Anomalous thermal expansion of iron borate crystals FeBO$_3$ near the Néel point

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Abstract. Study of the anomalous behavior of the linear thermal expansion coefficient near the antiferromagnetic phase transitions in iron borate crystals FeBO$_3$ are reported. The lattice parameters and volume of FeBO$_3$ have been measured in the temperature range 25–300°C by the X-ray diffraction method. The thermal expansion is evidently sharply anisotropic and spike near the Néel temperature.

1.Introduction
Iron borate, FeBO$_3$, represents a rare example of a magnetically ordered ferric oxide with a high transparency in the visible spectral region and with a Faraday rotation reaching 5000°/cm. From the magnetic point of view, FeBO$_3$ is a two-sublattice easy-plane antiferromagnetic with a weak in-plane moment and the Néel temperature $T_N = 348$ K [1]. The practical applications of the iron borate FeBO$_3$ requires knowledge of the particularities of thermal behavior.

In [1] for the first time was estimated the difference between the thermal expansions of FeBO$_3$ along the z and x axes to be determined from optical data. Previously, we have investigated anisotropy of the thermal expansion of FeBO$_3$ for temperatures 25, 400, 500 и 600 °С [2]. However, correct evaluations of the thermal expansion coefficients could be done in the temperature range from 400 to 600°C since below Néel point $T_N = 75$°C, FeBO$_3$ is an easy-plane weak antiferromagnetic with the anomalous behavior of physical properties near the region of phase transition into paramagnetic. Accordingly, it was study the characteristics of the thermal expansion of iron borate in the region of the Néel temperature, which was the aim of this study.

2.Object and method of research
The crystalline structure of iron borate, FeBO$_3$, grown by the vapor transport crystallization method, was first determined in work [3] and refined in [4]. Iron borate, FeBO$_3$, has rhombohedral calcite-type structure with point group symmetry 3m ($D_{3d}$) and space group $R3C$ ($D_{6d}$). The space group has an R-type Bravais lattice; thus, the unit cell parameters can be specified in both hexagonal and
rhombohedral settings. The structural rhombohedral parameters: $a_r = 5.52\, \text{Å}$, $\alpha_r = 49.54^\circ$, $V_r = 89.532\, \text{Å}^3$. The structural hexagonal parameters: $a_h = 4.626(1)\, \text{Å}$, $c_h = 14.496(6)\, \text{Å}$, $V_h = 268.596\, \text{Å}^3$. The rhombohedral and hexagonal FeBO$_3$ unit cells contain two and six formula units, respectively. The boron atoms are located in the center of plane of equilateral oxygen triangles, the oxygen atoms surround each iron atom forming a slightly distorted [FeO$_6$] octahedron, figure 1. The mean distances are $1.379\, \text{Å}$, for the B-O bonds and $2.028\, \text{Å}$, for the Fe-O bonds.

![Figure 1](image1.png)

**Figure 1.** The overview and top view of the rhombohedral unit cell of the FeBO$_3$.

For structural studies, samples of iron borate, FeBO$_3$, were ground into powder by standard technology. X-ray powder diffraction measurements of iron borate was executed at the Center of collective use of Institute of Metal Physics of the Ural Branch of the Russian Academy of Sciences. The in-situ powder X-ray diffraction was carried out with a Shimadzu XRD-7000 Maxima diffractometer (Cu (Kα) radiation, graphite monochromator with a thermal attachment (Anton Paar) in the temperature range 18–300°C under pressure of 10 Pa. SiO$_2$ were used as an external standard. The heating rate is 5 K / min, the exposure time before shooting at each point is 15 min. The temperature stability during the measurements was ±4°C. The diffraction angle $2\theta$ was varied from 22-85° range with step recording was 0.02°.

3. Analysis and discussion

The lattice parameters determined at different temperatures are given in Table 1. It can be seen that both the parameters $a$ and $c$ increase with temperature. The room temperature lattice constants obtained in the present study are compared with those available in the literature.
Table 1. Temperature dependence of hexagonal lattice constants «a», «c» and volume «V» of hexagonal cell of FeBO₃.

| t, °C | a, Å     | c, Å     | V, Å³    |
|-------|----------|----------|----------|
| 18    | 4.6285±0.0005 | 14.488±0.0012 | 268,79±0.03 |
| 68    | 4.6298±0.0005 | 14.499±0.0012 | 269,16±0.03 |
| 73    | 4.6295±0.0004 | 14.501±0.0012 | 269,145±0.03 |
| 77    | 4.6303±0.0005 | 14.502±0.0012 | 269,26±0.03 |
| 80    | 4.6292±0.0005 | 14.501±0.0012 | 269,11±0.03 |
| 200   | 4.6311±0.0003 | 14.5197±0.0011 | 269,69±0.03 |
| 300   | 4.6317±0.0003 | 14.5380±0.0014 | 270,01±0.03 |

The temperature range from 18 to 300°C includes the antiferromagnetic transition temperature Tₜₙ= 75°C, at which point our measurements show a kink in the temperature dependence curves of the cell parameters, figure 2.

The variation curves of parameters «a» and «c» in two ranges: from 18°C to 80°C and from 80°C to 300°C were approximated to the straight lines:

\[ a(t) = a₀ + a₁ \cdot t \quad (1) \]

were \( a₀ \) - lattice constant at room temperature;

\( a₁ \) - characteristic constants;

\( t \) - temperature in °C.

The values of characteristic constants determined by least-squares method are shown in table 2.

Table 2. Characteristic constants of the dependence of the hexagonal lattice constants «a», «c» and volume «V» of FeBO₃ on temperature.

| t, °C | Parameter | \( a₀ \) | \( a₁ \) |
|-------|-----------|----------|----------|
|       | a, Å      | 4.628    | 2.56·10⁻⁵ |
| 18 - 80| c, Å      | 14.484   | 2.35·10⁻⁴ |
|       | V, Å³     | 268,663  | 7.336·10⁻³ |
|       | a, Å      | 4.629    | 9.924·10⁻⁶ |
Figure 2. FeBO$_3$ hexagonal cell parameters between 18 and 300 °C.

With respect to the definition of the coefficient of the thermal expansion, [5]:

$$\alpha = \frac{1}{a_0} \frac{da}{dt} \quad (2)$$

were $da$ – difference of lattice parameters $a$ for the interval $dt$,

$dt$ - difference of temperature,

we obtain from (1) the thermal expansion coefficient, table 3.

| t, °C  | $\alpha_a$, $10^{-6}$ °C$^{-1}$ | $\alpha_c$, $10^{-6}$ °C$^{-1}$ | $\alpha_v$, $10^{-6}$ °C$^{-1}$ |
|-------|-------------------------------|-------------------------------|-------------------------------|
| 18 - 80 | 5,5                           | 16,2                          | 27,3                          |
| 80 - 300 | 2,1                           | 10,4                          | 14,7                          |
The three-dimensional thermal expansion diagrams of FeBO$_3$ drawing according to [6] is shown in figure 3.

![Diagram](image)

**Figure 3.** Indicatory surface of thermal expansion of FeBO$_3$: (a) from 18°C to 80°C; (b) from 80°C to 300°C.

The thermal expansion is evidently sharply anisotropic at room temperature ($\alpha_{\text{max}}/\alpha_{\text{min}} = 2.9$) and the anisotropy increases to $\alpha_{\text{max}}/\alpha_{\text{min}} = 4.8$ while heating above $T_N$.

A calculation of the thermal expansion coefficients along the «a» and «c» axes of FeBO$_3$ gave the following results, figure 4.

![Graph](image)

**Figure 4.** The thermal expansion coefficient of FeBO$_3$. 
4. Conclusion

It was found that near the Néel temperature of the phase transition of a magnetic-paramagnetic is accompanied by a sharp jump in the coefficients of thermal expansion along the «a» axis is \( \Delta \alpha_a = 3.39 \times 10^{-6} \, ^\circ C^{-1} \) and along the «c» axis is \( \Delta \alpha_c = 5.78 \times 10^{-6} \, ^\circ C^{-1} \) as shown in Figure 4. In fact, there are exchange striction along the z(«c») and x(«a») axes as the difference between of the regular contribution and of the contribution associated with the magnetic order to the thermal expansion. The value of exchange striction along the z, which was evaluated of \( \approx 0.53 \times 10^{-3} \) at \( T_N = 348 \, K \) in [1] are in good agreement with our results \( \approx 0.41 \times 10^{-3} \).

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