Light scattering near phase transition points

A. P. Levanyuk

Crystallography Institute, USSR Academy of Sciences
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The temperature dependence of the integral light-scattering intensity is investigated in the temperature region near the phase-transition point in which the scaling-theory relations are valid. Principal attention is paid to structural phase transitions in which the optical dielectric permittivity depends only quadratically on the order parameter. In this (the most interesting) case, first-order scattering by fluctuations of the order parameter occurs only in the less symmetric phase. Its intensity in the region of applicability of the Landau theory can increase appreciably only in a transition close to a tricritical point. On the other hand, in the scaling region for a second-order transition far from the tricritical point the critical index of the intensity turns out to be considerable: 0.5–0.8 (for the tricritical transition it is the same as in the Landau theory: 0.5). Second-order scattering is also considered. It is shown that the intensities of the first- and second-order scatterings are comparable on the boundary of the region of applicability of Landau theory, and on closer approach to the phase-transition point have the same temperature dependence. The spectral composition of the second-order light scattering near the transition point is investigated. In the case of both relaxational and vibrational dynamics of the order-parameter fluctuations the main part of the intensity is concentrated in the region of the central maximum, which increases in height and decreases in width as the phase-transition point is approached. The principal existing experimental data on light-scattering anomalies in structural phase transitions are discussed.

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Twenty years have passed since the first discussion of the possibility of critical scattering of light near second-order phase-transition points[1] and the experimental observation of "opalescence" in the $\alpha \rightleftarrows \beta$-transition in quartz.[2] During these years, and in particular more recently, a considerable number of experiments have been performed (cf., eg.,[3]); however, on the whole, the question of the character of the anomaly observed in the scattering is still not completely clear. In a number of cases it is not possible to interpret the experimental data using the simple phenomenological theory.[4-10] The limitations of this theory are connected, apparently, with several circumstances. First, in these papers[4-10] only the scattering thermal fluctuations (molecular scattering) was studied, i. e., the presence in the crystal of static inhomogeneities (twinning faces, dislocations, point defects) was not taken into account but can, in principle, be one of the reasons for the light-scattering anomaly.[11-14] Secondly, the temperature dependence of the relevant coefficients was taken to be the same as in the Landau theory of phase transitions.[15] Moreover, it is known that this theory is inapplicable in the immediate vicinity of a second-order phase-transition point and we must use in its place the well-known scaling relations.[16] The purpose of the present work is to consider light scattering in the scaling region. In addition, the second-order scattering, which turns out to be extremely important in the scaling region, is considered in more detail than before.

We note that for a phase transition in a solid the existence of a clearly defined scaling region is by no means obvious. It is known (e. g.,[17]) that a nonzero shear modulus can cause a change in the character of the transition—before we reach the point at which the thermodynamic quantities have singularities (the second-order transition point), a discontinuous change of density occurs, entailing the formation of a new phase, i. e., a first-order phase transition occurs. There are also other factors that can cause a change in the order of the transition.[18]

However, in the case of many phase transitions in solids, both the experimental data and theoretical considerations indicate the existence of a region in which deviations from the Landau theory are appreciable but the factors leading to a first-order transition can be disregarded. Thus, the existence of a sharply defined scaling region for many magnetic phase transitions is well known,[16] and there are sufficiently weighty reasons to assume that this region is observed in the case of the structural phase transition in $SrTiO_3$[19] and for certain other structural transitions.[3] In practice, in considering this region we can speak of a second-order phase transition, and this will be done below.

The intensity for scattering of light with a small change of frequency (into unit solid angle and for unit intensity of the incident wave) is given by the expression[4,20]

$$I=\left(\frac{V}{4\pi}\right)^2\left(\frac{2\pi}{\lambda_0}\right)^4\frac{n_2}{n_1}\cos^{-2}\delta_1\cos^{-2}\delta_2\langle|\Delta\varepsilon_{ik}(\mathbf{q})e_i^{(1)}e_k^{(2)}|^2\rangle$$
$$=Q\langle|\Delta\varepsilon_{ik}e_i^{(1)}e_k^{(2)}|^2\rangle, \qquad (1)$$

where V is the scattering volume (in the following we shall put $V=1$); λ_0 is the wavelength of the light in vacuo; n_1 and n_2 are the refractive indices for the incident and scattered normal waves, characterized by wave-vectors $\mathbf{k}_1$ and $\mathbf{k}_2$, unit electric-field intensity vectors $\mathbf{e}^{(1)}$ and $\mathbf{e}^{(2)}$, and angles δ_1 and δ_2 between the electric field and the electric induction; ε_{ik} is the dielectric-permittivity tensor in the range of optical frequencies; $\Delta\varepsilon_{ik}(\mathbf{q})$ is a Fourier component of the function $\Delta\varepsilon_{ik}(\mathbf{r})$, which is the difference between the local and equilibrium values of ε_{ik}; $\mathbf{q}=\mathbf{k}_1-\mathbf{k}_2$; the brackets

$\langle \ldots \rangle$ denote averaging over a statistical ensemble. The total scattering intensity is the sum of the expressions (1) for both normal waves (the incident wave is assumed to be normal). Naturally, the consideration of the light scattering is divided into two parts—the elucidation of the character of the dependence of ε_{ik} on the generalized coordinates of the system, and the calculation of the average thermal fluctuations of these coordinates.

1. DEPENDENCE OF ε_{ik} ON THE GENERALIZED COORDINATES

We first discuss the possibility of a linear dependence of ε_{ik} on the components η_j of the order parameter. Naturally, such a dependence can be possessed only by those components of the tensor ε_{ik} which are equal to zero in the high-symmetry phase and have the same transformation properties as the corresponding components η_j under the symmetry transformations of this phase. If we disregard the presence of absorption, which is unimportant for the following, the tensor ε_{ik} can be represented in the form of the sum of a symmetric tensor ε'_{ik}, invariant under time reversal R, and an antisymmetric tensor ε''_{ik}, which changes sign under this operation. Since $R\eta_j = -\eta_j$ for a transition accompanied by the appearance of magnetic order, while $R\eta_j = \eta_j$ for a structural phase transition, only ε''_{ik} can have a linear dependence on η_j in the case of magnetic transitions, and only ε'_{ik} in the case of structural transitions. Since ε''_{ik} has the same transformation properties as the magnetization vector, a linear relation between ε''_{ik} and η_j is possible for transitions in ferromagnets or in those antiferromagnets in which there is a linear relationship between the antiferromagnetism vector and the magnetization (in such antiferromagnets, the so-called weak ferromagnetism is possible).

A theory of critical light scattering in a ferromagnetic phase transition, in which fluctuations of ε''_{ik} were taken into account, is described in papers by L'vov and Moriya.[21] Since $\varepsilon''_{ik} \sim M_j$ (M_j is the magnetization), the light-scattering intensity is proportional, as can be seen from (1), to the Fourier component of the magnetization correlation function. This treatment can be improved only by refining the form of the correlation function, and this has been done repeatedly.[16]

In the case of a structural phase transition the existence of a linear relationship between ε'_{ik} and η_j implies that the order parameter is one or several components of the elastic-deformation tensor u_{lm} (which, like ε'_{ik}, is a symmetric second-rank tensor) or any other generalized coordinate (e. g., the polarization P_j) that is linearly related to u_{lm} in the high-symmetry phase[1]. In both cases, as shown by Sobyanin and the author,[22] the critical fluctuations are essentially suppressed and the Landau theory remains valid all the way to the phase transition. The light scattering in such transitions (the custom recently is to call them ferroelastic transitions) has been studied in[4] by Krivoglaz and Rybak using the example of a ferroelectric with a piezoeffect in the high-symmetry phase.

Thus, the possibilities for improving the theory pertain principally to those cases in which the dependence of ε_{ik} on η_j is quadratic. As follows from the discussion given above, for most phase transitions only such a relationship is possible. Moreover, for ferromagnetic transitions too, when a linear relationship is also possible, it follows from (1) that, by choosing the polarization of the incident and scattered rays in an appropriate way, we can study the part of the scattering which is associated with those fluctuations of the tensor components ε_{ik} which depend quadratically on η_j. Such an investigation, as will be shown below, is of undoubted interest.

In the expansion of ε_{ik} in powers of η_j, naturally, only those combinations of components of the order parameter which transform like the components of a second-rank tensor appear. Amongst the quadratic combinations of η_j there is certainly one that satisfies this condition—the second-order invariant $\eta_j\eta_j$; generally speaking, other combinations can also exist. We, however, shall take into account only the invariant combination, assuming the order parameter to have one component. In this case we can omit the tensor indices. In other words, we have

$$\varepsilon = \varepsilon_0 + a\eta^2, \tag{2}$$

$$\Delta\varepsilon(\mathbf{q}) = 2a\eta_0\eta(\mathbf{q}) + a\sum_{\mathbf{k}}\eta(\mathbf{k})\eta(\mathbf{q}-\mathbf{k}), \tag{3}$$

where η_0 is the equilibrium value of the order parameter. The coefficient a in formulas (2) and (3) can be assumed to be independent of temperature.

Since the dependence of ε on η is fairly weak (only quadratic), it may turn out that the contribution of fluctuations of η to the light-scattering anomaly is comparable to the contribution of fluctuations of some of the generalized coordinates on which ε depends linearly, although the fluctuations of these coordinates vary much more weakly with temperature than the fluctuations of η. As was shown in[4,9], precisely this situation is realized in the region of applicability of the Landau theory. The corresponding generalized coordinates can be the normal coordinates of the totally symmetric optical vibrations, the concentrations of the components in a many-component system, the density ρ of the substance, etc. Below, besides the fluctuations of η, only fluctuations of ρ are taken into account. The generalization is sufficiently obvious.

2. FIRST-ORDER SCATTERING INTENSITY

Taking into account the density dependence of ε, i. e., adding the term bu, where $u = \Delta\rho/\rho$, to the expression (2), for the first-order scattering intensity we have

$$I_1 = Q[4a^2\eta_0^2\langle\eta(\mathbf{q})\eta(-\mathbf{q})\rangle + 2ab\eta_0\langle u(\mathbf{q})\eta(-\mathbf{q}) + \text{c.c.}\rangle + b^2\langle u(\mathbf{q})u(-\mathbf{q})\rangle] \equiv I_{\eta\eta} + I_{\eta u} + I_{uu}. \tag{4}$$

As can be seen from formula (4), in the high-symmetry phase, i. e., for $\tau > 0$ ($\tau = (T - T_c)/T_c$), the first-order scattering is associated with the density fluctuations only. The temperature dependence of this part of the

scattering is the same as that of the compressibility, i. e., a logarithmic or weak power dependence.

For $\tau < 0$ it is necessary also to take into account the first two terms in formula (4): $I_{\eta\eta}$ and $I_{\eta u}$. We have (cf. the Appendix of[15])

$$\langle \eta(\mathbf{q})\eta(-\mathbf{q})\rangle = T\chi(\mathbf{q}) \tag{5}$$

where $\chi(\mathbf{q})$ is the generalized susceptibility corresponding to η. For sufficiently small $\mathbf{q}$, $\chi^{-1}(\mathbf{q}) = \chi^{-1}(0) + Dq^2$; this formula is true for $Dq^2 \ll \chi^{-1}(0)$, or, equivalently, for $qr_c \ll 1$, where r_c is the correlation length for η. When $qr_c \gg 1$ (q^{-1} is nevertheless much larger than the atomic dimensions). $\chi(\mathbf{q})$ can be regarded as independent of temperature and $\chi(\mathbf{q}) \sim q^{2-\tilde{\eta}}$, where the critical index $\tilde{\eta}$ is close to zero for three-dimensional systems.[16]

It follows from the above remarks and formulas (4) and (5) that in the region of values of $|\tau|$ so small that $qr_c > 1$ the intensity of the scattering by fluctuations of η decreases as the transition point is approached: $I_{\eta\eta} \sim \eta_0^2$. For $qr_c < 1$,

$$I_{\eta\eta} \sim \eta_0^2 \chi(0). \tag{6}$$

Taking[16] $\eta_0 \sim |\tau|^{\beta}$, $\chi(0) \sim |\tau|^{-\gamma}$ and using the relation (following from the scaling hypothesis) $2 - \alpha = \gamma + 2\beta$, where α is the critical index for the specific heat (compressibility), we find[23]

$$I_{\eta\eta} \sim |\tau|^{2(1-\gamma)-\alpha}. \tag{7}$$

According to the Landau theory, $\gamma = 1$, $\alpha = 0$, and $I_{\eta\eta}$ does not vary with temperature. In the general case $I_{\eta\eta}$ increases as $|\tau| \to 0$, since, as a rule, $\gamma > 1$. The latter is in any case fulfilled for both the Ising model and the Heisenberg model.[16] For the three-dimensional Ising model, $\gamma \approx 1.25$; for the Heisenberg model, $\gamma \approx 1.4$; for the transition to the superfluid state, $\gamma = 2.33$. In other words, since $\alpha \approx 0$,

$$I_{\eta\eta} \sim |\tau|^{-\psi}, \quad \psi = 0.5-0.8. \tag{8}$$

Thus, for fixed q and $|\tau| \to 0$, a fairly rapid increase in the intensity $I_{\eta\eta}$ first occurs and then $I_{\eta\eta}(\tau)$ passes through a maximum at $qr_c \approx 1$ and finally decreases on further decrease of $|\tau|$. We note that, since $q \approx 10^5 - 10^6$ cm^{-1} for light, it is evidently practically impossible to reach the region $qr_c \approx 1$ in the case of many transitions in solids, inasmuch as a first-order phase transition occurs at larger values of $|\tau|$ (cf.[17] and above).

As can be seen from (A.3) (cf. below), the mean fluctuation appearing in the expression for $I_{\eta u}$ is proportional to the derivative $\partial^2 G/\partial g \partial p$, where g is the generalized force conjugate to η and p is the pressure. According to the homogeneity hypothesis the thermodynamic potential is a generalized homogeneous function of the variables g and τ^*, where τ^* is the distance in the (p, T)-plane from the given point to the phase-transition line: $\tau^* = \tau - Kp$, $K = T_c^{-1} dT_c/dp$. Taking into account the properties of generalized homogeneous functions (cf., e. g.,[16]), we find

$$\frac{\partial^2 G}{\partial g\, \partial p} \sim \tau^{\beta-1}, \quad I_{\eta u} \sim \tau^{1-\gamma-\alpha}. \tag{9}$$

In the region of applicability of the Landau theory, $I_{\eta u}$, like $I_{\eta\eta}$, does not depend on the temperature, while in the region of applicability of the scaling relations $I_{\eta u}$ increases as $|\tau| \to 0$, but more slowly than $I_{\eta\eta}$. Taking into account the values given above for the critical indices for the Ising and Heisenberg models, we find that

$$I_{\eta u} \sim |\tau|^{-\varphi}, \quad \varphi = 0.25-0.4. \tag{10}$$

Thus, for a second-order transition far from the tricritical point, an appreciable anomaly, associated with the increase in $I_{\eta\eta}$, can be observed in the first-order scattering. It is interesting that the critical index for the intensity coincides in this case with that determined by the simple formula contained in the paper by Yakovlev *et al.*[2]:

$$I \sim \left(\frac{d\varepsilon}{dT}\right)^2 \langle (\Delta T)^2 \rangle \sim \left(\frac{d\varepsilon}{dT}\right)^2 c_V^{-1}, \tag{11}$$

if we take into account that near T_c we have $d\varepsilon/dT \sim a d\eta_0^2/dT$. We note that formula (11) is by no means universal; for example, for transitions corresponding to a tricritical point in solids, it leads (in the framework of the Landau theory) to a temperature dependence that is certainly incorrect.[10]

Using the scaling relations for a transition corresponding to a tricritical point, i. e., a point at which a line of second-order transitions merges with a line of first-order transitions,[24] we can convince ourselves that formulas (7) and (9) are also correct for a tricritical transition. We note that, as shown by theory[24] and experiment,[25] the indices γ and α in this case coincide with those given by the Landau theory of the tricritical point, i. e., $\gamma = 1$, $\alpha = \frac{1}{2}$. In this case $I_{\eta\eta}$, $I_{\eta u}$ and I_{uu} have the same temperature dependence, as has already been noted previously.[9]

We draw attention to the fact that the conclusions of the Landau theory and of scaling theory with respect to the critical indices of the thermodynamic quantities at a tricritical transition conicide only for the low-symmetry phase. In the high-symmetry phase, according to the Landau theory the first-order scattering intensity has practically no temperature dependence, while according to the scaling theory the critical indices for the scattering intensity are the same in both phases, i. e., $I_1 \sim |\tau|^{-1/2}$ for both signs of τ.

3. SECOND-ORDER SCATTERING

The character of the anomaly associated with the second-order scattering was first studied in a paper by Ginzburg and the author.[5] However, an approximate expression for the scattering intensity was used in it, and the temperature dependence of the material constants was assumed to be the same as in the Landau theory. In[6] we used exact formulas for the fourth-

order fluctuations, but in their final version certain terms were omitted in error (this does not affect the basic results of the paper, however). In the Appendix, improved formulas, obtained by the method used by us earlier,[6] are given for higher-order fluctuations. We shall make use of these formulas below, assuming that the constants that appear have the temperature dependence that agrees with the scaling hypothesis.[16]

For $\tau<0$ the second-order scattering intensity is determined by the second term of formula (3). We have

$$I_2(q)=Qa^2\sum_{\mathbf{k},\mathbf{k}'}\langle\eta(\mathbf{k})\eta(\mathbf{q}-\mathbf{k})\eta(\mathbf{k}')\eta(\mathbf{q}-\mathbf{k}')\rangle. \tag{12}$$

Using formula (A.9) and taking into account that the constant B' in this formula can be assumed equal to zero for $\tau>0$ (cf. the Appendix), we obtain

$$I_2(\mathbf{q})=Qa^2T^2\Big(2\int\chi(\mathbf{k})\chi(\mathbf{q}-\mathbf{k})\frac{d\mathbf{k}}{(2\pi)^3}-6T\int B(-\mathbf{k},\mathbf{k}-\mathbf{q},-\mathbf{k}',\mathbf{k}'+\mathbf{q})\times\chi(\mathbf{k})\chi(\mathbf{k}-\mathbf{q})\chi(\mathbf{k}')\chi(-\mathbf{k}'+\mathbf{q})\frac{d\mathbf{k}}{(2\pi)^3}\frac{d\mathbf{k}'}{(2\pi)^3}\Big). \tag{13}$$

In accordance with the scaling hypothesis, we assume that

$$\chi(\tau,\mathbf{k})=\tau^{-\nu}f(kr_c), \tag{14}$$

Where $f(x)$ is a temperature-independent function. Replacing the variable k by $x=kr_c$ in the first integral of formula (13), we find that for $q\approx0$ this integral is equal to

$$r_c^{-3}\tau^{-2\gamma}\frac{1}{\pi^2}\int x^2f^2(x)\,dx\sim\tau^{3\nu-2\gamma}. \tag{15}$$

The integral in (15) converges, since for $x\gg1$ we have $f(x)\sim x^{\tilde\eta-2}$, where, as already noted, $\tilde\eta$ is evidently close to zero in real systems.

Using next the homogeneity of the four-point function (cf. the Appendix), we have

$$B(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4)=Bb(\mathbf{k}_1r_c,\mathbf{k}_2r_c,\mathbf{k}_3r_c,\mathbf{k}_4r_c), \tag{16}$$

where $b(0,0,0,0)=1$. We shall determine the temperature dependence of B from the equation of state, which, in accordance with the scaling hypothesis, has the form

$$g=\eta\tau^{\gamma}h(\eta/\tau^{\beta}), \tag{17}$$

where $h(x)$ is a function that can be expanded in a series about the point $x=0$. Taking into account that $B=\frac{1}{2}(\partial^3g/\partial\eta^3)_0$, we find from (17) that the critical exponent of B is equal to $\gamma-2\beta$. It follows from this that the critical exponent of the second term in formula (10) is equal to $-3\gamma-2\beta+6\nu$.

In order that the expression for I_2 be positive-definite, this exponent should be no smaller than that of the first term, i. e., the inequality

$$3\nu\geqslant\gamma+2\beta. \tag{18}$$

should be fulfilled. Using one of the relations between the critical indices of the thermodynamic quantities ($\gamma+2\beta=2-\alpha$), we see that the inequality (18) is the Josephson inequality.[16] Thus, the requirement that the fourth-order fluctuations be positive leads to the Josephson inequality. In scaling theory this inequality is assumed to be an equality.[16] Calculations of the critical indices in the $(4-\varepsilon)$-approximation also lead to the equality.[26] Strictly speaking, however, it is not clear whether this equality is observed in the three-dimensional case. We recall that fulfillment of the equality does not follow from the assumption of homogeneity of the thermodynamic quantities and correlation functions—the additional assumption that the transformation properties under a scale transformation are the same for the correlation function and for the square of the order parameter is required.[16]

If the Josephson inequality becomes an equality, the mutual cancellation of the two terms in the right-hand side of formula (13) is possible. This would imply the existence of a relationship not only between the critical indices but also between the corresponding coefficients of the powers of τ. In such a case the temperature dependence of I_2 would be weaker than that of the first term in formula (13). In other cases these temperature dependences coincide. Making use of the relation $\gamma=\nu(2-\tilde\eta)$, which follows from the homogeneity of the correlation function, we have

$$I_2\sim\tau^{-\nu(1-2\tilde\eta)}. \tag{19}$$

Since $\tilde\eta$ is evidently extremely small for three-dimensional systems (for the Ising model $\tilde\eta\approx0.04$ and for the Heisenberg model $\tilde\eta\approx0.03$), the temperature dependence of I_2 is practically the same as that of the correlation length r_c. We note that a similar conclusion follows from the Landau theory.[5]

If the Josephson inequality becomes an equality (but the above-mentioned cancellation of terms of opposite signs in the expression for I_2 does not occur), then, as follows from a comparison of the expressions (7) and (19) taking (18) into account, the first- and second-order scattering intensities have the same temperautre dependence. Moreover, in the region in which the scaling relations are valid, $I_{\eta\eta}(-\tau)$ and $I_2(\tau)$ are the same in order of magnitude.

To convince ourselves of this we shall compare $I_{\eta\eta}(-\tau)$ and $I_2(\tau)$ in the region of applicability of the Landau theory, and also on the boundary between this region and the region of applicability of the scaling relations. According to the Landau theory, for $\tau<0$ we have

$$\chi(k)=-2A+Dk^2;\quad\eta_0^2=-A/B,$$

where $A=A'(T-T_c)$ and B, $D=\text{const}$; therefore, $I_{\eta\eta}=Qa^2T/2B$. The second-order scattering intensity can be expressed in the form[6]

$$I_2=Qa^2T^2S(1-\tfrac{3}{2}BTS), \tag{20}$$

where S is the first term of the expression in the brackets in formula (13). Since I_2 and S are positive-

definite quantities, the condition for applicability of the Landau theory is that the second term in the brackets in formula (20) be small compared with unity.[6] It can be seen that when this term becomes comparable with unity the intensities $I_{\eta\eta}$ and I_2 are also comparable in magnitude.

We have been concerned above with the second-order scattering for $\tau > 0$. Using the formulas contained in the Appendix, we can also examine the case $\tau < 0$. In this case,

$$I_2 = Q\left[2a^2\eta_0\sum_{\mathbf{k}}\langle\eta(\mathbf{k})\eta(\mathbf{q})\eta(-\mathbf{q}-\mathbf{k})\rangle + 2a^2\eta_0\sum_{\mathbf{k}}\langle\eta(\mathbf{q})\eta(-\mathbf{q}-\mathbf{k})\eta(\mathbf{k})\rangle + a^2\sum_{\mathbf{k},\mathbf{k}'}\langle\eta(\mathbf{q}-\mathbf{k})\eta(\mathbf{k})\eta(-\mathbf{k}')\eta(-\mathbf{q}+\mathbf{k}')\rangle\right]. \quad (21)$$

Carrying through arguments analogous to those given above, we can convince ourselves that in the region of applicability of the scaling relations the temperature dependences of all terms in the expression (21) are the same and coincide with the temperature dependence of $I_{\eta\eta}$.

We note that for $\tau < 0$ the use of the thermodynamic potential of the Landau theory leads (in contrast to the case $\tau > 0$; cf. above) to a positive-definite expression for the second-order scattering intensity (in the region, considered here, of small q).

Thus, in the region of applicability of the Landau theory the intensity I_2 increases as the transition point is approached, while $I_{\eta\eta}$ remains constant. On the boundary of the region of applicability of the Landau theory I_2 is comparable with $I_{\eta\eta}$ (for $\tau < 0$), and, still closer to the transition point, these two intensities are approximately the same, both in magnitude and in their temperature dependence.

We shall discuss now the question of the scattering of higher orders than the second. For example, inclusion of the term $a_4\eta^4$ in the expression (2) leads (for $q = 0$) to an expression proportional to

$$\int\chi(\mathbf{k}_1)\chi(\mathbf{k}_2)\chi(\mathbf{k}_3)\chi(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\,d\mathbf{k}_1\,d\mathbf{k}_2\,d\mathbf{k}_3. \quad (22)$$

Using the relation (14), we find that the critical index of the expression (22) is equal to $-4\gamma + 9\nu = \nu(1+4\bar{\eta})$. The positivity of the index means that the integral (22) remains finite as $\tau \to 0$. Expressions of a form analogous to (22) are also obtained when terms of still higher order are included in (2). In other words, the higher-order scattering intensities do not experience an anomalous temperature dependence as $T \to T_c$.

In the treatment given above it was assumed, in effect, that the order-parameter fluctuations are not accompanied by the appearance of long-range forces. However, in certain cases, when the order parameter is one of the components of the polarization vector (a uniaxial ferroelectric), and also when the order parameter is one of the components of the deformation tensor or equivalent to it in its transformation properties (a ferroelastic), such forces appear and substantially change the character of the fluctuations.[27-29,22] Substituting into formula (13) the known expressions for the $\chi(\mathbf{k})$ of a uniaxial ferroelectric,[27-29] we find that the second-order scattering intensity (for $q \to 0$) increases like $\ln\tau$ as the phase-transition point is approached. For a ferroelastic phase transition, as follows from (13) and the expression for $\chi(\mathbf{k})$ obtained by Villain and by Sobyanin and the author,[2] the second-order scattering intensity remains finite.

4. SECOND-ORDER SCATTERING. SPECTRAL DENSITY

As was shown above, in the scaling region the first- and second-order scattering intensities are the same in order of magnitude, and it is therefore worthwhile to analyze the spectral distribution of the second-order scattering intensity near T_c; so far as we know, this has not been done before. We shall carry out the analysis for the region of applicability of the Landau theory, in which the non-Gaussian character of the fluctuations can be disregarded, i.e., the second term in formula (13) can be omitted. The qualitative results evidently also remain valid on the boundary of this region. In addition, we confine ourselves to the case $\tau > 0$; in the approximation used, all the conclusions apply also to the nonsymmetric phase ($\tau < 0$). We have

$$I_2(\Omega, q) = 2Qa^2\int\langle\eta(\mathbf{k},\omega)\eta(-\mathbf{k},-\omega)\rangle\langle\eta(\mathbf{q}-\mathbf{k},\Omega-\omega)\eta(\mathbf{k}-\mathbf{q},\omega-\Omega)\rangle\,d\omega\,d\mathbf{k}. \quad (23)$$

We assume that the equation of motion of η is the equation of a harmonic oscillator with damping (this is close to reality for, e.g., a structural phase transition). In the usual way we find that

$$\langle\eta(\mathbf{k},\omega)\eta(-\mathbf{k},-\omega)\rangle = \frac{\Gamma T}{\pi m}\frac{1}{(\omega^2-\omega_0^2(\mathbf{k}))^2+\Gamma^2\omega^2}, \quad (24)$$

where $\omega_0(\mathbf{k})$, Γ and m are the characteristic-vibration frequency, damping constant and mass of the corresponding oscillator. In the following we shall neglect the wave-vector of the light, i.e., put $q = 0$.

As already noted, allowance for the fact that q differs from zero is important only in the region near the phase transition where the correlation length r_c is comparable with or greater than the wavelength of the light. For most phase transitions this region (putting aside the fact that the Landau theory is not applicable in it) is experimentally inaccessible. Using (24), we obtain

$$I_2(\Omega, 0) = 2Qa^2\left(\frac{\Gamma T}{m}\right)^2 \times\int\frac{d\omega\,d\mathbf{k}}{[(\omega^2-\omega_0^2(\mathbf{k}))^2+\Gamma^2\omega^2]\{[(\omega-\Omega)^2-\omega_0^2(\mathbf{k})]^2+\Gamma^2(\omega-\Omega)^2\}} = 2Qa^2\left(\frac{\Gamma T}{m}\right)^2\left[\frac{4\pi}{\Gamma(\Omega^2+\Gamma^2)}\int\frac{d\mathbf{k}}{[(2\omega_d-\Omega)^2+\Gamma^2][(2\omega_d+\Omega)^2+\Gamma^2]} + \frac{4\pi(\Omega^2+4\Gamma^2)}{\Gamma(\Omega^2+\Gamma^2)}\int\frac{d\mathbf{k}}{4\omega_0^2[(2\omega_d+\Omega)^2+\Gamma^2][(2\omega_d-\Omega)^2+\Gamma^2]}\right], \quad (25)$$

where $\omega_d^2 = \omega_0^2 - \Gamma^2/4$.

If there is no dispersion in the branch of oscillations of η, i.e., $\omega_d(\mathbf{k}) = \bar{\omega} = \text{const}$, then, as is easily seen, for $\bar{\omega} < \Gamma$, $I_2(\Omega)$ has three maxima: at $\Omega = 0$ and at $\Omega = \pm 2\bar{\omega}$. The central maximum is twice as high as the side maxima and the widths of the maxima are equal. The pres-

ence of dispersion in the oscillation branch leads to broadening and (in principle) disappearance of the side maxima. The width of the central maximum, however, is determined by the constant Γ, as before. Since for $\tilde{\omega} < \Gamma$ there are also side maxima in the first-order scattering intensity, at least three maxima should be present simultaneously in the spectrum of the scattered light, and these have approximately equal intensities and widths on the boundary of the region of applicability of the Landau theory. For real systems, when there are frequently several oscillation branches possessing the same symmetry as the oscillations of η, the situation, naturally, can become more complicated.

In the case when the fluctuations of η have a relaxational character, the Fourier transform of the correlation function can be written in the form

$$\langle \eta(\mathbf{k}, \omega)\, \eta(-\mathbf{k}, -\omega)\rangle = \frac{1}{\pi} \frac{\gamma T}{\chi^{-2}(\mathbf{k}) + \gamma^2 \omega^2}. \qquad (26)$$

This formula is obtained from (24) by taking the limit $m \to 0$, with $\gamma = m\Gamma$, $\omega_0^2(\mathbf{k}) = m^{-1}\chi^{-1}(\mathbf{k})$; for small k we have

$$\chi^{-1}(\mathbf{k}) = \chi^{-1}(0) + Dk^2.$$

The intensity distribution in the spectrum of the second-order scattering is given by the expression (the corresponding integral is calculated elsewhere[30]):

$$I_2(\Omega, 0) = \frac{Qa^2T^2}{4\pi^2} \frac{\chi^2(0)}{\omega_r r_c^3} \frac{1}{x^2} \left\{ \frac{1}{\sqrt{2}} [(1+x)^{1/2}+1]^{1/2} - 1 \right\}, \qquad (27)$$

where $x = \Omega^2/\omega_r^2$, $\omega_r = \gamma^{-1}\chi(0)$ is the inverse relaxation time of fluctuations of η, and $r_c = (D\chi(0))^{1/2}$.

According to (27), $I(\Omega, 0)$ has a maximum at $\Omega = 0$, the half-width of which amounts to $\sim 2.2\omega_r$. Since, in the region of applicability of the Landau theory, $\chi(0)$, $\omega_r \sim \tau^{-1}$ and $r_c \sim \tau^{-1/2}$, the height of the central maximum increases like $\tau^{-3/2}$. Consequently, the total intensity grows like $\tau^{-1/2}$ (cf. also[5]). Since the expression (26) satisfies the requirements of "dynamical scaling,"[16] formula (27) can also be used outside the region of applicability of the Landau theory. Only the temperature dependence of the coefficients $\chi(0)$ and γ will be different (cf. [31]). For a broad class of phase transitions, $\chi(0) \sim \tau^{-1.33}$ and $\gamma \sim \tau^{0.33}$ (cf., e.g., [31]), and therefore the temperature dependence of the width of the spectral maximum is the same in the region of applicability of the Landau theory and in the scaling region. The temperature dependences of the maximum intensity in these regions do, in fact, differ, but only by virtue of the differences in the critical indices for the correlation length r_c, since, as shown above, the temperature dependence of the integral intensity practically coincides with that of r_c in the scaling region. We recall, however, that in the scaling region, generally speaking, the non-Gaussian contribution to $I_2(\Omega, \mathbf{q})$, not taken into account here, becomes appreciable.

A separate treatment is necessary for a phase transition in a uniaxial ferroelectric or ferroelastic. Here it is important to take into account the dependence of ω_0^2 on the direction of $\mathbf{k}$.[22,27,28] The integral appearing in the formula for the second-order scattering intensity in a uniaxial ferroelectric (when the fluctuations of η have a relaxational character) has in fact been calculated in[32]. Using the result of this work, we have

$$I_2(\Omega, 0) = Qc^2a^2T \frac{\chi^{3/2}(0)}{r_c^3} \frac{1}{\omega_r} \frac{1}{x} \left[\operatorname{arctg} \frac{x}{2} - \frac{1}{x} \ln\left(1 + \frac{x^2}{4}\right) \right], \qquad (28)$$

where $c \approx 3 \times 10^{-4}$. Since, with logarithmic accuracy, $\chi(0) \sim \tau^{-1}$ and $r_c \sim \tau^{-1/2}$ for uniaxial ferroelectrics, it can be seen from (28) that the height of the spectral maximum grows like τ^{-1} as $\tau \to 0$, and its width decreases like τ. The total second-order scattering intensity then increases logarithmically (cf. Sec. 3).

In the case of a phase transition in a ferroelastic it has not been possible to obtain an expression for $I_2(\Omega, \mathbf{q})$ in explicit form. However, from the results of[33] by Shchedrina and the author, in which the same integral as the one appearing in the expression for $I_2(0, 0)$ was calculated for the ferroelastic case, it follows that when the fluctuations of η have a relaxational character we have $I_2(0, 0) \sim \tau^{-1/2}$. The total second-order scattering intensity in the ferroelastic does not experience a singularity near the transition point, and therefore the width of the central peak decreases in this case like $\tau^{1/2}$.

5. POSSIBILITIES OF COMPARISON WITH EXPERIMENT

Although a whole series of experimental studies of light scattering near phase-transition points in solids has by now been carried out,[3] it is evidently still too soon to make a direct comparison of the theory expounded above with experiment. In fact, strictly speaking, there are no grounds to suppose that it has been possible to observe critical scattering in the case of a quadratic relationship between ε_{ik} and η_j, although in a number of experiments it would have been possible, at first sight, to count on such observations. We shall discuss these experiments in more detail.

The clearest effect—the increase in the scattering intensity by four orders of magnitude in the region of the transition—has been observed in quartz.[2,11] At first, this "opalescence" was assumed to be due to fluctuations of the order parameter.[5,8,9] However, Shapiro and Cummins[11] then obtained data that indicate the static character of the inhomogeneities responsible for the "opalescence"; this, of course, would be impossible if thermal fluctuations were the cause of the scattering. The question of the nature of these inhomogeneities lies outside the scope of this paper (on the whole, it remains unclear[14]) and here it is pertinent only to discuss which part of the observed anomaly could be associated with scattering by thermal fluctuations.

We shall assume that the phase transition in quartz is second-order. As was shown above, the scattering intensity, in the region $qr_c < 1$, grows according to approximately the same law as the correlation length as $|\tau| \to 0$. Since the increase in intensity ceases when $qr_c \sim 1$, the intensity of the scattering by fluctuations of

η can be increased by, at best, three orders of magnitude. Far from the transition point the intensity of scattering by fluctuations of η is approximately equal to the intensity of one of one of the combination lines, i.e., is smaller than the total scattering intensity by one or two orders of magnitude. Thus, in the $\alpha \rightleftarrows \beta$-transition in quartz, the thermal-scattering anomaly due to the nonclassical temperature dependence of the constants of the crystal should be at least two orders of magnitude smaller than the observed anomaly.

The fact that the $\alpha \rightleftarrows \beta$-transition in quartz is, apparently, a first-order transition[3] can introduce additional restrictions on the magnitude of the molecular-scattering anomaly. If, however, as assumed by Larkin and Pikin, [17] the existence of the first-order transition is associated with the specific influence of the nonzero shear modulus on the behavior of the thermodynamic quantities in the scaling region, then a noticeable molecular-scattering anomaly could be observed in the $\alpha \rightleftarrows \beta$-transition in quartz. In addition, the intensities of the first- and second-order scatterings should be comparable. To check these conclusions, careful experiments to study the spectral composition of the scattered light are necessary.

The experimental data on the anomalies in the thermodynamic quantities in the $\alpha \rightleftarrows \beta$-transition in quartz are interpreted in a number of papers[5,9,3] as evidence of the closeness of the $\alpha \rightleftarrows \beta$-transition to a tricritical point. We shall discuss this possibility briefly. We note first of all that, in the framework of scaling theory, more or less definite conclusions about the character of the tricritical transition can be made only in those cases when either the shear modulus is equal to zero (a liquid) or its presence can be disregarded. [24] As already noted, in this case the critical indices of the thermodynamic quantities for the tricritical transition are the same as in the Landau theory. In particular, the compressibility of the substance increases like $|\tau|^{-1/2}$, and this should lead to a strong increase in the density fluctuations and to intensification of the molecular light scattering. The presence of the shear modulus changes this result in two respects. First, it has the effect that in the region of applicability of the Landau theory a large increase in compressibility does not lead to a corresponding increase in the level of the fluctuations, which, for parameters typical for structural transitions, becomes only a few times greater. [10] Secondly, the very existence of the tricritical point becomes problematical. The possibility that it exists has been demonstrated only for phase transitions occurring under very high pressure. [34] Thus, the assumption that the $\alpha \rightleftarrows \beta$-transition is close to a tricritical point is insufficiently certain at the present time.

An increase in the light scattering intensity near the phase-transition point in NH_4Cl has been observed in a number of experiments. [35,36] However, according to Shustin, [35] the dependence of the intensity on the wavelength of the light is much weaker than λ^{-4}, so that, in this case too, there are no grounds to assume that thermal fluctuations are the cause of the observed scattering (cf. also[12]). At atmospheric pressure the phase transition in NH_4Cl is first-order; the remarks just made concerning the $\alpha \rightleftarrows \beta$-transition in quartz can also be applied to this. It is interesting that this transition already becomes continuous at relatively low pressures. [37] According to the experimental data, the light-scattering intensity at the phase-transition point has a maximum at the pressure corresponding to the change in the character of the transition. [38] As follows from the formulas given in the articles by Ginzburg and the author, [10] the molecular-scattering intensity at the transition point (calculated using the Landau theory) is a maximum for the tricritical transition. It would seem, therefore, that we can expect that the maximum observed in NH_4Cl is associated with precisely the molecular scattering. However, such a conclusion requires careful experimental verification. In fact, it remains unclear whether the point on the $p-T$ diagram at which the character of the phase transition in NH_4Cl changes is tricritical in the strict sense of this word. In fact, the continuity of the transition could be associated with the presence of defects and inhomogeneities in the crystal; the fact that the first-order transition becomes continuous could correspond to a reduction of the discontinuities of the thermodynamic parameters to a certain magnitude in the first-order transition in the ideal crystal.

The discovery of an effect of the critical-opalescence type in the phase transition in $SrTiO_3$ has also been recently reported. [39] It was found, however, that the intensity has a substantial dependence on the scattering angle, so that if we associate this scattering with thermal fluctuations the correlation length of the fluctuations turns out to be extremely large: 4×10^{-6} cm for $\tau \approx 0.3$. This conclusion contradicts both the experimental data on neutron scattering[40] and the estimates from the EPR data of[19], according to which the correlation length in $SrTiO_3$ has the usual (i.e., atomic) order of magnitude (not too close to the phase-transition point). Thus, in the case of $SrTiO_3$ also, the molecular-scattering anomly is evidently masked by an anomaly of a different nature. In particular, if we assume that the latter is due to scattering by defects, the angular dependence of the intensity could be associated with correlations in the positions of the defects, which are determined by the conditions of the growing and annealing of the crystals. A value of the order of 10^{-6} cm for the corresponding correlation length is usual in this case, but the temperature dependence of the correlation length observed by Steigmeier *et al.* [39] remains incomprehensible.

Nor does it appear possible to compare the conclusions obtained above concerning the evolution of the spectral composition of the second-order scattering with experimental data. Evidently, this is connected with the fact that the scattering of interest to us is concentrated in the region of the central maximum, and experimental investigations of the anomalies in the light scattering in this region of frequencies are only just beginning.

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APPENDIX

Calculation of the mean fluctuations

The general method of calculating the average of the fluctuations of a certain macroscopic variable $\xi = \xi(X)$, where X is the complete set of microscopic coordinates, consists (cf., e.g., [41,42]) in considering the thermodynamic potential in the presence of an external force a, conjugate to ξ. It is obvious that

$$G(a) = -T \ln \int \exp\left(-\frac{H(X) - a\xi(X)}{T} \right) dX, \tag{A.1}$$

where $H(X)$ is the Hamiltonian of the system in the absence of the external force. Differentiating (A.1) a sufficient number of times, we can obtain exact formulas expressing the magnitudes of the fluctuations of arbitrarily high order in terms of the derivatives of $G(a)$. In many cases it is more convenient to consider not the thermodynamic potential G but the free energy F, defined by the relations

$$F(\xi) = G(a) - a\frac{\partial G}{\partial a}, \quad \xi = \frac{\partial G}{\partial a}. \tag{A.2}$$

An analogous procedure can be extended to the case of many variables.

For reference we give some formulas (cf.[37,38,6]):

$$\langle \Delta\xi_i \Delta\xi_k \rangle = -T\frac{\partial^2 G}{\partial a_i \partial a_k} = TF_{ik}^{-1}, \tag{A.3}$$

$$\langle \Delta\xi_i \Delta\xi_k \Delta\xi_l \rangle = T\frac{\partial^3 G}{\partial a_i \partial a_k \partial a_l} = T^2 F_{pl}^{-1} \frac{\partial F_{ik}^{-1}}{\partial \xi_p}, \tag{A.4}$$

$$\begin{aligned}\langle \Delta\xi_i \Delta\xi_k \Delta\xi_l \Delta\xi_m \rangle &= T^2 \frac{\partial^2 G}{\partial a_i \partial a_k}\frac{\partial^2 G}{\partial a_l \partial a_m} + T^2 \frac{\partial^2 G}{\partial a_i \partial a_l}\frac{\partial^2 G}{\partial a_k \partial a_m} \\ &+ T^2 \frac{\partial^2 G}{\partial a_i \partial a_m}\frac{\partial^2 G}{\partial a_k \partial a_l} - T^3 \frac{\partial^4 G}{\partial a_i \partial a_k \partial a_l \partial a_m} = T^2 F_{ik}^{-1} F_{lm}^{-1} + T^2 F_{il}^{-1} F_{km}^{-1} \\ &+ T^2 F_{im}^{-1} F_{kl}^{-1} + T^3 \frac{\partial F_{ik}^{-1}}{\partial \xi_p}\frac{\partial F_{pl}^{-1}}{\partial \xi_q} F_{qm}^{-1} + T^3 \frac{\partial^2 F_{ik}^{-1}}{\partial \xi_p \partial \xi_q} F_{pl}^{-1} F_{qm}^{-1}.\end{aligned} \tag{A.5}$$

The derivatives in formulas (A.3)–(A.5) are taken at the equilibrium values of all the variables, and F_{ik}^{-1} is an element of the inverse of the matrix with elements $F_{ik} = \partial^2 F / \partial\xi_i \partial\xi_k$.

The free energy also has the meaning of a free energy of nonequilibrium states, as this is defined by Lenontovich.[41] When the role of the variables ξ_i is played by the quantities $\eta(\mathbf{k})$, we have

$$\begin{aligned}F = F_0 + \frac{V}{2}\sum_{\mathbf{k}} A(T,\mathbf{k})\eta(\mathbf{k})\eta(-\mathbf{k}) + V\sum_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3=0} B'(T,\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3) \\ \times \eta(\mathbf{k}_1)\eta(\mathbf{k}_2)\eta(\mathbf{k}_3) + \frac{V}{4}\sum_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4=0} B(T,\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4)\eta(\mathbf{k}_1)\eta(\mathbf{k}_2)\eta(\mathbf{k}_3)\eta(\mathbf{k}_4)\end{aligned} \tag{A.6}$$

In the case $\tau < 0$ special clarification of the meaning of the expression (A.6) is necessary. This is connected with the fact that the equilibrium state here is degenerate, while the Leontovich definition of the free energy, like the derivation of formulas (A.3)–(A.5), stipulates averaging over a statistical ensemble of systems. It is obvious that the ensemble average of the quantity $\eta(0)$ is equal to zero both for $\tau > 0$ and for $\tau < 0$; but the system's being in the low-symmetry phase corresponds, in the language of the statistical ensemble, to the presence of large fluctuations that do not vanish as $V \to \infty$: $\langle \eta^2(0) \rangle = \eta_0^2$. According to (A.3) this means that if we consider the expression (A.6) as an expansion about the mean value of η, then $A(T,0) \to 0$ as $V \to \infty$. It can be shown that in this limit other coefficients in formula (A.6) also vanish.

There exists, however, a well-known procedure for eliminating such difficulties.[43] We assume that an external field, conjugate to η, is applied to the system. Passing first to the limit $V \to \infty$ and then letting the magnitude of the field tend to zero, we find that $\langle \eta(0) \rangle$ is nonzero and equal to one of the two equilibrium values of η, and the fluctuations of all quantities disappear when $V \to \infty$. The expression (A.6) now corresponds to an expansion about the corresponding equilibrium value of η. As an equivalent procedure, it can be assumed that the summation in (A.6) is performed over $\mathbf{k} \neq 0$, and $\eta(0)$ is a parameter of the Hamiltonian, i.e., in the calculation of F integration over this variable is not performed.

We emphasize that in neither of these approaches does the Leontovich-type free energy used in the calculation of the fluctuations have the form that is taken in the Landau theory of phase transitions. This follows not only from the arguments put forward above but also from the fact that, according to (A.3) and (A.6),

$$\langle |\eta(\mathbf{k})|^2 \rangle = TV^{-1}A^{-1}(T,\mathbf{k}), \tag{A.7}$$

i.e., $A(T,\mathbf{k}) > 0$ for all $\mathbf{k}$. At the same time, it is assumed in the Landau theory that for $\tau < 0$ the coefficient of $\eta(\mathbf{k})\eta(-\mathbf{k})$ in the expression for the free energy is negative in the region $kr_c < 1$. For the temperature region $\tau < 0$ the free energy figuring in the Landau theory can have the meaning of an incomplete free energy (cf., e.g., [44]).

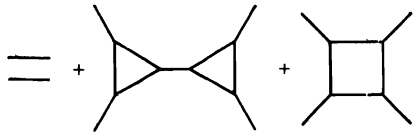
We shall write out formulas for the average fluctuations that appear in the expressions (12) and (21). In our previous paper[6] the calculation of the third-order fluctuation is annotated in detail. There it is shown that

$$\begin{aligned}&\langle \eta(\mathbf{q})\eta(-\mathbf{q}-\mathbf{k})\eta(\mathbf{k}) + \text{c.c.} \rangle \\ &= -6(T/V)^2 \chi(\mathbf{k})\chi(\mathbf{q})\chi(\mathbf{k}+\mathbf{q})\left(B'(-\mathbf{q},\mathbf{q}+\mathbf{k},\mathbf{k}) + B'(\mathbf{q},-\mathbf{q}-\mathbf{k},\mathbf{k})\right).\end{aligned} \tag{A.8}$$

Here $\chi(\mathbf{k})$ has the meaning of the generalized susceptibility corresponding to $\eta(\mathbf{k})$, and is defined by the relation

$$\frac{\partial^2 F}{\partial\eta(\mathbf{k})\partial\eta(-\mathbf{k})} = V\chi^{-1}(\mathbf{k}).$$

The calculations of the average fourth-order fluctuation are carried out analogously. We give the final result:



$$\langle\eta(\mathbf{k})\eta(\mathbf{q}-\mathbf{k})\eta(\mathbf{k}')\eta(-\mathbf{q}-\mathbf{k}')\rangle=(T/V)^3\chi(\mathbf{k})\chi(\mathbf{k}-\mathbf{q})$$
$$\times[\delta_{\mathbf{k}',\mathbf{k}-\mathbf{q}}+\delta_{\mathbf{k}',-\mathbf{k}}]+36(T/V)^3[B'(\mathbf{k}+\mathbf{k}',-\mathbf{k},-\mathbf{k}')$$
$$\times B'(-\mathbf{k}-\mathbf{k}',\mathbf{k}-\mathbf{q},\mathbf{k}'+\mathbf{q})\chi(\mathbf{k})\chi(\mathbf{k}-\mathbf{q})\chi(\mathbf{k}')\chi(\mathbf{k}'+\mathbf{q})\chi(\mathbf{k}+\mathbf{k}')$$
$$+B'(\mathbf{k}-\mathbf{k}'-\mathbf{q},-\mathbf{k},\mathbf{k}'+\mathbf{q})B'(\mathbf{q}-\mathbf{k}+\mathbf{k}',-\mathbf{q}+\mathbf{k},-\mathbf{k}')\chi(\mathbf{k})\chi(\mathbf{k}-\mathbf{q})$$
$$\times\chi(\mathbf{k}')\chi(\mathbf{k}'+\mathbf{q})\chi(\mathbf{k}-\mathbf{k}'-\mathbf{q})+B'(-\mathbf{q},-\mathbf{k}',\mathbf{q}+\mathbf{k}')$$
$$\times B'(-\mathbf{k},\mathbf{k}-\mathbf{q},\mathbf{q})\chi(\mathbf{q})\chi(\mathbf{k}-\mathbf{q})\chi(\mathbf{k}')\chi(\mathbf{k})\chi(\mathbf{k}'+\mathbf{q})]$$
$$-6(T/V)^3B(-\mathbf{k},\mathbf{k}-\mathbf{q},-\mathbf{k}',\mathbf{k}'+\mathbf{q})\chi(\mathbf{k})\chi(\mathbf{k}-\mathbf{q})\chi(\mathbf{k}')\chi(\mathbf{k}'+\mathbf{q}). \quad (A.9)$$

The structure of formula (A.9) can be elucidated by means of a diagram (the figure), in which the lines correspond to the quantities $TV^{-1}\chi(\mathbf{k})=\langle\eta(\mathbf{k})\eta(-\mathbf{k})\rangle$, the triangles to the complete three-point functions $6VT^{-1}B'(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3)$ and the square to the four-point function $6VT^{-1}B(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4)$.

[1)]From the point of view of symmetry theory, it does not matter which of P_j and u_{lm} is called the order parameter. In specific cases we start from a microscopic picture of the transition or from the experimentally determined temperature dependence of the corresponding constants of the crystal.

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