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Theory of Diffuse Scattering of X-rays by Solid Solutions. I.

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The intensity of the diffuse scattering of x-rays by mixed crystals has been determined by means of a phenomenological treatment. Thermodynamic quantities which may be found from other experiments appear in the expressions for the background intensity. Characteristic features of the scattering in the neighborhood of points of phase transitions of the second kind and of critical points on the dissociation curve have been investigated, and also the scattering by weak, by ideal and by almost completely ordered solid solutions has been examined.

X-RAYS scattered by a crystal* form sharp lines on an x-ray photograph corresponding to definite conditions of reflection, and also give rise to a diffuse background. Diffuse scattering of waves by a solid, which is not accompanied by a change in wavelength, is associated with some sort of deviations from ideal periodicity of the crystal: either thermal vibrations or static deviations from periodicity. In the present article we shall not take into account effects related to thermal and zero-point vibrations of the atom and also to Compton scattering. It is also assumed that all the atoms of the solid solution are situated exactly at the lattice points. The neglect of the geometric imperfections of the lattice introduced by these assumptions is approximately justified if the sizes of the various atoms of the solution differ little from each other, while the imperfections associated with a plastic deformation have been removed. Thus, the only cause for a deviation from periodicity of the crystal which is taken into account in this paper is the more or less random distribution of the atoms of the solution among the various lattice points. Because of the unequal scattering properties of the various kinds of atoms, this also leads to diffuse scattering.

An investigation of the scattering of x-rays presents a more complicated problem than the scattering of light, since the wavelengths of x-rays are of the same order of magnitude as the interatomic distances in the crystal. The situation is simplified considerably if the direction of the scattered wave, which corresponds to diffuse scattering, is

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* In what follows we shall examine the scattering of x-rays. However, all the results apply equally well to neutron scattering (not taking into account the background which is connected with the presence of isotopes and with magnetic scattering). In such a case the atomic scattering factors should be interpreted as the neutron scattering factors averaged over the isotopes. The results given below are also applicable in the study of scattering of other types of waves, provided the Born approximation is applicable and the scattering centers are situated at the lattice points. Thus, one may study the scattering of electrons, and the scattering of elastic waves by the fluctuations in the isotopic composition in a solution of isotopes. In an analogous way one may study the scattering of sound waves in the more general case of mixed crystals when not only the masses of the atoms are different, but also the forces acting between them.

close to the direction of the coherent wave corresponding to some particular condition for interference, or which is close to the direction of the incident beam. In such a case the differences in phase of waves scattered by different atoms begin to deviate appreciably from a value which is an integral multiple of π only if the distances between the atoms are much larger than the lattice constant. Therefore, a phenomenological examination of scattering becomes possible for the investigation of background near the lines on an x-ray photograph and near the incident beam. In such an investigation the crystal is regarded as a purely periodic structure which consists of effective atoms on top of which are superimposed fluctuations in the composition and in the degree of long range order. The periodic structure guarantees the production of the coherent wave, while the fluctuations give rise to the diffuse scattering. In calculating the intensity of the background near the lines on the x-ray photograph only those fluctuations are important which are spread over a large number of lattice constants. The probabilities of such fluctuations, and consequently the intensity of the scattered radiation, may be expressed in terms of certain thermodynamic quantities without using a specific model of the solution.

A phenomenological investigation of the scattering of x-rays by crystals was first carried out by Landau[1] who investigated the scattering in the neighborhood of superstructure lines at a temperature close to the temperature of a phase transition of the second kind. In this work it was assumed that the diffuse scattering is brought about by fluctuations in the degree of long range order. The results of Landau are applicable only to those crystals for which only fluctuations in the long range order are significant (for example, in the case of orientational ordering). In mixed crystals, and in particular in alloys, in addition to fluctuations in the long range order, there exist also fluctuations in composition. Since they are not statistically independent one should, in determining the probability of fluctuations, consider simultaneously the deviations from equilibrium values both of the composition and of the degree of long range order. Using a method analogous to that developed by Landau[1] we shall determine, by calculating such probabilities, the intensity of the background near the superstructural and the structural lines, and also for small scattering angles.

Calculations are carried out for those cases in which expressions for the thermodynamic potential Φ of the mixed crystal are known. Thus, we shall examine the scattering in the neighborhood of the points of ordering, which takes place as a phase transition of the second kind, when one may use Landau's thermodynamic theory. In a similar manner one may obtain an expression for Φ near the critical point on the dissociation curve. In addition, an investigation is made of the scattering by ideal, by weak, and by almost completely ordered solutions where the expressions for Φ are also known as functions of the composition and of the degree of ordering.

1. GENERAL EXPRESSIONS FOR THE INTENSITY OF THE BACKGROUND NEAR LINES ON AN X-RAY PHOTOGRAPH

We shall examine a binary solid solution $A-B$. In the disordered state it has a crystal lattice of the Bravais type; the probabilities of the various lattice points being occupied by atoms of a given kind are all the same, and are equal to the corresponding atomic concentrations $\bar{c}_A$ and $\bar{c}_B$. If the solution goes over into an ordered state, then its lattice points are subdivided into several different kinds, and the probabilities of the different types of lattice points being occupied are no longer the same. In what follows we shall restrict ourselves to the case when in the ordered state the crystal lattice is subdivided into points of only two types, with the number of points of the first and the second kinds being equal, and with the amplitudes of the radiation scattered by atoms situated at lattice points of either kind and leading to the formation of superstructure lines also being equal. In this case the probabilities of the lattice points being occupied by atoms A and B may be specified by means of a single degree of long range order $\bar{\eta}$:

$$p_A^{(1)} = \bar{c}_A + {}^1/_2\bar{\eta}; \quad p_A^{(2)} = \bar{c}_A - {}^1/_2\bar{\eta};$$

$$p_B^{(1)} = \bar{c}_B - {}^1/_2\bar{\eta}; \quad p_B^{(2)} = \bar{c}_B + {}^1/_2\bar{\eta}.$$

In spite of the limitations introduced above, this procedure will apparently include all the ordered solutions known at present that correspond to the stoichiometric composition AB, and all the disordered solutions.

As is well known, the amplitude of the monochromatic radiation scattered by a single crystal may be represented within the framework of the kinematic scattering theory in the form

$$a = \int \rho(\mathbf{r})\, e^{i(\mathbf{k}_2-\mathbf{k}_1,\, \mathbf{r})}\, d\tau. \tag{1}$$

Here a is expressed in electronic units, $\mathbf{k}_1$ and $\mathbf{k}_2$ are propagation vectors of the incident and the scattered waves, $\rho(\mathbf{r})$ is the density of the electronic charge in the crystal divided by the charge of the electron.

The calculation of the Fourier component of $\rho(\mathbf{r})$ which enters Eq. (1) is considerably simplified if one makes use of the assumption made above that all the atoms are situated exactly at the lattice points of an ideally periodic lattice, and if one also assumes that the distribution of the charge density of a given atom does not depend on the kind of atoms surrounding it, on the composition, or on the degree of order. The latter assumption holds with a sufficient degree of accuracy for almost all the atoms, with the exception of the lightest ones. The probability density $\rho(\mathbf{r})$ in a mixed crystal is a function of coordinates which has an extremely complicated variation in space. However, since the exponential factor (1) remains constant in the plane perpendicular to $\mathbf{k}_2 - \mathbf{k}_1$, the function $\rho(\mathbf{r})$ can be replaced for integration purposes by a function which is averaged over the different kinds of atoms in the plane referred to above. If one takes into account the simplifying assumptions made above, then this averaged function will have the following form:

$$\bar{\rho}(\mathbf{r}) = c_A \rho_A(\mathbf{r}) + c_B \rho_B(\mathbf{r}) + \eta \rho'(\mathbf{r}). \tag{2}$$

Here c_A, c_B and η denote the atomic concentration of the atoms A and B and the degree of long range order in the plane under consideration, the functions $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$ have a symmetry identical with the symmetry of the crystal lattice, while $\rho'(\mathbf{r})$ has the symmetry of the ordered crystal which is lower than the symmetry of the lattice; ρ_A, ρ_B and ρ' do not depend on c_A and η. Because of the fluctuations of composition and order present in the crystal, the values of the quantities c_A, c_B and η, corresponding to different planes, differ from the values $\bar{c}_A$, $\bar{c}_B$ and $\bar{\eta}$ averaged over the whole crystal, and are functions of the coordinate specifying the plane.

The periodic functions $\rho_A(\mathbf{r})$, $\rho_B(\mathbf{r})$ and $\rho'(\mathbf{r})$ may be expanded in Fourier series:

$$\rho_A(\mathbf{r}) = \sum_i \lambda_{Ai} e^{i\mathbf{K}_i \mathbf{r}}; \quad \rho_B(\mathbf{r}) = \sum_i \lambda_{Bi} e^{i\mathbf{K}_i \mathbf{r}}; \quad \rho'(\mathbf{r}) = \sum_j \lambda'_j e^{i\mathbf{K}'_j \mathbf{r}}. \tag{3}$$

Here $\mathbf{K}_i$ and $\mathbf{K}'_j$ are 2π times the lattice vectors of lattices which are respectively reciprocal to the lattices of the disordered and the ordered crystal, while in the expansion of $\rho'(\mathbf{r})$, those terms are missing for which $\mathbf{K}'_j$ coincides with any one of the $\mathbf{K}_i$. Substituting Eqs. (2) and (3) into (1) and breaking up the quantities c_A, c_B and η into their average values plus a fluctuating part we whall obtain

$$\begin{gathered} a = 8\pi^3 \sum_i (\bar{c}_A \lambda_{Ai} + \bar{c}_B \lambda_{Bi}) \delta(\mathbf{q}_i) + 8\pi^3 \bar{\eta} \sum_j \lambda'_j \delta(\mathbf{q}'_j) \\ + \sum_i (\lambda_{Ai} - \lambda_{Bi}) \int \Delta c_A e^{i\mathbf{q}_i \mathbf{r}} d\tau + \sum_j \lambda'_j \int \Delta\eta e^{i\mathbf{q}'_j \mathbf{r}} d\tau; \\ \mathbf{q}_i = \mathbf{K}_i + \mathbf{k}_2 - \mathbf{k}_1; \quad \mathbf{q}'_j = \mathbf{K}'_j + \mathbf{k}_2 - \mathbf{k}_1. \end{gathered} \tag{4}$$

Here $\delta(\mathbf{q})$ denotes the product of three δ-functions for the individual components of the vector, and it has been taken into account that $\Delta c_B = -\Delta c_A$.

The intensity of the scattered radiation is proportional to the square of the amplitude a. All the cross terms in the expression for a^2 drop out after statistical averaging. The square of the δ-function defined for a finite volume V (the crystal volume) is equal to this δ-function multiplied by $V/8\pi^3$. Below we shall calculate the intensity of scattering near the principal or the superstructure lines on an x-ray photograph. In this calculation one of the quantities q_i or q'_j is small, and in the expression for a^2 one may keep the square of only that Fourier component of Δc_A or of η, for which the corresponding q is small. As may be easily seen, the squares of all the other Fourier components are in order of magnitude smaller by a factor $q^2 a_0^2$ (where a_0 is the lattice constant) and are not taken into account in what follows. Noting further that

$$\lambda_{Ai} = (N/V) f_A;$$

$$\lambda_{Bi} = (N/V) f_B; \quad \lambda'_j = (N/2V)(f_A - f_B)$$

(N is the total number of all the lattice points, f_A and f_B are the atomic scattering factors of atoms A or B corresponding to the given angle of scattering), we shall find that the intensity of the scattered radiation, expressed in electronic units, near the principal line which corresponds to the $\mathbf{K}_i$ th Fourier component of the electron density is equal to

$$I = 8\pi^3 \frac{N^2}{V}\left[|\bar{c}_A f_A + \bar{c}_B f_B|^2 \delta(\mathbf{q}_i) + \frac{|f_A - f_B|^2}{8\pi^3 V}\left|\int \Delta c_A e^{i\mathbf{q}_i \mathbf{r}}\, d\tau\right|^2\right]. \quad (5)$$

In the same units, the intensity of radiation in the neighborhood of the superstructure line which corresponds to the $\mathbf{K}'_j$-th Fourier component of the electron density $\bar{\rho}(\mathbf{r})$ is determined by means of the formula:

$$I = 2\pi^3 \frac{N^2}{V} |f_A - f_B|^2 \left[\bar{\eta}^2 \delta(\mathbf{q}'_j) + \frac{1}{8\pi^3 V}\left|\int \Delta\eta e^{i\mathbf{q}'_j \mathbf{r}}\, d\tau\right|^2\right]. \quad (6)$$

The first terms in Eqs. (5) and (6) which contain δ-functions determine the intensities of the lines on the x-ray photograph while the second terms determine the intensity of diffuse scattering, i.e., of the background.

Thus the intensity of the background is determined by the distribution throughout the crystal of the fluctuations Δc_A and $\Delta\eta$. As is well known the probability of the occurrence of a certain distribution of fluctuations is proportional to $w \sim e^{-R/kT}$, where R is the minimum work required for the production in a reversible manner of this distribution of fluctuations, and T is the temperature of the external medium. In the case of a cubic crystal the expression for R can be written in the following form:

$$R = {}^1/_2 \int [\varphi_{\eta\eta}(\Delta\eta)^2 + 2\varphi_{\eta c}\Delta\eta\Delta c_A + \varphi_{cc}(\Delta c_A)^2 + \alpha(\nabla\eta)^2 + 2\gamma\nabla\eta\nabla c_A + \beta(\nabla c_A)^2]\, d\tau. \quad (7)$$

Here φ is the thermodynamic potential per unit volume of the crystal

$$\varphi_{\eta\eta} = \partial^2\varphi / \partial\eta^2; \quad \varphi_{\eta c} = \partial^2\varphi / \partial\eta\partial c_A; \quad \varphi_{cc} \equiv \partial^2\varphi / \partial c_A^2;$$

the terms which contain derivatives of c_A and η take into account the inhomogeneity of the fluctuations in space, and play a particularly important role in the neighborhood of critical points and of points of phase transition of the second kind, guaranteeing that the fluctuations at these points remain finite (see Refs. 1-3).

As may be seen from (5) and (6), in order to calculate the diffuse scattering, it is sufficient to know the Fourier components of the fluctuations Δc_A and $\Delta\eta$. Therefore, in what follows we shall determine not the distribution of the fluctuations in composition and in the degree of long range order, but directly the average values of the squares of the Fourier components of these fluctuations. In order to do this, we expand Δc_A and $\Delta\eta$ into Fourier series:

$$\Delta c_A = \sum_{\mathbf{f}} (c_{\mathbf{f}} e^{i\mathbf{f}\mathbf{r}} + c^*_{\mathbf{f}} e^{-i\mathbf{f}\mathbf{r}}), \quad (8)$$

$$\Delta\eta = \sum_{\mathbf{f}} (\eta_{\mathbf{f}} e^{i\mathbf{f}\mathbf{r}} + \eta^*_{\mathbf{f}} e^{-i\mathbf{f}\mathbf{r}}),$$

where $f_x > 0$. Substituting Eqs. (8) into Eq. (7) for the minimum work and performing the integration we shall find that the distribution of the probabilities of the Fourier components of the fluctuations Δc_A and $\Delta\eta$ has the form

$$w \sim \exp\left\{-\frac{V}{kT}\sum\left[(\varphi_{\eta\eta} + \alpha f^2)|\eta_{\mathbf{f}}|^2 + (\varphi_{cc} + \beta f^2)|c_{\mathbf{f}}|^2 + (\varphi_{\eta c} + \gamma f^2)(\eta_{\mathbf{f}} c^*_{\mathbf{f}} + \eta^*_{\mathbf{f}} c_{\mathbf{f}})\right]\right\}. \quad (9)$$

From formula (9) it may be seen that each term in the sum over f depends only on those $\eta_{\mathbf{f}}$ and $c_{\mathbf{f}}$ which correspond to the given f. Consequently, the fluctuations of the Fourier components corresponding to different f are statistically independent (but the fluctuations of the quantities $c_{\mathbf{f}}$ and $\eta_{\mathbf{f}}$ with the same f are statistically dependent), and therefore it is not difficult to find the average squares of these fluctuations. For the calculation of the latter we shall assume that f is sufficiently small (this assumption also justifies the neglect made in (7) of the higher derivatives of c_A and η). We may then retain terms which contain the factor f^2 only close to small terms which are independent of f (which vanish near the point under consideration in the phase diagram), and we may neglect terms proportional to f^4. Substituting the expression obtained in this way for $|\eta_{\mathbf{f}}|^2$ with $\mathbf{f} = \mathbf{q}'_{\mathbf{f}}$ into Eq. (6), and taking into account that

$$\int \Delta\eta e^{i\mathbf{q}'_j \mathbf{r}}\, d\tau = V\eta^*_{\mathbf{q}'_j} (\text{ or } V\eta_{-q_j}),$$

we shall find the following expression for the intensity of the background in the neighborhood of a superstructure line (for small q'_j):

$$I = 2\pi^3 \frac{N^2}{V} \left| f_A - f_B \right|^2 \Big\{ \bar{\eta}^2 \delta(\mathbf{q}'_j) + \tag{10}$$

$$+ kT / 8\pi^3 \Big[\varphi_{\eta\eta} - \frac{\varphi^2_{\eta c}}{\varphi_{cc}}$$

$$+ \left(\alpha - 2 \frac{\varphi_{\eta c}}{\varphi_{cc}} \gamma + \frac{\varphi^2_{\eta c}}{\varphi^2_{cc}} \beta \right) q'^2_j \Big]^{-1} \Big\}.$$

If we then determine $|c_{\mathbf{q}_i}|^2$ and take into account Eq. (5), we shall find an analogous expression for the intensity of the background near a principal line

$$I = 8\pi^3 \frac{N^2}{V} \big[\left| \bar{c}_A f_A + \bar{c}_B f_B \right|^2 \delta(\mathbf{q}_i)$$

$$+ \frac{\left| f_A - f_B \right|^2 kT}{8\pi^3}$$

$$\times \frac{\varphi_{\eta\eta} + \alpha q_i^2}{\varphi_{\eta\eta}\varphi_{cc} - \varphi^2_{\eta c} + (\alpha\varphi_{cc} + \beta\varphi_{c\eta} - 2\gamma\varphi_{\eta c}) q_i^2} \big] \tag{11}$$

or

$$I = 8\pi^3 \frac{N^2}{V} \big[\left| \bar{c}_A f_A + \bar{c}_B f_B \right|^2 \delta(\mathbf{q}_i) \tag{12}$$

$$+ \frac{kT \left| f_A - f_B \right|^2}{8\pi^3} \frac{1}{(d^2\varphi / dc_A^2) + \beta' q_i^2} \big].$$

In the above the derivative $\partial/\partial c_A$ (or $\partial/\partial\eta$) in (10) and (11) is evaluated for the equilibrium values of the degree of long range order $\eta = \bar{\eta}$ (or of composition). On the other hand, the derivative d/dc_A in Eq. (12) is calculated for the values of η, which correspond to the changed (due to fluctuations) composition of the alloy (and to the same temperature). The quantity β' denotes the coefficient of $(\nabla c)^2$ in the corresponding expansion of the thermodynamic potential. The equivalence of Eqs. (11) and (12) follows from the condition $\partial\varphi/\partial\eta = 0$.

The general formulas obtained above for the intensity of scattered radiation may be applied to various special cases for which expressions for thermodynamic potential as a function of c_A and η are known.

2. THE SCATTERING BY SOLID SOLUTIONS NEAR POINTS OF PHASE TRANSITION OF THE SECOND KIND

In this section we shall examine the distinctive features of diffuse scattering of x-rays by solid solutions in the order-disorder transition which takes place as a phase transition of the second kind. Phase transitions of this type occur in a number of alloys, for example, in CuZn, AgZn with an admixture of Au, Fe_3Al, etc. The distinctive features referred to above occur because at the point of a phase transition of the second kind, the derivatives $\varphi_{\eta\eta}$ and $\varphi_{\eta c}$ vanish. Because of this, anomalously large fluctuations in the degree of long range order should be observed, and also the very intense diffuse scattering in the neighborhood of the superstructure line which is connected with these fluctuations.

According to the thermodynamic theory of phase transitions of the second kind[3,4] the expression for φ in the neighborhood of the transition temperature T_0 may be represented in the form of an expansion in powers of η:

$$\varphi = \varphi_0 + {}^1\!/_2 A\eta^2 + {}^1\!/_4 B\eta^4, \tag{13}$$

$$A = a(T - T_0), \quad a > 0, \quad B > 0,$$

where φ_0, A and B are functions of c_A, T and P. The coefficients a and B may be determined from the experimental data on the discontinuity in the specific heat during the phase transition and on the temperature dependence of $\bar{\eta}$ by means of the formulas[3]:

$$\Delta C_p = a^2 T_0 / 2B; \quad \bar{\eta} = \sqrt{a(T_0 - T)/B}.$$

Evaluating the second derivatives of φ with respect to η and c_A near the transition point and substituting them into (10) we shall find that the intensity of scattered radiation near a superstructure line below the temperature of ordering ($T \leq T_0$) in the special case of cubic crystals is equal to

$$I = 2\pi^3 \frac{N^2}{V} \left| f_A - f_B \right|^2 \frac{aT_0}{B} \Big\{ \frac{T_0 - T}{T_0} \delta(\boldsymbol{q}'_j) \tag{14}$$

$$+ \frac{k}{16\pi^3 \Delta C_p} \Big[2 \frac{T_0 - T}{T_0} \Big[1 - \frac{\Delta C_p}{T_0} \left(\frac{dT_0}{dc_A} \right)^2 \left(\frac{d^2\varphi_0}{dc_A^2} \right)^{-1} \Big]$$

$$+ \frac{\alpha}{aT_0} q'^2_j \Big]^{-1} \Big\}.$$

For $T \geq T_0$ only the diffuse part of the scattered radiation remains

$$I = \frac{1}{8} \frac{N^2}{V} \left| f_A - f_B \right|^2 \frac{aT_0}{B} \frac{k}{\Delta C_p} \tag{15}$$

$$\times \left[\frac{T - T_0}{T_0} + \frac{\alpha}{aT_0} q'^2_j \right]^{-1}.$$

For crystals of different symmetry $\alpha q'^2_j$ should, in Eqs. (14) and (15), be replaced by

$$\sum_{k,l=1}^{3} \alpha_{kl} q'_{jk} q'_{jl}.$$

Expression (15) for the intensity of scattering from a solid solution in the disordered region agrees with the corresponding expression obtained by Landau[1] in the case when there are no fluctuations in composition. The presence of such fluctuations leads to a change in the expression for the intensity of scattering for $T < T_0$: formula (14) has acquired a square bracket in place of unity which appeared in the corresponding formula of Ref. 1. In the scattering from an ordered crystal a sharp line is formed whose shape is described by a δ-like function, and whose intensity is proportional to the temperature difference $T_0 - T$ and which vanishes at the temperature of ordering. At the same time, near the temperature T_0, both in the ordered and in the disordered region for small values of q_j, one should observe a very intense background on an x-ray photograph because of a sharp increase in the magnitude of fluctuations of long range order. The maximum of this intensity lies at $\mathbf{q}'_j = 0$ and is inversely proportional to the temperature difference $|T - T_0|$. For a given $\mathbf{q}'_j$, the intensity of the background is a maximum* at $T = T_0$, and its decrease is proportional to $|T - T_0|$. For alloys whose composition corresponds to a maximum temperature of ordering, the intensity of background decreases as we go away from T_0 twice as fast in the ordered region as in the disordered region**. In other cases the ratio of the rates of decrease in the intensity of the background is less than two.

All the parameters which occur in Eqs. (14) and (15) (with the exception of the quantity α/aT_0) may be determined if we know from other experiments the form of the functions $T_0(c_A)$, ΔC_p, the dependence on the concentration of the chemical potentials of the atoms of the crystal at $T \approx T_0$ and the temperature dependence of $\overline{\eta}(T)$ near the transition point. The only unknown parameter is determined by comparing the calculated background intensity with the experimental one (it may also be calculated by means of the statistical theory of solutions), and from this one may calculate the values of the intensity of scattered radiation for various angles of scattering (near superstructure lines) and for various temperatures (close to T_0) for all the superstructure lines.

As is shown in Ref. 4, at the point O where the curve of the points of phase transition of the second kind AO goes over into the curve of phase transitions of the first kind---the dissociation curve OB (Fig. 1), the condition

$$B = \tfrac{1}{2}(\partial A/\partial c_A)^2 \varphi_{cc}^{-1}$$

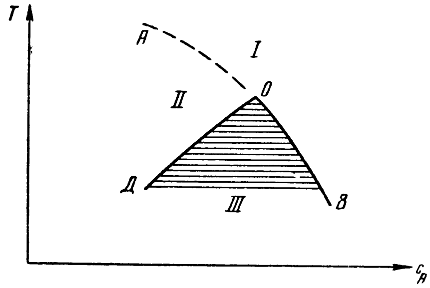

FIG. 1. *I* – Disordered crystal; *II* – Ordered crystal; *III* – Two phase region.

is fulfilled. This means that the expression which appears in the square brackets of Eq. (14) reduces to zero at the point O. Near such a point for $T \leq T_0$ the expression for the intensity of the radiation scattered by the ordered crystal may be represented near a superstructure line in the following form:

$$I = 2\pi^3 \frac{N^2}{V} |f_A - f_B|^2 \frac{aT_0}{B} \left\{ \frac{T_0 - T}{T_0} \delta(\mathbf{q}'_j) \right. \tag{16}$$

$$\left. + \frac{k}{16\pi^3 \Delta C_p} \left[2 \frac{T_0 - T}{T_0} \left(r_1 \frac{T_{\mathrm{cr}} - T}{T_0} + r_2 \frac{T_0 - T}{T} \right) + \frac{\alpha}{aT_0} q'^2_j \right]^{-1} \right\},$$

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* For $T = T_0$, the intensity of the background becomes infinite at the point $\mathbf{q}'_j = 0$ in accordance with Eqs. (14) and (15). This circumstance is related to the fact that for $\mathbf{q}'_j = 0$ the magnitude of the fluctuations in the long range order is not limited (as it is for $\mathbf{q}'_j \neq 0$) by the necessity of performing work related to the formation of an inhomogeneous fluctuation. However, in this case the finite dimensions of the crystal lead to a finite value of the intensity of the background and at the same time to the breakdown of Eqs. (14) and (15). This breakdown occurs only in a range of angles λ/L (where L is the size of the region of coherent scattering) and within a very narrow range of temperatures $\sim (\lambda/L)^2 T_0$.

**The quoted value for the ratio of the rates of change of the intensities of the background as we move away from T_0 in the ordered and in the disordered regions is only correct for sufficiently small values of $\mathbf{q}'_j$. For large values of $\mathbf{q}'_j$ this ratio will become larger because of the temperature dependence of α and of the factor kT in Eq. (10).

where T_{cr} is the temperature which corresponds to the point O, while r_1 and r_2 may be considered to be constant in the neighborhood of this point. Thus for $T < T_0$ the background intensity which corresponds to a given $\mathbf{q}_j'$ decreases extremely slowly as the temperature is decreased in the case under consideration. If $T > T_0$, then as T_0 is approached, the background intensity increases in accordance with Eq. (15), i.e., in accordance with the same law which holds far from the critical point O.

In contrast to the neighborhood of the ordinary points of phase transition of the second kind, the magnitude of the fluctuations of the composition in an ordered crystal also increases very markedly in the neighborhood of the point O, while the intensity of scattering near a principal line in accordance with Eq. (11) becomes equal to

$$I = 8\pi^3 \frac{N^2}{V} \left\{ |\bar{c}_A f_A + \bar{c}_B f_B|^2 \delta(\mathbf{q}_j') \right. \tag{17}$$

$$+ \frac{|f_A - f_B|^2}{8\pi^3} \frac{kT}{\varphi_{cc}} \times$$

$$\left. \frac{2(T_0 - T) + (\alpha/a) q_j'^2}{2(T_0 - T)[r_1(T_{cr} - T)/T_0 + r_2(T_0 - T)/T_0] + (\alpha/a) q_j'^2} \right\}.$$

Thus in the neighborhood of the critical point mentioned above, one should observe very intense diffuse scattering in the neighborhood of both the superstructure and the principal lines. For a disordered crystal in the neighborhood of the point at which ordering takes place $\varphi_{\eta c} = 0$, and since φ_{cc} does not vanish at the point O the diffuse scattering in the neighborhood of the principal lines is not large.

We[5] have also examined the special features of diffuse scattering by pure crystals near the point at which the curve of the points of phase transition of the second kind goes over into the curve of points of phase transition of the first kind, and also in the neighborhood of an isolated point of phase transitions of the second kind.

The formulas which have been obtained until now refer to the scattering of monochromatic x-rays by a single crystal. In order to be able to analyze a Debye photograph we must average the above expressions over all the orientations of the crystal. An averaging of this kind was carried out by Landau[1]. In the cases under consideration the result of Landau's calculation[1] for an ordered crystal in the neighborhood of superstructure lines has the form:

$$I = 4\pi^2 n \frac{N^2}{V} |f_A \tag{18}$$

$$- f_B|^2 \frac{aT_0}{B} \frac{1}{K_j'^3} \left\{ \frac{T_0 - T}{T_0} \operatorname{tg} \frac{\psi_j}{2} \delta(\psi - \psi_j) \right.$$

$$- \frac{kK_j'}{32\pi^2 \Delta C_p (\alpha / aT_0)}$$

$$\left. \times \ln \left[\frac{\operatorname{ctg}^2(\psi_j/2)}{16} (\psi - \psi_j)^2 + \frac{P}{4(\alpha/aT_0) K_j'^2} \right] \right\}.$$

Here ψ is the angle of scattering, ψ_j is the angle of scattering for the superstructure line under consideration, n is the number of families of atomic planes taking part in the formation of this line, while P denotes the term next to $(\alpha/aT_0)q_j'^2$ in the denominator of the corresponding Eq. (14) or (16) for an ordered crystal, and in the denominator of Eq. (15) for a disordered crystal. It is evident that in the last case the first term in (18) is absent.

3. SCATTERING NEAR A CRITICAL POINT ON THE DISSOCIATION CURVE, AND ALSO BY WEAK, IDEAL AND ALMOST COMPLETELY ORDERED SOLUTIONS

At critical points on dissociation curves (point K in Fig. 2) the concentrations of both phases become the same. At these points, as is well known, the derivatives $d^2\varphi/dc_A^2$ and $d^3\varphi/dc_A^3$ vanish, and therefore in the neighborhood of the critical point very large fluctuations in composition must take place, and very intense scattering of waves by such fluctuations should be observed.

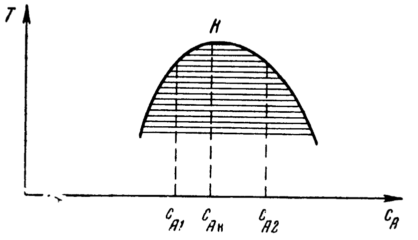

FIG. 2.

We expand the thermodynamic potential into a series in powers of $c_A - c_{Ak}$, where c_{Ak} is the composition which corresponds to the critical point*

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* For the sake of definiteness, we shall assume that the solution has an "upper" critical temperature, i.e., the state diagram has the form shown in Fig. 2. In the case of a "lower" critical temperature, the results will be altered in an obvious way.

$$\varphi = \varphi_0 + f_1 (c_A - c_{Ak}) + {}^1/_2 f_2 (c_A - c_{Ak})^2 + {}^1/_3 f_3 (c_A - c_{Ak})^3 + {}^1/_4 f_4 (c_A - c_{Ak})^4 + \ldots \tag{19}$$

In the neighborhood of the critical point one may take

$$f_2 = b(T - T_k); \quad f_3 = \gamma (T - T_k); \quad f_4 > 0,$$

where T_k is the critical temperature. In order to find the equation of the dissociation curve in the neighborhood of the critical point, one must substitute expression (19) into the conditions of equilibrium

$$\left.\frac{\partial \varphi}{\partial c_A}\right|_{c_A = c_{A1}} = \left.\frac{\partial \varphi}{\partial c_A}\right|_{c_A = c_{A2}};$$

$$\left.\frac{\partial \varphi}{\partial c_A}\right|_{c_A = c_{A1}} = \frac{\varphi(c_{A1}) - \varphi(c_{A2})}{c_{A1} - c_{A2}},$$

where c_{A1} and c_{A2} are the concentrations of atoms A in the first and in the second phases which are in equilibrium at a given T and P. On solving the resulting system of equations, and on neglecting in the expression for $c_A - c_{Ak}$ terms proportional to $|T - T_k|^{3/2}$, we shall find that the equation of the dissociation curve for small $|T - T_k|$ has the form:

$$T_k - T_p = Q (c_A - c_{Ak})^2 - (2\gamma/3b)(c_A - c_{Ak})(T_k - T_p) \approx Q (c_A - c_{Ak})^2; \quad Q = f_4/b. \tag{20}$$

Here T_p is the dissociation temperature for a solution of given composition c_A.

Thus b and f_4 may be determined from experimental data if the curvature of the dissociation curve in the neighborhood of the critical point and the discontinuity in the specific heat at that point are both known. Using (19) and (20), and determining the amounts of both phases by means of "the rule of the lever", we shall find that the thermodynamic potential of the solution of critical composition in a two-phase region is equal to $\varphi = \varphi_0 - (b^2/4f_4)(T - T_k)^2$. Consequently, in going over into a two-phase region the specific heat at the critical point increases discontinuously by an amount $\Delta C_p = T_k b^2/2f_4$. The derivative $d^2\varphi/dc_A^2$ in the neighborhood of the critical point may also be expressed in terms of ΔC_p and Q:

$$d^2\varphi/dc_A^2 = 2\Delta C_p Q (T + 2T_k - 3T_p)/T_k.$$

Substituting this expression into (12) we shall obtain the following formula for the intensity of scattering from cubic crystals in the neighborhood of the critical point for small q_i:

$$I = 8\pi^3 \frac{N^2}{V} \left\{ |\bar{c}_A f_A + \bar{c}_B f_B|^2 \delta(\mathbf{q}_i) + \frac{kT_k |f_A - f_B|^2}{16\pi^3 Q \Delta C_p} \left[\frac{T + 2T_k - 3T_p}{T_k} + \frac{\beta'}{bT_k} q_i^2 \right]^{-1} \right\}. \tag{21}$$

The formula obtained above contains only one unknown parameter $\beta' bT_k$ and allows one to dermine the intensity of scattered radiation near the principal lines and for small angles for solutions of different compositions at various temperatures near the critical point. This formula shows that in the case indicated above, as in the case of a phase transition of the second kind, the background intensity is anomalously large when ordering takes place. It attains a maximum at the critical point for $T = T_p = T_k$.

The formula takes on a particularly simple form in the case of small angle scattering when

$$q_i^2 = |\mathbf{k}_1 - \mathbf{k}_2|^2 = (4\pi/\lambda)^2 \sin^2(\psi/2).$$

In this case

$$I = \frac{1}{2} \frac{\Lambda'^2}{V} |f_A - f_B|^2 \frac{kT_k}{Q\Delta C_p} \left[\frac{T + 2T_k - 3T_p}{T_k} + \frac{\beta'}{bT_k} \frac{16\pi^2}{\lambda^2} \sin^2 \frac{\psi}{2} \right]^{-1}. \tag{22}$$

The intensity of the scattered radiation near the principal lines on a Debye photograph (calculated for a portion of the ring equal to its radius) for a solution which is near the critical state is determined by a formula of type (18)

$$I = 4\pi^2 n \frac{N^2}{V} \frac{1}{K_i^3} \left\{ |\bar{c}_A f_A + \bar{c}_B f_B|^2 \operatorname{tg} \frac{\psi_i}{2} \delta(\psi - \psi_i) - \frac{kT_k K_i |f_A - f_B|^2}{32\pi^2 \Delta C_p Q (\beta'/bT_k)} \ln \left[\frac{\operatorname{ctg}^2 \frac{\psi_i}{2}}{16} (\psi - \psi_i)^2 + \frac{T + 2T_k - 3T_p}{T_k} \frac{1}{(\beta'/bT_k) K_i^2} \right] \right\}, \tag{23}$$

where the angle ψ_i corresponds to a principal line. From (23) it follows that the background intensity falls off comparatively slowly as $|\psi - \psi_i|$ increases: the distance at which the intensity of the background is reduced by a factor 2 in the close neighborhood of the critical point is proportional to $[(T + 2T_k - 3T_p)/T_k]^{1/4}$, with the coefficient of proportionality being equal to unity in order of magnitude. The background intensity in the neighborhood of the Roentgen lines also depends weakly on the temperature--logarithmically. A more pronounced dependence on the temperature and on angles of the background on a Debye photograph near a critical point should be observed at small angles. In this case the intensity of radiation scattered by an individual crystal does not depend on its orientation, and therefore the averaging over orientations will not change expression (22), and it will be applicable also for the calculation of the intensity of the background in a Debye photograph. From (22) it follows that at very small angles (or large λ), when the second term in the denominator of this formula is considerably less than the first term, I is inversely proportional to the difference $T + 2T_k - 3T_p$. The background intensity decreases with increasing ψ faster than in the neighborhood of lines on a Roentgen photograph, and the distance at which I attains half of its maximum value is proportional to

$$[(T + 2T_k - 3T_p)/T_k]^{1/2}.$$

Equation (22) is evidently applicable not only to the scattering of x-rays but also to the scattering of light by transparent dielectric solutions near the critical point. Since the wavelength of a light wave is considerably larger than the lattice constant, Eq. (22) in this case is applicable not only for small, but for arbitrary scattering angles. The effective cross sections for scattering of visible light at frequencies considerably smaller than the frequency of self-absorption are in this case inversely proportional to λ^4 and far from the critical point $I \sim \lambda^{-4}$. Near the critical point because of the last factor in (22) the intensity of the scattered radiation depends more weakly on λ (the dependence is λ^{-2} right at the critical point).

We note that the results for small angle scattering obtained above are applicable not only to solids, but also to liquids. It is true that in liquids density fluctuations play a significant role. However, in the neighborhood of the critical dissociation point the scattering by density fluctuations is considerably smaller than by composition fluctuations (which we consider to be statistically independent). Therefore, Eq. (22) may also be applied for the determination of small angle scattering of x-rays by liquid solutions in the neighborhood of the critical point, and for the scattering of light by liquid solutions through arbitrary angles.

As is well known, the general expression for the thermodynamic potential of a solution may be obtained without utilizing a specific statistical model of the solution in the case of small concentration of one of the components ($c_A \ll 1$). Neglecting terms quadratic in c_A^2 we shall write the expression for φ in the form (see, for example, Ref. 3):

$$\varphi = \varphi_B + N_0 c_A kT \ln c_A + c_A f(P, T). \qquad (24)$$

Here φ_B is the thermodynamic potential per unit volume of the pure crystal B, N_0 is the number of atoms per unit volume, and $f(P, T)$ does not depend on c_A. The derivative of the thermodynamic potential (24) $d^2\varphi/dc_A^2 = N_0 kT/c_A$ for sufficiently small c_A is considerably larger than the second term in the denominator of Eq. (12), and therefore in this case the following formula is valid for the determination of the intensity of scattering at all angles

$$I = 8\pi^3 (N^2/V) \sum_i |c_A f_A + c_B f_B|^2 \delta(\mathbf{q}_i) + N|f_A - f_B|^2 c_A. \qquad (25)$$

As should be expected in the case of weak solutions the background intensity does not depend on the temperature at which the crystal becomes ordered, and is proportional to c_A.

The expression for φ has a simple form also in the case of ideal solutions

$$\varphi = \varphi^0 + kTN_0 (c_A \ln c_A + c_B \ln c_B), \qquad (26)$$

where φ^0 does not depend on the composition. Since the coefficient β' in the expansion of φ in powers of Δc_A is equal to zero in the ideal solution approximation, it follows from (12) and (26) that the following formula holds for the intensity of scattering by ideal solutions at arbitrary angles of scattering

$$I = 8\pi^3 (N^2/V) \sum_i |c_A f_A + c_B f_B|^2 \delta(\mathbf{q}_i) + N|f_A - f_B|^2 c_A(1 - c_A). \qquad (27)$$

In this case the background intensity also does not depend on the temperature and has a simple dependence on the composition. We note that (27) agrees with the formula obtained by a different method by Laue[6] on the assumption of a completely random distribution of atoms of different kinds among the lattice points. This assumption is evidently fulfilled in the case of an ideal solution.

The thermodynamic expression for φ may also be obtained for ordered solid solutions whose composition is close to the stoichiometric, at low temperatures, when the numbers of atoms at "wrong" lattice points may be considered as small parameters. In this case for the solid solutions of the structure under examination in which the numbers of lattice points of the first and second kinds are the same, the thermodynamic potential is equal to (Ref. 7):

$$\varphi = \varphi' + \chi_1 c_A + \chi_2 \eta + \frac{kTN_0}{2}[p_A^{(1)} \ln p_A^{(1)} + p_A^{(2)} \ln p_A^{(2)} + p_B^{(1)} \ln p_B^{(1)} + p_B^{(2)} \ln p_B^{(2)}] + kTN_0[(p_B^{(1)})^2 e_1 + p_B^{(1)} p_A^{(2)} e_2 + (p_A^{(2)})^2 e_3]. \tag{28}$$

Here φ', χ_1, χ_2, e_1, e_2, e_3 depend only on T and P and do not depend on c_A and η. For sufficiently low temperatures, and for compositions sufficiently close to the stoichiometric one, i.e., in the region of applicability of Eq. (28), χ may be considered to be constant, while $p_B^{(1)}$ and $p_A^{(2)}$ decrease rapidly as the temperature is decreased--faster than e_1, e_2 and e_3 increase. The coefficients of $(\Delta\eta)^2$, $\nabla\eta\, \Delta c_A$ and $(\nabla c_A)^2$ in the expansion of φ also increase more slowly as $T \to 0$ than $p_B^{(1)}$ and $p_A^{(2)}$ decrease. Therefore, at sufficiently low temperatures the background intensity for arbitrary scattering angles has the form:

$$I = 8\pi^3 (N^2/V) \left[\sum_i |c_A f_A + c_B f_B|^2 \delta(\mathbf{q}_i) + {}^1/_4\, \eta^2 \sum_j |f_A - f_B|^2 \delta(\mathbf{q}_j) \right] + N |f_A - f_B|^2 (c_A c_B - {}^1/_4\, \eta^2). \tag{29}$$

The background intensity in a Debye photograph in the case of weak, ideal and almost completely ordered solutions is also determined by Eqs. (25), (27) and (29), respectively. Equation (29) agrees with the expression for the intensity of diffuse radiation scattered by an ordered crystal which was obtained by Lifshitz[8] on the assumption of the absence of correlation in the alloy. Thus the correlation in the alloy becomes of small importance not only at high but also at low temperatures in the neighborhood of the state of complete ordering.

It should be emphasized that all the above results have been obtained for the scattering by a system which is in a condition of equilibrium (corresponding to a certain annealing temperature).

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