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# Anharmonic interaction in the Raman and polariton lattice spectra of solids

A M Yaremko and D I Ostrovskii

Institute of Semiconductor Physics, National Academy of Science, Ukraine, 45 Prospect Nauki, 252028 Kiev-28, Ukraine

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**Abstract.** The peculiarities of polariton light scattering under strong anharmonic interaction of the fundamental vibration with the complex transition (i.e. polariton Fermi resonance) are investigated. It is shown that the polariton Fermi resonance influences the polariton band shape and dispersion curves. A detailed comparison with experimental results for a BaTiO<sub>3</sub> crystal is carried out.

## 1. Introduction

During the last few years the approaches to the investigation of low-frequency vibrations with pulse techniques, e.g. pulsed stimulated Raman scattering, have been intensively developed [1–5]. The application of such techniques is very attractive and useful for phonon–polariton light scattering. By changing the wavevector value, one can investigate lattice excitations of crystals down to decades of reciprocal centimetres where traditional Raman scattering or IR absorption cannot be successfully used if considerable damping of excitations takes place. The technique advanced becomes especially useful for investigations in the range of temperatures near phase transitions. It follows from [1–3] that the proposed approach is based on the fact that vibrational properties of a crystal in a low-frequency range can be described by a model of one, two or several oscillators. The probable situation when the combined frequencies fall into the fundamental vibrations range and the interaction between these vibrations takes place at proper symmetry is not considered here.

The well known phenomenon of Fermi resonance (FR) has been discovered in the CO<sub>2</sub> molecule and has also been investigated later for the phonon and polariton spectra of crystals [6–9] (and references therein). It may be noted that the problem of FR and two-phonon intramolecular excitations were studied in [8, 9] for CO<sub>2</sub> and CS<sub>2</sub> crystals by time-resolved spectroscopy, similar to [1–5]. In particular the relaxation rates for components of Fermi doublets were measured in a wide temperature region and conclusions concerning the mechanism of relaxation were made. However, the polaritonic problem was not investigated in these articles.

The polariton spectrum band shape and dispersion curves become especially complicated at FR since the intensity of polariton scattering is determined not only by fundamental vibration but also by new states which arise owing to FR, namely

(i) by the range of two-particle states (TPSs) which is formed by a pair of ‘free’ phonons and

(ii) by biphonons, i.e. by a pair of phonons which are 'bonded' by anharmonic interaction. The ratio of band intensities depends strongly on the angle of light scattering. So it may be that the lower polariton branch is not determined by the fundamental vibration but is determined by the biphonon which appears owing to FR.

Therefore in the present paper we would like to pay attention to that in particular. According to this idea we develop the theory of light scattering by polaritons in crystals taking into account FR and carry out the calculations for the BaTiO<sub>3</sub> crystal. This theory allows one to obtain the frequency dependence of damping parameters and to clarify the role of the crystal parameters including anharmonic interaction in the formation of the polariton spectrum.

The paper consists of the following. In section 2 the microtheory of a crystal is considered, and the light-scattering differential cross section, expressed by appropriate Green functions, is calculated. In section 3, analysis of the experimental results is carried out, and dispersion curves for the BaTiO<sub>3</sub> crystal are plotted.

The time dependences of the light-scattering intensity will be considered elsewhere.

## 2. Energy operator and light-scattering cross section

Interaction of the polariton with the TPS band, i.e. the polariton FR, was firstly considered in [10, 11] in which the abrupt changes in the shape of the polariton dispersion curve inside the TPS range have been predicted. These changes are caused by critical points in the density-of-states function.

The question about the polariton band shape under the resonance interaction of a polariton with the two-phonon band was considered for the simple case when only cubic anharmonic terms in the power series expansion of potential energy was taken into account [12]. In this case, dispersion curves plotted according to the maxima of scattering techniques [6, 7] do not exhibit the 'inverse' portion of the curve inside the TPS band predicted by [11].

In the present paper the generalization of this new approach which was developed in [6, 7, 12] is carried out taking into consideration all the main factors responsible for FR in crystals. We avoid the traditional polariton representation [12, 13] in the calculations. As was discussed by Tait [14], this description of polaritons is very convenient for investigation of the damping of the excitations. It provides additional advantages in the case of polariton FR. This description allows one to introduce explicitly the important constant of optical anharmonism and electro-optical constant.

Using the second quantization formalism, the Hamiltonian operator, which describes the polariton excitation in a crystal lattice, may be written in the form (for  $\hbar = c = 1$ )

$$\begin{aligned}
 H = & \sum_{sq} \omega_{sq} a_q^{+s} a_q^s + \frac{1}{3! \sqrt{N}} \sum_{\substack{ss's'' \\ qq'q''}} V \left( \begin{matrix} ss's'' \\ qq'q'' \end{matrix} \right) \varphi_q^s \varphi_{q'}^{s'} \varphi_{q''}^{s''} \delta(q + q' + q'') \\
 & + \frac{1}{4! N} \sum_{\substack{ss's''s''' \\ qq'q''q'''}} V \left( \begin{matrix} ss's''s''' \\ qq'q''q''' \end{matrix} \right) \varphi_q^s \varphi_{q'}^{s'} \varphi_{q''}^{s''} \varphi_{q'''}^{s'''} \delta(q + q' + q'' + q''') \\
 & + \sum_{sk\lambda} D(sk\lambda) \gamma_{k\lambda} \pi_k^\delta + \sum_{k\lambda} \frac{\omega_0^2}{2|k|} \gamma_{k\lambda} \gamma_{k\lambda}^+ + \sum_{k\lambda} |k| b_{k\lambda}^+ b_{k\lambda}
 \end{aligned} \tag{1}$$

where

$$\varphi_q^s = \frac{1}{\sqrt{2}}(a_q^s + a_{-q}^s) \quad \pi_q^s = \frac{1}{\sqrt{2}}(a_q^{+s} - a_{-q}^s) \quad (2)$$

$$\gamma_{k\lambda} = \frac{1}{\sqrt{2}}(b_{k\lambda} + b_{-k\lambda}^+) \quad P_{k\lambda} = \frac{1}{\sqrt{2}}(b_{k\lambda}^+ - b_{-k\lambda}) \quad (3)$$

$$D(sk\lambda) = -id_{-k}^{s\lambda} \omega_{sk} \sqrt{\frac{4\pi}{v|k|}} \quad (4)$$

$$\omega_0^2 = \frac{4\pi}{v} \sum_i \frac{e_j}{m_j} \quad j = 1, \dots, \sigma. \quad (5)$$

Here  $a_q^{+s}$ ,  $a_q^s$  and  $b_{k\lambda}^+$ ,  $b_{k\lambda}$  are the creation and annihilation operators for a phonon of  $s$  lattice branch number with wavevector  $q$  and for a quantum of electromagnetic field with polarization  $\lambda$ ;  $\omega_{sq}$  is the frequency of  $s$  and  $q$  phonon types;  $\omega_0$  is the plasmon frequency;  $v$  is the volume of the unit cell;  $V \begin{pmatrix} ss' \dots \\ qq' \dots \end{pmatrix}$  is the anharmonicity constant;  $D(sk\lambda)$  is the constant of phonon-photon interaction;  $\delta(q' + q'' + \dots)$  is the delta function;  $N$  is the number of unit cells in the crystal.

The intensity of the incident light scattered by crystal lattice is given by [7, 15]

$$\frac{d^2\sigma}{d\omega d\Omega} \sim [1 + n(\omega)] \text{Im} \langle \langle W_q^+(t), W_q(0) \rangle \rangle_\omega. \quad (6)$$

In this formula  $\langle \langle \dots \rangle \rangle_\omega$  is the Fourier component of the retarded Green function of operators  $W_q^+$  and  $W_q$  which is proportional to the product of the electronic polarizability tensor  $\chi_{ij}$ , incident-light polarization vector  $e_L$  and scattered-light polarization vector  $e_S$ .

Expanding the tensor  $\chi_{ij}$  in the power series and restricting the row by second-order terms in the atom displacements and by the linear terms in electromagnetic field, one can obtain

$$W_q^+ = \sum_s \chi_s^{(1)}(q) \varphi_q^s + \sum_\lambda \left( -i \sqrt{\frac{4\pi|q|}{v}} \right) \chi_\lambda^{(1)}(q) P_{-q\lambda} + \frac{1}{\sqrt{N}} \sum_{ss't} \chi_{ss't}^{(2)}(t, q-t) \varphi_t^s \varphi_{q-t}^{s'} + \dots \quad (7)$$

In equation (7),  $\chi_s^{(1)}(q)$  and  $\chi_\lambda^{(1)}(q)$  are the values described by the third-order tensor, and they depend on the displacement of atoms and on the electromagnetic field, respectively; the  $\chi_{ss't}^{(2)}(t, t-q)$ -value depends on the displacement of atoms and is described by the fourth-order tensor.

In the case of FR, among all the Green functions in (6), one should take into account only those which have resonance in the actual frequency region  $\omega \sim \omega_{\mu k} \sim 2\omega_{pq}$ . Thus equation (6) is reduced to the following expression ( $\lambda = 1$ ):

$$\begin{aligned} \frac{d^2\sigma}{d\omega d\Omega} \sim [1 + n(\omega)] \text{Im} \left\{ (\chi_\mu^{(1)})^2 [ \langle \langle \varphi_k^\mu + z_k P_{-k\lambda}, \varphi_k^{+\mu} + z_k^* P_{-k\lambda}^+ \rangle \rangle_\omega \right. \\ \left. + \frac{\beta}{\sqrt{N}} \sum_t ( \langle \langle \varphi_k^\mu + z_k P_{-k\lambda}, \varphi_t^{+p} \varphi_{k-t}^{+p} \rangle \rangle_\omega + \langle \langle \varphi_t^p \varphi_{k-t}^p, \varphi_k^{+\mu} + z_k^* P_{-k\lambda}^+ \rangle \rangle_\omega \right. \\ \left. + \frac{\beta^2}{N} \sum_{tt'} \langle \langle \varphi_t^p \varphi_{k-t}^p, \varphi_{k-t'}^{+p} \varphi_{k-t'}^{+p} \rangle \rangle_\omega \right\} \quad (8) \end{aligned}$$

where

$$z_k = -i\sqrt{\frac{4\pi|k|}{v}}z. \quad (9)$$

$z = \chi_\lambda^{(1)}/\chi_\mu^{(1)}$  is the electro-optic constant;  $\beta = \chi_{pp}^{(2)}/\chi_\mu^{(1)}$  is the parameter of optical anharmonicity; in the following, we assume that  $\chi_\mu^{(1)}(k)$ ,  $\chi_\lambda^{(1)}(k)$  and  $\chi_{pp}^{(2)}(t, k-t)$  do not depend on the wavevector.

To obtain the equations of motion for Green functions of type

$$\begin{aligned} G_k^{\nu\mu}(t) &= \langle\langle \varphi_k^\nu(t), \varphi_k^{+\mu}(0) \rangle\rangle \\ G_k^{\lambda\mu}(t) &= \langle\langle P_{-k\lambda}(t), \varphi_k^{+\mu}(0) \rangle\rangle \end{aligned}$$

it is convenient to perform a twofold differentiation on time. Then in Fourier representation the system of equations for the above-mentioned Green functions reads as

$$\omega^2 G_k^{\nu\mu} = \omega_{\nu k} \delta_{\nu\mu} + \left\{ \tilde{\omega}_{\nu\mu}^2 G_k^{\nu\mu} - |k| D(\nu k \lambda) G_k^{\lambda\mu} + \frac{1}{\sqrt{N}} \omega_{k\nu} \Gamma \sum_q G^{p\mu} \left( q, \begin{matrix} k-q \\ k \end{matrix} \right) \right\} \quad (10)$$

$$\begin{aligned} \omega^2 G_k^{\lambda\mu} &= D(\mu k \lambda) + \left\{ (k^2 + \omega_0^2) G_k^{\lambda\mu} \right. \\ &\quad \left. + \sum_s D(\mu k \lambda) \tilde{\omega}_{sk} G_k^{s\mu} + \frac{1}{\sqrt{N}} \Gamma D(\mu k \lambda) \sum_q G^{p\mu} \left( q, \begin{matrix} k-q \\ k \end{matrix} \right) \right\}. \quad (11) \end{aligned}$$

Here

$$\tilde{\omega}_{\nu k}^2 = \omega_{\nu k}^2 + 2\omega_{\nu k} R^\nu(k\omega) \quad \tilde{\omega}_{\nu k} = \omega_{\nu k} + 2R^\nu(k\omega) \quad R^\nu(k\omega) = R_1^\nu + iR_2^\nu$$

are the shift and damping, respectively, of frequency due to interaction of the vibration with other lattice phonons.

One can obtain the Fourier component  $G^{p\mu} \left( q, \begin{matrix} k-q \\ k \end{matrix} \right)$  of the Green function as follows:

$$G^{p\mu} \left( q, \begin{matrix} k-q \\ k \end{matrix} \middle| t \right) = \langle\langle \varphi_q^p(t) \varphi_{k-q}^p(t), \varphi_k^{+\mu}(0) \rangle\rangle$$

which describes the contribution of two-phonon states to the intensity of light scattering and may be determined from the second system of equations:

$$\omega G^{p\mu} = -\{ \tilde{\omega}_{pq'} \langle\langle \pi_{-q'}^p \varphi_{q'}^p, \varphi_k^{+\mu} \rangle\rangle + \tilde{\omega}_{pq''} \langle\langle \varphi_{q'}^p \pi_{-q''}^p, \varphi_k^{+\mu} \rangle\rangle \} \quad (12)$$

$$\begin{aligned} \omega \langle\langle \pi_{-q'}^p \varphi_{q'}^p, \varphi_k^{+\mu} \rangle\rangle &= -\left\{ \omega_{pq'} \langle\langle \varphi_{q'}^p, \varphi_{q''}^p, \varphi_k^{+\mu} \rangle\rangle + \left( \frac{1}{2} + n_{q''}^p \right) \left[ \frac{2\Gamma}{\sqrt{N}} \langle\langle \varphi_{q'+q''}^\mu, \varphi_k^{+\mu} \rangle\rangle \right. \right. \\ &\quad \left. \left. - \frac{2A}{N} \sum_t \langle\langle \varphi_t^p \varphi_{q'+q''-t}^p, \varphi_k^{+\mu} \rangle\rangle \right] + \tilde{\omega}_{pq''} \langle\langle \pi_{-q'}^p \pi_{q''}^p, \varphi_k^{+\mu} \rangle\rangle \right\} \quad (13) \end{aligned}$$

$$\omega \langle\langle \pi_{-q'}^p \varphi_{q''}^p, \varphi_k^{+\mu} \rangle\rangle = -\{ \tilde{\omega}_{pq'} \langle\langle \varphi_{q'}^p \pi_{-q''}^p, \varphi_k^{+\mu} \rangle\rangle + \tilde{\omega}_{pq''} \langle\langle \pi_{-q'}^p \varphi_{q''}^p, \varphi_k^{+\mu} \rangle\rangle \}. \quad (14)$$

The equation for the function  $\langle\langle \varphi_{q'}^p \pi_{-q''}^p, \varphi_k^{+\mu} \rangle\rangle$  differs from (13) only by the exchange  $q' \rightarrow q''$ . In equation (13),  $n_{q''}^p$  is the filling number of phonons with frequency  $\tilde{\omega}_{pq} = \omega_{pq} + i\gamma_p$ ; the anharmonic constant  $A$  and  $\Gamma$  are given by [9]

$$A = -\frac{1}{4}V \begin{pmatrix} p & p & p & p \\ -q & q & t & -t \end{pmatrix} \quad \Gamma = \frac{1}{2}V \begin{pmatrix} p & p & v \\ -q & q-k & k \end{pmatrix}.$$

From equations (12)–(14), one can obtain

$$G_k^{p\mu} = \frac{1}{\sqrt{N}} \sum_q G^{p\mu} \left( \begin{matrix} q, k - q \\ k \end{matrix} \right) = \frac{2\Gamma f(k\omega)}{1 + 2Af(k\omega)} G_k^{\mu\mu} \quad (15)$$

where the following notation is introduced:

$$f(k\omega) = f_1 + if_2 = \frac{1}{N} \sum_q \frac{1}{\bar{\Delta}(\omega k q)} \quad (16)$$

$$\bar{\Delta}(\omega k q) = \frac{[\omega^2 - (\bar{\omega}_{pq} + \bar{\omega}_{p,k-q})^2][\omega^2 - (\bar{\omega}_{pq} - \bar{\omega}_{p,k-q})^2]}{(\frac{1}{2} + n_{k-q}^p)(\omega^2 + \bar{\omega}_{pq}^2 - \bar{\omega}_{p,k-q}^2)\bar{\omega}_{p,k-q} + (\frac{1}{2} + n_{k-q}^p)(\omega^2 - \bar{\omega}_{pq}^2 + \bar{\omega}_{p,k-q}^2)\bar{\omega}_{p,q}}$$

Inserting (15) into (10) and (11) and taking into account the notation

$$\begin{aligned} \bar{\omega}_{\mu k} &= \bar{\omega}_{\mu k} + \frac{2\Gamma^2 f(k\omega)}{1 + 2Af(k\omega)} \\ \Omega_{\mu k}^2 &= \omega_{\mu k} \bar{\omega}_{\mu k} \quad (\nu = \mu) \\ \Omega_{\nu k}^2 &= \bar{\omega}_{\nu k}^2 \quad (\nu \neq \mu) \end{aligned} \quad (17)$$

one can obtain the following system of equations for the functions  $G_k^{\nu\mu}$  and  $G_k^{\lambda\mu}$ :

$$(\omega^2 - \Omega_{\nu k}^2)G_k^{\nu\mu} + |k|D(\nu k \lambda)G_k^{\lambda\mu} = \omega_{\nu k}\delta_{\nu\mu} \quad (18)$$

$$- \sum_s D(s k \lambda)\bar{\omega}_{s k}G_k^{s\mu} + (\omega^2 - |k|^2 - \omega_0^2)G_k^{\lambda\mu} = D(\mu k \lambda). \quad (19)$$

The solution of this system gives the following expression for the Green functions:

$$G_k^{\mu\mu} = \frac{\omega_{\mu k}\alpha}{\alpha(\omega^2 - \Omega_{\mu k}^2) - \omega^2\omega_0^2 F_k^{\mu\lambda}} \quad (20)$$

$$G_k^{\lambda\mu} = \frac{\omega^2 D(\mu k \lambda)}{\omega_{\mu k}\alpha} G_k^{\mu\mu} \quad (21)$$

where  $\alpha = \varepsilon_0\omega^2 - |k|^2$ ,  $F_k^{\mu\lambda} = \omega_{\mu k}(d_k^{\mu\lambda})^2(\sum_i e_i/m_i)^{-1}$  is the oscillator strength of the  $0 \rightarrow \mu$  transition.

The traditional procedure for extracting the ground dielectric function [16] and the orthogonality conditions for amplitudes of the lattice atom shift [17] were used to obtain (20) and (21).

One can obtain a system of equations for the second group of Green functions in a similar way:

$$\begin{aligned} G^{\nu p} \left( \begin{matrix} k \\ q, k - q \\ t \end{matrix} \right) &= \langle\langle \varphi_k^\nu(t), \varphi_q^{+p}(0)\varphi_{k-q}^{+p}(0) \rangle\rangle \\ G^{\lambda p} \left( \begin{matrix} k \\ q, k - q \\ t \end{matrix} \right) &= \langle\langle P_{-k\lambda}(t), \varphi_q^{+p}(0)\varphi_{k-q}^{+p}(0) \rangle\rangle \\ G^{pp} \left( \begin{matrix} q, k - q \\ q', k - q' \\ t \end{matrix} \right) &= \langle\langle \varphi_q^p(t)\varphi_{k-q}^p(t), \varphi_{q'}^{+p}(0)\varphi_{k-q'}^{+p}(0) \rangle\rangle. \end{aligned}$$

The solution of the system above produces expressions for the corresponding Fourier components:

$$G_k^{\mu p} = \frac{1}{\sqrt{N}} \sum_q G^{\mu p} \left( \begin{matrix} k \\ q, k - q \end{matrix} \right) = \frac{2\Gamma f(k\omega)}{1 + 2Af(k\omega)} G_k^{\mu\mu} \quad (22)$$

$$G_k^{pp} = \frac{1}{N} \sum_{qq'} G^{pp} \left( \begin{matrix} q, k-q \\ q', k-q' \end{matrix} \right) = \left[ \frac{2\Gamma f(k\omega)}{1+2Af(k\omega)} \right]^2 G_k^{\mu\mu} + \frac{2\Gamma f(k\omega)}{1+2Af(k\omega)} \quad (23)$$

$$G_k^{\lambda p} = \frac{1}{\sqrt{N}} \sum_q G^{\lambda p} \left( \begin{matrix} k \\ q, k-q \end{matrix} \right) = \frac{D(\mu k \lambda) \omega^2}{\omega_{\mu k} \alpha} G_k^{\mu p}. \quad (24)$$

It is clear that equation (22) coincides with (15). This is natural because both equations describe similar processes.

Finally for the Fourier components of the third group of Green functions given by

$$G_k^{\nu\lambda}(t) = \langle\langle \varphi_k^\nu(t), P_{-k\lambda}^+(0) \rangle\rangle$$

$$G_k^{\lambda\lambda}(t) = \langle\langle P_{-k\lambda}(t), P_{-k\lambda}^+(0) \rangle\rangle$$

one can obtain

$$G_k^{\mu\lambda} = -\frac{D(\mu k \lambda) \omega^2}{\omega_{\mu k} \alpha} G_k^{\mu\mu} = -G_k^{\lambda\mu} \quad (25)$$

$$G_k^{\lambda\lambda} = \frac{|k|^2 - (\varepsilon_0 - 1)\omega^2}{|k|\alpha} + \frac{\omega^4 \omega_0^2 F_k^{\mu\lambda}}{\alpha^2 |k| \omega_{\mu k}} G_k^{\mu\mu}. \quad (26)$$

The first term in (26) is real; hence only the second term gives the contribution to the intensity of light scattering.

Substituting equations (21)–(26) into equation (8) and taking into account the relations

$$\frac{4\pi |k| \omega_0^2 F_k^{\mu\lambda}}{v |k| \omega_{\mu k}} = \left( \frac{4\pi}{v} d_k^{\mu\lambda} \right)^2 \quad \left( -i\sqrt{\frac{4\pi |k|}{v}} \right) \left( -\frac{D(\mu k \lambda)}{\omega_{\mu k}} \right) = \frac{4\pi}{v} d_k^{\mu\lambda}$$

equation (8) may be written as follows:

$$\begin{aligned} \frac{d^2\sigma}{d\omega d\Omega} &\sim [1+n(\omega)][\tilde{\chi}_\mu^{(1)}]^2 \text{Im}\{G_k^{\mu\mu} + \tilde{\beta}(G_k^{\mu p} + G_k^{p\mu}) + \tilde{\beta}^2 G_k^{pp}\} \\ &= [1+n(\omega)][\tilde{\chi}_\mu^{(1)}]^2 \text{Im} \left\{ \left[ 1 + \frac{2\Gamma \tilde{\beta} f(k\omega)}{1+2Af(k\omega)} \right]^2 G_k^{\mu\mu} + \frac{2\tilde{\beta}^2 f(k\omega)}{1+2Af(k\omega)} \right\} \quad (27) \end{aligned}$$

where

$$\begin{aligned} \tilde{\beta} &= \beta \left( 1 - \frac{4\pi z \omega^2}{v\alpha} d_k^{\mu\lambda} \right)^{-1} \\ \tilde{\chi}_\mu^{(1)} &= \chi_\mu^{(1)} \left( 1 - \frac{4\pi z \omega^2}{v\alpha} d_k^{\mu\lambda} \right). \quad (28) \end{aligned}$$

Substituting equation (20) into equation (27) and using equations (16) and (17) for  $f(k\omega)$  and  $\Omega_{\mu k}^2$  the expression for light scattering may be written in the standard form for the case of FR [8, 9] as

$$\frac{d^2\sigma}{d\omega d\Omega} \sim [1+n(\omega)][\tilde{\chi}_\mu^{(1)}]^2 \frac{R_2^\mu a^2 + 2f_2 b^2}{c^2 + d^2} \quad (29)$$

where the values of  $a$ ,  $b$ ,  $c$  and  $d$  are given by the following expressions:

$$a^2 = 2\alpha^2 \omega_{\mu k}^2 \{ [1 + 2f_1(A + \tilde{\beta}\Gamma)]^2 + 2f_2(A + \tilde{\beta}\Gamma) \}^2 \quad (30a)$$

$$b^2 = [\alpha \omega_{\mu k} \Gamma + \tilde{\beta} \Delta_{\mu k}]^2 + [2\alpha \omega_{\mu k} \tilde{\beta} R_2^\mu]^2 \quad (30b)$$

$$c = \Delta_{\mu k} (1 + 2Af_1) + 4\alpha \omega_{\mu k} A f_2 R_2^\mu - 2\alpha \omega_{\mu k} \Gamma^2 f_1 \quad (30c)$$

$$d = 2\Delta_{\mu k} A f_2 - 2\alpha \omega_{\mu k} (1 + 2Af_1) R_2^\mu - 2\alpha \omega_{\mu k} \Gamma^2 f_2 \quad (30d)$$

$$\Delta_{\mu k} = \alpha(\omega^2 - \omega_{\mu k}^2) - \omega^2 \omega_0^2 F_k^{\mu\lambda}. \quad (30e)$$

The expression for the cross section, equation (29), includes all the main factors responsible for the FR phenomenon in the Raman process. It describes the light scattering by lattice phonons for small and large angles. Here it should be noted that, in accordance with the definition of operators  $\varphi_{sq}$  and  $\pi_{sq}$  accepted in this paper, they differ from those used in the previous work [18] by a factor of  $1/\sqrt{2}$ . This means that the anharmonic parameters  $\beta$ ,  $\Gamma$ ,  $A$  and  $\chi_{\mu}^{(1)}$  should be enhanced by a factor of  $(\sqrt{2})^n$ , where  $n = 2, 3, 4$  and  $1$ , respectively. When this is taken into account, the result of the present work fully coincides with the appropriate expression in [18].

We would like to emphasize that the results of Raman light scattering for large angles (about  $90^\circ$ ) are very similar to IR formulae. However, we should take into consideration that the meanings of the parameter of optical anharmonicity in the two cases are different; for Raman scattering  $\beta = \chi_{pp}^{(2)}/\chi_{\mu}^{(1)}$  is the ratio of second- to first-order terms in the power series for tensor polarizability; for IR,  $\beta$  is the ratio of analogous terms in the expansion of the dipole momentum of the crystal unit cell.

From equations (29) and (30a)–(30e) one can see that intensity of light scattering by a polariton at FR conditions has a complex dependence on the frequency  $\omega$ , the wavevector  $k$ , the anharmonic parameters  $\beta$ ,  $\Gamma$  and  $A$  and the function of the two-phonon density of states. For this reason we shall consider some examples to analyse the principal features of light scattering for small and large angles.

### 3. Experimental results

As an example we consider the BaTiO<sub>3</sub> crystal. In the low-temperature phase ( $T < 115^\circ\text{C}$ ) this ferroelectric has the  $C_{4v}^2$  space group and has one formula molecule in the elementary cell. Detailed studies of the Raman spectra of the BaTiO<sub>3</sub> crystal have been described in [19–22]. The experimental results and assignment of bands are discussed intensively and, in principle, are in agreement with each other. The polariton spectra were studied in more detail in [20] (see also [23]), and so we shall follow these studies in our investigations.

The polariton curves in [20] were constructed taking into account the presence of several (three) fundamental vibrations. We paid attention to the fact that in the region of spectrum considered, overlapping of one- and two-phonon excitations takes place. Therefore the effect of FR can be important to the understanding of the spectral features in the region studied.

In accordance with [20–22] the following assignment of the frequency is accepted (figure 1): the bands 170, 270 and 520  $\text{cm}^{-1}$  are the one-phonon excitations while the broad bands  $\alpha \simeq 270 \text{ cm}^{-1}$  and  $\beta \simeq 520 \text{ cm}^{-1}$  are the second-order vibrations. There are also three narrow bands 185, 475 and 725  $\text{cm}^{-1}$  assigned to the first order which are observed in the LO phonon spectrum. Such an assignment was confirmed in the review in [23].

However, not all the TO (170, 270 and 520  $\text{cm}^{-1}$ ) and LO (185, 475 and 725  $\text{cm}^{-1}$ ) bands mentioned above may be attributed to first-order transitions (fundamental frequencies). The reason is that complex mixing of one- and two-phonon vibrations takes place in the BaTiO<sub>3</sub> crystal for the spectral range under consideration. In particular, the polaritonic Fermi resonance (PFR) occurs due to the coincidence of the intensive fundamental vibration  $\omega = 270 \text{ cm}^{-1}$  with two-phonon  $\alpha$ -band vibrations.

The experimental spectra for different angles  $\theta$  of light scattering are plotted in figure 2 (solid curves). For the theoretical description of the band shape at FR conditions the function  $f(k\omega)$  of the two-phonon density of states is very important. It is determined by



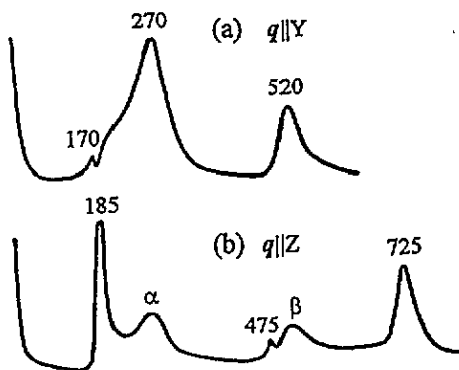


Figure 1. The spectrum of Raman scattering of the BaTiO<sub>3</sub> crystal in the A<sub>1</sub> excitation geometry (from [20]): (a) TO phonons in the X(ZZ)X + ΔY geometry; (b) LO phonons in the X(ZZ)X + ΔZ geometry.

the dispersion law  $\omega_{pk}(2\omega_{pq} \sim \omega_{\mu k})$ . For model calculations the frequency  $\omega_{pq}$  may be taken in the generalized form

$$\omega_{pq} = \omega_p + M_1^p \cos(q_x a_x) + M_2^p \cos(q_y a_y) + M_3^p \cos(q_z a_z). \quad (31)$$

Varying the values of  $M_1^p$ ,  $M_2^p$  and  $M_3^p$ , one can obtain different structures of the two-phonon bands which significantly influence the spectrum.

It is necessary to emphasize that the light-scattering cross section  $d^2\sigma/(d\omega d\Omega) = S''$  is the function of two variables  $k$  and  $\omega$ . Thus it is convenient to investigate  $S''$  as a function of one variable (the other variable, e.g.  $k$ , being fixed). The successive set of such functions  $S''(k_i = \text{constant})$  makes it possible to obtain the dependence of the polariton band shape on wavevector (or scattering angle  $q$ ). Experiments are usually carried out at constant angle  $q$  between the directions of incident ( $\omega_L$ ) and scattered ( $\omega_S$ ) light. The relation between  $k$  and  $q$  follows from the conservation law for the wavevector:  $k = k_L - k_S$ . Then  $|k|^2 = \epsilon_0(\omega^2 + \omega_L^2 q^2)$ ,  $q \ll 1$ . Using the values of frequencies corresponding to the maxima of light scattering for given  $k$ , reconstruction of the polariton dispersion curve is possible.

Analysis of the experimental spectra and its comparison with the theoretical curves obtained according to equations (29) and (30a)–(30d) shows that the best fitting takes place if we use the ratio  $M_1^p \gg M_2^p, M_3^p$  in the description of the dispersion law  $\omega_{pq}$ . Fitting of the theoretical results to the experimental spectra is fulfilled in the following way: firstly we achieve good agreement for large-angle scattering ( $q \simeq 90^\circ$ ) (curve 4' in figure 2), and then we generate curves 3'–1' by varying  $q$  from  $90^\circ$  to  $0^\circ$ . The fitting parameters are the following:  $G = 0.42$ ,  $A = 0.11$ ,  $b = 0.08$  and  $\omega_0^2 F_k^{\mu\lambda} = 1250$  (the energy parameters are given in units of  $2M^p = 2(M_1^p + M_2^p + M_3^p) = 45 \text{ cm}^{-1}$ ).

The value of  $\omega_{\text{TO}}$  unperturbed by FR is  $265 \text{ cm}^{-1}$ . The small maximum at  $\omega \simeq 170 \text{ cm}^{-1}$  observed for large scattering angles  $q$  (figure 2, curve 4) is the biphonon split from the two-phonon  $\alpha$  band due to its anharmonic interaction with the fundamental vibration  $\omega_{\text{TO}}$ . In the region of very small scattering angles ( $q < 1^\circ$ ) the increase in the calculated biphonon maxima is significant. This is evident from curves 1–3 in figure 2. The shifts of the maxima at  $\omega = 170 \text{ cm}^{-1}$  and  $\omega = 270 \text{ cm}^{-1}$  versus  $k$  (i.e.  $q$ ), which are obtained from the data in figure 2, are plotted in figure 3 (broken parts of curves 1 and 2) and show good agreement with the experimental data (solid curves with open circles).

Figure 3 shows an additional polariton curve 4 which begins at about  $700 \text{ cm}^{-1}$ . This means that the experimentally observed band at  $\omega \simeq 715 \text{ cm}^{-1}$  (LO) can be considered as the LO component of the fundamental  $\omega_{\text{TO}} = 270 \text{ cm}^{-1}$ . The sharp maxima at  $\omega \simeq 170 \text{ cm}^{-1}$  and  $\omega \simeq 185 \text{ cm}^{-1}$  (in figure 1) can be assigned then to the TO and LO components of the biphonon, split from the two-phonon  $\alpha$  band. The maximum at  $\omega \simeq 520 \text{ cm}^{-1}$  is due

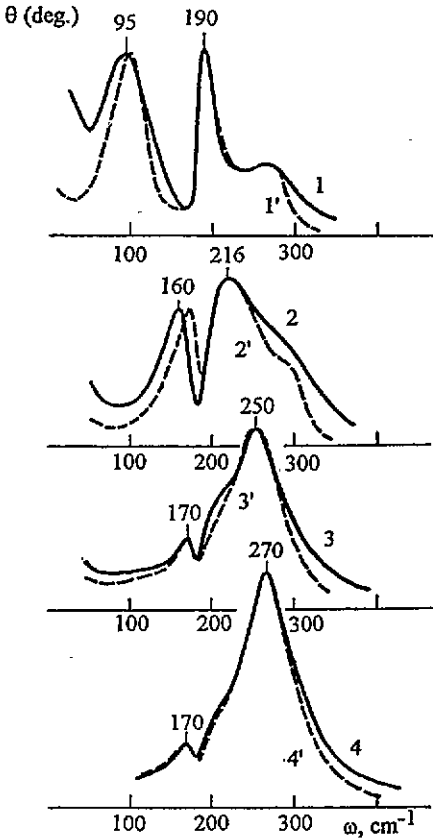


Figure 2. The spectra of polariton scattering of the BaTiO<sub>3</sub> crystal in the A<sub>1</sub> excitation geometry for various scattering angles  $\theta$ : curve 1,  $\theta = 0.85^\circ$ ; curve 2,  $\theta = 2^\circ$ ; curve 3,  $\theta = 4^\circ$ ; curve 4,  $\theta = 8^\circ$ ; —, experimental results [20]; - - -, our calculation.

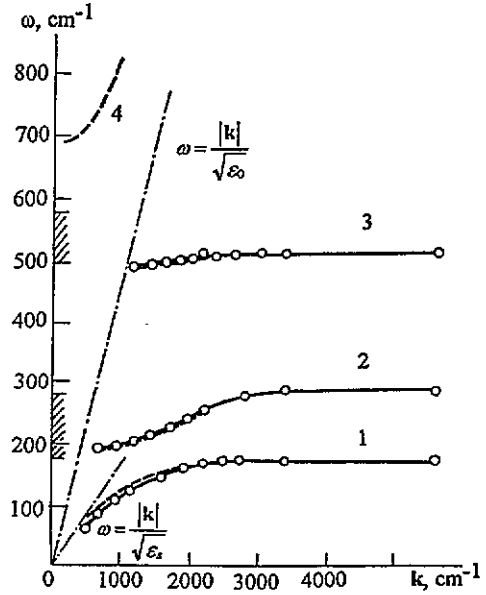


Figure 3. Comparison of experimental (—○—) and theoretical (— —) dispersion curves of polaritons in the frequency range of fundamental TO vibration and of TPS bands (regions indicated on the frequency axis) of the BaTiO<sub>3</sub> crystal.

to the maximum in the density of two-phonon states in the *b* zone, which corresponds to  $2\omega_{TO} \simeq 540 \text{ cm}^{-1}$  transitions.

Thus, for BaTiO<sub>3</sub>, taking into account the anharmonic interactions between vibrations, i.e. PFR, makes it possible to explain the principal feature in the polariton and Raman spectra for A<sub>1</sub>-type symmetry in the frequency range  $\omega \simeq 1800\text{--}800 \text{ cm}^{-1}$ .

#### 4. Summary

For the correct description of polariton scattering under the conditions of FR it is necessary (as is seen for the example of a BaTiO<sub>3</sub> crystal) to consider accurately the cross section spectral dependence. This procedure is necessary since the cross section maxima may disagree with the denominator minima due to the complicated frequency dependence of equations (29) and (30a)–(30e). This is obviously the main reason for the inconsistency between the results of [12] and the conclusions obtained in [11] about the regularity of polariton scattering inside TPS bands. Outside this band, where the influence of the two-

phonon-states density function  $f(k\omega)$  is small, these inconsistencies are less significant and the dispersion dependences obtained by both methods of calculation are similar.

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