Raman scattering of light in ammonium chloride under conditions of polariton Fermi resonance

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We investigated Raman scattering at small angles in the low-temperature modification of ammonium chloride in the range 2500–3200 cm^{-1}. We studied the polariton Fermi resonance in the region of the bound dipole-active state of the crystal near $\nu_2(E)+\nu_4(F_2)$, and also studied in greater detail than in the earlier investigations the polariton Fermi resonance in the region of two-particle states. The investigation was carried with an STÉ-1 spectrograph and an argon laser. The existence of a gap on the polariton branch is established in the region of the bound dipole active state, and the character of the variation of the intensity and width of the polariton satellites in Raman scattering as the Fermi resonance is approached is studied. The results are compared with the theory.

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Any number of recent theoretical papers [1-5] have demonstrated the possible existence of phonon excitations—biphonons or vibrational biexcitons—in the vibrational spectra of crystals (in the case of intramolecular vibrations). In addition, the existence [4,5] of bound states was predicted in the polariton region under conditions of polariton Fermi resonance. Polariton Fermi resonance takes place when the polariton branch "intersects" with the branch of the dipole-active bound state (vibrational biexciton) or the band of the dissociated vibrational excitations in the crystal. Theory [4,5] has predicted the formation of a gap in the polariton spectrum in the region of the "intersection" of the dispersion curve of the polaritons and the bound dipole-active vibration of the crystal. We note that in crystals it is possible to have also Fermi resonance as a result of pure mechanical anharmonicity, when the frequencies of the fundamental oscillations of corresponding symmetry fall in the region of the overtones or composite tones. As shown in [3,4], in this case effects of hybridization of single-particle states with two-particle states can take place, accompanied by formation of bound states and by increasing intensities of the corresponding Raman scattering (RS) lines.

Of particular interest is the situation when both the purely mechanical anharmonicity and interaction of the mechanical vibrations with the electromagnetic ones are large. This cannot occur in that part of the spectrum in which the polariton branch "intersects" with the branches of the dipole-active overtones or composite tones, which are enhanced as a result of hybridization effects. This type of resonance will henceforth be called complex polariton Fermi resonance.

The appearance of bound states in the region of vibrational excitons in the investigation of RS at large angles was reported earlier [6-9]. In particular, the effects of hybridization of single-particle excitations with two-particle excitations were observed [8,9] in the investigation of RS in ammonium chloride. Thus, the existence of bound states for mechanical vibrational excitations can be regarded as established.

Polariton Fermi resonance was investigated in a number of experimental studies [10,11]. In particular, it was observed in [11] that in the region of the two-particle state band $2\nu_4(F_2)$ a gap is observed in the polariton spectrum of ammonium chloride. The question of the existence of the gap in the region of the dipole-active bound states, predicted by the theory [4], has so far remained open, as noted in [11].

In the present study we investigated RS at small angles in the low-temperature phase of ammonium chloride. We investigated the complex polariton Fermi resonance in the region of high-frequency oscillations of the $(NH_4)^+$ group. In addition, we studied in greater detail[1)] than in [11] the region of the polariton Fermi resonance with the two-particle state band (2800 cm^{-1}).

EXPERIMENTAL PROCEDURE

The polaritons were studied by photographing the RS spectra. Since we investigated polaritons due to intermolecular vibrations with high frequencies (~3000 cm^{-1}), it was necessary to ensure sufficiently large angles of gathering the scattered radiation. We used accordingly a telescopic system with direct (along the optical axis of the spectrograph) and oblique passage of the exciting-light beam (Figs. 1a and 1b).

To excite the RS spectra we used an argon laser of power ~2 W in each of the most intense lasing lines (λ = 5145 Å and λ = 4880 Å). The spectra where photographed with an STÉ-1 spectrograph with dispersion 10 Å/mm. After passing through the investigated crystal, the exciting radiation was attenuated by an absorption filter. The maximum exposure was one hour. The ammonium-chloride single crystals were right-angle

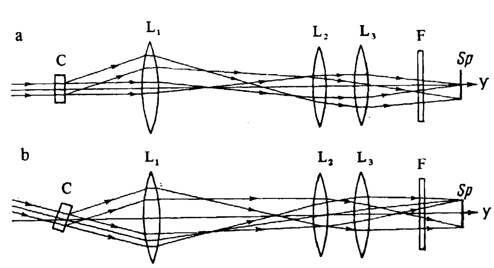

FIG. 1. Experimental setup. a—laser beam propagates along the optical axis Y of the spectrograph and is incident perpendicular to the (010) surface of the crystal C; L_1, L_2, L_3—lenses, F—filter, Sp—spectrograph slit (the Z axis is in the plane of the figure); b—laser beam directed at an angle to the optical axis.

prisms (~1 cm) with faces (100), (010), and (001). The measurements were performed using a vacuum nitrogen cryostat; the sample temperature was about 80°K.

EXPERIMENTAL RESULTS

Figure 2 shows sections of the RS spectra at small scattering angles in the investigated single crystal; Fig. 2a corresponds to passage of the exciting-radiation beam along the system axis (Fig. 1a); the spectra in Figs. 2b and 2c were obtained for oblique incidence of the laser beam (Fig. 1b). The use of a polarizer and analyzer has made it possible to separate the polar oscillations of type F_2, which appear in the geometry Y(Z, X)Y (the indices in the parentheses specify the polarization of the incident and scattered light, the outside indices specify the direction of propagation of the incident and scattered radiation), from the nonpolar oscillations of type A_1 and E. In all the figures one can clearly see the polariton sections in the region of the two-particle state band (2800 cm^{-1}), near the fully-symmetrical oscillation $\nu_1(A_1) = 3042$ cm^{-1} and in the region of the complex polariton Fermi resonance a composite tone $\nu_2(E) + \nu_4(F_2)$ ($\nu_2(E) = 1716$ cm^{-1}, $\nu_{4t} = 1400$ cm^{-1}, $\nu_{4l} = 1418$ cm^{-1}) with fundamental dipole-active oscillation $\nu_3(F_2)$ ($\nu_{3t}(F_2) = 3122$ cm^{-1}, $\nu_{3l}(F_2) = 3159$ cm^{-1}). The general form of the polariton spectrum in the region of the two-particle state band (2800 cm^{-1}) agrees with the earlier results.[11] In particular, one can clearly see the gap in the polariton branch in the region of the discussed band.[2)] A small polariton section is noticeable also in the dissociated-state band (near the low-frequency boundary of this band). A strong smearing of the polariton branch on "entering" the band is also seen, in agreement with the theoretical results.[5]

It can also be concluded from the presented spectrum that the polariton branch touches the high-frequency boundary of the dissociated-state band.

The intensity of RS by polaritons (Fig. 2) increases when the polariton branch approaches the lower edge of the band; after "leaving" the band, the intensity turns out to be somewhat lower than at the lower edge of the same band. With further increase of frequency, the intensity of the RS by the polaritons increases sharply, apparently as a result of the approach to the region of the complex polariton Fermi resonance.[3)]

This region of the spectrum contains a transverse and longitudinal component ($\nu_t' = 3052$ cm^{-1}, $\nu_l' = 3070$ cm^{-1}) of the bound state enhances the result of the effects of hybridization of the composite tone $\nu_2(E) + \nu_4(F_2)$ with the fundamental oscillation $\nu_3(F_2)$.[8] The bound states are followed by a dipole-active band of dissociated states, surrounded on both sides by smeared polariton sections (ν_{3t} and $\tilde{\nu}$). Just as for the band in the 2800 cm^{-1} region, a gap is observed here for the polariton branch as a result of the Fermi resonance of the polaritons with the band; in this case, however, the picture of the formation of the gap is less clearly seen because of the strong broadening of the polariton curve.

The polariton branch that follows the discussed band becomes constant in frequency with increasing scattering angle. This corresponds to the transformation of the polariton into a pure mechanical oscillation ($\nu_{3t}(F_2) = 3122$ cm^{-1}). The intensity of the RS by this branch turns out to be somewhat smaller than the intensity of

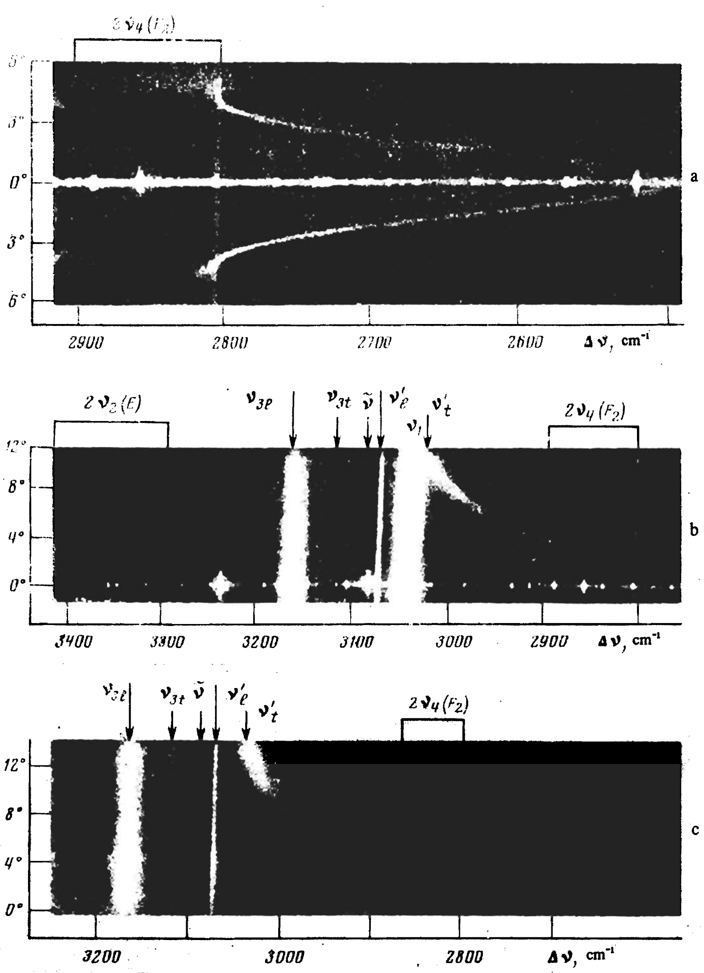

FIG. 2. Sections of the SR spectrum at small scattering angles in single-crystal ammonium chloride (T = 80°K; a, b—without polarization attachments; c—with polarization attachments (geometry Y(ZX)Y + ΔZ). The small arrows correspond to polaritons and the large arrows to longitudinal vibrations.

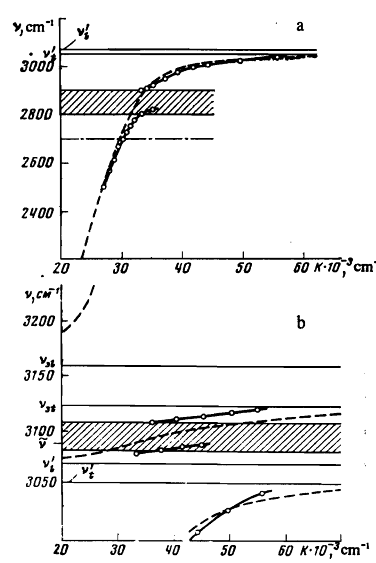

FIG. 3. Dispersion curve for polaritons; a—region of Fermi resonance of the polaritons with the two-particle state band $2\nu_4(F_2)$; b—region of complex polariton Fermi resonance. The solid curves represent the experimental data of the present study; the theoretical curves are dashed; the dash-dot line marks the position of a break that is noted only at large exposures.

the scattering by polaritons at the low-frequency edge of the region of the complex Fermi resonance.

The observed spectrum shows also a longitudinal oscillation $\nu_{3l}(F_2) = 3155\ cm^{-1}$ and a fully-symmetrical oscillation $\nu_1(A_1) = 3042\ cm^{-1}$ (the latter oscillations are strongly suppressed in the Y(Z, X)Y geometry). In addition, two bands are present near the frequency $\nu_{3l}(F_2)$ (Fig. 2b, narrow on the right and broad on the left) due to combinations of $\nu_1(A_1)$ with the translational lattice vibrations. [8] A weak band is also observed in the region $2\nu_2(E)$.

DISCUSSION OF RESULTS AND CONCLUSIONS

From the experimental dependence of the polariton frequency on the scattering angle it is possible to plot dispersion curves (the dependence of the frequency ν on the wave vector K) for the polaritons in the discussed region of the spectrum (see [11]).

The obtained curves are drawn solid in Fig. 3. The same figure shows the theoretical plot [4] constructed in exactly the same manner as in [11]. On Figs. 3a and 3b are marked the frequencies of the corresponding transverse and longitudinal polar oscillations and the positions of two dipole-active bands of the two-particle excitations in accordance with the obtained spectrum.

A gap of width $\sim 100\ cm^{-1}$ is observed on the polariton curve (Fig. 3a) in the region of $2800\ cm^{-1}$. As already noted, its presence is due to Fermi resonance of the polaritons with the dissociated-state band. With further increase of the frequency, the polariton branch is bent as a result of the bound transverse oscillation $\nu'_t(F_2)$. After the longitudinal component $\nu'_l(F_2)$ there is a small region of the dispersion curve with a gap produced resulting from the Fermi resonance of the polaritons with the polar band of two-particle states located in this region. Finally, with further increase of the frequency, the polariton branch tends to the value $\nu_{3t}(F_2) = 3122 = 3122\ cm^{-1}$.

As seen from Fig. 3, there is an appreciable difference between the dispersion curve plotted on the basis of the experimental results obtained in the present study and the corresponding theoretical curve. This is quite natural, inasmuch as no account is taken of the two-particle vibrational excitations in the latter case.

It follows from the presented data that a gap is observed in the polariton spectrum of the investigated crystal in the region of dipole-active bound state ($\nu'_t = 3052\ cm^{-1}$ corresponds to the transverse and $\nu'_l = 3070\ cm^{-1}$ to the longitudinal component of the bound state). The bound states can also be enhanced in the RS spectrum as a result of hybridization (owing to the proximity of the frequency of the fundamental oscillation $\nu_3(F_2)$ to the composite tone $\nu_2(E) + \nu_4(F_2)$). The observed spectrum in the region of the bound state agrees qualitatively with the conclusions of the theories [4,5] concerning the polariton RS by a dipole-active bound state under the conditions of Fermi resonance.

It was observed in experiment that the RS lines corresponding to the bound state on the polariton section turn out to be quite narrow and polarized (in accordance with the F_2 type of symmetry). It was also observed that the intensity of the RS by polaritons near the frequencies of the bound dipole-active oscillations increases strongly in this case. In the observed polariton spectrum, we identified also a band of two-particle states, which follows the dipole-active bound state. The values of the binding energy ($\nu_2(E) + \nu_{4t}(F_2) - \nu'_t$ and $\nu_2(E) + \nu_{4l}(F_2) - \nu'_l$) turned out to be the same for the transverse and the longitudinal oscillations, namely $64 \pm 2\ cm^{-1}$. The large binding energy is apparently the result of a strong mechanical anharmonicity which arises under conditions of hybridization of the fundamental oscillation $\nu_3(F_3)$ with the two-particle states.

The obtained spectra confirm also the conclusions of [11] concerning the formation of a gap in the polariton spectrum in the region of the $2\nu_4(F_2)$ band. In addition, an analogous gap is observed in the region of another polar band (which follows the bound states ν'_t and ν'_l). As follows from the data on infrared spectra [12], strong absorption takes place in thin films of NH_4Cl in the region of the discussed two-particle state band. It must therefore be concluded that the observed gaps in the region of the two-particle states differ significantly in their nature from the gaps due to dipole-active bound fundamental oscillations. In the case of a gap due to bound or fundamental oscillations, the region of the gap is characterized by a strong reflection coefficient. On the other hand, in the case of a gap due to the two-particle state band there is apparently a strong absorption caused by the rapid decay of the light quanta to mechanical excitations of the crystal.

We have thus shown the need for taking both dissociated and bound states into account when plotting the dispersion curves for polaritons in crystals.

In conclusion, we are grateful to Yu. I. Galinkovskiĭ and A. I. Pisanskiĭ for growing the single crystals of ammonium chloride, and to V. M. Agranovich for a discussion of the results and for valuable remarks.

1) The investigations in [11] were made with an instrument having a smaller dispersion, and a smaller range of wide-scattering angles was studied.

2) We note that in the same branch an additional small gap is observed in the $2700\ cm^{-1}$ region; the nature of this gap has not been established by us.

3) We note that the attenuation of the RS by the polaritons in the region of very small scattering angles ($2500\ cm^{-1}$) is connected with the form of the RS tensor for oscillations of type F_2.

4) Account is taken here of three pairs (longitudinal and transverse components) of the fundamental polar oscillations, and also the frequencies $\nu'_t = 3052\ cm^{-1}$ and $\nu'_l = 3070\ cm^{-1}$ corresponding to the bound dipole-active excitation.

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