Pis'ma v ZhETF, vol. 75, iss. 1, pp. 25 – 27

# Equation of state and structural phase transition in $FeBO_3$ at high pressure

*A. G. Gavriliuk, I. A. Trojan, R. Boehler$^+$, M. Eremets$^+$, A. Zerr$^*$, I. S. Lyubutin$^{\square 1)}$, V. A. Sarkisyan$^\square$*

*Institute for High Pressure Physics RAS, 142190 Troitsk, Moscow reg., Russia*

$^+$*Max-Planck Institut fuer Chemie, 55020 Mainz, Germany*

$^*$*Technische Universität Darmstadt, FB Material- und Geowissenschaften, FG Disperse Feststoffe, 64287 Darmstadt, Germany*

$^\square$*A. V. Shubnikov Institute of Crystallography RAS, 117333 Moscow, Russia*

Submitted 23 November 2001

Evolution of X-ray diffraction patterns in $FeBO_3$ under high pressures up to 63 GPa has been investigated at room temperature in a diamond anvil cell. A structural phase transition at pressure of $53 \pm 2$ GPa was found for the first time. The transition is of the first- order type with the hysteresisless drop of the reduced unit cell volume of about 8.6%. Apparently, the transition is isostructural. At pressures below the transition, the equation of state for $FeBO_3$ was fitted. In approximation of the third order Birch-Murnagan equation of state, the bulk modulus $K$ and its first pressure derivative $K'$ were found to be $255 \pm 25$ GPa and $5.0 \pm 1.2$, respectively.

PACS: 61.50.Ks, 64.60.–i, 64.70.Kb

At ambient conditions, the crystal lattice of iron borate $FeBO_3$ has the rhombohedral symmetry with space group $R\bar{3}c\,(D^6_{3d})$ and with lattice parameters $a = 4.612$ Å, $c = 14.47$ Å [1, 2]. Iron ions $Fe^{3+}$ are in an octahedral oxygen surrounding, and interionic distances are $(\mathrm{Fe-O}) = 2.028$ Å and $(\mathrm{Fe-Fe}) = 3.601$ Å, while the angles of the bonds $(\mathrm{O-Fe-O})$ are 91.82° and 88.18° [2]. $FeBO_3$ is an antiferromagnet with week ferromagnetism and with Neel temperature of about 348 K [3]. This material has very interesting electronic, magnetic and magneto-optical properties. Recently the transition from magnetic to non-magnetic state has been discovered at pressures of about 46 GPa in the $FeBO_3$ single crystal [4]. Nature and a mechanism of this transition are not known yet. It is interesting to know whether this transition is accompanied with a structural transition, and it is important to investigate how changes of interionic distances and a crystal structure under pressure influence the electronic and magnetic properties in this compound.

In the present paper we have investigated in details the room temperature X-ray diffraction (XRD) spectra in $FeBO_3$ at high pressures up to $P = 63$ GPa using a diamond anvil cell (DAC). The powder sample was obtained by grinding the $FeBO_3$ single crystal. The diameter of culets of diamond anvils was about 300 $\mu$m. The diameter of the gasket hole was about 100 $\mu$m. At different scans of pressure, tungsten or rhenium was used as a gasket material. As a pressure medium we used silicon organic liquid, which is quite appropriate for maintenance of quasi-hydrostatic conditions. The gasket hole was filled up with the sample powder to about one third to be sure that all powder grains were surrounded by pressure liquid. The shift of ruby fluorescence was used to determine pressure. To estimate the pressure distribution along the sample, several ruby chips were placed inside the hole at different distances from the center of the hole. It was found that the pressure gradient at the sample was not more than 4–5 GPa at maximal pressures. DAC, applied in this work, allowed to collect X-ray data in the angle range of about 30 degrees of $2\Theta$. X-ray patterns were recorded in the transmission geometry on image plate and then were treated with a standard procedure. As an X-ray source we used a rotating Mo anode equipped with the specially designed focusing X-ray optics.

Fig.1 shows changes in XRD patterns of $FeBO_3$ with higher pressure. It can be seen that new peaks appear at about 52 GPa indicating an onset of phase transition to a new crystal structure. Both initial and new crystal structures coexist in the pressure range 52–55 GPa, apparently, due to a pressure gradient. In the measured range of diffraction angles $2\Theta$, we have found that the high-pressure phase at $P > 55$ GPa has the similar set of X-ray peaks as the low-pressure phase at $P < 52$ GPa (Figs.1a and 1b). Fig.2 shows the experi-

---

[1] e-mail: lyubutin@ns.crys.ras.ru

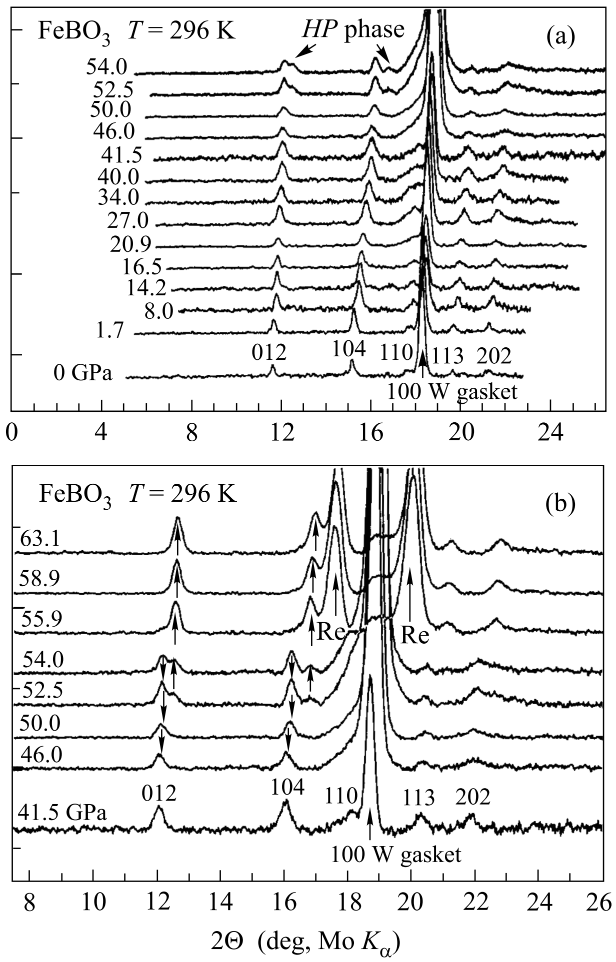

Fig.1. Evolution of the XRD-pattern of $FeBO_3$ at high pressures: (a) below phase transition, (b) in the region of the phase transition and at higher pressures. The peaks of W and Re gaskets are also seen

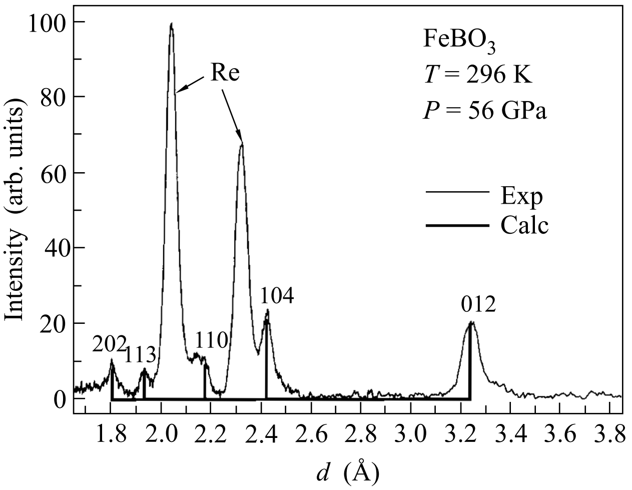

Fig.2. X-ray pattern of the high-pressure phase of $FeBO_3$ at $P = 56$ GPa. Solid line is an experimental pattern, bars are a theoretical calculation of interplanar $d_{hkl}$-spaces in a hexagonal representation for $R\bar{3}c$ space group with the lattice parameters $a = 4.3539$ Å and $c = 12.6642$ Å. The other peaks fit well to reflexes of the compressed Re gasket

Table 1

**Interplanar distances, peak intensities and the corresponding Miller-indices of the high-pressure phase of $FeBO_3$ at $P = 56$ GPa calculated in an approximation of the space group $R\bar{3}c$ with the unit cell parameters $a = 4.3539$ Å and $c = 12.66422$ Å. (Mo-radiation, $T = 296$ K)**

| $h\ k\ l$ | Intensity | $d_{\rm exp}$ (Å) | $d_{\rm calc}$ (Å) | $d_{\rm calc} - d_{\rm exp}$ (Å) |
|---|---|---|---|---|
| 1 0 2 | 90 | 3.24420 | 3.23971 | −0.00449 |
| 1 0 4 | 100 | 2.42443 | 2.42466 | +0.00023 |
| 1 1 0 | 30 | 2.17300 | 2.17695 | +0.00395 |
| 1 1 3 | 20 | 1.93562 | 1.93483 | −0.00079 |
| 2 0 2 | 20 | 1.80583 | 1.80691 | +0.00108 |

mental XRD-pattern obtained at 56 GPa and positions of the calculated reflexes for the structure of space group $R\bar{3}c$. The calculated data fit well the experimental peaks when the lattice parameters $a$ and $c$ are 4.3539 Å and 12.6642 Å, respectively. Five reflexes of the new high-pressure phase fit very well to the same symmetry as the low-pressure phase. The interplanar distances and the peak intensities of XRD-pattern of $FeBO_3$ recorded at 56 GPa are given in Table 1. Though, the measured range of angles 2Θ is not enough to make a final conclusion, it is more likely that the transition is isostructural. Recently, Parlinski [5] have calculated a possible change of the crystal structure in $FeBO_3$ using the density functional theory and found that the phase transition to the same space group $R\bar{3}c$ should exist at certain pressure.

At this assumption we have calculated the unit cell volume and the $V(P)$ dependence for the high pressure phase of $FeBO_3$. Figs.3a and 3b show the pressure dependence of the unit cell parameters $a$ and $c$ and the reduced unit cell volume $V/V_0$. It is obvious that the observed structural transition is the first order one, and the drop of $V/V_0$ value is about 8.6%. To determine possible hysteresis of the transition, we also measured the XRD-patterns at the pressure release regime. It was found that the hysteresis is in the limit of pressure distribution along the sample due to non-hydrostatisity.

At pressures below the transition, four types of equations of state (the 2-nd power polynom, Murnagan, Birch-Murnagan, and Vinet) were fitted to the experimental dependence $V(P)$. The results of calculations are given in Table 2. It seems that the fit of the Birch-Murnagan equation of state with the bulk modulus $K = 255 \pm 25$ GPa and its first pressure derivative $K' = 5.0 \pm 1.2$, gives the most reliable result. The value of bulk modulus is close to that estimated for an oxygen octahedron surrounding iron ion in other iron oxides

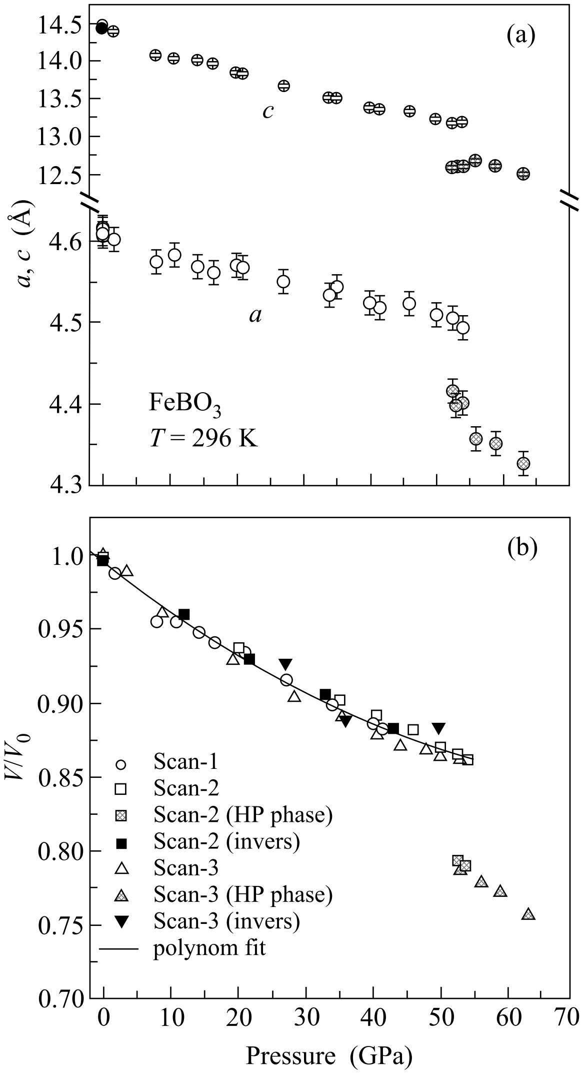

Fig.3. The experimental pressure dependence of the unit cell parameters $a$ and $c$ and the reduced unit cell volume $V/V_0$ of $FeBO_3$ measured at room temperature in DAC. Pressure medium is poly-ethyl-silicon. At pressures above the phase transition $P > 52.5$ GPa, the $V(P)$-relation was calculated assuming that the crystal structure of the high-pressure phase has the same symmetry as the low-pressure one

(≈ 280 GPa) [6, 7]. It correlates with possible freedoms of change of crystal structure in $FeBO_3$. Under pressure, only compression of oxygen octahedron is possible in $FeBO_3$. The same is valid for $\alpha$-$Fe_2O_3$, in contrast, for example, to the rare-earth orthoferrites $RFeO_3$ where, besides compression, there is a freedom of rotation of oxygen octahedrons.

A special attention should be paid to the problem of different values of pressure for the structural transition found in the present work at $53 \pm 2$ GPa and the magnetic transition found at $46 \pm 2$ GPa in Ref.[4]. The powder sample (a grained single crystal) was used in the present studies, while the single crystal specimen of $FeBO_3$ enriched with Fe-57 isotope was used in the magnetic measurements [4]. It is important to verify whether the pressure difference of the structural and magnetic transitions is a sample effect or it is a physical effect. Now we are caring out the Mössbauer spectroscopy experiments with powder sample with the aim to clarify this problem.

Table 2

**The bulk modules $K$ and its first pressure derivative $K'$ calculated from different types of EOS fitted to experimental $V(P)$ of $FeBO_3$ measured at $T = 296$ K**

| Equation of state | $K$ (GPa) | $K'$ |
|---|---|---|
| 2-nd power polynom | $273 \pm 4$ | 4.0 (fixed) |
| Murnagan | $254 \pm 23$ | $4.6 \pm 1.0$ |
| Birch-Murnagan | $255 \pm 25$ | $5.0 \pm 1.2$ |
| Vinet | $250 \pm 25$ | $5.2 \pm 1.2$ |

In summary, the XRD spectra and $V(P)$ dependence for $FeBO_3$ were measured at room temperature at pressures up to 63 GPa. The bulk modules calculated using the Birch-Murnagan equation of state is $255 \pm 25$ GPa, and its first pressure derivative $K'$ is $5.0 \pm 1.2$. At pressure of $53 \pm 2$ GPa we observed the first order phase transition (apparently of the isostructural type) with the unit cell volume decrease of about 8.6%. The isostructural character of the transition is in an agreement with the density functional theory calculations [5]. The pressure value of the structural transition differs from that of the transition from magnetic to non-magnetic state, found recently in $FeBO_3$ [4].

We are grateful to Professor R.Rüffer for useful discussions. This work was partially supported by NATO grant #PST.CLG.976560 and by Russian Foundation for Basic Research grants #00-02-17710-a, #01-02-17543-a and #02-02-17364-a. This study was also partly supported by grants CRDF-11209 and INTAS-710.

1. Database PDF-II, record 21-0423; I. Bernal, C. W. Struck, and J. G. White, Acta Cryst. **16**, 849 (1963).
2. R. Diehl, Solid State Comm. **17**, 743 (1975).
3. R. Wolff, A. J. Kurtzig, and R. C. LeCraw, J. Appl. Phys. **41**, 1218 (1970).
4. I. A. Trojan, A. G. Gavriliuk, V. A. Sarkisyan et al., JETP Lett. **74**, 24 (2001).
5. K. Parlinski, submitted for publication in Europ. Phys. J. **B**.
6. R. M. Hazen and L. W. Finder, *Comparative Crystal Chemistry*, Wiley, New York, 1982.
7. A. G. Gavriliuk, G. N. Stepanov, I. S. Lyubutin et al., JETP **90**, 330 (2000).