

## Analysis of the electronic polarizability of ions in weak ferromagnetic FeBO<sub>3</sub> crystals

*M.B.Strugatskii, A.A.Yatsenko, A.V.Yatsenko*

Taurida National University, 4 Vernadsky Ave.,  
95007 Simferopol, Ukraine

Basing on the analysis of the FeBO<sub>3</sub> crystal refractive indices, the electron dipole polarizability (DEP) in the crystal structure has been calculated and the effective ion charges have been estimated. Within the frame of the model used, the ferric borate ionic formula Fe<sup>+2.5</sup>B<sup>+2.4</sup>O<sub>3</sub><sup>-1.63</sup> has been established to be the most preferable. The following cation DEP values answer to that formula:  $\alpha_{Fe} \approx 0.30 \cdot 10^{-24}$  cm<sup>3</sup>,  $\alpha_B \approx 0.45 \cdot 10^{-24}$  cm<sup>3</sup>. The DEP of oxygen anions has been shown to be anisotropic, the main components of oxygen DEP tensor being  $\alpha_{11} \approx 1.81 \cdot 10^{-24}$  cm<sup>3</sup> and  $\alpha_{33} \approx 1.43 \cdot 10^{-24}$  cm<sup>3</sup>.

На основе анализа показателей преломления кристаллов FeBO<sub>3</sub> проведено вычисление дипольной электронной поляризуемости (ДЭП) ионов в структуре этого кристалла и выполнена оценка их эффективных зарядов. Установлено, что в рамках использованной модели наиболее обоснованной является следующая ионная формула бората железа: Fe<sup>+2.5</sup>B<sup>+2.4</sup>O<sub>3</sub><sup>-1.63</sup>. Этой формуле отвечают следующие значения ДЭП катионов:  $\alpha_{Fe} \approx 0.30 \cdot 10^{-24}$  см<sup>3</sup>,  $\alpha_B \approx 0.45 \cdot 10^{-24}$  см<sup>3</sup>. Показано, что ДЭП ионов кислорода анизотропна и установлены главные компоненты тензора ДЭП:  $\alpha_{11} \approx 1.81 \cdot 10^{-24}$  см<sup>3</sup> и  $\alpha_{33} \approx 1.43 \cdot 10^{-24}$  см<sup>3</sup>.

Weak ferromagnetic FeBO<sub>3</sub> crystal is a promising material for practical applications in various magneto-optical and magneto-acoustical devices [1]. The magnetic and acoustical properties of this material are widely studied due to its practical importance. Computer simulations of ionic or partially ionic systems are widely used now in solid state physics [2], but no attempts to investigate the peculiarities of FeBO<sub>3</sub> physical properties and crystal structure by this method were done. In computer simulations, empirical, semi-empirical or *ab initio* methods are used to analyze the intracrystal interactions. The commercially available computer program packages for the analysis of single crystal properties (GAUSSIAN, CRYSTAL, GAMESS, etc.) are based on the cluster calculation methods, but the application thereof results in some cases in ambiguous results [3]. However, if correct information is available on the so-called "effective" charges of ions  $q_{eff}$ , their electronic polarizability and short-range interaction parameters, the computer simulation using

the empirical approach can be productive enough [4, 5]. So the main aim of this study is to calculate the possible sets of dipole electronic polarizability (DEP) of ions in FeBO<sub>3</sub> structure and the evaluation of their effective charges.

It is well-known that the  $q_{eff}$  and DEP values of the same ion are influenced strongly by its chemical environment and differ significantly for different compounds [6, 7], therefore, the chemical bonds in the compound under investigation are to be considered previously. The length of the shortest (Fe–O) bonds in FeBO<sub>3</sub> structure is comparable to the sum of the of Fe<sup>3+</sup> and O<sup>2-</sup> ionic radii, so that bond is close to pure ionic one. Therefore, the effective charge of Fe ions,  $q_{Fe}$ , must be close to its formal charge  $+3|e|$  where  $|e|$  is the electron charge modulus, and DEP of this ion  $\alpha_{Fe}$  seems to be close to the corresponding value for a free Fe<sup>3+</sup> ion:  $\alpha_{Fe} = 0.248 \cdot 10^{-24}$  cm<sup>3</sup> [8]. The shortest (B<sup>3+</sup>–O<sup>2-</sup>) distance in FeBO<sub>3</sub> crystal is 0.13415 nm [1] and it is known [9] that if this bond length is less than

0.143 nm, the bond must be an ionic-covalent one. It was shown before that partially covalent binding of an  $O^{2-}$  ion results in a significant anisotropy of its DEP [5, 10, 11]. So it is reasonable to believe that the anisotropy of the oxygen ion DEP must be presented in  $FeBO_3$ , too. Proceeding from symmetry considerations, we believe that the principal '3' axis of oxygen ion DEP tensor must be coincide with the shortest (B–O) bond direction and this tensor likely has an axial symmetry, so that  $\alpha_{11} = \alpha_{22} \neq \alpha_{33}$ .

To calculate the possible DEP sets of ions in  $FeBO_3$ , a method was used based on modified Lorenz-Lorentz equation [10]:

$$\frac{n_k^2 - 1}{n_k^2 + 2} = \frac{1}{3\epsilon_0} \sum_{i=1}^S N_i (\alpha_{eff})_{ik}, \quad (1)$$

where  $n_k$  is the experimental refractive indices of the crystal ( $n_o = 2.09$ ;  $n_e = 2.02$  for  $\lambda = 1.06$  nm) at the light wave electric component directed along the  $\mathbf{k}$  direction ( $\mathbf{k} = x, y, z$ );  $S$ , the number of structurally non-equivalent ions in the crystal;  $N_i$ , the volume concentration of the  $i$ -th ion species;  $(\alpha_{eff})_{ik}$ , so-called effective DEP of  $i$ -th ion species [10] influenced by the nearest ( $\leq 10$  nm) dipole surrounding of that ion. If  $\mathbf{E}$  is directed along the  $x$  crystal axis,  $(\alpha_{eff})_{ix}$  is expressed as:

$$\begin{aligned} (\alpha_{eff})_{ix} = & \sum_{l=1}^3 (\alpha_{ll})_i \cdot \cos^2 \theta_{lxi} \cdot \left[ 1 + \sum_{j=1}^S (T_{ijx})_x \right] + \\ & + \sum_{l=1}^3 (\alpha_{ll})_i \cdot \cos \theta_{lxi} \cdot \cos \theta_{lyi} \cdot \sum_{j=1}^S (T_{ijx})_y + \\ & + \sum_{l=1}^3 (\alpha_{ll})_i \cdot \cos \theta_{lxi} \cdot \cos \theta_{lzi} \cdot \sum_{j=1}^S (T_{ijx})_z, \end{aligned} \quad (2)$$

where  $(\alpha_{ll})_i$  are the DEP tensor components of the  $i$ -th ion kind in its own coordinate system;  $\theta_{lfi}$ , the angles between  $l$ -th main axis of DEP tensor and  $f$  direction, where  $f = x, y, z$ . The structure sums  $(T_{ijx})_x$ ,  $(T_{ijx})_y$  and  $(T_{ijx})_z$  are defined as:

$$\begin{aligned} (T_{ijx})_g = & \frac{1}{4\pi\epsilon_0} \left[ \sum_{l=1}^3 \sum_f (\alpha_{ll})_j \cdot \cos \theta_{lxj} \cos \theta_{lfi} \times \right. \\ & \left. \times \sum_{m=1}^{M_j} \frac{3 \cdot G_{ijm} \cdot F_{ijm} - \delta_{gf} \cdot R_{ijm}^2}{R_{ijm}^5} \right], \end{aligned} \quad (3)$$

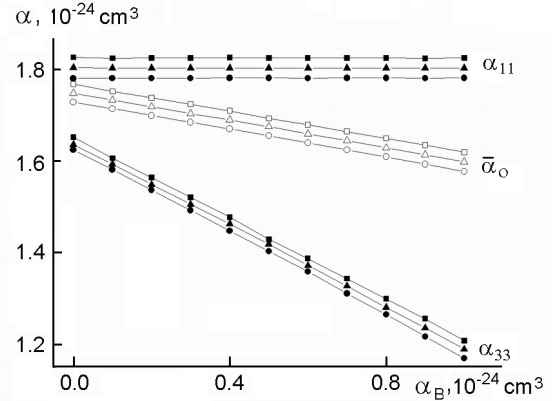


Fig. 1. Dependences of oxygen ion DEP tensor main components on  $\alpha_B$  at  $\alpha_{Fe}$  values ( $\cdot 10^{-24}$  cm<sup>3</sup>): 0.256 (squares), 0.307 (triangles), 0.358 (circles).

where  $g = x, y, z$ ;  $R_{ijm}$  is the distance between the specified ion of  $i$ -th species to the  $m$ -th ion of  $j$ -th species;  $G_{ijm}$  and  $F_{ijm}$  are the projections of  $R_{ijm}$  onto  $g$  and  $f$  directions;  $\delta_{gf}$  is the Kronecker symbol. A similar equation for  $(\alpha_{eff})_{iz}$  can be derived from Eq.(2) by relabelling the ( $x \leftrightarrow z$ ) indices.

The calculations were done under variation of  $\alpha_B$  and  $\alpha_{Fe}$  within reasonable areas of their values. In spite of the fact that DEP of isolated  $B^{3+}$  ion is very small ( $\alpha_B^{3+} \cong 0.03 \cdot 10^{-24}$  cm<sup>3</sup>), the real total charge of boron ion must be smaller than  $+3|e|$  due to the partially covalent character of (B–O) bonds. It is to note that the configuration of the outer electron shells affects strongly the ion polarizability; for example, DEP of  $Li^+$  ion  $\alpha_{Li}^+$  is  $0.032 \cdot 10^{-24}$  cm<sup>3</sup>, but it increases by two orders for non-ionized Li atom [12]. Therefore, the calculations were done under assumption that boron DEP in  $FeBO_3$   $\alpha_B$  lies within the limits of 0.1 to  $1.00 \cdot 10^{-24}$  cm<sup>3</sup>.

The dependences of calculated  $\alpha_{11}$  and  $\alpha_{33}$  principal components of oxygen ion DEP tensor in  $FeBO_3$  crystal on the  $\alpha_B$  value at  $T = 293$  K and three different values of  $\alpha_{Fe}$  are presented in Fig. 1. According to [13], we can introduce into consideration the average polarizability  $\bar{\alpha}$  of oxygen ion  $\bar{\alpha} = 1/3(\alpha_{11} + \alpha_{22} + \alpha_{33})$ ; the corresponding dependences are presented in Fig. 1, too. The fact of decreased oxygen DEP  $\bar{\alpha}$  in  $FeBO_3$  as compared to its value for free  $O^{2-}$  ion ( $\alpha_{O^{2-}} = 2.402 \cdot 10^{-24}$  cm<sup>3</sup>) agrees well with other results obtained for oxygen

DEP in mixed borate oxide ( $\text{BO}_3$ ) glasses [14].

It is possible to believe as a first approximation that DEP of any ion must be proportional to the charge of its outer electron shells deformed by an external electric field [15]. Let the results obtained be considered using this principle. It is assumed that the charge of the outer electron shells (dipole forming charge, DFC) of  $\text{O}^{2-}$  ion is equal to  $-2.848|e|$  [16], thus, the effective charge of oxygen ion  $q_{\text{O}}$  can be expressed as:

$$q_{\text{O}} = -\frac{2.848 \cdot \bar{\alpha}}{\alpha_{\text{O}^{2-}}} + 0.848. \quad (4)$$

Dependences of  $q_{\text{O}}$  on the  $\alpha_{\text{B}}$  value obtained using Eq.(4) for some fixed  $\alpha_{\text{Fe}}$  values are shown in Fig. 2. According to the electroneutrality condition for the crystal unit cell, the effective charges of ions are connected as  $q_{\text{Fe}^+} + q_{\text{B}} + 3 q_{\text{O}} = 0$ , so assuming  $q_{\text{Fe}} = +3|e|$ , it is possible to calculate the same dependences for the effective charge of boron  $q_{\text{B}}$ , which are shown in Fig. 2, too.

A certain contradiction is contained in these results — the discrepancy between  $q_{\text{B}}$  value and DEP of boron ion, which can be partially excluded by assuming that the  $q_{\text{Fe}} = (2.4 \text{ to } 2.6)|e|$ , that is, the (Fe–O) bonds are the mixed ionic-covalent ones. A certain compromise between all the considered conditions can be obtained by introducing the following approximated ionic formula for iron borate:  $\text{Fe}^{+2.5}\text{B}^{+2.4}\text{O}_3^{-1.63}$ . The following values of DEP are consistent with this ionic formula:  $\alpha_{\text{Fe}} \cong 0.30 \cdot 10^{-24} \text{ cm}^3$ ;  $\alpha_{\text{B}} \cong 0.45 \cdot 10^{-24} \text{ cm}^3$ ;  $\alpha_{11} \cong 1.81 \cdot 10^{-24} \text{ cm}^3$ ;  $\alpha_{33} \cong 1.43 \cdot 10^{-24} \text{ cm}^3$ .

Although the values of effective charges and DEP of ions in  $\text{FeBO}_3$  crystal estimated by us are results of the calculations under "first approximation", those can be used for the simplified calculations of local electric fields in this crystal. The electrical parameters of ions can be corrected by taking into account the possible anisotropy of boron ion DEP due to peculiarities of  $\text{BO}_3$  complex electron configuration, or by using one of the above-mentioned program packages

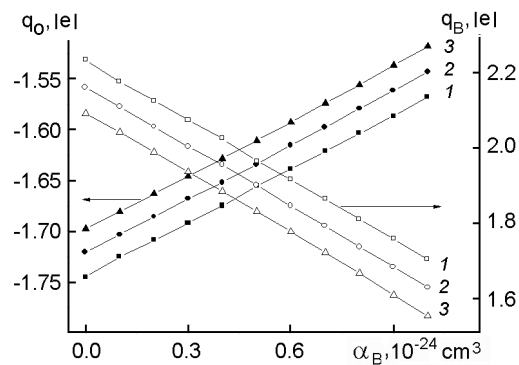


Fig. 2. Dependence of effective charges of oxygen ( $q_{\text{O}}$ ) and boron ( $q_{\text{B}}$ ) on  $\alpha_{\text{B}}$  at  $\alpha_{\text{Fe}}$  values ( $\cdot 10^{-24} \text{ cm}^3$ ): 0.256 (1), 0.307 (2), 0.358 (3).

based on the first-principle methods of calculations.

### References

1. R.Diehl, W.Jantz, B.Nolang, W.Wettling, *Current Topics in Mat. Science*, Elsevier (1984).
2. A.Bosenick, M.T.Dove, C.A.Geiger, *Phys. Chem. Minerals*, **27**, 398 (2000).
3. Th.Gog, P.Schotters, J.Falta et al., *J. Phys.:Condens. Matter.*, **7**, 6971 (1995).
4. S.V.Yevdokimov, A.V.Yatsenko, *Crystallography Reports*, **48**, 594 (2003).
5. A.V.Yatsenko, *Crystallography Reports*, **50**, 1047 (2005).
6. P.W.Fowler, P.A.Madden, *J. Phys. Chem.*, **89**, 2581 (1985).
7. R.Kirsch, A.Gerard, M.Wautelet, *J. Phys. C.:Solid State Phys.*, **7**, 3633 (1974).
8. P.W.Fowler, A.J.Sadlej, *Phys. Rev. B.*, **43**, 6386 (1991).
9. A.Takada, C.R.A.Catlow, G.D.Price, C.L.Hayward, *Phys. Chem. Minerals*, **24**, 423 (1997).
10. A.V.Yatsenko, *Physica B*, **305**, 287 (2001).
11. A.A.Yatsenko, A.V.Yatsenko, *Functional Materials*, **11**, 586 (2004).
12. C.Pouchan, D.M.Bishop, *Phys. Rev. A*, **29**, 1 (1984).
13. S.Canuto, M.Castro, P.Mukherjee, *Phys. Rev. A*, **49**, 3515 (1994).
14. J.Qi, D.Xue, H.Ratajczak, G.Ning, *Physica B*, **349**, 265 (2004).
15. H.Chaib, T.Otto, L.M.Eng, *Phys. Rev. B*, **67**, 174109 (2003).
16. N.H.de Leeuw, S.C.Parker, C.R.A.Catlow, *Phys. Chem. Minerals*, **27**, 332 (2000).

## **Аналіз електронної поляризованості іонів в слабкому ферромагнетикі $\text{FeVO}_3$**

***М.Б.Стругацький, А.А.Яценко, А.В.Яценко***

На підставі аналізу показників заломлення кристалів  $\text{FeVO}_3$  проведено обчислення дипольної електронної поляризованості (ДЕП) іонів у структурі цього кристала та зроблено оцінку їх ефективних зарядів. Встановлено, що у рамках моделі, яка була використана, найбільш обґрунтованою є наступна іонна формула борату заліза:  $\text{Fe}^{+2.5}\text{V}^{+2.4}\text{O}_3^{-1.63}$ . Цій формулі відповідає таке значення катіонів:  $\alpha_{\text{Fe}} \approx 0.30 \cdot 10^{-24} \text{ см}^3$ ,  $\alpha_{\text{V}} \approx 0.45 \cdot 10^{-24} \text{ см}^3$ . Показано, що ДЕП іонів кисню анізотропна та встановлено головні компоненти тензору ДЕП:  $\alpha_{11} \approx 1.81 \cdot 10^{-24} \text{ см}^3$  та  $\alpha_{33} \approx 1.43 \cdot 10^{-24} \text{ см}^3$ .