Electron-phonon resonances in the spectrum of a rare-earth impurity ion

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Splitting of the phonon-free lines was observed in the absorption and fluorescence spectra of the Yb^{3+} ion in the $YAlO_3$ crystal. It is shown that this effect may be due to the electron-phonon resonance.

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The resonance or quasi-resonance of the local electron states with a phonon spectrum of the crystal matrix produces a number of specific effects, including the appearance of bound phonons states—dielectric modes. The theory of these effects[1-4] was used for small impurity centers of semiconductors that absorb light in the far IR region; the corresponding experimental results were reviewed in Refs. 3 and 5. Below, we report the observation of an electron-phonon resonance (EPR) in the absorption and fluorescence spectra of an ionic crystal doped with rare-earth (RE) ions when the optical transitions occurs in the 1 to 2-eV energy region, and the Stark structure of the final-electron state coincides with the phonon resonance. As far as we know, the only reported occurrence of the EPR in this case is the temperature broadening of the phonon-free lines (PFL), which is due to single-phonon, nonradiative transitions between the Stark levels of the RE ion.[6,7]

We shall examine the optical transition from the nondegenerate isolated state $|\Gamma_i\rangle$ to the $|\Gamma\rangle$ level, which is, generally degenerated and isolated from the neighboring level $|\Gamma'\rangle$ by the energy gap $\Omega_{\Gamma'\Gamma} > 0$.[1)] In the case of weak electron-phonon interaction (EPI), which is characteristic for the RE ions, this transition corresponds to a series of Lorentz PFL whose maxima Ω_α are the roots of the equation

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$$\Omega - \Omega_{\Gamma\Gamma_i} = \Sigma(\Omega). \tag{1}$$

Here, $\Sigma(\Omega)$ is the real part of the self-energy function which for the center of the small radius can be written in the form ($T = 0\ K$):

$$\Sigma(\Omega) = \sum_{\bar{\Gamma}} |\langle \Gamma || V_{\bar{\Gamma}} || \Gamma' \rangle|^2 \int \frac{\rho_{\bar{\Gamma}}(\omega) d\omega}{\omega(\Omega - \Omega_{\Gamma'\Gamma_i} - \omega)}, \tag{2}$$

where $\langle \Gamma || \cdots || \Gamma' \rangle$ is a normalized matrix element of the tensor EPI operator, $\bar{\Gamma} \in \Gamma \times \Gamma'$ is the irreducible vibrational representation of the point group of the center, and $\rho_{\bar{\Gamma}}(\omega)$ is the projected phonon density.[7] The PFL function with the subscript α, with an accuracy to a factor that is almost independent of the optical frequency Ω, has the form:

$$F_\alpha(\Omega) = \frac{\bar{\Delta}_\alpha \left(1 - \frac{\partial \Sigma}{\partial \Omega}\Big|_{\Omega = \Omega_\alpha}\right)^{-1}}{(\Omega - \Omega_\alpha)^2 + \bar{\Delta}_\alpha^2/4}, \tag{3}$$

where

$$\bar{\Delta}_\alpha = \Delta(\Omega_\alpha)\left(1 - \frac{\partial \Sigma}{\partial \Omega}\Big|_{\Omega = \Omega_\alpha}\right)^{-1}, \tag{4}$$

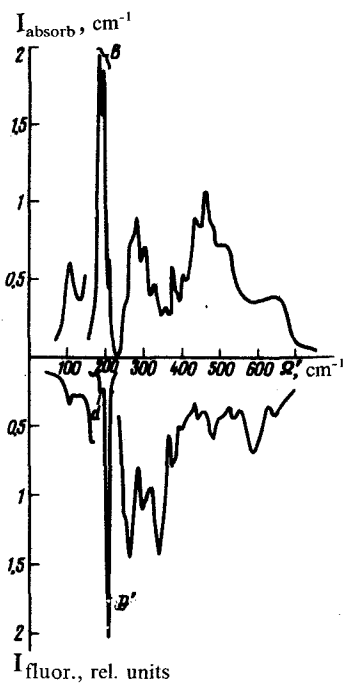

FIG. 1. Absorption and fluorescence spectra of the Yb^{3+} ion in the $YAlO_3$ crystal at 77 K. The wave numbers, which were measured from the location of line C, are plotted along the X axis. The intensities of the D', d and B lines are reduced by a factor of 5 and 7, respectively.

$\Delta(\Omega)$ is the imaginary part of the self-energy function. In the conventional approximation $\Delta(\Omega_{\Gamma\Gamma'})$ is the probability of a single-phonon nonradiative transition $\Gamma \to \Gamma'$.

For the nondegenerate electron states Γ and Γ', which are mixed by a single vibrational mode with the frequency ω_0, Eq. (1) reduces to the quadratic equation

$$\Omega' - \Omega_{\Gamma\Gamma'} - \frac{b}{\Omega' - \omega_0} = 0, \tag{5}$$

where $\Omega' \equiv \Omega - \Omega_{\Gamma'\Gamma_i}$, and we come to the well-known quantum-mechanical problem of quasi-resonant perturbation of a two-level system (see Ref. 8, Sec. 40). The dispersion of crystal vibrations and the degeneracy of the electron states Γ and Γ' greatly complicate the splitting. In this report, we confine ourselves to the analysis of the observed doublet splitting of the B and D' lines in the absorption and fluorescence spectra of the Yb^{3+} ion in $YAlO_3$ (Fig. 1), using the simplified Eq. (5) and the basic relations for the roots $\Omega_{1,2}$ of this equation

$$\Omega_1 + \Omega_2 = \Omega_{\Gamma\Gamma'} + \omega_0, \tag{6}$$

$$\Omega_1 \Omega_2 = \Omega_{\Gamma\Gamma'} \omega_0 - b \tag{7}$$

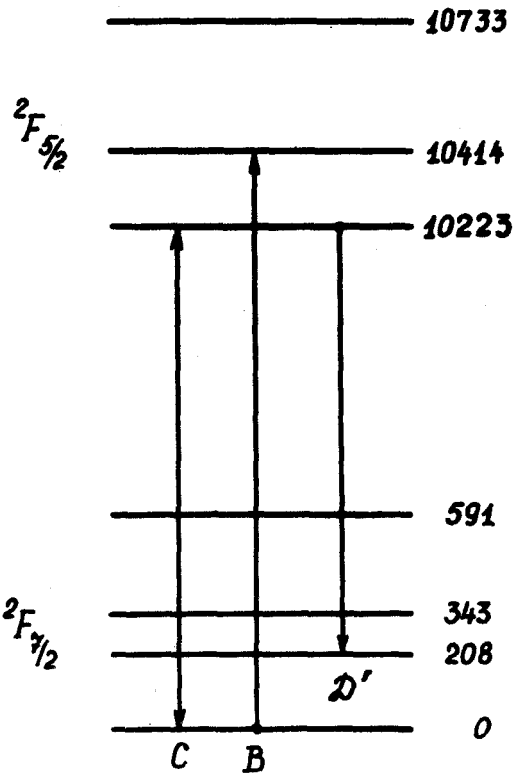

FIG. 2. Stark splitting of the $^2F_{5/2;7/2}$ states of $YAlO_3$:Yb^{3+}. The energies of the Stark components are in cm^{-1}.

and the intensity ratio

$$I_1/I_2 = (\Omega_2 - \Omega_{\Gamma\Gamma'})/(\Omega_{\Gamma\Gamma'} - \Omega_1), \tag{8}$$

which holds for $\bar{\Delta}_1 \approx \bar{\Delta}_2$. It follows from Eq. (8) that for $\omega_0 = \Omega_{\Gamma\Gamma'}$, i.e., for a precise resonance, $I_1 = I_2$; for an imprecise resonance, the split PFL is asymmetrical.

We note that the two-peaked B line and the strong satellite d in the short-wave wing of the D' line cannot be explained in terms of the accepted picture of the Stark splitting of the Yb^{3+} ion states in $YAlO_3$ (Fig. 2).[9] It is unreasonable to attribute these peculiarities to the phonon spectrum of the crystal matrix because of the high intensity of the indicated peaks. For PFL B $\Omega_1 = 185$ cm^{-1}, $\Omega_2 = 198$ cm^{-1}, and $I_1/I_2 = 1.05$. Substituting these data in Eqs. (8), (6), and (7), we obtain $\Omega_{\Gamma\Gamma'} = 191$ cm^{-1}, $\omega_0 = 192$ cm^{-1}, and $b = 42$ cm^{-2}. For this value of ω_0 we obtain from Eq. (6) $\Omega_{\Gamma\Gamma'} = 208$ cm^{-1} for PFL D' for which $\Omega_1 = 190$ cm^{-1}, and $\Omega_2 = 210$; thus, we obtain from Eq. (8) $I_1/I_2 = 0.11$, in good agreement with the experiment. For the D' transition, $b = 36$ cm^{-2}.

Our estimate leads us to think that the indicated features of the spectrum of the Yb^{3+} ions in $YAlO_3$ are actually determined by the EPR, especially since a well-defined peak of the electron-vibrational structure of the R line of the Cr^{3+} ion can be observed in this crystal in the region of 190–200 cm^{-1}.[10] A peak of the Raman scattering of IR radiation can be observed in the same frequency region.[11]

We conclude that the exact location of the electron levels in the resonance with the phonon spectrum does not coincide with any of the observed maxima of the structural PFL. This procedure makes it possible to determine the true location of the electron levels and of the resonance peak of the phonon density.

[1)]The notations of the electron states correspond to the irreducible representations of the point group of the local center.

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