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Electron-phonon interaction in huntite iron borates

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ABSTRACT

In this presentation, the results on the study of electron-phonon coupling in rare-earth iron borates $RFe_3(BO_3)_4$, R = Pr, Sm, Tb, and Gd, which was carried out in our laboratory in a cooperation with other Russian and foreign institutions, are briefly reviewed.

1. Introduction

The electron-phonon interaction being a basic interaction in solid-state physics governs many fundamental properties and phenomena. Thermal and electronic conductivity of materials [1,2] as well as energy dissipation [2] depend on the electron-phonon interaction. Classical superconductivity [3] and different kinds of the Jahn – Teller effect [4] take place due to the electron-phonon interaction. The homogeneous broadening of zero-phonon spectral lines in rare-earth-doped crystals is caused by the electron-phonon coupling in a majority of cases [5]. The same coupling is responsible for the crystal-field levels' relaxation and, hence, the lifetimes. The values of these effects and of the multiphonon relaxation rates (also dependent on the electron-phonon interaction) are of primary importance for laser applications, because they influence the gain, output frequency stability, and thermal tunability of a laser [5].

If the frequency of an electronic transition coincides with or is near to the phonon frequency, the electron-phonon interaction forms coupled electron-phonon excitations [6–9]. Formation of coupled electron-phonon modes is accompanied by a mutual energy renormalization and appearance of new branches in the excitation spectrum. Typically, these processes arise in the terahertz (far infrared) frequency region and can affect properties of optical materials for this spectral range.

In this presentation, I'll briefly review results on the study of electron-phonon coupling in rare-earth (RE) iron borates $RFe_3(BO_3)_4$, R = Pr, Sm, Tb, and Gd, which was carried out in our laboratory in a cooperation with other Russian and foreign institutions [10–12].

RE borates with general formula $RM_3(BO_3)_4$ (R = RE or Y, M = Al, Ga, Sc, Cr, Fe) crystallize in a noncentrosymmetric trigonal structure of the natural mineral huntite (space group $R32$) [13]. The structure contains helical chains of edge-sharing MO_6 octahedra running along the c-axis of the crystal, interconnected by two kinds of BO_3 triangles and RO_6 distorted prisms. Different RO_6 units do not have common oxygen atoms, which results in a low luminescence quenching. A technology of crystal growth by the solution-melt method is well developed for aluminum and iron borates and big single crystals of good optical quality can be obtained. They are chemically stable and possess good thermal and mechanical properties. Nd and Yb aluminum borates from this family are used as nonlinear active media for self-frequency-doubling and self-frequency-summing lasers [14,15]. Having excellent nonlinear optical properties and a broad optical gap, aluminum borates are effective frequency doublers up to the UV range. Many compounds from the family exhibit multiferroic properties and are considered for applications in modern electronics [16].

2. Experimental

The $RFe_3(BO_3)_4$, R = Pr, Sm, Tb, and Gd single crystals were grown in the Kirensky Institute of Physics in Krasnoyarsk, as described in Ref. [17]. Big transparent single crystals were green in

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color and had a good optical quality. They were oriented using the crystal morphology and optical polarization methods. Polished plane-parallel plates with dimensions up to 5 × 5 × 10 mm and with the *c*-axis lying in the *ab* plane were prepared. Temperature-dependent reflection spectra in the spectral range from 20 to 4400 cm^{-1}, at a resolution 2 cm^{-1} were measured for the π-(k⊥*c*, E||*c*) and σ- (k⊥*c*, E⊥*c*) polarizations of the incident light. To register the spectra of $PrFe_3(BO_3)_4$ and $SmFe_3(BO_3)_4$ in the range of temperatures 2–300 K, we used a Fourier spectrometer Bruker IFS 125 HR with a liquid helium bolometer (4.2 K) as a detector and a closed-cycle cryostat Cryomech ST403. For spectral measurements of $TbFe_3(BO_3)_4$ and $GdFe_3(BO_3)_4$ in the temperature interval from 7 to 300 K, a Fourier spectrometer Bruker 113 and a helium-flow cryostat were used. In what follows, we concentrate on the spectral intervals where manifestations of the electron-phonon interaction in $PrFe_3(BO_3)_4$ and $TbFe_3(BO_3)_4$ are observed, namely, intervals 20–80 and 180–220 cm^{-1}, respectively.

3. The rare-earth iron borates as mirrors for the terahertz radiation

At room temperature, all the studied RE iron borates $RFe_3(BO_3)_4$, R = Pr, Sm, Gd, Tb, possess the trigonal structure described by the space group $R32$ (D_3^7), with one formula unit in the primitive crystal cell. The group-theoretical analysis reveals the following set of optical modes [18]:

$$\Gamma_{\rm opt}(R32) = 7A_1(xx, yy, zz) + 12A_2(\mathrm{E}||\mathrm{z}) + 19E(\mathrm{E}||\mathrm{x}, \mathrm{E}| \times |\mathrm{y};\ xz, yz, xy). \qquad (1)$$

Among them, A_2 and E modes are infrared-active in the π- and σ-polarizations, respectively. The lowest-frequency phonon mode is nondegenerate, has the A_2 symmetry and is associated, mainly, with translational motions of the heavy R^{3+} ions [19]. It manifests itself as a strong π-polarized reflection band with maximum reflectivity close to unity in the frequency region 50–70 cm^{-1} for different $RFe_3(BO_3)_4$ compounds [12,20]. We would like to note that the $RFe_3(BO_3)_4$ crystals can serve as almost ideal mirrors for the terahertz radiation having the bandwidth of about 0.3 THz and the frequency 1.5, 1.65. 1.8, or 2.1 THz when using iron borates with R = Pr, Sm, Gd, or Tb, respectively.

4. Coupled electron-phonon modes in praseodymium iron borate

The praseodymium and samarium iron borates preserve the $R32$ (D_3^7) structure down to the lowest temperatures. Both compounds undergo an antiferromagnetic phase transition at the same temperature of 32 K. In $PrFe_3(BO_3)_4$, the lowest-frequency phonon mode falls into resonance with an electronic excitation corresponding to the transition from the singlet ground Γ_2 state of the Pr^{3+} ion to the first excited Γ_1 one (these states are well isolated from the other crystal-field states) [17]. The 4f electronic and phonon excitations have the same symmetry (Γ_2 and A_2 irreducible representations of the crystal factor group D_3, in the notations accepted for electronic excitations and phonons, respectively) and, thus, are allowed to interact. On the contrary, no electronic excitations exist for $SmFe_3(BO_3)_4$ in this frequency region [21].

To detect spectral signatures of a possible electron-phonon coupling in $PrFe_3(BO_3)_4$, we have compared its temperature-dependent reflection spectra in the frequency range of the considered A_2 phonon with those of $SmFe_3(BO_3)_4$. Fig. 1 demonstrates this comparison. While the corresponding reflection band in $SmFe_3(BO_3)_4$ practically does not change with lowering the temperature [see Fig. 1(a) and (b)], drastic changes are observed in the spectra of $PrFe_3(BO_3)_4$ [Fig. 1(c) and (d)]. A new more narrow band appears at the high-frequency side of this phonon band below ~100 K (well above T_N = 32 K) and grows in intensity with further lowering the temperature [Fig. 1(c) and (d)]. This picture is caused by a growing interaction between the phonon and the 4f crystal-field electronic excitation, accompanied by a mutual frequency repulsion and intensity redistribution. We note that purely electronic 4f excitations cannot be observed in reflection because of their low oscillator strengths. Here, coupled electron-phonon modes are formed. The quasi-electronic mode borrows its intensity from the quasi-phonon mode. Frequencies of the coupled electron-phonon excitations in $PrFe_3(BO_3)_4$ can be found as roots of the following equation [10,22]:

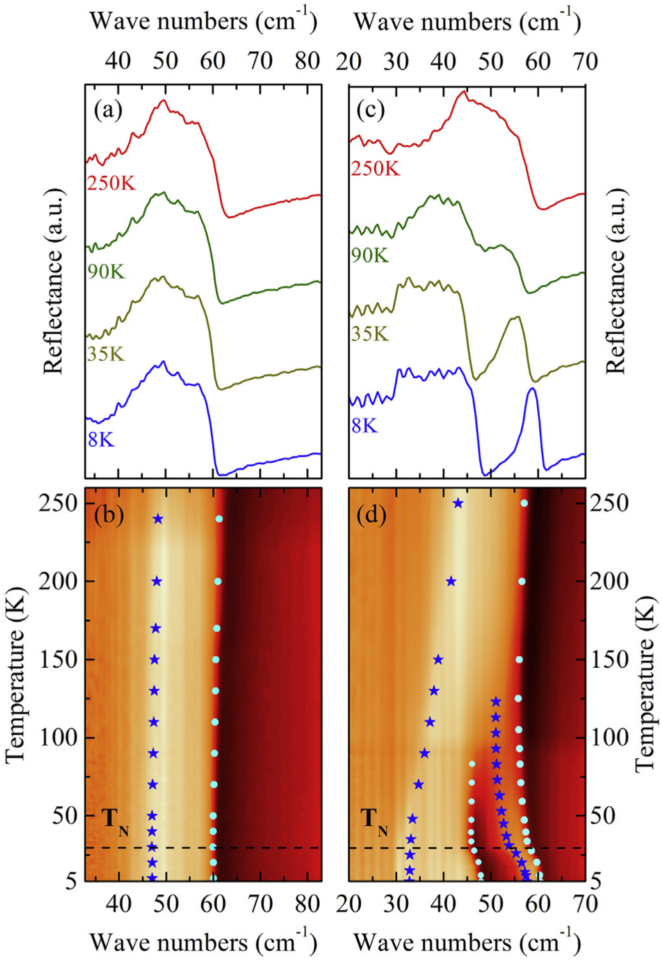

Fig. 1. The π-polarized FIR reflection spectra and the corresponding reflection intensity maps in the frequency-temperature axes for (a,b) $SmFe_3(BO_3)_4$ and (c,d) $PrFe_3(BO_3)_4$, T_N = 32 ± 1 K for both compounds. (b,c) Navy-blue (dark) stars represent ω_{TO} frequencies, blue (gray) circles denote ω_{LO} frequencies. A splitting of the $PrFe_3(BO_3)_4$ phonon reflection band near 50 cm^{-1} below ~ 100 K is seen. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$$\omega^2 - \omega_0^2 + \frac{2\omega_0\omega_{12}(n_1 - n_2)|W|^2}{\omega^2 - \omega_{12}^2} = 0, \qquad (2)$$

where ω_0 and ω_{12} are the frequencies (in cm^{-1}) of the vibrational and electronic excitations, respectively, in the absence of interaction; n_1 and n_2 are relative populations of the excited $|\Gamma_1>$ and ground $|\Gamma_2>$ CF states of Pr^{3+}, respectively; W is the interaction constant between the electronic excitation ω_{12} and the Γ-point A_2^1

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