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RAMAN SCATTERING OF LIGHT NEAR SECOND-ORDER PHASE-TRANSITION POINTS

V. I. GINZBURG and A. P. LEVANYUK

P. N. Lebedev Physics Institute, Academy of Sciences, U.S.S.R.

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The spectral composition of light scattered in crystals near second-order phase-transition points is studied (quartz, ferroelectrics). It is shown that the "critical opalescence" which appears in such cases when the critical Curie point is approached is closely related to the Raman scattering of light.

NEAR second-order phase-transition points there appear, as is well known, fluctuations of the parameters η_i, characteristic of the given transition (for instance, in the case of ferroelectrics the η_i are usually the components of the vector of the spontaneous electrical polarization P_i). Inasmuch as changes of these parameters lead, generally speaking, to changes of the index of refraction, an increase in the intensity of the scattered light should also be observed near transition points. In the event of the transition being near the critical Curie point, the phenomenon will have the character of a "critical opalescence" in a solid. This effect indicated in reference 1, and considered in more detail in references 2, 3, and 4, has been experimentally observed[5,6] in the $\alpha \rightleftarrows \beta$ transition in quartz ($T_c = 573°C$). However, in all the above references the problem of the fluctuation kinetics, and thereby also of the spectral constitution of the scattered light, were not investigated, although, as will be shown below, this aspect of the phenomenon is also of great interest.

The scattering at an angle θ to the incident light is due to the Fourier component $\Delta\epsilon_{\mathbf{q}}$ of the fluctuations of $\Delta\epsilon \equiv \Delta n^2$ with a wave vector $q = (4\pi/\lambda_0) \sin(\theta/2)$. The medium will be considered here for simplicity optically isotropic (cf. references 2 and 3 for a generalization to the anisotropic case); $n(\lambda_0)$ is the index of refraction, and $\lambda_0 = 2\pi c/\omega_0$ is the wavelength of the light in vacuo. If the phase transition is characterized by one parameter η, as in the case of quartz, then

$$\Delta\varepsilon = a\,(\Delta\eta^2 - \overline{\Delta\eta^2}), \quad \Delta\varepsilon_{\mathbf{q}} = a\{2\eta_0 A_{\mathbf{q}} + \sum_{\mathbf{k}} A_{\mathbf{k}} A_{\mathbf{k}-\mathbf{q}}\},$$

where $\eta = \Sigma A_{\mathbf{k}} \exp(i\mathbf{k}\cdot\mathbf{r})$, and $\eta_0(T)$ is the equilibrium value of η. As a result, with statistical averaging,

$$\overline{|\Delta\varepsilon_{\mathbf{q}}|^2} = \overline{|\Delta\varepsilon_{\mathbf{q}}|_1^2} + \overline{|\Delta\varepsilon_{\mathbf{q}}|_2^2},$$

where the main first term is proportional to $\overline{|A_{\mathbf{q}}|^2}$, and the second term is proportional to the sum $\Sigma\, \overline{|A_{\mathbf{k}}|^2}\, \overline{|A_{\mathbf{k}-\mathbf{q}}|^2}$ (cf. reference 2). Thus the spectrum of the main part of the scattering I_1 is determined by the propagation velocity and the damping of the wave $\eta_{\mathbf{q}}(\mathbf{r}) = A_{\mathbf{q}} \exp(i\mathbf{q}\cdot\mathbf{r})$. As the parameter η in quartz we can choose the displacement of the mean position of the silicon atom in α quartz compared with its position in β quartz. Since the nonequilibrium change of η corresponds to a mutual displacement of various sublattices, this displacement will vary with the frequency of the optical vibration of the crystal $\Omega_i(q)$.

At the transition point $\eta_0 = 0$, that is, there is no elastic force (see below), and the frequency of the vibration $\Omega_i(0)$ becomes zero; here $\Omega_i(0) \approx \Omega_i(q)$, since $q \ll q_{max} = \pi/d \sim 10^8$ ($d \sim 3 \times 10^{-8}$ is the lattice constant). Unfortunately we cannot uniquely state the corresponding frequency Ω_i at room temperature. In α quartz the lattice symmetry does not change for lines with frequencies $\tilde{\nu}_i = \Omega_i/2\pi c$ equal to 207, 356, 466, and 1082 cm^{-1} (reference 7); the 466-cm^{-1} line was also observed in β quartz.[8] The frequency of at least one of the remaining three lines should become zero at the transition point. It is known that the frequencies $\tilde{\nu}_i$ decrease with increasing temperature;[9] the $\tilde{\nu}_i$ = 207 cm^{-1} line is shifted and broadened particularly strongly. In addition, Landsberg and Mandel'shtam have already shown[8] that this line is lacking in β quartz. This is completely understandable, since this vibration is asymmetrical in β quartz, and is consequently inactive in first-order Raman scattering. The 356- and 1082-cm^{-1} lines should also be lacking in β quartz.

As $T \rightarrow T_c$, the line corresponding to the vibration with vanishing frequency approaches the undisplaced line and its intensity I_1 is in fact determined by the formulas given in references 1 and 2. If the frequencies of two of the aforementioned

207-, 356-, and 1082-cm^{-1} lines do not become zero, then the intensity of these lines in α quartz should tend to zero as $T \to T_c$. From the experiments of Yakovlev and Velichkina[5,6] it follows that the depolarization of the scattering in the immediate neighborhood of the transition point is considerably smaller than for $T < T_c$. This becomes understandable in the light of what has been said; for $T \approx T_c$ the basic contribution to the scattering is due to the line with $\Omega_i(0) \approx 0$, and the depolarization of this line is zero (in contrast, the depolarization of the Rayleigh scattering amounts to 12–13% at room temperature and apparently still increases with increasing temperature).

Therefore, what has actually been considered in the previous investigations[1–6] is Raman light scattering which has the character of critical opalescence at the $\alpha \rightleftarrows \beta$ transition in quartz. The scattering by the $\overline{|\Delta\epsilon_{\mathbf{q}}|_2^2}$ fluctuations, with an intensity I_2 (cf. reference 2), is the second-order Raman scattering, which has a broad spectrum not very weak only very near the transition point, but present also above it. The reason why higher-order scattering is not taken into account in reference 2 is because the relation $\Delta\epsilon = a(\Delta\eta^2 - \overline{\Delta\eta^2})$, which does not contain higher powers of $\Delta\eta^2$, is used.

There is likewise no first-order Raman scattering in ferroelectrics of the $BaTiO_3$ type above the transition point (we are referring to the vibration of Ba relative to the TiO_3 group, due to the appearance of polarization along the cube axes). The picture is therefore analogous to that in quartz. True, the difference consists in the fact that in a free $BaTiO_3$ crystal the transition to the tetragonal phase is a first-order transition near the critical Curie point. Therefore, although the frequency $\Omega_i(0)$ at the transition point is anomalously small, it is not zero. Disregarding this point[10] for simplicity, we can approximately write down the dielectric constant for frequencies near Ω_i in the form[10,11]

$$T > T_c\colon \varepsilon \approx 2\pi/(\alpha - \mu\Omega^2 + ig\Omega), \quad \Omega_i^2(0) = \alpha/\mu,$$
$$T < T_c\colon \varepsilon_z \approx 2\pi/(-2\alpha - \mu\Omega^2 + ig\Omega), \quad \Omega_i^2(0) = 2|\alpha|/\mu, \tag{1}$$

where $\alpha = \alpha'(T_c)(T_c - T)$ is the coefficient in the expansion of the thermodynamic potential in terms of the polarization

$$\Phi = \Phi_0 + \alpha P^2 + \frac{\beta}{2}P^4 + \ldots;$$

the connection of μ and g with the atomic constants is indicated in references 10 and 11. The dependence of Ω_i^2 on q was neglected. When $T < T_c$, the polarization in (1) is taken to be directed along the z axis. The value of $\epsilon_x = \epsilon_y$ differs from ϵ_z, i.e., a splitting of the characteristic frequencies takes place. The corresponding expressions for first- and second-order transitions are given in reference 10. We also note that here we do not differentiate between the adiabatic and isothermal coefficients α. These differences are, generally speaking, not large; for not too low a frequency Ω the adiabatic values appear in (1). Inasmuch as the constant electric field and the elastic stresses affect the properties of ferroelectrics in the region of a transition considerably, the same can also be said about the effect of these factors on the vanishing frequencies $\Omega_i(0)$.

When account is taken of the field equations, the transverse optical vibrations in a crystal, due to the change in the polarization, turn out to be, as is known, simply "normal" electromagnetic waves in the given medium; the index of refraction here is $n(\Omega) = \sqrt{\epsilon(\Omega)}$. Furthermore, $q^2 = (\Omega/c^2\epsilon(\Omega)$, and with sufficiently small absorption $(g \to 0)$ we obtain from (1)

$$\Omega^2 = \Omega_i^2(0) / (1 + 2\pi/\mu c^2 q^2).$$

For visible light $q \sim 10^5 [\lambda_0 \sim 5000$ A, $\theta \sim \pi/2$, $n(\lambda_0) \sim 1]$; at the same time in $BaTiO_3$ $\mu \sim 10^{-27}$ (reference 10). Therefore, the frequency of the light-scattering electromagnetic waves is, with great precision,[*] $\Omega = \Omega_i(0)$. In other words, these transverse optical vibrations in a crystal can practically be considered purely mechanical; indeed this is usually done in studying Raman scattering. For ferroelectrics that exhibit piezoelectric effects also outside the ferroelectric region (Rochelle salt, KH_2PO_4, etc), the first-order Raman scattering does not disappear even in the more symmetric phase. The intensity of such scattering was calculated by Krivoglaz and Rybak;[3] it increases on approaching the transition point from either side (at the same time the frequency Ω_i for a second-order transition also tends to zero as $T \to T_c$).

We shall now take into account the attenuation of the light-scattering waves, which leads to a broadening of the lines. The scattered light field

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[*] In taking account of the dependence of Φ on the gradient of P, i.e., of the dependence of Ω_i on q, a term δq^2 is added in the denominator of expressions (1) for ε. Therefore

$$\Omega^2 = \Omega_i^2 (1 + \delta q^2/\mu\Omega_i^2)/(1 + 2\pi/\mu c^2 q^2),$$

where $\delta \sim d^2 \sim 3 \times 10^{-16}$ (cf. reference 10). Hence $\delta q^2/\mu\Omega_i^2 = \delta q^2/\alpha \sim 3 \times 10^{-2}$ for $\alpha \sim 10^{-4}$, and we can assume, just as when the term δ is not taken into account, that $\Omega = \Omega_i(0)$.

is in a first approximation proportional to

$$\Delta\varepsilon_q e^{i\omega_0 t} = 2a\eta_0 A_q e^{i\omega_0 t}$$

(ω_0 is the frequency of the incident light) and its spectrum is determined by the Fourier components

$$G_\omega = \frac{1}{2\pi}\int_{-\infty}^{+\infty} A_{\mathbf{q}}(t)\, e^{i(\omega_0-\omega)t}\,dt = A_\Omega,$$

where

$$\Omega = \omega - \omega_0,\quad A_\Omega = \frac{1}{2\pi}\int_{-\infty}^{+\infty} A_{\mathbf{q}}(t)\, e^{-i\Omega t}\,dt.$$

Furthermore, to a first approximation we can assume

$$\ddot{A}_{\mathbf{q}} + \gamma\dot{A}_{\mathbf{q}} + \Omega_i(0)A_{\mathbf{q}} = f,$$

where $\gamma = g/\mu$ [cf. (1)], and f is the generalized random force due to thermal motion. Hence

$$A_\Omega = f_\Omega / (\Omega_i^2 - \Omega^2 + i\gamma\Omega)$$

and the scattering intensity $I(\Omega)$ is proportional to $|A_\Omega|^2$ and equal to

$$I(\Omega) = \frac{(\gamma\Omega_i^2/\pi)I_1}{(\Omega_i^2 - \Omega^2)^2 + \gamma^2\Omega^2},\quad I_1 = \int_{-\infty}^{+\infty} I(\Omega)\,d\Omega, \tag{2}$$

where I_1 has been calculated in reference 2.

If the red and violet satellites do not overlap, i.e., $\Omega_i \gg \gamma$, then for each satellite

$$I_c(\Omega) = \frac{\gamma I_1/4\pi}{(\Omega - \Omega_i)^2 + \gamma^2/4}$$

(I_1 is the total intensity of both satellites; in the classical approximation considered the intensities of these satellites are equal).

According to (2), it is obvious that

$$I(0) = \gamma I_1/\pi\Omega_i^2,\quad I(\Omega_i) = I_1/\pi\gamma.$$

Therefore, for $\Omega_i > \gamma$ but at the same time $\Omega_i \sim \gamma$, the satellites essentially overlap; when $\Omega_i < \gamma$ the function $I(\Omega)$ has a maximum only when $\Omega = 0$. It is interesting that the intensity for this maximum, $I(0) = \gamma I_1/\pi\Omega_i^2$, is strongly temperature dependent. Thus, for second-order transitions far from the critical Curie point I_1 depends weakly on T (cf. reference 2) and

$$\Omega_i^2 = -2\alpha/\mu = 2\alpha'(T_k)(T_k - T).$$

With regard to the coefficient $\gamma = g/\mu$, we note that it apparently should not have any singularities at the transition point. In ferroelectrics γ increases with increasing electric conductivity. In the absence of conductivity γ is determined by the relation of the given vibration with all the remaining vibrations, i.e., by the anharmonicity. In either case one can expect an increase of γ (more precisely of $g = \mu\gamma$) with increasing temperature. Experimentally γ can be determined, for example, by measuring the electrical losses [cf. (1)], or from the additional relaxation absorption of elastic (sound) waves in the crystal (cf. reference 6). In the latter case it is usually assumed that $\Omega_i = 0$ near T_c and the equation

$$\dot{\eta} = -\frac{1}{2g}\frac{\partial\Phi}{\partial\eta} = -\frac{1}{2g}\left(\frac{\partial^2\Phi}{\partial\eta^2}\right)_0(\eta - \eta_0) = -\frac{1}{\tau}(\eta - \eta_0),$$

is employed, from which

$$\dot{A}_{\mathbf{q}} + A_{\mathbf{q}}/\tau = 0,$$

where

$$\tau = g/\alpha = g/\alpha'(T_k)(T - T_k)\quad \text{for } T > T_k,$$
$$\tau = g/2\alpha'(T_k)(T_k - T)\quad \text{for } T < T_k.$$

The relaxation absorption of sound takes place only for $T < T_c$ when $\eta_0 \neq 0$; measuring τ and $\alpha'(T_c)$ one can obviously find g for $T \approx T_c$. From here we can then find γ, if the value $\Omega_i^2(0) = 2|\alpha|/\mu$ is known [cf. (1)].

The Raman lines which we are discussing are connected in ferroelectrics with the fluctuations of the polarization, i.e., they are also known to be active in the "infrared" absorption (in $BaTiO_3$ the frequency corresponding to the vibrations of Ba relative to the TiO_3 group becomes zero). However, when the transition is approached the frequencies Ω_i are in the difficultly accessible millimeter or submillimeter portions of the spectrum. Therefore the method of Raman scattering can here too compete with and complement the measurements on the absorption and reflection of electromagnetic waves (Raman scattering has already been observed in some ferroelectrics,[12] but not for all lines and outside the transition region).

Besides, the study of the spectrum and of the intensity of the scattered light near second-order transition points close to the critical Curie point* is also most interesting in other respects, as is clear from what has already been said in earlier papers.[1-6]

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*A related effect is, for instance, neutron scattering in ferro- and antiferroelectric substances near the Curie point (cf. references 13 and 1). We note that the existence of analogous phenomena also appears possible in macromolecules and polymer chains and structures (when the structure is changed, say the chain is lengthened, and also when the temperature is increased, some characteristic frequencies may become anomalously small; this may lead to a strong increase in the scattering intensity).

[1] V. L. Ginzburg, Dokl. Akad. Nauk SSSR **105**, 240 (1955).

[2] V. L. Ginzburg and A. P. Levanyuk, J. Phys. Chem. Solids **6**, 51 (1958), Coll. in memoriam G. S. Landsberg, Acad. of Sci. Press, 1959, p. 104.

[3] M. A. Krivoglaz and S. A. Rybak, JETP **33**, 139 (1957), Soviet Phys. JETP **6**, 107 (1958).

[4] A. P. Levanyuk, JETP **36**, 810 (1959), Soviet Phys. JETP **9**, 571 (1959).

[5] Yakovlev, Velichkina, and Mikheeva, Кристаллография (Cristallography) **1**, 123 (1956), Dokl. Akad. Nauk SSSR **107**, 675 (1956), Soviet Phys.-Doklady **1**, 215 (1956).

[6] I. A. Yakovlev and T. S. Velichkina, Usp. Fiz. Nauk **63**, 411 (1957).

[7] B. D. Saksena, Proc. Indian Acad. Sci. **A12**, 93 (1940).

[8] G. S. Landsberg and L. I. Mandel'shtam, Z. Physik **58**, 250 (1929).

[9] P. K. Narayanaswamy, Proc. Indian Acad. Sci. **A26**, 521 (1947).

[10] V. L. Ginzburg, Физ. тв. тела (Solid State), in press.

[11] V. L. Ginzburg, JETP **19**, 36 (1949), Usp. Fiz. Nauk **38**, 490 (1949).

[12] Baryshanskaya, Landsberg, and Motulevich, Izv. Akad. Nauk SSSR, Ser. Fiz. **12**, 573 (1948).

[13] L. Van Hove, Phys. Rev. **95**, 1374 (1954).

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