ON THE SCATTERING OF X-RAYS AND THERMAL NEUTRONS BY SINGLE-COMPONENT CRYSTALS NEAR PHASE-TRANSITION POINTS OF THE SECOND KIND

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A study is made of peculiarities of the scattering of x-rays and thermal neutrons by single-component crystals near phase-transition points of the second kind. Explicit account is taken of geometric distortions of the crystal lattice owing to fluctuations of the internal parameters characterizing long-range order. The general case is considered, in which the long-range order is characterized not by just one parameter, but by several. Inclusion of the geometrical distortions can lead to a decided change of the qualitative pattern of intensity distribution of the diffuse scattering in the reciprocal lattice space, and in particular to the appearance of components that are inversely proportional to the distance from a point of the reciprocal lattice, i.e., that become infinite with approach to such points. Near a phase-transition point of the second kind peculiarities can be observed in the distribution of the diffuse scattering both near superlattice reflections and also near the main regular reflections. The type of temperature dependence shown by the scattering and its position in the reciprocal lattice space depend in an essential way on the symmetry of the crystal. Ferroelectric crystals are discussed in greater detail. In this case the parameters that determine the intensity of the diffuse scattering near reciprocal lattice points can be found by means of independent experiments.

In the preceding paper[1] (cited hereafter as I) the discussion of the geometrical distortions of the crystal lattice of a solid solution was based on a method in which the distortions were related to waves of variation of composition or of the long-range order parameters. Important lattice distortions can also arise from fluctuations of the internal parameters that characterize the long-range order in single-component crystals (ferroelectric, ferromagnetic, antiferroelectric, and antiferromagnetic substances, quartz, etc.). As Landau has shown,[2] particularly large fluctuations of the long-range order parameters, giving rise to anomalously large scattering of x-rays, must occur near a phase-transition point of the second kind. In Ref. 2 the calculation of the scattering was carried out without including the geometrical distortions of the lattice, and the case considered was that in which the long-range order can be characterized by only one parameter. In a number of cases, however, as can be seen from the results obtained for solid solutions (cf. I), the presence of geometrical distortions leads to the appearance of qualitatively new effects. Therefore the purpose of the present paper is to discuss the scattering of x-rays and thermal neutrons near phase-transition points of the second kind, including the effects of geometrical distortions of the crystal lattice. In addition, the results of Landau will be extended to the case in which the change of the long-range order in the crystal is characterized not by just one, but by several parameters. The scattering by ferroelectric crystals is considered in greater detail.

We consider the case of scattering of monochromatic radiation by a single crystal, and take into account neither scattering by thermal vibrations, nor Compton scattering of x-rays and magnetic scattering of neutrons by the electron shells of atoms. The calculation is carried out in the framework of the kinematic theory of scattering. For definiteness the formulas given will be written in terms appropriate to the scattering of x-rays. Formulas for the scattering of neutrons can be obtained from them essentially by just a simple change of notation.

Let us first consider the case in which the values of the long-range order parameters that are subject to anomalously large fluctuations can be uniquely specified by giving the values of the components of the spontaneous polarization, P_i. This is the case, for example, in $BaTiO_3$. In addition to the long-range order parameters, there can also be fluctuations in the internal parameters that characterize the local order in the distribution of

atoms at the lattice points. But in the cases considered with below, in which the fluctuations of the P_i lead to anomalously large scattering, fluctuations of the local-order parameters evidently play a relatively small part and will not be taken into account.

The fluctuations $P_i - \overline{P}_i$ of the polarization components can be expanded in Fourier series:

$$P_{it} - \overline{P}_i = \sum_{\mathbf{k}}' [P_{\mathbf{k}i} \exp(-i\mathbf{k}\mathbf{R}_t) + P^*_{\mathbf{k}i} \exp(i\mathbf{k}\mathbf{R}_t)]. \quad (1)$$

Here $\overline{P}_i$ is the average equilibrium value of the i-th component of the polarization vector, P_{it} is the value of P_i corresponding to cell number t, $\mathbf{R}_t$ is the radius vector of this cell, and the prime on the summation sign means that the summation is taken over values of the vector $\mathbf{k}/2\pi$ that lie in a half-cell of the reciprocal lattice and satisfy cyclic conditions, the term with $\mathbf{k} = 0$ being excluded. The polarization wave for each value of $\mathbf{k}$ corresponds to a wave of displacements of the atoms. In what follows we shall study the diffuse scattering only in the neighborhood of the regular Laue reflections (where this scattering is anomalously large). Because of this we can restrict ourselves to the consideration of long waves of fluctuation. For these waves the displacements of lattice points of different types are almost identical (cf. Sec. 2 in I), so that the displacements of the various atoms of cell number t corresponding to the $\mathbf{k}$-th polarization wave are practically the same and can be written in the form:

$$\delta\mathbf{R}_{t\mathbf{k}} = i \sum_{i=1}^{3} a_{\mathbf{k}i} \mathbf{k} k^{-2} [P_{\mathbf{k}i} \exp(-i\mathbf{k}\mathbf{R}_t) - P^*_{\mathbf{k}i} \exp(i\mathbf{k}\mathbf{R}_t)], \quad (2)$$

where $\mathbf{k}'$ is a vector along the displacement of the atoms in the $\mathbf{k}$-th wave, with $k' = k$.

The intensity of the x-ray scattering in the neighborhood of the Laue reflections, expressed in electronic units, can be represented in the following form:

$$I = \overline{\left| \sum_t f_{lt} \exp(i\mathbf{q}_1, \mathbf{R}_t + \delta\mathbf{R}_t) \right|^2}. \quad (3)$$

Here $\mathbf{q}_1$ is the difference of the wave vectors of the scattered and incident waves, the averaging is taken over all possible configurations of the atoms, and f_{lt} is the structure factor of cell number t corresponding to the l-th Laue reflection and calculated with inclusion of effects of geometrical distortions. The quantity f_{lt} can be written as the sum of the average value of the structure factor corresponding to the l-th reflection, $\overline{f}_l$, and the departure from the average value, Δf_{lt}, corresponding to cell number t. In the calculation of f_{lt} the atomic factors for the individual lattice points must be multiplied by factors $\exp(-L_\gamma/2)$ for each type γ of lattice point, to take account of the weakening of the amplitude because of the geometrical distortions (cf. Sec. 2 in I). Since in the determination of the L_γ one must include not only the long but also the short waves, we shall not give formulas for these quantities, recalling that the structure factor $\overline{f}_l$ can be determined directly from x-ray data on the intensities of the regular reflections.

When the components of the polarization vector are changed by amounts ΔP_i the average structure factor $\overline{f}_l$ is changed by the amount $d_{li}\Delta P_i$, where d_{li} depends on the number of the reflection (for some reflections $d_{li} = 0$). Here and in what follows, summation over repeated indices i is understood. The deviation of the atomic factor of cell number t from the average value is $(P_{it} - \overline{P}_i) d_{li}$. (Some difference is possible between the values of d_{li} that are involved in the change of the f_{lt} by fluctuations and are defined for unchanged values of the short-range order parameters and the values of d_{li} that correspond to the equilibrium values $\overline{f}_l$ and are defined for values of the short-range order parameters that do not vary with changes of the $\overline{P}_i$.) For the neighborhood of a regular reflection, where we can use for the calculation of the diffuse reflection the d_{li} corresponding to that reflection and the displacements of the atoms can be determined according to Eq. (2) without taking account of the atomic structure, by Eqs. (3) and (2) the contribution to the scattering amplitude from elementary cell number t is given by

$$\left[\overline{f}_l + \sum_{\mathbf{k}}' (d_{li} - \overline{f}_l a_{\mathbf{k}i} \mathbf{k}'\mathbf{q}_1/k^2) P_{\mathbf{k}i} \exp(-i\mathbf{k}\mathbf{R}_t) + \sum_{\mathbf{k}}' (d_{li} + \overline{f}_l a_{\mathbf{k}i} \mathbf{k}'\mathbf{q}_1/k^2) P^*_{\mathbf{k}i} \exp(i\mathbf{k}\mathbf{R}_t) \right] \exp(i\mathbf{q}_1\mathbf{R}_t). \quad (4)$$

In the summation of the expression (4) over the elementary cells (over t) near regular reflections (where a condition of the type of Eq. (9) of I is satisfied), the most important part in the sum over $\mathbf{k}$ is played by the term with $\mathbf{k} = \mathbf{q}$ or $\mathbf{k} = -\mathbf{q}$, where $\mathbf{q} = \mathbf{q}_1 - 2\pi\mathbf{K}_l$, and $\mathbf{K}_l$ is the vector of the reciprocal lattice lying closest to the end of the vector $\mathbf{q}_1/2\pi$ and corresponding to the l-th reflection (the "reduced" vector $\mathbf{q}/2\pi$ lies in the first cell of the reciprocal lattice). Therefore, squaring the indicated sum in accordance with Eq. (3), we find that the intensity of the scattering is given by

$$I = 8\pi^3 \frac{N_0}{\Delta'} \overline{|f_l|^2} \delta(\mathbf{q}_l) + N_0^2 \left| (\overline{f}_l \frac{\mathbf{q}_1\mathbf{q}}{q^2} a_{\mathbf{q}i} - d_{li}) P_{\mathbf{q}i} \right|^2, \quad (5)$$

where N_0 is the number of elementary cells in the crystal and Δ' is the volume of a cell. The

first term, involving the δ function, gives the intensity of the regular reflection, and the second term gives the intensity I_F of the diffuse scattering.

To carry out the averaging in Eq. (5) one can use the probability distribution for the Fourier components $P_{\mathbf{ki}}$ of the polarization fluctuations for small $\mathbf{k}$:

$$w \sim \exp\left[-\frac{V}{kT}\sum_{\mathbf{k}}{}'\left(\frac{\partial^2\varphi}{\partial P_i \partial P_j} + A_{ijmn}k_m k_n\right)P_{\mathbf{k}i}P^*_{\mathbf{k}j}\right]. \quad (6)$$

Here φ is the thermodynamic potential per unit volume, and A_{ijmn} is a tensor of the fourth order. Using the fact that $\partial^2\varphi/\partial P_i \partial P_j = \kappa^{-1}_{ij}$, where κ^{-1}_{ij} is a tensor, the reciprocal of the electric susceptibility tensor,[3] we get from Eqs. (5) and (6):

$$I = 8\pi^3 \frac{N_0}{\Delta'}|\bar{f}_l|^2 \delta(\mathbf{q}_l) + \frac{N_0 kT}{\Delta'}\left(\bar{f}_l a_{\mathbf{q}i}\frac{\mathbf{q}_l\mathbf{q}'}{q^2} - d_{li}\right)\left(\bar{f}_l a_{\mathbf{q}j}\frac{\mathbf{q}_l\mathbf{q}'}{q^2} - d_{lj}\right) \times (\kappa^{-1} + A_{mn}q_m q_n)^{-1}_{ij}. \quad (7)$$

Here $(\kappa^{-1} + A_{mn}q_m q_n)^{-1}_{ij}$ are the components of a tensor, the reciprocal of the tensor $\kappa^{-1}_{ij} + A_{ihmn}q_m q_n$. For sufficiently small values of q the last factor in Eq. (7) is just the electric susceptibility κ_{ij}.

The quantities $d_{\ell i}$ appearing in Eq. (7) can be determined from the dependence of the structure factors (i.e., the intensities of the regular reflections) on the polarization (or on the intensity of the external electric field). One can find the quantities $a_{\mathbf{q}i}$ by considering the expression for the stress tensor in an inhomogeneously polarized crystal. If we note that in the presence of fluctuations $\delta\mathbf{P}$ the expression for the free energy of the deformed crystal contains the term $-\epsilon_{ijm}u_{ij}\delta P_m$, we get for the components σ_{ij} of the stress tensor the expression

$$\sigma_{ij} = \lambda_{ijmn}u_{mn} - \varepsilon_{ijm}\delta P_m, \quad (8)$$

where u_{mn} are the components of the deformation tensor and λ_{ijmn} are the components of the elastic modulus tensor. In order to get the formula for $a_{\mathbf{q}m}$ we must insert in Eq. (8) instead of δP_m a periodic function corresponding to the $\mathbf{k}$-th fluctuation wave, and instead of u_{mn} the components of the deformation tensor corresponding to the wave of geometrical distortion produced by the fluctuation wave in question when the boundaries of the crystal are kept motionless. Then, noting that $\partial\sigma_{ij}/\partial x_j = 0$, and carrying out the same argument as for the derivation of Eq. (16) of I, we get three equations for $a_{km}k'_r$:

$$\lambda_{ijpr}n_i n_p a_{km}k'_r/k = \varepsilon_{ijm}n_j \quad (i = 1,2,3), \quad (9)$$

where n_i are the direction cosines of the wave vector $\mathbf{k}$. Here it is clear that the third-order tensor ϵ_{ijm} is to be determined from the dependence of the stresses (or deformations) on the polarization (i.e., on the external electric field). Thus, just as in the case of scattering by solid solutions, all the parameters appearing in the expression for the diffuse scattering, with the exception of A_{ijmn}, can be determined from independent experiments.

As follows from the thermodynamic theory of ferroelectricity,[4] at a phase transition point of the second kind the components of the reciprocal dielectric susceptibility tensor κ^{-1}_{ij} go to zero, and by Eq. (7) this has the consequence that an anomalously large diffuse scattering should appear near this point. In this connection the nature of the dependences of I_F on the temperature and on $\mathbf{q}$ depends on the symmetry of the crystal. Near the temperature T_0 of a phase transition of the second kind the tensor ϵ_{ijm} can be written in the form

$$\varepsilon_{ijm} = \varepsilon^0_{ijm} + \delta_{ijmn}P_n.$$

Let us first consider the case in which the tensor components ϵ^0_{ijm} are different from zero (i.e., in which there is a piezoelectric effect in the non-ferroelectric phase). For this case Eqs. (7) and (9) show that for reflections for which $\bar{f}_\ell \neq 0$ in the non-ferroelectric phase, both above and below the temperature T_0 there is a term in the expression for I_F that has the factor q^{-2} and thus goes to infinity as we approach a point of the reciprocal lattice. For sufficiently small q the coefficient of this term contains κ_{ij}, i.e., it becomes anomalously large for $T \to T_0$ (this coefficient is, of course, decidedly dependent on the quantity ϵ^0_{ijm}). The terms containing the factor q^{-2} must lead to a strong anisotropy of the intensity distribution of the diffuse scattering, regarded as a function of position in the space in the reciprocal lattice, since they are proportional to $\cos^2\varphi$, where φ is the angle between the vectors $\mathbf{q}'$ and $\mathbf{q}_l$. Since according to Eq. (9) the $a_{\mathbf{q}m}$ can also depend strongly on the orientation of the vector $\mathbf{q}$, this anisotropy does not reduce to just a proportionality to $\cos^2\varphi$, and the pattern of the intensity distribution of the diffuse scattering will be different in the neighborhoods of different reciprocal lattice points. The term proportional to q^{-2} is absent for small scattering angles, when $\mathbf{q} = \mathbf{q}_l$, and the coefficient of this term increases with increase of the order of the reflection (with increase of $|\mathbf{q}_l|$).

Besides the terms containing factors q^{-2} and q^{-1}, for reflections with $d_{\ell i}$ different from zero there is also a sharp increase near the temperature T_0 in a term proportional to $d_{\ell i}^2$, which plays an important role for somewhat larger values of q. If $\bar{f}_\ell = 0$ for $T > T_0$, only this term remains in the non-ferroelectric phase, and near such regular reflections the intensity of the diffuse scattering does not go to infinity for $q \to 0$, but reaches its maximum value (which increases rapidly as $T \to T_0$) at the point $\mathbf{q} = 0$. For $T < T_0$ the quantity $\bar{f}_\ell$ in this case is small near the temperature T_0, so that the terms proportional to q^{-2} have a small proportionality coefficient. Along with the sharp increase of I_F, near the temperature T_0 there must be an increase of the quantities L_γ that determine the intensities of the regular reflections. It can be shown that near the temperature T_0 these quantities contain terms proportional to $\kappa^{1/2}$. This sort of qualitative picture of the intensity distribution should be found, for example, in scattering by crystals of the type of Rochelle salt, KH_2PO_4, etc.

The qualitative picture of the temperature dependence of I_F is changed if the ϵ^0_{ijm} vanish identically because of requirements imposed by the symmetry of the crystal. This occurs if the crystal in the non-ferroelectric phase has a center of symmetry. In this case in the non-ferroelectric phase Eqs. (7) and (9) indicate that even in the neighborhoods of reflections at which $\bar{f}_\ell \neq 0$ the coefficients of q^{-2} and q^{-1} arising from the polarization fluctuations considered here are equal to zero (there can be some nonvanishing contributions to these coefficients, arising from fluctuations in the short-range order). In the ferroelectric phase the coefficient in question is proportional to $\bar{P}^2$ (since $a_{\mathbf{q}m} \sim \bar{P}$), where $\bar{P}$ is the spontaneous polarization, and because of this for small values of $\bar{P}$, near an ordinary phase transition point of the second kind, the term proportional to q^{-2} does not become as large as in the case considered above. The term proportional to $d_{\ell i}^2$ here gives the anomalously large scattering at the transition point. But near the critical point at which the curve of points of phase transition of the second kind goes over into a curve of phase transition of the first kind, the product $\bar{P}^2\kappa_{ij}$ is very large, so that just as in the case considered above ($\epsilon^0_{ijm} \neq 0$) the term containing the factor q^{-2} becomes anomalously large for the ferroelectric phase as we approach the critical point (the same thing happens for phase transitions of the first kind, near the critical point). In the non-ferroelectric phase the coefficient of q^{-2} must be considerably smaller. The scattering proportional to q^{-2} should appear particularly strongly in crystals with a large discontinuity of the coefficient of thermal broadening. Crystals with $\epsilon^0_{ijm} = 0$ include, for example, ferroelectrics of the type of $BaTiO_3$. In these crystals the polarization is directed along the cubic axis (the z axis), and the only nonvanishing components of the electric susceptibility tensor are $\kappa_{11} = \kappa_{22}$ and κ_{33}. In this case the explicit form of the temperature dependence of I_F can be found if we substitute for κ_{ij} and $\bar{P}$ (involved in $a_{\mathbf{q}m}$) in Eq. (7) the expressions for these quantities obtained in the theory of ferroelectricity [for example, Eqs. (19) and (20) of Ref. 3].

One can deal in the same way with the general case of crystals observed near phase transition points of the second kind. Here the inhomogeneity of the crystal is characterized by the fluctuations of the quantities c_i which determine the change of the symmetry of the crystal in the phase transition. These quantities can be taken to be the coefficients in the expansion of the change $\delta\rho$ of the density function of the crystal in the transition: $\delta\rho = \sum c_i\varphi_i$, where the φ_i form the basis of the irreducible representation of the symmetry group of the more symmetrical phase which is manifested in the transition to the less symmetrical phase.[5] It is clear that the intensity of the scattering arising from the fluctuations of the c_i can be determined in the same way as the intensity of the scattering arising from the fluctuations of the P_i, i.e., by a formula analogous to Eq. (7):

$$I = 8\pi^3 \frac{N_0}{\Delta'} |\bar{f}_l|^2 \delta(\bar{\mathbf{q}}_l) + \frac{N_0 kT}{\Delta'} \left(\bar{f}_l a_{\mathbf{q}i} \frac{\mathbf{q}_l\mathbf{q}'}{q^2} - d_{li}\right)\left(\bar{f}_l a_{\mathbf{q}j} \frac{\mathbf{q}_l\mathbf{q}'}{q^2} - d_{lj}\right) \varphi^{-1}_{\mathbf{q}ij}. \quad (10)$$

The summations over i and j are here taken from 1 to p, where p is the number of functions forming the basis of the irreducible representation in question. The $\varphi^{-1}_{\mathbf{q}ij}$ are the elements of the matrix reciprocal to the matrix $\partial^2\varphi/\partial c_i \partial c_j + A_{ijmn}q_m q_n$. The quantities $d_{\ell i}$ are the coefficients in the expansion of the $\bar{f}_\ell$ in terms of the c_i, so that they can be determined from the change of the $\bar{f}_\ell$ (the intensities of the regular reflections) below the transition temperature. The coefficients $a_{\mathbf{q}i}$ can be found from Eq. (9) if we substitute instead of the ϵ_{ijm} the quantities ϵ'_{ijm} that give the dependence of the stress tensor components on the c_i:

$$\sigma_{ij} = \lambda_{ijmn}u_{mn} - \varepsilon'_{ijm}c_m. \quad (11)$$

The application of these formulas to various systems (antiferroelectrics, ferromagnetic sub-

stances, antiferromagnetics, quartz near the point of the $\alpha-\beta$ transition, and so on) and the determination of the connections between the c_i and the macroscopic parameters of the crystal require special considerations involving the concrete changes of symmetry in the various transitions. A qualitative picture of the dependence of the intensity of the scattering on the temperature and on $\mathbf{q}$ can, however, be obtained from the general formulas given here. As is well known,[5] the derivatives $\partial^2\varphi/\partial c_i \partial c_j$ go to zero at a phase transition point of the second kind. Because of this an anomalously large scattering should be observed near the temperature T_0. As in the case of ferroelectric crystals considered above, the type of dependence of I_F on T and $\mathbf{q}$ depends essentially on whether or not there is a term of degree zero in the expansion of ϵ'_{ijm} in powers of the c_i. Depending on this, one gets a qualitative picture of the intensity distribution of the scattering which is of some one of the types discussed above. In particular, in the neighborhoods of those regular reflections at which $d_{\ell i} = 0$ (in the case of x-ray scattering by ferromagnetic and antiferromagnetic crystals $d_{\ell i} = 0$ for all reflections), there must be characteristic peculiarities of I_F near the temperature T_0 in crystals for which $\epsilon'^{0}_{ijm} \neq 0$, and also in those for which $\epsilon'^{0}_{ijm} = 0$ but at the transition point there is a large change of the thermal expansion coefficient (neighborhood of the critical point). In the neighborhoods of reflections for which $d_{\ell i} \neq 0$ the expressions for I_F always contain large terms not proportional to q^{-2}. In particular, characteristic peculiarities in the intensity distribution of the diffuse scattering should be found in quartz near the point of the $\alpha-\beta$ transition.

In conclusion we remark that near a phase transition point of the second kind there should also be characteristic peculiarities in the intensity distribution of the diffuse scattering by the thermal vibrations. This problem will be dealt with elsewhere.

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75