

Effect of a Rare-Earth Ion on the Structural Instability in $R\text{Fe}_3(\text{BO}_3)_4$ Crystals

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The dynamics of the crystal lattice of $R\text{Fe}_3(\text{BO}_3)_4$ ($R = \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}, \text{and Ho}$) compounds in the high-symmetry $R32$ phase has been calculated. Significant changes in spectra of compounds with various rare-earth ions have been obtained only near the edge Λ point of the Brillouin zone ($\mathbf{q}_\Lambda = 1/3(-2\mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3)$, where \mathbf{b}_1 , \mathbf{b}_2 , and \mathbf{b}_3 are the reciprocal lattice vectors) for acoustic oscillation branches. A decrease in the frequency of an acoustic mode at the point Λ has been revealed in all studied compounds. This frequency depends on the type of rare-earth ion and decreases from a compound with Pr to a compound with Ho down to imaginary values. Such a behavior of the frequency of the unstable acoustic mode is in good agreement with experimental data on the dependence of the temperature of the $R32 \rightarrow P3_121$ structural phase transition on the type of rare-earth ion in ferroborates.

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Compounds $R\text{Fe}_3(\text{BO}_3)_4$ (R is a rare-earth element) with huntite structure attract attention in view of the diversity of their magnetic properties because of the presence of two magnetic subsystems—rare-earth and iron [1–4]. The magnetic structure in crystals of this family demonstrating various features depending on the type of rare-earth ion was studied in numerous works. Recent interest is also stimulated by the discovery of a magneto-electric effect in these compounds and appearance of electric polarization at magnetic ordering and/or at the application of an external magnetic field [5, 6].

Crystals $R\text{Fe}_3(\text{BO}_3)_4$ with $R = \text{Eu–Er}$ and Y undergo a temperature-induced unusual structural phase transition from a phase with the space symmetry group $R32$ to a phase with the space group $P3_121$ [7, 8]. The peculiarity of this phase transition is that the point symmetry (group $D3$) of the crystal does not change in this transition, only the translational symmetry changes, and the volume of the cell is tripled. Depending on the rare-earth ion, the transition temperature varies in a very wide range from 88 to 450 K [7]. The structural transition is not experimentally observed in crystals with $R = \text{La–Sm}$. It is noteworthy that the phase transition is accompanied by change in the point symmetry of the local environment of the rare-earth ion: point group $D3$ in phase $R32$ changes to point group $C2$ in phase $P3_121$. Thus, at low temperatures, the crystal electric field acting on the rare-earth ion in ferroborate compounds in which the high-sym-

metry phase $R32$ holds will be significantly different from that in compounds that undergo a structural transition to the phase $P3_121$. This fact can apparently affect the difference in the magnetic, magnetoelastic, and magnetoelectric properties of compounds having groups $R32$ and $P3_121$ at low temperatures.

An anomaly of the temperature behavior of the specific heat in $R\text{Fe}_3(\text{BO}_3)_4$ crystals that corresponds to the structural phase transition was observed in [7]. The dynamics of the crystal lattice of the $\text{GdFe}_3(\text{BO}_3)_4$ compound was studied in [8] by Raman spectroscopy. Below the temperature of the structural phase transition, a soft mode was recovered from low frequencies to frequencies of 50–60 cm^{-1} (6–8 meV). Similar results on Raman spectra were obtained in [9] for other crystals of this family that undergo the $R32 \rightarrow P3_121$ phase transition. Changes in infrared spectra at the phase transition were detected in [10].

In our previous work [11], the phonon spectrum of the $\text{HoFe}_3(\text{BO}_3)_4$ crystal in a high-temperature phase with the space symmetry group $R32$ was calculated within a nonempirical model of polarizable ions. Near the edge point Λ ($\mathbf{q}_\Lambda = 1/3(-2\mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3)$, where \mathbf{b}_1 , \mathbf{b}_2 , and \mathbf{b}_3 are the reciprocal lattice vectors) of the Brillouin zone, we revealed an anomalous softening of one of the transverse acoustic modes. It was shown that the distortion in the phase $R32$ of holmium ferroborate in the eigenvector of this mode leads to the space group $P3_121$ with three molecules in a unit cell, which corre-

sponds to the experimentally observed structure below the transition temperature in this crystal.

In [12], the dynamics of the crystal lattice of the $\text{TbFe}_3(\text{BO}_3)_4$ crystal was studied by the method of inelastic neutron scattering in the temperature range $180 \text{ K} < T < 350 \text{ K}$, including a structural transition temperature of 192 K. A significant but incomplete softening of the transverse acoustic oscillation branch near the point Λ of the Brillouin zone was obtained experimentally.

In this work, the dynamics of the crystal lattice of $\text{RFe}_3(\text{BO}_3)_4$ compounds ($\text{R} = \text{Pr, Nd, Sm, Gd, Tb, Dy, Ho}$) in the high-symmetry phase $R32$ is calculated in order to establish the effect of the rare-earth ion on phonon spectra and the anomalous behavior of the acoustic oscillation mode.

The calculations were performed within the density functional theory with Perdew–Burke–Ernzerhof exchange correlation functionals with the generalized gradient approximation (PBE–GGA) implemented in VASP [13, 14]. The number of plane waves was limited by an energy of 600 eV. A $7 \times 7 \times 7$ Monkhorst–Pack grid was used [15]. The GGA + U method in the Dudarev approximation [16] for iron with $U = 4 \text{ eV}$ was used in the calculations. To calculate the oscillation frequencies, we constructed a $2 \times 2 \times 2$ supercell and calculated the force constants by the small displacement method implemented in PHONOPY [17].

Compounds considered in this work at high temperatures have a structure with the space group $R32$. A primitive cell has the shape of a rhombohedron with an angle between the lattice vectors $\alpha > 90^\circ$. For this case, the shape of the Brillouin zone and its edge points are shown in Fig. 1. The third-order symmetry axis passes through the points Γ and Q , and the second-order symmetry axis passes through the points Γ and F . The points Λ and Λ_1 are symmetric with respect to the second-order symmetry axis. According to the group theoretical analysis (see, e.g., the ISOTROPY Software Suite [18]), the $R32 (Z = 1) \rightarrow P3_121 (Z = 3)$ phase transition is attributed to one component of the complete two-dimensional representation Λ_3 (the star of the representation Λ_3 contains two vectors $\mathbf{q}_\Lambda = 1/3(-2\mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3)$ and $\mathbf{q}_{\Lambda_1} = -1/3(-2\mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3)$).

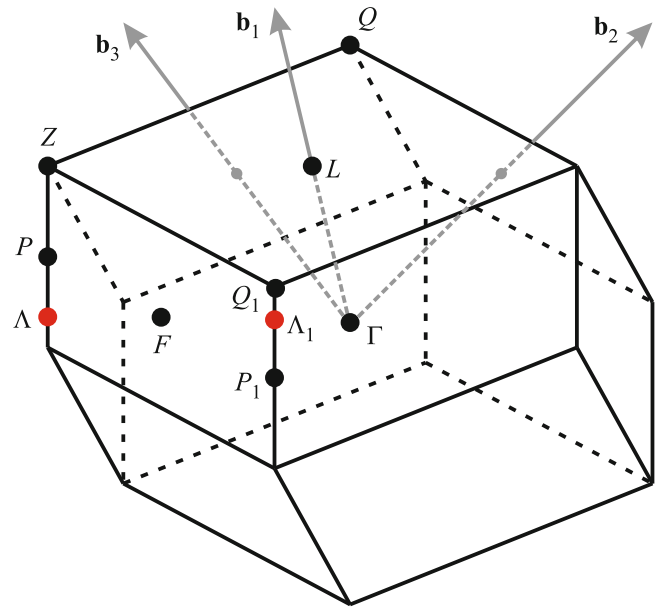


Fig. 1. (Color online) Brillouin zone for the rhombohedral lattice.

The equilibrium values of the lattice parameters and atomic coordinates for the $\text{RFe}_3(\text{BO}_3)_4$ ($\text{R} = \text{Pr, Nd, Sm, Gd, Tb, Dy, Ho}$) compounds were calculated and were used for the further calculation of the dynamics of the lattice. These lattice parameters are in good agreement with the experimental data [7] (Table 1).

Using the calculation of the dynamics of the crystal lattice, we plot the total phonon spectra in the $R32$ phase for all studied crystals. No significant changes in the phonon spectra for compounds containing various rare-earth ions were revealed (except for the vicinity of the Λ_1 point) either in the frequencies of phonon modes or in the behavior of their dispersion. Differences in the frequencies of phonon modes in compounds with rare-earth ions neighboring in the periodic table are no more than 1 meV. Figure 2 shows the phonon spectra of the $\text{PrFe}_3(\text{BO}_3)_4$ and $\text{HoFe}_3(\text{BO}_3)_4$ crystals (compounds with the maximum and minimum radii of the rare-earth ion in the compounds considered in this work). The maximum differences between oscillation frequencies in these crystals are no

Table 1. Lattice parameters in the rhombohedral lattice of $\text{RFe}_3(\text{BO}_3)_4$ compounds calculated in this work and determined experimentally in [7]

	Pr	Nd	Sm	Gd	Tb	Dy	Ho
$a_{\text{calc}} (\text{\AA})$	6.152	6.143	6.127	6.113	6.107	6.101	6.097
α_{calc}	103.78°	103.80°	103.85°	103.87°	103.88°	103.89°	103.90°
$a_{\text{exp}} (\text{\AA})$	6.096	6.091	6.078	6.068	6.062	6.053	6.046
α_{exp}	103.83°	103.85°	103.86°	103.89°	103.89°	103.89°	103.89°

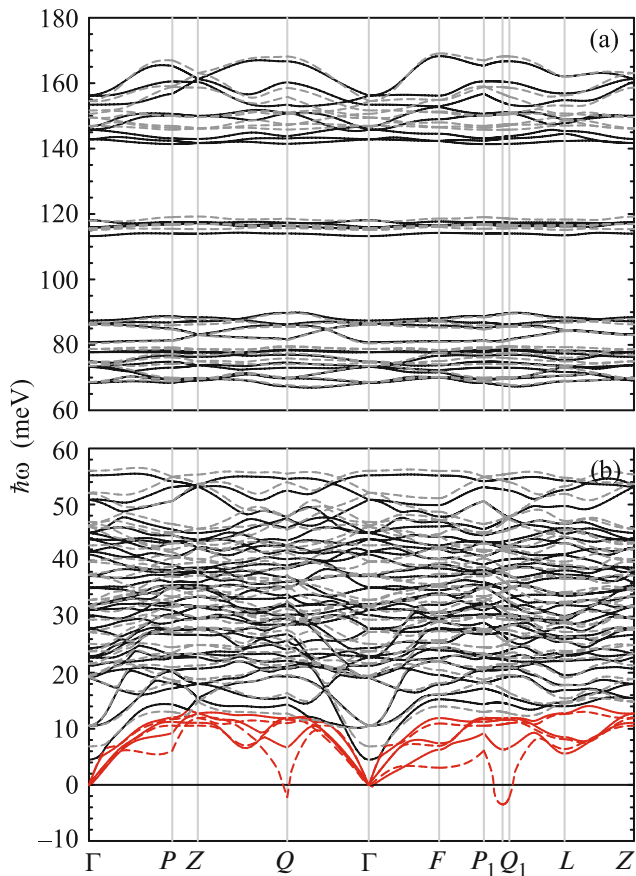


Fig. 2. (Color online) (a) Middle- and high-frequency parts of the total phonon spectrum for (solid line) $\text{PrFe}_3(\text{BO}_3)_4$ and (dashed line) $\text{HoFe}_3(\text{BO}_3)_4$ crystals. (b) Middle- and low-frequency part of the total phonon spectrum for (solid line) $\text{PrFe}_3(\text{BO}_3)_4$ and (dashed line) $\text{HoFe}_3(\text{BO}_3)_4$ crystals; acoustic modes are shown in red; imaginary frequencies are represented as negative values. The Λ_1 point is between the P_1 and Q_1 points.

more than 5 meV in the high-frequency part of the spectrum and no more than 3 meV in the remaining part of the spectrum.

The main peculiarity of all found phonon spectra is the presence of a bend in the acoustic oscillation branch near the Λ (and Λ_1) point; i.e., an anomaly in the dispersion dependence of the acoustic mode is present even in compounds where no structural phase transition is observed.

Figure 3 shows the low-frequency part of the phonon spectrum for the $\Gamma \rightarrow \Lambda$ direction for each of the studied crystals. The bend in one of the transverse acoustic branches with a minimum at the Λ point is clearly seen. The frequency at the Λ point in the $\text{RFe}_3(\text{BO}_3)_4$ compounds with $\text{R} = \text{Pr}, \text{Nd}, \text{Sm},$ and Gd decreases gradually from a compound with praseodymium to a compound with gadolinium and its value in gadolinium ferroboration becomes almost zero. The

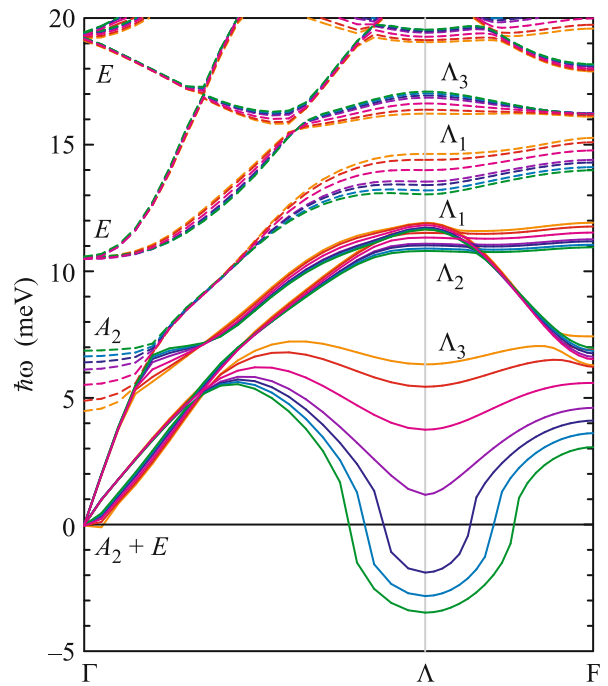


Fig. 3. (Color online) Low-frequency part of the phonon spectrum for the $\Gamma \rightarrow \Lambda$ direction demonstrating the anomalous behavior of acoustic oscillation branches in crystals with rare-earth ions (orange line) Pr, (red line) Nd, (pink line) Sm, (violet line) Gd, (blue line) Tb, (azure line) Dy, and (green line) Ho. Imaginary modes are represented as negative values. Solid and dashed lines are acoustic and optical modes, respectively.

frequency at the Λ point in the $\text{RFe}_3(\text{BO}_3)_4$ compounds with $\text{R} = \text{Tb}, \text{Dy},$ and Ho becomes imaginary (a soft mode appears), increasing gradually in absolute value from terbium ferroboration to holmium ferroboration. The appearance of an imaginary mode in these calculations indicates the instability of the crystal lattice against the distortion of the structure in the corresponding eigenvector. Indeed, the displacement of ions along the eigenvector of the soft mode at the Λ point with the corresponding tripling of the cell is energy favorable for the compounds with $\text{R} = \text{Tb}, \text{Dy},$ and Ho and leads to a structure with the symmetry group $P3_121$. A structural phase transition is observed experimentally not only in these compounds but also in compounds with gadolinium [7, 8]. A soft mode in $\text{GdFe}_3(\text{BO}_3)_4$ does not appear in this calculation, but an almost zero frequency of the acoustic mode exists at the Λ point. Thus, the resulting picture is in qualitatively good agreement with experimental data.

In work [12] on the inelastic neutron scattering in the $\text{TbFe}_3(\text{BO}_3)_4$ crystal, a significant energy broadening of the acoustic mode was observed at the Λ point when approaching the transition temperature. We believe that this can be attributed to the anharmonic interaction between the acoustic and optical modes

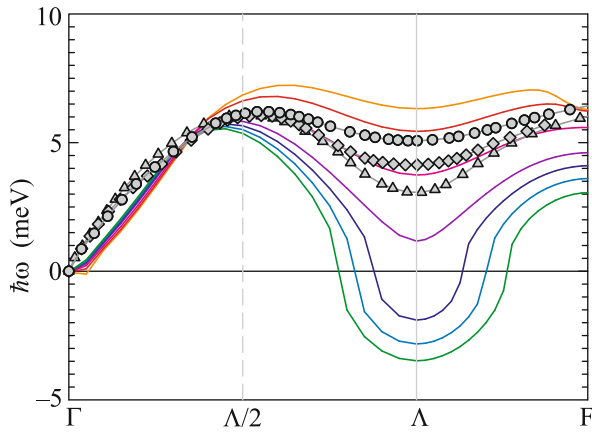


Fig. 4. (Color online) Dispersion dependences calculated in this work for acoustic modes of ferroborates with rare-earth ions (orange line) Pr, (red line) Nd, (pink line) Sm, (violet line) Gd, (blue line) Tb, (azure line) Dy, and (green line) Ho and dispersion dependences obtained experimentally in [12] for $\text{TbFe}_3(\text{BO}_3)_4$ at temperatures of (triangles) 198, (diamonds) 250, and (circles) 350 K. Imaginary modes are represented as negative values.

with the same symmetry at the Λ point; in this case, the optical mode is really unstable. This statement cannot be tested within these calculations because they were performed in the harmonic approximation. However, an optical mode whose symmetry coincides with that of the unstable acoustic mode was observed in the low-frequency part of the calculated spectra of the studied compounds (Fig. 3). The decomposition of the vibrational representation into irreducible representations for the center of the Brillouin zone has the form $\Gamma = 7A_1 + 13A_2 + 20E$, including the acoustic modes $A_2 + E$. The decomposition of the vibrational representation at the Λ point has the form $\Lambda = 20\Lambda_1 + 20\Lambda_2 + 20\Lambda_3$. The modes A_1 and A_2 are shifted from the center of the zone to the Λ_1 point at the edge of the zone, and doubly degenerate modes E are split into single modes Λ_2 and Λ_3 . An unstable acoustic mode refers to the representation Λ_3 . The optic mode Λ_3 has a frequency of 16–17 meV depending on the type of rare-earth ion (Fig. 3).

The dispersion dependences of unstable acoustic modes for the $\Gamma \rightarrow \Lambda$ direction of the Brillouin zone calculated in this work for the $\text{RFe}_3(\text{BO}_3)_4$ crystals ($R = \text{Pr, Nd, Sm, Gd, Tb, Dy, and Ho}$) are shown in Fig. 4 in comparison with the dispersion dependences for the acoustic oscillation branch at temperatures of 198, 250, 350 K obtained from the experimental spectra of inelastic neutron scattering in the $\text{TbFe}_3(\text{BO}_3)_4$ crystal from [12]. It is seen that the character of the bend on the calculated and experimental curves is the same. Indeed, up to the wave vector $\mathbf{q}_{\Lambda/2} \approx 1/6(-2\mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3) = 1/2\mathbf{q}_\Lambda$, all dispersion curves (cal-

culated and experimental) are close to each other and reach values near 6 meV at $\mathbf{q} \approx 1/6(-2\mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3)$ with the subsequent softening in the range $\mathbf{q}_{\Lambda/2} \leq \mathbf{q} \leq \mathbf{q}_\Lambda$.

To summarize, we have calculated the dynamics of the crystal lattice and plotted the total phonon spectra of the $\text{RFe}_3(\text{BO}_3)_4$ compounds ($R = \text{Pr, Nd, Sm, Gd, Tb, Dy, and Ho}$) in the $R32$ phase. Significant changes in the spectra of compounds with different rare-earth ions have been obtained only near the Λ point of the Brillouin zone for acoustic oscillation branches. A decrease in the frequency of the acoustic mode at the Λ point has been revealed in all studied compounds (even in those where no structural phase transition is observed). This frequency depends on the type of rare-earth ion and decreases from the compound with Pr to the compound with Ho down to imaginary values. Such a dependence of the frequency of the unstable acoustic mode is in good agreement with experimental data on the dependence of the temperature of the $R32 \rightarrow P3_121$ structural phase transition on the type of rare-earth ion in ferroborates.

The dynamics of the crystal lattice of $\text{HoFe}_3(\text{BO}_3)_4$ was calculated within the polarized ion model in [11], where it was shown that the frequency of the transverse acoustic branch at the Λ point of the Brillouin zone is sensitive to the free z coordinate of oxygen at the 18f Wyckoff position (hexagonal lattice). In this work, the relaxation of the lattice parameters and coordinates of ions has been performed for all considered compounds. It has been found that the z coordinate of oxygen at the 18f Wyckoff position varies smoothly with increasing number of the rare-earth ion in the periodic table from 0.48038 for the compound with praseodymium to 0.48657 for the compound with holmium. Such an increase in the z coordinate results in approach of oxygen to the rare-earth ion and, according to this calculation, apparently in an increase in the instability of the lattice at the Λ point (see Fig. 3), which is in qualitative agreement with the results reported in [11].

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