Interference between overtone states of an impurity and the host lattice in an NH_4Cl crystal

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The case when an impurity that does not give rise to a local vibration in the first-order spectrum produces a sharp singularity in the two-phonon transition spectrum is investigated for the first time ever. It is observed that introduction of $N^{15}H_4^+$ ions in an $N^{14}H_4Cl$ crystal produces a narrow dip in the band of the quasibound two-phonon $\omega_4 + \omega_4$ transition.

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The spectrum of combination transitions of a shallow impurity center is determined both by the resonant interaction of the impurity vibrations with the host lattice and by the anharmonic interaction of the vibrations. We have found in an earlier experiment[1] that in the case of partially delocalized vibrations of the impurity the anharmonicity can lead to their localization and to the appearance of an additional band of local vibrations in the spectrum of the combination transitions. As shown theoretically by Agranovich,[2] the stronger anharmonicity that causes formation of a bound two-phonon state (biphonon) can lead to the appearance in the second-order spectrum of a local vibration also in the case when in first order the vibrations will be delocalized. Preliminary estimates have shown that this situation is possibly realized in the vibrational spectrum of the NH_4Cl containing $N^{15}H_4^+$ ions as impurities.

We report here an experimental investigation of the Raman scattering of light (RSL) of the ω_4 vibration and of its overtone in natural and isotopically substituted crystals of ammonium chloride (space group T_d^1, one formula unit per cell). To register the RSL spectra we used a monochromator with Spex–Ramolog holographic gratings at a spectral width of the slit from 0.25 to 1 cm^{-1}. The excitation was with an argon laser of wavelength 514.5 nm and power up to 1 W. All the spectra were investigated at a sample temperature $T \approx 80$ K.

The first- and second-order spectra of the NH_4Cl crystal have been investigated in sufficient detail (see, e.g., Refs. 3 and 4). In the region of the ω_4 oscillation, two narrow lines (width not larger than 0.2 cm^{-1}) are observed, corresponding *TO* (1402 cm^{-1}) and *LO* (1420 cm^{-1}) phonons. When isotopically substituted $N^{15}H_4^+$ ions (up to 10%) are introduced into the crystal, these lines broaden insignificantly and shift towards the lower frequencies; in addition, a weak continuous spectrum appears in the region 1400–1450 cm^{-1} as a result of the presence of the impurity. The width of the induced spectrum agrees with the width of the ω_4 band in the NH_4Cl crystal. An additional argument confirming the considerable dispersion of the ω_4 vibration is the width, approximately 100 cm^{-1}, of the spectrum of its overtone transition (see below). Thus, the width of the ω_4 band is 50 cm^{-1}. No local ω_4' vibration of the $N^{15}H_4^+$ ions is observed, a fact attributed to the small isotopic shift [$\Delta = -6$ cm^{-1} (Ref. 5)] compared with the width of the band, i.e., the spectra of the crystal $N_x^{15}N_{1-x}^{14}H_4Cl$ exhibit in the ω_4 region a typical single-mode behavior.

We consider now the $\omega_4 + \omega_4$ overtone transition. The forms of the RSL spectra, in polarizations corresponding to the A and F_2 irreducible representations, are quite different (Fig. 1a).[1)] In the polarization $z(yz)y$ (F_2), a broad band is observed in the interval 2800–2900 cm^{-1}. In the spectrum of symmetry A, the low-frequency edge of the broad band has a sharp peak (2804 cm^{-1}), which was interpeted in Ref. 3 as manifestation of a biphonon. The biphonon is produced on account of the anharmonicity, which in the case of an isolated molecule leads to an anharmonic shift of the frequencies of the combination transitions. The difference between the spectra of the A and F_2 symmetry is due to different selection rules for two-phonon transitions and to the different values of the anharmonicity constants for different types of vibrations.

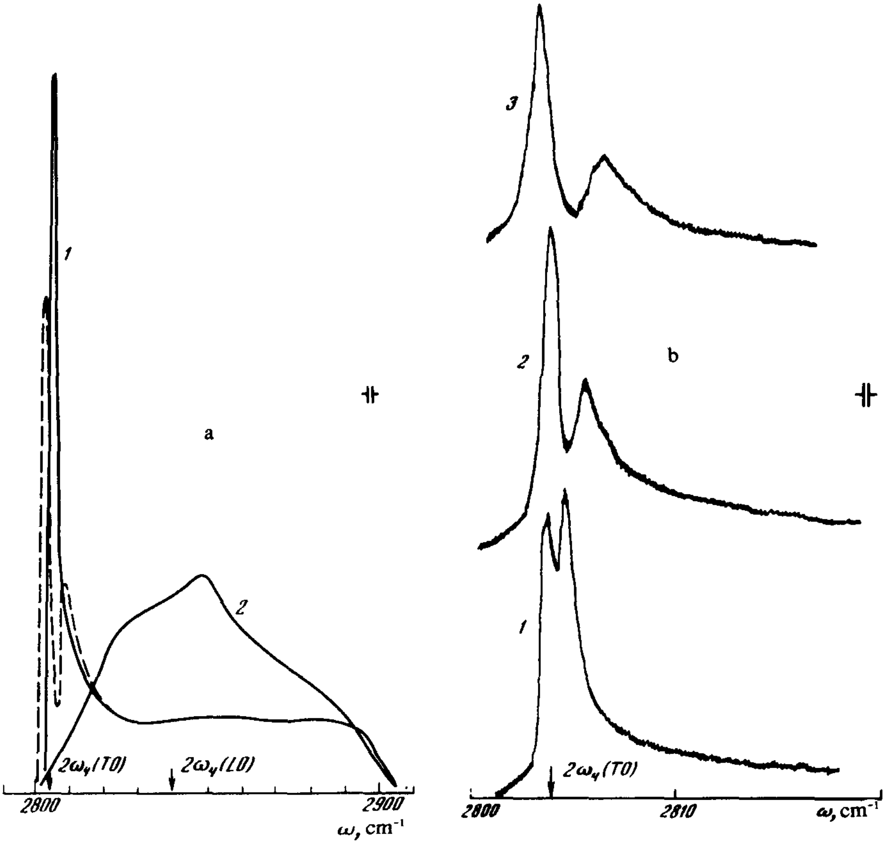

FIG. 1. RSL spectra of NH_4Cl crystal in the region of the $\omega_4 + \omega_4$ two-phonon transitions at $T = 80$ K: a1) $z(xx)y$ geometry ($A + E$ symmetry), a2) $z(yz)y$ geometry (F_2 symmetry). Solid line—crystal with natural content of N^{15}, dashed—10% N^{15}. b) $z(xx)y$ geometry, spectral width of the slit 0.25 cm^{-1}: 1—0.37%, 2—2%, 3—5% of the N^{15} isotope.

According to the theory,[2] if there is no local vibration in the first-order spectrum this vibration may be detached from the biphonon band, since this band must be much narrower than the band of the main transition. In this case an additional weak line should be located at an approximate distance 2Δ below the biphonon band.

The experimentally observed picture, however, does not fit the case considered in Ref. 2. Introduction of the isotopic ions $N^{15}H_4^+$ does not produce an addition line in the A-symmetry spectrum, but produces a narrow dip on the biphonon band with a frequency almost equal to double the $\omega_4(TO)$ frequency (see Fig. 1). When the concentration of the impurity ions is increased, the spectrum shifts towards the low-frequency side, and the dip stays practically in place but broadens substantially. Measurements with an extremely narrow spectral slit (0.25 cm^{-1}) have shown that even the natural content of N^{15} (0.37%) leads to the appearance of a dip at the very maximum of the $2\omega_4$ band (Fig. 1b).

It is still impossible to estimate quantitatively the effect observed in the present study, that of the influence of the impurity in the spectrum of second order, since there is no corresponding theoretical analysis. However, using the results obtained by Rashba[6] for vibronic spectra of molecular crystals we can propose the following qualitative explanation.

We note first, that the 2804 cm^{-1} peak observed in the spectrum of the pure NH_4Cl lies on the edge of the band of the dissociated states, the lower limit of which is determined by double the frequency of the TO oscillation [$2\omega_4(TO) = 2804$ cm^{-1}]. The low-frequency edge of this line is very sharp, whereas the high-frequency edge goes over smoothly into the continuum of the dissociated states. All this is evidence that not a biphonon but a quasibound state has been observed in the A-symmetry spectrum. One can then expect the introduction of $N^{15}H_4^+$ ions (the isotopic shift for $2\omega_4$ is -12 cm^{-1}) to lead to formation of a quasilocal quasibound state of the impurity. The spectrum of such a state should have an even narrower peak with frequency likewise on the lower edge of the band. The appearance of a narrow dip in the spectrum of a crystal with isotopic impurity is apparently due to interference between resonant (in frequency) states of the host crystal and of the impurity.

[1)] There is practically no spectrum if the polarization corresponds to the E irreducible representation.

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