

Local biphonon in an NH_4Br crystal

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It has been observed experimentally for the first time that the phonon-phonon interaction can lead to localization of two phonons on an impurity, each of which separately is not localized on it.

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Three types of interactions make the main contribution to the overtone or combination-transition spectrum of a fine isotropic impurity: phonon-phonon interaction, which strives to combine two phonons into a biphonon; phonon-impurity interaction, which strives to localize the phonon; and, resonant interaction, which leads to delocalization of the excitations. In general, the problem of the spectrum of two-particle states of a crystal with an impurity leads to a three-body problem. The simplest situation occurs for an isolated impurity and point interaction of quasiparticles (Frenkel excitons, intramolecular phonons). However, even in this case, an exact solution was obtained¹ only if one of the quasiparticles has an infinitely large effective mass, i.e., it is stationary. The theory developed in Ref. 1 agrees well with experiment^{2,3} and yields important new information on the interaction of quasiparticles and their density of states.³ For two mobile quasiparticles, the problem is greatly complicated.⁴ As noted in Ref. 5, a strong phonon-phonon interaction, leading to the appearance of a biphonon, forms a localized state in the two-phonon spectrum, even if the phonon-impurity interaction is not strong enough to form a local state in the single-phonon spectrum.⁵ In this paper, we report for the first time an experimental investigation of this situation.

We studied experimentally the Raman light scattering spectra for the internal vibration ω_4 and its overtone in the low-temperature δ phase of the NH_4Br crystal with the isotope ^{15}N as the impurity (symmetry T_d^1). The Raman spectra were excited by an argon laser ($\lambda = 514.5$ nm, with power up to 1 W) and were recorded by a Spex Ramalog spectrometer. All spectra were obtained at $T = 77$ K.

Two narrow lines (with a width not exceeding 0.2 cm^{-1}), corresponding to TO (1397.5 cm^{-1}) and LO (1413.5 cm^{-1}) phonons, are observed in the crystal with the natural content of the ^{15}N isotope in the region of single-phonon $\omega_4(\mathbf{k} \cong 0)$ transitions. In the isotropically mixed crystal $^{15}\text{N}_x$ $^{14}\text{N}_{1-x}\text{N}_4\text{Br}$ ($x = 0.05$ and 0.3), there is an insignificant broadening and shift of these lines. The absence of local vibration and the typically single-mode behavior of the spectrum are explained by the fact that the phonon-impurity interaction, which is characterized by the isotropic shift $\Delta_4 = -6$ cm^{-1} ,⁶ in the case studied, is small compared to the resonant interaction, which is characterized by a single-phonon bandwidth $T_4 = 36$ cm^{-1} [estimates from the width of the $\omega_4(\mathbf{k}) + \omega_4(-\mathbf{k})$ band].

The Raman spectra of the completely symmetrical overtones of transitions in the crystal with a natural content of the isotope ^{15}N (0.37%) is presented in Fig. 1a. The 2795 to 2867 - cm^{-1} band corresponds to the two-particle transitions $\omega_4(\mathbf{k}) + \omega_4(-\mathbf{k})$. Its

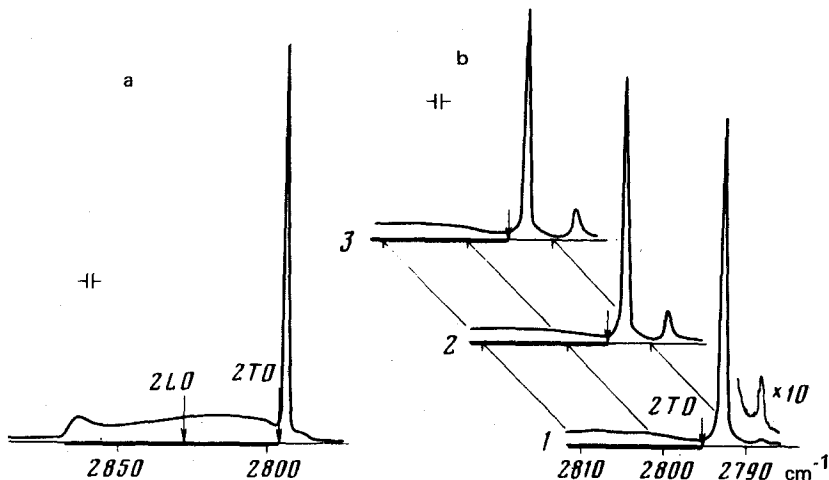


FIG. 1. Raman scattering spectra of $^{15}\text{N}_x^{14}\text{N}_{1-x}\text{H}_4\text{Br}$ crystals in the region of $\omega_4(\mathbf{k}) + \omega_4(-\mathbf{k})$ transitions at $T = 77$ K and a $K(XX)Y$ geometry; the region of two-particle transitions is separated: the arrows indicate the doubled frequencies $\omega_4(\mathbf{k} \cong 0)$ to TO and LO phonons. a) $x = 0.0037$; b) 1 is for $x = 0.0037$, 2 is for $x = 0.05$, and 3 is for $x = 0.3$.

low-frequency boundary coincides with the doubled frequency of the TO phonon $\omega_4(\mathbf{k} \cong 0)$, while the width (according to the selection rules) is equal to the double d width of the spectrum of $\omega_4(\mathbf{k})$ states. The narrow 2792.5-cm^{-1} line, which is situated below the region of two-particle transitions, belongs to the single-particle (biphonon) transition $\omega_{44}(\mathbf{k} \cong 0)$. Its presence in the spectrum indicates the strong phonon-phonon interaction. The anharmonic shift characterizing this interaction is $\Delta_{44} = -30$ to -35 cm^{-1} (according to estimates presented in Ref. 3).

The observed spectrum and its interpretation as a whole agree with the results in Ref. 7. In addition, an additional line $\omega'_{44} = 2788\text{ cm}^{-1}$, whose intensity is about 1.5% of the biphonon line intensity (Fig. 1b), was discovered in the crystal with the natural content of the ^{15}N isotope. When the isotope concentration increases, the relative integral intensity of the line ω'_{44} increases (up to approximately 15% with $x = 0.05$ and 33% with $x = 0.3$). Therefore, this line corresponds to a two-phonon state localized on the impurity (local biphonon).

We point out the following characteristics of the picture observed.

1) the distance between the biphonon and local biphonon lines $\omega_{44}(\mathbf{k} \cong 0) - \omega'_{44} = 4.5\text{ cm}^{-1}$ is much shorter than the isotopic shift of the overtone in the isolated ion $2\Delta_4 = -12\text{ cm}^{-1}$.⁶ This fact can apparently be explained by an incomplete localization of the overtone excitation, which is also indicated by the small splitting of the biphonon from the two-particle transition spectrum and the appreciable intensity of the latter.

2) In the crystal with the natural isotopic composition, the ratio of the local and principal biphonon line intensities exceeds by almost a factor of 4 the relative content of the impurity. Taking into account the fact that the splitting of the local biphonon is less than the isotopic shift, the amplification of this line can be explained by the manifesta-

tion of the second-order Rashba effect in the spectra.⁸ Until now, the amplification of the impurity band was observed only in spectra of the principal transitions (electronic⁸ and phonon³). The results obtained here show that in the presence of a bound state the Rashba effect can also occur in the two-phonon spectra.

3) An increase in the impurity concentration leads to a low-frequency shift in the line ω'_{44} (by 1 cm^{-1} for $x = 0.3$), its broadening (up to 1.8 cm^{-1} at $x = 0.3$), and the appearance of a low-frequency wing in its profile (Fig. 1b). The spectra $\omega_4(\mathbf{k}) + \omega_4(-\mathbf{k})$ and $\omega_{44}(\mathbf{k} \cong 0)$, in this case remain essentially constant. The reasons for such a concentration dependence of the spectra require further theoretical analysis.

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