Interference effects in Fermi resonance of optical phonons with the band of two-particle states

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Using a lithium formiate crystal as an example, we demonstrate for the first time that, under Fermi-resonance conditions, dips can appear in the intensity of the light scattered by two-particle states.

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Fermi resonance (FR) in crystals has a number of distinguishing features in comparison with isolated molecules. [1–4] The reason is that the phonon dispersion in the Brillouin zone leads in the general case to the appearance, in the second-order phonon spectra, of broad energy bands of two-particle states, which are absent from the spectra of the free molecules. We report experimental observation of new singularities that appear in crystals in the case of FR of optical phonons with the band of two-particle states and manifest themselves in the spectra of the Raman scattering of light (RSL).

We investigated RSL in the biaxial crystal lithium formiate monohydrate Li HCOO·H_2O, belonging to the point group $mm2$. In the crystals of this group, oscillations of four symmetry types are active in the RSL, and three of them are polar. The unit cell of lithium formiate contains four formula units, and this leads to a rich phonon spectrum. In particular, a situation is realized wherein the frequencies of the longitudinal and transverse components of a weak polar vibration land in the two-particle-state band.

To register the RSL spectra we used a Coderg double monochromator with holographic gratings at a spectral slit width 2.5 cm^{-1}. The excitation was by a 514.5-nm argon laser.

Figure 1 shows fragments of the RSL spectra of lithium formiate and the scattering geometries corresponding to these spectra.

Spectrum 1 was obtained with light scattering by transverse (TO) oscillations of symmetry $A_1(z)$. The line $\nu_4(\text{TO}) = 1580$ cm^{-1} pertains to the asymmetric valence vibration of the formiate ions (O—C—O). [5]

Spectrum 2 was obtained with RSL by longitudinal (LO) vibrations of symmetry $A_1(z)$. The frequency $\nu_4(\text{LO})$ of the longitudinal component of the fundamental oscillation is 1665 cm^{-1}.

The broad band observed in these spectra in the region from 1520 to 1750 cm^{-1} is attributed by us to the two-particle-state band produced by two optical phonons. Favoring this assumption are the following considerations:
a) The appreciable width of the band situated in the region of narrow intramolecular oscillations (the assumption that this band is due to the presence of the water of crystallization is not confirmed by the fact that a similar band is
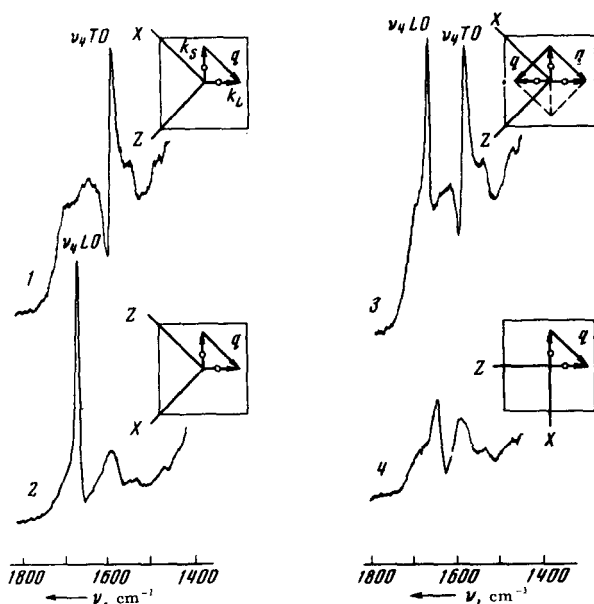
FIG. 1. Spectra of the Raman scattering of light in a lithium formiate crystal; ν—frequency of the Stokes shift. The scattering geometry relative to the crystallographic axes X and Z is shown for each spectrum. k_L, k_S, and q are the wave vectors of the incident, scattered, and phonon waves, respectively. Spectrum 2 is plotted at half the light intensity.

observed in the spectra of the barium and strontium anhydrous formiate investigated by us). b) The results of an investigation of RSL of formiates[6] indicate that in the considered frequency region there is only one fundamental oscillation (the weak lines observed in this region by a number of workers[6] were classified as second-order lines. c) The singularities of the temperature dependence of the shape and intensity of the band[1] favor the assumption that this is a two-particle-state band.

In the presented spectrum 1 we call attention to the singularities of the FR observed by us. These singularities constitute interference between the transverse optical phonon and the two-particle-state band, and lead to the appearance of a sharp dip (at a frequency 1592 cm^{-1}) in the broad band at the location of the high-frequency edge of the fundamental vibration.

At another position of the crystal, in spectrum 2 of the pure LO oscillation, the interference leads only to a noticeable asymmetry of the shape of the longitudinal-oscillation line. In this spectrum, in contrast to spectrum 1, no dip is observed at all at 1592 cm^{-1}, and a second-order line shape can be traced.

Spectrum 3 corresponds to a scattering geometry in which TO and LO oscillations are simultaneously excited (to this end, the light incident on scattered light in the crystal was reflected with the aid of mirrors in the opposite

direction). It is clearly seen that the character of the resonant interaction has not changed. A strong cancellation due to the interference between the single-particle and two-particle states is observed (frequency 1592 cm^{-1}) only at the location of the high-frequency edge ν_4(TO) of the line of the transverse oscillation.

We have realized one more scattering geometry, in which the dipole-active phonon propagated in the crystal in the XZ plane at an angle 45° to the Z axis. In this case the phonon excitation corresponds to a mixed oscillation $A_1(z)$ $+B_1(x)$. The frequency of such a phonon should be intermediate between the frequencies of the pure TO and LO oscillations. In spectrum 4, recorded in such a scattering geometry, total cancellation of the first-order line is observed. The reason why the dip frequency (1620 cm^{-1}) differs from that of spectrum 1 is the influence exerted on the FR condition by the spatial anisotropy of the crystal.

Fermi resonance of optical phonons with the two-particle-state band was observed also earlier. [7] Then, however, the FR condition was realized in the interaction of the soft mode of a ferroelectric crystal with the band made up of two acoustic phonons. Owing to the apparently weak interaction of the optical phonons with the bands of two acoustic phonons, all that was observed in[7] was a change in the line shape and a redistribution of the intensity of the light scattered by the single-particle and two-particle excitations. [4,7]

Thus, we have demonstrated experimentally that in crystals, under FR conditions, interference of the contributions of the single-particle and two-particle excitations can give rise to dips (cancellation) in the intensity of the scattered light. This phenomenon, according to the theory, [1-3] is possible in principle if the interaction between the single-particle and two-particle states, due to anharmonicity effects, is strong enough. Analytic expressions that describe the RSL intensity under FR conditions contain a large number of indeterminate parameters, which makes it difficult for the time being to carry out a quantitative comparison of the results of theory and experiment.

1)The results of the investigation of the temperature dependence of the RSL spectra of lithium formiate monohydrate will be published later.

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