unit cell volume of the AFM phase is larger then that of the LM phase. The volume change of 9% is exceptionally large. This difference can be compared with the 8.6% found by X-ray diffraction [7].

At the pressure of 30 GPa the electronic density of states for the AFM and LM phases have been calculated. The AFM phase shows an energy gap, while the LM phase is clearly metallic. Hence, the phase transition involves also the insulator-metal transition.

In reference [11] we have shown that the AFM and the non-magnetic states provide quite different phonon spectra. Using these data we have estimated the difference in free energy of the AFM and the LM phases at $T = 0$ and $T = 300$ K. The phonon free energy of the LM phase is 0.13 eV, and 0.18 eV higher then that of the AFM phase, at $T = 0$ and $T = 300$ K, respectively. The correction of 0.13 eV originates from the harmonic zero-motion. These quantities together with the enthalpies of Figure 1 tell us that the phase transition pressure 22.7 GPa will be shifted to higher pressures of 26 and 27.5 GPa at $T = 0$ and $T = 300$ K, respectively, if the phonon contributions will be taken into account.

Concluding we found the phase transition in $FeBO_3$ crystal, observed under high pressure. The space group $R\bar{3}c$ does not change across the transition point. It is a first order phase transition accompanied by a large change of the unit cell volume, and by a change of the magnetic moment of the antiferromagnetic structures. Simultaneously the metal-insulator phase transition occurs.

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