Fermi resonance between polaritons and a two-particle state band in the vibrational spectrum of ammonium chloride

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The Raman scattering spectrum for an ammonium chloride single crystal at $T = 80°K$ is measured in the range of small scattering angles. That region of the dissociated-state band, which is due to overtone transitions $2\nu_4(F_2)$, is investigated. The study is carried out with an argon laser and photographic recording of the spectrum. The dispersion law for the polariton branches near the two-particle state band is formulated on the basis of the spectrum obtained, and the theory is compared with the experimental results. A small section of the polariton branch is observed in the dissociated-state band itself. A "gap" in the polariton scattering spectrum is found to arise within the band.

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INTRODUCTION

The phenomenon of Fermi resonance is observed in isolated molecules if the frequencies of the overtone (the composite tone) is close to another fundamental oscillation.[1)] In the case of crystals, a polariton Fermi resonance is also possible[1-9] and arises when the frequencies of the polariton and of the overtone (composite tone) active in the absorption spectrum are close. One of the most effective methods of investigating Fermi resonance is Raman scattering (RS), and polariton Fermi resonance was investigated by this method in a number of studies.[4-9]

It should be noted that in crystals, in contrast to liquids, in the region of overtones and composite tones there can appear broad bands due to the dissociated two-phonon excitations of the crystal. In addition, under conditions of strong anharmonicity, sharp intensity peaks can appear near broad bands, owing to the formation of bound states[2,10] corresponding to biphonons or vibrational biexcitons (in the case of intramolecular vibrations).

The polariton branches can intersect either with the biphonon branches or with the bands of the two-particle states (broad bands). In the general case it is therefore necessary to distinguish between two types of polariton Fermi resonance, namely resonance of the polaritons with the branch of the bound states, and resonance of the polaritons with the band of the two-particle (dissociated) states.

The singularities of the polariton Fermi resonance were theoretically investigated by a number of workers.[1-3] In particular, Agranovich has concluded that in the case of polariton resonance with a dipole-active biphonon a characteristic "gap" should appear in the polariton spectrum; on the other hand, if the polaritons intersect with the band of the two-particle states, no gap should appear. In the latter case one should expect only the possibility of a nonmonotonic change of the polariton frequency, and also a strong broadening of the corresponding Raman lines.

The gap in the polariton spectrum in the region of the overtones and composite tones was observed in [4-6]. The results of these experiments, however, can have an ambiguous interpretation, owing to the presence in the investigated spectral region of a weak first-order Raman scattering line with a symmetry different from the polariton symmetry.[2)]

Three closely-lying gaps were observed in $LiIO_3$ crystal[9] in an overtone region far from the frequencies of the fundamental vibrations. The behavior of the polariton branches near the gaps was described by introducing additional oscillators with frequencies corresponding to the positions of these gaps. We note that this is valid only if bound states are present. To ascertain the presence of bound states in this crystal, however, a detailed investigation is necessary of the spectra of the 90° RS, as well as more accurate information on the dispersion of the polarization in the region of the gaps.

The presence of a gap in the polariton branch under the conditions of Fermi resonance was observed also in crystalline $LiNbO_3$.[7,8] The presence of a gap in this crystal was attributed in [7], in accord with the theory,[8] to the existence of a biphonon. Another argument in favor of the assumption was that the position of the gap in the polariton spectrum turned out to be shifted 13 cm^{-1} relative to the end point of the two-particle state band as observed in 90° scattering.[3)] The results of the cited experimental papers seem to us, however, to be insufficient to prove the existence of phonon bound states in the investigated crystals. We therefore consider it quite important to investigate the behavior of the polariton branch of the dissociated state of the phonons under conditions of polariton Fermi resonance.

In this paper we present the results of an investigation of polariton Fermi resonance in the region of the band of two-particle states in the low-temperature modification of ammonium chloride.

1. STRUCTURE AND VIBRATIONAL SPECTRUM OF AMMONIUM CHLORIDE

Ammonium chloride exists at room temperature[13] in the form of a structure of the CsCl type with disordered groups of ammonium (phase II). Cooling produces a phase transition (at 243°K) into the low-temperature modification (phase IV[4)]). The low-temperature modification constitutes[14] a structure of the CsCl type with ordered $(NH_4)^+$ groups. The space group for this modification is $T_d^1(P\bar{4}3m)$, and the symmetry group

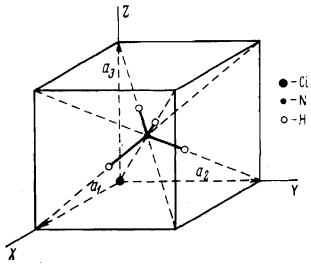

FIG. 1. Unit cell of low-temperature (IV) phase of ammonium chloride.

of the directions is $T_d(\bar{4}3m)$; the unit cell (Fig. 1) contains one formula unit.

The RS spectrum of phase IV of ammonium chloride reveals[15-17] external vibrations (motions of the $(NH_4)^+$ group relative to the chlorine) and internal vibrations of the ammonium group.[5)] In the region of the internal vibrations, there is a polar vibration of type F_2, which gives rise to transverse (ν_{4t} = 1400 cm^{-1}) and longitudinal (ν_{4l} = 1418 cm^{-1}) components, nonpolar degenerate vibration ($\nu_2(E)$ = 1716 cm^{-1}), nonpolar fully-symmetrical vibration ($\nu_1(A_1)$ = 3042 cm^{-1}), and also two pairs of transverse and longitudinal components resulting from Fermi resonance in the region of the polar vibration $\nu_3(F_2)$ (3100 cm^{-1}).

In the same spectral region there appear second-order satellites. In particular, two-particle RS scattering processes are observed[16,17] and are connected with an overtone of the first polar oscillation in the 2800 cm^{-1} region. The RS spectrum contains in this case a broad band (2805–2925 cm^{-1}) corresponding to dissociated two-particle excitations, and a sharp peak due to the bound state (vibrational biexciton). Polarization measurements have shown[17] that the bound state corresponds in this case to a dipole-inactive transition; thus, the presence of vibrational biexciton should not lead to a gap in the polariton spectrum. On the other hand, it was established[17] that the discussed two-particle dissociated excitations are dipole-active and can accordingly interact strongly with polaritons.

2. EXPERIMENTAL PROCEDURE

The polariton RS spectra were investigated by a known procedure[6] using a telescope system; the scattering was investigated in the angle range from 0 to 8°. We used a scattering geometry $Y(ZX)Y + \Delta Z$, which made it possible to separate the dipole-active oscillations. To excite the RS spectra we used a Spectra-Physics argon laser of power up to 2 W in the λ = 5145Å line. The spectra were photographed with an ISP-51 spectrograph. The excited radiation past the investigated crystal was attenuated with the aid of a CdS single crystal. The exposure amounted to several times ten minutes.

The investigated single crystals, grown from the saturated solution, were right-angle prisms (~1 cm) with face orientations (100), (010), and (001). The measurements were performed at a crystal temperature T = 80° K.

3. EXPERIMENTAL RESULTS AND THEIR REDUCTION

Figure 2 shows a section of the RS spectrum at small angles in NH_4Cl. The lowest-frequency satellite in the figure corresponds to the first polar vibrational exciton

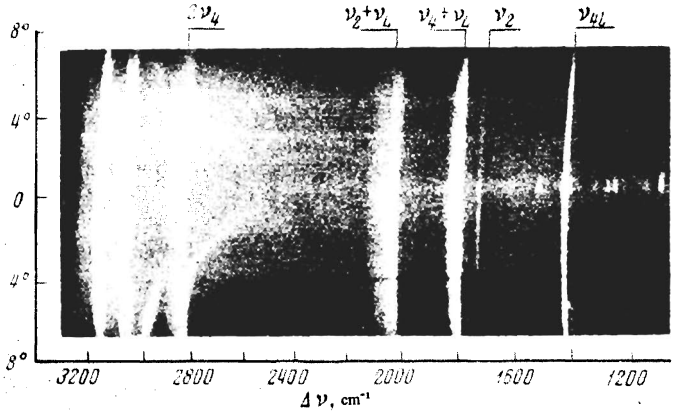

FIG. 2. Spectrum of the Raman scattering of light at small angles in phase IV of ammonium chloride in the region of intramolecular vibrations; the polariton section is seen in the region = 2800 cm^{-1}.

$\nu_4(F_2)$; the next weak line corresponds to the degenerate nonpolar vibration $\nu_2(E)$; next there are two bands of two-particle excitations due to combinations of $\nu_4(F_2)$ and $\nu_2(E)$ with vibrational oscillations of the $(NH_4)^+$ group; in the 2800 cm^{-1} region we see a broad band[6)] due to scattering by the dissociated states ($2\nu_4(F_2)$). A characteristic polariton "bell" is seen in the same region.

As seen from Fig. 2, near the band of the two-particle states ($2\nu_4(F_2)$) there is observed an appreciable distortion of the polariton sections of the spectrum; in the band itself, the polariton satellites become rapidly smeared out and merge with the general background due to the two-photon scattering processes.

The observed spectrum shows also the weakening of the intensity in the polariton section when the scattering angle is decreased; this is due to the form of the RS tensor for the considered vibrations.

The obtained spectra were used to deduce the dispersion law for the polariton branch near the band of the two particle states ($2\nu_4(F_2)$). We used here the relation

$$k=2\pi[(\nu_0 n_0)^2+[(\nu_0-\nu)n']^2-2\nu_0(\nu_0-\nu)\times n_0 n'\cos\theta]^{1/2},$$

obtained from the conservation laws in the elementary scattering process in a cubic crystal. Here k and ν are the wave vector and the wave number of the polariton (in cm^{-1}); ν_0 is the wave number of the exciting radiation; n_0 and n' are the corresponding refractive indices for the exciting and scattered radiation; θ is the angle of the scattering in the crystal. To find the refractive indices n_0 and n' we used an approximation in the form

$$n=B+A/\lambda^2,$$

where the parameters A and B were determined with the aid of data given in [18] on the refractive index of ammonium.

The obtained experimental plot of $\nu(k)$ is shown in Fig. 3. The same figure shows an analogous plot (dashed) constructed using the known dispersion law for polaritons in cubic crystals:

$$\nu=\frac{k}{2\pi\sqrt{\varepsilon(\nu)}},\quad \varepsilon(\nu)=\varepsilon(\infty)\prod_j\frac{\nu_{jl}^2-\nu^2}{\nu_{jt}^2-\nu^2}.$$

In the last expression, account is taken of four polar

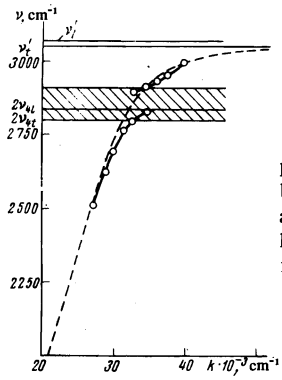

FIG. 3. Dispersion law $\nu = \nu(k)$ for the polariton branch in the region of the band of the two-particle states; ν_t' and ν_l' are the frequencies of the transverse and longitudinal iscillations of type F_2 that follow the band of the two-particle states.

oscillations with frequencies ν_{jl} = 275, 1418, 3070, and 3159 cm^{-1} and ν_{jl} = 188, 1400, 3052, and 3122 cm^{-1} (the frequencies were taken from experiments on 90° Raman scattering;[16,17] for $\epsilon(\infty)$ we used the value $\epsilon(\infty) = 2.7$ given in [16]). The limits of the investigated band of the two-particle states are marked in Fig. 3 in accordance with the results of [17]. As seen from this figure, on the low-frequency end there is small section of RS by polaritons in the band of the two-particle states itself. With further increase of frequency we observe (see Fig. 2) a broadening of the RS line by the polaritons. This broadening increases with increasing wave vector of the polariton, and this leads in final analysis to a merging of the polariton band with the two-particle state band. Raman scattering by polariton then appears again near the upper end of the two-particle state band at lower values of the wave vectors.

We note that the merging of the upper and lower sections of the polariton band with the band of the two-particle states (Fig. 2) occurs at greatly differing values of the polariton wave vectors, and this corresponds to the presence of a gap in the region of the dissociated states.

4. DISCUSSION OF RESULTS AND CONCLUSION

We have thus established in this study that a gap can appear in the polariton spectrum in the case of Fermi resonance of polaritons with the band of the two-particle states. We have observed, in addition, the existence of a small section of a polariton branch in the two-particle state band itself; the accompanying strong broadening agrees with the predictions of the theory.[3]

In accordance with the results, it must be concluded that the presence of the gap in the polariton scattering spectrum under conditions of Fermi resonance is not always due to the existence of bound states of the phonons in the crystal. To prove the existence of bound states in the polariton region it is necessary to identify in the RS spectrum, besides the gap due to the single-particle excitations, also the band of the dissociated states.

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[1)] A necessary resonance condition is in this case also that the symmetry types of the interacting vibrational terms coincide.

[2)] In this case the gap in the frequency-angle spectrum can result also from anti-intersection of the branches [11,12].

[3)] No two-particle-state band was observed in [7] in the polariton RS spectrum.

[4)] Phase III, which is characterized by antiparallel ordering of the $(NH_4)^+$ groups, is not produced under ordinary conditions.

[5)] The internal vibrations in the crystal lead to vibrational excitations called vibrational excitons.

[6)] The sharp peak due to the vibrational biexciton does not appear in the employed scattering geometry.

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