

THE SCATTERING OF LIGHT NEAR POINTS OF PHASE TRANSITION IN SOLIDS¹⁾

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AS is well known, the study of the scattering of light was one of G. S. Landsberg's central interests. His works were devoted to the study of the scattering in gases, in liquids, and in solids. His most important results, however, were those for crystals, and in particular for crystalline quartz. In 1927 Landsberg was the first to distinguish the molecular scattering of light in a solid from the scattering by foreign inhomogeneities, by measuring the intensity of the scattering in quartz at different temperatures. In 1928, using crystals of quartz, G. S. Landsberg and L. I. Mandel'shtam discovered combination scattering of light. It was also by the use of quartz that they obtained the first results on the fine structure of the Rayleigh scattering line (for details see the report by I. L. Fabelinskii on page 667). Finally, in 1929 a brief note by G. S. Landsberg and L. I. Mandel'shtam^[1] reported a change of intensity and shape of the lines of combination (Raman) scattering in quartz when it was heated above the point of the $\alpha \rightleftharpoons \beta$ transition.

In this phase transition, which occurs at 846°K, the "low-temperature" rhombohedral α -quartz goes over into the hexagonal "high-temperature" phase called β -quartz. In the spectrum of the combination scattering of α -quartz there are present, among other lines, lines (satellites) with frequencies $\tilde{\nu}_i = \Omega_i/2\pi c$ of 207 cm^{-1} and 466 cm^{-1} ; these lines are the ones that were studied, at temperatures up to 900°K. It was found that with increasing temperature the line $\tilde{\nu}_i = 466 \text{ cm}^{-1}$ becomes somewhat broader and more diffuse, but remains clearly marked in the β -quartz. On the other hand the line $\tilde{\nu}_i = 207 \text{ cm}^{-1}$ becomes rapidly more diffuse with increase of the temperature, and at 800°K one can detect only intensity maxima at places where at room temperature there were quite distinct satellites (red and violet). At 900°K, i.e., in β -quartz, no trace of the 207 cm^{-1} line remains.

The cited paper by Landsberg and Mandel'shtam^[1] essentially raised the question of studying the peculiarities of the scattering of light near phase transitions in solids. For many years, however, this problem received no attention, or at any rate was not solved. It may be supposed that there are two reasons for this. First, for a long time the only object accessible to study was crystalline quartz, in which the transition occurs at an extremely high temperature. Therefore there were great difficulties in the way of experimen-

tal studies. Second, so far as is known to the author of this report, up until the time of his paper in 1955^[2] no attention was given to the possibility of observing the interesting phenomenon of critical opalescence at certain phase transitions in solids. Namely, this sort of opalescence must occur near the Curie critical point, at which the line of second-order phase transitions on a pT diagram goes over into the line of first-order transitions.^[3]

It is rather strange that this fact did not attract attention much earlier. In fact, the existence of the Curie critical point for transitions in solids has been known for a comparatively long time. Attention had also been called to the appearance of an additional scattering of x-rays near a point of second-order phase transition.^[4] Even earlier it had been known that there is opalescence near other critical points—the critical point in a liquid-vapor system^[5] and the critical point for the mixing of two liquids.^[6,7] It must be pointed out, by the way, that the experimental study^[8] of the scattering of light near the $\alpha \rightleftharpoons \beta$ transition point in quartz was not undertaken through the influence of^[2], but from independent considerations.

A comparison of the experimental data^[8] with the results of calculations^[2,9] shows that there is good agreement between theory and experiment, and leaves no doubt that near the point of the $\alpha \rightleftharpoons \beta$ transition in quartz there is a sort of critical opalescence. Analogous effects must also exist in other cases, in particular for certain ferroelectric transitions.^[2,10]

In the work mentioned^[2,8-10] attention was given only to the problem of the intensity and the polarization of the scattered light. The same is true of the review article^[11]. It is also interesting to find out the spectral composition of the light scattered near phase-transition points.^[12] Furthermore, precisely this problem is closely connected with the combination scattering of light in crystals, and in particular with the work of G. S. Landsberg and L. I. Mandel'shtam^[1] to which we have already referred. Therefore we would like here to give special attention to the problem of the spectral composition of the scattered light. It is, however, desirable also to give attention to other aspects of the subject, in order to elucidate the character of the scattering of light at phase transitions in solids in a rather broad way, but without getting buried in some of the details of the calculations.

1. At an "ordinary" first-order phase transition, a transition far from the Curie critical point, a crystal undergoes a sharp change, for example from cubic to tetragonal structure. In that case the cell length c

¹⁾Report at session of the Scientific Council, Physical Institute of the Academy of Sciences of the U.S.S.R., held February 12, 1962, in memory of G. S. Landsberg.

along the fourfold axis differs considerably from the cell length a of the cubic phase, even right at the transition point (Fig. 1, a). At the point of an equilibrium first-order transition (at $T = \theta$) the thermodynamical potentials of the two phases are equal, and in a certain range of temperatures near θ both phases can exist as metastable phases (the states in question, corresponding to superheating or undercooling, are indicated by dashed lines in Fig. 1). For example, in the neighborhood of the transition from a cubic to a tetragonal crystal the indices of refraction (or, more exactly, their squares, $n^2 = \epsilon$) behave in the way shown in Fig. 1, b (all the diagrams except Figs. 7 and 9, are schematic only). In a first-order transition a latent heat of transition is evolved (or absorbed), and also there is a change of the specific volume of the crystal. For the latter reason the crystal will as a rule crack during the transition. Even if we ignore this fact, which hinders the study of a single-crystal specimen on both sides of the transition point, the study of the scattering of light at an "ordinary" first-order transition is of no particular interest. In fact, the scattering is different in the two phases, but it is about the same as in these phases at some distance from the transition point. Therefore there is no reason to try to get as close as possible to the transition point, unless of course one is interested in some such question as that of the kinetics of the phase transition.

The picture is different for second-order transitions and for first-order transitions close to the Curie critical point. The qualitative character of such transitions is clear from Figs. 2 and 3. Figure 4 provides a reminder of the behavior of the phase-transition lines in the pT diagram; the Curie critical point corresponds to the values p_c, θ_c . Physically it is rather obvious that a first-order transition sufficiently close to the Curie critical point (this means at values of p

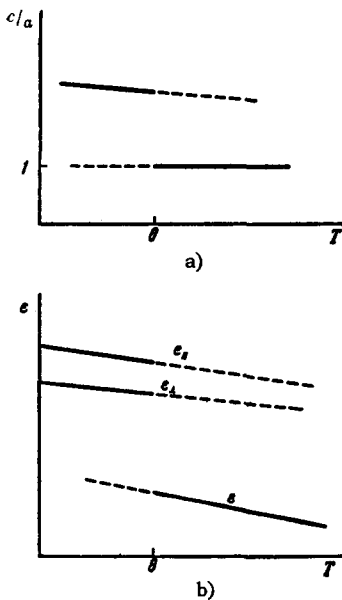


FIG. 1. First-order transition.

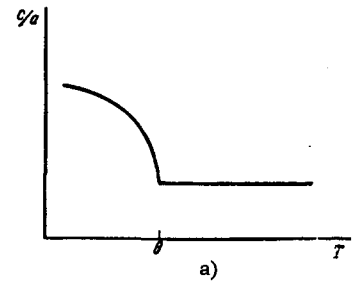


FIG. 2. Second order transition far from the Curie critical point.

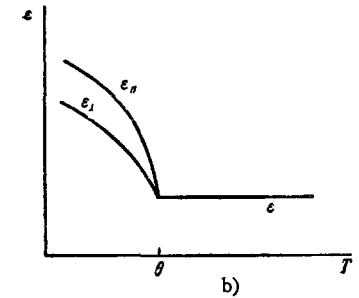


FIG. 3. Transitions near the Curie critical point.

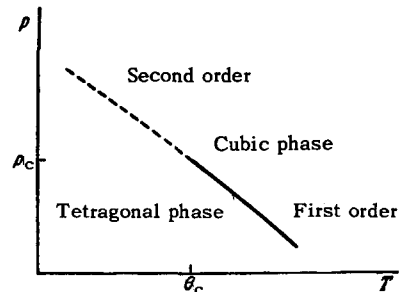


FIG. 4. Position of the Curie critical point ($p = p_c, T = \theta_c$).

and θ close to p_c, θ_c) will differ only slightly from a second-order transition which also occurs near the critical point (more exactly, the differences cancel out when considered at small distances from the transition point). Therefore for simplicity we shall hereafter discuss only second-order phase transitions,

which we divide into "ordinary" transitions far from the critical point and transitions near this point.

The problem of second-order phase transitions, which occur mainly in solids, cannot as yet be regarded as solved, even if we consider only questions of principle. There is no doubt that since the nature of superconductivity was finally cleared up in 1957 the theory of second-order phase transitions is the main unsolved problem of the physics of macroscopic systems. This problem is primarily that of determining the dependence of the thermodynamic potential of a system (for example, a crystal) on various variables—the temperature, the pressure, the degree of order, and so on. For example, in the case of the second-order phase transition mentioned above, in which a cubic crystal goes over into a tetragonal crystal, one must determine the temperature dependence of the parameter $\eta = c/a - 1$ near the transition point.

The assertion that the dependence $\eta(T)$ is unknown may arouse some surprise, since there are available many experimental studies of phase transitions, and in addition there is a certain body of theory, to which we have indeed made reference.^[3] This theory, however, is of limited applicability and can be regarded only as a certain kind of approximation. The point is that in the existing theory of second-order transitions it is assumed that the thermodynamic potential has no singularities in the neighborhood of the transition point and therefore can be expanded in a series in the parameter η :

$$\Phi(p, T, \eta) = F + \alpha\eta^2 + \frac{\beta}{2}\eta^4 + \frac{\gamma}{\sigma}\eta^6 + \delta(\text{grad } \eta)^2. \quad (1)$$

Here F , α , β , γ , and δ can depend on p and T , and the quantity η is the difference $c/a - 1$, the spontaneous polarization (in the case of a ferroelectric transition), or some other quantity characterizing the difference between one phase of the crystal ("the ordered phase") and the other ("the disordered phase") generally speaking, there are several parameters η_i , but in Eq. (1) we are confining ourselves to the case of one parameter, particularly since this is indeed the case for the $\alpha \rightleftharpoons \beta$ transition in quartz.

The situation which corresponds to a second-order transition is that the coefficient α in Eq. (1) becomes zero at a certain temperature θ , where $\alpha > 0$ for $T > \theta$, and in a small temperature range we can set

$$\alpha(T) = \alpha'_0(T - \theta), \quad \alpha'_0 = \text{const} > 0. \quad (2)$$

The potential (1) is the thermodynamic potential of a nonequilibrium state for which η has the given value [we are speaking here of a spatially homogeneous problem, for which the last term in Eq. (1) is zero]. In equilibrium $\partial\Phi/\partial\eta = 0$, $\partial^2\Phi/\partial\eta^2 > 0$, and consequently in equilibrium $\eta = \eta_0$, with the values

$$T > \theta: \quad \eta_0 = 0, \quad T < \theta: \quad \eta_0^2 = \frac{-\beta + \sqrt{\beta^2 - 2\alpha\gamma}}{\gamma}. \quad (3)$$

Far from the Curie critical point the coefficient β can be regarded as constant in the transition region and equal to β_θ ; moreover, in the transition region $\gamma \approx \gamma_\theta$. In other words, for an "ordinary" second-order transition only the coefficient α is small, and near the transition point [cf. Eqs. (2) and (3)]

$$T < \theta: \quad \eta_0^2 = -\frac{\alpha}{\beta_\theta} = \frac{\alpha'_0(\theta - T)}{\beta_\theta}. \quad (4)$$

At the Curie critical point $\beta_\theta = \beta_{\theta_C} = 0$, and near this point β_θ is small; furthermore for second-order transitions $\beta_\theta > 0$ (moreover, $\gamma_\theta > 0$).

Thus the expansion (1) leads to a quite definite temperature dependence of η_0 ; for an "ordinary" second-order transition we have simply $\eta_0^2 \sim (\theta - T)$, and there is a finite discontinuity of the specific heat.^[3] Moreover, above the transition point (for $T > \theta$) we have $\eta_0 = 0$, and there is no additional specific heat associated with the transition. Meanwhile it is known from the measurements that for a number of second-order transitions (for example, those corresponding to ordering transitions in alloys, to the λ point in liquid helium, and so on) an anomaly of the specific heat is observed also for $T > \theta$, while the jump of the specific heat is larger than the theoretical value, and evidently infinite.^[13]

The lack of agreement between the theory based on the expansion (1) and the experimental data indicates that it is not permissible to expand the potential Φ in a power series in η near the transition point; i.e., it indicates that the transition point is a singular point of the thermodynamic potential. This is also indicated by the unbounded increase of the fluctuations of the parameter η as the transition point is approached, as follows from the expression (1) itself. In fact, the fluctuations of any thermodynamic quantity (in particular, the parameter η) are determined by the value of the second derivative of the potential Φ with respect to the quantity. In a concrete case, we have for the fluctuations $\Delta\eta = \eta - \eta_0$,^[3,9]

$$\overline{(\Delta\eta)^2} = \frac{kT}{\left(\frac{\partial^2\Phi}{\partial\eta^2}\right)_{\eta_0} \Delta V}, \quad (5)$$

where the bar indicates statistical averaging, k is Boltzmann's constant, and ΔV is the volume element for which the value of $\overline{(\Delta\eta)^2}$ is determined. According to Eqs. (1) and (3)

$$\left. \begin{aligned} T > \theta: & \quad \left(\frac{\partial^2\Phi}{\partial\eta^2}\right)_{\eta_0} = 2\alpha, \\ T < \theta: & \quad \left(\frac{\partial^2\Phi}{\partial\eta^2}\right)_{\eta_0} = -4(2\alpha + \beta\eta_0^2) = 4\sqrt{\beta^2 - 2\alpha\gamma}\eta_0^2. \end{aligned} \right\} \quad (6)$$

It is clear from Eqs. (5) and (6) that at the transition point $\overline{(\Delta\eta)^2} \rightarrow \infty$, since $\alpha \rightarrow 0$. For a transition near the Curie critical point, for $T < \theta$ the increase of the fluctuations is especially large, since for $T \rightarrow \theta$ we not only have $\alpha \rightarrow 0$, $\eta_0 \rightarrow 0$, but also the parameter

β_θ is small, and is equal to zero right at the Curie critical point (for $\theta = \theta_c$).

The increase of the fluctuations of the parameter η corresponds as it were to a "smearing out" of the regular picture of the transition which follows from Eq. (1). Therefore the results (3) and (4) are incorrect in a certain region, which contains the transition point itself. It is also not possible at present to determine the dependence $\eta_0(T)$ in this neighborhood from the experimental data, both because of technical difficulties and for reasons of a more general nature: from experimental data relating to macroscopic bodies it is in general very difficult to find limiting forms of laws, for example the value of the derivative $d\eta_0/dT$ for $T \rightarrow \theta$. It may be supposed that only the creation of a consistent theory of second-order transitions will bring clarity into questions of the nature of the singularity of the potential Φ at $\eta = 0$, and also of the temperature dependences of η_0 , $(\Delta\eta)^2$, and other quantities.

What is the role of the theory based on the expansion (1), and in what sense can its results be regarded as an approximation to reality? An unambiguous answer to this question will also be obtained only after the construction of an exact theory, but it seems to us that the situation is already rather clear. The presence of a singular point of the potential Φ at $\eta = 0$ does not prevent the expansion of Φ in series near values of η which though small are different from zero. Moreover, for $\eta_0 \neq 0$ the fluctuations $(\Delta\eta)^2$ are finite. From this it is clear that the expansion (1) and the results obtained from it may be valid in a certain region near the transition point but excluding this point itself and its immediate neighborhood. The whole question is only whether there exists an interval, and if so, how wide an interval, of values of η in which we may use the expansion (1) and keep only the terms $\alpha\eta^2 + (\beta/2)\eta^4$, or in extreme cases also the term $(\gamma/6)\eta^6$. It is natural to suppose^[14] that the smaller the fluctuations, the closer to the transition point one can use the expansion (1), and the wider the region where the parameter η is relatively small and it is permissible to stop at terms of the order η^4 or η^6 (when higher powers of η are included the expansion (1) contains so many unknown coefficients that in general one cannot get any concrete results from it). We cannot discuss this interesting question in detail here, and shall confine ourselves to a few remarks.^[14] According to what we have said, to find the region of applicability of the expansion (1) we must compare the values of η_0^2 and $(\Delta\eta)^2$. It can be supposed that the expansion is surely legitimate when $(\Delta\eta)^2 \ll \eta_0^2$. Here we cannot use the expression (5) for $(\Delta\eta)^2$, since it contains the arbitrary volume ΔV and applies only to the spatially homogeneous case. A calculation of the fluctuations $(\Delta\eta)^2$ free from these limitations gives as the criterion for the validity of the expansion (1) the inequality^[14]

$$\frac{\Delta T}{\theta} \gg \zeta_T = \frac{k^2 \beta_0^2}{\delta^2 \alpha_0} \quad (7)$$

Here $\Delta T = (\theta - T)$ is the distance (in the temperature scale) from the transition point at which the theory based on the expansion (1) is already valid. We see that the value of ΔT will be smaller for large values of the coefficient δ which characterizes the so-called correlation energy [cf. Eq. (1)]. An extremely curious fact is that the values of δ are altogether different in different cases. A more convenient and consistent procedure, however, is to compare not the values of δ , but the actual characteristic parameters ζ_T for various transitions [cf. Eq. (7)]. For superconductors $\zeta_T \sim 3 \times 10^{-16}$, in liquid helium $\zeta_T \sim 0.3$, and in solids ordinarily $\zeta_T \sim 0.03$, but sometimes it is much smaller [e.g., in ferroelectrics $\zeta_T \sim (1-3) \times 10^{-3}$]. Owing to this the expansion (1) and all of the corresponding theory of second-order transitions can be applied practically without any restrictions for superconducting transitions. Also for some other transitions in solids, though there are limitations they are sometimes of little practical importance. For example, in the case of ferroelectric transitions we have to do with an incorrectness of Eq. (4) in a region with a width of one degree or a few degrees near the transition point. In the case of the $\alpha \rightleftharpoons \beta$ transition in quartz the situation is still not clear, since this transition is close to the Curie critical point. For quartz the expansion (1) is evidently already good at a distance of several degrees from the transition point.²⁾ It must also be kept in mind that as a rule the applicability of any particular theory is not universal, in the sense that it depends strongly on the physical quantity under consideration. In this connection it is very important for our thesis here that the intensity of scattering of light is one of the quantities for which the theory of Eq. (1) gives particularly good results (cf. [9] and footnote 7). Thus not only for lack of a more exact theory, but also with some justification in the nature of the case considered, we can discuss the scattering of light near points of second-order phase transition on the basis of the expansion (1).

2. As is well known, light is scattered by the fluctuations of the dielectric constant, $\Delta\epsilon$ (we are of course speaking of a homogeneous medium, for example a single crystal without foreign inclusions). More exactly, even in an isotropic medium the fluctuations are of a tensor nature, i.e., we must consider

²⁾The temperature variation of the specific heat in the transition region takes very different forms, depending on the value of the parameter ζ_T (when one uses a single scale on the axis of abscissas, on which the ratio $\Delta T/\theta$ is measured off). In our opinion precisely this is the explanation of the quite different shapes of the specific-heat curves (and curves of other quantities) for various transitions.^[14] From this point of view all second order transitions are essentially of the same type, with the same dependence of any physical quantity on the ratio $\Delta T/\theta\zeta_T$.

a tensor $\Delta\epsilon_{ij}$. For simplicity, however, we shall confine ourselves here to the case in which we can, with sufficient accuracy, set $\Delta\epsilon_{ij} = \Delta\epsilon\delta_{ij}$. Besides this, of course, the values of ϵ and $\Delta\epsilon$ must be taken for the frequency of the light being scattered, $\omega_0 = 2\pi c/\lambda_0$, and we must write $\epsilon = n^2$ and $\Delta\epsilon = 2n\Delta n$, where n is the index of refraction. In a medium whose state is characterized by the density ρ , the temperature T , and the parameter η , we have

$$\Delta\epsilon = \left(\frac{\partial\epsilon}{\partial\rho}\right)_{T,\eta} \Delta\rho + \left(\frac{\partial\epsilon}{\partial T}\right)_{\rho,\eta} \Delta T + \left(\frac{\partial\epsilon}{\partial\eta^2}\right)_{\rho,T} \Delta\eta^2. \quad (8)$$

Here we have used the fact that ϵ depends only on η^2 , since replacement of η by $-\eta$ corresponds to twinning and cannot affect the value of ϵ (for example, in the case of a ferroelectric crystal, if $\eta = P_z$ is the component of the polarization along the z axis, the states P_z and $-P_z$ differ in the direction of the polarization parallel or antiparallel to the z axis). We note that in Eq. (8) it is more correct to write $\Delta\eta^2 - \overline{\Delta\eta^2}$ instead of $\Delta\eta^2$ in the last term, but in the region below the transition point in which we are interested this is unimportant, and the term $\overline{\Delta\eta^2}$ is omitted for simplicity (for details see [9]).

Near a point of second-order transition the fluctuations of the quantity η increase, whereas there are no important changes in the fluctuations of density and temperature. Therefore near the transition point we can set

$$\Delta\epsilon = a\Delta\eta^2 = 2a\eta_0\Delta\eta, \quad (9)$$

where $a = (\partial\epsilon/\partial\eta^2)_{\rho,T}$ and we have used the facts that $\Delta\eta = \eta - \eta_0$ and $\Delta\eta^2 = \eta^2 - \eta_0^2 = 2\eta_0\Delta\eta + (\Delta\eta)^2$. Moreover, the term $(\Delta\eta)^2$ in Eq. (9), like the term $\overline{\Delta\eta^2}$ in Eq. (8), has been dropped; it is important only above the transition point, where $\eta_0 = 0$. The intensity I of the scattered light is proportional to $(\Delta\epsilon)^2$ and, as is clear from Eqs. (5), (6), and (9),

$$I(T) \propto \frac{a^2\eta_0^2 T}{\left(\frac{\partial^2\Phi}{\partial\eta^2}\right)_{\eta_0}} \propto \frac{a^2 T}{V\beta^2 - 2\alpha\gamma}. \quad (10)$$

Right at the transition point $\alpha_\theta = 0$ and

$$I(\theta) \propto \frac{a^2\theta}{\beta_\theta}. \quad (11)$$

It is clear from this that for "ordinary" second-order transitions, i.e., transitions far from the Curie critical point, the scattering below the transition point has a weak dependence on the temperature (Fig. 5, a). This result may be surprising at first glance, since for ordinary second-order transitions the fluctuations $(\Delta\eta)^2 \rightarrow \infty$ for $T \rightarrow \theta$. The point is, however, that the intensity of the scattering is proportional to $(\Delta\eta^2)$ and is therefore determined by the product $\eta_0^2(\Delta\eta)^2$ [cf. Eq. (9)]. As for this product, it does not increase, because $\eta_0^2 \rightarrow 0$ for $T \rightarrow \theta$. The situation changes near the Curie critical point, at which $\beta_\theta = 0$. It is obviously for this last reason that for transitions close to

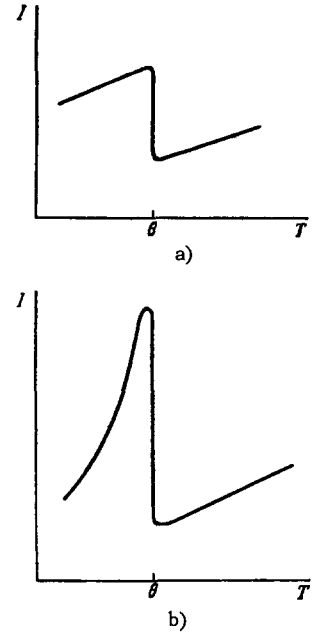


FIG. 5. Intensity of the scattering for an "ordinary" second-order transition (a) and for a second-order transition close to the Curie critical point (b). Besides the scattering by fluctuations of η , in both cases the scattering by density fluctuations has also been taken into account.

the critical case the intensity $I(T)$ is temperature dependent (Fig. 5, b) and increases sharply as β_θ decreases, i.e., as the transition approaches the critical case. It is precisely in this region that critical opalescence should be observable in a solid.

If we use the expressions (9)–(11) we find that at $T = \theta$ the intensity I falls discontinuously from the value (11) for $T < \theta$ to the value $I = 0$ for $T > \theta$ (by I we of course mean only the intensity of the scattering by the fluctuations $\Delta\eta$). It is true that inclusion of the omitted terms of the order of $(\Delta\eta)^2$ leads to the appearance of some weak scattering in second order even for $T > \theta$, but this does not invalidate the conclusion that there is a jump in the first-order scattering [scattering by the fluctuations (9)].

At the same time it is clear from physical considerations that the temperature variation of the scattered intensity cannot have any "jump" (this has already been taken into account in Fig. 5). Moreover, the limitations of the formula (11) are also obvious owing to the fact that according to this formula $I \rightarrow \infty$ at the Curie critical point itself. In fact, of course, the intensity of the scattering is always finite. In order to obtain expressions free from these shortcomings, it is necessary to take into account the correlation between the fluctuations in adjacent volumes. This conclusion has been known for a long time in the case of fluctuations near the critical point in a liquid-vapor system. [5] Under the conditions of second-order transitions the inclusion of the correlations can be accomplished automatically, if we do not drop from the expression (1) the gradient term $\delta(\text{grad } \eta)^2$: by its very meaning this term leads to a connection between the changes of η in adjacent regions. We shall not concern ourselves here with the calculations, [9] and only recall the approach which is used in making them and is im-

portant for what follows; this goes back to the classic work of A. Einstein on the scattering of light by density fluctuations.^[15]

It follows from the calculation that the scattering of light of frequency ω_0 in a given direction involves only a definite Fourier component of the fluctuation $\Delta\epsilon(\mathbf{r})$; namely the intensity of the scattered light is given by

$$\left. \begin{aligned} I &= \left(\frac{V}{4\pi}\right)^2 \left(\frac{2\pi}{\lambda_0}\right)^4 |\Delta\epsilon_{\mathbf{q}}|^2 \sin^2 \varphi, \\ \Delta\epsilon_{\mathbf{q}} &= \frac{1}{V} \int_V \Delta\epsilon(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}, \quad \mathbf{q} = \frac{2\pi}{\Lambda} = \frac{4\pi n}{\lambda_0} \sin \frac{\theta}{2}. \end{aligned} \right\} \quad (12)$$

Here V is the volume of the scattering medium with index of refraction $n(\omega_0)$; $\lambda_0 = 2\pi c/\omega_0$; φ is the angle between the electric vector of the incident wave and the direction of observation, and θ is the scattering angle (Fig. 6). Thus the scattering through the angle θ is due only to the Fourier component of the function $\Delta\epsilon(\mathbf{r})$ that corresponds to the wave vector $\mathbf{q} = \mathbf{k}_0 - \mathbf{k}$ (and also to the vector $-\mathbf{q}$, since $\Delta\epsilon_{-\mathbf{q}} = (\Delta\epsilon_{\mathbf{q}})^*$ owing to the fact that $\Delta\epsilon$ is a real function). In other words, the scattering is produced only by the "inhomogeneity wave" of the dielectric constant with length $\Lambda = 2\pi/q = \lambda_0/[2n \sin(\theta/2)]$; this corresponds to the well known interference condition

$$2\Lambda \sin \frac{\theta}{2} = \frac{\lambda_0}{n}.$$

According to Eq. (9) the component $\Delta\epsilon_{\mathbf{q}}$ is proportional to the component $\Delta\eta_{\mathbf{q}}$. The value of $|\Delta\eta_{\mathbf{q}}|^2$ itself can be calculated by the method usual in statistical physics, by using the expression (1) for the thermodynamic potential and including the gradient term. The result is^[9]

$$I(T) = \frac{V}{(4\pi)^2} \left(\frac{2\pi}{\lambda_0}\right)^4 \frac{a^2 k T \sin^2 \varphi}{\sqrt{\beta^2 - 2\alpha\gamma} + \frac{\delta\gamma q^2}{2(\sqrt{\beta^2 - 2\alpha\gamma} - \beta)}}. \quad (13)$$

For $\delta = 0$, i.e., when the "correlation energy" is not included in Eq. (1), the expression (13) goes over into (10), where a temperature-dependent factor which is clear from comparison with Eq. (13) was omitted. For $\delta \neq 0$ the intensity is always finite, and at the transition point (where $\alpha = \alpha_\theta = 0$), and in particular at the Curie critical point (with $\alpha_{\theta_C} = 0$, $\beta_{\theta_C} = 0$) the intensity $I(\theta) = 0$. Above the transition point (in the region $T > \theta$) this first-order scattering is also absent, and thus the continuity of the function $I(T)$ is preserved, as it must be. The width of the region in

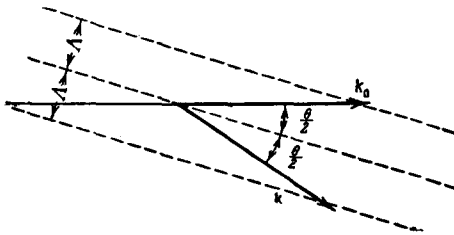


FIG. 6. Scattering of light through angle θ .

which the intensity falls is determined (away from the Curie critical point itself) from the condition

$$\frac{\delta q^2}{2\alpha'_0(\theta - T)} \sim 1. \quad (14)$$

The value of δ is unknown for the majority of transitions, but usually in solids (except in the case of superconducting transitions) the characteristic length $l \sim (\delta/\alpha'_0\theta)^{1/2} \sim 10^{-7} - 10^{-8}$ cm. Under such conditions the width of the region in which the intensity falls is $\Delta T = (\theta - T) \sim 10^{-4} - 10^{-1}$ deg. Thus the fall of intensity of the scattered light occurs practically right at the transition "point," which in fact is always somewhat smeared out owing to stresses, nonuniformity of the temperature, and so on. Therefore in first approximation we can compare theory with experiment by using the formula (13) with $\delta = 0$. Here it is convenient to use not the absolute value of the intensity, but the ratio of the intensity of the scattering by the fluctuations of η to the intensity I_0 of the scattering far from the transition point. For an isotropic body, taking into account only the scattering by density fluctuations, we must use for I_0 Einstein's formula^[15]

$$I_0(T) = \frac{V}{(4\pi)^2} \left(\frac{2\pi}{\lambda_0}\right)^4 \left(\epsilon \frac{\partial \epsilon}{\partial \rho}\right)_T b_T k T \sin^2 \varphi, \quad (15)$$

where $b_T = \rho^{-1}(\partial\rho/\partial p)_T$ is the isothermal compressibility.

According to Eqs. (13) and (15), with $\delta = 0$,

$$\frac{I(T_2)}{I_0(T_1)} = \frac{a^2 T_2}{\sqrt{\beta^2 - 2\alpha\gamma} b_T \left(\epsilon \frac{\partial \epsilon}{\partial \rho}\right)_T^2 T_1}, \quad \frac{I(\theta)}{I_0(T_1)} = \frac{a^{2\theta}}{\beta_\theta b_T \left(\epsilon \frac{\partial \epsilon}{\partial \rho}\right)_T^2 T_1}, \quad (16)$$

where the values of a , β , α , and γ must be taken at the temperature $T_2 \approx \theta$, and the values of b_T and $(\rho \partial\epsilon/\partial\rho)_T$ at the temperature T_1 . The quantities b_T and $(\rho \partial\epsilon/\partial\rho)_T$ can be measured directly or can be connected with other measureable quantities. Away from the Curie critical point, but close to it as well as far from it, the jump of the specific heat at the transition is

$$\Delta c = \frac{\theta}{\beta_\theta} (\alpha'_0)^2. \quad (17)$$

The value of $a = (\partial\epsilon/\partial\eta^2)_\rho, T$ can be determined from measurements of $\epsilon = n^2$ near the transition point. In fact, near the transition point the dependence $\epsilon(T)$ is practically the dependence $\epsilon(\eta_0^2(T))$, where $\eta_0(T)$ is the equilibrium value of η , which near the transition is given by Eq. (4). The changes of ϵ owing to fluctuations of η and owing to the change of the equilibrium value $\eta = \eta_0$ with the temperature are of entirely the same character, and therefore near the transition point (in the region $T < \theta$) we have in accordance with Eq. (9)

$$\epsilon(T) - \epsilon(\theta) = 2n\Delta n = a\eta_0^2 = \frac{a\alpha'_0(\theta - T)}{\beta_\theta}. \quad (18)$$

From this it follows that [see Eqs. (17) and (18), with $\Delta n = n(T) - n(\theta)$]

$$\frac{\alpha^2}{\beta_0} = \frac{4n^2 (\Delta n)^2 \beta_0}{(\alpha_0')^2 (\theta - T)^2} = \frac{4n^2 (\Delta n)^2 \theta}{\Delta c (\theta - T)^2} \quad (19)$$

For the $\alpha \rightleftharpoons \beta$ transition in quartz:

$$\theta = 846^\circ \text{K}, \quad n = 1.56,$$

$$\Delta n = 1.2 \cdot 10^{-3} \text{ in the range } (\theta - T) = 0.1^\circ,$$

$$\Delta c = 0.4 \frac{\text{cal}}{\text{g deg}} = 4.2 \cdot 10^7 \frac{\text{erg}}{\text{deg cm}^3} \quad \left(\rho = 2.51 \frac{\text{g}}{\text{cm}^3} \right),$$

$$\left(\rho \frac{\partial \epsilon}{\partial \rho} \right)_T \approx 1.6, \quad b_T \approx 3.3 \cdot 10^{-12} \frac{\text{cm}^2}{\text{dyne}} \quad (20)$$

All of these values are taken from the sources indicated in [9] and [11], and here we shall confine ourselves to presenting a curve of $n(T)$ for quartz in the transition region, taken from [11] (Fig. 7). Besides this we emphasize that in all probability the $\alpha \rightleftharpoons \beta$ transition in quartz is a second-order transition (and not a first-order transition close to the Curie critical point). It cannot be doubted that this transition is close to the Curie critical point, as is clear from the steepness of the function $n(T)$ in Fig. 7 and from other data. [11] This is most clearly evidenced by the critical opalescence which is also observed in the region of the $\alpha \rightleftharpoons \beta$ transition. [8,11]

Using the values (20) and the expression (19), we can find the ratio of intensities (16). The result is

$$\frac{I(\theta)}{I_0(20^\circ \text{C})} \approx 1.1 \cdot 10^4, \quad (21)$$

whereas experimentally $I(\theta)/I_0(20^\circ \text{C}) \approx 1.4 \times 10^4$. As T. S. Velichkina has kindly informed the writer, the accuracy of this experimental value is 20 to 30 percent (the intensity $I(\theta)$ was experimentally determined as the average intensity in a range of 0.1° near the transition point). In view of the size of the error and the known inaccuracies of the value (21), caused by neglect of anisotropy and the lack of precision of the values (20), we must for the present regard the agreement between theory and experiment as complete. A more detailed comparison will primarily require the securing of more accurate values of all the parameters and new measurements of the intensity of the scattering in the region of the $\alpha \rightleftharpoons \beta$ transition in quartz. It would also be very interesting to observe the scattering near other second-order transitions. Measurements in the neighborhood of certain ferroelectric transitions are evidently especially promising in this connection.

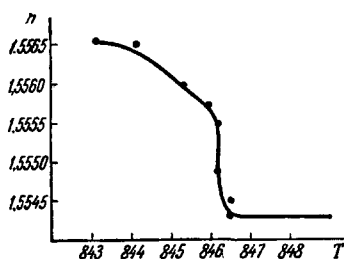


FIG. 7. Temperature dependence of the index of refraction of quartz ($\lambda_0 = 4057 \text{ \AA}$).

3. The intensity of the scattered light is a physical quantity whose measurement is undoubtedly of interest. But the determination of the spectral composition of the scattered light makes it possible to get much more information about the properties of the scattering medium.

The spectrum of the scattered light depends on the kinetics of the fluctuations $\Delta \epsilon$; that is, in our case of the region near second-order transition points, on the kinetics of the fluctuations of the parameter η . Since the scattering through angle θ involves the wave [cf. Eq. (12)]

$$\Delta \epsilon = \Delta \epsilon_q e^{i\mathbf{q} \cdot \mathbf{r}} = 2a\eta_0 \Delta \eta_q e^{i\mathbf{q} \cdot \mathbf{r}} \text{ with } q = \frac{4\pi n}{\lambda_0} \sin \frac{\theta}{2},$$

the spectral composition of the light depends on the form of the function $\Delta \eta_q(t)$ —on the variation with time of the amplitude of the wave of $\Delta \eta$ with the wave vector \mathbf{q} [this fact, which is also the basis for the analysis of the spectrum of the Rayleigh scattering, is also elucidated in the report by I. L. Fabelinskii (see page 667)]. Concretely, the field in the scattered light wave is proportional to $\Delta \epsilon_q e^{i\omega_0 t} = 2a\eta_0 \Delta \eta_q e^{i\omega_0 t}$, and its spectral composition is determined by the Fourier components

$$G_\Omega = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \Delta \eta_q(t) e^{-i\Omega t} dt, \quad (22)$$

where $\Omega = \omega - \omega_0$; ω is the frequency of the scattered light, and ω_0 is that of the incident light.

What are the kinetics of the fluctuations $\Delta \eta_q$? In the case of quartz we can take as the parameter η the displacement of the position of a definite Si atom in the α quartz relative to its position in the β quartz. In a ferroelectric such as BaTiO_3 , for example, one of the parameters is proportional or equal (this depends on the normalization) to the electric polarization of the crystal along the tetragonal axis. This quantity is in turn proportional to the displacement of a Ba atom (more exactly, ion) relative to the TiO_3 group.

Thus in these and similar cases a nonequilibrium change (fluctuation) corresponds to the displacement of various sublattices, and consequently will be of an oscillatory nature. In fact, as is well known, it is precisely through the displacement of sublattices relative to each other that optical (Born) vibrations occurring at some frequency $\Omega_i(\mathbf{q})$ arise in a crystal. Thus we arrive at the conclusion that the scattering of light by fluctuations is a special case of combination scattering of light. This conclusion is quite obvious if we follow the ideas developed by G. S. Landsberg and L. I. Mandel'shtam, who interpreted combination scattering as the result of modulation of a light wave by the optical vibrations of a lattice. [16]³ With a differ-

³Here and in what follows we use classical ideas and classical theory. This is completely justified for transitions occurring at temperatures $T \gg \hbar \Omega_i / k$, and these are basically the transitions

ent approach to the problem, if we calculate the intensity of the scattering by the fluctuations of η without thinking of their kinetics, the connection of this scattering with combination scattering^[12] remains obscure, and was not noted in^[2,9], and some other papers.

In quartz, where the phase transition is characterized by one parameter η , we must expect a connection of only one branch of the optical vibrations with the oscillations of η . At the same time there are 16 optical vibrations in α quartz, 12 of which are active in combination scattering.^[18] Thus the need arises to determine the optical normal vibration which corresponds to fluctuations (oscillations) of the parameter η .

A change of the quantity η in α quartz is not associated with a change of the symmetry of the lattice. There are 4 vibrations in quartz which do not change the symmetry; their frequencies $\tilde{\nu}_i = \Omega_i/2\pi c$ at room temperature are 207, 357, 466, and 1082 cm^{-1} . As was already mentioned at the beginning of this article, the combination line 466 cm^{-1} can also be seen in β quartz,^[1] so that the oscillation of η with which we are concerned cannot be connected with it (in β quartz oscillations of η do not give first-order scattering). The behavior of the other three lines can be traced theoretically only in the framework of calculations which use the model of a lattice with definite force constants, etc. Such an analysis has not yet been made completely, but some conclusions can already be drawn.

First, and this is especially important, the frequency Ω_i associated with changes of η must go to zero at the transition point of the second kind. The basis for this conclusion is presented below, but we emphasize here that thus it is clear that it must be possible to find the relevant frequency Ω_i from measurements of the frequencies of lines at various temperatures. Unfortunately, measurements of the positions of a number of combination lines in α quartz have been made^[19] only up to 685°K, which is still rather far from the transition temperature $\theta = 846^\circ\text{K}$. Nevertheless it is clear from the measurements that the greatest decrease of frequency with increase of temperature is shown by the line $\nu_1 = 207 \text{ cm}^{-1}$ ($\nu_1 = 207 \text{ cm}^{-1}$ at 300°K and $\nu_1 = 173 \text{ cm}^{-1}$ at 685°K). At the same time the line 357 cm^{-1} (at $T = 300^\circ\text{K}$) has a frequency 351 cm^{-1} at $T = 685^\circ\text{K}$, i.e., is displaced very little (we have no data for the line 1082 cm^{-1}). Besides this, according to^[1] the line 207 cm^{-1} also has the largest increase in width with rising

of interest to us here (as is shown below, the frequency Ω_i with which we are concerned is small near the transition point). From the quantum point of view^[16,17] combination scattering is associated with the absorption (violet satellite) or production (red satellite) of a quantum of the optical vibrations (an optical phonon) by a photon of energy $\hbar\omega_0$ and momentum $\hbar\omega_0 n_{k_0}/k_0 c$ incident on the medium. In the scattering the momentum of the photon is changed by the amount of the phonon momentum $\hbar q$.

temperature.^[19] Thus the experimental data, together with the general theoretical conclusion just stated, point to the line 207 cm^{-1} as the one whose frequency goes to zero at the $\alpha \rightleftharpoons \beta$ transition point. Second, the same conclusion can be drawn from a brief note^[20]^[4] which states that calculations on the basis of a definite microscopic model indicate a great resemblance between the vibrations responsible for the line 207 cm^{-1} and the displacements in the $\alpha \rightleftharpoons \beta$ transition.

We shall now present the arguments which indicate that the frequency Ω_i corresponding to oscillations of the parameter η goes to zero at $T = \theta$.

At a second-order transition point $\eta_0(\theta) = 0$ and $\alpha \equiv \alpha(\theta) = 0$, which means that the "generalized elastic energy"—the term $\alpha\eta^2$ in the expansion (1)—goes to zero. To make this interpretation of the expression $\alpha\eta^2$ clearer, we recall that the equilibrium value $\eta = \eta_0$ is determined from the condition $\partial\Phi/\partial\eta = 0$, i.e., from the condition $\alpha\eta + \beta\eta^3 = 0$ (we set $\delta = 0$ and neglect the term $\gamma\eta^6/6$). This equation, however, is analogous to the equilibrium condition for an anharmonic oscillator with the equation of motion $\ddot{z} + a\dot{z} + bz + cz^3 = 0$ (differentiation d/dt is indicated by a dot). This analogy is particularly deep because the parameter η is proportional to some displacement in the lattice (we are speaking of quartz, ferroelectrics, and some other cases). Thus to a certain approximation we can write an equation of motion for η in the form $\mu\ddot{\eta} + \mu\nu\dot{\eta} + \alpha\eta + \beta\eta^3 = 0$. From this we have for small oscillations $\Delta\eta = \eta - \eta_0$ about an equilibrium value η_0 ⁵⁾

$$\left. \begin{aligned} \frac{d^2}{dt^2}(\Delta\eta) + \nu \frac{d}{dt}(\Delta\eta) + \Omega_i^2(\Delta\eta) &= 0, \\ T > \theta: \quad \eta_0 &= 0, \quad \Omega_i^2 = \frac{\alpha}{\mu} = \frac{\alpha'_0(T-\theta)}{\mu}, \\ T < \theta: \quad \eta_0^2 &= -\frac{\alpha}{\beta_0}, \quad \Omega_i^2 = \frac{2|\alpha|}{\mu} = \frac{2\alpha'_0(\theta-T)}{\mu}. \end{aligned} \right\} \quad (23)$$

The linear dependence on the difference $\theta - T$ which holds near the transition point (Fig. 8) is connected with the expansion (1), and is probably only approximate (see above). There can scarcely be any doubt, however, that one of the optical frequencies goes to zero at a second-order transition point.⁶⁾

⁴⁾The same conclusion is indicated by the detailed paper, which appeared later and is cited in the list of literature also under^[20].

⁵⁾To avoid misunderstanding we make one comment regarding the notation. The Ω_i denote both frequencies of optical vibrations in general, and also the frequency of the vibration of special interest to us, which is connected with changes of η . This should not lead to confusion, since in what follows the notation Ω_i occurs only with the second meaning. The parameters μ and ν in Eq. (23) refer only to the vibration connected with changes of η , and for simplicity carry no index.

⁶⁾The scattering of light involves the frequency $\Omega_i(q)$, whereas in Eq. (23) we were essentially concerned with the limiting frequency $\Omega_i(0)$, i.e., with an optical vibration with wavelength

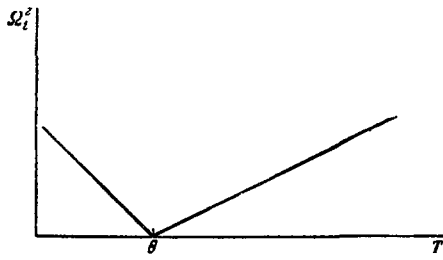


FIG. 8. Temperature dependence of the square of the frequency Ω_i associated with oscillations of η .

This fact was pointed out long ago^[21] for the ferroelectric transition (see also^[14,22,23]). In this case, if $\eta = P_z$ and a cubic crystal goes over into a tetragonal crystal, the complex dielectric constant is of the form

$$\left. \begin{aligned} T > \theta: \quad \epsilon = \epsilon' - i\epsilon'' \approx \frac{2\pi\mu}{\Omega_i^2 - \Omega^2 + i\nu\Omega}, \quad \Omega_i^2 = \frac{\alpha}{\mu}, \\ T < \theta: \quad \epsilon_z = \epsilon'_z - i\epsilon''_z \approx \frac{2\pi\mu}{\Omega_i^2 - \Omega^2 + i\nu\Omega}, \quad \Omega_i^2 = \frac{2|\alpha|}{\mu}. \end{aligned} \right\} \quad (24)$$

For $T < \theta$ we have $\epsilon_x = \epsilon_y \neq \epsilon_z$, i.e., there is a splitting of the characteristic frequencies (for the corresponding expressions see^[14]). One easily gets the formulas (24) from Eq. (23) by setting $\Delta\eta = P_{i,z}$, where $P_{i,z} = (\epsilon - 1)E_z/4\pi \approx (\epsilon/4\pi)E_z$ is the polarization induced by an external field $E_z = E_z^{(0)}e^{i\Omega t}$ along the axis z in the direction of the spontaneous polarization $P_{0,z}$ (we note that when the electric field is taken into account one must add to the expression (1) for this case a term $-P_z E_z$, which leads to the appearance of a generalized force E_z in the right member of Eq. (23) for $\Delta\eta = P_{i,z}$). The frequency Ω_i in Eq. (24) is the characteristic frequency of the optical vibration in which the electric polarization oscillates along the z axis (above the transition point the crystal is isotropic in its dielectric properties and the z axis is of course not singled out). Such an optical vibration obviously is active in infrared absorption, as can indeed be seen from Eq. (24): the presence of the frequency Ω_i leads to a resonance and an absorption maximum both for $T < \theta$ and for $T > \theta$. In first-order combination scattering the vibration with frequency Ω_i is active only for $T < \theta$. This sort of ferroelectric transition of a cubic crystal to a tetragonal crystal is close to the case found in BaTiO_3 (for which it is a matter of vibrations of Ba relative to the TiO_3 group). The only difference is that in pure BaTiO_3 the phase transition is a first-order transition close to the Curie point [therefore $\Omega_i(\theta) \neq 0$, although this frequency is indeed anomalously small^[14]].

In the case of quartz the parameter η is not connected with an electric polarization, and consequently

$\Lambda = 2\pi/q \rightarrow \infty$. For light, however, $q = (4\pi n/\lambda_0) \sin \theta/2 \leq 4\pi n/\lambda_0 \leq 5 \times 10^5 \ll q_{\text{max}} \sim \pi/d \sim 10^8$ ($d \sim 3 \times 10^{-8}$ is the lattice parameter). Therefore with good accuracy $\Omega_i(q) \approx \Omega_i(0)$ (for details see^[12,24]; in^[24] there is also information on the problem of the connection between optical vibrations and "normal" electromagnetic waves and the theory of excitons in crystals; we cannot go into this here).

the optical vibration in which we are interested is not active in infrared absorption, but appears in the combination scattering for $T < \theta$. For $T > \theta$ this vibration is inactive also in first-order combination scattering.⁷⁾ In the experiments with quartz^[8] the spectral composition was not obtained, but besides the intensity measurements there were measurements of the degree of depolarization Δ of the scattered light. At room temperature $\Delta \approx 0.12$ near the transition point, but at some distance from this point (for $T < \theta$), $\Delta \approx 0.18$. In the immediate region of the transition $\Delta \approx 0.06$. In view of what has been said, this large decrease of Δ is quite understandable. Outside the transition region the scattering is mainly Rayleigh scattering. In the transition region (near the transition point), on the other hand, the main contribution is that of combination scattering, with degree of depolarization $\Delta = 0$ for the 207 cm^{-1} line (the fact that even in the transition region we see that $\Delta = 0$ does not contradict our conclusion and calls for special analysis, since the depolarization of the scattered light was not calculated in^[9] and the usual calculation for combination lines cannot be used here).

For ferroelectrics which have a piezoelectric effect even below the ferroelectric region (Rochelle salt, KH_2PO_4 , and so on) the first-order combination scattering does not vanish even in the more symmetrical (nonferroelectric) phase. The intensity of this scattering is calculated in^[10]; it increases as the transition point is approached from either side (furthermore the corresponding frequency Ω_i for the second-order transition also goes to zero for $T = \theta$).

In the foregoing we have essentially assumed that the optical vibration associated with changes of η is undamped and occurs with the frequency Ω_i . Then the frequency of the combination line (more exactly, the distance between the satellite and the unchanged line, $\Omega = \omega - \omega_0$) is also equal to Ω_i . Actually, however, every vibration is damped, and consequently the combination lines have nonvanishing widths. This broadening is ordinarily given no attention if it is not the object of special investigation. One cannot, however, in general neglect the width for a frequency Ω_i which rapidly decreases and even goes to zero for $T \rightarrow \theta$.

Thus we need to determine the spectrum of the scattered light in more detail. This has been done in^[12], but we would like to carry out this simple calculation here also.

Obviously what we are to find is the spectral density $J(\Omega)$ of the intensity of the scattered light; this is proportional to $|G_\Omega|^2$, where G_Ω is the Fourier

⁷⁾Second-order combination scattering, which in quantum language corresponds to the production or absorption of two optical phonons in the scattering of a photon, has a broad spectrum and is in general very weak (exceptions can occur in only a few substances, and in these only very near the transition point^[9]). To keep the exposition from being unwieldy we shall not go into the details of this question.

component (22). To do this we must remember that the fluctuations of the parameter η are caused by the thermal motion in the crystal. This means that the vibrations of the quantity $\Delta\eta = \eta - \eta_0$ are forced, not free vibrations, and obey the equation⁸⁾

$$\frac{d^2}{dt^2}(\Delta\eta) + \nu \frac{d}{dt}(\Delta\eta) + \Omega_i^2(\Delta\eta) = f. \quad (25)$$

Here f is a random force which arises from the thermal motion, or specifically from the thermal vibrations of all the degrees of freedom connected with vibrations of η through weak interactions of nonlinear character. Equation (25) differs from Eq. (23) only by the inclusion of the force f —in Eq. (23) we were interested only in the characteristic vibrations of the crystal and did not take the force f into account [but in getting (24) we actually already used (25) with f replaced by the electric field E_z (see above)].

It follows from Eqs. (25) and (22) that⁹⁾

$$G_\Omega = \frac{f_\Omega}{\Omega_i^2 - \Omega^2 + i\nu\Omega}, \quad f_\Omega = \frac{1}{2\pi} \int_{-\infty}^{+\infty} f(t) e^{-i\Omega t} dt. \quad (26)$$

As has already been pointed out, we have for the spectral density of the intensity of the scattering $J(\Omega) \sim |G_\Omega|^2$, and thus

$$J(\Omega) = \frac{\left(\frac{\nu\Omega_i^2}{\pi}\right) I}{(\Omega_i^2 - \Omega^2)^2 + \nu^2\Omega^2}, \quad I = \int_{-\infty}^{+\infty} J(\Omega) d\Omega. \quad (27)$$

Here we have introduced the factor I proportional to $|f_\Omega|^2$, and by definition of the quantity $J(\Omega)$, I is equal to the total intensity of the light scattered by the fluctuations in question. Therefore we do not need to make a new calculation of the value of I ; it has been found earlier [see item 2, and in particular Eq. (13)]. If the red and violet satellites do not overlap, i.e., if $\Omega_i \gg \nu$, then for each satellite

$$J_c(\Omega) = \frac{\frac{\nu}{4\pi} I}{(\Omega_i - \Omega)^2 + \frac{\nu^2}{4}}. \quad (28)$$

Here I is obviously the total intensity of both satel-

⁸⁾The quantity appearing in Eq. (22) is $\Delta\eta_{\mathbf{q}}$, but in Eq. (25) we omit the index \mathbf{q} . This is due to our neglect of the difference between $\Omega_i(\mathbf{q})$ and $\Omega_i(0)$, which we have already mentioned. Along with this we must emphasize that from other points of view it is very important to consider the fluctuations with $\mathbf{q} \neq 0$, and not with $\mathbf{q} = 0$. The point is that when the term $\delta(\text{grad } \eta)^2$ in Eq. (1) is included the fluctuations with $\mathbf{q} \neq 0$ do not become infinite even right at the transition point (cf. [9]). For this reason it is legitimate to use the theory based on the expansion (1) for the analysis of the problem of the scattering of light over a much wider range^[9] than it could be used to calculate quantities such as the specific heat. On the other hand, the value of \mathbf{q} which is important for the scattering of light is small in comparison with $q_{\text{max}} \sim \pi/d$, and this diminishes the values of integrals of the type $\int_{\mathbf{q}} F(\mathbf{q}) d\mathbf{q}$.

⁹⁾ $\Delta\eta_{\mathbf{q}}(t)$ and $f(t)$ are random functions and do not go to zero as $|t| \rightarrow \infty$. Nevertheless it is permissible to use the usual Fourier transformation in the present calculations.

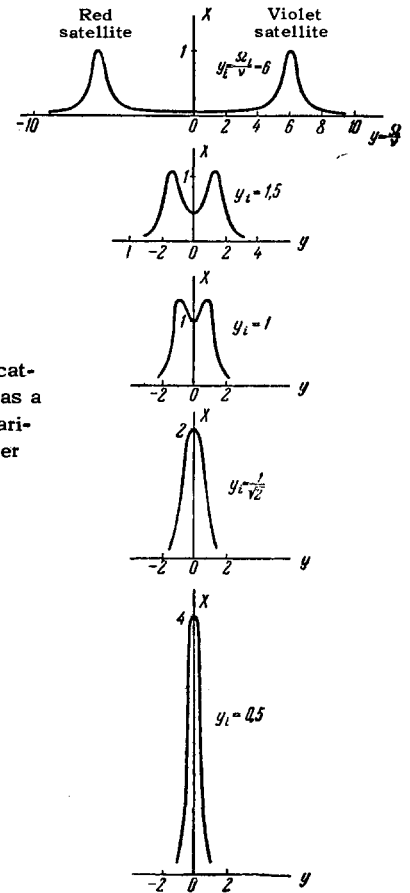


FIG. 9. Spectrum of scattered light, $X = \pi\nu J(y)/I$, as a function of $y = \Omega/\nu$ for various values of the parameter $y_i = \Omega_i/\nu$.

lites taken together (in this classical approximation the intensities of the satellites are equal).

We also note that according to Eq. (27)

$$\left. \begin{aligned} J(0) &= \frac{\nu I}{\pi\Omega_i^2}, \quad J(\Omega_i) = \frac{I}{\pi\nu}, \\ J(\Omega_{\text{max}}) &= \frac{I}{\pi\nu \left(1 - \frac{\nu^2}{4\Omega_i^2}\right)}, \end{aligned} \right\} \quad (29)$$

where the frequencies $\Omega_{\text{max}} = \pm(\Omega_i^2 - \nu^2/2)^{1/2}$ correspond to maxima of the function $J(\Omega)$ when $\Omega_i > \nu/2^{1/2}$. For $\Omega_i < \nu/2^{1/2}$ the function $J(\Omega)$ has only one maximum, at $\Omega = 0$. The dependence of $J(\Omega)$ on the ratio $y_i = \Omega_i/\nu$ is shown in Fig. 9, where the ordinate is the quantity X :

$$X(y, y_i) = \frac{\pi\nu J(\Omega)}{I} = \frac{y_i^2}{(y_i^2 - y^2)^2 + y^2}, \quad y = \frac{\Omega}{\nu}, \quad y_i = \frac{\Omega_i}{\nu}. \quad (30)$$

An important point is that the intensity of the scattering without frequency shift, $J(0) = \nu I/\pi\Omega_i^2$, depends strongly on the temperature. For second-order transitions far from the Curie critical point the intensity I for $T < \theta$ is approximately constant (Fig. 5,a), but $\Omega_i^2 = 2\alpha'_\theta(\theta - T)/\mu$. In this case the temperature dependence of $J(\Omega)$ is given by the curves of Fig. 9, since the decrease of Ω_i as the transition point is approached is associated with a change of the parameter $y_i = \Omega_i/\nu \sim (\theta - T)^{1/2}$. When the Curie critical point is approached a temperature dependence of the inten-

sity I appears (Fig. 5,b) and the effect becomes still sharper. As for the coefficient ν which characterizes the damping, generally speaking it must be "well-behaved" near the transition point, i.e., must not have any singularities. One can determine ν by various methods.^[12] In particular, it is obvious that the basis parameters Ω_i and ν for the normal vibration responsible for a phase transition can be found by spectral analysis of the scattered light. In cases in which this vibration is active in infrared absorption one can in principle determine these same parameters by the methods of infrared spectroscopy. It is well known, however, that these two methods—combination scattering and infrared spectroscopy—only supplement each other. Furthermore for low frequencies the infrared method (which could then be more correctly called the microwave method) encounters great difficulties, especially in the submillimeter part of the spectrum.

Summarizing, we want to point a conclusion about the possible fruitfulness, and in any case the great interest, which would be presented by spectral studies of the scattered light near points of second-order phase transition and first-order ones close to the Curie critical point. Clearly ferroelectrics are of particular importance in this connection; the combination scattering of light in ferroelectrics has already been observed,^[26] but not for all lines and outside the transition region.

The main feature which determines the peculiarities of the scattering of light at second-order phase transitions and transitions closely resembling them is essentially the sharp decrease of one of the frequencies of the normal vibrations. Such an effect, however, is also possible in liquids for macromolecules and polymer chains. Owing to this these substances clearly also deserve attention in work such as that suggested here.

But why are there no experimental researches on the spectrum of the scattered light near second-order phase transition points? It is hard to give a completely definite answer to this question. In our opinion there are three facts to be mentioned in explanation. First, there is still too little recognition of the potentialities of measurements made along the lines we have suggested. Second, these measurements are by no means simple. Third, the study of the scattering of light is, so to speak, an old classical problem and has "gone out of style."

There are, however, many examples of "old" and "unstylish" fields of research which have again come to the center of attention as the result of the appearance of more modern experimental resources, new ideas, or new objects of study. It may be that this will also be the fate of the study of the scattering of light, especially in solids. Here there are many new materials which have second-order phase transitions (ferroelectrics, so-called antiferroelectrics, and

others). We hope that it is clear that the study of the scattering of light in these substances is important. Finally, remarkable new light sources have been developed (quantum generators—lasers), which are as it were especially predestined for the spectral analysis of scattered light.

Will all of these favorable conditions be enough to make work on the scattering of light again lead to great advances in the study of crystals and molecules? We shall of course know the answer to this question only in the future.

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