



Article Magnetic-Field-Tunable Intensity Transfer from Optically Active Phonons to Crystal-Field Excitations in the Reflection Spectra of the PrFe₃(BO₃)₄ Antiferromagnet

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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 quasielectronic 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; PrFe₃(BO₃)₄; theory of intensity transfer



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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 CeF₃ 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 electronphonon 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 PrFe₃(BO₃)₄ Crystals

The Praseodymium iron borate crystallizes in a noncentrosymmetric trigonal structure of the natural mineral huntite with the space symmetry group *R*32 [19,20]. FeO₆ octahedra share edges forming helical chains along the *c* axis of the crystal. These isolated chains are interconnected by two kinds of BO₃ triangles and by PrO₆ distorted prisms. The Pr³⁺ 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 Pr³⁺ are characterized by the Γ_1 and Γ_2 nondegenerate and Γ_3 doubly degenerate irreducible representations of the D_3 point symmetry group. The ground and the first excited CF states of Pr³⁺ in PrFe₃(BO₃)₄ are the Γ_2 and Γ_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, Fe³⁺ spins of PrFe₃(BO₃)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 Pr³⁺ ions, $V = \pm g_0 \mu_B J_z B_{int}$ (here $g_0 = 4/5$ is the Lande factor of the ground multiplet ${}^{3}H_4$, μ_B is the Bohr magneton, and the \pm sign denotes that one half of the Pr³⁺ ions experiences a positive field and the other half experiences a negative field). A non-zero matrix element of the J_z component of the angular momentum, $<\Gamma_1 | J_z | \Gamma_2 >$, 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 Fe³⁺ ions flop onto the *ab* plane [12,24].

The frequency 48 cm⁻¹ of the electronic CF excitation corresponding to the symmetryallowed for the π -polarized ($k \perp c$, $E \parallel c$) light $\Gamma_2 \rightarrow \Gamma_1$ optical electric dipole transition in \Pr^{3+} ions falls into the region between the TO and LO frequencies ($\omega_{TO} = 38 \text{ cm}^{-1}$ and $\omega_{LO} = 55 \text{ cm}^{-1}$, respectively; all frequencies at T = 120 K) of the lowest infrared-active in the π polarization Γ_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 ($\sim 10^{-6}$) 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 π -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 $B \parallel c$, we used the earlier obtained [12] π -polarized far-infrared (terahertz) reflection spectra in the region of 25–100 cm⁻¹ (0.75–3 THz) of a PrFe₃(BO₃)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 quasielectronic 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. The π -polarized far-infrared reflection spectra of PrFe₃(BO₃)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 (ω_1 and ω_2) of the coupled mode (see the text).



Figure 2. Measured (black symbols) and fitted by Equation (1) (red dashed line) π -polarized farinfrared reflection spectra of PrFe₃(BO₃)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:

$$R(\omega) = \left(\frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1}\right)^2,\tag{1}$$

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

$$\varepsilon(\omega) = \varepsilon_{\infty} + \sum_{p=1}^{K} \frac{\omega_{0p}^2 f_p}{\omega_{0p}^2 - \omega^2 + i\omega\gamma_p}.$$
(2)

Here, *K* is the total number of oscillators, ω_{0p} , f_p , and γ_p are the transverse optical (TO) mode frequency, the oscillator strength, and the damping constant of the *p*-th oscillator, respectively, and ε_{∞} 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 $B \parallel c$, $B < B_{SF}$. Symbols represent the experimental data; solid red lines are calculated according to Equation (15).

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 $\boldsymbol{B} || c, B < B_{SF}$, 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,

$$\omega_{el,s}^{2} = E^{2} + 4\mu_{B}^{2}g_{0}^{2}|\langle\Gamma_{1}|J_{Z}|\Gamma_{2}\rangle|^{2}|B_{\text{eff}}^{(s)}|^{2}, s = 1, 2,$$
(3)

where *E* is the energy of the Γ_1 first excited CF level of Pr^{3+} in paramagnetic $PrFe_3(BO_3)_4$, $B_{eff}^{(1)} = B_{int} + B$ at one half of the praseodymium sites, $B_{eff}^{(2)} = -B_{int} + B$ at the other half ($B_{int} \approx 10.5 \text{ T}$ 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:

$$H = H_Q + \sum_{s=1,2} (H_{el,s} + V_s),$$
(4)

where

$$H_Q = \frac{1}{2} \left(\dot{Q}^2 + \omega_Q^2 Q^2 \right) \tag{5}$$

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

$$H_{el,s} = \sum_{n=1}^{N} \sum_{M=1,2} E_{M,s} P_{MM}^{n,s}$$
(6)

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

$$V_s = \sum_n \frac{1}{\sqrt{N}} Q \left(w P_{12}^{n,s} + w^* P_{21}^{n,s} \right) \tag{7}$$

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 $w = 2\pi c (\hbar \omega_{\Omega})^{\frac{1}{2}} W$.

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 ω 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 $G_{QQ}(t) = i\vartheta(t) < [Q(t), Q(0)] >$:

$$I(\omega) \sim Im G_{QQ}(\omega), \ G_{QQ}(\omega) = \frac{1}{2\pi} \int G_{QQ}(t) e^{i\omega t} dt.$$
(8)

Equations for the Green's function can be written as

$$\frac{d^2}{dt^2}G_{QQ}(t) = \hbar\delta(t) + i\vartheta(t) < \left[\frac{d^2Q(t)}{dt^2}, Q(0)\right] >.$$
(9)

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

$$\frac{d^2Q}{dt^2} = \frac{1}{i\hbar} \left[\frac{dQ}{dt}, H \right] = -\omega_Q^2 Q - \sum_{n,s} \frac{1}{\sqrt{N}} \left(w P_{12}^{n,s} + w^* P_{21}^{n,s} \right), \tag{10}$$

$$\frac{dP_{12}^{n,s}}{dt} = \frac{dP_{21}^{n,s*}}{dt} = -i\omega_{el,s}P_{12}^{n,s} - \frac{iQ}{\hbar\sqrt{N}}w^*(P_{11}^{n,s} - P_{22}^{n,s}).$$
(11)

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 $P_{MM}^{n,s}$,

$$< P_{MM}^{n,s} > = \rho_{M,s} = \exp(-E_{M,s}/k_BT) / \sum_{M} \exp(-E_{M,s}/k_BT),$$

where $\rho_{M,s}$ 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:

$$G_{QQ}(\omega) = \frac{\hbar}{2\pi \left[\left(\omega_Q^2 - \omega^2 \right) + 2\sum_s \frac{\omega_{el,s}(\rho_{1,s} - \rho_{2,s})|w|^2}{\hbar \left(\omega^2 - \omega_{el,s}^2 \right)} \right]}.$$
(12)

The poles of this function, i.e., the roots ω_1 , ω_2 and $\widetilde{\omega}_Q$ of the equation

$$\left(\omega^{2} - \omega_{Q}^{2}\right) - 2\sum_{s} \frac{\omega_{el,s}(\rho_{1,s} - \rho_{2,s})|w|^{2}}{\hbar\left(\omega^{2} - \omega_{el,s}^{2}\right)} = \left(\omega^{2} - \omega_{1}^{2}\right)\left(\omega^{2} - \omega_{2}^{2}\right)(\omega - \widetilde{\omega}_{Q}^{2}) = 0, \quad (13)$$

are the frequencies of coupled excitations.

Equation (13) was analyzed in Ref. [12]. The magnetic-field-dependent values of $\tilde{\omega}_Q$, ω_1 , and ω_2 were found from Equation (13) using the experimentally determined values $E = 49 \text{ cm}^{-1}$ and $g_0 \langle \Gamma_1 | J_Z | \Gamma_2 \rangle = 1.9$ 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 $\text{PrFe}_3(\text{BO}_3)_4$ at T = 1.5 K in the external magnetic field $B \parallel c$ coincide with the roots of Equation (13) $\tilde{\omega}_Q$, ω_1 and ω_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

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

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

$$I(\omega) \sim \frac{\left(\widetilde{\omega}_{Q}^{2} - \omega_{el,1}^{2}\right)\left(\widetilde{\omega}_{Q}^{2} - \omega_{el,2}^{2}\right)}{\left(\widetilde{\omega}_{Q}^{2} - \omega_{1}^{2}\right)\left(\widetilde{\omega}_{Q}^{2} - \omega_{2}^{2}\right)}\delta\left(\omega^{2} - \widetilde{\omega}_{Q}^{2}\right) + \frac{\left(\omega_{1}^{2} - \omega_{el,1}^{2}\right)\left(\omega_{1}^{2} - \omega_{el,2}^{2}\right)}{\left(\omega_{1}^{2} - \widetilde{\omega}_{Q}^{2}\right)\left(\omega_{1}^{2} - \omega_{2}^{2}\right)}\delta\left(\omega^{2} - \omega_{1}^{2}\right) + \frac{\left(\omega_{2}^{2} - \omega_{el,1}^{2}\right)\left(\omega_{2}^{2} - \omega_{el,2}^{2}\right)}{\left(\omega_{2}^{2} - \widetilde{\omega}_{Q}^{2}\right)\left(\omega_{2}^{2} - \omega_{1}^{2}\right)}\delta\left(\omega^{2} - \omega_{2}^{2}\right).$$
(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 fielddependent spectra of PrFe₃(BO₃)₄ [12] using the Drude–Lorentz model revealed the oscillator strengths of the quasi-phonon and quasi-electronic branches of the coupled electronphonon mode. An excellent agreement between the experimental and theoretical results was demonstrated. The developed theory can be applied to optically active coupled modes in the infrared spectra of other compounds, in particular, rare-earth magnetodielectric materials [29] and can be used to analyze their magnetodielectric response.

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