

RAMAN SCATTERING OF LIGHT IN CRYSTALS

V. S. GORELIK and M. M. SUSHCHINSKIĬ

P. N. Lebedev Physics Institute, USSR Academy of Sciences

Usp. Fiz. Nauk 98, 237-294 (June, 1969)

1. INTRODUCTION

RAMAN scattering (RS) of light is one of the most interesting interactions between electromagnetic radiation and matter. RS in liquids, gases, and solids is usually described as inelastic interaction between light and a quantum system (atom, molecule, crystal), as a result of which the light is scattered at an altered frequency, and the quantum system goes over to a different energy level (say, vibrational). In the study of RS in crystals, this phenomenon is conveniently represented also as a process of interaction between the quasiparticles of the crystal. For example, Stokes RS can be described as the decay of a quantum of light of energy $\hbar\omega_0$ into an optical phonon of energy $\hbar\Omega$ and a photon of energy $\hbar\omega'$, while anti-Stokes scattering can be described as a collision between a light quantum of energy $\hbar\omega_0$ and an optical phonon of energy $\hbar\Omega$, resulting in a light quantum of energy $\hbar\omega''$ (Fig. 1). The energy and quasimomentum conservation laws for the foregoing processes are of the form

$$\left. \begin{aligned} \hbar\omega_0 &= \hbar\omega' + \hbar\Omega, \\ \hbar\mathbf{k}_0 &= \hbar\mathbf{k}' + \hbar\mathbf{k}, \end{aligned} \right\} \quad (1.1)$$

$$\left. \begin{aligned} \hbar\omega_0 + \hbar\Omega &= \hbar\omega'', \\ \hbar\mathbf{k}_0 + \hbar\mathbf{k} &= \hbar\mathbf{k}''; \end{aligned} \right\} \quad (1.2)$$

here \mathbf{k}_0 , \mathbf{k}' , and \mathbf{k}'' are the wave vectors of the quasiparticles of the incident and scattered radiation, \mathbf{k} is the wave vector of the optical phonon, and $\hbar\omega_0$, $\hbar\omega'$, $\hbar\omega''$, and $\hbar\omega$ are the energies of the corresponding quasiparticles.

We note that other quasiparticles of the crystal, for example polaritons,^[1] acoustic phonons (Mandel'shtam-Brillouin scattering), magnons,^[2,3] plasmons^[4,5] etc. can participate in the scattering process in place of the optical phonon. We shall consider mainly scattering processes in which optical phonons take part.

Since the crystal lattice vibrations take part in the RS, it has become possible to obtain with the aid of this phenomenon important information concerning the dynamics of the motion of atoms and molecules of the crystal. One of the advantages of RS over other methods of studying vibrations in crystals (infrared absorption, the slow-neutron method, etc.) is that in the former the "tool" of the investigation is visible light.

However, observation of RS in crystals is made difficult by the fact that the effective cross section and accordingly the RS intensity are very small. The order of magnitude of the effective RS cross section per unit cell is 10^{-27} - 10^{-28} cm²; it turns out here that the scattered-radiation power reaching the receiver amounts to 10^{-11} - 10^{-12} W. Thus, to observe RS it is necessary to have powerful sources of monochromatic radiation and very sensitive receivers.

The exciting-light source used for the study of RS has for a long time been mainly the mercury arc-discharge line ($\lambda = 2537, 4358, \text{ or } 5461 \text{ \AA}$). Difficult and laborious

experiments have made it possible to investigate RS in very many samples that are transparent to the indicated mercury lines. The processes mainly investigated were of first order, i.e., RS in which only one phonon takes part. It follows from (1.1) and (1.2) that the modulus of the wave vector of the optical phonon taking part in the scattering has the same order of magnitude as the modulus of the wave vector of the photon, i.e., $|\mathbf{k}| \ll \pi/d$, where d is the linear dimension of the unit cell. Thus, a study of the first-order RS spectra is in essence a study of the spectrum of long-wave optical phonons ($|\mathbf{k}| \approx 0$). A partial study was made also of the distribution of the line intensity in the spectrum, the line polarization, and a few other line parameters. There are many reviews devoted to the results of these measurements.^[6,9]

Later on, second-order RS spectra were observed, and yielded important information concerning phonons with $\mathbf{k} \neq 0$, i.e., the entire Brillouin zone. However, in view of the large experimental difficulties, second-order RS spectra were investigated only in a small number of crystals.^[9]

The discovery of lasers, which are sources of monochromatic directional and polarized radiation, has led to entirely new possibilities in RS spectroscopy. The first investigations, which demonstrated the prospects of using lasers for the excitation of RS in crystals, were investigations of colored crystalline powders with the aid of ruby^[10,11] ($\lambda = 6943 \text{ \AA}$) and helium-neon^[12,13] ($\lambda = 6328 \text{ \AA}$) lasers. At the present time, the use of lasers in RS spectroscopy has made it possible to solve many new experimental problems. The wide range of wavelengths of laser-radiation lines has made it possible to study substances that are not transparent to the already-mentioned mercury lines, particularly a number of colored organic substances,^[10-13] and certain semiconducting materials with a forbidden band width of the order of 2 eV.^[4,14,15]

Owing to the small divergence of the laser beam, it became possible to trace the variation of the scattered-radiation frequency as a function of the direction of propagation of the incident and scattered radiation.^[16] The possibility of concentrating intense laser radiation in a small volume of matter has made it possible to observe second-order processes in many new substances, as well as stimulated RS of light. In recent years, interest arose also in temperature investigations, particularly near phase-transition points in crystals.

The theory of RS has developed further in keeping with the new accomplishments in the experimental techniques. One of the principal tasks of the theory of RS is to calculate the effective cross section of this process, which determines the intensity of the scattered light. At the present time there are many approaches to the solution of this problem, but all leads to such

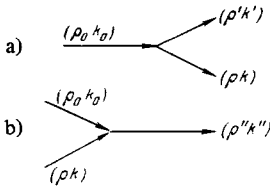


FIG. 1. Scheme of Raman scattering. a) Stokes RS; b) anti-Stokes RS.

cumbersome final formulas, that an actual calculation of the intensity of the scattered light is extremely difficult and can be performed only in the simplest cases, with allowance for many simplifying assumptions. In this connection, the establishment of selection rules, i.e., of the conditions for the vanishing of the effective cross section, which follow from the concrete symmetry of the crystal, [17-19] becomes highly valuable.

Of great importance is the interpretation of the RS spectra, and in connection with it also the classification of the vibrational levels of the crystal. This problem is likewise solved by using the symmetry of the crystal with the aid of the formalism of the theory of group representations. [20, 21] It should be noted that several trends have been noted in the literature devoted to these questions; some of these trends frequently appear to be mutually contradictory. For further development of the theory, it is of interest to make a critical comparison of different points of view and to establish their mutual relationship.

In this review we attempt to summarize the results of recent investigations in the field of RS spectroscopy in crystals.

2. CRYSTAL LATTICE VIBRATIONS

2.1. One-dimensional Lattice Vibrations

Many important properties of crystal vibrations can be clarified by considering the simple case of a one-dimensional lattice model. [22, 23] Let us consider a chain of identical atoms of mass m , the distance between which are equal to a . We denote by u_n the displacement of the n -th atom from its equilibrium position. If we take into account the interaction of only the nearest neighbors, then the force F_n acting on the n -th atom can be represented in the form

$$F_n = f(u_{n+1} - u_n) - f(u_n - u_{n-1}), \quad (2.1)$$

where f is the force constant of the lattice. The equation of motion of the n -th atom can be written in the form

$$m\ddot{u}_n = f(u_{n+1} + u_{n-1} - 2u_n). \quad (2.2)$$

The solution of this equation can be sought in the form

$$u_n = u_0 e^{i(\omega t + kna)}. \quad (2.3)$$

Substituting (2.3) in (2.2), we obtain the condition

$$\omega^2 = \pm 2 \sqrt{\frac{f}{m}} \sin\left(\frac{ka}{2}\right). \quad (2.4)$$

Formula (2.4), which connects the oscillation frequency ω with the wave number k , is the dispersion equation for the problem under consideration. It follows from (2.4) that the maximum frequency ω_m which can be possessed by vibrations of a chain of identical atoms is $\omega_m = 2\sqrt{f/m}$. This frequency corresponds to wave-vector values $k_m = \pm\pi/a$. Usually in crystals $k_m = \pm\pi/a \approx 10^8 \text{ cm}^{-1}$ and $\omega_m \approx 10^{13} \text{ sec}^{-1}$. This limiting frequency lies in the infrared region of the spectrum.

We shall assume that the chain in question consists of N atoms and that periodic boundary conditions (cyclic conditions) are satisfied, i.e.,

$$u(na + Na) = u(na). \quad (2.5)$$

We then obtain from (2.3) the possible values of the wave vector k :

$$k = \pm \frac{2\pi}{Na}, \pm \frac{4\pi}{Na}, \dots, \frac{N/2 \cdot 2\pi}{Na}. \quad (2.6)$$

These values of k determine the N natural oscillations of the chain.

Let us determine the distribution function of the number of oscillations with respect to frequency; this distribution function describes the spectrum of the natural oscillations. Let $g(\omega)d\omega$ give the number of oscillations in the interval from ω to $\omega + d\omega$, and $w(k)dk$ the number of oscillations in the wave-number interval from k to $k + dk$. Then

$$g(\omega)d\omega = w(k) \frac{dk}{d\omega} d\omega. \quad (2.7)$$

The value of $dk/d\omega$ can be readily obtained from (2.4):

$$\frac{dk}{d\omega} = \frac{2}{a \sqrt{\omega_m^2 - \omega^2}}. \quad (2.8)$$

Thus, since according to (2.6) there is one oscillation in the interval $2\pi/Na$, we get

$$g(\omega) = \frac{N}{\pi \sqrt{\omega_m^2 - \omega^2}}. \quad (2.9)$$

Let us consider now a more complicated case, that of a linear chain of atoms that are equally spaced but have different alternating masses m_1 and m_2 . We denote the force constants of the interaction of the neighboring atoms by f . In this case the unit cell contains two atoms and the equations of motion become more complicated. In place of (2.2), we have a system of two equations (we again take into account only the interaction of the nearest neighbors)

$$\left. \begin{aligned} m_1 \ddot{u}_{2n} &= f(u_{2n+1} + u_{2n-1} - 2u_{2n}), \\ m_2 \ddot{u}_{2n+1} &= f(u_{2n+2} + u_{2n} - 2u_{2n+1}). \end{aligned} \right\} \quad (2.10)$$

We seek the solution of these equations in the form

$$\left. \begin{aligned} u_{2n} &= A_1 e^{i(\omega t + 2nka)}, \\ u_{2n+1} &= A_2 e^{i(\omega t + (2n+1)ka)}. \end{aligned} \right\} \quad (2.11)$$

Substituting this solution in (2.10), we obtain a system of two homogeneous equations

$$\left. \begin{aligned} -\omega^2 m_1 A_1 &= f A_2 (e^{ika} + e^{-ika}) - 2f A_1, \\ -\omega^2 m_2 A_2 &= f A_1 (e^{ika} + e^{-ika}) - 2f A_2. \end{aligned} \right\} \quad (2.12)$$

This system has nontrivial solutions with respect to A_1 and A_2 if

$$\begin{vmatrix} 2f - m_1 \omega^2 & -2f \cos ka \\ -2f \cos ka & 2f - m_2 \omega^2 \end{vmatrix} = 0. \quad (2.13)$$

Then

$$\omega^2 = f \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \pm f \left[\left(\frac{1}{m_1} + \frac{1}{m_2} \right)^2 - \frac{4 \sin^2 ka}{m_1 m_2} \right]^{\frac{1}{2}}. \quad (2.14)$$

The dependence of ω on k , determined by formula (2.14), is shown in Fig. 2 (it is assumed that $m_1 > m_2$). We see that in this case the dispersion curve has two branches. One is called acoustic and the other optical.

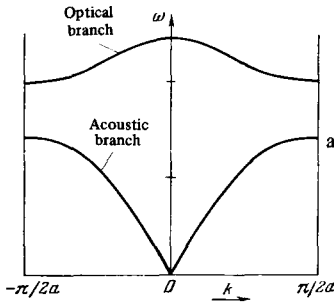


FIG. 2. Oscillation frequencies of a two-atom chain.

Similar branches arise also in two-dimensional and three-dimensional lattices.

2.2. Three-dimensional Lattice Oscillations

An ideal crystal is a mechanical system with an infinitely large number of degrees of freedom. To simplify the problem one considers, in accordance with the Born hypothesis,^[24] not the vibrations of an infinite crystal but those of a sufficiently large finite volume of the crystal (cyclic volume), which contains $N = L^3$ unit cells, with account taken of the cyclic boundary conditions. Let us consider the harmonic oscillations of the cyclic volume.

The position of an arbitrary atom of the crystal can be specified by means of the vector

$$\mathbf{R} \left(\begin{matrix} 1 \\ \kappa \end{matrix} \right) = \mathbf{X} \left(\begin{matrix} 1 \\ \kappa \end{matrix} \right) + \mathbf{u} \left(\begin{matrix} 1 \\ \kappa \end{matrix} \right) = \mathbf{l} + \mathbf{X}_\kappa + \mathbf{u} \left(\begin{matrix} 1 \\ \kappa \end{matrix} \right), \quad (2.15)$$

where $\mathbf{l} = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3$ is a vector that determines the position of the unit cell in which the atom under consideration is situated, and l_i are integers satisfying the inequality $0 \leq l_i < L$. The vector \mathbf{X}_κ defines the equilibrium position of the atom numbered κ ($\kappa = 1, 2, \dots$) inside the unit cell specified by the vector \mathbf{l} ; the vector $\mathbf{u} \left(\begin{matrix} 1 \\ \kappa \end{matrix} \right)$ characterizes the deviation of this atom from the equilibrium position.

As the generalized coordinates of the considered mechanical system we can choose the $3Nn$ coordinates of the displacements $u_\alpha \left(\begin{matrix} 1 \\ \kappa \end{matrix} \right)$ of the atoms from their equilibrium position in the direction of the α axis ($\alpha = 1, 2, 3$) of a Cartesian system. The Hamiltonian and the Lagrangian of the system have then in the harmonic approximation the form

$$H = \frac{1}{2} \sum_{l \times \alpha} m_\kappa \left[u_\alpha \left(\begin{matrix} 1 \\ \kappa \end{matrix} \right) \right]^2 + \frac{1}{2} \sum_{\substack{l \times \alpha \\ l' \times \alpha'}} \Phi_{\alpha\alpha'} \left(\begin{matrix} 1 \\ \kappa\kappa' \end{matrix} \right) u_\alpha \left(\begin{matrix} 1 \\ \kappa \end{matrix} \right) u_{\alpha'} \left(\begin{matrix} 1 \\ \kappa' \end{matrix} \right), \quad (2.16)$$

$$L = \frac{1}{2} \sum_{l \times \alpha} m_\kappa \left[\dot{u}_\alpha \left(\begin{matrix} 1 \\ \kappa \end{matrix} \right) \right]^2 - \frac{1}{2} \sum_{\substack{l \times \alpha \\ l' \times \alpha'}} \Phi_{\alpha\alpha'} \left(\begin{matrix} 1 \\ \kappa\kappa' \end{matrix} \right) u_\alpha \left(\begin{matrix} 1 \\ \kappa \end{matrix} \right) u_{\alpha'} \left(\begin{matrix} 1 \\ \kappa' \end{matrix} \right); \quad (2.17)$$

here m_κ is the mass of the atom numbered κ , $\Phi_{\alpha\alpha'} \left(\begin{matrix} 1 \\ \kappa\kappa' \end{matrix} \right)$ are the coefficients of second order in the expansion of the potential energy in the displacements of the atoms.

The equations of motion are accordingly

$$m_\kappa \ddot{u}_\alpha \left(\begin{matrix} 1 \\ \kappa \end{matrix} \right) + \sum_{l' \times \alpha'} \Phi_{\alpha\alpha'} \left(\begin{matrix} 1 \\ \kappa\kappa' \end{matrix} \right) u_{\alpha'} \left(\begin{matrix} 1 \\ \kappa' \end{matrix} \right) = 0. \quad (2.18)$$

The solution of (2.18) is of the form

$$u_\alpha \left(\begin{matrix} 1 \\ \kappa \end{matrix} \right) = u_\alpha^{(0)} \left(\begin{matrix} 1 \\ \kappa \end{matrix} \right) e^{-i\omega t}. \quad (2.19)$$

After substituting (2.19) in (2.18) we obtain

$$\sum_{l' \times \alpha'} \left[\Phi_{\alpha\alpha'} \left(\begin{matrix} 1 \\ \kappa\kappa' \end{matrix} \right) - \omega^2 m_\kappa \delta_{\alpha\alpha'} \delta_{\kappa\kappa'} \delta_{ll'} \right] u_{\alpha'}^{(0)} \left(\begin{matrix} 1 \\ \kappa' \end{matrix} \right) = 0. \quad (2.20)$$

The condition for the solvability of the system (2.20) is the vanishing of the determinant

$$\left| \Phi_{\alpha\alpha'} \left(\begin{matrix} 1 \\ \kappa\kappa' \end{matrix} \right) - \omega^2 m_\kappa \delta_{\alpha\alpha'} \delta_{\kappa\kappa'} \delta_{ll'} \right| = 0. \quad (2.21)$$

Equation (2.21) is an algebraic equation of degree $3Nn$ relative to ω^2 . The solution of the system (2.20) yields $3Nn$ eigenvectors. It is possible to go over from the quantities $u_\alpha^{(0)} \left(\begin{matrix} 1 \\ \kappa \end{matrix} \right)$ to other more convenient variables. Owing to the translational symmetry, such variables are the quantities $u_\alpha^{(0)} \left(\begin{matrix} \mathbf{k} \\ \kappa \end{matrix} \right)$, determined from the expansion of $u^{(0)} \left(\begin{matrix} 1 \\ \kappa \end{matrix} \right)$ in plane waves

$$u_\alpha^{(0)} \left(\begin{matrix} 1 \\ \kappa \end{matrix} \right) = \sum_{\mathbf{k}} \frac{1}{\sqrt{m_\kappa N}} u_\alpha^{(0)} \left(\begin{matrix} \mathbf{k} \\ \kappa \end{matrix} \right) e^{i\mathbf{k}\cdot\mathbf{l}}. \quad (2.22)$$

It follows from (2.22) that

$$u_\alpha^{(0)} \left(\begin{matrix} \mathbf{k} \\ \kappa \end{matrix} \right) = \sqrt{\frac{m_\kappa}{N}} \sum_{\mathbf{l}} u_\alpha^{(0)} \left(\begin{matrix} 1 \\ \kappa \end{matrix} \right) e^{-i\mathbf{k}\cdot\mathbf{l}}. \quad (2.23)$$

Owing to the cyclicity conditions, the vector \mathbf{k} assumes a number of discrete values, such that

$$\left. \begin{aligned} k_x &= \pm \frac{2\pi}{La_1}, \pm \frac{2\pi}{La_1} \cdot 2, \pm \frac{2\pi}{La_1} \cdot 3, \dots, \pm \frac{2\pi}{La_1} \frac{L}{2}, \\ k_y &= \pm \frac{2\pi}{La_2}, \pm \frac{2\pi}{La_2} \cdot 2, \pm \frac{2\pi}{La_2} \cdot 3, \dots, \pm \frac{2\pi}{La_2} \frac{L}{2}, \\ k_z &= \pm \frac{2\pi}{La_3}, \pm \frac{2\pi}{La_3} \cdot 2, \pm \frac{2\pi}{La_3} \cdot 3, \dots, \pm \frac{2\pi}{La_3} \frac{L}{2}. \end{aligned} \right\} \quad (2.24)$$

where a_1 , a_2 , and a_3 are the linear dimensions of the unit cell. Substituting (2.22) and (2.19) in (2.18), we obtain

$$\sum_{\alpha' \times \kappa'} \left[D_{\alpha\alpha'} \left(\begin{matrix} \mathbf{k} \\ \kappa\kappa' \end{matrix} \right) - \omega^2 \delta_{\alpha\alpha'} \delta_{\kappa\kappa'} \right] u_{\alpha'}^{(0)} \left(\begin{matrix} \mathbf{k} \\ \kappa' \end{matrix} \right) = 0. \quad (2.25)$$

where

$$D_{\alpha\alpha'} \left(\begin{matrix} \mathbf{k} \\ \kappa\kappa' \end{matrix} \right) = \frac{1}{\sqrt{m_\kappa m_{\kappa'}}} \sum_{\mathbf{l}} \Phi_{\alpha\alpha'} \left(\begin{matrix} 0 \\ \kappa \kappa' \end{matrix} \right) e^{-i\mathbf{k}\cdot\mathbf{l}}.$$

The condition for the solvability of (2.25) is the vanishing of the determinant

$$\left| D_{\alpha\alpha'} \left(\begin{matrix} \mathbf{k} \\ \kappa\kappa' \end{matrix} \right) - \omega^2 \delta_{\alpha\alpha'} \delta_{\kappa\kappa'} \right| = 0. \quad (2.26)$$

We denote the eigenvectors of the system (2.25) by $e \left(\begin{matrix} \mathbf{k} \\ j \end{matrix} \right)$, and the corresponding eigenvalues are $\omega^2 \left(\begin{matrix} \mathbf{k} \\ j \end{matrix} \right)$. Then

$$\sum_{\alpha' \times \kappa'} D_{\alpha\alpha'} \left(\begin{matrix} \mathbf{k} \\ \kappa\kappa' \end{matrix} \right) e_{\alpha'} \left(\begin{matrix} \mathbf{k} \\ j \end{matrix} \right) = \omega^2 \left(\begin{matrix} \mathbf{k} \\ j \end{matrix} \right) e_\alpha \left(\begin{matrix} \mathbf{k} \\ j \end{matrix} \right). \quad (2.27)$$

Equation (2.26) is of order $3n$, so that $j = 1, 2, \dots, 3n$.

Thus, in the case of a three-dimensional lattice consisting of $3nN$ particles, there are $3nN$ oscillation frequencies, which are grouped in $3n$ branches. The relation $\omega = \omega(\mathbf{k})$ obtained from (2.26) is a multiply-valued function that has $3n$ different values of \mathbf{k} (in the absence of degeneracy) for each value of the vector \mathbf{k} ; each of these values pertains to one of the $3n$ branches. It can be shown that the three branches have frequencies ω that tend to zero when \mathbf{k} tends to zero; these branches are

called acoustic; the remaining $3n - 3$ branches are optical.

The system (2.25) makes it possible to determine the eigenvectors $e\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$ only accurate to a constant factor. They can therefore be chosen such as to satisfy the orthonormalization condition

$$\left. \begin{aligned} \sum_{\kappa'} e_{\alpha}^{\kappa'}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) e_{\alpha}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) &= \delta_{j\kappa'}, \\ \sum_j e_{\alpha}^{\kappa'}\left(\kappa' \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) e_{\alpha}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) &= \delta_{\alpha\alpha'} \delta_{\kappa\kappa'}. \end{aligned} \right\} \quad (2.28)$$

The Hamiltonian of the crystal is the sum of two quadratic forms which can be reduced simultaneously to diagonal form. Such a transformation can be realized with the aid of the expansion

$$u_{\alpha}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) = \frac{1}{\sqrt{m_{\alpha} N}} \sum_{\kappa', j} e_{\alpha}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) Q\left(\kappa' \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) e^{i\mathbf{k}\cdot\mathbf{r}}. \quad (2.29)$$

It follows from the fact that $u_{\alpha}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$ is real that

$$Q^*\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) = Q\left(\kappa \left| \begin{smallmatrix} -\mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right). \quad (2.30)$$

Substituting (2.23) in the Hamiltonian and Lagrangian, we obtain

$$\left. \begin{aligned} H &= \frac{1}{2} \sum_{\mathbf{k}, \mathbf{j}} \left[\dot{Q}^*\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) \dot{Q}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) - \omega^2\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) Q^*\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) Q\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) \right], \\ L &= \frac{1}{2} \sum_{\mathbf{k}, \mathbf{j}} \left[\dot{Q}^*\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) \dot{Q}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) - \omega^2\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) Q^*\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) Q\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) \right]. \end{aligned} \right\} \quad (2.31)$$

From this we obtain the equations of motion

$$\ddot{Q}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) + \omega^2\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) Q\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) = 0 \quad (2.32)$$

with solution

$$Q\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) = Q^{(0)}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) e^{-i\omega t + i\varphi_0}, \quad (2.33)$$

where $Q^{(0)}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$ is the amplitude of the oscillation and φ_0 is the initial phase.

The coordinates $Q\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$ are called normal coordinates, and the vibrations of the crystal atoms with frequency $\omega\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$ are called the principal vibrations.

The normal coordinates $Q\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$ and the corresponding canonically conjugate momenta $P\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) = \dot{Q}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$, generally speaking, are complex. It is possible to change over to real coordinates with the aid of the transformation

$$Q\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) = \frac{1}{2} [q\left(\kappa \left| \begin{smallmatrix} -\mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) + q\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)] + \frac{i}{2\omega\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)} [\dot{q}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) - \dot{q}\left(\kappa \left| \begin{smallmatrix} -\mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)]. \quad (2.34)$$

It can be shown that such a transformation is canonical. The variables $q\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$ and $\dot{q}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$ are then canonically conjugate.

As a result of the substitution (2.34), the Hamiltonian reduces to the form

$$H = \frac{1}{2} \sum_{\mathbf{k}, \mathbf{j}} \left[p^2\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) + \omega^2\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) q^2\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) \right],$$

where $p\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) = \dot{q}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$, with the variables $p\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$ and $q\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$ real.

On going over to the quantum-mechanical analysis, the quantities $u_{\alpha}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$ and $p_{\alpha}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \right.\right)$ are regarded as operators $\hat{u}_{\alpha}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$ and $\hat{p}_{\alpha}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$ satisfying the following commutation relations

$$[\hat{u}_{\alpha}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right), \hat{p}_{\alpha}\left(\kappa' \left| \begin{smallmatrix} \mathbf{k}' \\ \mathbf{j}' \end{smallmatrix} \right.\right)] = i\hbar \delta_{\mathbf{k}\mathbf{k}'} \delta_{\mathbf{j}\mathbf{j}'} \delta_{\alpha\alpha'}.$$

Accordingly, the variables $Q\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$, $P\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$ and $q\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$, $p\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$ should also be regarded as operators, and it follows from (2.28) that

$$\left. \begin{aligned} [\hat{Q}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right), \hat{P}\left(\kappa' \left| \begin{smallmatrix} \mathbf{k}' \\ \mathbf{j}' \end{smallmatrix} \right.\right)] &= i\hbar \Delta(\mathbf{k} - \mathbf{k}') \delta_{j\mathbf{j}'}, \\ [\hat{q}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right), \hat{p}\left(\kappa' \left| \begin{smallmatrix} \mathbf{k}' \\ \mathbf{j}' \end{smallmatrix} \right.\right)] &= i\hbar \Delta(\mathbf{k} - \mathbf{k}') \delta_{j\mathbf{j}'}. \end{aligned} \right\} \quad (2.35)$$

($\Delta(\mathbf{k}) = 1$ if \mathbf{k} vanishes or equals the reciprocal-lattice vector; $\Delta(\mathbf{k}) = 0$ in all other cases.)

In particular, in the coordinate representation we have the well known relation

$$\hat{p}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) = -i\hbar \frac{\partial}{\partial q\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)}, \quad \hat{q}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) = q\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right),$$

so that the Schrödinger equation takes the form

$$\frac{1}{2} \sum_{\mathbf{k}, \mathbf{j}} \left\{ -\hbar^2 \frac{\partial^2}{\partial q^2\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)} + \omega^2\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) q^2\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) \right\} \psi = E\psi.$$

The solution of this equation is well known and can be written in the form

$$\psi = \prod_{\mathbf{k}, \mathbf{j}} \psi_{m(\mathbf{k})}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right),$$

where $m\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$ is the vibrational quantum number of the oscillator with index $\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$. Each of the functions $\psi_{m(\mathbf{k})}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$ satisfies the equation

$$\left\{ -\hbar^2 \frac{\partial^2}{\partial q^2\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)} + \frac{1}{2} \omega^2\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) q^2\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) \right\} \psi_{m(\mathbf{k})}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) = E_{m(\mathbf{k})} \psi_{m(\mathbf{k})}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right). \quad (2.36)$$

The total energy $E\{m\}$ of the crystal in the state described by $3Nn$ quantum numbers $m\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$ is

$$E\{m\} = \sum_{\mathbf{k}, \mathbf{j}} E_{m(\mathbf{k})}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right).$$

The solution of (2.36) is of the form

$$\psi_m(q) = \left(\frac{\alpha}{\pi^{1/2} 2^m m!} \right)^{1/2} \exp\left(-\frac{1}{2} \beta^2 q^2\right) H_m(\beta q), \quad (2.37)$$

where $\beta^2 = \beta_j^2(\mathbf{k}) = (1/\hbar) \omega\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$, and $H_m(x)$ is a Hermite polynomial of order m .

The corresponding energy levels are determined by the formula

$$E_m\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) = \left[m\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) + \frac{1}{2} \right] \hbar \omega\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right),$$

where $m\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right) = 0, 1, 2, \dots$. The matrix elements of the operators $\hat{q}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$ and $\hat{p}\left(\kappa \left| \begin{smallmatrix} \mathbf{k} \\ \mathbf{j} \end{smallmatrix} \right.\right)$, calculated with the aid of the wave function (2.37), are

$$\left. \begin{aligned} \langle m | q | m' \rangle &= \sqrt{\frac{\hbar}{2\pi}} (V\overline{m+1} \delta_{m', m+1} + V\overline{m} \delta_{m', m-1}), \\ \langle m | p | m' \rangle &= -\sqrt{\frac{\hbar\omega}{2}} (V\overline{m+1} \delta_{m', m+1} - V\overline{m} \delta_{m', m-1}). \end{aligned} \right\} (2.38)$$

Let us consider now the so-called second-quantization representation. To this end, we introduce first new canonical variables $a(\mathbf{k}_j)$ and $a^*(\mathbf{k}_j)$, defined by the relations

$$\left. \begin{aligned} a(\mathbf{k}_j) &= \left[\left(\frac{\omega(\mathbf{k}_j)}{2\hbar} \right)^{1/2} Q(\mathbf{k}_j) + i \left(\frac{1}{2\hbar\omega(\mathbf{k}_j)} \right)^{1/2} P(\mathbf{k}_j) \right], \\ a^*(\mathbf{k}_j) &= \left[\left(\frac{\omega(\mathbf{k}_j)}{2\hbar} \right)^{1/2} Q^*(\mathbf{k}_j) - i \left(\frac{1}{2\hbar\omega(\mathbf{k}_j)} \right)^{1/2} P^*(\mathbf{k}_j) \right]. \end{aligned} \right\} (2.39)$$

On going over to the quantum-mechanical analysis, the quantities $a(\mathbf{k}_j)$ and $a^*(\mathbf{k}_j)$ are replaced by operators. Using (2.35), we readily find that

$$\begin{aligned} [\hat{a}(\mathbf{k}_j), \hat{a}^*(\mathbf{k}'_j)] &= \Delta(\mathbf{k}-\mathbf{k}') \delta_{jj'}, \\ [\hat{a}(\mathbf{k}_j), a(\mathbf{k}'_j)] &= [\hat{a}^*(\mathbf{k}_j), \hat{a}^*(\mathbf{k}'_j)] = 0. \end{aligned}$$

Thus, the operators \hat{a} can be regarded as Bose operators. The matrix elements of these operators, in the representation given by formula (2.37), can be obtained by using (2.38) and (2.39):

$$\begin{aligned} \langle m | a^* | m' \rangle &= V\overline{m} \delta_{m', m-1}, \\ \langle m | a | m' \rangle &= V\overline{m+1} \delta_{m', m+1}. \end{aligned} (2.40)$$

The Hamiltonian operator takes the form

$$\hat{H} = \sum_{kj} \hbar\omega(\mathbf{k}_j) \left[\hat{a}^*(\mathbf{k}_j) \hat{a}(\mathbf{k}_j) + \frac{1}{2} \right].$$

Since any stationary state of the crystal is determined by specifying $3nN$ quantum numbers $\{m(\mathbf{k}_j)\}$, any quantum state of the system can be described by a set of these numbers. The corresponding wave function $\psi\{m(\mathbf{k}_j)\}$ depends on $3nN$ variables and specifies the second-quantization representation. It follows from (2.40) that in the second-quantization representation the operator $\hat{a}^*(\mathbf{k}_j) \hat{a}(\mathbf{k}_j)$ is diagonal, with

$$\hat{a}^*(\mathbf{k}_j) \hat{a}(\mathbf{k}_j) \psi\{m(\mathbf{k}_j)\} = m(\mathbf{k}_j) \psi\{m(\mathbf{k}_j)\}. (2.41)$$

Accordingly, the action of the Hamiltonian operator on the function $\psi\{m(\mathbf{k}_j)\}$ yields

$$\hat{H}\psi\{m(\mathbf{k}_j)\} = E_{\{m\}} \psi\{m(\mathbf{k}_j)\},$$

where

$$E_{\{m\}} = \sum_{kj} \hbar\omega(\mathbf{k}_j) \left[m(\mathbf{k}_j) + \frac{1}{2} \right].$$

The last expression can be interpreted as the energy of the aggregate of the interacting oscillators, for each of which there are $m(\mathbf{k}_j)$ quasiparticles with energies

$\hbar\omega(\mathbf{k}_j)$, and a vacuum with energy

$$E_0 = \frac{1}{2} \sum_{kj} \hbar\omega(\mathbf{k}_j).$$

The indicated quasiparticles are called phonons; they were first introduced by I. E. Tamm.

From the form of the matrix elements (2.38) it follows that

$$\begin{aligned} \hat{a}^*(\mathbf{k}_j) \psi\{m(\mathbf{k}_j)\} &= \sqrt{m(\mathbf{k}_j)+1} \psi\{m(\mathbf{k}_j)+1\}, \\ \hat{a}(\mathbf{k}_j) \psi\{m(\mathbf{k}_j)\} &= \sqrt{m(\mathbf{k}_j)} \psi\{m(\mathbf{k}_j)-1\}. \end{aligned}$$

Therefore the operators $\hat{a}^*(\mathbf{k}_j)$ and $\hat{a}(\mathbf{k}_j)$ are appropriately called the quasiparticle creation and annihilation operators; the operator $\hat{m}(\mathbf{k}_j) = \hat{a}^*(\mathbf{k}_j) \hat{a}(\mathbf{k}_j)$, in accordance with (2.41), is called the quasiparticle-number operator.

2.3. Raman's Theory of Crystal-lattice Dynamics

In a number of papers,^[25] Raman and his co-workers^[26-28] developed for the crystal lattice vibrations a theory different from Born's. The main idea of this theory consists in the following.

Raman foregoes the aforementioned Born's cyclic boundary conditions, assuming that the normal oscillations of the crystal particles should not be identified with all the wave motions that follow from the cyclic condition. He postulates instead that the ratios of the displacements (α, β, γ) of any two neighboring equivalent atoms, located along any of the three principal axes of the Bravais lattice and taking part in the normal oscillations, are real and the same for each pair of such atoms:

$$\alpha, \beta, \gamma = \pm 1.$$

This means that the phases of the oscillations of the indicated atoms can either coincide or be opposite. If $\alpha = \beta = \gamma = 1$, i.e., the oscillations of equivalent atoms are the same, and if the primitive cell contains n nonequivalent particles, then n interpenetrating Bravais lattices vibrate relative to each other with the same oscillation phase as the neighboring equivalent atoms. Altogether there are $3n$ such oscillations; the seven remaining possible values of α, β , and γ have $21n$ more degrees of freedom, corresponding to oscillations in which not all the neighboring planes made up of equivalent atoms move in phase (some of them move in phase opposition). It is thus assumed that the crystal has altogether $24n - 3$ degrees of freedom corresponding to real physical oscillations (among all the normal oscillations, three correspond simply to translation of the crystal as a whole). Accordingly, the problem reduces to a study of the oscillations of a system consisting of $8n$ atoms located in eight neighboring unit cells, making it possible to apply the same reasoning as in the analysis of polyatomic molecules.

At first glance, Raman's theory and Born's theory of crystal lattice dynamics are mutually exclusive. However, the development of the theory of critical points makes it possible to establish a correspondence between these two theories.

2.4. Polar Oscillations of a Crystal Lattice

It has been assumed so far that the ions oscillate independently of the electromagnetic normal oscillations that propagate in the crystal. This, however, is not satisfied for polar oscillations, which are connected with changes of the dipole moment. Let us consider the singularities of polar oscillations on the basis of Born's theory of the crystal lattice dynamics.

Polar oscillations of ions are accompanied by the occurrence of electromagnetic waves that interact strongly with the purely mechanical oscillations, and the equations of motion for such oscillations describe the displacements of the ions relative to each other as well as the components of the electromagnetic field. The formulation and solution of such equations for crystals of various types has been carried out in a number of papers. According to Born's results,^[24] in the case of a polar diatomic lattice of a cubic crystal, the simultaneous solution of the equations of motion for the mechanical displacements of the atoms and for the components of the electromagnetic fields, with Maxwell's equations taken into account, leads to the presence of two branches of polar oscillations—longitudinal and transverse. The dependence of the frequency ω on the wave vector k for these oscillations is shown schematically in Fig. 3. The longitudinal oscillations are essentially oscillations of the crystal polarization vector \mathbf{P} , which occur in the direction of propagation of the oscillation wave. The frequency of the longitudinal oscillation is determined from the relation

$$\omega_l^2 = \frac{\epsilon_0}{\epsilon_\infty} \omega_0^2, \quad (2.42)$$

where ω_l is the frequency of the longitudinal oscillation, $\epsilon_0 = \epsilon(0)$ is the static dielectric constant, $\epsilon_\infty = \epsilon(\infty)$ is the dielectric constant at frequencies much higher than infrared but much lower than the electron-absorption frequencies; ω_0 is the frequency of the mechanical oscillations without allowance for the interaction with the electromagnetic field (the dispersion infrared frequency). The longitudinal oscillations are nondegenerate.

For the doubly-degenerate transverse branch of the oscillations, the dependence of the frequency on the wave vector k is determined from the relation

$$\frac{k^2 c^2}{\omega^2} = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{\omega_0^2 - \omega^2} \omega_0^2, \quad (2.43)$$

where c is the velocity of light and the remaining quantities have been defined earlier. We see that the values of the frequencies change with changing absolute magnitude of the wave vector k .

In Fig. 3, all the solutions of (2.43) are represented by solid lines; the dashed lines show the corresponding curves for non-interacting electromagnetic and purely-mechanical subsystems.

In this case we actually have a typical example of resonance of two oscillating subsystems. On the right of the resonance point the frequency of the electromagnetic oscillations (branch 1) becomes so large that the ions are not set in motion by the field, owing to their large mass; the corresponding ion oscillations (branch 2) are purely mechanical. To the contrary, near resonance, the mechanical oscillations "mix" with the electromagnetic ones. The crystal quasiparticles corresponding to

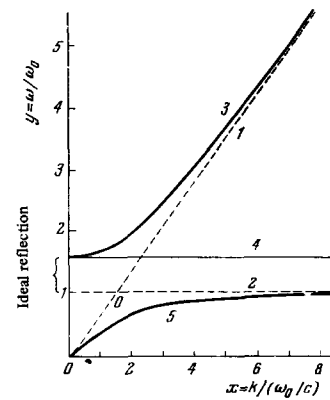


FIG. 3. Optical and mechanical waves in a crystal. 1 – Optical waves without allowance for dispersion; 2 – mechanical oscillations without allowance for the interaction with the electromagnetic field; 3 – optical waves with allowance for dispersion; 4 – longitudinal lattice oscillation; 5 – transverse lattice oscillations.

the section of the dispersion curve 5 near the point O are called polaritons.

Equations (2.42) and (2.43) were generalized and investigated for more complicated cubic crystals in^[23]. According to the results of that paper, each triply degenerate oscillation of the vector type (i.e., active in the infrared absorption spectrum) is split into nondegenerate longitudinal and doubly-degenerate transverse oscillations. For a crystal having n optical oscillations of the vector type, the following relation holds true:

$$\prod_{j=1}^n \left(\frac{\omega_{lj}}{\omega_{tj}} \right)^2 = \frac{\epsilon_0}{\epsilon_\infty}, \quad (2.44)$$

where ω_{lj} and ω_{tj} are the frequencies of the longitudinal and transverse oscillations at sufficiently large values of the wave vector k ($k \gg \omega/c$).

For noncubic crystals, the dispersion curves of the vibrational branches have a more complicated form. In this case the frequencies of the polar oscillations depend not only on the absolute value of the vector k , but also on its direction; the separation of the oscillations into longitudinal and transverse is valid only for certain of the most symmetrical directions of the vector k . When the direction of the vector k changes, the oscillation may become transformed from transverse into longitudinal and vice versa. Let us consider by way of an example a uniaxial crystal, in which there is only one group of three vibrational branches active in the spectrum of the infrared absorption. Owing to the anisotropy of the crystal, in the absence of long-wave electric forces, the oscillation in which the atoms are displaced along the z axis of the crystal have a frequency $\omega_{||}$, which differs from the frequency ω_{\perp} of the doubly-degenerate oscillation occurring in the (x, y) plane.

Equations (2.44) were generalized for noncubic uniaxial crystals in the presence of three polar branches in^[30,31]. Two solutions are obtained for an arbitrary orientation of the wave vector k of the phonon relative to the z axis. In one of them, the vectors \mathbf{E} and \mathbf{P} are perpendicular both to the vector k and to the z axis. This solution corresponds to the ordinary wave, for which the following relation holds true

$$\frac{k^2 c^2}{\omega^2} = \frac{\omega_{\perp}^2 \epsilon_{0\perp} - \omega^2 \epsilon_{\infty\perp}}{\omega_{\perp}^2 - \omega^2}. \quad (2.45)$$

The second solution corresponds to the extraordinary wave. The frequencies of the extraordinary wave depend on the angle θ between the vector \mathbf{k} and the z axis.

$$\frac{k^2 c^2}{\omega^2} = \frac{\left(\frac{\omega_{\parallel}^2 \epsilon_{0\parallel} - \omega^2 \epsilon_{\infty\parallel}}{\omega_{\parallel}^2 - \omega^2} \right) \left(\frac{\omega_{\perp}^2 \epsilon_{0\perp} - \omega^2 \epsilon_{\infty\perp}}{\omega_{\perp}^2 - \omega^2} \right)}{\left(\frac{\omega_{\parallel}^2 \epsilon_{0\parallel} - \omega^2 \epsilon_{\infty\parallel}}{\omega_{\parallel}^2 - \omega^2} \right) \cos^2 \theta + \left(\frac{\omega_{\perp}^2 \epsilon_{0\perp} - \omega^2 \epsilon_{\infty\perp}}{\omega_{\perp}^2 - \omega^2} \right) \sin^2 \theta}; \quad (2.46)$$

$\epsilon_{0\perp}$, $\epsilon_{\infty\perp}$, $\epsilon_{0\parallel}$ and $\epsilon_{\infty\parallel}$ are the corresponding values of the dielectric constants.

It is convenient to introduce the following notation:

$$\omega_{\parallel}^l = \omega_{\parallel} \sqrt{\frac{\epsilon_{0\parallel}}{\epsilon_{\infty\parallel}}}, \quad \omega_{\perp}^l = \omega_{\perp} \sqrt{\frac{\epsilon_{0\perp}}{\epsilon_{\infty\perp}}}. \quad (2.47)$$

It follows from (2.45) and (2.46) that when $\mathbf{k} = 0$ the phonon frequencies are ω_{\parallel}^l and ω_{\perp}^l . At large wave vectors ($\mathbf{k} \gg \omega/c$) we have from (2.45) $\epsilon = \epsilon_{\perp}$ for the ordinary phonon and

$$\left(\frac{\omega_{\parallel}^2 \epsilon_{0\parallel} - \omega^2 \epsilon_{\infty\parallel}}{\omega_{\parallel}^2 - \omega^2} \right) \cos^2 \theta + \left(\frac{\omega_{\perp}^2 \epsilon_{0\perp} - \omega^2 \epsilon_{\infty\perp}}{\omega_{\perp}^2 - \omega^2} \right) \sin^2 \theta = 0 \quad (2.48)$$

for the extraordinary phonons.

Since the last equation has in general two different roots ω_1 and ω_2 , we obtain when $\mathbf{k} \gg \omega/c$ three nondegenerate vibrational branches with frequencies ω_{\perp} , ω_1 , and ω_2 .

To analyze the general formula (2.48), let us consider two limiting cases: 1) $|\omega_{\parallel} - \omega_{\perp}| \ll \omega_{\parallel}^l - \omega_{\parallel}$, $\omega_{\perp}^l - \omega_{\perp}$. In this case the difference between the mechanical elastic coefficients of the vibrational branches, due to the anisotropy of the crystal, is much smaller than the additions due to the electrostatic forces. Examples of such crystals are hexagonal-modification ZnO and SiC and others. Under the condition that ϵ_{\parallel} and ϵ_{\perp} differ insignificantly, we obtain from (2.48)

$$\omega_1^2 = \omega_{\parallel}^2 \sin^2 \theta + \omega_{\perp}^2 \cos^2 \theta, \quad \omega_2^2 = (\omega_{\parallel}^l)^2 \cos^2 \theta + (\omega_{\perp}^l)^2 \sin^2 \theta. \quad (2.49)$$

The form of the dispersion curves for different directions of the wave vector \mathbf{k} is shown schematically in Figs. 4a and 4c.

2) $|\omega_{\parallel} - \omega_{\perp}| \gg \omega_{\parallel}^l - \omega_{\parallel}$, $\omega_{\perp}^l - \omega_{\perp}$. In this case the solutions of (2.48) are given by

$$\omega_1^2 = \omega_{\perp}^2 \sin^2 \theta + \omega_{\parallel}^2 \cos^2 \theta, \quad \omega_2^2 = \omega_{\perp}^2 \cos^2 \theta + \omega_{\parallel}^2 \sin^2 \theta. \quad (2.50)$$

The corresponding curves are shown in Figs. 4d and 4f. Formulas similar to (2.49) and (2.50) were first obtained in [32]. The subsequent development of the theory for the case when there are more than three polar vibrational branches is also given in [32]. In the general case the frequencies of the polar oscillations depend both on the direction of the wave vector and on its magnitude.

2.5. Oscillations of Individual Molecules or Group of Atoms in Crystals

In some crystals the unit cell may contain many atoms; individual atoms are strongly attracted to each other and combine into separate groups. Such groups can be either neutral (molecules) or charged formations (CO_3^{--} , H_2PO_4^- , etc.). In first approximation it can be assumed that the individual molecules in the molecular-crystal lattice are

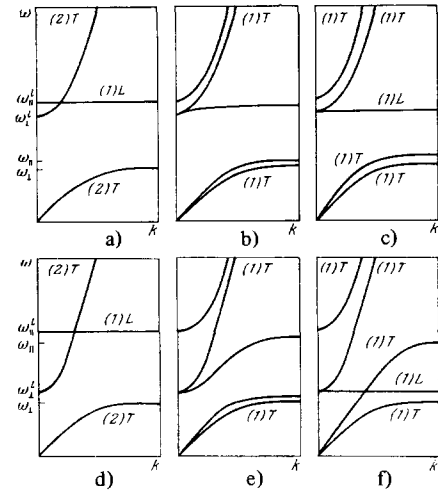


FIG. 4. Dispersion curves of optical vibrational branches at small wave vectors \mathbf{k} for a uniaxial crystal with different placements of the phonon wave vector: a), d) parallel to the z axis; c), f) in the (x, y) plane; e) and e) in the intermediate position; d) corresponds to the case when the anisotropic interatomic forces prevail over the electrostatic forces.

individual atomic groups constitute rigid formations which, as a unit, execute translational and rotational oscillations. Let us stop to discuss in greater detail the case of molecular crystals. A. I. Ansel'm and N. N. Perfir'eva [33] performed calculated the oscillations of a one-dimensional model of a molecular lattice; these calculations make it possible to gain new ideas concerning the singularities of our problem.

Let us consider first a one-dimensional lattice with one molecule per unit cell. We assume that the position of the center of gravity and the orientation of the n -th molecule are specified by the coordinates x_n and θ_n respectively (the molecule can rotate only in one plane). The potential energy of the n -th molecule is then equal to

$$u_n = u_0 + \frac{1}{2} a (\theta_{n-1}^2 + \theta_n^2) + \frac{1}{2} b (\theta_n^2 + \theta_{n+1}^2) + c (\theta_{n-1} \theta_n + \theta_n \theta_{n+1}) + \frac{1}{2} f [(x_{n-1} - x_n)^2 + (x_n - x_{n+1})^2] + g [\theta_{n-1} (x_{n-1} - x_n) + \theta_n (x_n - x_{n+1})] + h [\theta_n (x_{n-1} - x_n) + \theta_{n+1} (x_n - x_{n+1})] + \dots; \quad (2.51)$$

Here a, b, c, f, g, h —ordinary dynamic constants. The equations of motion are

$$\left. \begin{aligned} m\ddot{x}_n &= -f(2x_n - x_{n-1} - x_{n+1}) - g(\theta_{n-1} - \theta_{n+1}) - h(\theta_{n-1} - \theta_n), \\ I\ddot{\theta}_n &= -(a+b)\theta_n - c(\theta_{n-1} + \theta_{n+1}) - g(x_n - x_{n+1}) - h(x_{n-1} - x_n) \end{aligned} \right\} \quad (2.52)$$

(m —mass, I —moment of inertia of the molecule).

We seek the solution of this system in the form of orientational-translational waves

$$x_n = x e^{i(\omega t - n\varphi)}, \quad \theta_n = \theta e^{i(\omega t - n\varphi)}, \quad (2.53)$$

where the phase of the wave is $\varphi = 2\pi a/\lambda$ and a is the lattice constant. Substituting (2.53) and (2.52), we obtain a system of two linear homogeneous equations for the amplitudes x and

$$\left. \begin{aligned} [m\omega^2 - 2f(1 - \cos \varphi)] x - [g(1 - e^{i\varphi}) - h(1 - e^{-i\varphi})] \theta &= 0, \\ [g(1 - e^{i\varphi}) - h(1 - e^{-i\varphi})] x - [I\omega^2 - (a+b+2c \cos \varphi)] \theta &= 0. \end{aligned} \right\} \quad (2.54)$$

Equating, as usual, the determinants of this system to

zero, we get

$$\omega^2 = \frac{1}{2} \Omega_1^2 (1 - \cos \varphi) + \frac{1}{2} \Omega_2^2 (1 + q \cos \varphi) \pm \left\{ \left[\frac{1}{2} \Omega_2^2 (1 + q \cos \varphi) - \frac{1}{2} \Omega_1^2 (1 - \cos \varphi) \right]^2 + (g_0 - h_0)^2 (1 - \cos \varphi)^2 + (g_0 + h_0)^2 \sin^2 \varphi \right\}^{1/2}; \quad (2.55)$$

Here

$$g_0 = g_l \sqrt{mI}, \quad h_0 = h_l \sqrt{mI}, \quad \Omega_1^2 = 2f/m, \quad \Omega_2^2 = (a+b)I, \quad q = 2c/(a+b).$$

The quantities Ω_1 and Ω_2 are the translational and orientational frequencies of the molecule when its nearest neighbors are secured in their equilibrium positions.

It can be seen from (2.55) that in the general case the oscillations have a mixed character of translational-orientational oscillations. The spectrum separates into orientational and translational components if $g = h = 0$. Then

$$\left. \begin{aligned} \omega_{or} = \omega_+ = \Omega_2 \sqrt{1 + q \cos \varphi}, \\ \omega_{tr} = \omega_- = \Omega_1 \sqrt{1 - \cos \varphi}. \end{aligned} \right\} \quad (2.56)$$

The limiting frequencies for long waves $\lambda \rightarrow \infty$ (or $\varphi = 0$) are

$$\omega_{tr}^2 = \frac{a+b}{I} (1+q), \quad \omega_{or}^2 = 0. \quad (2.57)$$

Thus, the translational frequencies give in this case the ordinary acoustic branch.

In the case of a linear molecular lattice with two molecules per unit cell, the calculations of Ansel'm and Porfir'eva^[33] lead to the following expressions for the limiting frequencies:

$$\begin{aligned} \omega_1^2 = 0, \quad \omega_2^2 = \Omega_2^2 (1-q), \\ \omega_3^2 = \frac{1}{2} (1+q) \Omega_2^2 - \Omega_1^2 + \left\{ \left[\frac{1}{2} (1+q) \Omega_2^2 - \Omega_1^2 \right]^2 + 4 (g_0 + h_0)^2 \right\}^{1/2}, \\ \omega_4^2 = \frac{1}{2} (1-q) \Omega_2^2 + \Omega_1^2 - \left\{ \left[\frac{1}{2} (1-q) \Omega_2^2 - \Omega_1^2 \right]^2 + 4 (g_0 + h_0)^2 \right\}^{1/2}. \end{aligned}$$

The first frequency pertains to the purely translational acoustic branch and the second is purely orientational. The third and fourth branches are mixed, and their separation into translational and orientational occurs only if $g_0 + h_0 = 0$.

In later papers,^[34] Porfir'eva considered two-dimensional and three-dimensional models of the molecular crystal lattice. The oscillations are divided into purely translational and orientational only at the limiting frequencies and only under the additional condition $g + h = 0$. The limiting frequencies of the acoustic branches of purely translational oscillations are then equal to zero, and those of purely orientational ones are proportional to $\sqrt{R_i/I_i}$ ($i = x, y, z$). The limiting frequencies of the optical branches are proportional in this case to $\sqrt{f_i/m}$ (translational oscillations) and $\sqrt{R_i^f/I_i}$ (orientational oscillations) (here I_x, I_y, I_z — moments of inertia of the molecule about the corresponding axis, and R_i, R_i^f, f_i — certain combinations of the quasielastic lattice constants). Similar conclusions were obtained in^[35].

3. CLASSIFICATION OF THE PRINCIPAL OSCILLATIONS OF A CRYSTAL IN ACCORDANCE WITH THE IRREDUCIBLE REPRESENTATIONS OF THE SPACE GROUPS

3.1. Crystal Lattice Symmetry. Irreducible Representation of Space Groups

The aggregate of all the transformations of the space occupied by the crystal, which do not change the equilib-

rium configuration (which reduce to interchange of places of identical atoms) is called the symmetry group of the crystal. The lattice always has a definite translational symmetry and can, in addition, have symmetry axes and planes.* The aggregate of all these symmetry elements of the crystal lattice is called its space group. Different space groups are distributed over the crystal classes. Altogether, 230 different space groups are possible.

Each space group contains a translation subgroup, which includes all the possible parallel transfers that realign the crystal lattice with itself. The elements of the translation subgroup can be written in the form $\{h_1 | \mathbf{a}\}$, where h_1 is the unit element of the group of crystal directions, and $\mathbf{a} = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3$ (l_i — integers, \mathbf{a}_i — basis vectors of the unit cell).

The space groups are infinite groups, and are therefore difficult to investigate. However, the crystal symmetry groups can be regarded as finite groups, if one assumes the cyclicity condition advanced by Born.^[24] According to the Born hypothesis, it can be assumed that when the number L of the translations along each of the vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ is sufficiently large, the crystal becomes aligned with itself, i.e.,

$$\{h_1 | \mathbf{a}_1\}^L = \{h_1 | \mathbf{a}_2\}^L = \{h_1 | \mathbf{a}_3\}^L = \{h_1 | 0\}. \quad (3.1)$$

From the cyclicity condition it follows that

$$0 \leq l_1, l_2, l_3 < L. \quad (3.2)$$

Thus, the translation subgroup can be regarded as a finite group of order $N = L^3$. In addition, since all the translations are commutative, this group is an Abel group and all its irreducible representations are one-dimensional and their number is also equal to N . It is convenient to describe these irreducible representations in the space of wave vectors \mathbf{k} or in reciprocal space, the unit vectors of which are the vectors

$$\mathbf{b}_i = 2\pi \frac{[\mathbf{a}_j \mathbf{a}_k]}{\mathbf{a}_i \mathbf{a}_j \mathbf{a}_k} \quad (i, k, l = 1, 2, 3). \quad (3.3)$$

Two reciprocal-space vectors that differ from each other by an integer number of basis vectors \mathbf{b}_i are called equivalent. The aggregate of nonequivalent reciprocal-space vectors can be obtained by confining oneself to the Brillouin zone, which is constructed in the following manner. We draw from the origin vectors to all the sites of the reciprocal lattice (i.e., the lattice constructed with the aid of the vectors $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$) and construct planes perpendicular to these vectors and passing through their midpoints. It can be shown that the smallest part of space bounded by these planes and containing the origin is fully equivalent to the unit cell made up of the vectors $\mathbf{b}_1, \mathbf{b}_2$, and \mathbf{b}_3 . The symmetrical polyhedron constructed in this manner is called the first Brillouin zone or simply the Brillouin zone. According to (2.24), the wave vectors of all the plane waves propagating in a crystal turns out to be located in the first Brillouin zone; the number of such vectors, and accordingly the number of points of the Brillouin zone, is equal to $N = L^3$. Each of the indicated points corresponds to an irreducible representation of the translation subgroup, the operators of which are simply numbers and are given by

*The aggregate of rotations and reflections in the symmetry planes of the crystal (proper and improper rotations) forms the group of directions F , or the group of macroscopic symmetry of the crystal.

$$T(\{h_j | a\}) = e^{ik_a} \quad (3.4)$$

and the basis functions are

$$\psi_k(a) = e^{ik_a}.$$

Reciprocal space has a simple physical meaning. In the system of units in which $\hbar = 1$, it coincides with the momentum space of the crystal quasiparticles, whose quasimomentum can assume only a set of N discrete values.

The complete space group G is obtained by adding to the translation subgroup also $f - 1$ elements of the form

$$g_j = \{h_j | \alpha_j\} \quad (j = 2, 3, \dots, f);$$

here h_j are elements of the group of directions

$$\alpha_j = p_1 a_1 + p_2 a_2 + p_3 a_3 \quad (0 \leq p_1, p_2, p_3 \leq 1). \quad (3.5)$$

In the particular case when all $\alpha_j = 0$, the space group is called symmorphic. In this case the proper and improper rotations in the crystal are elements of the symmetry group of the entire crystal and cause coincidence not only of the equivalent direction but also of the equivalent points. On the other hand, if $\alpha_j \neq 0$, then screw axes or glide planes are included among the elements of the crystal group.

The theory of irreducible representations of the direction group F makes it possible to solve a number of problems arising in the investigation of Raman scattering in crystals. Frequently, however, it is necessary to use the representation of the entire space group G . A description of the irreducible representation of space groups is given in a number of papers.^[36-42] We shall make use of the results of^[39, 40]

Each representation τ of the space group G is characterized by a set $\{\mathbf{k}\}$ of reciprocal-space vectors; this set is invariant against the rotational part of the elements of the space group. Thus, if $\mathbf{k}_i \in \{\mathbf{k}\}$, then also $h_j \mathbf{k}_i \in \{\mathbf{k}\}$ ($j = 1, 2, \dots, f$). This aggregate of vectors is called the "star" of the representation τ . The star $\{\mathbf{k}\}$ is called irreducible if for any of the vectors $\mathbf{k}_i, \mathbf{k}_j \in \{\mathbf{k}\}$, there exists a rotational element that carries to \mathbf{k}_j into \mathbf{k}_i . An irreducible representation of the group G corresponds to an irreducible star $\{\mathbf{k}\}$.

To each vector \mathbf{k} of the star there corresponds a certain subgroup of group G of such elements, the rotational part of which does not change the vector \mathbf{k} . The aggregate of these elements is called the group $G_{\mathbf{k}}$ of the vector \mathbf{k} or the "small" group. The irreducible representations of the group $G_{\mathbf{k}}$ will be denoted by $\tau_{\mathbf{k}}$. It turns out that knowledge of these irreducible representations is sufficient to find the matrix elements of the entire irreducible representation of the group G . Moreover, for applications it is frequently necessary to have the characters of the irreducible representations of only the group $G_{\mathbf{k}}$.

In practice, great interest attaches to the group $\hat{G}_{\mathbf{k}}$, the elements of which are the rotational elements h_j , which leave the vector \mathbf{k} invariant (accurate to the reciprocal-lattice vector). When $\mathbf{k} = 0$, the group $\hat{G}_{\mathbf{k}}$ coincides with the direction group F .

The problem of constructing the irreducible representations of the group $G_{\mathbf{k}}$ is conveniently solved by the method of built-up representations of the group $G_{\mathbf{k}}$, which is described in detail in^[39, 40].

3.2. General Classification of Principal Oscillations of Crystals

In the general theory of small oscillations, the principal oscillations (i.e., the oscillations of all the particles with the same frequency) are classified in accordance with the irreducible representations of the symmetry group G of the equilibrium configuration of the system.^[39] This classification is realized in the following manner.

Each element of the symmetry group transforms a system, whose equilibrium position has been disturbed, from one configuration into another, generally speaking different configuration. The space $u_i(\mathbf{r})$ ($i = 1, 2, \dots, 3s$, s —number of particles of the system, \mathbf{r} —vectors of the equivalent positions of the particles) of the displacements of the particles of the system from the equilibrium positions is called the mechanical space L_M . In symmetry transformations, the aggregate of the displacements $u_i(\mathbf{r})$ goes over into $\sum_{i'} T_{ii'}(g) u_{i'}(g\mathbf{r})$, where g is an element of the symmetry group of the system, and $T_{ii'}(g)$ are the coefficients of a matrix that depends on the elements of the group G .

If we introduce the linear operators $T(g)$ defined by

$$T(g) u_i(\mathbf{r}) = \sum_{i'} T_{ii'}(g) u_{i'}(g\mathbf{r}), \quad (3.6)$$

and set each element g of group G in correspondence with an operator $T(g)$:

$$g \rightarrow T(g),$$

then we obtain the representation of the group G , called the mechanical representation G_M . The mechanical representation G_M is reducible, and accordingly the displacement space L_M is also reducible.

The main results of the group-theoretical classification of the principal oscillations are as follows:

1) To each principal oscillation there corresponds a basis vector of a certain space L_j , which transforms in accordance with the irreducible representation T_j of the group G ; L_j is here one of the subspaces in terms of which the reducible space L_M is expanded; $L_M = \Sigma L_j$, (the summation sign stands for the direct sum of spaces).

2) All the principal oscillations connected in the indicated manner with the same representation T_j and space L_j have the same frequency. In addition, if the representation T_j is not real, then all the principal oscillations corresponding to the representation that is complex conjugate to T_j have the same frequency as the principal oscillations corresponding to T_j . Accordingly, if the representation T_j is real, then the degeneracy multiplicity of the corresponding frequency is equal to the dimensionality of the space L_j ; on the other hand, if T_j is not real, then the multiplicity of the degeneracy of this frequency is equal to double the dimensionality of the space.

It follows from the foregoing that the problem of the group-theoretical classification of the principal oscillations is solved by expanding the reducible mechanical representation T_M into irreducible representation T_j and determining whether they are real.

Bhagavantam^[43] developed a classification in terms of the irreducible representation of the direction group F (this corresponds to the case $\mathbf{k} = 0$) and in terms of the irreducible representation of the finite group of the

Raman supercell (see below).

The classification of the principal oscillations with allowance for all the crystal symmetry elements is given in the book by G. Ya. Lyubarskiĭ.^[89] Poulet^[20] considered a classification of crystal oscillations for $\mathbf{k} \neq 0$, but the final formulas of this paper were obtained only for the simplest cases.

Let us stop to discuss the classification of the principal oscillations at $\mathbf{k} \neq 0$ on the basis of the results obtained in^[39].

For crystals, the mechanical space L_M is the $3mN$ -dimensional space of displacements $u_\alpha \begin{pmatrix} 1 \\ \kappa \end{pmatrix}$. The operators of the mechanical representation are defined by the relations

$$T_M(g) u_\alpha \begin{pmatrix} 1 \\ \kappa \end{pmatrix} = \sum_\beta A_{\alpha\beta}(h_j) u_\beta \left[g \begin{pmatrix} 1 \\ \kappa \end{pmatrix} \right], \quad (3.7)$$

where g is the element of group G , $A_{\alpha\beta}(h_j)$ are the coefficients of the transformation matrix of the components of the vector, and $\alpha, \beta = 1, 2, 3$.

The arbitrary displacement $u_\alpha \begin{pmatrix} 1 \\ \kappa \end{pmatrix}$ can be expanded in terms of basis vectors that transform in accordance with the irreducible representation of the translation group:

$$u_\alpha \begin{pmatrix} 1 \\ \kappa \end{pmatrix} = \sum_k \frac{1}{\sqrt{m_\kappa N}} u_\alpha^{(0)} \begin{pmatrix} \mathbf{k} \\ \kappa \end{pmatrix} e^{i\mathbf{k}\cdot\mathbf{r}} = \sum_k u_\alpha \begin{pmatrix} \mathbf{k} \\ \kappa \end{pmatrix}, \quad (3.8)$$

where m_κ is the mass of the corresponding atom.

The expansion (3.8) shows that the star of the representation T_M is the reducible star $\{\mathbf{k}\}$, the irreducible components of which are represented by all the irreducible stars of the first Brillouin zone. From (3.8) we can also conclude that the mechanical space L_M can be expanded into N subspaces L_k , each of which is invariant relative to the group G_k of the vector \mathbf{k} (the "small" group), but is not invariant relative to all the elements of the group G . Each vector from L_k is transformed by the operator $T_M(g)$ into vectors from the same space. We can therefore define in space L_k operators $\tau_k(g)$ with the aid of the relations

$$\tau_k(g) u_\alpha \begin{pmatrix} \mathbf{k} \\ \kappa \end{pmatrix} = T(g) u_\alpha \begin{pmatrix} \mathbf{k} \\ \kappa \end{pmatrix}.$$

We shall say that the operator $T_M(g)$ induces in the invariant subspace L_k an operator $\tau_k(g)$ (see^[39]). The representation $\tau_k(g)$ is the reducible representation of the group G_k . In order to expand it into irreducible components, it is necessary to calculate the characters $\chi_k(g)$ of this representation. According to^[21], they are obtained from the general formula

$$\chi_k(\{h_j | \alpha\}) = (\pm 1 + 2 \cos \varphi) \left[\sum_x \delta(x) e^{i\mathbf{k}_0 \cdot \mathbf{x}} \right] e^{i\mathbf{k}\alpha}, \quad (3.9)$$

where the signs are chosen in accordance with whether the rotation is proper or improper; the summation is carried out over all the nonequivalent atoms of the unit cell, $\alpha = \alpha_j + \mathbf{a}$. The symbol $\delta(x)$ is defined as follows: $\delta(x) = 1$ if the atom remains in its place accurate to pure translation, and $\delta(x) = 0$ if non-equivalent identical atoms interchange places; $\mathbf{k}_0 = h_j^{-1}\mathbf{k} - \mathbf{k}$ (the vector \mathbf{k}_0 is equal to the reciprocal-space vector or is equal to zero, since $\{h_j | \alpha\} \in G_k$). If $\mathbf{k}_0 = 0$, which holds true in particular

for all the points inside the Brillouin zone, then formula (3.5) assumes the simpler form, which coincides with the corresponding result of^[20]:

$$\chi_k(\{h_j | \alpha\}) = (\pm 1 + 2 \cos \varphi) n_0 e^{i\mathbf{k}\alpha}, \quad (3.10)$$

where n_0 is the number of nonequivalent atoms within the unit cell, which remain in place accurate to pure translation as a result of the symmetry transformation.

The general formula (3.9) makes it possible to change over conveniently to the characters of the built-up representation $\hat{\chi}_k(h_j)$ of the group \hat{G}_k (the point group of the vector \mathbf{k}):

$$\hat{\chi}_k(h_j) = \chi_k(\{h_j | \alpha\}) e^{-i\mathbf{k}\alpha} = (\pm 1 + 2 \cos \varphi) \left(\sum_x \delta(x) e^{i\mathbf{k}_0 \cdot \mathbf{x}} \right). \quad (3.11)$$

For the number n_p of the irreducible built-up representations of character $\hat{\chi}^p(h_j)$, contained in the reducible representation $\hat{\chi}_k(h_j)$ we obtain, with allowance for the build-up,

$$n_p = \frac{1}{f'} \sum_{h_j \in \hat{G}_k} \hat{\chi}_k(h_j) \overline{\hat{\chi}^p(h_j)} e^{i(\mathbf{k}-h_j)\alpha}, \quad (3.12)$$

where $\hat{\chi}_k(h_j)$ is obtained from (3.11), and f' is the number of elements of the group \hat{G}_k .

Let us examine in somewhat greater detail the final formula (3.12). If the wave vector \mathbf{k} is located inside the Brillouin zone, then $\mathbf{k} - h_j\mathbf{k} = 0$ (the built-up representations do not differ from the ordinary representations of the point group \hat{G}_k) and (3.12) takes the form

$$n_p = \frac{1}{f'} \sum_{h_j \in \hat{G}_k} (\pm 1 + 2 \cos \varphi) n_0 \overline{\chi^p(h_j)}, \quad (3.13)$$

where $\chi^p(h_j)$ is the character of the ordinary representation of the point group \hat{G}_k .

In the particular case $\mathbf{k} = 0$, Eq. (3.13) simplifies to:

$$n_p = \frac{1}{f} \sum_{h_j \in F} (\pm 1 + 2 \cos \varphi) n_0 \overline{\chi^p(h_j)}, \quad (3.14)$$

where F is the group of directions of the crystal and f is the number of elements of this group.

Formula (3.14) coincides with the analogous result of^[43,44], in which the crystal oscillations were classified in accordance with irreducible representations of the point group F of the crystal directions. We can therefore conclude that the classification of the crystal oscillations in accordance with the irreducible representations of the group has a classification of phonons at $\mathbf{k} = 0$.

Once the irreducible representations τ_k^p of the group G_k , which enter in the irreducible representation τ_k are found, the irreducible representations of the entire space group, which enter in T_M can be constructed by uniting all the representations pertaining to the same irreducible star $\{\mathbf{k}\}$, in accordance with the well-known method^[39] of constructing the irreducible representations of a space group. To each principal oscillation of the crystal there corresponds an irreducible representation τ_k^p obtained in this manner.

It now remains to determine whether the irreducible representations τ_k^p , in accordance with which the spaces L_k^p are transformed, are real. This problem can be easily solved with the aid of the reality criterion^[39,45]

$$\frac{1}{f} \sum_{h, \mathbf{k}=-\mathbf{k}} \chi_k(q^2) = \begin{cases} 1, & \text{if } \tau_{\{\mathbf{k}\}}^p \text{ is real,} \\ 0 \text{ or } -1, & \text{if } \tau_{\{\mathbf{k}\}}^p \text{ is not real.} \end{cases} \quad (3.15)$$

The summation is carried out over all the elements of the point group F , for which the relation $h\mathbf{k} = -\mathbf{k}$ is satisfied (\mathbf{k} is any vector of the star $\{\mathbf{k}\}$).

The degeneracy multiplicity of the principal oscillation is equal to the dimensionality of the corresponding space $L_{\{\mathbf{k}\}}^p$, if the representation $\tau_{\{\mathbf{k}\}}^p$ is real, and is equal to double the dimensionality of this space if the representation $\tau_{\{\mathbf{k}\}}^p$ is not real. Physically this means that all the discrete plane waves corresponding to the principal oscillations of the crystal are characterized by a polarization that is specified by the index p , and the direction of propagation \mathbf{k} corresponds to one and the same oscillation frequency.

We note that the classification of the vibrational levels corresponding to excitations with $\mathbf{k} = 0$ was sufficient in most cases at the first stage of the experiments on Raman scattering, when the spectrum $\omega_1(0)$ for different optical branches was investigated.

The classification of the vibrational levels for arbitrary wave vectors is necessary in the study of second-order spectra.

3.3. Classification of Oscillations in Crystals Containing Complex Atomic Groups

The general theory described above makes it possible to realize a classification of the principal oscillations of the crystal for any number of nonequivalent atoms in the unit cell. It turns out frequently, however, that, owing to the forces acting between the particles, it is advantageous to separate individual groups of atoms, which can be regarded as new structural units of the crystal. Such groups may be complex ions, and in molecular crystals also individual molecules. The normal oscillations can be subdivided in this case into internal and external ones. The external oscillations are oscillations of groups of particles relative to each other. The internal oscillations are oscillations of pointlike particles within the indicated groups.

The vectors of the displacements from the equilibrium particle positions of the internal oscillations characterize the displacements of the atoms within the groups. The vectors of the displacements of the external oscillations are three-dimensional if the considered group can be regarded as a point, and six-dimensional if this group is regarded as a solid body with six degrees of freedom.

The next step is to subdivide the external oscillations into oscillations of the translational type and oscillations of the orientational type, or rotary rocking. We note that such a subdivision of the oscillations, if physically justified, leads to a corresponding subdivision of the irreducible subspaces $L_{\mathbf{k}}$, but the possibility of the indicated subdivision may turn out to be incorrect for spaces $L_{\mathbf{k}}$ corresponding to certain values of the vectors \mathbf{k} . In practice, the indicated subdivision is important only for principal oscillations with $\mathbf{k} = 0$. The formulas for the characters of the corresponding representations are given in Table I.

Normal Raman oscillations were classified by the group-theory method in a number of papers.^[46-48] The classification is usually effected in two stages. At first, $3n$ normal oscillations corresponding to $\alpha = \beta = \gamma = 1$

Table I

| Investigated object | Name of representation | Formulas for characters* |
|--|--|---|
| Unit cell contains n pointlike particles | Mechanical representation $\tau_{\mathbf{k}}$, \mathbf{k} belongs to first Brillouin zone. | $\chi(h) = n_0 (1 + 2 \cos \varphi)$ |
| | Vibrational representation, $\mathbf{k} = 0$. | $\chi(h) = (n_0 - 1) (\pm 1 + 2 \cos \varphi)$ |
| Unit cell contains n pointlike particles, the external oscillations are realized by m groups. | Representation of external oscillation (without the acoustic ones) | $\chi(C_\varphi) = (2m_0 - 1) (1 + 2 \cos \varphi)$, $\chi(S_\varphi) = 1 - 2 \cos \varphi$ |
| | Representation of internal oscillations | $\chi(C_\varphi) = (n_0 - 2m_0) (1 + 2 \cos \varphi)$, $\chi(S_\varphi) = n_0 (-1 + 2 \cos \varphi)$ |
| | Translational-vibrational representation | $\chi(C_\varphi) = (m_0 - 1) (1 + 2 \cos \varphi)$, $\chi(S_\varphi) = (m_0 - 1) (-1 + 2 \cos \varphi)$ |
| | Rotational-vibrational representation | $\chi(C_\varphi) = m_0 (1 + 2 \cos \varphi)$, $\chi(S_\varphi) = m_0 (1 - 2 \cos \varphi)$ |
| Unit cell contains n pointlike particles, external oscillations are realized by m asymmetrical groups and p pointlike particles. | External-vibrational representation | $\chi(C_\varphi) = (2m_0 + p_0 - 1) (1 + 2 \cos \varphi)$, $\chi(S_\varphi) = (p_0 - 1) (-1 + 2 \cos \varphi)$ |
| | Translational-vibrational representation | $\chi(C_\varphi) = (p_0 + m_0 - 1) (1 + 2 \cos \varphi)$, $\chi(S_\varphi) = (p_0 + m_0 - 1) (-1 + 2 \cos \varphi)$ |
| | Rotational-vibrational representation | $\chi(C_\varphi) = m_0 (1 + 2 \cos \varphi)$, $\chi(S_\varphi) = -m_0 (1 - 2 \cos \varphi)$ |
| | Internal-vibrational representation | $\chi(C_\varphi) = (n_0 - p_0 - 2m_0) (1 + 2 \cos \varphi)$, $\chi(S_\varphi) = (n_0 - p_0) (-1 + 2 \cos \varphi)$ |

* n_0, m_0, p_0 - numbers of particles that remain stationary apart from translation equal to the vector of the direct lattice.

are classified. To this end, the nonequivalent atoms of one unit cell are considered; the symmetry group of the system is taken to be the factor group of group G (i.e., the group of directions of the crystal), and formulas are derived for the characters of the mechanical and other representations,^[43] which coincide with the corresponding results of Table I for $\mathbf{k} = 0$.

All the normal Raman oscillations are classified by considering eight neighboring unit cells (the so-called supercell) and using as the symmetry group the crystal direction group supplemented with those translations that transform neighboring equivalent atoms into each other. For example, for diamond, such a symmetry group contains 384 elements (of which only 48 elements belong to the crystal direction group). The formulas for the characters of the mechanical representation are the same as in Table I, with allowance for the numbers of all the atoms contained in the supercell.

A discussion of the experimental data on Raman scattering of light in crystals, from the point of view of the Raman theory, will be given in the succeeding sections.

We note that a group-theoretical classification of polar oscillations at $\mathbf{k} = 0$ by means of the formulas of Table I would be incorrect, since the mechanical system is not independent but interacts strongly with electromagnetic field.

3.4. Example of Application of the Group-theoretical Classification of Lattice Vibrations

Examples of the application of a group-theoretical classification of the vibrational levels corresponding to $\mathbf{k} = 0$ are described in detail in the literature.^[43, 49] We shall therefore stop to discuss only the classification of the vibrational levels in the general case (for any \mathbf{k}). We consider crystals of the ZnS type (cubic modification). The ZnS crystal belongs to the symmetry group T_d^2 .

Figure 5 shows the unit cell of the Zn crystal and the Brillouin zone. If 2τ is the length of the edge of the cube, then the elementary-translation vectors have the following coordinates:

$$a_1 = \tau(0, 1, 1), \quad a_2 = \tau(1, 0, 1), \quad a_3 = \tau(1, 1, 0).$$

The reciprocal lattice vectors are given by

$$b_1 = \frac{\pi}{\tau}(-1, 1, 1), \quad b_2 = \frac{\pi}{\tau}(1, -1, 1), \quad b_3 = \frac{\pi}{\tau}(1, 1, -1).$$

The vectors of the principal points of the Brillouin zone are of the form (see [20, 40])

$$k_2 = \mu(b_1 + b_2) + \mu_3 b_3 = \frac{\pi}{\tau}(\mu_3, \mu_3, (2\mu - \mu_3)),$$

$$k_5 = \mu(b_1 + b_2 + b_3) = \frac{\pi}{\tau}(\mu, \mu, \mu),$$

$$k_8 = \mu(b_1 + b_2) = \frac{\pi}{\tau}(0, 0, 2\mu),$$

$$k_7 = \frac{1}{2}(b_1 + b_3) + \mu(b_1 + b_2) = \frac{\pi}{\tau}(0, 1, 2\mu),$$

$$k_8 = \frac{1}{2}(b_1 + b_2) + \frac{1}{2}(b_2 + b_3) = \frac{\pi}{\tau}\left(1, 0, \frac{1}{2}\right),$$

$$k_9 = \frac{1}{2}(b_1 + b_2 + b_3) = \frac{\pi}{\tau}\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right),$$

$$k_{10} = \frac{1}{2}(b_1 + b_2) = \frac{\pi}{\tau}(0, 0, 1),$$

$$k_{11} = 0 = \frac{\pi}{\tau}(0, 0, 0).$$

They are characterized by different groups G_k . Applying the elements of group F of the crystal to the vectors k , we obtain all the irreducible stars of group G. The characters of the representations $\hat{\tau}_k(h_j)$ corresponding to the indicated vectors are obtained with the aid of formula (3.11). Using relation (3.13), we expand the reducible representations $\hat{\tau}_k(h_z)$ in terms of the irreducible one. The results for all the vectors listed above are given in Table II.

The representation T_M consists accordingly of a set of the following irreducible representations:

$$\begin{aligned} &3\tau_{\{k_2\}}^{(1)} + 3\tau_{\{k_2\}}^{(2)}, \quad \tau_{\{k_5\}}^{(1)} + \tau_{\{k_5\}}^{(2)} + 2\tau_{\{k_5\}}^{(3)}, \\ &\tau_{\{k_8\}}^{(1)} + 2\tau_{\{k_8\}}^{(5)} + \tau_{\{k_8\}}^{(4)}, \quad 3\tau_{\{k_7\}}^{(1)} + 3\tau_{\{k_7\}}^{(2)}, \\ &2\tau_{\{k_8\}}^{(2)} + 2\tau_{\{k_8\}}^{(3)} + 2\tau_{\{k_8\}}^{(4)}, \quad \tau_{\{k_9\}}^{(1)} + \tau_{\{k_9\}}^{(2)} + 2\tau_{\{k_9\}}^{(3)}, \\ &\tau_{\{k_{10}\}}^{(1)} + 2\tau_{\{k_{10}\}}^{(5)} + \tau_{\{k_{10}\}}^{(4)}, \quad 2\tau_{\{k_{11}\}}^{(3)}. \end{aligned}$$

The numbering of the irreducible representations $\tau_{\{k\}}^{(p)}$ is in accordance with the numbering of the built-up representations $\hat{\tau}^{(p)}$ of the group T_d^2 , given in [40].

By using the criterion (3.15), it is possible to check whether these representations are real. Analogous calculations were performed by Poulet [20] for four points of the Brillouin zone: $\Gamma(k_{11})$, $X(k_{10})$, $L(k_9)$, $W(k_2)$. The general formulas (3.11) in (3.12) make it possible to

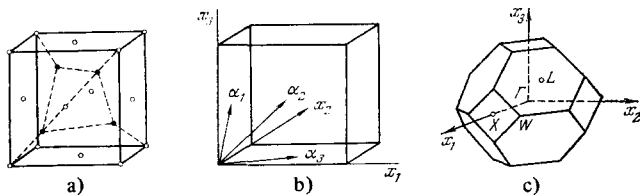


FIG. 5. ZnS crystal lattice (cubic modification). a, b) Unit cell; c) Brillouin zone.

Table II

| Vector $k_2 = \mu(b_1 + b_2) + \mu_3 b_3$ | | | Vector $k_7 = \frac{1}{2}(b_1 + b_3) + \mu(b_2 + b_3)$ | | | | | | | | |
|---|---|---------------|--|--------------------|-------------|--------------------------|-------|----------------|--------|-----------|----------------|
| G_k | E | σ | G_k | E | C_2 | | | | | | |
| $\hat{\chi}^{(1)}$ | 1 | 1 | $\hat{\chi}^{(1)}$ | 1 | 1 | | | | | | |
| $\hat{\chi}^{(2)}$ | 1 | -1 | $\hat{\chi}^{(2)}$ | 1 | -1 | | | | | | |
| $\hat{\chi}_k$ | 6 | 2 | $\hat{\chi}_k$ | 6 | -2 | | | | | | |
| $\tau_k = 4\tau_k^{(1)} + 2\tau_k^{(2)}$ | | | $\tau_k = 2\tau_k^{(1)} + 4\tau_k^{(2)}$ | | | | | | | | |
| Vectors $k_5 = \mu(b_1 + b_2 + b_3)$, $k_9 = \frac{1}{2}(b_1 + b_2 + b_3)$ (L) | | | Vector $k_8 = \frac{1}{4}(b_1 + b_2) + \frac{1}{2}(b_2 + b_3)$ (W) | | | | | | | | |
| G_k | E | $C_3^{\pm 1}$ | 3σ | G_k | E | C_2 | S_4 | $S_6^{\pm 1}$ | | | |
| $\hat{\chi}^{(1)}$ | 1 | 1 | 1 | $\hat{\chi}^{(1)}$ | 1 | 1 | 1 | 1 | | | |
| $\hat{\chi}^{(2)}$ | 1 | 1 | -1 | $\hat{\chi}^{(2)}$ | 1 | -1 | 1 | -1 | | | |
| $\hat{\chi}^{(3)}$ | 2 | -1 | 0 | $\hat{\chi}^{(3)}$ | 1 | 1 | -1 | -1 | | | |
| $\hat{\chi}_k$ | 6 | 0 | 2 | $\hat{\chi}^{(4)}$ | 1 | -1 | -2 | -2 | | | |
| $\tau_k = 2\tau_k^{(1)} + 2\tau_k^{(3)}$ | | | $\tau_k = \tau_k^{(1)} + 2\tau_k^{(2)} + 2\tau_k^{(3)} + \tau_k^{(4)}$ | | | | | | | | |
| Vectors $k_6 = \mu(b_1 + b_2)$, $k_{10} = \frac{1}{2}(b_1 + b_2)$ (X) | | | Vector $k_{11} = 0$ (Gamma) | | | | | | | | |
| G_k | E | C_2 | $2S_4$ | $2C_2'$ | $2\sigma_d$ | G_k | E | $4C_3^{\pm 1}$ | $3C_2$ | 6σ | $3S_6^{\pm 1}$ |
| $\hat{\chi}^{(1)}$ | 1 | 1 | 1 | 1 | 1 | $\hat{\chi}^{(1)}$ | 1 | 1 | 1 | 1 | 1 |
| $\hat{\chi}^{(2)}$ | 1 | 1 | 1 | -1 | -1 | $\hat{\chi}^{(2)}$ | 1 | 1 | 1 | -1 | -1 |
| $\hat{\chi}^{(3)}$ | 1 | 1 | -1 | 1 | -1 | $\hat{\chi}^{(3)}$ | 2 | -1 | 2 | 0 | 0 |
| $\hat{\chi}^{(4)}$ | 1 | 1 | -1 | -1 | 1 | $\hat{\chi}^{(4)}$ | 3 | 0 | -1 | -1 | 1 |
| $\hat{\chi}^{(5)}$ | 2 | 0 | -2 | 0 | 0 | $\hat{\chi}^{(5)}$ | 3 | 0 | -1 | 1 | -1 |
| $\hat{\chi}_k$ | 6 | -2 | -2 | 2 | 2 | $\hat{\chi}_k$ | 6 | 0 | -2 | 2 | -2 |
| $\tau_k = \tau_k^{(1)} + 2\tau_k^{(5)} + \tau_k^{(4)}$ | | | | | | $\tau_k = 2\tau_k^{(5)}$ | | | | | |

realize a similar classification also for crystals of the non-symmorphic symmetry groups at any point of the Brillouin zone.

We shall consider below several other examples of a group-theoretical classification of the principal oscillations in certain crystals, during the course of the discussion of the results of RS in these crystals.

4. FIRST-ORDER RAMAN SCATTERING IN CRYSTALS

4.1. Theory of RS Intensity in Crystals

The calculation of the intensity of scattered light is one of the main problems of the theory of RS of light. In solving this problem, different methods of considering RS of light have been developed.

One of the first investigations of the theory of RS in crystals is that of Tamm. [50] In this paper, RS of light is regarded as a result of interaction between normal oscillations, corresponding to electromagnetic waves, and mechanical normal oscillations of the crystal lattice — phonons. Formally, such processes occur when the Hamiltonian of the system made up of the electrons, nuclei, and their radiation field includes, besides the quadratic terms, also terms of third and higher order in the amplitudes of the crystal oscillations.

In spite of the general approach to the problem, Tamm's theory was essentially semiphenomenological,

since it led to no explicit expressions for the anharmonicity constants of the crystal. The development of a microscopic theory for molecular crystals and concrete calculations of the anharmonicity coefficient were carried out by L. N. Ovander.^[51] He obtained from the Hamiltonian of the molecular crystal, by using a third-order canonical transformation under the condition that the interaction between the crystal molecules is sufficiently small,

$$H = H^{(2)} + H^{(3)}, \quad (4.1)$$

where

$$H^{(2)} = \sum_{\rho, \mathbf{k}} E_{\rho}(\mathbf{k}) \xi_{\rho}^{\dagger}(\mathbf{k}) \xi_{\rho}(\mathbf{k}), \quad (4.2)$$

$$H^{(3)} = \sum_{\rho_1 \rho_2 \rho_3} Q_{\rho_1 \rho_2 \rho_3}(\mathbf{k}_1, \mathbf{k}_2) \xi_{\rho_1}(\mathbf{k}_1) \xi_{\rho_2}(\mathbf{k}_2) \xi_{\rho_3}^{\dagger}(\mathbf{k}_3) + \text{c.c.}; \quad (4.3)$$

here the operators $\xi_{\rho}^{\dagger}(\mathbf{k})$ and $\xi_{\rho}(\mathbf{k})$ are the Bose operators of creation and annihilation of the quasiparticles in the crystal, ρ is the polarization index, \mathbf{k} is the wave vector, and $Q_{\rho_1 \rho_2 \rho_3}(\mathbf{k}_1, \mathbf{k}_2)$ are the anharmonicity coefficients. The Hamiltonian of the system, with second-order terms included, is regarded as the zeroth approximation; it yields the energy spectrum of the crystal quasiparticles obeying Bose statistics. i.e., the exciton spectrum. Allowance for third-order terms is based on perturbation theory. These terms lead to processes in which three quasiparticles take part simultaneously (the decay of one quasiparticle into two others and the inverse process).

Let us consider from this point of view the RS of light. Assume that the radiation-exciting incident photon is characterized by the indices (ρ_0, \mathbf{k}_0) , the photon taking part in the RS process by the indices (ρ, \mathbf{k}) , and the scattered phonon by the indices (ρ', \mathbf{k}') for the Stokes RS and (ρ'', \mathbf{k}'') for the anti-Stokes RS. The corresponding constants in (4.3) take the form $Q_{\rho' \rho \rho_0}(\mathbf{k}', \mathbf{k})$ and $Q_{\rho_0 \rho \rho''}(\mathbf{k}_0, \mathbf{k})$. In the first order of perturbation theory, the increase of the number of quasiparticles with time is determined, for the processes under consideration, by the expressions

$$\frac{dn(\rho', \mathbf{k}')}{dt} = \frac{2\pi}{\hbar} \sum_{\rho_0 \rho} |Q_{\rho' \rho \rho_0}(\mathbf{k}', \mathbf{k})|^2 n(\rho_0, \mathbf{k}_0) \times \\ \times [n(\rho', \mathbf{k}' + 1) + 1] \delta\{E(\rho_0, \mathbf{k}_0) - E(\rho', \mathbf{k}')\}, \quad (4.4)$$

$$\frac{dn(\rho'', \mathbf{k}'')}{dt} = \frac{2\pi}{\hbar} \sum_{\rho_0 \rho} |Q_{\rho_0 \rho \rho''}(\mathbf{k}_0, \mathbf{k})|^2 n(\rho_0, \mathbf{k}_0) n(\rho, \mathbf{k}) \times \\ \times [n(\rho'', \mathbf{k}'') - 1] \delta\{E(\rho_0, \mathbf{k}_0) + E(\rho, \mathbf{k}) - E(\rho'', \mathbf{k}'')\}; \quad (4.5)$$

here $n(\rho_0, \mathbf{k}_0)$, $n(\rho, \mathbf{k})$, $n(\rho', \mathbf{k}')$, and $n(\rho'', \mathbf{k}'')$ are the numbers of quasiparticles of the exciting light, of the phonons, and of the Stokes and anti-Stokes scattered light, respectively.

The explicit form of the anharmonicity coefficients is very cumbersome and will not be presented here. The intensity of the scattered light is proportional to the probability of the indicated processes. Expressions for the scattered-light intensity, obtained in^[51], are complicated and will not be written out here. The extension of the exciton theory to the case of semiconductor crystals is given in^[52].

An essential feature of the theory^[52] is that the interaction of the electromagnetic radiation with the electron and vibrational subsystems is not assumed to be small. This makes it possible to investigate RS under conditions

when the frequency of the incident light is close to the exciton-absorption band.

Another approach to the RS phenomenon is based on the smallness of the perturbation of the electron subsystem of the crystal by the electromagnetic field of the radiation. The direct interaction between the light and the vibrations of the nuclei is generally not taken into account, in view of the large mass of the nuclei. It is assumed, however, that the lattice vibrations can interact with the light indirectly, via the electronic subsystem. The solution of the problem of RS of light under the indicated assumptions was considered in detail in^[24, 53, 54]. By regarding the crystal as a "giant molecule," it can be shown that the intensity of the Raman scattering with polarization σ is equal to

$$I_{RS}(\omega') = \frac{I_0 \omega'^4}{4\pi c^3} |\beta_{\rho\sigma}|^2, \quad (4.6)$$

where ρ and σ are the indices of the axes x , y , and z of the stationary coordinate system, in which the scattered light is observed, I_0 is the intensity of the exciting line with polarization ρ , and ω' is the frequency of the scattered radiation. If the conditions for the applicability of the polarizability theory are satisfied, then the scattering tensor $\beta_{\rho\sigma}$ is equal to the matrix element of the transition between the ground and excited vibrational levels of the tensor $\alpha_{\rho\sigma}$ of the polarizability of the crystal, the explicit form of which is obtained on the basis of the microscopic theory in the cited papers.

One of the shortcomings of the method described above, in which the RS process is considered in second-order perturbation theory, is the fact that the eigenfunctions of the unperturbed electronic subsystem pertain to the non-equilibrium configuration of the nuclei. The concrete form of such functions remains unknown, and it is therefore impossible to estimate the matrix elements that enter in the expressions for the scattering tensor. It is more natural to use as the unperturbed functions of the electronic subsystem functions that pertain to the equilibrium configuration of the nuclei, and to take the influence of the vibrations of the nuclei into account by introducing an additional perturbation due to the interaction of the electrons and the phonons. The first such description of Raman scattering was presented by I. I. Sobel'man.^[55] A detailed development of the indicated method for simple crystals is given in^[56, 57].

In this method the RS probability differs from zero only in third order of perturbation theory. The probability of the Stokes RS per unit time is determined by the expression

$$w_{RS} = \frac{2\pi}{\hbar^3} \sum_{\mathbf{k}_0 \mathbf{k}'} \left| \sum_{a, b} \frac{\langle n_0 - 1, 1; n + 1; 0 | v | a \rangle \langle a | v | b \rangle \langle b | v | n_0, 0; n; 0 \rangle}{(\omega_a - \omega_0)(\omega_b - \omega_0)} \right|^2; \quad (4.7)$$

here a and b are the indices of the intermediate states of the entire system, \mathbf{k}_0 and \mathbf{k}' are the wave vectors of the incident and scattered light, $v = H_{\text{rad}} + H_{\text{lat}}$ is the perturbation operator, which consists of the perturbation of the electronic subsystem by the radiation field and by the phonon field. In spite of the complicated form of (4.7), this particular method yielded concrete estimates of the scattering cross section in the case of simple crystals, since the values of the electron-photon and electron-phonon interactions are known for certain crystals.

Direct measurement data on the absolute cross section

of RS of light in crystals are presently available for a very small number of crystals.^[58-60]

4.2. Selection Rules in First-order RS Spectra

According to the general theory,^[61] the matrix element $(f_\lambda)_{ik}$ of a certain operator f_λ differs from zero only if the product of the representations $\Gamma^{i*} \times \Gamma^\lambda \times \Gamma^k$ contains a unit representation, i.e.,

$$\Gamma^{i*} \times \Gamma^\lambda \times \Gamma^k \supset A, \tag{4.8}$$

where Γ^i is the representation of the symmetry group of the quantum system, in accordance to which the wave function of the initial state is transformed, Γ^k is the representation according to which the wave function of the final state is transformed (the initial and final states are assumed to be different), Γ^λ is the representation in accordance with which the operator f_λ is transformed, and A is a unit representation. In the case of RS, the operator f_λ is, in the polarizability-theory approximation, a symmetrical tensor of second rank $\alpha_{\rho\sigma}$, the components of which transform in accordance with the irreducible representation $[V]^2$ of the direction group of the crystal. As was already indicated, for the first-order RS process the transition occurs between the long-wave vibrational levels, which are classified approximately in accordance with the irreducible representations of the point group F of the crystal. Thus, to clarify the selection rules in the first-order RS spectra, it is sufficient to know the irreducible representations of the group F.

Let us consider Stokes RS (the analysis for anti-Stokes RS is similar). The initial state is the ground state and corresponds to the unity representation. Therefore (4.8) takes the form

$$[V]^2 \times \Gamma^k \supset A. \tag{4.9}$$

In accordance with the general theory of representation,^[39] this is equivalent to

$$[V]^2 \supset \Gamma^k, \tag{4.10}$$

i.e., the RS turns out to be allowed for the transition $A \rightarrow \Gamma^k$ if the representation $[V]^2$ contains at least one irreducible representation Γ^k . The expansion of the representation $[V]^2$ into irreducible components can be realized by using the relation

$$n_{\Gamma^k} = \frac{1}{f} \sum_h \chi^{[V]^2}(h) \chi^{\Gamma^k}(h), \tag{4.11}$$

where

$$\chi^{[V]^2}(h) = 2 \cos \varphi (\pm 1 \pm 2 \cos \varphi), \quad \varphi -$$

φ is the rotation angle, the signs depends on whether the rotation is proper or improper, and $\chi^{\Gamma^k}(h)$ are the characters of the irreducible representations of the group F.

If $N_{\Gamma^k} \neq 0$, then the components of the polarizability tensor, which transform in accordance with this representation, are also different from zero. Using (4.11), it is easy to ascertain which components of the RS tensor differ from zero for the given crystal. The results for the most important crystal classes are presented in Table III. The irreducible representations that are active in the first-order RS spectra are listed against each crystal class.

As indicated above, the Raman scattering tensor is in

Table III. Selection rules in first-order Raman-scattering spectra of the most important crystals (from the data of^[56])

| System | Class | Raman scattering tensor | | | |
|--------------|--------------|---|--|--|---|
| Monoclinic | 2 | $\begin{pmatrix} a & 0 & d \\ 0 & b & 0 \\ d & 0 & e \end{pmatrix}$ | $\begin{pmatrix} 0 & e & 0 \\ e & 0 & f \\ 0 & f & 0 \end{pmatrix}$ | | |
| | m $2/m$ | $A(y)$ $A'(x, z)$ A_g | $B(x, z)$ $A''(y)$ B_g | | |
| Orthorhombic | 222 | $\begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}$ | $\begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$ | $\begin{pmatrix} 0 & 0 & e \\ 0 & 0 & 0 \\ e & 0 & 0 \end{pmatrix}$ | $\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & f \\ 0 & 0 & 0 \end{pmatrix}$ |
| | $nm2$ | A | $B_1(z)$ | $B_2(y)$ | $B_3(x)$ |
| | mmm | A_g | B_{1g} | B_{2g} | B_{3g} |
| Trigonal | 3 | $\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}$ | $\begin{pmatrix} c & d & e \\ d & -c & f \\ e & f & 0 \end{pmatrix}$ | $\begin{pmatrix} d & -c & -f \\ -c & -d & e \\ -f & e & 0 \end{pmatrix}$ | |
| | $\bar{3}$ | A_1 | E_g | E_g | |
| | 32 | $\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}$ | $\begin{pmatrix} c & 0 & 0 \\ 0 & -c & d \\ 0 & d & 0 \end{pmatrix}$ | $\begin{pmatrix} 0 & -c & -d \\ -c & 0 & 0 \\ -d & 0 & 0 \end{pmatrix}$ | |
| | $3m$ | A_1 | $E(x)$ | $E(y)$ | $E(-x)$ |
| | $\bar{3}m$ | A_{1g} | E_g | E_g | E_g |
| Tetragonal | 32 | $\begin{pmatrix} a & 0 & 0 \\ 0 & d & 0 \\ 0 & 0 & b \end{pmatrix}$ | $\begin{pmatrix} c & 0 & 0 \\ 0 & -c & d \\ 0 & d & 0 \end{pmatrix}$ | $\begin{pmatrix} 0 & -c & -d \\ -c & 0 & 0 \\ -d & 0 & 0 \end{pmatrix}$ | |
| | $3m$ | A_1 | $E(x)$ | $E(y)$ | $E(-x)$ |
| | $\bar{3}m$ | A_{1g} | E_g | E_g | E_g |
| | 4 | $\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}$ | $\begin{pmatrix} c & d & 0 \\ d & -c & 0 \\ 0 & 0 & 0 \end{pmatrix}$ | $\begin{pmatrix} 0 & 0 & e \\ 0 & 0 & f \\ e & f & 0 \end{pmatrix}$ | $\begin{pmatrix} 0 & 0 & -f \\ 0 & 0 & e \\ -f & e & 0 \end{pmatrix}$ |
| | $\bar{4}$ | A | $B(z)$ | $E(x)$ | $E(-y)$ |
| $4/m$ | A_g | B_g | E_g | E_g | |

the general case not symmetrical. Ovander^[51] gives non-zero elements of the scattering tensor, regarded as a second-rank tensor. The results of^[51] differ from those given in Table III in the presence of additional nonvanishing components.

To calculate the effective cross section s or the intensity I of the Raman-scattering lines with the aid of the tables it is necessary to use the formula

$$s = A \left[\sum_{\rho\sigma} e_\rho \beta_{\rho\sigma} e'_\sigma \right]^2, \tag{4.12}$$

where A is a proportionality factor, e_ρ and e'_σ are the components of the unit vectors of the polarization of the electric field of the incident and scattered light, and $\beta_{\rho\sigma}$ is the Raman-scattering tensor components.

By way of an example let us consider Raman scattering for the geometry shown in Fig. 6.

We consider first scattering by vibrations of type B of group C_4 . The effective Raman scattering cross section is

$$s = A (e_x \beta_{xx} e'_x + e_x \beta_{xy} e'_y + e_x \beta_{xz} e'_z + e_y \beta_{yx} e'_x + e_y \beta_{yy} e'_y + e_y \beta_{yz} e'_z)^2.$$

Table III (cont.)

| System | Class | Raman scattering tensor | | | | | | |
|-----------------|-------------|---|--|---|--|--|--|--|
| Tetra- gonal | | $\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}$ | $\begin{pmatrix} c & 0 & 0 \\ 0 & -c & 0 \\ 0 & 0 & 0 \end{pmatrix}$ | $\begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$ | $\begin{pmatrix} 0 & 0 & e \\ 0 & 0 & 0 \\ e & 0 & 0 \end{pmatrix}$ | $\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & e \\ 0 & e & 0 \end{pmatrix}$ | | |
| | $4mm$ | C_{4v} | $A_1(z)$ | B_1 | B_2 | $E(x)$ | $E(y)$ | |
| | 422 | D_4 | A_1 | B_1 | B_2 | $E(-y)$ | $E(x)$ | |
| | $\bar{4}2m$ | D_{2d} | A_1 | B_1 | $B_2(z)$ | $E(y)$ | $E(x)$ | |
| $4/mmm$ | D_{2h} | A_{1g} | B_{1g} | B_{2g} | E_g | E_g | | |
| Hexa- gonal | | $\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}$ | $\begin{pmatrix} 0 & 0 & c \\ 0 & 0 & d \\ c & d & 0 \end{pmatrix}$ | $\begin{pmatrix} 0 & 0 & -d \\ 0 & 0 & c \\ -d & c & 0 \end{pmatrix}$ | $\begin{pmatrix} e & f & 0 \\ j & -e & 0 \\ 0 & 0 & 0 \end{pmatrix}$ | $\begin{pmatrix} 0 & f & -e \\ 0 & -e & -f \\ 0 & 0 & 0 \end{pmatrix}$ | | |
| | 6 | C_6 | $A(z)$ | $E_1(x)$ | $E_1(y)$ | E_2 | E_2 | |
| | $\bar{6}$ | C_{3h} | A' | E'' | E'' | $E'(x)$ | $E'(y)$ | |
| | $6/m$ | C_{6h} | A_g | E_{1g} | E_{1g} | E_{2g} | E_{2g} | |
| | | | $\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}$ | $\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & c \\ -c & 0 & 0 \end{pmatrix}$ | $\begin{pmatrix} 0 & 0 & -c \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$ | $\begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$ | $\begin{pmatrix} d & 0 & 0 \\ 0 & -d & 0 \\ 0 & 0 & 0 \end{pmatrix}$ | |
| | 622 | D_6 | A_1 | $E_1(x)$ | $E_1(y)$ | E_2 | E_2 | |
| | $6mm$ | C_{3v} | $A_1(z)$ | $E_1(y)$ | $E_1(-x)$ | E_2 | E_2 | |
| | $\bar{6}m2$ | D_{3h} | A'_1 | E'' | E'' | $E'(x)$ | $E'(y)$ | |
| $6/mmm$ | D_{6h} | A_{1g} | E_{1g} | E_{1g} | E_{2g} | E_{2g} | | |
| Cubic | | $\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix}$ | $\begin{pmatrix} b & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & b \end{pmatrix}$ | $\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$ | $\begin{pmatrix} 0 & 0 & d \\ 0 & 0 & d \\ d & 0 & 0 \end{pmatrix}$ | $\begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$ | | |
| | 23 | T | A | E | E | $F(x)$ | $F(y)$ | |
| | $m\bar{3}$ | T_h | A_g | E_g | E_g | F_g | F_g | |
| | 432 | O | A_1 | E | E | F_2 | F_2 | |
| | $\bar{4}3m$ | T_d | A_1 | E | E | $F_2(x)$ | $F_2(y)$ | |
| | $m\bar{3}m$ | O_h | A_{1g} | E_g | E_g | F_{2g} | F_{2g} | |

$$\left. \begin{aligned} s_{||} &= Ad^2 [(e_x \sin \psi)^2 + e_y^2], \\ s_{\perp} &= Ad^2 e_x^2. \end{aligned} \right\} \quad (4.14)$$

In the particular case when $\psi = \pi/2$, the obtained expressions simplify greatly.

An important characteristic of the scattered light is the degree of depolarization ρ , defined as the ratio $\rho = s_{||}/s_{\perp}$. The degree of depolarization in the general case depends on the angle ψ and makes it possible to estimate the symmetry of the oscillations that take part in the radiation transport. Calculations of the degree of depolarization for different types of crystals and different geometries of illumination are found in a number of papers.^[62,63]

Experimentally, to analyze the Raman scattering tensor, one usually obtains the so-called two-dimensional intensity table.^[64] To construct this table, one measures the intensity of the scattered light for different orientations of the crystal and of the polarizing devices in the paths of the incident and scattered light. The observation is carried out in a direction perpendicular to the incident light. For a theoretical calculation of the components of the indicated table, in the case of nondegenerate oscillations, it is necessary to take the square of the corresponding component of the Raman-scattering tensor. For example, the intensity-table component corresponding to the fact that the polarizing devices of the receiver and of the illuminator are oriented along the x axis is proportional to β_{xx}^2 , etc. If the oscillation that takes part in the Raman scattering process is degenerate, then the component of the intensity table is obtained by summing the corresponding squares of the Raman-scattering tensor components.

We note that in the literature there is frequent mention of cases when the selection rules in Raman spectra of crystals are violated. These violations can be divided into two types. On the one hand, the appearance of "forbidden" RS line may be due to components of the RS tensor which are equal to zero in the table. Such "forbidden" lines may be observed when the crystal is heated,^[65,66] when the exciting line approaches the actual resonant absorption band of the crystal (resonant RS). Violation of the selection rules at sufficiently high temperatures is quite natural, for it was assumed in the derivation of these rules that the crystal is in the ground state prior to the scattering process, a condition strictly satisfied only at $T = 0^\circ K$.^[61] In the case of resonant RS, it is necessary to take into account the fact that the RS tensor is not symmetrical.^[51]

On the other hand, violation of the quasimomentum selection rules in the RS spectra is possible as a result of violation of the translational invariance of the crystal in the presence of inhomogeneities or vacancies.^[67] As a result it is possible to observe RS in which one lattice phonon with arbitrary quasimomentum takes part. The main contribution to the scattering should be made in this case by phonons corresponding to the critical points of the Brillouin zone (see Ch. 6). A violation of the selection rules of this type has apparently, made it possible to observe first-order lines in $SrTiO_3$ crystals. The appearance of additional sharp but very weak lines near strong RS lines^[69,70] is also due to a violation of the selection rules of this type (see Sec. 4.3).

The selection rules can be violated following applica-

According to Table III

$$\beta_{xz} = \beta_{yz} = 0, \quad \beta_{xx} = c, \quad \beta_{xy} = \beta_{yx} = \alpha, \quad \beta_{yy} = -c.$$

If we consider scattering polarized in the (x, z) plane (parallel scattering), we obtain for the effective cross section

$$s_{||} = A (e_x c + e_y d)^2 \cos^2 \psi. \quad (4.13a)$$

Accordingly, for scattering polarized perpendicular to the (x, z) plane we have

$$s_{\perp} = A (e_x d - e_y c)^2. \quad (4.13b)$$

It is assumed here that the scattered light is transverse. Let us consider also an example of scattering by triply degenerate oscillations of the type F_{2q} of group O_h . In this case the total effective cross section can be represented in the form of a sum of three terms, each of which is obtained from the corresponding matrix of Table III. As a result of the calculations we obtain

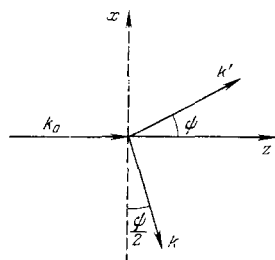


FIG. 6. Geometrical scattering conditions.

tion of external fields^[71] that lower the symmetry of the crystal. This is very useful for the study of oscillations that are not active in the RS spectrum.

4.3. Results of Investigation of First Order RS Spectra of Simplest Crystals

a) **Calcite (CaCO₃).** The RS spectrum of calcite has been the subject of many investigations, since large single crystals of calcite are readily accessible for investigation, are transparent in the wide region of the spectrum, are homogeneous, and can be easily worked. The unit cell of the calcite crystal is shown in Fig. 7. It contains two CaCO₃ molecules. The coordinates of the atoms are:

$$\begin{aligned} \text{Ca (1; 2): } & \frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{3}{4}, \frac{3}{4}, \frac{3}{4}; \\ \text{C (3; 4): } & 0, 0, 0, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}; \\ \text{O: } & (5, 6, 7, 8, 9, 10). \end{aligned}$$

The symmetry space group of the crystal is D_{3d}⁶, the direction group is D_{3d}. The limiting oscillations (k = 0) of the unit cell can be subdivided in the following manner. The CO₃ groups can be regarded as a unit and accordingly one can separate the translation oscillations (motions of the CO₃ groups relative to each other at relative to the Ca atoms), orientation oscillations (rocking of the CO₃ groups relative to each other in phase and in counter-phase), and internal oscillations of the CO₃ groups. The characters of the corresponding vibrational representations, and also of the representations of the vector and of the symmetrical second-rank tensor, can be calculated by using Fig. 7 and Table I. The results of the calculations are shown in Table IV.

Expanding the reducible representations in terms of the irreducible ones, we obtain

$$\left. \begin{aligned} \Gamma_{\text{нов}} &= A_{2g} + A_{1u} + E_g + E_u, \\ \Gamma_{\text{TP}} &= A_{2g} + A_{1u} + A_{2u} + 2E_u + 2E_g, \\ \Gamma_{\text{нотр}} &= A_{1g} + 3A_{2g} + A_{1u} + A_{2u} + 2E_u + 2E_g, \\ \Gamma_{\text{но.ин}} &= A_{1g} + 3A_{2g} + 3A_{1u} + 2A_{2u} + 5E_u + 4E_g. \end{aligned} \right\} \quad (4.15)$$

Comparing with the representations of the vector $\Gamma_V = A_{2u} + E_u$ and of the symmetrical tensor $\Gamma_{\beta\rho\sigma} = 2A_{1g} + 2E_g$, we arrive at the conclusion that the oscillations of type A_{1g} and E_g are active in the RS spectrum and are inactive in the infrared-absorption spectrum. At high frequencies (internal oscillations) one should expect three RS lines, and in the low-frequency spectrum two lines.

The RS spectrum of calcite has revealed five lines

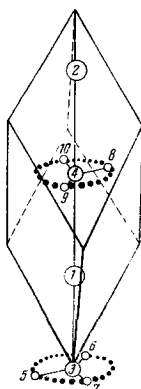


FIG. 7. Unit cell of calcite crystal.

Table IV. Characters of representations for calcite crystal (group D_{3d}⁶)

| Name of representation | E | 2S ₆ | 2C ₃ | i | 3σ _v | 3C ₂ |
|--|----|-----------------|-----------------|----|-----------------|-----------------|
| Vibration representation | 27 | 0 | 0 | -3 | -1 | -3 |
| Translation vibrational representation | 9 | 0 | 0 | -3 | -1 | -1 |
| Orientation vibrational representation | 6 | 0 | 0 | 0 | 0 | -2 |
| External vibration representation | 15 | 0 | 0 | -3 | -1 | -3 |
| Internal vibration representation | 12 | 0 | 0 | 0 | 0 | 0 |
| Vector representation | 3 | 0 | 0 | -3 | 1 | -1 |
| Symmetrical tensor representation | 6 | 0 | 0 | 6 | 2 | 2 |
| A _{1g} | 1 | 1 | 1 | 1 | 1 | 1 |
| A _{1u} | 1 | -1 | 1 | -1 | -1 | 1 |
| A _{2g} | 1 | -1 | 1 | 1 | -1 | -1 |
| A _{2u} | 1 | 1 | -1 | -1 | 1 | -1 |
| E _g | 2 | -1 | -1 | 2 | 0 | 0 |
| E _u | 2 | 1 | -1 | -2 | 0 | 0 |

with frequencies 155, 282, 712, 1086, and 1436 cm⁻¹.^[72-74] The last two frequencies obviously correspond to internal vibrations of the CO₃ group, the strongest line $\Delta\nu = 1086$ cm⁻¹ corresponds to a fully symmetrical oscillation of the type A_{1g}, and the lines 712 and 436 cm⁻¹ to oscillations of type E_g. The remaining two low-frequency lines correspond to oscillations of the type E_g.

The succeeding investigations of the RS spectrum of calcite^[69-70,75] have shown that this spectrum has a much more complicated structure. Additional many weak sharp lines as well as a continuous background in certain sections of the spectrum were observed in the indicated investigations. Thus, weak satellites with frequencies 1067, 1072, and 1075⁻¹ near the 1086 cm⁻¹ line; lines at 1399, 1412, and 1418 cm⁻¹ were observed near the 1436 cm⁻¹ line, etc.

The appearance of additional lines is explained in^[76,77] on the basis of Raman's theory of crystal lattice dynamics. These lines are connected with scattering by additional degrees of freedom of the Raman supercell. It should be noted that the appearance of additional lines can be explained also on the basis of the Born theory, as a result of violation of the quasimomentum conservation owing to the inhomogeneities of the crystal lattice.

b) **Quartz (SiO₂).** A large number of papers are devoted to an experimental study of the RS spectra of quartz, and the studies covered not only the frequencies but also the intensities, the state of polarization, and the line widths.^[78-82,82,76]

The crystal lattice of α-quartz is made up of silicon-oxygen tetrahedra: each silicon ion is connected with four surrounding oxygen ions, and each oxygen ion is connected with two silicon ions. The direction group of α-quartz is D₃, and the unit cell contains three SiO₂ molecules. Accordingly, four oscillations of type A₁ and eight doubly-degenerate oscillations of type E are allowed in the Raman scattering spectra at k = 0. The remaining degrees of freedom yield four oscillations of type A₂ which are active in the infrared spectrum, and three acoustic branches.

The customarily investigated quartz crystals are in the form of a cube with edges directed along the crystallographic axes. We shall henceforth assume the optical axis of the α-quartz to coincide with the z axis. According to Table III, we then have for the scattering-tensor component $\beta_{xx} = \beta_{yy} \neq \beta_{zz}$; $\beta_{\rho\sigma} = 0$ when $\rho \neq \sigma$ (oscillations of type A₁), $\beta_{xx} = -\beta_{yy} = -\beta_{xy}$, $\beta_{xz} = -\beta_{yz}$, $\beta_{zz} = 0$ (oscillations of type E). Experimentally, 12 lines were observed

Table V. Relative intensities of RS lines of α -quartz

| Symmetry class | Width $\Delta\nu$, cm^{-1} | Frequency, $\delta \text{ cm}^{-1}$ | $I_{\infty}(z)$ | $I_{\infty}(x)$ | $I_{\infty}(y)$ | $I_0(z)$ | $I_0(x)$ | $I_0(y)$ |
|----------------|--------------------------------------|-------------------------------------|-----------------|-----------------|-----------------|----------|----------|----------|
| E | 128 | 4.4 | 90 | 55 | 55 | 100 | 60 | 60 |
| A | 206 | 21 | 51 | 66 | 61 | 28 | 30 | 31 |
| E | 266 | 4.4 | 6.2 | 6.5 | 6.0 | 12 | 11 | 12 |
| A | 357 | 4 | 5.3 | 5.7 | 6.1 | 12 | 14 | 13 |
| A | 466 | 6.6 | 180 | 210 | 210 | 180 | 220 | 220 |
| E | 696 | 6.4 | 3.1 | 2.4 | 2.4 | 4.4 | 3 | 3 |
| E | 795 | 8.4 | 7.3 | 6.4 | 6.2 | 3 | 3.4 | 3.4 |
| E | 805 | 11.3 | | | | | | |
| E | 1061 | 7.9 | 2.7 | 1.8 | 1.5 | 3.1 | 1.9 | 2.1 |
| A | 1081 | 11.5 | 1.5 | 3.3 | 3.1 | 1.1 | 2.8 | 2.7 |
| E | 1159 | 8.4 | 10 | 7.2 | 7 | 10 | 6.9 | 6.5 |
| E | 1228 | 11.6 | 1.4 | 1.6 | 1.4 | 1.3 | 1.1 | 1.2 |

in the RS spectrum of α -quartz. Table V lists the results of measurements of the parameters of the α -quartz lines, performed in ^[80] by a photographic method. In that investigation, the intensities of the RS lines were measured at three sample positions, with each of the three axes coinciding in succession with the scattering direction (other conditions being equal). The symbols z, x, and y in the table denote the data obtained when the indicated axis coincides with the scattering direction and the sample was uniformly illuminated in the plane perpendicular to this axis.

Using a polarization measurement procedure, D. F. Kiselev and L. P. Osipova^[81] obtained the values of the intensities for the Raman scattering lines of α -quartz. These measurements, generally speaking, can be carried out by several methods: 1) the crystal is illuminated with linearly-polarized light, and a polaroid with a polarization direction parallel and perpendicular to the spectrometer slit is alternately placed in the path of the scattered light; 2) the crystal is alternately illuminated with linearly polarized light having a polarization direction parallel and perpendicular to the observation direction; this method is usually realized using "tubular" polaroids; 3) the crystal is illuminated with unpolarized light, and polaroids with polarization directions parallel and perpendicular to the instrument slit are alternately placed in the path of the scattered light. Each of these methods makes it possible to compile from the measured intensity values an intensity table whose components are proportional to the squares of the components of the scattering tensor (the measurement methods, the calculations, and the introduction of the necessary corrections are described in ^[81,83]; see also the supplement to the book ^[84]). By using the intensity table, it is easy to find the absolute values of the scattering-tensor components. The signs of the components of this tensor can sometimes be determined on the basis of simple symmetry considerations, but in many cases it is necessary to perform additional calculations and measurements. According to Table III, $I_{zx} = I_{zy}$ and $I_{xx} = I_{yy}$. Thus, in the intensity table and accordingly in the scattering tensor there are only four components that differ in absolute magnitude. For the lines of class A, all the scattering-tensor components can be regarded as positive. For the most intense 466 cm^{-1} line, according to the data of ^[81], the RS tensor is given by

$$\beta(466) = \begin{bmatrix} 103 \pm 3 & 14 \pm 12 & 22 \pm 2 \\ 14 \pm 12 & 103 \pm 3 & 22 \pm 2 \\ 22 \pm 2 & 22 \pm 2 & 100 \pm 2 \end{bmatrix}.$$

Similar data are given in ^[81] for other lines of class A. We call attention to the fact that the mixed components $\beta_{\rho\sigma}$ ($\rho \neq \sigma$) do not equal to zero, i.e., there are deviations from the selection rules.

As shown by the measurements,^[81] the scattering tensors for the 206, 357, and 466 cm^{-1} lines are approximately spherically symmetrical ($\beta_{zz} \approx \beta_{xx} \approx \beta_{yy}$). The fourth line of type H, has an appreciably differing scattering tensor (the values of the components are given in the same scale as for the tensor $\beta(466)$):

$$\beta(1081) = \begin{bmatrix} 6 & 0 & 5 \\ 0 & 6 & 5 \\ 5 & 5 & 15,3 \end{bmatrix}.$$

The form of this tensor shows that the oscillations of the induced electric moment occur in this case predominantly along the z axis.

For degenerate oscillations, the experimental determination of the Raman scattering tensor of α -quartz was carried out by Kiselev.^[82] In the measurements, two identical cubic samples were used, which differed in the direction of the crystallographic axes x and y. The axes of one sample were directed along the edges of the cube, while the axes of the second sample made an angle of 45° with the crystallographic axes x and y.

The measurements have shown that, within the limits of errors, the intensity tables of both investigated samples are the same for the most intense type lines, E 128, 696, 795-805, and 1159 cm^{-1} .

For degenerate oscillations, the Raman scattering tensor can be written in the form

$$\beta_{\rho\sigma} = \beta'_{\rho\sigma} + \beta''_{\rho\sigma},$$

where the tensors β' and β'' each pertain to one of the degenerate oscillations with a given frequency ω . Inasmuch as two oscillations of type E with frequency ω are normal oscillations, i.e., independent of each other, it follows that

$$I_{\rho\sigma} = (\beta'_{\rho\sigma})^2 + (\beta''_{\rho\sigma})^2 = I'_{\rho\sigma} + I''_{\rho\sigma}.$$

The reduction of the experimental material in ^[82] was based on the assumption that $I'_{\rho\sigma} = I''_{\rho\sigma}$, as a result of which the scattering tensors β' and β'' differ only in the signs of certain components. The scattering tensors obtained in this case were for type-E lines.

5. CERTAIN TYPICAL CASES OF RS OF LIGHT IN CRYSTALS

Investigations of RS of light in crystals involve great experimental difficulties. First, it is necessary to have for the investigations sufficiently large and very pure samples, thus greatly limiting the number of possible objects. Work with powders and polycrystals is possible, but entails additional difficulties. The RS lines in crystals are very weak, and in addition lie near the exciting line, which produces a strong background, and also "ghosts" when instruments with diffraction gradients are used. In spite of this, more than 100 different crystals have been investigated to date, and the number of RS in-

vestigations amounts to several hundred. It is not our task to present a systematic review of all these investigations, all the more since there are several review papers on this question, [5-7, 56, 85] where an extensive bibliography is cited. We consider below only several typical cases of RS in crystals which in our opinion are of greatest physical interest.

5.1. Molecular Crystals

An intensive investigation of lattice vibrations of molecular crystals was initiated by the discovery of the low-frequency RS spectrum by E. F. Gross and M. F. Vuks. [86] The lines of this spectrum have two important features:

1) The region of lines of this spectrum lies in the immediate vicinity of the exciting line, and consequently correspond to very low natural frequencies of the medium.

2) In the crystal spectrum, the lines are quite clearly pronounced; on the other hand, only a continuous spectrum is observed in the spectrum of the same substance in the liquid state in the region under consideration (the wings of the Rayleigh line).

Gross and his co-workers expressed the opinion, even in their first papers, that the low-frequency spectrum is due to intermolecular vibrations—vibrations of the crystal lattice of the investigated substance. This conclusion was confirmed by a number of experiments. [87]

A comparison of the spectra of crystals whose quasi-elastic constants can be assumed to be close in magnitude makes it possible in principle to assign the observed lines to definite oscillations. Systematic investigations of this kind were performed by E. F. Gross, A. V. Korshunov, M. F. Vuks, and their co-workers. [88-92] In these investigations, a comparison was made of the low-frequency spectra of crystals having similar structure, primarily isomorphous crystals, particularly paradihalide derivatives of benzene. A group theoretical analysis of the oscillations of these crystals can be based on the general theory developed in [49]. The theory of crystal-lattice vibrations of molecular crystals has been developed in [93-97].

It should be noted that the subdivision of vibrations into internal and external is not rigorous. Coupling between the internal and external vibrations, which usually is very difficult to control, can lead to a shift of the position and to a change of other parameters of the lines in the low-frequency spectra. According to the data of Porfir'eva, [93] in those cases when the external limiting vibrations can be fully separated into translational and orientational, a coupling between the internal and orientational vibrations still remains.

Besides the study and comparison of the spectra of similar crystals (primarily isomorphous), of great importance for the investigation of crystal-lattice dynamics is the study of the small-oscillation spectra at different temperatures and pressures. Such investigations make it possible also in a number of cases to relate the lines to various lattice vibrations.

According to the data of [96, 98, 99], when the temperature decreases an increase of the frequencies is observed. This effect is apparently due to the approach of the molecules as a result of compression of the substance when

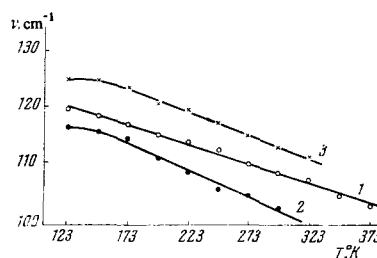


FIG. 8. Temperature dependence of the frequencies: 1 — stilbene 110 cm^{-1} line; 2 — tolane 105 cm^{-1} line; 3 — tolane 116 cm^{-1} line (at 273°K).

the temperature is lowered, causing an increase in the quasi-elastic constants of the crystal. The frequency shift has a smooth almost linear character, slowing down somewhat at low temperatures. By way of illustration, Fig. 8 shows plots of the temperature dependence of the frequencies of stilbene and tolane, obtained in [99]. A similar effect is observed under hydrostatic compression of the medium. According to the data of Fröhling, [98] the lines of crystalline benzene, which have under ordinary conditions frequencies 63 and 105 cm^{-1} , have frequencies 66 and 112 cm^{-1} respectively at 720 atm.

With increasing temperature, the integral intensity of the low-frequency Raman-scattering lines increases, in accordance with the data of [96], and the temperature dependence of the intensity agrees with the theoretical one.

The line widths in low-frequency Raman spectrum were investigated by A. V. Korshunov and A. F. Bondarev [100-102] and by P. A. Bazhulin, A. V. Rakov, and A. A. Rakhimov. [99, 103] Of particular interest are measurements of the width of these lines, carried out at different temperatures.

The main causes of line broadening in the low-frequency spectrum are apparently the anharmonicity of the oscillations and the jumplike reorientation of the molecules. The influence of the anharmonicity on the temperature dependence of the width was qualitatively considered in [104]. The expression obtained for the line width is

$$\delta_{\text{anh}} = \frac{aT\nu}{f}, \quad (5.1)$$

where a is a constant, T the absolute temperature, ν the frequency of the given line, and f the quasi-elastic constant.

The influence of reorientation of molecules in the liquid on the widths of Raman-scattering lines for which the tensor of the derivative of the polarizability has an anisotropic part was investigated experimentally and theoretically in a number of papers. Unlike a liquid, where rotations of the molecules through any angle are possible in principle, only rotations that do not violate the crystal-lattice symmetry are realized in crystals. Rakov [105] demonstrated for the first time, by an optical method, that in many crystalline substances there actually occur random reorientations of the molecules, and calculated the reorientation barriers U . The following formula was obtained for the temperature dependence of the line width, in analogy with liquids,

$$\delta_{\text{reor}} = A \exp\left(-\frac{U}{kT}\right). \quad (5.2)$$

Special interest attaches to investigations of the reorientation of molecules in the crystal lattice by means of the low-frequency spectra.^[99] According to (5.1) and (5.2), the temperature dependence of the line width is determined in the general case by the sum of the anharmonic and reorientational terms:

$$\delta = \delta_{\text{anh}} + \delta_{\text{reor}} = AT + B \exp\left(-\frac{U}{kT}\right), \quad (5.3)$$

where A and B are certain constants. In accordance with the ratio of the indicated two terms, the temperature dependence of the line width is linear or exponential to a lesser or a greater degree.

Figure 9 shows a typical dependence of the low-frequency spectral line width on the temperature in accordance with the data of^[99]. It can be readily seen that for most lines this dependence is linear, but for the 90 cm⁻¹ frequency the dependence is close to exponential, i.e., the principal role for this line is played by reorientation of the molecules in the lattice. Reduction of the experimental data makes it possible to find the potential barriers of the orientation U and the average reorientation time τ .

We have used above rather crude qualitative notions concerning the causes of line broadening in the low-frequency spectra. A more rigorous solution of the problem is given in^[106] on the basis of the theory of random rotary wandering of the molecule in the crystal lattice. According to this theory, one considers first scattering by a molecule taken individually, after which one considers the total scattering by an aggregate of molecules making up the crystal. In spite of the classical approach, to this problem, the correlation theory^[106] leads to good agreement with the experiment. The quantum mechanical theory was developed by A. A. Rakhimov and L. A. Shelepin.^[103] The physical meaning of the formulas of the quantum and correlation theory is essentially the same.

Let us consider now the perturbations of the intramolecular oscillations by the field of the crystal lattice. Usually these perturbations are small and can be attributed to two mechanisms: a) the influence of the static field of the crystal, which leads to a shift of the frequency and to a change in the selection rules for the intramolecular oscillations (as a result, certain forbidden frequencies may become active and degenerate frequencies may split); b) resonant interaction of identical oscillations of molecules in the unit cell, as a result of which frequency splitting takes place (the number of components of the split line cannot exceed the number of molecules in the unit cell).

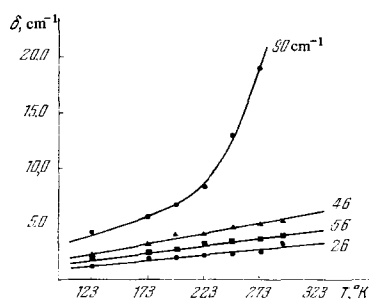


FIG. 9. Dependence of low-frequency spectral line width on the temperature.

The first effect is called static splitting, and the second dynamic or Davydov splitting (it was first proposed by A. S. Davydov to explain the structure of the electronic spectra of molecular crystals^[49]).

Investigations of the splitting of vibrational frequencies under the influence of the indicated perturbing factors were carried out so far mainly by using the absorption spectra.^[107] In some cases it was possible to observe splitting due to only one of these factors. Thus, for example, O. V. Fialkovskii^[108] investigated the spectrum of infrared absorption of single-crystal anthracene, and observed splitting of the 740 cm⁻¹ into the components 742 and 728 cm⁻¹. The anthracene molecule has no degenerate vibrations. Therefore the effect observed in this investigation may be only the Davydov splitting. The static splitting of degenerate lines in infrared spectra has the same order of magnitude.

From the point of view of a study of the influence of the lattice field on the intramolecular oscillations, great interest attaches to investigations of cyclohexane crystals. At 46°C, cyclohexane crystallizes in a cubic system (form I) with four molecules per unit cell, and there is no splitting of the lines in the region of the fundamental frequency. At -87°C, a first-order phase transition takes place, with formation of crystals of the monoclinic system (form II) with eight molecules per unit cell. Many of the lines of the infrared spectrum of form II are split.^[109] A similar splitting occurs in the Raman scattering spectrum of this form. According to the data of M. Ito,^[110] lines of type E_g, which have in liquid cyclohexane the frequencies 1025, 1266, 1345, and 1441 cm⁻¹, split respectively into 1023, and 1032, 1264 and 1276, 1335 and 1347, and 1439 and 1445 cm⁻¹. Microphotographs of three lines of form II are shown in Fig. 10. In addition, lines of type A_g, 1055 and 1422 cm⁻¹, which are forbidden by the selection rules in the liquid phase, appear in the spectrum of form II. These effects can be attributed to a lowering of the symmetry of the crystal lattice and help in turn refine the symmetry group of the crystal.^[110]

5.2. Investigation of RS Spectra in Phase Transitions

As far back as in one of the earliest studies of RS in crystals, G. S. Landsberg and L. I. Mandel'shtam^[111] observed a change in the intensity and width of the lines of quartz near the point of the phase transition at T = 573°C. In that investigation, they studied the 207 and 466 cm⁻¹ line. It turned out that the 466 cm⁻¹ line becomes broader and more diffuse with increasing temperature, but the position of its maximum hardly changes above the transition point. The 207 cm⁻¹ line becomes strongly smeared out with increasing temperature, and shifts towards the exciting line. Near the transition point, this line becomes hardly noticeable, and above the transition point, i.e., in β -quartz, it disappears completely.

Owing to the experimental difficulties, no systematic investigations were made in this field for a long time following publication of^[111]. The detailed study of RS spectra near second order phase transition points began only after V. L. Ginzburg pointed out the singularities in the behavior of certain lines at these points.^[112]

In the case of second-order phase transitions between different crystal modifications, there occurs either a displacement of the sublattices of the crystal in the direction

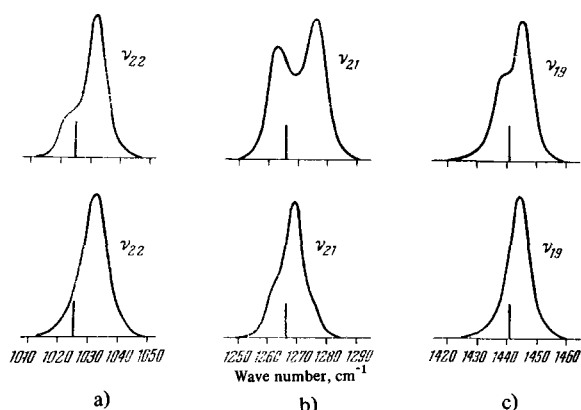


FIG. 10. Microphotographs of three lines (a - c) of cyclohexane at 77°K in a supercooled crystal of form I (top) and a crystal of form II (bottom).

of one of the normal oscillations, or an ordering of the positions of the sublattices along certain oscillations. It turns out here that the shape of the potential curve of the normal oscillation is of great significance. In the case of a potential with one minimum, the phase transition is a transition of the displacement type, and in the case of two minima it is of the "order-disorder" type. The nature of the phase transition in the indicated sense can be established on the basis of the exact structure investigations. However, in the case of ferroelectrics, as shown in ^[113], it is sufficient for this purpose to know the results of electrical measurements; the Curie-Weiss constant is of the order of 10^5 deg for displacement-type transitions and 10^3 deg for "order-disorder" transitions. In particular, the phase transitions in the crystals BaTiO_3 , Li_2TiO_3 , KTaO_3 , and quartz can be credited to this type of displacement and phase transitions in the crystals NaNO_2 , NaClO_3 , KH_2PO_4 , $\text{NH}_4\text{H}_2\text{PO}_4$, Rochelle salt, triglycin sulfate, etc. belong to the second type.

The theory developed by V. L. Ginzburg and A. P. Levanyuk^[112] relates the second-order phase transitions, due to displacements of the sublattices, with the crystal-lattice dynamics. According to this theory, in the case of second order phase transitions the frequency of one (or several) SR lines tends to zero as the transition point is approached, and its intensity increases if the transition point is critical. Similar results with respect to the anomalous decrease of certain frequencies is obtained in the semiphenomenological theory of ferroelectrics developed by W. Cochran.^[114]

The theoretical investigations of Ginzburg and Levanyuk,^[112] and also of Cochran,^[114] stimulated numerous experimental investigations of the vibrational spectra of crystals near phase-transition points.

One of the most interesting objects is barium titanate BaTiO_3 . In the BaTiO_3 crystal, the ferroelectric phase transition is of first order (of the displacement type), and is close to the critical Curie point; therefore the frequency of the oscillation responsible for the transition does not vanish. This frequency pertains to the oscillations of Ba relative to the TiO_3 group. At room temperature, the frequencies 12, 174, 182, and 491 cm^{-1} appear in the infrared spectrum of single-crystal barium titanate,^[115] and the 174 cm^{-1} frequency vanishes above the transition point. The splitting of the frequency in the region of 180 cm^{-1}

can be attributed to the change of the crystal symmetry, which is cubic above the transition point ($\Theta \approx 120^\circ\text{C}$) and tetragonal below it. With increasing temperature, the frequencies 182 and 491 cm^{-1} remain unchanged, whereas the frequency of the first oscillation decreases near the transition point to 6 cm^{-1} . The decrease of the frequency in the phase-transition region was observed also somewhat earlier in ^[116]. The RS spectra of barium titanate were also investigated. In ^[65], in the tetragonal phase, the frequencies 235, 306, 512, and 718 cm^{-1} were found near the transition point. Only the first of these frequencies changes appreciably with temperature, shifting from 271 to 235 cm^{-1} when the temperature is increased from 290 to 390°K. The authors ascribe this frequency to a longitudinal oscillation connected with a low-frequency transverse ferroelectric oscillation. An investigation of the high-frequency oscillation responsible for the ferroelectric transition in single-crystal BaTiO_3 was reported in ^[117]. Since the oscillation in question is strongly damped and has a very low frequency ($\sim 15 \text{ cm}^{-1}$), it was impossible to register the corresponding line reliably.

The anomalous shift of one of the RS lines towards the exciting line on approaching the phase-transition temperature was investigated also in ^[71,118]. It was observed in ^[71] that the frequency of the oscillation responsible for the ferroelectric transition* shifts towards the exciting frequency by $\sim 60 \text{ cm}^{-1}$ when the crystal is cooled from 300° to 8°K. It turns out, however, that the frequency of the oscillation in question, while decreasing appreciably, does not vanish at the very transition point. A line that varies in accordance with the theory of ^[112] was observed in ^[118]. However, the fact that the indicated line is an "extra" line according to the group-theoretical classification of the normal oscillations, and has an intensity comparable with the intensity of the forbidden lines and second-order lines, is still unexplained.

The case of transitions of the "order-disorder" type was considered by V. G. Vaks, V. M. Galitskiĭ, and A. I. Larkin,^[119] who have shown that in this case the magnitude of the frequency shift of the oscillation responsible for the phase transition depends on the shape of the potential curve. An appreciable decrease is expected only for low potential barriers; in general, however, this quantity tends to a finite limit. This result was obtained only in the "classical" variant of the indicated theory, but in our opinion it is worthy of attention.

P. A. Bazhulin and I. M. Aref'ev^[120] investigated the RS spectrum of the ferroelectrics KH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$. A 34 cm^{-1} line was observed in the spectra of both crystals. Upon cooling to the transition point, the frequency of this line decreased by 4 cm^{-1} in both spectra. It should be noted that in accordance with the calculations of Cochran,^[114] in KH_2PO_4 the frequency of the oscillation connected with the ferroelectric transition should decrease from 85 cm^{-1} at room temperature to 14 cm^{-1} at the transition point.

The RS spectra of ferroelectrics, triglycin sulfate, and Rochelle salt, were investigated at low frequencies in ^[121]. No changes were observed in the spectra of these single crystals following changes of the temperature and passage

*We note that the indicated oscillation is inactive in the RS spectrum, but violation of the selection rule was attained in ^[71] by applying an external electric field.

through the phase-transition point. Similar results were obtained in [122].

Certain changes in the Raman scattering spectra at the phase-transition points were observed in [66,123] in investigations of single-crystal NaNO_2 . The measurements performed in [66] have shown that when the NaNO_2 crystal is heated all the lines shift towards the exciting line and broaden. These effects are most strongly pronounced at the lowest-frequency lines $\Delta\nu_1 = 121 \text{ cm}^{-1}$, $\Delta\nu_2 = 158 \text{ cm}^{-1}$ and $\Delta\nu_3 = 184 \text{ cm}^{-1}$ (the frequencies are given at room temperature). At the ferroelectric phase transition point ($\Theta = 160^\circ\text{C}$), the aforementioned lines have frequencies $\Delta\nu_1 = 110 \text{ cm}^{-1}$, $\Delta\nu_2 = 143 \text{ cm}^{-1}$, and the line $\Delta\nu_3$ becomes so smeared out that it can no longer be registered. Above the transition point, the spectrum in the low-frequency region is represented by a broad asymmetrical band with maximum near 110 cm^{-1} . The intensity of this band decreases uniformly with increasing distance from the exciting line. In addition, certain lines with higher frequencies vanish above the transition point, in agreement with the selection rules.

The broadening of the Raman scattering lines and their shift towards the exciting line upon heating of the crystal are ordinary temperature effects. No line with an anomalously decreasing frequency near the transition point was observed in [66].

Much stronger changes than in the cited investigations were observed in the RS spectrum in [124] following heating of an NaClO_3 crystal. This crystal has a ferroelectric transition at $\Theta = 593^\circ\text{K}$. Investigations at higher temperatures were difficult, since the melting point of the crystal is 537°K .

The observed spectrum of the NaClO_3 crystal can be subdivided into three groups of lines: 1) weak lines with lowest frequencies $\Delta\nu_1 = 72 \text{ cm}^{-1}$, $\Delta\nu_2 = 81 \text{ cm}^{-1}$, and $\Delta\nu_3 = 107 \text{ cm}^{-1}$, corresponding apparently to translational oscillations; 2) the lines $\Delta\nu_4 = 123 \text{ cm}^{-1}$, $\Delta\nu_5 = 131 \text{ cm}^{-1}$, and $\Delta\nu_6 = 179 \text{ cm}^{-1}$, corresponding to orientational oscillations; 3) lines with higher frequencies, corresponding to internal oscillations of the NaClO_3 molecule (the values of the frequencies are given at a temperature 45°C). All the oscillations are active in the Raman-scattering spectrum.

When the crystal is heated, all the lines except $\Delta\nu_6$ shift only slightly in frequency (by $3\text{--}5 \text{ cm}^{-1}$) and broaden. Appreciable changes with temperature are observed in the $\Delta\nu_6$ line.

The results of measurements of the parameters of the $\Delta\nu_6$ line are shown in Table VI and are illustrated in Fig. 11. On heating from 83° to 423°K , the $\Delta\nu_6$ line shifts towards the exciting line by 45 cm^{-1} , and its width increases from 5 to 44 cm^{-1} . The integral intensity of this line, which is approximately proportional to the product $I_0\delta$, also increases with increasing temperature. Thus, all the effects predicted by the theory are qualitatively confirmed.

Table VI

| $T, ^\circ\text{K}$ | $\Delta\nu_6, \text{cm}^{-1}$ | δ, cm^{-1} | I_0 , arb. un. | $I_0\delta$ | $T, ^\circ\text{K}$ | $\Delta\nu_6, \text{cm}^{-1}$ | δ, cm^{-1} | I_0 , arb. un. | $I_0\delta$ |
|---------------------|-------------------------------|--------------------------|------------------|-------------|---------------------|-------------------------------|--------------------------|------------------|-------------|
| 83 | 202 | 5 | 70 | 350 | 373 | 172 | 26 | — | — |
| 113 | 198 | 6 | 62 | 370 | 423 | 161 | 32 | 28 | 900 |
| 203 | 192 | 8 | 49 | 392 | 483 | 157 | 44 | — | — |
| 318 | 179 | 16 | 25 | 400 | | | | | |

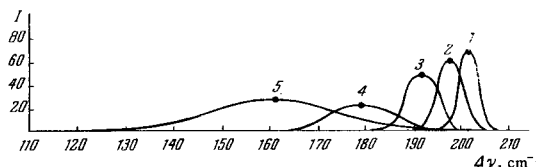


FIG. 11. Change of shift of the $\Delta\nu_6$ line with increasing temperature. 1 - $T = 83^\circ\text{K}$; 2 - $T = 113^\circ\text{K}$; 3 - $T = 203^\circ\text{K}$; 4 - $T = 318^\circ\text{K}$; 5 - $T = 423^\circ\text{K}$.

A new effect observed experimentally in [124] is the appreciable line broadening connected with the ferroelectric transition. At high temperatures, this line spreads out to such an extent that the harmonic approximation for the crystal lattice is apparently no longer valid.

Further theoretical and experimental investigations are needed for a more complete explanation of the mechanisms of the phase transitions in solids.

Besides the study of phase transitions between different crystal modifications, RS is used to study transitions from crystals to liquids and also from liquid crystals to liquid crystals. [125]

5.3. Scattering of Light in Piezoelectric Crystals

If the crystal has a symmetry center, then all the oscillations active in the RS are inactive in the infrared absorption spectrum. However, if there is no symmetry center, as is the case for piezoelectric crystals, scattering by polar lattice vibrations becomes possible. RS by polar vibrations has many specific properties.

In accordance with the features of the dispersion curves of the optical branches of the polar oscillations, the frequency of scattered light changes as a function of the magnitude and direction of the wave vector of the vibrational quantum that takes part in the scattering process. By exciting various points in reciprocal space during the RS, it is possible to study the shape of these dispersion curves. This is done by choosing a suitable scattering geometry. As seen from Fig. 6, the modulus of the wave vector of the scattered light decreases with decreasing angle θ between the directions of the incident and scattered radiation. If this angle is very small, then the scattering is called longitudinal. In longitudinal Raman scattering it is possible to excite not only purely mechanical oscillations, but also "mixed" vibrational quanta—polaritons, the frequency of which decreases strongly with decreasing wave vector. RS on polaritons was observed experimentally in [1] in the cubic piezoelectric crystal GaP. The difficulty of the indicated experiment lies in the fact that the divergence of the beams of the incident and scattered radiations should be very small ($\sim 0.5\%$), which greatly reduces the intensity of the scattered light; the light source used in [1] was a helium-neon laser. The observed polariton frequency shift was 20% when the angle θ changed from zero to several degrees. In [126], a study was made of the longitudinal Raman scattering in a uniaxial ZnO crystal with the aid of an argon laser ($\lambda = 4880 \text{ \AA}$). The laser beam propagated along the x axis, and the scattered light propagated in the (x, z) plane at an angle θ to the direction of the incident light (Fig. 12). The incident and scattered beams were polarized. The case in which the exciting ray is ordinary and the scattered extraordinary is designated in Fig. 12 by yz; the symbol for the

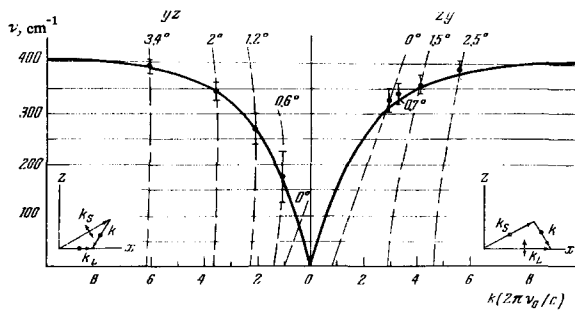


FIG. 12. Dispersion curve for the 407 cm^{-1} oscillation obtained with the aid of RS. yz – incident beam polarized along the y axis (ordinary beam) and beam scattered along the z axis (extraordinary beam); zy – reversed polarizations of the incident and scattered light; k_L – wave vector of incident beam; k_S – wave vector of scattered beam; k – wave vector of phonon; the dashed lines were obtained from the energy-quasi-momentum conservation law; solid line – dispersion curve obtained by calculation.

opposite polarization of the incident and scattered radiation is zy .

Regardless of the polarization of the incident and scattered light, an extraordinary transverse polariton, polarized along the y axis, was excited. The solid line in Fig. 12 shows the dispersion curve calculated with the aid of the relation

$$\frac{k^2 c^2}{\omega^2} = \frac{\nu_0^2 \epsilon_{0\perp} - \nu_l^2 \epsilon_{\infty\perp}}{\nu_0^2 - \nu^2},$$

where $\omega = 2\pi\nu$, $\epsilon_{0\perp} = 8.15$ and $\epsilon_{\infty\perp} = 4.0$ are the static and high-frequency dielectric constants, respectively, and ν_0 is the dispersion frequency, equal to 407 cm^{-1} and expressed in units of $2\pi\nu_0/c$.

According to the energy and quasimomentum conservation law, at small θ the following relations are satisfied:

$$k = \{[\nu_l(n_e - n_o) + \nu n_o]^2 + \nu_l(\nu_l - \nu)n_e n_o \theta^2\}^{1/2}$$

in the case zy and

$$k = -\{[\nu n_e - \nu_l(n_e - n_o)]^2 + \nu_l(\nu_l - \nu)n_o n_e \theta^2\}^{1/2}$$

in the case yz ; here ν_l is the laser frequency and n_o and n_e are the refractive indices for the ordinary and extraordinary beams. The energy and quasimomentum conservation law curves corresponding to these relations are shown in Fig. 12 by dashed lines. Figure 13 shows spectrograms for the yz polarization. We see that the observed frequencies change from 407 to 160 cm^{-1} when the angle is changed from 0.6° to 3.4° .

In the described experiments, RS of light was used to study the dependence of the frequencies of the polar oscillations on the absolute magnitude of the wave vector. However, for non-cubic crystals, as indicated in Sec. 2.4, the frequency of the polar oscillations depends also on the direction of the wave vector k . An effect of this kind was observed in the Raman scattering spectra of a number of crystals.^[127-137]

A feature of RS of light in piezoelectric crystals is also the anomalous degree of depolarization of a number of lines,^[134] which does not agree with the theoretical values. These anomalies are discussed in^[135, 51, 66]. As already noted above, degenerate polar oscillations split under the influence of electrostatic forces into longitudi-

nal and transverse oscillations (in a cubic crystal). The intensity of the RS by the longitudinal and transverse oscillations is different. This follows, for example, from the form of the RS tensor, obtained with the aid of third-order perturbation theory,^[56] since the electron-phonon interaction is different for the longitudinal and transverse oscillations.

5.4. Scattering With Participation of Magnons, Plasmons, and Other Quasiparticles

Not only phonons, but also all other quasiparticles of the crystal can take part in the RS process.

The scattering of light in magnetic crystals has been the subject of a number of theoretical papers.^[136-139] Recently, RS with participation of one and two magnons was experimentally observed^[2, 3] in the antiferromagnets FeF_2 and MnF_2 . The RS spectra were excited with the aid of the 4880 \AA line of an argon laser of 50 mW power; the temperature of the FeF_2 sample, which was an oriented single crystal measuring $5 \times 5 \times 7 \text{ mm}$, ranged from 10° to 70° K ; the antiferromagnetic transition point of FeF_2 corresponds to 78.5° K . At sufficiently low temperatures, two satellites were registered with frequencies $\nu_1 = 52 \text{ cm}^{-1}$ and $\nu_2 = 154 \text{ cm}^{-1}$, corresponding to single-magnon (magnon wave vector $k = 0$) and two-magnon scattering (the magnon wave vectors k and $-k$ are on the boundary of the Brillouin zone). In the case of MnF_2 the first-order spectrum could not be observed, since the frequency of the magnon with zero wave vector turned out to be very small, but a second-order RS line was registered in this case, too. The intensity of the first-order magnon satellites was 10^{-4} of the intensity of the 992 cm^{-1} RS line of liquid benzene, and the order of magnitude of the two-magnon scattering coincided with that of the intensity of the single-magnon process. Although the latter fact was theoretically demonstrated,^[138, 139] in our opinion additional experimental confirmation of this singularity is necessary.

The feasibility of scattering of light with participation of plasmons, which are longitudinal oscillations of the electron density, was investigated in^[55]. Usually the plasmon frequencies are much higher than the optical-phonon frequencies. In semiconductors, however, these frequencies may be small. The RS effect with participation of the plasmons that interact with the longitudinal optical phonons was observed in^[4, 5] and also in^[140, 141], where a CO_2 laser was used as the source of the exciting radiation. The value of the RS method in this case is enhanced by the fact that the longitudinal oscillations of the electron density, which do not interact with the transverse electromagnetic waves, cannot be investigated with the aid of infrared absorption.

Single-crystal gallium arsenide was investigated in^[4]. When the electron density is increased in this sample from 2.3×10^{15} to $2.9 \times 10^{18} \text{ cm}^{-3}$, the values of the plasma frequency and the frequencies of the longitudinal optical phonons turn out to be close in magnitude; when the plasma frequency approaches the phonon frequency as the electron density is increased, the RS line corresponding to the longitudinal optical phonons broadens and shifts from 300 to 540 cm^{-1} ; at the same time, a weak broad line whose frequency approaches that of the transverse optical oscillation is produced. The observed effects are

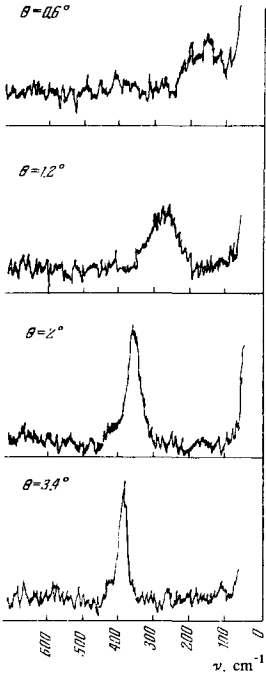


FIG. 13. Microphotograph of longitudinal RS in ZnO at different angles θ between the incident and scattered rays (yz).

in good agreement with the theory. The intensity of the lines of RS on plasmons turns out to be much larger than in ordinary RS; the effective scattering cross section is $\sim 10^{-25}$ cm² per molecule,^[141] which is 100–1000 times larger than the corresponding figure for scattering by phonons; the plasma RS line width is also very large (~ 30 cm⁻¹), this being connected with the rapid damping of the plasma waves.

A theory of RS of light in the electron-spectrum energy gap produced in superconductors below the superconducting transition point was developed in^[143]. An experimental attempt to observe RS of this kind ended in failure.^[144] In such a case the experiment is made complicated by the fact that: 1) the width of the gap turns out to be very small ($5\text{--}10$ cm⁻¹); 2) the RS effective cross section is smaller by several orders of magnitude than the usual one; 3) since the investigated object is a metal, the exciting light can penetrate to a very small depth (10^{-5} cm), which additionally decreases the intensity of the scattered light.

Mention should also be made of RS by electronic transitions of impurity paramagnetic ions that enter the crystal lattice^[145–147] of scattering by local oscillations^[148] and by Landau levels,^[140–141] and of scattering connected with the spectral manifestations of crystallites in glass,^[129] all of which are of independent interest.

6. SECOND ORDER SR SPECTRA

Two phonons take part simultaneously in second-order RS. The following process can occur in this case.

1) A photon of frequency ω_0 (incident radiation) decays into a photon of frequency ω' (scattered radiation) and two phonons of frequencies Ω_1 and Ω_2 . The energy and quasi-momentum conservation laws for such a process are given by

$$\left. \begin{aligned} \hbar\omega_0 &= \hbar\omega' + \hbar\Omega_1 + \hbar\Omega_2, \\ \hbar\mathbf{k}_0 &= \hbar\mathbf{k}' + \hbar\mathbf{k}_1 + \hbar\mathbf{k}_2. \end{aligned} \right\} \quad (6.1)$$

2) A photon of frequency ω_0 interacts with a phonon of

frequency Ω_1 . The scattering results in a photon of frequency ω'' and a phonon of frequency Ω_2 . The conservation laws are

$$\left. \begin{aligned} \hbar\omega_0 + \hbar\Omega_1 &= \hbar\omega'' + \hbar\Omega_2, \\ \hbar\mathbf{k}_0 + \hbar\mathbf{k}_1 &= \hbar\mathbf{k}'' + \hbar\mathbf{k}_2. \end{aligned} \right\} \quad (6.2)$$

3) A photon of frequency ω_0 interacts simultaneously with two phonons of frequency Ω_1 and Ω_2 . The result is a scattered photon of frequency ω''' . The conservation laws take the form

$$\left. \begin{aligned} \hbar\omega_0 + \hbar\Omega_1 + \hbar\Omega_2 &= \hbar\omega''', \\ \hbar\mathbf{k}_0 + \hbar\mathbf{k}_1 + \hbar\mathbf{k}_2 &= \hbar\mathbf{k}'''. \end{aligned} \right\} \quad (6.3)$$

Since the absolute magnitude of the wave vectors of the photons is small compared with the linear dimensions of the first Brillouin zone, it follows from (6.1) and (6.2) that the wave vectors of the phonons taking part in the scattering process satisfy the following approximate relations

$$\mathbf{k}_1 + \mathbf{k}_2 = 0 \quad \text{or} \quad \mathbf{k}_1 - \mathbf{k}_2 = 0. \quad (6.4)$$

It follows from (6.4) that in the second-order Raman scattering there can take part not only phonons from the start of the first Brillouin zone, but from any point of the zone, particularly points lying on the boundary of the zone. Thus, the study of second-order spectra yields information on the phonon spectrum of the entire first Brillouin zone.

The processes (6.1)–(6.3) can be taken into account by introducing into the Hamiltonian of the crystal fourth-order anharmonic terms describing processes in which four crystal quasiparticles, two photons and two phonons, take part simultaneously. In particular, the scattering of type (6.1) turns out to be due to the term

$$\begin{aligned} H^{(4)} &= \sum_{\rho_0\rho'\rho_1\rho_2} Q_{\rho_0\rho'\rho_1\rho_2}(\mathbf{k}_0, \mathbf{k}', \mathbf{k}_1, \mathbf{k}_0 - \mathbf{k}' - \mathbf{k}_1) \\ &\times \xi_{\rho_0}(\mathbf{k}_0) \xi_{\rho'}^+(\mathbf{k}') \xi_{\rho_1}^+(\mathbf{k}_1) \xi_{\rho_2}^+(\mathbf{k}_0 - \mathbf{k}' - \mathbf{k}_1); \end{aligned} \quad (6.5)$$

here ξ and ξ^+ are Bose operators of annihilation and creation of the quasiparticles of the crystal, $\rho_0, \rho', \rho_1,$ and ρ_2 are the polarization indices of the corresponding quasiparticles, and $\mathbf{k}_0, \mathbf{k}',$ and \mathbf{k}_1 are their wave vectors. The increase in the number of scattered photons $n(\rho', \mathbf{k}')$ per unit time can be obtained by using first-order perturbation theory:

$$\begin{aligned} \frac{dn(\rho', \mathbf{k}')}{dt} &= \frac{2\pi}{\hbar} \sum_{\rho'\rho_1\rho_2} |Q_{\rho_0\rho'\rho_1\rho_2}|^2 n(\rho_0, \mathbf{k}_0) \{n(\rho', \mathbf{k}') + 1\} \\ &\times \{n(\rho_1, \mathbf{k}_1) + 1\} \{n(\rho_2, \mathbf{k}_2) + 1\} \delta\{E_{\rho_0\mathbf{k}_0} - E_{\rho'\mathbf{k}'} - E_{\rho_1\mathbf{k}_1} - E_{\rho_2\mathbf{k}_2}\} \dots; \end{aligned} \quad (6.6)$$

here $n(\rho, \mathbf{k})$ is the number of quasiparticles per oscillator (ρ, \mathbf{k}) . Analogous expressions can be obtained for the processes (6.2) and (6.3). Explicit expressions for the anharmonicity coefficients of fourth order have not been obtained so far. The corresponding formulas would apparently be very complicated.

The second order RS of light can be described also on the basis of polarizability theory.^[150,151] As already noted, the main result of polarizability theory is the fact that the intensity of the scattered light is expressed in terms of the matrix elements of the polarizability of the electron subsystem, which depends on the coordinates of the nucleus as parameters. For the process of type (6.1), the indicated matrix element is taken between the ground

state of the crystal and the state corresponding to the doubly excited vibrational level. In this case the non-vanishing matrix element is that of the term

$$\frac{1}{\alpha} \left(\frac{\partial^2 \alpha \rho \sigma}{\partial Q_\mu \partial Q_\nu} \right)_0 Q_\mu Q_\nu$$

in the expansion of the electronic polarizability in normal coordinates. Thus, the intensity of the second-order lines is proportional to the quantity

$$\left(\frac{\partial^2 \alpha \rho \sigma}{\partial Q_\mu \partial Q_\nu} \right)_0.$$

We note that it is possible also to calculate the intensity of the second-order RS by starting from the electronic wave functions corresponding to the equilibrium configuration of the nuclei; the motion of the nuclei is taken into account here as an additional small perturbation. In this method, the nonzero scattering probability appears only in fourth order of perturbation theory. Owing to the complexity of the final formulas, the completion of such a program appears to be little likely, but an important qualitative result of such an approach is the fact that the value of the RS cross section is determined by the constants of the electron-phonon and electron-photons interactions.

In a concrete calculation of the second-order RS cross section, the following difficulties arise: 1) the fourth-order anharmonicity constants are unknown, 2) the density of the two-phonon states of the crystal, which enters in the final perturbation-theory formula, is unknown (the probability of the scattering process is proportional to the density of the final states, i.e., to the number of states per unit energy interval).

The density function of the single-phonon states of the crystal can be determined from the secular equation (2.26) if one knows the elastic constants characterizing the interaction of the atoms (ions) of the crystal lattice with one another. In the general case this function is given by

$$g(\omega) = \frac{2\omega v_0}{3n} \int_{S(\omega^2)} \frac{dS}{|\text{grad}_{\mathbf{k}} \omega^2(\mathbf{k})|}, \quad (6.7)$$

where v_0 is the volume of the unit cell, n the number of atoms per unit cell, and $S(\omega^2)$ is the surface in the Brillouin zone for which $\omega^2(\mathbf{k}) = \omega^2$.

The final expression for the function $g(\omega)$ can be obtained only under a number of simplifying assumptions and only for the simplest crystal lattices. (It was calculated directly for a one-dimensional lattice in Sec. 2.1.) In [150, 151], calculations of this type were performed for cubic lattices of the NaCl and of the diamond type with account taken of only the nearest-neighbor interaction. As a result of the calculations, it was found that the dependence of the state density on the frequency (the function $g(\omega)$) is sufficiently smooth, although it does have several maxima. Thus, the second-order Raman-scattering spectrum should be quasicontinuous.

It was learned recently that the density function of the single-phonon states of a crystal always has a number of characteristic points, called critical. A critical point is a point in \mathbf{k} -space such that each component $\text{grad}_{\mathbf{k}} \omega(\mathbf{k})$ is either equal to zero or reverses sign. According to (6.7), the density of states becomes infinite at this point. This property of critical points was first pointed out in [152]. Subsequently, Loudon and Johnson [153] established that the singularities of the single-phonon state-density function coincide with the singularities of the two-phonon

state-density function $\mathbf{k} = 0$, the latter being needed for the calculation of the probability of second-order Raman scattering. Knowing the critical points we can thus determine the contributions of various sections of the Brillouin zone to the scattering process, without calculating in detail the entire state-density function. Methods of finding the critical points were developed in [152, 154]. Thus, for crystals of the ZnS type (cubic modification) and of the diamond type, the critical points are the points Γ , L, W, X (see Fig. 5c). Thus, owing to the presence of critical points, sharp intensity maxima should occur in the second-order RS spectra. The contribution of the remaining points of the Brillouin zone constitutes only a continuous weak background of scattered light.

The experimental data on the second-order spectra have heretofore been interpreted from two points of view: starting from the crystal-lattice dynamics developed by Born, and from the point of view of the Raman theory. The most investigated were the second-order spectra of alkali-halide salts. [9, 155-158] An example of second-order spectra is given below in Fig. 15. The presence of sharp maxima in second-order spectra is interpreted in [156] from the point of view of Raman's theory as the result of the appearance of additional degrees of freedom of the Raman supercell. At the same time, it is noted in [155, 157, 158] that the second-order spectrum has a quasi-continuous character, and the experimentally obtained spectra agree satisfactorily in the form with the state-density function obtained by Born, although the number of sharp maxima observed experimentally is larger than would follow from the theory.

The method of analyzing the critical points is more fruitful than theoretical calculations based on simplified crystal-lattice models, and eliminates the seeming disparity between the crystal-lattice dynamics developed by Born and experiment. We note that allowance for the critical points makes it also possible to explain the presence of sharp additional lines of "zero" intensity, which appear in the RS spectra of a number of crystals (for example, calcite [75, 77]). These lines are the result of single-phonon scattering and are due apparently to violation of the quasimomentum conservation law, owing to violation of translational invariance of the crystal lattice in the presence of impurities or defects (see Sec. 4.2). The scattering probability turns out to be largest for critical points, and therefore the observed spectrum consists of sharp lines. On the other hand, it turns out that the additional degrees of freedom of the Raman supercell can coincide with the normal crystal-lattice oscillations corresponding to the critical point of the Brillouin zone.

Let us consider from this point of view the normal oscillations of ZnS and diamond crystals, corresponding to the points Γ , L, and X. At the point Γ ($\mathbf{k} = 0$), the atoms (ions) of the neighboring cells move in phase, thus satisfying the Raman requirement. Corresponding to this point are six normal oscillations (two atoms per unit cell). At the point L,

$$\mathbf{k}_0 = \frac{1}{2} (b_1 + b_2 + b_3) = \left\{ \frac{\pi}{2\tau}, \frac{\pi}{2\tau}, \frac{\pi}{2\tau} \right\}.$$

Accordingly

$$\mathbf{k}_0 \mathbf{a}_1 = \pi, \quad \mathbf{k}_0 \mathbf{a}_2 = \pi, \quad \mathbf{k}_0 \mathbf{a}_3 = \pi.$$

since

$$\mathbf{a}_1 = \{0, \tau, \tau\}, \quad \mathbf{a}_2 = \{\tau, 0, \tau\}, \quad \mathbf{a}_3 = \{\tau, \tau, 0\}.$$

Thus, the oscillations of atoms of neighboring cells are in phase opposition, and consequently also satisfy the Raman condition ($\alpha = \beta = \gamma = -1$). Since the star $\{\mathbf{k}_9\}$ consists of four vectors, the Brillouin-zone points corresponding to these vectors cause additional normal oscillations of the Raman type. The total number of such oscillations, corresponding to the star $\{\mathbf{k}_9\}$, is obviously 24. The oscillations corresponding to the point X also satisfy the Raman criterion:

$$\mathbf{k}_{10a_1} = \pi, \quad \mathbf{k}_{10a_2} = \pi, \quad \mathbf{k}_{10a_3} = 0, \quad \mathbf{k}_{10} = \frac{1}{2}(\mathbf{b}_1 + \mathbf{b}_2);$$

since in this case the number of vectors of the star is equal to three, the corresponding number of Raman normal oscillations is 18. Thus, all the normal oscillations corresponding to the critical points Γ , L, and X are normal oscillations of the Raman supercell; moreover, since the total number of the degrees of freedom of the Raman supercell is in this case 48, the aforementioned normal oscillations account for all the oscillations according to Raman. It is clear that a useful fact in Raman's theory is that the postulated normal oscillations indeed turn out in this case to be among the most important ones and make the main contribution to the second-order scattering processes. Therefore the calculated frequencies of the corresponding oscillations agree with the experimental data. On the other hand, it is obvious that the normal oscillations corresponding to the critical point may also not coincide with the Raman normal oscillations. In particular, for the example indicated above, the point W ($\mathbf{k}_8 = \frac{1}{4}(\mathbf{b}_1 + \mathbf{b}_2) + \frac{1}{2}(\mathbf{b}_2 + \mathbf{b}_3)$) does not correspond to oscillations of the Raman type, even though it is a critical point. Thus, the crystal-lattice theory developed by Born, supplemented by the concept of the critical point, is apparently the most correct and in best agreement with experiment.

Let us consider now the selection rules in the second-order RS spectra. On the basis of (6.4), phonons of the entire first Brillouin zone take part in the RS processes. Let us examine the selection rules for the processes of type (6.1).^{*} For the overtone transitions (scattering in which two identical phonons take part), the wave function of the final state is transformed in accordance with the representation $[\tau^2]$, which is a symmetrical square of the physically irreducible representation τ , in accordance with which the considered normal oscillation of the crystal lattice is classified. On the basis of the general rules (see Sec. 4.2), assuming that the initial state of the crystal is the ground state and is classified in accordance with a fully-symmetrical representation, we obtain in this case the selection rule

$$[V]_{\alpha}^2 \times [\tau]^2 \supset A. \quad (6.8)$$

Correspondingly, for the remaining transitions we obtain

$$[V]_{\alpha}^2 \times \tau_1 \times \tau_2 \supset A. \quad (6.9)$$

The rules (6.8) and (6.9) can be rewritten in the form

$$[\tau]^2 \supset [V]_{\alpha}^2, \quad (6.10)$$

$$\tau_1 \times \tau_2 \supset [V]_{\alpha}^2, \quad (6.11)$$

where $[V]_{\alpha}^2$ are the irreducible representations that enter

in $[V]^2$. According to ^[39], the physically irreducible representation τ is either an irreducible real representation of the group G, or else is written in the form of a direct sum of two complex-conjugate representations τ' and τ'' . In the latter case $[\tau^2]$ can be represented in the following manner (see ^[39]):

$$[\tau]^2 = [\tau']^2 + [\tau'']^2 + \tau' \tau''. \quad (6.12)$$

In this case (6.8) is equivalent to the relations

$$[\tau']^2 \supset [V]_{\alpha}^2, \quad (6.13a)$$

$$[\tau'']^2 \supset [V]_{\alpha}^2, \quad (6.13b)$$

$$[\tau' \tau''] \supset [V]_{\alpha}^2. \quad (6.13c)$$

Accordingly, the representation $\tau_1 \times \tau_2$ can be written in the form of a sum of products of irreducible representations of the group G. Therefore the selection rules reduce in both cases to a clarification of relations of the type (6.10) and (6.11), where τ , τ_1 , and τ_2 are irreducible representations of the group G.

Thus, the problem of the selection rules in second-order RS spectra can be solved only by determining the structure of the products of the irreducible representations of the entire space group. Only in the particular case when phonons with wave vector $\mathbf{k} = 0$ are excited in the scattering process can the representation τ be regarded as the representation of the point group of directions of the crystal F, and only then can the procedure employed for molecules be used.

The problem of expanding the product of representations of space group was solved in a number of papers ^[17,18,159] connected with concrete physical applications. In particular, a general procedure was developed in ^[17] for expanding products of two and three irreducible representations of the space group into irreducible ones, and selection rules were obtained in the case of crystals of group T_d^2 for Raman scattering in which two and three phonons, corresponding to the critical points of the Brillouin zone, take part. The procedure developed in ^[17] is based on the construction of the characters of the product of irreducible representations of the entire space group on the basis of the characters of the small representations. The general method developed in ^[17], however, is quite cumbersome and its use for the calculation of the selection rules in second-order RS spectra is not essential.

Let us stop in greater detail on another method, ^[19] analogous to that used in ^[39] to ascertain the feasibility of second-order phase transitions. The latter method, besides being simple to use in practice, has also the advantage that it yields final results in the form of formulas that are convenient for an investigation of a number of particular cases and for obtaining general relations.

Let us consider the method of obtaining general representations of the symmetrical square of the irreducible representation $[\tau]^2$ of group G and of the representation $[V]^2$ of a symmetrical second-rank tensor, which expands into irreducible representations $[V]_{\alpha}^2$. The star $\{\mathbf{k}\}^2$ of the representation $[\tau]^2$ consists of all the possible vectors of the type $\mathbf{k}_i + \mathbf{k}_j$ (\mathbf{k}_i and \mathbf{k}_j are the vectors of the star $\{\mathbf{k}\}$ of the representation τ). If there is no null vector among the latter vectors, then (6.10) is certainly not satisfied, since the star of the representation $[V]^2$ is $\{0\}$. Thus, to satisfy (6.10) it is necessary that among the vectors of the star $\{\mathbf{k}\}$ there be present simultaneously

^{*}The selection rules for the processes of the type (6.2) and (6.3) are derived in similar fashion.

the vectors \mathbf{k}_i and $\mathbf{k}_i' = -\mathbf{k}_i$. This requirement is an expression of the condition for quasimomentum conservation in the RS process. If the representation τ satisfies the foregoing condition, then the star $\{\mathbf{k}\}^2$ breaks up into two stars: one of them contains only the null vector, and the other all the remaining vectors. Accordingly the representation τ breaks up into two representations τ_0 and τ_1 , and only τ_0 can have common representations with $[V]_\alpha^2$, a condition necessary for the satisfaction of (6.10). Let us consider first only such representations τ , whose stars contain vectors \mathbf{k}_i that are not equivalent to $-\mathbf{k}_i$. For this case, in accordance with [39], we obtain

$$n([V]_\alpha^2) = \frac{l}{2f} \sum_{h_j \in G_{k_1}} \{ \chi^{(1)}(g) \chi^{(1)}(g_1^{-1} a g_1) \chi_{[V]_\alpha^2}(g) + \chi^{(1)}(g_{11} g g_{11}^{-1} g) \chi_{[V]_\alpha^2}(g_{11}^{-1} g) \}, \quad (6.14)$$

where $g = \{h_j | \alpha_j\}$; l is the number of vectors of the star $\{\mathbf{k}\}$; f is the number of elements of the point group of the vector $\mathbf{k}_1 \in \{\mathbf{k}\}$; $g_{11} \mathbf{k}_1 = \mathbf{k}_1, -\mathbf{k}_1, g_{11} \in G, \chi^{(1)}(g)$ are the characters of the small representation of the group G_{k_1} ; $\chi_{[V]_\alpha^2}$ is the character of the irreducible representation $[V]_\alpha^2$, which enters in the representation $[V]^2$; $n([V]_\alpha^2)$ is the number of irreducible representations $[V]_\alpha^2$ contained in the representation τ_0 . If the vectors of the star of the representation are such that each vector \mathbf{k}_i is equivalent to the vector $-\mathbf{k}_i$, then we have in accordance with [39]

$$n([V]_\alpha^2) = \frac{l}{2f} \sum_{h_j \in G_{k_1}} \{ |\chi^{(1)}(g)|^2 + \chi^{(1)}(g^2) \} \chi_{[V]_\alpha^2}(g). \quad (6.15)$$

The notation is the same as in formula (6.14).

To satisfy the relation $\tau_1 \times \tau_2 \subset [V]_\alpha^2$, where τ_1 and τ_2 are the irreducible representations of the group G , it is necessary that the star $\{\mathbf{k}\} \times \{\mathbf{k}_2\}$ of the representation $\tau_1 \times \tau_2$ contain the star $\{0\}$. This is satisfied if the stars $\{\mathbf{k}_1\}$ and $\{\mathbf{k}_2\}$ can be represented in the form

$$\left. \begin{aligned} \{\mathbf{k}_1\} &= \{\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_l\}, \\ \{\mathbf{k}_2\} &= \{-\mathbf{k}_1, -\mathbf{k}_2, \dots, -\mathbf{k}_l\}. \end{aligned} \right\} \quad (6.16)$$

If there exists an element $g \in G$ such that $g\mathbf{k}_1 = -\mathbf{k}_1$ ($\mathbf{k} \in \{\mathbf{k}_1\}$), then the stars $\{\mathbf{k}\}_1$ and $\{\mathbf{k}\}_2$ consist of the same vectors \mathbf{k} . Under this condition, the product of the representations $\tau_1 \times \tau_2$ can be expanded into a representation τ_0 with star $\{0\}$ and a representation τ_1 whose star contains all the remaining vectors. The number of irreducible representations $[V]_\alpha^2$ contained in the representation $\tau_1 \times \tau_2$ is determined from the formula

$$n([V]_\alpha^2) = \frac{l}{2f} \sum_{h_j \in G_{k_1}} \chi^{(1)}(g) \chi^{(1)'}(g) \chi_{[V]_\alpha^2}(g). \quad (6.17)$$

where $g = \{h_j | \alpha_j\} \in G, \chi^{(1)}(g)$ is the character of the small representation $\tau_{k_1}(g)$, and $\chi^{(1)'}$ (g) is the character of the small representation $\tau_{-\mathbf{k}_1}(g)$.

We note that if τ_1 and τ_2 are complex-conjugate non-real representations, then the following relation is satisfied

$$\tau_1 \times \tau_2 \supset A, \quad (6.18)$$

i.e., the product of complex-conjugate representations always contains the unit representation.

Using relations (6.14) and (6.15) we can easily determine the selection rules for the overtone transitions, and obtain with the aid of (6.17) the selection rules for the component transitions. In the particular case when the

vectors of the star $\{\mathbf{k}\}$ are arranged in arbitrary manner inside the Brillouin zone, the only element of the point group F with the aid of which the vector \mathbf{k} can be transformed into the vector $-\mathbf{k}$ is inversion. Using the general formulas (6.14) and (6.17), we obtain in both cases

$${}^{(n)}[V]_\alpha^2 = \chi_{[V]_\alpha^2}(e) \neq 0,$$

i.e., the Raman scattering is always allowed for the overtone and component transitions of the indicated symmetry in the case of crystals having an inversion center. This result agrees with the analogous conclusion of [18], which was obtained by directly constructing the characters of the irreducible representations of the entire space group. We note also that in accordance with formula (6.18), the overtone transition for the reducible representation τ , which consists of two complex-conjugate irreducible representations, is always allowed as a result of the scalar component of the polarizability tensor.

By way of an example, let us consider the selection rules in the second-order RS spectra for the group C_{2h}^5 . Each element of this group represents a product of the translation $\{e | \mathbf{a}\}$ ($\mathbf{a} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3, n_1, n_2, n_3 = 0, \pm 1, \dots$) by one of the elements of the type

$$\{e | 0\}, \{c_2 | \mathbf{a}_1\}, \{i | \mathbf{a}_2\}, \{\sigma_h | \mathbf{a}_3\}; \quad (6.19)$$

here

$$\mathbf{a}_1 = \frac{1}{2} \mathbf{a}_3, \mathbf{a}_2 = \frac{1}{2} (\mathbf{a}_1 + \mathbf{a}_3), \mathbf{a}_3 = \frac{1}{2} \mathbf{a}_1; \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 -$$

are the vectors of the elementary translations (see [39]). The group of directions of the crystal is the point group $C_{2h} = \{e, C_2, i, \sigma_h\}$. According to [39], in the Brillouin zone of the group under consideration there are 14 characteristic points, each of which can be set in correspondence with the corresponding star of the irreducible representation of the group G . Let us consider some of these points.

a) The point $\mathbf{k}_1 = \frac{1}{2}(\mathbf{b}_1 + \mathbf{b}_2)$. The corresponding star of the irreducible representation τ consists only of one vector ($l = 1$), since all elements of the group F leave the vector \mathbf{k}_1 invariant. The point group of the vector \mathbf{k}_1 is therefore the group C_{2h} . It is also easy to verify that the relation $\mathbf{k} = -\mathbf{k}$ is satisfied (accurate to within equivalence). Thus, it is necessary to use the general formula (6.15). Using the results of [39], we find that the group C_{2h} has only one built-up two-dimensional representation $\hat{\tau}$ at the point under consideration. In Table VII are indicated the matrix elements of the representations $\hat{\tau}$ and $\tau_{\mathbf{k}}$, and the characters of the representation $\tau_{\mathbf{k}}$, which are needed for the calculation in accordance with formula (6.15). From the reality criteria we ascertain

Table VII

| $\hat{G} = C_{2h}$ | e | c_2 | i | σ_h |
|---------------------|--|---|---|--|
| $\hat{\tau}$ | $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ | $\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ | $\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$ | $\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ |
| $G_{\mathbf{k}}$ | $\{e 0\}$ | $\{C_2 \frac{1}{2} \mathbf{a}_3\}$ | $\{i \frac{1}{2} (\mathbf{a}_1 + \mathbf{a}_2)\}$ | $\{\sigma_h \frac{1}{2} \mathbf{a}_1\}$ |
| $\tau_{\mathbf{k}}$ | $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ | $\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ | $\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$ | $\begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix}$ |
| $\chi(g)$ | 2 | 0 | 0 | 0 |

with the aid of Table IX that the irreducible representation $\hat{\tau}$ of the space group G is real. Using (6.15) and (6.17), we obtain in this case

$$[\tau] \supset A_g, \quad \tau \times \tau \supset A_g + B_g.$$

Thus, the overtone transition is allowed as a result of the fully-symmetrical components of the polarizability tensors $\alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}$; the composite transition is allowed for all the components of this tensor.

b) The point $\mathbf{k} = \frac{1}{2}(\mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3)$. This point, like the preceding one, is on the boundary of the Brillouin zone. The symmetry point group is the group C_{2h} . The built-up representations of this group from the vector $\mathbf{k} = \frac{1}{2}(\mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3)$ are one-dimensional (Table VIII). Using the reality criterion (Table IX) we find that all the irre-

Table VIII

| $G = C_{2h}$ | e | C_2 | i | σ_h |
|--|-------------|-----------------------------|-----------------------------------|----------------------------------|
| $\hat{\tau}^{(1)}$ | 1 | 1 | 1 | -1 |
| $\hat{\tau}^{(2)}$ | 1 | 1 | -1 | 1 |
| $\hat{\tau}^{(3)}$ | 1 | -1 | 1 | 1 |
| $\hat{\tau}^{(4)}$ | 1 | -1 | -1 | -1 |
| $g \in G_k$ | | | | |
| $\mathbf{k} = \frac{1}{2}(\mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3)$ | $\{e 0\}$ | $\{C_2 \frac{1}{2} a_3\}$ | $\{i \frac{1}{2} (a_1 + a_3)\}$ | $\{\sigma_h \frac{1}{2} a_1\}$ |
| $\tau_k^{(1)}$ | 1 | i | -1 | - i |
| $\tau_k^{(2)}$ | 1 | i | 1 | i |
| $\tau_k^{(3)}$ | 1 | - i | -1 | - i |
| $\tau_k^{(4)}$ | 1 | - i | 1 | i |
| $\chi_1(g)$ | 1 | i | -1 | - i |
| $\chi_2(g)$ | 1 | i | 1 | i |
| $\chi_3(g)$ | 1 | - i | -1 | - i |
| $\chi_4(g)$ | 1 | - i | 1 | i |

Table IX

| $g \in G$ | $\{e 0\}$ | $\{C_2 \frac{1}{2} a_3\}$ | $\{i \frac{1}{2} (a_1 + a_3)\}$ | $\{\sigma_h \frac{1}{2} a_1\}$ |
|--|-------------|-----------------------------|-----------------------------------|----------------------------------|
| g^2 | | | | |
| $\chi(g^2)$ | $\{e 0\}$ | $\{e a_3\}$ | $\{e 0\}$ | $\{e a_1\}$ |
| $\mathbf{k} = \frac{1}{2}(\mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3)$ | 2 | 2 | 2 | -2 |
| $\chi_1(g^2), \chi_2(g^2), \chi_3(g^2), \chi_4(g^2)$ | 1 | -1 | 1 | -1 |

ducible representations $\tau_1, \tau_2, \tau_3,$ and τ_4 of the space group, which correspond to $\hat{\tau}^{(1)}, \hat{\tau}^{(2)}, \hat{\tau}^{(3)},$ and $\hat{\tau}^{(4)}$ are nonequivalent to their complex conjugates. Combining the complex-conjugate representations, we obtain the physically irreducible representations $\tau_I = \tau_1 + \tau_3$ and $\tau_{II} = \tau_2 + \tau_4$. On the basis of formula (6.18) we can already state that the overtone transitions are active in Raman scattering, owing to the symmetry of the polarizability tensor components. Using the general formulas (6.15) and (6.17) as well as Tables VIII-IX, we obtain

$$[\tau_I]^2 \supset A_g + B_g, \quad [\tau_{II}]^2 \supset A_g + B_g, \\ \tau_I \times \tau_I \supset A_g + B_g, \quad \tau_{II} \times \tau_{II} \supset A_g + B_g.$$

Thus, the overtone and composite transitions in the spectra of the Raman scattering are allowed for all components of the polarizability tensor.

Knowledge of the critical points and of the selection

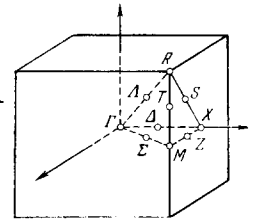


FIG. 14. Brillouin zone with characteristic points for crystals of the CsBr type.

rules in the RS spectrum, and also data of infrared absorption, neutron scattering, and calculations of the type of the dispersion curves, make it possible, generally speaking, to assign the observed lines to the second-order spectra, although concrete implementation of such a program is frequently difficult.

Let us stop to discuss several examples of interpretation of second-order spectra.

In [158, 160] they investigated the second-order spectrum in the crystal CsBr. The symmetry group of this crystal is the space group O_h^1 . The unit cell contains two non-equivalent atoms. The Brillouin zone for the group under consideration is shown in Fig. 14. The vibrational levels are classified in this investigation with the aid of the compatibility relations for the irreducible representations of the group G_k . In accordance with their polarizations, the oscillations are separated into transverse and longitudinal. According to the selection rules, the second-order RS spectrum of this crystal is allowed both for the overtones and for the composite tones at the points $\Gamma, \Delta, T, X, A, R, \Sigma, S, Z, M$. From the calculation of the dispersion curves given in [160], it follows that the points $\Gamma, M, X, A, R, S, \Sigma,$ and T are critical. As a result of the satisfaction of the selection rules and of the presence of a large number of critical points, a rather large number of sharp maxima are observed in the spectrum (Fig. 15). Using the calculated values of the frequencies, the authors of [160] attempt to interpret all the observable lines (Table X). A feature of the discussed spectrum is the fact that many combinations of phonon pairs contribute to the same intensity maximum, thus making their unique assignment difficult.

The second-order RS spectrum of the crystal GaP was investigated in [161]. The lattice of this crystal is exactly the same as of the cubic modification of ZnS (see Fig. 5). The points $\Gamma, L, X,$ and W are critical points of the

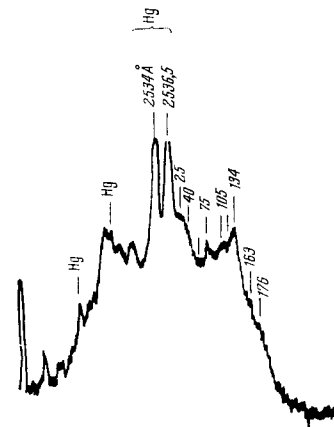


FIG. 15. Second-order RS spectrum of the CsBr crystal [160].

Table X. Second order RS spectrum in the CsBr crystal

| Experiment 158, $\Delta\nu$, cm ⁻¹ | Calculation Av, cm ⁻¹ | Assignment |
|--|----------------------------------|--|
| 25 | 24 | LA(M) - TA ₂ (M), LO(T) - LA(T) |
| | | LO(S) - LA(S), TO ₁ (Z) - TA ₁ (Z) |
| 40 | 41 | LO(Γ) - TO(Γ), LO(X) - TO(X), LO(T) - LA(T) |
| | | LO(S) - TA ₂ (S), LO(Z) - TA ₁ (Z) |
| 54 | 52 | LO(M) - TA ₂ (M), LO(X) - TA(X), LO(S) - TA ₁ (S) |
| | | LO(Z) - TA ₂ (Z) |
| 75 | 83 | LA(M) + TA ₂ (M), 2LA(T), TA(S) + TA ₂ (S) |
| 105 | 105 | 2TO ₂ (M), TO ₁ (T) + LA ₁ (T), TO ₂ (S) + TA ₁ (S) |
| | | LA(Z) + TA ₁ (Z) |
| 125 | 125 | LO(X) + TA(X), LO(T) + LA(T), TO ₁ (S) + LA(S) |
| | | TO ₁ (S) + LA(S), TO ₁ (Z) + TA ₁ (Z) |
| 134 | 134 | TO(X) + LA(X), LO(M) + TO ₂ (M) |
| 134 | 135 | LO(M) + LA(M) |
| 134 | 133 | LO(R) + LA(R), LO(T) + TO(T) |
| | | TO ₁ (S) + TA ₁ (S), LO(Z) + TA ₁ (Z) |
| | | 2LA(Z), 2LO(T), LO(S) + TO ₁ (S), 2TO ₁ (Z) |
| 163 | 163 | 2LO(M), 2LO(T), LO(S) + TO ₁ (S), LO(Z) + TO ₁ (Z) |
| 176 | 182 | 2LO(X), 2LO(S), 2LO(Z) |

LO, LA - longitudinal optical and acoustical branches, TO, TO₁, TO₂, TA₁, TA₂, TA - transverse optical and acoustic branches.

Table XI. RS spectrum of GaP crystal

| Frequency cm ⁻¹ | Assignment | Frequency cm ⁻¹ | Assignment |
|----------------------------|---|----------------------------|---|
| 804 | Maximum of two-phonon density of states | 548 | Maximum of TA + TO combinations |
| 802 | 2 × TO(W) | 546 | TO ₁ (W) + TA ₁ (W) |
| 786 | 2 × TO(X) | 533 | TO ₂ (W) + TA ₂ (W) |
| 770 | 2 × TO(W) | 570 | 2 × LA(X) |
| 756 | 2 × TO(L) | 495 | TO(X) + TA(X) |
| 745 | TO(X) + LO(X) | 471 | 2 + LA(L) |
| 740 | TO(L) + LO(L) | 460 | LO(X) + TA(X) |
| 721 | 2 × LO(L) | 450 | TO(L) + TA(L) |
| 705 | 2 × LO(X) | 402 | } First-order lines |
| 687 | 2 × LO(W) | 366 | |
| 650 | } LA + TO | 309 | TA(L) + LA(L) |
| 618 | | 289 | Maximum of 2 × TA combinations |
| 613 | | 285 | 2 × TA(W) |
| 607 | | 209 | 2 × TA(X) |
| 582 | | 151 | 2 × TA(L) |
| 567 | } LA + LO | | |
| | | | |

LO, LA - longitudinal optical and acoustic branches; TO, TA, TA₁, TA₂ - transverse optical and acoustic branches.

Brillouin zone. According to [159], all the overtone and composite transitions are allowed in RS at each of these points. Figure 16 shows the spectrum of this crystal at 20°K. According to calculations of the dispersion curves of the GaAs crystal, it turns out that the longitudinal optical branch (LO) and the transverse optical branch (TO) intersect, so that LO > TO at the beginning of the Brillouin zone, and TO > LO and almost reaches the optical branch on the edge of the Brillouin zone. It is assumed in [161] that the dispersion curves of the vibrational branches for GaP have approximately the same form. Under this condition, it is possible to explain in the following manner the observed RS spectrum of this crystal (see Fig. 16). The observed spectrum can be subdivided into three regions. The interval 670-800 cm⁻¹ corresponds to summary transitions of pairs of optical phonons, the second region extends from 293 to 613 cm⁻¹; the corresponding lines are the results of the summary combinations of pairs of optical and acoustic phonons; in the 289-150 cm⁻¹ interval, apparently, there appear phonons of the transverse acoustic branch. The difference processes do not lead to the appearance of Raman scattering, owing to the sufficiently low temperature of the crystal. Lines with frequencies 366 and 422 cm⁻¹ result from first-order RS scattering on transverse and longitudinal long-wave optical oscillations. The intensity peak at 289 cm⁻¹ probably corresponds to the summary

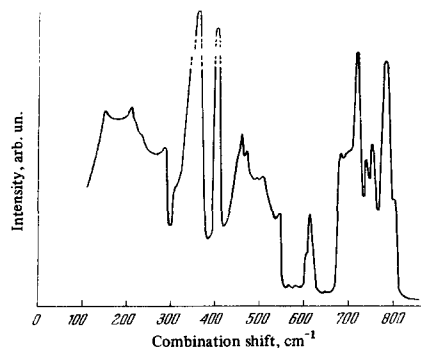


FIG. 16. Second order RS spectrum of the crystal GaP at 20°K [159].

process of phonon pairs of the edge of the transverse acoustic branch. The intensity peak at 804 cm⁻¹ corresponds to an overtone transition on a longitudinal long-wave optical oscillation. The presence of several maxima in the region of 786 cm⁻¹ is evidence that the transverse optical branch is strongly shifted when the edge of the Brillouin zone is reached. In Table XI are indicated the possible assignments of the remaining observed lines. Thus, the study of the second-order RS spectra can yield useful information on the dispersion curves of the vibrational branches of crystals.

* * *

Recently, new interesting results on RS of light in crystals were obtained. These include [162] in which RS was first observed in the metal Be and in the alloy AuAl₂, data on light scattering near the phase transition point in SrTiO₃, [163] which confirm the general theory of light scattering near a second order phase transition point, [112] new work on RS in quartz, [164] in which the authors propose that the oscillation responsible for the phase transition in this crystal is the result of resonant interaction of lines of first and second order, and also a detailed theory of RS of light in crystals. [165]

¹C. H. Henry and T. T. Hopfield, Phys. Rev. Lett. 15, 964 (1965).

²P. A. Fleury, S. P. S. Porto, L. E. Gheesman, and H. T. Guggenheim, Phys. Rev. Lett. 17, 84 (1966).

³P. A. Fleury, S. P. S. Porto, and R. Loudon, Phys. Rev. Lett. 18, 658 (1967).

⁴A. Mooradian and G. B. Wright, Phys. Rev. Lett. 16, 999 (1966).

⁵B. Tell and R. Martin, Phys. Rev. 167, 381 (1968).

⁶A. C. Menzies, Rept. Progr. Phys. 16, 83 (1953).

⁷S. Bhagavantam and S. Venkatarayudu, Proc. Ind. Acad. Sci. A9, 224 (1939).

⁸J. P. Mathieu, Phys. Soc. Year Book, vol. 23, 1956; Proc. of the Conf. on Optics and Spectroscopy at all Wavelengths, 1962, p. 476.

⁹E. F. Gross, P. P. Pavinskiĭ, and A. I. Stekhanov,

Usp. Fiz. Nauk 43, 536 (1951).

¹⁰P. E. Danil'tseva, V. A. Zubov, M. M. Sushchinskiĭ, and I. K. Shuvalov, Zh. Eksp. Teor. Fiz. 44, 2193 (1963), [Sov. Phys.-JETP 17, 1473 (1963)].

¹¹P. E. Danil'tseva, V. A. Zubov, M. M. Sushchinskiĭ, and I. K. Shuvalov, Tr. Komissii po spektroskopii AN SSSR (VINITI) (Proceedings of Commission on Spectroscopy, USSR Academy of Sciences) (VINITI) 1, 696 (1965).

¹²A. S. L'vova, V. A. Zubov, M. M. Sushchinskiĭ, and V. A. Chirkov, Opt. Spektrosk. 23, 168 (1967).

¹³I. Brandmuller, H. Hacker, and Schrotter, Chem. Ber. 22, 765 (1966).

¹⁴I. P. Russel, J. Phys. 26, 620 (1965).

¹⁵R. C. C. Leite and S. P. S. Porto, Phys. Rev. Lett. 17, 10 (1966).

¹⁶S. P. S. Porto, B. Tell, and T. C. Damen, Phys. Rev. Lett. 16, 450 (1966).

¹⁷I. L. Birman, Phys. Rev. 127, 1033 (1962); 131, 1489 (1963).

¹⁸R. Loudon, Phys. Rev. 137, 1784 (1965).

¹⁹V. S. Gorelik, Kristallografiya 13, 696 (1968) [Sov. Phys.-Crystallogr. 13, 591 (1969)].

²⁰H. Poulet, J. Phys. 26, 684 (1965).

²¹V. S. Gorelik, Kristallografiya 13, 841 (1968) [sic!].

²²M. Born and T. Karman, Phys. Z. 13, 297 (1912).

²³M. Born and M. Goepfert-Mayer, Solid State Theory (Russ. transl.) Gostekhizdat, 1938.

²⁴M. Born and K. Huang, Dynamical Theory of Crystal Lattices, Oxford, 1953.

²⁵C. V. Raman, Proc. Ind. Acad. Sci. A14, 459 (1941); A18, 237 (1943); A26, 356, 359, 370, 383, 391, 396 (1947); A34, 61, 141 (1951); A44, 99 (1956).

²⁶K. C. Ramanathan, Proc. Ind. Acad. Sci. A28, 454 (1948).

²⁷R. S. Krishnan and R. S. Katiyar, J. Phys. 26, 630 (1965).

²⁸R. S. Krishnan and N. Krishnamurty, J. Phys. 26, 633 (1965).

²⁹W. Cochran and R. A. Cowley, J. Phys. and Chem. Solids 23, 447 (1962).

³⁰L. Merten, Zs. Naturforsch. A15, 47 (1960).

³¹R. Loudon, Proc. Phys. Soc. (Lond.) 82, 393 (1963).

³²H. Poulet, Ann. de phys. (Paris) 10, 908 (1955).

³³A. I. Ansel'm and N. N. Porfir'eva, Zh. Eksp. Teor. Fiz. 19, 439 (1949).

³⁴N. N. Porfir'eva, Ibid. 19, 692 (1949) and 22, 590 (1952).

³⁵A. M. Raskin, A. V. Sechkarev, and F. I. Skripov, Dokl. Akad. Nauk SSSR, 66, 837 (1949); F. I. Skripov, ibid. 66, 1075 (1949).

³⁶N. V. Belov, Strukturnaya kristallografiya (Structural Crystallography), AN SSSR (1960).

³⁷L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Ch. XIII, Nauka, 1964 [English translation, Addison-Wesley].

³⁸C. F. Koster, Solid State Phys. 5, 230 (1957).

³⁹G. Ya. Lyubarskii, Teoriya grupp i ee primeneniya v fizike (Group Theory and Its Applications in Physics), Fizmatgiz, 1958.

⁴⁰O. V. Kovalev, Neprivodimye predstavleniya prostranstvennykh grupp (Irreducible Representations of Space Groups), Kiev, AN UkrSSR, 1961.

⁴¹D. K. Faddeev, Tablitsy osnovnykh unitarnykh predstavleniy fedorovskikh grupp (Tables of Fundamental

Units or Representations of Fedorov Groups), AN SSSR, 1961.

⁴²I. S. Lomont, Application of Finite Groups, New York, 1959.

⁴³S. Bhagavantam and T. Venkatarayudu, Theory of Groups and Its Application to Physical Problems, Andhra Univ., Waltair, 1951.

⁴⁴S. Bhagavantam, Proc. Ind. Acad. Sci. A37, 350 (1953).

⁴⁵M. Hamermesh, Group Theory and Its Application to Physical Problems, Addison-Wesley, 1964.

⁴⁶K. G. Ramanathan, Proc. Ind. Acad. Sci. A28, 454 (1948).

⁴⁷R. S. Krishnan and R. S. Katiyar, J. Phys. 26, 630 (1965).

⁴⁸R. S. Krishnan and N. Krishnamurte, J. Phys. 26, 600 (1965).

⁴⁹A. S. Davydov, Teoriya pogloshcheniya sveta v molekulyarnykh kristallakh (Theory of Absorption of Light in Molecular Crystals), Kiev, AN UkrSSR, 1951, Usp. Fiz. Nauk 82, 393 (1964) [Sov. Phys.-Usp. 7, 145 (1964)].

⁵⁰I. E. Tamm, Z. Physik 60, 345 (1930).

⁵¹L. N. Ovander, Usp. Fiz. Nauk 86, 3 (1965) [Sov. Fiz.-Usp. 8, 337 (1965)] Fiz. Tverd. Tela 3, 2394 and 5, 89 (1963) [Sov. Phys.-Solid State 3, 1737 (1962) and 5, 656 (1963)].

⁵²I. L. Birman and A. E. Ganguly, Phys. Rev. Lett. 17, 647 (1966).

⁵³V. L. Strizhevskii, Fiz. Tverd. Tela 3, 2932 (1961) [Sov. Phys.-Solid State 3, 2141 (1962)].

⁵⁴O. Theimer and A. C. Saxman, J. Phys. 26, 697 (1965).

⁵⁵I. I. Sobel'man, in: Issledovanie po eksperimental'noi i teoreticheskoi fizike (Research in Experimental and Theoretical Physics), AN SSSR, 1959, p. 192.

⁵⁶R. Loudon, Adv. Phys. 13, 423 (1964).

⁵⁷R. Loudon, J. Phys. 26, 677 (1965).

⁵⁸V. S. Ryazanov and M. N. Sushchinskiĭ, Opt. Spektrosk. 23, 580 (1964).

⁵⁹V. S. Ryazanov and M. F. Sushchinskiĭ, Zh. Eksp. Teor. Fiz. 54, 1099 (1968) [Sov. Phys.-JETP 27, 589 (1968)].

⁶⁰V. S. Ryazanov, V. S. Gorelik, T. V. Peregudov, V. A. Chirkov, and M. M. Sushchinskiĭ, Fiz. Tverd. Tela 10, 1909 (1968) [Sov. Phys.-Solid State 10, 1508 (1969)].

⁶¹L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics), Fizmatgiz, 1963, p. 422 [English translation, Addison-Wesley].

⁶²B. D. Saksena, Proc. Ind. Acad. Sci. A11, 229 (1940), A12, 93 (1940).

⁶³N. Chandrasekharen, Zs. Phys. 175, 63 (1963).

⁶⁴I. P. Mathie, Spectres de vibration et symetrie des molecules et des cristaux, Paris, 1945.

⁶⁵C. H. Perry and D. B. Hall, Phys. Rev. Lett. 15, 700 (1965).

⁶⁶V. S. Gorelik, I. S. Zheludev, and M. M. Sushchinskiĭ, Kristallografiya 11, 604 (1966) [Soviet Phys.-Crystallogr. 11, 527 (1966)].

⁶⁷R. Loudon, Proc. Phys. Soc. 84, 379 (1964).

⁶⁸P. S. Narayanan and K. Vedam, Zs. Phys. 168, 158 (1951).

⁶⁹R. S. Krishnan, Proc. Ind. Acad. Sci. A22, 182 (1945).

- ⁷⁰ N. Krishnamurty, Proc. Ind. Acad. Sci. A46, 183 (1957).
- ⁷¹ P. A. Fleury and G. M. Worlock, Phys. Rev. Lett. 18, 665 (1967).
- ⁷² I. Cabannes, Compt. Rend. 188, 1041 (1929).
- ⁷³ H. Nisi, Proc. Imp. Acad. Tokyo 5, 127 (1928).
- ⁷⁴ F. Rasetti, Nature 127, 626 (1931); Nuovo Cimento 9, 72 (1932).
- ⁷⁵ A. I. Stekhanov, Opt. Spekt. 3, 143 (1957).
- ⁷⁶ N. Chandrasekharen, Proc. Ind. Acad. Sci. A128, 409 (1948).
- ⁷⁷ D. Krishnamurty, Proc. Ind. Acad. Sci. A46, 183 (1957).
- ⁷⁸ G. S. Landsberg, Izbr. trudy (Selected Works), AN SSSR, 1958, p. 101.
- ⁷⁹ D. Krishnamurty, Proc. Ind. Acad. Sci. A47, 276 (1958).
- ⁸⁰ V. G. Zubov and L. P. Osipova, Kristallografiya 6, 418 (1961) [Sov. Phys.-Crystallogr. 6, 330 (1961)].
- ⁸¹ D. F. Kiselev and L. P. Osipova, ibid. 11, 279, 401 (1966) [11, 255, 000 (1966)].
- ⁸² D. F. Kiselev, ibid 11, 886 (1966) [11, 752 (1967)].
- ⁸³ Yu. M. Naberezhnykh, Opt. Spektrosk. 13, 483 (1962).
- ⁸⁴ I. Brandmuller and T. Moser, Introduction to the Spectroscopy of Raman Scattering of Light (Russ. transl.), Mir, 1964.
- ⁸⁵ E. Burstein, Lattice Dynamics, in: Proc. Intern. Conference on Lattice Symmetry, 1963, p. 315.
- ⁸⁶ E. F. Gross and M. F. Vuks, Nature 135, 100, 431 (1935); J. phys. radium 7, 113 (1936).
- ⁸⁷ E. F. Gross and E. Komarov, Acta Physicochimica URSS 6, 637 (1937).
- ⁸⁸ E. F. Gross and A. I. Raskin, Dokl. Akad. Nauk SSSR 24, 105 (1939); A. I. Raskin, Izv. AN SSSR ser. fiz. 11, (1947).
- ⁸⁹ E. F. Gross and A. V. Korshunov, Izv. AN SSSR ser. fiz. 4, 32 (1940).
- ⁹⁰ E. F. Gross and Korshunov, Zh. Eksp. Teor. Fiz. 20, 292 (1950) and 22, 579 (1952).
- ⁹¹ M. F. Vuks, ibid. 7, 270 (1937) and 16, 410 (1946).
- ⁹² A. V. Korshunov and V. E. Volkov, Fizich. probl. spektroskopii (Physical Problems of Spectroscopy), Vol. 1, AN SSSR, 1962, p. 398.
- ⁹³ N. N. Perfir'eva, Zh. Eksp. Teor. Fiz. 33, 47 (1957) [Sov. Phys.-JETP 6, 35 (1958)].
- ⁹⁴ S. Bhagavantam, Proc. Ind. Acad. Sci. 13A, 543 (1941).
- ⁹⁵ F. I. Skripov, Candidate's Dissertation, Leningrad, 1962.
- ⁹⁶ A. A. Rakhimov, Candidate's Dissertation, Moscow, Physics Institute of the Academy of Sciences, 1966.
- ⁹⁷ M. S. Shur, Fiz. Tverd. Tela 8, 57, 1291, 2504 (1966) [Sov. Phys.-Solid State 8, 43, 1034 (1966) and 2007 (1967)].
- ⁹⁸ A. Frühling, Recherches sur le spectre Raman de quelques monocristaux aromatiques, Theses a la faculté des Sciences de Université de Paris, Serie A, Nr. 2308, 1950.
- ⁹⁹ P. A. Bazhulin and A. A. Rakhimov, Fiz. Tverd. Tela 7, 94 (1965) [Sov. Phys.-Solid State 7, 69 (1965)].
- ¹⁰⁰ A. V. Korshunov, Proceedings Siberian Forestry Institute 18, 27 (1958).
- ¹⁰¹ A. V. Korshunov and A. F. Bondarev, Opt. Spekt. 15, 182 (1963).
- ¹⁰² A. V. Korshunov, A. F. Bondarev, and E. K. Tustanovskaya, Spektroskopiya Metody in primeneniya (Spectroscopy, Methods and Applications), Nauka, 1964.
- ¹⁰³ P. A. Bazhulin, A. V. Rakov, and A. A. Rakhimov, Opt. Spekt. 16, 1027 (1964). P. A. Bazhulin, A. A. Rakhimov, and L. A. Shelepin, Fiz. Tverd. Tela 7, 2088 (1965) [Sov. Phys.-Solid State 7, 1681 (1966)].
- ¹⁰⁴ A. F. Bondarev, Izv. Sibirskogo otd. AN SSSR, ser. khim. (Bulletin, Siberian Division USSR Academy of Sciences, Chemistry Series 7, 74, 196 (1963).
- ¹⁰⁵ A. V. Rakov, Trudy FIAN 27, 111 (1964).
- ¹⁰⁶ E. I. Ivanov and K. A. Volkov, Opt. Spektrosk. 19, 897 (1965).
- ¹⁰⁷ D. A. Dows, Physics and Chemistry of Organic Solid State 1, 658 (1963).
- ¹⁰⁸ O. V. Fialkovskaya, Opt. Spektrosk. 17, 397 (1964).
- ¹⁰⁹ T. N. Zhishin, Candidate's Dissertation, FIAN, 1965.
- ¹¹⁰ M. Ito, Spectrochim. Acta 21, 2063 (1965).
- ¹¹¹ G. S. Landsberg and L. I. Mandel'shtam, Z. Physik 58, 250 (1929).
- ¹¹² V. L. Ginzburg, Dokl. Akad. Nauk SSSR 105, 240 (1955); Fiz. Tverd. Tela 2, 2031 (1960) [Sov. Phys.-Solid State 2, 1824 (1961)]. Usp. Fiz. Nauk 77, 621 (1962) [Sov. Phys.-Usp. 5, 649 (1963)]; V. L. Ginzburg and A. P. Levanyuk, Zh. Eksp. Teor. Fiz. 39, 132 (1960) [Sov. Phys.-JETP 12, 138 (1961)].
- ¹¹³ P. P. Jona and G. Shirane, Ferroelectric Crystals, Pergamon, 1962.
- ¹¹⁴ W. Cochran, Adv. Phys. 9, 387 (1960); 10, 401 (1961).
- ¹¹⁵ I. M. Ballantyne, Phys. Rev. A136, 429 (1964).
- ¹¹⁶ V. I. Murzin and A. I. Demeshina, Opt. Spekt. 13, 826 (1962); Fiz. Tverd. Tela 6, 182 (1964) [Sov. Phys.-Solid State 6, 144 (1964)].
- ¹¹⁷ M. Di Domenico, S. P. S. Porto, and S. U. Wemple, Phys. Rev. Lett. 19, 855 (1967).
- ¹¹⁸ S. M. Shapiro, D. C. O'Shea, and H. Z. Cummins, Phys. Rev. Lett. 19, 361 (1967).
- ¹¹⁹ V. G. Vaks, M. V. Galitskiĭ, and A. I. Larkin, Preprint, iAE-1141, 1966.
- ¹²⁰ P. A. Bazhulin and I. M. Aref'ev, Fiz. Tverd. Tela 7, 407 (1965) [Sov. Phys.-Solid State 7, 326 (1965)].
- ¹²¹ A. I. Arbatskaya, I. S. Zheludev, U. A. Zirnit, and M. M. Sushchinskiĭ, Kristallografiya 10, 335 (1965) [Sov. Phys.-Crystallogr. 10, 270 (1965)].
- ¹²² R. S. Krishnan and P. S. Narayanan, Crystallography and Crystal Perfection, London-New York, 1963.
- ¹²³ É. V. Chisler, Fiz. Tverd. Tela 7, 2258 (1965) [Sov. Phys.-Solid State 7, 1825 (1966)].
- ¹²⁴ V. S. Gorelik, I. V. Gavrilov, I. N. Zheludev, G. V. Peregodov, V. S. Ryazanov, and M. M. Sushchinskiĭ, ZhETF Pis. Red. 5, 214 (1967) [JETP Letters 5, 171 (1967)].
- ¹²⁵ V. S. Gorelic, G. V. Peregodov, V. S. Rjasanov, and M. M. Suschinsky, Modern Optica, New York, 1968, p. 349; M. M. Sushchinskiĭ and A. S. L'vova, Preprint FIAN, A-92, 1965.
- ¹²⁶ S. P. S. Porto, B. Tell, and T. C. Damen, Phys. Rev. Lett. 16, 11 (1955).
- ¹²⁷ L. Couture-Mathieu and J. P. Mathieu, Compt. Rend. 231, 838 (1952).
- ¹²⁸ L. Couture-Mathieu and J. P. Mathieu, J. Phys. 13, 271 (1952).

- ¹²⁹A. Well and J. P. Mathieu, *Compt. Rend.* **238**, 251 (1954).
- ¹³⁰A. Tramer, *Compt. Rend.* **249**, 2531 (1959).
- ¹³¹Y. Corre, *Compt. Rend.* **257**, 3352 (1964).
- ¹³²B. Tell, T. C. Damen, and S. P. S. Porto, *Phys. Rev.* **144**, 771 (1966).
- ¹³³L. Couture and J. P. Mathieu, *Ann. Phys.* **8**, 521 (1948).
- ¹³⁴J. P. Mathieu, *J. Chem. Phys.* **46**, 58 (1949).
- ¹³⁵H. Poulet, *Ann. Phys. (Paris)* **10**, 908 (1955).
- ¹³⁶F. G. Bass and M. I. Kaganov, *Zh. Eksp. Teor. Fiz.* **37**, 1390 (1959) [*Sov. Phys.-JETP* **10**, 986 (1960)].
- ¹³⁷Y. R. Shen and N. Bloembergen, *Phys. Rev.* **143**, 372 (1966).
- ¹³⁸V. S. L'vova, *Fiz. Tverd. Tela* **9**, 2693 (1967) [*Sov. Phys.-Solid State* **9**, 2114 (1968)].
- ¹³⁹V. M. Genkin, G. M. Genkin, and V. M. Faïn, *ibid* **10**, 66 (1968) [**10**, 47 (1968)].
- ¹⁴⁰R. E. Slusher, C. K. N. Patel, and P. A. Fleury, *Phys. Rev. Lett.* **18**, 77 (1967).
- ¹⁴¹C. K. N. Patel and R. E. Slusher, *Phys. Rev.* **167**, 413 (1968).
- ¹⁴²B. B. Varge, *Phys. Rev.* **137**, A1896 (1965).
- ¹⁴³A. A. Abrikosov and L. A. Fal'kovskii, *Zh. Eksp. Teor. Fiz.* **40**, 262 (1960) [*Sov. Phys.-JETP* **13**, 179 (1960)].
- ¹⁴⁴M. S. Khaikin and V. P. Boikov, *ibid* **3**, 119 (1965) [sic!].
- ¹⁴⁵R. T. Elliot and R. Loudon, *Physics Lett.* **3**, 189 (1963).
- ¹⁴⁶I. T. Hougen and S. Singh, *Phys. Rev. Lett.* **10**, 406 (1963).
- ¹⁴⁷I. T. Hougen and S. Singh, *Proc. Roy. Soc.* **A277**, 193 (1964).
- ¹⁴⁸D. W. Feldman, M. Ashkin, and J. H. Parker, *Phys. Rev. Lett.* **17**, 1200 (1966).
- ¹⁴⁹M. Haas and H. B. Rosenstock, *Appl. Opt.* **6**, 2079 (1967).
- ¹⁵⁰M. Born and B. Bradburn, *Proc. Roy. Soc.* **A188**, 161 (1947).
- ¹⁵¹H. M. Smith, *Phil. Trans.* **A241**, 105 (1948).
- ¹⁵²L. Van Hove, *Phys. Rev.* **89**, 1189 (1953).
- ¹⁵³R. Loudon and F. A. Johnson, *Proc. Roy. Soc.* **A281**, 274 (1964).
- ¹⁵⁴I. C. Phillips, *Phys. Rev.* **104**, 1263 (1956).
- ¹⁵⁵E. Fermi and F. Rosetti, *Zs. Phys.* **71**, 689 (1931).
- ¹⁵⁶R. S. Krishnan, *Proc. Ind. Acad. Sci.* **A18**, 298 (1943); *Proc. Roy. Soc.* **A187**, 188 (1946); *Nature* **159**, 266 (1947).
- ¹⁵⁷E. F. Gross and A. I. Stekhanov, *Izv. AN SSSR, ser. fiz.* **11**, 364 (1947).
- ¹⁵⁸H. L. Welsh, M. F. Crawford, and W. I. Staple, *Nature* **164**, 737 (1949); A. I. Stekhanov and A. P. Korol'kov, *Fiz. Tverd. Tela* **4**, 3156 (1962) [*Sov. Phys.-Solid State* **4**, 3211 (1963)].
- ¹⁵⁹M. Lax and J. J. Hopfield, *Phys. Rev.* **124**, 125 (1961).
- ¹⁶⁰S. Ganesan, E. Burstein, A. U. Karo, and I. R. Hardy, *J. Phys.* **26**, 668 (1965).
- ¹⁶¹J. P. Russel, *J. Phys.* **26**, 620 (1965).
- ¹⁶²D. W. Feldman, G. H. Parker, and M. Ashkin, *Phys. Rev. Lett.* **21**, 607 (1968).
- ¹⁶³P. A. Fleury, G. F. Scott, and G. M. Worlock, *Phys. Rev. Lett.* **21**, 16 (1968).
- ¹⁶⁴S. M. Shapiro and H. Z. Cummins, *Phys. Rev. Lett.* **21**, 1578 (1968).
- ¹⁶⁵A. K. Gaugaly and J. L. Birman, *Phys. Rev.* **162**, 806 (1967).

Translated by J. G. Adashko