

Breaking of the Selection Rules for Optical Transitions in the Dielectric $\text{PrFe}_3(\text{BO}_3)_4$ Crystal by a Praseodymium-Iron Exchange Interaction

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We report on the emergence of new lines in the optical spectrum of the $\text{PrFe}_3(\text{BO}_3)_4$ single crystal at the magnetic ordering temperature. The transitions between singlet crystal-field sublevels of Pr^{3+} ion with the same transformational properties, strictly forbidden for the trigonal D_3 point symmetry of this ion in $\text{PrFe}_3(\text{BO}_3)_4$, appear below the Néel temperature and grow in intensity as a square of the order parameter. We show that the phenomenon originates from the mixing of wave functions of different Pr^{3+} sublevels by the Pr-Fe exchange interaction.

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Optical spectra of crystals are governed by selection rules for optical transitions that follow from symmetry considerations. In the case of infrared (IR) absorption or Raman scattering by phonons (as well as in the case of the interband absorption), the space group of the crystal lattice is of importance. New lines in the IR and Raman spectra appear at proper and improper ferroelastic phase transitions. In the case of proper transitions (the deformation tensor is an order parameter), degeneration of highly symmetric vibrations is lifted. This effect is well known. It was observed, for example, in the Raman spectra of the rare-earth (RE) compounds with tetragonal zircon structure which undergo cooperative Jahn-Teller phase transitions to the low-temperature orthorhombic structure [1]. In the case of improper transitions, new vibrational frequencies in the Brillouin zone center and, correspondingly, new lines in optical spectra appear due to folding of the Brillouin zone when the primitive cell doubles (triples). These so-called “folded modes” are also well known and were observed in several crystals, e.g., in Hg_2Cl_2 [2], NaV_2O_5 [3], and CuGeO_3 [4], and, recently, in the RE iron borates $R\text{Fe}_3(\text{BO}_3)_4$ ($R = \text{Eu-Er, Y}$) at the spontaneous structural phase transition from the trigonal D_3^7 phase to the also trigonal but less symmetric D_3^4 one [5].

In the case of radiative transitions between energy levels of localized electrons, the point symmetry group of an optical center is of importance. Again, lowering of the point symmetry leads to the appearance of new spectral lines. This effect has been observed, e.g., in the spectrum of the Eu^{3+} ion in $\text{EuFe}_3(\text{BO}_3)_4$ at the already mentioned structural phase transition $D_3^7 \rightarrow D_3^4$ [6], when the positional symmetry for the RE ion lowers from the D_3 point group to the C_2 one [5,7] (the threefold symmetry axis disappears, but from the three axes of the second order only one survives). We note that in the RE iron borates RE-RE interactions can be neglected, not only because $4f$ electrons are well shielded by the closed $5p$ and $5s$ shells but

also because the RE ions are well isolated having no connections through one oxygen. As a result, optical transitions in RE ions that stoichiometrically enter the RE iron borates can be explained in the framework of the positional point symmetry group.

In this Letter, on the example of $\text{PrFe}_3(\text{BO}_3)_4$ we demonstrate a fundamentally different effect. Forbidden spectral lines appear not due to changes in the symmetry of the crystal lattice structure as the magnetic phase transition is crossed but due to mixing of wave functions of an optical center by the exchange interaction in the magnetically ordered state. Of course, the overall symmetry (that includes the magnetic symmetry) lowers in this case; the violation of the selection rules can be explained by a global symmetry lowering and, thus, does not contradict general symmetry concepts. However, as far as we know, we present the first experimental observation of such an effect. This effect is not connected with the considered crystal or similar materials but should be observed in many other compounds containing magnetically ordered sublattices of transition metal ions and RE non-Kramers ions (i.e., RE ions with an even number of electrons).

The $R\text{Fe}_3(\text{BO}_3)_4$ crystals ($R = \text{Y, La-Nd, Sm-Er}$) have received much attention recently because of their extremely interesting optical, magnetic, and magnetoelectric properties that may lead to a new class of multifunctional materials [5,7–21]. The structure of these crystals features helical chains of the edge-sharing FeO_6 octahedra running along the trigonal symmetry axis c and interconnected by the R^{3+} and boron ions [7]. While the majority of the $R\text{Fe}_3(\text{BO}_3)_4$ compounds undergo the structural phase transition $D_3^7 \rightarrow D_3^4$, $\text{PrFe}_3(\text{BO}_3)_4$ is known to preserve the D_3^7 space symmetry down to at least 2 K [7,20]. Studies of the magnetic susceptibility have shown that the Fe^{3+} magnetic moments order antiferromagnetically along the c axis of the crystal at the Néel temperature $T_N \approx 32$ K and polarize the Pr^{3+} ions via the Pr-Fe exchange interaction [21]. The

same result followed from our optical study by the method of an erbium spectroscopic probe [6]. In a strong magnetic field $\mathbf{B} \parallel c$ ($B_{\text{cr}} = 4.3$ T at $T = 4.2$ K, $B_{\text{cr}} = 6.5$ T at $T = 31$ K), the spin-flop transition takes place; i.e., Fe^{3+} spins reorient to the basal plane [21].

The $\text{PrFe}_3(\text{BO}_3)_4$ crystals of good optical quality were grown by the flux method as described in Ref. [22]. Figures 1 and 2 show the spectra of the $\text{PrFe}_3(\text{BO}_3)_4$ single crystal at 50 K $> T_N$ and 5 K $< T_N$ for the α ($\mathbf{k} \parallel c$, $\mathbf{E} \perp c$), σ ($\mathbf{k} \perp c$, $\mathbf{E} \perp c$), and π ($\mathbf{k} \perp c$, $\mathbf{E} \parallel c$) polarizations of the incident radiation in the regions of the transitions from the ground ${}^3\text{H}_4$ multiplet to the ${}^3\text{F}_2$ and, respectively, ${}^3\text{F}_3$ excited multiplets of the electronic $4f^2$ configuration of the Pr^{3+} ion [23]. The multiplets of a free non-Kramers Pr^{3+} ion are split by the crystal field (CF) of the D_3 symmetry into Γ_1 and Γ_2 singlets and Γ_3 doublets (Γ_k is the irreducible representation of the D_3 point group). We follow the notations that the CF sublevels of the ground multiplet are labeled by Roman numerals and those of a given excited multiplet by capital letters (A, B, etc.). The electric dipole $\Gamma_1 \leftrightarrow \Gamma_2$ transitions are allowed in the π polarization, the $\Gamma_1, \Gamma_2 \leftrightarrow \Gamma_3$ ones are allowed in the α and σ polarizations, while the $\Gamma_3 \rightarrow \Gamma_3$ transitions are allowed

in all of the polarizations, but the $\Gamma_1 \rightarrow \Gamma_1$ and $\Gamma_2 \rightarrow \Gamma_2$ ones are *strictly forbidden*, both as the electric dipole and as the magnetic dipole.

Let us first consider the ${}^3\text{F}_2 = \Gamma_1 + 2\Gamma_3$ multiplet (Fig. 1). At low temperatures, when only the ground state is populated, three lines are observed in the ${}^3\text{H}_4 \rightarrow {}^3\text{F}_2$ optical transition, which rules out the Γ_1 symmetry for the ground state. As the electric dipole transitions dominate for the considered ${}^3\text{H}_4 \rightarrow {}^3\text{F}_2, {}^3\text{F}_3$ spectra (this follows from our finding that σ - and α -polarized spectra coincide), the selection rules point unambiguously to Γ_2 as the symmetry of the ground state and lead to the following symmetry assignments for the ${}^3\text{F}_2$ sublevels: $A(\Gamma_3^A)$, $B(\Gamma_1^B)$, and $C(\Gamma_3^C)$. The assignment of the Γ_3 sublevels is confirmed by the observed splittings of these doublets below T_N (we shall return to this point later). Two new lines IIA and IIC emerge in the σ -polarized spectrum with rising temperature. They are shifted by 48 cm^{-1} to the low frequency side from the IA and IC lines and originate from the first excited CF level thus situated at 48 cm^{-1} . The absence of the IIB line in both σ - and π -polarized 50 K spectra points to the Γ_1 symmetry of the level at 48 cm^{-1} .

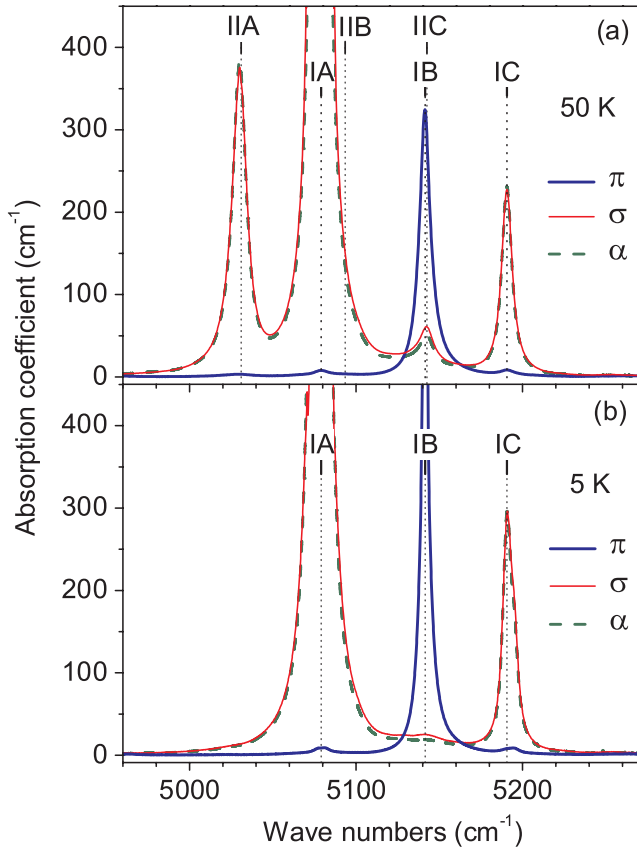


FIG. 1 (color online). Region of the ${}^3\text{F}_2$ multiplet of the Pr^{3+} ion in the absorption spectrum of $\text{PrFe}_3(\text{BO}_3)_4$ at $T = 50$ K $> T_N$ (a) and $T = 5$ K $< T_N$ (b). The spectral lines IIA and IIC freeze out with lowering temperature.

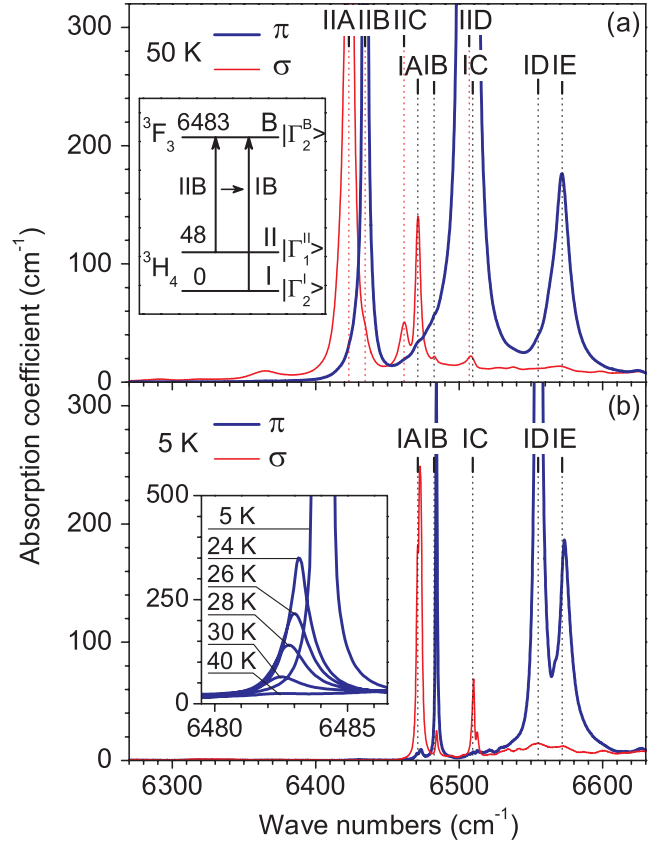


FIG. 2 (color online). Region of the ${}^3\text{F}_3$ multiplet of the Pr^{3+} ion in the absorption spectrum of $\text{PrFe}_3(\text{BO}_3)_4$ at $T = 50$ K (a) and 5 K (b). New spectral lines IB and ID emerge below $T_N = 31$ K in the π -polarized spectrum. Inset in (a): Scheme of the Pr^{3+} energy levels. Inset in (b): Rise of the line IB below T_N .

We now turn to the ${}^3F_3 = \Gamma_1 + 2\Gamma_2 + 2\Gamma_3$ multiplet (Fig. 2). At elevated temperatures $T > T_N$, transitions from the lowest two levels Γ_2^I and Γ_1^II of the ground multiplet to the Γ_3 and Γ_1 sublevels of the 3F_3 multiplet are observed, together with two strong π -polarized lines IIB and IID that have to be assigned to the $\Gamma_1^II \rightarrow \Gamma_2$ transitions. The $\Gamma_2 \rightarrow \Gamma_2$ lines are absent, in complete agreement with the selection rules. However, below T_N , two new π -polarized lines IB and ID appear and grow in intensity with further lowering of the temperature [see Fig. 2(b)]. The lines IB and ID arise at the positions shifted precisely 48 cm^{-1} to higher frequencies from the lines IIB and IID, respectively and, thus, have to be assigned to the forbidden $\Gamma_2 \rightarrow \Gamma_2$ transitions.

Let us discuss possible physical reasons for the observed phenomenon. First of all, we investigate the possibility that the new spectral lines arise because of the symmetry lowering at the Pr^{3+} position, caused by a low-symmetry striction below T_N . Indeed, in $\text{PrFe}_3(\text{BO}_3)_4$, the forced magnetostriction and electric polarization were observed, induced by the external magnetic field aligned along the c axis. However, these phenomena take place only in the case of strong fields ($> 4.3 \text{ T}$ at 4.2 K) [21]. The symmetry analysis also confirms the absence of the spontaneous low-symmetry striction and electric polarization when the magnetic moments are ordered along the c axis [11,21]. Thus, the crystal lattice symmetry does not lower at the magnetic phase transition, and the symmetry of the crystal field at the Pr^{3+} position remains the same (D_3).

The most probable reason of the selection rule breaking for the $\Gamma_2 \rightarrow \Gamma_2$ transitions in the easy-axis magnet $\text{PrFe}_3(\text{BO}_3)_4$ is, to our mind, the admixture of the $|\Gamma_1\rangle$ states to the $|\Gamma_2\rangle$ ones by the Pr-Fe exchange interaction. At temperatures $T < T_N$, the average spin moments $\langle S \rangle$ of the Fe^{3+} ions ($S = 5/2$) are parallel to the c axis [21]. In the framework of the molecular field approximation, the exchange Hamiltonian of the Pr^{3+} ions in the Cartesian system of coordinates with the z and x axes parallel to the crystallographic c and a axes, respectively, has the form [24]: $H_{\text{ex}} = F_z \langle S_z \rangle$, with

$$F_z = \sum_k \left[a_0^0 + \sum_{p=2,4,6} a_0^p C_0^p(k) + \sum_{p=4,6} i a_3^p [C_3^p(k) + C_{-3}^p(k)] + a_6^6 [C_6^6(k) + C_{-6}^6(k)] \right] s_{k,z}. \quad (1)$$

Here the first sum is taken over $4f$ electrons with the spin moments s_k , $C_q^p(k)$ are the one-particle spherical tensor operators of the rank p , and the orbital operator in square brackets determined by seven parameters a_q^p is invariant under the D_3 symmetry operations and has the same structure as the CF Hamiltonian. We consider the Hamiltonian H_{ex} as a perturbation.

First of all, this perturbation shifts the CF energy levels and splits the Γ_3 doublets at temperatures $T < T_N$. The inset in Fig. 3 shows the absorption spectrum in the region

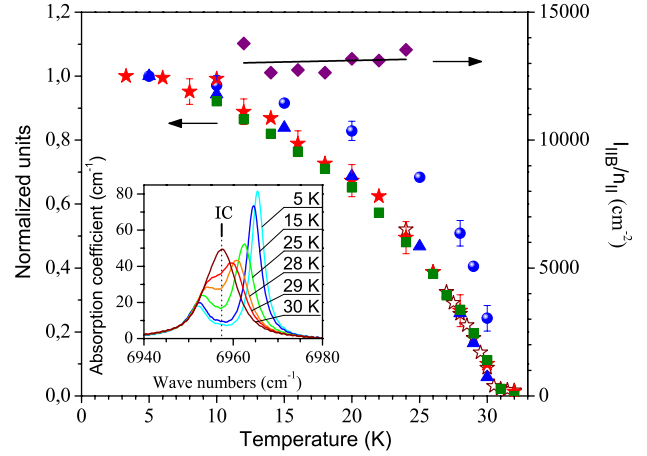


FIG. 3 (color online). Temperature dependences of exchange splitting of the Γ_3 level (balls), the same splitting squared (triangles), increase of the energy gap between the lowest two levels Γ_2^I and Γ_1^II of the ground multiplet (squares), ratio I/n_I for different $\Gamma_2^I \rightarrow \Gamma_2$ transitions (stars), and ratio $I_{\text{IB}}/n_{\text{II}}$ (diamonds). Inset: Absorption caused by transitions from the ground state Γ_2^I to the Γ_3^C doublet in the 3F_4 multiplet, at different temperatures.

of the Γ_3 doublet near 6957 cm^{-1} at $T < T_N$. This doublet in the 3F_4 multiplet demonstrates the largest splitting observed in the spectrum of $\text{PrFe}_3(\text{BO}_3)_4$. The temperature dependence of the splitting is plotted in Fig. 3. To the first order, the splitting Δ of an isolated Γ_3 doublet is proportional to the order parameter of the magnetic phase transition $\Delta(T) \sim \langle S_z \rangle$. The first-order corrections to the energies of the Γ_1 and Γ_2 singlets vanish in our case of the D_3 symmetry, and the second-order corrections have to be taken into account. In particular, the increase of the energy gap between the lowest two levels Γ_2^I and Γ_1^II of the ground multiplet, neglecting their mixing with other CF states, equals

$$\delta(T) = 2|\alpha|^2 [E(\Gamma_1^II) - E(\Gamma_2^I)], \quad (2)$$

with $\alpha = \frac{\langle \Gamma_1^II | H_{\text{ex}} | \Gamma_2^I \rangle}{E(\Gamma_2^I) - E(\Gamma_1^II)}$, $|\alpha| \ll 1$, and is proportional to the square of the order parameter $\delta(T) \sim \langle S_z \rangle^2$. From the experimentally measured difference between the frequencies of the lines IA and IIA, IB and IIB, etc., we really find $\delta_{\text{exp}}(T) \sim \Delta(T)^2 \sim \langle S_z \rangle^2$ (see Fig. 3).

The perturbation H_{ex} influences also the wave functions and hence the integral intensities of optical transitions, which are determined by matrix elements of the effective electric dipole operator \mathbf{d} of the Pr^{3+} ion. In particular, for the π -polarized intensity of the transition IB that arises below T_N [see Fig. 2(b)],

$$I_{\text{IB}}(T) \sim n_1(T) |\langle \Gamma_2^B | d_z | \Gamma_2^I(T) \rangle|^2. \quad (3)$$

Here $n_1(T)$ is the relative population of the ground level with the temperature-dependent perturbed wave function $|\Gamma_2^I(T)\rangle = (1 + |\alpha|^2)^{-1/2} (|\Gamma_2^I\rangle + \alpha |\Gamma_1^II\rangle)$. Note that we ne-

glect in Eq. (3) variations of the excited state Γ_2^B in the magnetically ordered phase (see below). The matrix element $\langle \Gamma_2^B | d_z | \Gamma_2^I \rangle$ between the unperturbed states is exactly zero, and we obtain from Eq. (3) the following relation (again, to the second order in $|\alpha|$) between the intensities of the forbidden (IB) and allowed (IIB) transitions:

$$I_{IB}(T) = |\alpha|^2 \frac{n_I(T)}{n_{II}(T)} I_{IIB}(T), \quad (4)$$

where $n_{II}(T)$ is the relative population of the level Γ_1^{II} .

From Eq. (2), using the measured temperature-dependent shift $\delta(T) = 2.6 \text{ cm}^{-1}$ of the IB line relative to the IIB line at the temperature $T = 26 \text{ K}$, we obtain $|\alpha|^2 = 0.0271$. Almost exactly the same value $|\alpha|^2 = 0.0274$ is obtained when substituting into Eq. (4) the measured intensities $I_{IB}/n_I = 357$ and $I_{IIB}/n_{II} = 13000$ at the same temperature. The consistency between the observed temperature dependences of the intensity of the forbidden transition IB and of the gap between the Γ_2^I and the Γ_1^{II} states gives evidence for a negligible effect of the exchange interaction on the wave function of the final state Γ_2^B (3F_3) of the considered optical transition. As one can see from Fig. 3, the ratio $I_{IIB}(T)/n_{II}(T)$ practically does not depend on the temperature. This is quite natural because this ratio equals the probability of the allowed optical transition. Thus, as it follows from Eq. (4), the intensity of the forbidden line divided by the population of the initial level of the transition behaves as a square of the average iron magnetic moment. For the experimentally measured intensities of the $\Gamma_2 \rightarrow \Gamma_2$ transitions (see Fig. 3), indeed, we find $I_{IB}(T)/n_I(T) \sim \Delta(T)^2 \sim \langle S_z \rangle^2$, which is in favor of the proposed mechanism.

Only the first term (a_0^0) in the square brackets in Eq. (1) corresponds to the isotropic exchange interaction that involves the total spin moment (proportional to the total angular momentum \mathbf{J} within the space of states $|LSJJ_z\rangle$ of the fixed multiplet) of the Pr^{3+} ion. However, the operators F_z and J_z have the same transformational properties and, correspondingly, the nonzero matrix elements of the same type ($\langle \Gamma_1 | \dots | \Gamma_2 \rangle$ and $\langle \Gamma_3 | \dots | \Gamma_3' \rangle$). Thus, when considering the matrix element $\langle \Gamma_1^{II} | H_{ex} | \Gamma_2^I \rangle$, we can compare the exchange Hamiltonian with the Zeeman energy of the Pr^{3+} ion in the so-called “exchange magnetic field” B_{ex} : $H_{ex} = -\mu_B g_0 J_z B_{ex}$, where μ_B is the Bohr magneton and g_0 is the Landé factor. Using the value $g_0 \langle \Gamma_1^{II} | J_z | \Gamma_2^I \rangle = 2.234$ (obtained from the crystal-field analysis), we get an estimate for the maximum value of the exchange field B_{ex} (5 K) $\approx 11.7 \text{ T}$. This value is close to $B_{ex} \approx 11.5 \text{ T}$ obtained from the magnetic susceptibility measurements [21].

The more detailed analysis of the observed effect and of the obtained from the experimental data parameters of the crystal field and the anisotropic exchange interaction will be presented in a separate publication.

In conclusion, on the example of $\text{PrFe}_3(\text{BO}_3)_4$ we have demonstrated an effect which is new, to our knowledge, namely, emergence of forbidden transitions in the optical spectrum of a RE ion in a dielectric crystal at the magnetic ordering temperature, induced by the exchange interaction. We explain this effect by the intensity borrowing from an allowed transition that results from mixing of wave functions of different Pr^{3+} CF sublevels in the antiferromagnetic phase of $\text{PrFe}_3(\text{BO}_3)_4$. This effect should be observed also in any other compounds containing magnetically ordered sublattices of transition metal ions and RE non-Kramers ions in the positions with the D_2 , D_{2d} , D_4 , D_3 , D_{3h} , D_6 , T_d , and O point symmetry.

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