Article

Magnetic-Field-Tunable Intensity Transfer from Optically Active Phonons to Crystal-Field Excitations in the Reflection Spectra of the PrFe$_3$(BO$_3$)$_4$ Antiferromagnet

Kirill N. Boldyrev 1,*; Boris Z. Malkin 2; and Marina N. Popova 1

1 Institute of Spectroscopy, Russian Academy of Sciences, Troitsk, 108840 Moscow, Russia; popova@isan.troitsk.ru
2 Institute of Physics, Kazan Federal University, 420008 Kazan, Russia; boris.malkin@kpfu.ru
* Correspondence: kn.boldyrev@gmail.com

Abstract: We analyze the field-dependent intensities of the coupled electron-phonon modes observed in the low-temperature far-infrared (terahertz) reflection spectra of PrFe$_3$(BO$_3$)$_4$ and develop a theory based on the Green’s function approach. An excellent agreement between the experimental and theoretical data is achieved. The developed theory of the intensity transfer from phonons to quasi-electronic excitations can be applied to the electron-phonon modes in other compounds, in particular, in magnetodielectric materials, where it can be used to analyze the magnetodielectric response.

Keywords: intensities of coupled electron-phonon modes; PrFe$_3$(BO$_3$)$_4$; theory of intensity transfer

1. Introduction

A strong interaction between electronic, magnetic, and lattice degrees of freedom in multiferroics results in a vast variety of phases and phenomena [1–4], including electronic-structural phase transitions [5], coupled magnon-phonon [6,7] and electron-magnon modes [8], and formation of electromagnons [9,10]. Coupled electron-phonon modes in a terahertz spectral region and related new phenomena were recently discovered in an antiferromagnetic PrFe$_3$(BO$_3$)$_4$ single crystal [11–13], a member of a new family of multiferroics [14–17]. The peculiarity of PrFe$_3$(BO$_3$)$_4$ is that the 4f electronic excitation corresponding to the transition from the ground state to the first excited crystal-field (CF) level of the Pr$^{3+}$ ion falls into the region between the TO and LO phonon frequencies. In this case, the electronic mode is inverted: the LO frequency becomes lower than the TO frequency. It was the first observation of an inverted electronic mode [13]. A new effect was observed—the splitting of the “reststrahlen” band corresponding to a non-degenerate phonon mode [11]. Investigation of the behavior of the coupled electron-phonon modes of PrFe$_3$(BO$_3$)$_4$ in an external magnetic field made it possible to discover another new effect caused by the electron-phonon interaction, namely, the existence of a gap in the spectrum of quasi-electronic excitations of an easy-axis antiferromagnet in an arbitrarily small external magnetic field directed along the easy axis of magnetization [12]. As a result, the field behavior of the spectrum of excitations differs qualitatively from the behavior in the absence of electron-phonon coupling. How the formation of coupled electron-phonon modes affects the magnetic, magnetoelectric, and magnetodielectric properties of a multiferroic depends not only on the frequencies but also on the intensities of the coupled excitations. The magnetic field dependence of the far-infrared reflectivity of the rare-earth compound CeF$_3$ was observed more than thirty years ago [18], but, to the best of our knowledge, the intensity transfer from optically active phonons to quasi-electronic excitations in coupled electron-phonon modes has not been theoretically analyzed in the literature.

Here, we investigate the intensity vs. magnetic field dependence for coupled electron-phonon modes of PrFe$_3$(BO$_3$)$_4$ at low temperatures and develop a theory that describes the experimental findings well.
2. Structure and Properties of PrFe$_3$(BO$_3$)$_4$ Crystals

The Praseodymium iron borate crystallizes in a noncentrosymmetric trigonal structure of the natural mineral huntite with the space symmetry group R32 [19,20]. FeO$_6$ octahedra share edges forming helical chains along the c axis of the crystal. These isolated chains are interconnected by two kinds of BO$_3$ triangles and by PrO$_6$ distorted prisms. The Pr$^{3+}$ ions occupy a single $D_3$ symmetry position. The threefold symmetry axis z of the local $D_3$ point symmetry group is parallel to the crystallographic c axis [19–21]. A detailed illustrated description of the huntite structure can be found, e.g., in Ref. [21]. Crystal-field levels of Pr$^{3+}$ are characterized by the $\Gamma_1$ and $\Gamma_2$ nondegenerate and $\Gamma_3$ doubly degenerate irreducible representations of the $D_3$ point symmetry group. The ground and the first excited CF states of Pr$^{3+}$ in PrFe$_3$(BO$_3$)$_4$ are the $\Gamma_2$ and $\Gamma_1$ singlets, respectively, well isolated from other CF levels [22,23], which determines the magnetic and magnetoelectric properties of this compound [23–25].

At $T_N = 32 \pm 1$ K, Fe$^{3+}$ spins of PrFe$_3$(BO$_3$)$_4$ order into an easy-axis antiferromagnetic structure [20,24], and effective sign-alternative internal magnetic fields directed along the z axis appear at the praseodymium sites inducing the Zeeman term in the Hamiltonian of the Pr$^{3+}$ ions, $V = \pm g_0 \mu_B I_z B_{\text{int}}$ (here $g_0 = 4/5$ is the Lande factor of the ground multiplet $^3H_4$, $\mu_B$ is the Bohr magneton, and the $\pm$ sign denotes that one half of the Pr$^{3+}$ ions experiences a positive field and the other half experiences a negative field). A non-zero matrix element of the $I_z$ component of the angular momentum, $\langle \Gamma_1 | I_z | \Gamma_2 \rangle$, results in a growing mutual repulsion of the lowest CF levels at temperatures below the second-order antiferromagnetic phase transition [22,23] accompanied by the unit cell doubling along the c-axis. In an external magnetic field applied along the c axis, the crystal undergoes a spin-flop transition at $B_{SF} \approx 4.5$ T, at which the antiferromagnetically ordered along the c axis magnetic moments of Fe$^{3+}$ ions flop onto the ab plane [12,24].

The frequency $48 \text{ cm}^{-1}$ of the electronic CF excitation corresponding to the symmetry-allowed for the $\pi$-polarized ($k \perp c, E || c$) light $\Gamma_2 \rightarrow \Gamma_1$ optical electric dipole transition in Pr$^{3+}$ ions falls into the region between the TO and LO frequencies ($\omega_{\text{TO}} = 38 \text{ cm}^{-1}$ and $\omega_{\text{LO}} = 55 \text{ cm}^{-1}$, respectively; all frequencies at $T = 120$ K) of the lowest infrared-active in the $\pi$ polarization $\Gamma_2$ ($A_2$ in notations accepted in lattice dynamics) phonon mode. This mode is associated mainly with motions of the heavy Pr$^{3+}$ ions in PrFe$_3$(BO$_3$)$_4$ [26]. Electric dipole optical transitions within the ground $4f^2$ configuration of Pr$^{3+}$ are forbidden by the parity selection rule; a non-zero electric dipole moment appears due to mixing of the $4f^2$ configuration with excited configurations of opposite parity in the non-centrosymmetric crystal field. The oscillator strength of such f–f electronic transition is small (~$10^{-6}$) and it cannot be observed in the reflection spectra. However, the electron-phonon interaction results in the intensity borrowing from a phonon mode and frequency renormalization, i.e., in a formation of the coupled electron-phonon mode in PrFe$_3$(BO$_3$)$_4$, which is observed in the $\pi$-polarized reflection spectra [11,12].

3. Experimental Results

To get information on the intensities for the quasi-phonon and quasi-electronic branches of the coupled mode as a function of the strength of an external magnetic field $B || c$, we used the earlier obtained [12] $\pi$-polarized far-infrared (terahertz) reflection spectra in the region of 25–100 cm$^{-1}$ (0.75–3 THz) of a PrFe$_3$(BO$_3$)$_4$ single crystal at the temperature of 1.5 K. Figure 1 shows the spectra.

At any nonzero value of the external field below $B_{SF}$ ($B || c$), there are two quasi-electronic branches in the spectrum of coupled modes in the easy-axis antiferromagnetic phase of PrFe$_3$(BO$_3$)$_4$, with a gap between them at $B \rightarrow 0$. This gap is mediated by the electron-phonon coupling and can be regarded as its signature. The physical nature of the gap was considered in detail in Ref. [12]. The low-frequency quasi-electronic branch appears at $B > 0$ and gradually gains its intensity with a growing magnetic field (see Figure 1). Above the spin-flop transition, at $B > B_{SF}$, all praseodymium ions experience the same effective field, so that only one quasi-electronic mode remains [12] (see Figures 1 and 2). Though the
spin-flop is the first-order magnetic transition, weak traces of this single quasi-electronic mode are visible well below \( B_{SF} \), due to inhomogeneity of the magnetic field.

![Figure 1](image1.png)

**Figure 1.** The π-polarized far-infrared reflection spectra of \( \text{PrFe}_3(\text{BO}_3)_4 \) at \( T = 1.5 \) K in the external magnetic field \( B \parallel c \) (a) represented as a reflection intensity map [black (white) color corresponds to the reflectance close to unity (zero)] in the frequency—magnetic field axes and (b) for several selected values of \( B \) in the region shown by a rectangle in (a). The spin-flop transition in the field \( B_{SF} \approx 4.5 \) T is clearly observed in the spectra. Dotted lines in (a) represent the calculated transverse optical (TO) frequencies of the quasi-phonon (\( \tilde{\omega}_Q \)) and two quasi-electronic branches (\( \omega_1 \) and \( \omega_2 \)) of the coupled mode (see the text).

![Figure 2](image2.png)

**Figure 2.** Measured (black symbols) and fitted by Equation (1) (red dashed line) π-polarized far-infrared reflection spectra of \( \text{PrFe}_3(\text{BO}_3)_4 \) at several values of the external magnetic field \( B \parallel c \) at \( T = 1.5 \) K. Thin arrows point to the two quasi-electronic branches below \( B_{SF} \approx 4.5 \) T. Above \( B_{SF} \), they convert into a single quasi-electronic mode (indicated by a bold arrow).

To obtain quantitative information on the intensities, the spectra were fitted using the RefFIT software [27,28]. The least-squares method was applied, and calculations were performed according to the equation:

\[
R(\omega) = \left( \frac{\sqrt{\frac{\varepsilon(\omega)}{\varepsilon(\omega)}} - 1}{\sqrt{\frac{\varepsilon(\omega)}{\varepsilon(\omega)}} + 1} \right)^2, \tag{1}
\]
where $R(\omega)$ is the reflection coefficient, $\varepsilon(\omega)$ is the dielectric function represented in the form of a sum of independent damped oscillators (Drude–Lorentz model) as

$$
\varepsilon(\omega) = \varepsilon_\infty + \sum_{p=1}^{K} \frac{\omega_0^2 f_p}{\omega_0^2 - \omega^2 + i\omega\gamma_p}. \tag{2}
$$

Here, $K$ is the total number of oscillators, $\omega_0$, $f_p$, and $\gamma_p$ are the transverse optical (TO) mode frequency, the oscillator strength, and the damping constant of the $p$-th oscillator, respectively, and $\varepsilon_\infty$ is the dielectric constant at high frequencies.

Figure 2 shows the fitting results for the spectra taken at several values of the magnetic field.

Symbols in Figure 3 represent the relative oscillator strengths for two quasi-electronic branches of the coupled mode (see Figure 1), found from the described fitting procedure.

![Figure 3. Relative intensities of the two quasi-electronic branches of the coupled mode in PrFe$_3$(BO$_3$)$_4$ at $T = 1.5$ K vs. the external magnetic field $B||c$, $B < B_{SF}$. Symbols represent the experimental data; solid red lines are calculated according to Equation (15).](image_url)

4. Theory

Our goal is to derive an analytical expression for relative intensities of quasi-phonon and quasi-electronic coupled electron-phonon modes in the far-infrared reflection (absorption) spectra of PrFe$_3$(BO$_3$)$_4$ in the antiferromagnetic phase, under an applied external magnetic field. As far as we know, a theoretical analysis of the intensity transfer from optically active phonons to quasi-electronic excitations in coupled electron-phonon modes has not yet been presented in the literature.

In the antiferromagnetic phase, the crystallographic unit cell of PrFe$_3$(BO$_3$)$_4$ doubles along the trigonal symmetry axis, a new unit cell contains two Pr$^{3+}$ ions with antiparallel magnetic moments along the $c$-axis. In an external magnetic field $B||c$, $B < B_{SF}$, these ions have different energy spectra. In the absence of the electron-phonon interaction, the differences between energies of their first excited and ground CF levels are $\hbar \omega_{el,1}$ and $\hbar \omega_{el,2}$, respectively,

$$
\omega_{el,s}^2 = E^2 + 4\mu_B^2 g_0^2 |\langle \Gamma_1 | J_z | \Gamma_2 \rangle|^2 |B_{\text{eff}}(s)|^2, \ s = 1, 2, \tag{3}
$$

where $E$ is the energy of the $\Gamma_1$ first excited CF level of Pr$^{3+}$ in paramagnetic PrFe$_3$(BO$_3$)$_4$, $B_{\text{eff}}^{(1)} = B_{\text{int}} + B$ at one half of the praseodymium sites, $B_{\text{eff}}^{(2)} = -B_{\text{int}} + B$ at the other half ($B_{\text{int}} \approx 10.5$ T at 1.5 K [23] is an internal staggered magnetic field at the praseodymium sites).
The Hamiltonian of the considered system is written as follows:

\[ H = H_Q + \sum_{s=1,2} (H_{e,s} + V_s), \]  

where

\[ H_Q = \frac{1}{2} Q^2 + \omega_Q^2 Q^2 \]

is a phonon Hamiltonian for the normal mode \( Q \) with the wave vector \( q = 0 \) (at the Brillouin zone center) and the frequency \( \omega_Q \);

\[ H_{e,s} = \sum_{n=1}^{N} \sum_{M=1,2} E_{M,s} p_{MK}^{n,s} \]

is the Hamiltonian for the \( s \)-th two-level electronic center in the \( n \)-th unit cell with energies \( E_{1,s} \) and \( E_{2,s} \) (\( E_{2,s} - E_{1,s} = \hbar \omega_{e,s} \)) and corresponding wave functions \( |1_{n,s}> \) and \( |2_{n,s}> \), respectively, but \( p_{MK}^{n,s} = |M_n > < K_{n,s}| \) are projection operators;

\[ V_s = \frac{1}{\sqrt{N}} Q (\omega_{P_{12}} p_{12}^{n,s} + \omega_{P_{21}} p_{21}^{n,s}) \]

is the Hamiltonian of the electron-phonon interaction, \( w \) is the coupling constant related to the parameter \( W \) (measured in wave numbers and determined in [12]) by the relation \( w = 2\pi c(\hbar \omega_Q)^2 W \).

We assume the effective electric dipole moment of the TO phonon mode to be proportional to the normal mode displacement \( Q \). In this case, the intensity of the electric dipole absorption at the frequency \( \omega \) is proportional to the imaginary part of the dynamic susceptibility of the \( Q \) mode, i.e., the imaginary part of the spectral representation of the thermodynamic Green’s function \( G_{QQ}(t) = i \theta(t) < [Q(t), Q(0)] > : \)

\[ I(\omega) \sim ImG_{QQ}(\omega), \quad G_{QQ}(\omega) = \frac{1}{2\pi} \int G_{QQ}(t) e^{i\omega t} dt. \]  

Equations for the Green’s function can be written as

\[ \frac{d^2}{dt^2} G_{QQ}(t) = \hbar \delta(t) + i \theta(t) < \frac{d^2 Q(t)}{dt^2}, Q(0) >. \]  

Here, the relation \( [\frac{dQ}{dt}, Q] = -i\hbar \) was used. Equations of motion for considered operators are:

\[ \frac{d^2 Q}{dt^2} = \frac{1}{\hbar} \left[ \frac{dQ}{dt}, H \right] = -\omega_Q^2 Q - \sum_{n,s} \frac{1}{\sqrt{N}} (\omega_{P_{12}} p_{12}^{n,s} + \omega_{P_{21}} p_{21}^{n,s}), \]  

\[ \frac{dP_{12}^{n,s}}{dt} = \frac{dP_{21}^{n,s}}{dt} = -i \omega_{e,s} p_{12}^{n,s} - \frac{iQ}{\hbar \sqrt{N}} \omega^* (P_{11}^{n,s} - P_{22}^{n,s}). \]  

Next, to decouple the equations of motion of electronic and phonon dynamic variables, we linearize Equation (11) substituting non-zero average values for diagonal components of projection operators \( p_{MK}^{n,s} \):

\[ < p_{MK}^{n,s} > = \rho_{M,s} = \exp(-E_{M,s}/k_BT) / \sum_M \exp(-E_{M,s}/k_BT), \]
where $\rho_{M,i}$ are relative populations of the corresponding electronic states at the temperature $T$. Substituting (10) into (9) and passing to spectral representations, we obtain the following expression for the Green’s function:

$$G_{QQ}(\omega) = \frac{\hbar}{2\pi} \left[ \frac{\omega_Q^2 - \omega^2}{\omega_Q^2 - \omega^2} + 2 \sum_{\rho} \frac{\omega_{\rho,\delta}(\rho_{1,\delta} - \rho_{2,\delta})}{\hbar(\omega^2 - \omega_{\rho,\delta}^2)} \right].$$  \hfill (12)

The poles of this function, i.e., the roots $\omega_1$, $\omega_2$ and $\omega_Q$ of the equation

$$\left(\omega^2 - \omega_Q^2\right) - 2 \sum_{\rho} \frac{\omega_{\rho,\delta}(\rho_{1,\delta} - \rho_{2,\delta})}{\hbar(\omega^2 - \omega_{\rho,\delta}^2)} |\omega|^2 = \left(\omega^2 - \omega_1^2\right)\left(\omega^2 - \omega_2^2\right)(\omega - \omega_Q^2) = 0,$$  \hfill (13)

are the frequencies of coupled excitations.

Equation (13) was analyzed in Ref. [12]. The magnetic-field-dependent values of $\omega_Q$, $\omega_1$, and $\omega_2$ were found from Equation (13) using the experimentally determined values $E = 49 \text{ cm}^{-1}$ and $g_0 \langle F_1 | z | F_2 \rangle = 1.9$ and obtained from the fitting procedure values $|W| = 14.8 \text{ cm}^{-1}$, $\omega_Q = 40 \text{ cm}^{-1}$ [12]. The calculated frequencies are shown by dotted lines in Figure 1. It was shown that the experimentally observed frequencies of the quasi-phonon and two quasi-electronic modes in the far-infrared reflection spectra of PrFe$_3$(BO$_3$)$_4$ at $T = 1.5 \text{ K}$ in the external magnetic field $B \parallel c$ coincide with the roots of Equation (13) $\omega_Q$, $\omega_1$, and $\omega_2$, respectively. We note that the value of the effective electron-phonon coupling constant $|W|$ presented above does not contradict the estimates of derivatives of the crystal-field parameters with respect to the ligand distances from Pr$^{3+}$ ions.

Furthermore, to get insight into the intensities of the coupled modes, we represent (12) in the form

$$G_{QQ}(\omega) = -\frac{\hbar}{2\pi} \frac{\left(\omega^2 - \omega_{\rho,1}^2\right)\left(\omega^2 - \omega_{\rho,2}^2\right)}{\left(\omega^2 - \omega_1^2\right)\left(\omega^2 - \omega_2^2\right)}.$$  \hfill (14)

Replacing the excitation frequency with a complex variable, $\omega^2 \rightarrow \omega^2 + i\epsilon$, $\epsilon \rightarrow 0$, we obtain the following expression for the absorption intensity:

$$I(\omega) \sim \left(\omega_Q^2 - \omega_{\rho,1}^2\right)\left(\omega_Q^2 - \omega_{\rho,2}^2\right) \delta(\omega^2 - \omega_Q^2) + \frac{\left(\omega_1^2 - \omega_{\rho,1}^2\right)\left(\omega_2^2 - \omega_{\rho,2}^2\right)}{\left(\omega_Q^2 - \omega_{\rho,1}^2\right)\left(\omega_Q^2 - \omega_{\rho,2}^2\right)} \delta(\omega^2 - \omega_1^2) + \frac{\left(\omega_1^2 - \omega_Q^2\right)\left(\omega_2^2 - \omega_Q^2\right)}{\left(\omega_Q^2 - \omega_{\rho,1}^2\right)\left(\omega_Q^2 - \omega_{\rho,2}^2\right)} \delta(\omega^2 - \omega_2^2).$$  \hfill (15)

Above, we did not consider the widths of the excitations; they can be taken into account by replacing in (15) frequencies of phonon and electronic excitations with complex quantities.

The coefficients at the delta-functions in (15) determine the relationship between the intensities of the quasi-phonon mode and the intensities of the two quasi-electronic modes. Solid lines in Figure 3 show the theoretical field dependence of the two quasi-electronic modes. An excellent agreement with the experimental data is evident.

5. Conclusions

To summarize, the theory is developed of the intensity transfer from optically active phonons to quasi-electronic excitations in coupled electron-phonon modes. The theory is applied to the magnetic-field-dependent coupled crystal-field and phonon excitations observed in the terahertz frequency region in the low-temperature reflection spectra of the easy-axis antiferromagnet PrFe$_3$(BO$_3$)$_4$ [12]. Analysis of the earlier obtained field-
References


2. Liang, X.; Chen, H.; Sun, N.X. Magnetoelectric materials and devices. APL Mater. 2021, 9, 041114. [CrossRef]


Author Contributions: Conceptualization, K.N.B. and M.N.P.; methodology, K.N.B. and B.Z.M.; data acquisition K.N.B.; theory and calculations, B.Z.M.; writing—original draft preparation, M.N.P. and K.N.B.; writing—review and editing, M.N.P. and B.Z.M.; figures, K.N.B. All authors have read and agreed to the published version of the manuscript.

Funding: Financial support from the Russian Science Foundation (Grant No. 19-12-00413) was given.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data that support the plots within the paper and other findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.


23. Popova, M.N.; Stanislavchuk, T.N.; Malkin, B.Z.; Bezmernykh, L.N. Optical Spectroscopy of PrFe$_3$(BO$_3$)$_4$: Crystal-Field and Anisotropic Pr-Fe Exchange Interactions. Phys. Rev. B 2009, 80, 195101. [CrossRef]


