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28

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THEORY OF DIFFUSE SCATTERING OF X-RAYS AND THERMAL NEUTRONS IN SOLID SOLUTIONS. III. ACCOUNT OF GEOMETRICAL DISTORTIONS OF THE LATTICE

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A method for treatment of various problems connected with static distortions of crystal lattices is proposed, in which the distortions are related to fluctuation waves of the composition and of the internal parameters. Scattering of x-rays and thermal neutrons in binary solutions of arbitrary composition and with arbitrary values of the short and long range order parameters is considered. Anisotropy of the crystal and its atomic structure are taken into account explicitly. The scattering intensity can be expressed in terms of the thermodynamical characteristics of the solution (or correlation parameters), elastic moduli (or interatomic interaction constants), and also in terms of parameters characterizing the dependence on the concentration of the cell shape and dimensions. The particular cases of ideal, dilute, almost completely ordered solutions and also of solutions located near the critical point on the decay curve or near phase-transition points of the second kind are investigated. The diffuse scattering intensity distribution in a Cu_3Au solution, calculated without making use of the theoretical parameters, agrees satisfactorily with the experimental distribution.

IN earlier papers[1,2] (quoted in the following as I and II) the diffuse scattering of x-rays and neutrons in solid solutions was investigated within the framework of phenomenological[1] and microscopic[2] theories. In the course of these investigations it was assumed that the sole cause giving rise to diffuse scattering was the random distribution of the atoms among the lattice points of a geometrically ideal lattice. In this article we shall investigate the influence of geometrical distortions of the lattice, associated with the difference in the size of atoms of different kinds, on the scattering. During the last few years an intensive experimental study was begun of the diffuse scattering due to the above cause and of the weakening of the lines in an x-ray photograph (see, for example, Ref. 3 where references to other work are given). These problems have been studied theoretically for several particular cases in a number of papers.[4-9]

In this article we investigate the general case of substitution solutions of arbitrary composition with arbitrary values of the parameters of long and short range order without making use of the approximation of an elastic isotropic continuum. For the calculation of intensity we use a simple method, which is a generalization to the case when distortions are present of the method used in I and II. In this method, which can be called the method of fluctuation waves, we consider Fourier components of fluctuations of the composition, of the degree of long-range order, or of other internal parameters characterizing the state of the crystal. The equations which relate these fluctuation waves to waves of geometrical distortions turn out to be simple ones. This leads to the possibility of easily expressing the scattering intensity, which is related to the differences in the atomic factors and to the geometric distortions, in terms of the above Fourier components. The probability distribution of the fluctuations is obtained by means of the thermodynamic theory of fluctuations, as a result of which the intensity turns out to be expressed in terms of quantities determined from independent experiments. By means of this method the anisotropy of the crystal and its atomic structure have been taken into account explicitly. As in I and II, we have not taken into account in the present article Compton scattering, nor scattering by thermal vibrations, and the calculations are carried out within the framework of the kinematic scattering theory. The scattering of monochromatic radiation by a single crystal is considered.

1. DISORDERED SOLID SOLUTIONS

We consider a disordered solid substitution solution AB of arbitrary composition, and with arbitrary values of the parameters of short-range order, an elementary cell of which contains one atom. The distribution of the atoms A and B among the lattice points of the lattice is determined by assigning the numbers c_s, where s is the index of the lattice point, with $c_s = 1$ if an atom A occupies the s-th lattice point, and $c_s = 0$ if an atom B is situated there. The distribution of atoms can also be specified by giving not the c_s themselves, but their Fourier components defined by the relations:

$$c_s - c = \sum_{\mathbf{k}}{}' \left[c_{\mathbf{k}} \exp(-i\mathbf{k}\mathbf{R}_s) + \overset{*}{c}_{\mathbf{k}} \exp(i\mathbf{k}\mathbf{R}_s)\right];$$

$$c_{\mathbf{k}} = \frac{1}{N} \sum_s (c_s - c) \exp(i\mathbf{k}\mathbf{R}_s). \tag{1}$$

Here c is the atomic concentration of atoms A, $\mathbf{R}_s$ is the position vector of the s-th lattice point, the summation over k is taken over the vectors $\mathbf{k}/2\pi$ lying in one half of the first cell of the reciprocal lattice space and satisfying cyclic conditions.

The geometric distortions may be characterized by the displacements $\delta\mathbf{R}_s$ of atoms from the lattice points of an ideal periodic lattice having the same structure and the same lattice constant as the solution. To each distribution of atoms there corresponds a definite distribution of displacements. The $\delta\mathbf{R}_s$ may be represented in the form of a superposition of displacements corresponding to individual fluctuation waves. The discussion is considerably simplified if one assumes that the boundaries of the crystal are held by infinitely rigid walls and cannot be displaced. We denote by $\mathbf{k}'$ a vector parallel to the displacements of atoms in the k-th wave and equal to k in absolute value. Then

$$\delta\mathbf{R}_s = \sum_k{}' \frac{a_{\mathbf{k}}\mathbf{k}'}{k^2} i \left[c_{\mathbf{k}} \exp(-i\mathbf{k}\mathbf{R}_s) - \overset{*}{c}_{\mathbf{k}} \exp(i\mathbf{k}\mathbf{R}_s)\right] \tag{2}$$

When $\mathbf{k} \to 0$ the $a_{\mathbf{k}}$ cease to depend on k (but do depend on the direction of **k**). Explicit expressions for $a_{\mathbf{k}}$ are given below. Strictly speaking, we should also have taken into account in the expansion quadratic and higher-order terms in $c_{\mathbf{k}}$. Instead of this, in an alternative formulation of the problem, we could have taken into account fluctuations of short-range order parameters as well as fluctuations in composition in determining $\delta\mathbf{R}_s$, and could have also taken into account the fact that the quantities $a_{\mathbf{k}}$ should be evaluated for constant values of these parameters and may differ from the equilibrium values given below. The approximation adopted in the present article is valid if

$$|\partial v/\partial c| \gg |\partial^2 v/\partial c^2| \sqrt{c(1-c)},$$

where v is the molar volume. This condition is fulfilled for solutions obeying Vegard's rule (linear dependence of v on c), and also for all solutions of low concentration of one of the components.

As is well known, the x-ray scattering intensity expressed in electronic units can be given in the form

$$I = \left|\sum_s f_s \exp(i\mathbf{q}_1, \mathbf{R}_s + \delta\mathbf{R}_s)\right|^2. \tag{3}$$

Here $f_s = c_s f_A + (1 - c_s) f_B$ is the atomic scattering factor for an atom situated at the s-th lattice point, f_A and f_B are the atomic factors for atoms A and B, $\mathbf{q}_1$ is the difference between the wave vectors of the scattered and the incident waves, and the bar indicates averaging over all the permutations of the atoms among the lattice points.*

In calculating I by means of formula (3) it is convenient to break up f_s into its average value and its deviation from the average:

$$f_s = \bar{f} + (c_s - c)(f_A - f_B), \quad \bar{f} = cf_A + (1-c) f_B.$$

The expression for I is then broken up into three terms each of which we shall evaluate separately:

$$\begin{aligned} I &= I_1 + I_2 + I_3 \\ &= |\bar{f}|^2 \sum_{s,\, s'=1}^{N} \exp(i\mathbf{q},\, \mathbf{R}_s - \mathbf{R}_{s'}) \overline{\exp(i\mathbf{q}_1, \delta\mathbf{R}_s - \delta\mathbf{R}_{s'})} \\ &+ [\bar{f}(f_A^* - f_B^*) + \bar{f}^*(f_A - f_B)] \sum_{s,\, s'=1}^{N} \exp(i\mathbf{q},\, \mathbf{R}_s - \mathbf{R}_{s'}) \\ &\times \overline{(c_s - c)\exp(i\mathbf{q}_1,\, \delta\mathbf{R}_s - \delta\mathbf{R}_{s'})} \\ &+ |f_A - f_B|^2 \sum_{s,\, s'=1} \exp(i\mathbf{q},\, \mathbf{R}_s - \mathbf{R}_{s'}) \\ &\times \overline{(c_s - c)(c_{s'} - c)\exp(i\mathbf{q}_1,\, \delta\mathbf{R}_s - \delta\mathbf{R}_{s'})}. \end{aligned} \tag{4}$$

Here $\mathbf{q} = \mathbf{q}_1 - 2\pi\mathbf{K}_n$, where $\mathbf{K}_n$ is the vector of the reciprocal lattice lying in the same cell as the vector $\mathbf{q}_1/2\pi$ (so that $\mathbf{q}/2\pi$ lies in the first cell).

It can be seen from (4) that in order to evaluate I_1 it is necessary to find the statistical average of the expression $\exp(i\mathbf{q}_1,\, \delta\mathbf{R}_s - \delta\mathbf{R}_{s'})$. Such an average may be easily evaluated if one notes that in accordance with (2) this exponential breaks up into a product of factors corresponding to different **k** and adopts for the probability distribution of the quantities $c_\mathbf{k}$ the Gaussian distribution (cf. Refs. 11 and I):

$$w \sim \exp\Big(-\sum_{\mathbf{k}}{}' g_\mathbf{k} |c_\mathbf{k}|^2\Big). \tag{5}$$

(The formulas relating $g_\mathbf{k}$ to the thermodynamic characteristics of the solution are given below). Then

$$\begin{aligned} M(\mathbf{R}_s - \mathbf{R}_{s'}) &= \overline{\exp(i\mathbf{q}_1,\, \delta\mathbf{R}_s - \delta\mathbf{R}_{s'})} \\ &= \exp\Big[-2 \sum_{\mathbf{k}}{}' \frac{(\mathbf{q}_1\mathbf{k}')^2}{k^4 g_\mathbf{k}} a_\mathbf{k}^2 (1 - \cos \mathbf{k},\, \mathbf{R}_s - \mathbf{R}_{s'})\Big]. \end{aligned} \tag{6}$$

Substituting (6) into the first term of formula (4), factoring out e^{-L} where

$$L = 2 \sum_{\mathbf{k}}{}' k^{-4} (\mathbf{q}_1\mathbf{k}')^2 a_\mathbf{k}^2 / g_\mathbf{k}, \tag{7}$$

and expanding the exponential expression remaining in (6) into a series we obtain:

$$I_1 = 8\pi^3 \frac{N}{\Delta} |\bar{f}|^2 e^{-L} \delta(\mathbf{q}) + N^2 |\bar{f}|^2 e^{-L} \frac{(\mathbf{q}_1\mathbf{q}')^2}{q^4} \frac{a_\mathbf{q}^2}{g_\mathbf{q}}. \tag{8}$$

Here Δ is the volume of an elementary cell, the first term containing the δ function (which appears in the limiting case of an infinite crystal) determines the intensity of the regular Laue scattering, while the second term determines the intensity of the diffuse scattering.

In calculating I_1 terms in (8) are neglected which correspond to terms which appear in the expansion of the expression $M(\mathbf{R}_s - \mathbf{R}_{s'})e^{L}$ and which contain products of two or more cosines. The discarded terms are much smaller than the term retained in (8) if the following condition holds

$$(Lq/k_m)\cos^{-2}(\mathbf{q}'\mathbf{q}_1) \ll 1, \tag{9}$$

where k_m is the maximum value of k lying in the first cell of the reciprocal lattice. In many cases condition (9) is satisfied for arbitrary **q**, and it is always satisfied for sufficiently small **q** (with the exception of directions for which $\cos(\mathbf{q}'\mathbf{q}_1) = 0$). It is evident that if it should turn out to be necessary, it would not be difficult within the framework of the procedure outlined above to take into account also these discarded terms.

For the calculation of I_2 and I_3 one may make use of the relations obtained from (2), (5) and (6):

$$\begin{aligned} &\overline{c_\mathbf{k} \exp(i\mathbf{q}_1,\, \delta\mathbf{R}_s - \delta\mathbf{R}_{s'})} \\ &= (\mathbf{q}_1\mathbf{k}'/k^2 g_\mathbf{k}) a_\mathbf{k} [\exp(i\mathbf{k}\mathbf{R}_s) - \exp(i\mathbf{k}\mathbf{R}_{s'})] M(\mathbf{R}_s - \mathbf{R}_{s'}), \\ &\overline{c_\mathbf{k}^* \exp(i\mathbf{q}_1,\, \delta\mathbf{R}_s - \delta\mathbf{R}_{s'})} = -(\mathbf{q}_1\mathbf{k}'/k^2 g_\mathbf{k}) a_\mathbf{k} \\ &\times [\exp(-i\mathbf{k}\mathbf{R}_s) - \exp(-i\mathbf{k}\mathbf{R}_{s'})] M(\mathbf{R}_s - \mathbf{R}_{s'}). \end{aligned} \tag{10}$$

Substituting (1), (5) and (10) into the second and third terms in (4) we obtain:

$$\begin{aligned} I_2 + I_3 &= -N^2 [\bar{f}(f_A^* - f_B^*) + \bar{f}^*(f_A - f_B)] \\ &\times e^{-L} \frac{\mathbf{q}_1\mathbf{q}'}{q^2 g_\mathbf{q}} a_\mathbf{q} + N^2 |f_A - f_B|^2 e^{-L} \frac{1}{g_\mathbf{q}}. \end{aligned} \tag{11}$$

In calculating I_2 and I_3 we have also neglected terms containing products of two or more cosines. However it may be shown that if condition (9) is satisfied for a given **q** then the neglected terms are much less than I_3 (if $L \ll 1$) or I_1 (if $L \gtrsim 1$).

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*To obtain the neutron scattering cross-section per unit solid angle one should replace f_A and f_B in the formulas for I by A_A and A_B, which are constants describing the interaction of the neutron with the nuclei (see Ref. 10), averaged over the isotopes and independent of the spin directions of the neutron and the nucleus, and one should multiply the result by $m^2/4\pi\hbar^2$, were m is the neutron mass.

It follows from (4), (8), and (11) that the expression for the intensity of scattering by a disordered solution may be written in the form:

$$I = 8\pi^3 \frac{N}{\Delta} |\bar{f}|^2 e^{-L} \delta(\mathbf{q}) + N^2 \frac{e^{-L}}{g_{\mathbf{q}}} \left| \bar{f} a_{\mathbf{q}} \frac{\mathbf{q}_1 \mathbf{q}'}{q^2} - f_A + f_B \right|^2. \quad (12)$$

In order to be able to apply formula (12) we must find expressions for the quantities $a_{\mathbf{q}}$ and $g_{\mathbf{q}}$. We consider first the quantities $a_{\mathbf{q}}$ which characterize the degree of deformation associated with the **q**-th fluctuation wave. For this purpose we shall make use of the conditions of equilibrium with respect to the displacement of the atoms of the solution. In the approximation of an elastic isotropic continuum the expression for the density F of the free energy of a solution, in which there is a non-uniform distribution of concentration $\delta c(\mathbf{r})$, may be written in the form (cf. Ref. 12, part II, Ch. 1):

$$F = F_0 - \varkappa K \delta c u_{ll} + \mu (u_{ij} - {}^1\!/_3\, \delta_{ij} u_{ll})^2 + {}^1\!/_2\, K u_{ll}^2,$$

where i, j, and ℓ denote Cartesian coordinates, u_{ij} is the deformation tensor, F_0 does not depend on u_{ij} and δc, k is the bulk modulus of elasticity, μ is the shear modulus, δ_{ij} is the Kronecker delta. In this and in the following expressions it is understood that summation is to be carried out over repeated indices. From this we obtain the following equation for the components of the stress tensor:

$$\sigma_{ij} = \partial F / \partial u_{ij} = -\varkappa K \delta c \delta_{ij} + K u_{ll} \delta_{ij} + 2\mu (u_{ij} - {}^1\!/_3\, \delta_{ij} u_{ll}). \quad (13)$$

In the case when δc is constant along the sample and $\sigma_{ij} = 0$, Eq. (13) enables us to relate κ to the equilibrium change in the volume as the composition is changed. In this case $u_{ij} \sim \delta_{ij}$, and setting (13) equal to zero we find that $\kappa = u_{\ell\ell}/\delta c = (1/v)\, \partial v/\partial c$. If δc is a wave of fluctuations of composition along the x axis, then in planes perpendicular to this axis the displacements are equal to zero (the crystal boundaries do not move) and all the u_{ij} with the exception of u_{xx} are equal to zero. Substituting in (13) $c_{\mathbf{k}} \exp(-i\mathbf{k}\mathbf{R}_s)$ in place of δc, and the expression $a_{\mathbf{k}} c_{\mathbf{k}} \exp(-i\mathbf{k}\mathbf{R}_s)$ obtained from (2) in place of u_{xx}, setting σ_{xx} equal to zero and making use of the well known relations between k, μ and the Poisson ratio σ, we obtain:

$$a_{\mathrm{k}} = \frac{1+\sigma}{3(1-\sigma)} \varkappa = \frac{1+\sigma}{3(1-\sigma)} \frac{1}{v} \frac{\partial v}{\partial c}; \quad \mathrm{k}' = \mathrm{k}. \quad (14)$$

Thus, in the approximation of an isotropic continuum, $a_{\mathbf{k}}$ does not depend on **k**.

In the case of a single crystal

$$F = F_0 - \lambda_{ijlm} k_{lm} u_{ij} \delta c + {}^1\!/_2\, \lambda_{ijlm} u_{ij} u_{lm},$$

where $\lambda_{ij\ell m}$ is the elasticity tensor. In order to determine $k_{\ell m}$ we may, as above, consider the case when $\delta c(\mathbf{r}) = \text{const}$ and $\sigma_{ij} = 0$. The equation obtained from this shows that the $k_{\ell m}$ are equal to the result of dividing by δc the components of the deformation tensor $u_{\ell m}$ which arises as a result of changing the composition by δc. Evidently the tensor $k_{\ell m}$ is completely determined if we know the dependence on the composition of the dimensions and the shape of the ideal elementary cell. If the fluctuation wave is directed along the X′ axis with the unit vector $\mathbf{n} = \mathbf{k}/k$, then in the system of coordinates x′y′z′, only $u_{x'x'} \neq 0$, $u_{x'y'} \neq 0$, $u_{x'z'} \neq 0$. The quantities σ_{ij} are expressed in terms of the $u_{\ell m}$ by means of the formula

$$\sigma_{ij} = -\lambda_{ijlm} k_{lm} \delta c + \lambda_{ijlm} u_{lm}. \quad (15)$$

Replacing δc and $u_{x'x'}$ by periodic functions and taking into account that $\partial\sigma_{ij}/\partial x_j = 0$ we obtain from (15), (1), and (2) three equations for the $a_{\mathbf{k}} n_i'$, where $n' = \mathbf{k}/k$:

$$\lambda_{ijlm} n_j n_l a_k n'_m = \lambda_{ijlm} k_{lm} n_j. \quad (16)$$

Thus the $a_{\mathbf{k}}$ may be determined if we know the moduli of elasticity and the dependence on the composition of the dimensions and the shape of the elementary cell. The expressions for $a_{\mathbf{k}}$ become simplified for various specific structures. Thus in the case of cubic crystals

$$k_{lm} = \frac{1}{3} \frac{1}{v} \frac{\partial v}{\partial c} \delta_{lm}$$

and there exist only three different elastic moduli

$$\lambda_{xxxx} = c_{11}, \quad \lambda_{xxyy} = c_{12} \text{ И } \lambda_{xyxy} = c_{44}.$$

In this case, for directions of the type (100), expression (16) takes on the following form:

$$a_{\mathrm{k}} = \frac{1}{3} \frac{1}{v} \frac{\partial v}{\partial c} \frac{c_{11} + 2c_{12}}{c_{11}}. \quad (17)$$

In determining the quantities $a_{\mathbf{k}}$ for short wavelengths, the continuum approximation may no longer be used, and the atomic structure of the crystal must be taken into account explicitly. In the approximation under discussion, where the relation between $\delta\mathbf{R}_s$ and $c_{\mathbf{k}}$ is assumed to be linear, the expression for the free energy of the solution considered as a function of the static displacements of the atoms (positions of equilibrium for their vibrations) takes on the following form:

$$F' = F_0' - w_{ss'i} (c_{s'} - c) \delta R_{si} + {}^1\!/_2\, V_{ss'ij} \delta R_{si} \delta R_{s'j}, \quad (18)$$

where the coefficients $w_{ss'i}$ and $V_{ss'ij}$ depend on the relative position of the lattice points s and

s', on the temperature and on c. The force $\mathbf{F}_s$ which acts on the s-th atom due to all the other atoms is equal to:

$$F_{si} = -\partial F' / \partial \delta R_{si} = -w_{ss'i}(c_{s'} - c) + V_{ss'ij}\,\delta R_{s'j}. \quad (19)$$

Substituting into (19) in place of $c_{s'} - c_s$ and $\delta R_{s'j}$ the partial ($\mathbf{k}$-th) waves appearing in the expansions (1) and (2), and equating to zero the components of the vectors $\mathbf{F}_s$, we obtain:

$$\begin{aligned} &a_{\mathbf{k}} n'_j V_{ss'ij} \exp(i\mathbf{k},\ \mathbf{R}_s - \mathbf{R}_{s'}) \\ &= (k/i)\, w_{ss'i} \exp(i\mathbf{k},\ \mathbf{R}_s - \mathbf{R}_{s'}) \quad (i = 1, 2, 3). \end{aligned} \quad (20)$$

Restricting ourselves to the few nonvanishing constants $V_{ss'ij}$ and $w_{ss'i}$, we can express these constants in terms of the moduli of elasticity and of quantities which characterize the dependence of the dimensions and the shape of the cell on the concentration. Subsequently the $a_{\mathbf{k}}$ will be determined for arbitrary $\mathbf{k}$.

We now go on to the determination of $g_{\mathbf{k}}$ and to the investigation of the expressions obtained for I in various special cases. In accordance with (5), $1/g_{\mathbf{k}} = \overline{|c_{\mathbf{k}}|^2}$. For ideal and for weak solutions (when the atoms are distributed among the lattice points at random) these quantities may be determined either directly from formula (1) (taking into account that $\overline{c_s^2} = \overline{c_s} = c$, $\overline{c_s c_{s'}} = 0$ for $s \neq s'$) or with the aid of the usual formulas of the thermodynamic theory of fluctuations (cf. I):

$$1/g_{\mathbf{k}} = c(1-c)/N.$$

Substituting this expression into (12) we shall find that the intensity of diffuse scattering I_φ by ideal solutions is equal to:

$$I_\varphi = Nc(1-c)e^{-L}|a_{\mathbf{q}}\bar{f}\mathbf{q}_1\mathbf{q}'/q^2 - f_A + f_B|^2, \quad (21)$$

where the $a_{\mathbf{q}}$ in various special cases are determined by formulas (14), (16), (17), and (20). For $a_{\mathbf{q}} = 0$ formula (21), and also the formulas given below for non-ideal solutions, reduce to the corresponding formulas of Refs. I and II. Therefore in solutions with components having nearly equal atomic radii, and not too closely equal atomic factors (for example in Ag—Au) one may use formulas given in I and II for all values of $\mathbf{q}$, with the exception of values lying in the immediate neighborhood of lattice points of the reciprocal lattice.

In the case of non-ideal solutions, when the correlation between the occupation of different lattice points by atoms of different kinds is significant, we have in accordance with (1):

$$1/g_{\mathbf{k}} = \overline{|c_{\mathbf{k}}|^2} = \frac{1}{N}\Big[c(1-c) - \sum_{\rho \neq 0} \varepsilon(\rho)\cos \rho\mathbf{k}\Big]. \quad (22)$$

Here $\boldsymbol{\rho} = \mathbf{R}_{s'} - \mathbf{R}_s$ take on the values of all the position vectors of the lattice, and the correlation parameters are

$$\varepsilon(\rho) = -(\overline{c_s c_{s'}^{(\rho)}} - c^2),$$

where the averaging is carried out over all pairs of lattice points separated from one another by the distance ρ. In accordance with (12) and (22), I_φ is in this case equal to:

$$\begin{aligned} &I_\varphi \\ &= N\Big[c(1-c) - \sum_{\rho \neq 0} \varepsilon(\rho) \overline{\cos \mathbf{q}\rho}\Big] e^{-L}|a_{\mathbf{q}}\bar{f}\mathbf{q}_1\mathbf{q}'/q^2 - f_A + f_B|^2. \end{aligned} \quad (23)$$

Formula (23) is a generalization of the well-known formula (see, for example, Ref. 13) which expresses I_φ in terms of c and $\epsilon(\rho)$ to the case when geometrical distortions are present. This formula also enables us to determine $\epsilon(\rho)$ from the experimentally obtained distribution of intensity of diffuse scattering taking geometrical distortions into account. For this one has to carry out the Fourier transformation of I_φ divided by the last factor of formula (23). As a consequence of this the expressions for $\epsilon(\rho)$ can be obtained from the corresponding expressions of Ref. 13 by making the following replacements in the latter:

$$f_A - f_B \rightarrow f_A - f_B - a_{\mathbf{q}}\bar{f}\mathbf{q}_1\mathbf{q}'/q^2, \quad (24)$$

i.e.,

$$\varepsilon(\rho) = -\frac{1}{2}\int d\mathbf{k}\,\frac{I_\Phi}{N}\left|a_{\mathbf{k}}\bar{f}\,\frac{\mathbf{q}_1\mathbf{k}'}{k^2} - f_A + f_B\right|^{-2}\cos \mathbf{k}\rho, \quad (25)$$

where in the course of integration $\mathbf{k}/2\pi$ take on values which lie inside the volume of an arbitrary elementary cell of the reciprocal lattice.

As was shown in II, certain thermodynamic constants (for example the energies of ordering) can be obtained directly from the experimentally-determined distribution of diffuse scattering. The inclusion of geometrical distortions in this method will also reduce to carrying out the replacement (24) in formulas (23) of II. The correction for the distortions is particularly important in the case of decaying solutions with appreciably different atomic radii. It should be noted that in the case of weak dependence of v on c and of not too similar atomic scattering factors ($a_{\mathbf{q}}|\bar{f}| < 0.1\,|f_A - f_B|$) the correction due to the distortions in the formulas for $\epsilon(\rho)$ and for the energies of ordering is significant only for small q ($q \ll k_m$) when the macroscopic formulas (16) and (17) can be used for $a_{\mathbf{q}}$. In the more general case when the correction is significant also for large q, $a_{\mathbf{q}}$ should be found with the aid of formula (20).

If the constants characterizing the thermodynamic properties of the solution, e.g. the energies of ordering, are known, then I_φ may be calculated with the aid of the formulas of II upon making the replacement (24). In the general case, the determination of I_φ by this method will not be sufficiently accurate, since it is based on a simplified statistical model of the solution. However, in the neighborhood of the lattice points of the reciprocal lattice (where the distortions play the most significant role), the evaluation of I_φ from the thermodynamic data can be carried out quite accurately. In this case [compare (9) of I with (5) of this article] $g_\mathbf{k}$ is determined for cubic crystals by means of the following formula:

$$g_\mathbf{k} = (V/kT)(\varphi_{cc} + \beta k^2). \tag{26}$$

Here V is the volume of the crystal, $\varphi_{cc} = d^2\varphi/dc^2$, φ is the thermodynamic potential per unit volume, the derivative with respect to c is calculated for a given number of atoms (and not for a given volume), and β is of the order of magnitude of $(kT/\Delta)r_0^2$, where r_0 is the interatomic distance. Substituting (26) into (12) we find that for $q \ll k_m$

$$I_\Phi = \frac{N}{\Delta}\frac{kTe^{-L}}{\varphi_{cc} + \beta q^2}\left| a_\mathbf{q}\bar{f}\frac{\mathbf{q}_1\mathbf{q}'}{q^2} - f_A + f_B \right|^2. \tag{27}$$

In the general case of crystals of non cubic symmetry, βq^2 is replaced by the sum $\beta_{ij}q_iq_j$. If the dependence on concentration of the activity a_A of atoms A in solution AB is known, then φ_{cc} may be found from the formula:

$$\varphi_{cc} = \frac{kT}{(1-c)\Delta}\frac{1}{a_A}\frac{da_A}{dc}.$$

Thus, for $\mathbf{q} \to 0$, I may be calculated with the aid of parameters obtained from independent experimental data on the dependence of a_A on c, on the moduli of elasticity, and on the dependence on concentration of the dimensions and shape of the elementary cell. Within a certain region $q \ll k_m$, in accordance with (27), I_Φ depends only on the single unknown parameter β. It is evident that formula (27) also provides a method for an independent determination of activities from experimental data obtained from x-ray photographs.

Geometrical distortions are particularly significant if the molar volume depends strongly on c ($a_\mathbf{q}$ is large), and if f_A and f_B are nearly equal. Even if $a_\mathbf{q} \ll 1$ and $|f_A - f_B| \ll |\bar{f}|$, still for sufficiently small q, i.e., in the vicinity of the lattice points of the reciprocal lattice, the first term in the binomials of formulas (21), (23), or (27), which is determined by the distortions, becomes dominant. In this case, just as in the case of weak solutions discussed by Huang,[5] I_Φ tends to infinity like q^{-2} when a lattice point of the reciprocal lattice is approached. The coefficient of q^{-2} is proportional to $\mathbf{q}_1^2 = (4\pi\lambda^{-1}\sin\theta)^2$, where λ is the wavelength and 2θ is the scattering angle. Therefore, the intensity, divided by $|f_A - f_B|^2$, of the background associated with distortions, in contrast to the intensity of the background associated with a difference in the atomic factors, does not recur periodically in the different cells of the reciprocal lattice, but grows with an increase in θ and with a decrease in λ (i.e., with an increase in the cell index). For small θ, when $\mathbf{q}_1 = \mathbf{q}$, I_Φ in accordance with (27) tends to a constant limit and does not vary proportionally to q^{-2}. The term in I_Φ which is proportional to q^{-2} contains $\cos^2\varphi$ as a factor where φ is the angle between $\mathbf{q}'$ and $\mathbf{q}_1$. Therefore, for small q, I_Φ depends appreciably not only on the distance to the nearest lattice point of the reciprocal lattice, but also on the mutual orientation of the vectors $\mathbf{q}'$ and $\mathbf{q}_1$. Since $a_\mathbf{q}$ also changes appreciably as the orientation of $\mathbf{q}$ with respect to the crystal axes is varied, the above behavior of I_Φ is determined not only by the factor $\cos^2\varphi$, but also by the factor $a_\mathbf{q}^2$, and will be different in the vicinity of the different lattice points of the reciprocal lattice. It should be noted that the small terms neglected in the derivation of formulas (8) and (11) have a different dependence on the direction of $\mathbf{q}$ than the terms which are retained; in particular, they do not vanish when $\cos\varphi = 0$. Therefore the characteristic form of the isodiffusion curves will be somewhat altered if we take into account the neglected terms, whose relative importance in accordance with (9) increases with increasing q and becomes insignificant as $q \to 0$. The cross products obtained on squaring the binomials in formulas (21), (23), and (27) change sign when $\mathbf{q}$ is replaced by $-\mathbf{q}$ and lead to an asymmetry in the distribution of intensity of diffuse scattering with respect to the lattice points of the reciprocal lattice.

It can be seen from formula (21) that, even in the case of ideal solutions, the dependence of I_Φ on concentration is, generally speaking, not simple, since it is determined by the factor $c(1-c)$, by the linear dependence of $\bar{f}$ on c, and also by the dependence on the concentration of $a_\mathbf{q}$ which is different for different solutions. If the correlation in the solution is significant, then the dependence of I_Φ on the concentration, as may be seen from (23) and (27), becomes even more complicated, owing to the fact that $\epsilon(\rho)$ and φ_{cc} depend strongly on c. Moreover, I_Φ also depends strongly on the annealing temperature T′ at which short range order is established. Apparently, for small q, a typical behavior will be an increase of I_ϕ with diminishing T′ for decaying solutions, and an increase of I_ϕ for solutions that are becoming ordered (although exceptions are possible).

The intensity of diffuse scattering in the vicinity of lattice points of the reciprocal lattice becomes particularly great for solutions which are in the neighborhood of a critical point on the decay curve (point K in Fig. 2 of I). As is well known, $\varphi_{cc} = 0$ at a critical point. Therefore, right at the critical point, I_ϕ increases for small q proportionally to q^{-4} since $\beta q^2 \ll 1$ ($\beta k_m^2 \sim 1$) for $q \ll k_m$ and in this case I_ϕ is considerably larger than, say, for ideal solutions.* In the neighborhood of the critical point φ_{cc} is very small and for small q, when $\beta q^2 < \varphi_{cc}$, I_ϕ is proportional to q^{-2}, but with a very large coefficient of proportionality.†
If the sizes of the atoms A and B are nearly equal and $a_\mathbf{q}$ is small, then the dependence of I_ϕ on **q** agrees with that obtained in I for not too small q, when $|a_\mathbf{q} f q_1/q| \ll |f_A - f_B|$ (but $q \ll k_m$).

In order to calculate L, which determines the reduction in the intensity of the regular reflections, it is necessary in the general case, as follows from (7), to know $a_\mathbf{k}$ and $g_\mathbf{k}$ not only for long, but also for short wavelengths, i.e., it is necessary to utilize a specific atomic model. Such calculations will be carried out elsewhere. Here we shall merely quote the formula for L obtained by Huang[5] for weak solutions (and also applicable to ideal solutions) with a face-centered cubic lattice and improved in accordance with formula (14) by the addition of the factor $(1 + \sigma)^2/9(1 - \sigma)^2$, which takes into account the difference in the displacements brought about by a point defect in an infinite and a finite crystal (cf. Ref. 14):

$$L = 2B\frac{\sin^2\theta}{\lambda^2} = \frac{16\pi^2}{\lambda^2}u_i^2 n_i^2$$

$$= 0.234c(1-c)\left(\frac{1+\sigma}{1-\sigma}\right)^2\left(\frac{1}{v}\frac{\partial v}{\partial c}\right)^2\frac{d_0^2}{\lambda^2}\sin^2\theta. \qquad (28)$$

Here u_i^2 is the mean square of the i-th component of the static displacements of the atom, and d_0 is the length of an edge of the cubic cell. In deriving formula (28) atomic structure was taken into account explicitly, but the displacements of each atom were calculated in the approximation of an isotropic continuum and may differ considerably from the true displacements. In the case of non-ideal solutions L, generally speaking, decreases when short-range order, which is characteristic of decaying solutions, is established.

The evaluation of L can be carried out without taking atomic structure into account if the solution is near a critical point on the decay curve. Since, in accordance with (26), $1/g_\mathbf{k}$ decreases rapidly in this case (maximum value at $\mathbf{k} = 0$), the region of small **k** is the most important one in the summation (7). Making the transition in (7) from summation to integration over **k**, extending the region of integration to infinity, and making use of (14), we find in the approximation of the isotropic continuum that near the critical point

$$L = \frac{8\pi}{27}\left(\frac{1+\sigma}{1-\sigma}\right)^2\frac{kT}{\sqrt{\varphi_{cc}\beta}}\frac{1}{\lambda^2}\sin^2\theta.$$

In the case of specific crystals, it is not difficult to obtain L near a critical point, even without using the approximation of an isotropic continuum, by making use of (16) or (17) and by carrying out numerical integration over the angles. The above formula allows us to calculate L if the value of β has been previously determined from the data on diffuse scattering. As the critical point is approached the intensity of regular reflection is reduced in proportion to

$$\exp(-\text{const}\,\varphi_{cc}^{-1/2}).$$

This law ceases to hold in the immediate neighborhood of the critical point L > 1 and the stricter criterion (9) (see note†) is no longer satisfied.

It follows from (7), (16), and (20) that for the same $\sin\theta/\lambda$ (same q_1), but for different directions of $\mathbf{q}_1$, the values of L for non-cubic crystals may differ appreciably. Formula (28), while giving a correct estimate of L, may, generally speaking, lead to appreciable quantitative error. An evaluation of L, taking atomic structure into account by means of formulas (7) and (20), yields an improved expression for L and permits us to investigate its dependence on the direction of $\mathbf{q}_1$ and on the correlation parameters.

Expression (27) for I_ϕ in the vicinity of regular reflections was compared with experimental data by Borie[9] for a disordered solution Cu_3Au quenched at 600°C. The value of $a_\mathbf{q}$ for **q** direc-

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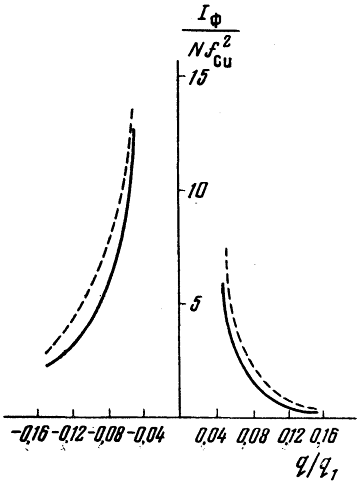
*For crystals of finite size in the region of very small q ($qa \sim 1$, where a are the dimensions of the crystal) the formulas obtained above cease to hold at the critical point. The region indicated above in the space of the reciprocal lattice is occupied by extended Laue reflection as a result of diffraction by a crystal of finite size.

†It should be noted that in the neighborhood of the critical point it is necessary to satisfy in place of the criterion (9) a more strict criterion, which is obtained from (9) by replacing k_m by $\sqrt{\varphi_{cc}/\beta}$.

ted parallel to a cubic axis is computed by means of formula (17). In doing this it was assumed in accordance with Ageev and Shoikhet[15] that $v^{-1}\partial v/\partial c = 0.4$, and in accordance with the data of Siegel[16] (for ~ 400°C.) it was assumed that $(c_{11} + 2c_{12})/3c_{11} = 0.87$. With the aid of thermodynamic data on the activity of Cu in Cu — Au (Ref. 17) it was found that at 600°C. $\varphi_{cc} = 13kT/\Delta$. For small q it was possible to neglect βq^2 in comparison with φ_{cc}. For the ratio of the atomic factors corresponding to the reflection (200), the value $f_{Au}/f_{Cu} = 3.0$ was adopted. According to Borie,[9] the factor e^{-L} for the reflection under discussion practically does not differ from unity (~ 0.96). With the aid of these values for the parameters, we have calculated by means of formula (27) the theoretical curve of the dependence of I_ϕ/Nf^2_{Cu} on q/q_1 for the direction (100) in the reciprocal lattice in the vicinity of the (200) reflection (the solid curve in the figure). In the same figure we have also shown the experimental curve (dotted line) obtained by Borie[9] after subtracting the Compton and the thermal scattering. The difference between the calculated and the measured values of I_ϕ lies within the limits of error of the experimental determination of the parameters of the theory (the inaccuracy in the determination of φ_{cc} may be particularly significant). Therefore the agreement between theory and experiment may be considered to be good, particularly if we take into account the fact that in constructing the theoretical curve all the parameters have been determined from independent experimental data.



For the same solution Cu_3Au we have also evaluated the factor 2B with the aid of formula (28). In doing this we have assumed $\sigma = 0.36$ (calculated on the assumption that σ depends linearly on c). The calculated value of 2B is equal to $0.43\,A^{-2}$, while the measured value is equal to $0.42\,A^{-2}$ according to the data of Borie,[9] and is equal to $0.34\,A^{-2}$ according to the data of Herbstein, Borie and Auerbach.[3] The agreement of the measured values of 2B with those calculated with the aid of the formula for ideal solutions obtained in the approximation of an isotropic continuum is apparently related to the smaller influence of short range order on L than on I_ϕ, and also to a partial compensation of errors introduced by the different approximations.

2. ORDERED SOLUTIONS

It is not difficult to generalize the results obtained above to the case of ordered solutions of arbitrary structure having a center of symmetry. The distribution of atoms A and B among the lattice points of the solution may, as before, be characterized by the numbers c_s or by their Fourier components $c_{\mathbf{k}}$. However, in ordered solutions the lattice is subdivided into lattice points of several kinds and the average atomic concentrations $\overline{c}_\gamma$ of atoms A on the lattice points of different kinds γ become different. The coefficients w and V in the expansion (18) for the free energy now depend not only on the distance between the lattice points s and s′, but also on the kind of lattice points. Therefore the wave of displacements of the lattice corresponding to the **k**-th fluctuation wave has different amplitudes $a_{\mathbf{k}\gamma}$ [see formula (2)] for lattice points of different kinds. These amplitudes are determined from a system of linear equations which are obtained by substituting values corresponding to the **k**-th wave into expressions of the type (19) for lattice points of different sorts, in place of $c_s - c_\gamma$ and $\delta R_{s'j'}$, and by equating F_{si} to zero:

$$iV^{\gamma\gamma'}_{ss'ij}n'_{j\gamma'}\frac{a_{\mathbf{k}\gamma'}}{k}\exp(i\mathbf{k},\ \mathbf{R}_s - \mathbf{R}_{s'}) = w^{\gamma\gamma'}_{ss'i}\exp(i\mathbf{k},\ \mathbf{R}_s - \mathbf{R}_{s'}) \tag{29}$$

In the limit of long wavelengths, it may be easily seen that $a_{\mathbf{k}\gamma}$ for different γ are the same and, as before, are determined by formula (16) of the theory of elasticity.

In decomposing the atomic factors into their average values and deviations from the average in an ordered crystal, one must introduce the average atomic factors $\overline{f}_\gamma = \overline{c}_\gamma f_A + (1 - \overline{c}_\gamma) f_B$ for lattice points of each kind. The averaged structure obtained in this way possesses lower symmetry than the solution with a disordered distribution of atoms among the lattice points of the same lattice, as a result of which each elementary cell of the reciprocal lattice of the above disordered solution will contain lattice points corresponding to superstructural reflections, in addition to the lattice points corresponding to structural reflections (which remain when disordering takes place). With the aid of formulas (3) and (2), the expression for the intensity of scattering by an ordered solution in the approximation adopted above may be written in the form:*

$$I = 8\pi^3 \frac{N_0}{\Delta'} \sum_l |f_l|^2 \delta(\mathbf{q}_l)$$

$$+ N_0^2 \overline{\left| \sum_{l=0}^{\nu-1} c_{\mathbf{q}l} f'_l \frac{\mathbf{q}_1 \mathbf{q}'_l}{q_l^2} a_{\mathbf{q}l1} - \nu (f_A - f_B) c_{\mathbf{q}0} \right|^2}. \qquad (30)$$

Here N_0 is the number of elementary cells of the ordered solution; Δ' is the volume of these cells; the index ℓ denotes lattice points in any cell of the reciprocal lattice of the above solution which are characterized by the vectors $\mathbf{K}_\ell$ (with the value $\ell = 0$ corresponding to a structural reflection); $\mathbf{q}_\ell = \mathbf{q}_1 - 2\pi \mathbf{K}_\ell$ is the vector $\mathbf{q}_1$ "reduced" to one of the elementary cells of the reciprocal lattice of the ordered crystal lying in the central elementary cell of the disordered crystal; $c_{\mathbf{q}\ell}$ is the Fourier coefficient of the quantities c_s corresponding to the vector $\mathbf{q}_\ell$; $a_{\mathbf{q}\ell_1}$ is the coefficient $a_{\mathbf{q}\gamma}$ for lattice points of the first kind ($\gamma = 1$) corresponding to this vector;

$$f_l = \sum_{\gamma=1}^{\nu} \bar{f}_\gamma \exp(2\pi i \mathbf{K}_l \mathbf{h}_\gamma) \exp(-L_\gamma/2)$$

is the structure factor for the ℓ-th reflection; ν is the number of lattice points in a cell; $\mathbf{h}_\gamma$ is a vector drawn from the central lattice point of the cell to the lattice point of index γ;

$$\mathbf{q}'_l f'_l = \sum_{\gamma=1}^{\nu} \bar{f}_\gamma (a_{\mathbf{q}l\gamma}/a_{\mathbf{q}l1}) \exp(-L_\gamma/2) \cdot \exp(2\pi i \mathbf{K}_l \mathbf{h}_\gamma) q_l \mathbf{n}'_\gamma$$

($f'_\ell \rightarrow f_\ell$ as $\mathbf{q} \rightarrow 0$), and $\exp(-L_\gamma/2)$ is a factor which takes into account the reduction in the scattering amplitude by atoms situated at lattice points of the γ kind, owing to geometrical distortions. L_γ are different for lattice points of different kind. In the interest of brevity we shall not give here formulas for these quantities. (They may be determined experimentally from the reduction in the intensity of lines on an x-ray photograph by means of the usual methods of analyzing such x-ray photographs.) We note that $L_\gamma \sim (\sin\theta/\lambda)^2$ and that for non-cubic crystals they are anisotropic.

In calculating the average value of (30) it should be kept in mind that, in contrast to the case of disordered solutions, nonzero values are obtained not only for mean squares but also for the mean values of the products of the Fourier components $c_{\mathbf{q}}$ with different $\mathbf{q}_\ell$ and $\mathbf{q}_j$ which, however, correspond to the same value of the vector $\mathbf{q}_1$. These mean values can be easily expressed in terms of the correlation parameters, starting with formula (1) for $c_{\mathbf{k}}$ (in which in the terms involving lattice points of each kind one should replace c by the corresponding value of c_γ):

$$\overline{|c_{\mathbf{q}l}|^2} = \frac{1}{N\nu} \sum_{\gamma=1}^{\nu} [\bar{c}_\gamma (1 - \bar{c}_\gamma) - \sum_{\rho \neq 0}^{\bullet} \varepsilon_\gamma(\rho) \cos \mathbf{q}_l \rho],$$

$$\frac{1}{2} \overline{(c_{\mathbf{q}l} c^*_{\mathbf{q}j} + c^*_{\mathbf{q}l} c_{\mathbf{q}j})} = \frac{1}{N\nu} \sum_{\gamma=1}^{\nu} [\bar{c}_\gamma (1 - \bar{c}_\gamma) \cos(2\pi \mathbf{h}_\gamma, \mathbf{K}_l - \mathbf{K}_j)$$

$$- \sum_{\rho \neq 0} \varepsilon_\gamma(\rho) \cos(\mathbf{q}_l \rho + 2\pi \mathbf{h}_\gamma, \mathbf{K}_l - \mathbf{K}_j)]. \qquad (31)$$

Here $\mathbf{q}_\ell - \mathbf{q}_j = 2\pi(\mathbf{K}_j - \mathbf{K}_\ell)$, while the correlation parameters are given by

$$\varepsilon_\gamma(\rho) = [\bar{c}_\gamma \bar{c}_{\gamma'} - \overline{c_s c_{s'}^{(\gamma\rho)}}],$$

where the averaging is carried out over pairs of lattice points separated from each other by the distance ρ, while s is a lattice point of the γ kind. Substituting (31) into (30) we obtain

$$I = 8\pi^3 \sum_l |f_l|^2 \delta(\mathbf{q}_l) + \frac{N_0}{\nu^2} \Big\{ \sum_{l=0}^{\nu-1} \sum_{\gamma=1}^{\nu} [\bar{c}_\gamma (1 - \bar{c}_\gamma)$$

$$- \sum_{\rho \neq 0} \varepsilon_\gamma(\rho) \cos \mathbf{q}_l \rho] [a_{\mathbf{q}l1} f'_l \mathbf{q}_1 \mathbf{q}'_l q_l^{-2} - \nu (f_A - f_B) \delta_{l0}]^2$$

$$+ \sum_{l,j=1}^{\nu-1} \sum_{\gamma=1}^{\nu} [\bar{c}_\gamma (1 - \bar{c}_\gamma) \cos(2\pi \mathbf{h}_\gamma, \mathbf{K}_l - \mathbf{K}_j)$$

$$- \sum_{\rho \neq 0} \varepsilon_\gamma(\rho) \cos(\mathbf{q}_l \rho + 2\pi \mathbf{h}_\gamma, \mathbf{K}_l - \mathbf{K}_j)]$$

$$\times [a_{\mathbf{q}l1} f'_l \mathbf{q}_1 \mathbf{q}'_l q_l^{-2} - \nu (f_A - f_B) \delta_{l0}]$$

$$\times [a_{\mathbf{q}j1} f'_j \mathbf{q}_1 \mathbf{q}_j q_j^{-2} - \nu (f_A - f_B) \delta_{j0}]. \qquad (32)$$

Thus, just as in the case of absence of distortions, the scattering intensity is expressed in terms of the concentrations on lattice points of different kinds and in terms of the correlation parameters. Formula (32) together with equations (29) enables us to determine I_ϕ from given values of $\bar{c}_\gamma$ and $\epsilon_\gamma(\rho)$ and also enables us, in a number of cases, to determine $\epsilon_\gamma(\rho)$ (or certain combinations of them) from an experimentally determined intensity distribution I_ϕ. From (32) it can be seen that in the neighborhood of both the structural and the superstructural reflections I_ϕ increases proportionally to q^{-2}. The principal terms proportional to q^{-2} may be represented in the neighborhood of the lattice points of the recip-

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*In the discussion of ordered solutions it is assumed that there are no anti-phase domains in the crystal. The existence of such non-equilibrium domains, which arise if the relaxation times for ordering are large, leads to a smearing of the intensity distribution.

rocal lattice in a simple form if one makes use of formula (26) for $|\overline{c_{\mathbf{q}_\ell}}|^2$:

$$I_\Phi \approx (N_0/\Delta')\, a_{\mathbf{q}l}^2(\mathbf{q}_1\mathbf{q}'_l)^2\, q_l^{-4}\, |f_l|^2\, kT\, (\varphi_{cc} + \beta q^2)^{-1}. \quad (33)$$

As may be seen from (33), the intensity of this part of the diffuse scattering, just like the intensity of the corresponding regular reflection, is proportional to the square of the modulus of the structure factor f_ℓ. If $|a_{\mathbf{q}\ell}\overline{f}_\ell| \ll |f_A - f_B|$, then in the neighborhood of structural reflections one may, as before, use formula (27) for the determination of I_ϕ (and not only of its part proportional to q^{-2}), i.e , one may determine I_ϕ with the aid of independent thermodynamic measurements.

For a more detailed investigation of the dependence of I_ϕ on the temperature in the vicinity of regular reflections it is convenient to introduce parameters of long-range order. Such a discussion will be carried out for the sake of simplicity for ordered solutions with two lattice points in an elementary cell (for example solutions of the type of β-brass or NaCl), in which one may restrict oneself to specifying a single long-range order parameter η. In this case one may characterize the distribution of atoms A and B among the lattice points of the lattice by specifying the numbers c'_t and η_t, where t is the cell index, c'_t is equal to the arithmetic mean of the numbers c_s for the two lattice points of the cell, and η_t is equal to the difference of these numbers. The average values of the quantities c'_t and η_t coincide with c and η (which are related to $\overline{c}_\gamma$ by the expressions $\overline{c}_1 = c + \eta/2$, $\overline{c}_2 = c - \eta/2$). In place of c'_t and η_t one may introduce their Fourier components $c'_\mathbf{k}$ and $\eta_\mathbf{k}$ for $\mathbf{k}/2\pi$ lying in the first cell of the reciprocal lattice of the ordered crystal. Then instead of (2) the $\delta\mathbf{R}_s$ are determined by the formula

$$\delta\mathbf{R}_s = \sum_\mathbf{k} p_\gamma a_\mathbf{k} \mathbf{k}' k^{-2} i\, [c'_\mathbf{k} \exp(-i\mathbf{k}\mathbf{R}_s) - c'^{*}_\mathbf{k} \exp(i\mathbf{k}\mathbf{R}_s)]$$
$$+ \sum_\mathbf{k} p'_\gamma b_\mathbf{k} \mathbf{k}' k^{-2} i\, [\eta_\mathbf{k} \exp(-i\mathbf{k}\mathbf{R}_s) - \eta^{*}_\mathbf{k} \exp(i\mathbf{k}\mathbf{R}_s)]. \quad (34)$$

Here p_γ and p'_γ reduce to unity as $\mathbf{k} \to 0$ and $a_\mathbf{k}$, as in the case of disordered solutions, is determined by formulas (16), (17), while $b_\mathbf{k}$ is determined by analogous formulas in which c is replaced by η.

Evaluating the average value of (4) by means of (34) and of the Gaussian probability distribution for $c'_\mathbf{k}$ and $\eta_\mathbf{k}$ [formula (9) of I], in the same way in which this was done for disordered solutions, we find that, in the neighborhood of structural reflections, I_ϕ is equal to

$$I_\Phi = \frac{N}{\Delta}\,\frac{kT}{(\varphi'_{\eta\eta} + \alpha q^2)(\varphi'_{cc} + \beta' q^2) - (\varphi'_{\eta c} + \gamma q^2)^2}\Big\{(\varphi'_{\eta\eta} + \alpha q^2)\Big[\frac{a_\mathbf{q}\overline{f}(\mathbf{q}_1\mathbf{q}')}{q^2} - f_A + f_B\Big]^2 - 2(\varphi'_{\eta c} + \gamma q^2)\, b_\mathbf{q}\frac{(\mathbf{q}_1\mathbf{q}')}{q^2}\overline{f}\Big[\frac{a_\mathbf{q}\overline{f}(\mathbf{q}_1\mathbf{q})}{q^2} - f_A + f_B\Big]$$
$$+ (\varphi'_{cc} + \beta' q^2)\, b_\mathbf{q}^2 \frac{(\mathbf{q}_1\mathbf{q}')^2}{q^4}\overline{f}^2\Big\} \approx \frac{N}{\Delta}\,\frac{kT}{(\varphi'_{cc} + \beta' q^2) - (\varphi'_{\eta c} + \gamma q^2)^2/(\varphi'_{\eta\eta} + \alpha q^2)^2}\Big[\frac{a_\mathbf{q}\overline{f}(\mathbf{q}_1\mathbf{q}')}{q^2} - f_A + f_B\Big]^2 \quad (35)$$

In the neighborhood of superstructural reflections I_ϕ is given by the formula

$$I_\Phi = \frac{N}{4\Delta}\,\frac{(f_A - f_B)^2 kT}{(\varphi'_{\eta\eta} + \alpha q^2)(\varphi'_{cc} + \beta' q^2) - (\varphi'_{\eta c} + \gamma q^2)^2}\Big[(\varphi'_{cc} + \beta' q^2)\Big(1 - \eta b_\mathbf{q}\frac{\mathbf{q}_1\mathbf{q}'}{q^2}\Big)^2 - 2(\varphi_{\eta c} + \gamma q^2)\,\eta a_\mathbf{q}\frac{\mathbf{q}_1\mathbf{q}'}{q^2}\Big(\eta b_\mathbf{q}\frac{\mathbf{q}_1\mathbf{q}'}{q^2} - 1\Big)$$
$$+ (\varphi_{\eta\eta} + \alpha q^2)\, a_\mathbf{q}^2\eta^2\frac{(\mathbf{q}_1\mathbf{q}')^2}{q^4}\Big] \approx \frac{N}{4\Delta}\,\frac{(f_A - f_B)^2 kT}{(\varphi'_{\eta\eta} + \alpha q^2)(\varphi'_{cc} + \beta' q^2) - (\varphi'_{\eta c} + \gamma q^2)^2}$$
$$\times\Big[\varphi'_{cc} + \beta' q^2 + 2(\varphi'_{\eta c} + \gamma q^2)\,\eta a_\mathbf{q}\frac{\mathbf{q}_1\mathbf{q}'}{q^2} + (\varphi'_{\eta\eta} + \alpha q^2)\, a_\mathbf{q}^2\eta^2\frac{(\mathbf{q}_1\mathbf{q}')^2}{q^4}\Big]. \quad (36)$$

In the above, $\mathbf{q}/2\pi$ characterizes in both cases the deviation of a point in the space of the reciprocal lattice from the corresponding lattice point. In the expressions, which appear in (35) and (36) after the sign of approximate equality, terms containing $b_\mathbf{q}$ have been neglected. For small q these terms are proportional to ϵ^2, where ϵ is a parameter which characterizes the difference in the atomic radii of atoms A and B in the solution (for small $\eta b_\mathbf{q}$ they are also proportional to η), while $a_\mathbf{q} \sim \epsilon$. Therefore the retention of terms containing $b_\mathbf{q}$ would not be quite consistent within the framework of the approximation under discussion, when fluctuations in the short-range order parameters, which also lead to effects proportional to ϵ^2, are not taken into account (the short range order itself is, of course, taken into account). The possibility of neglecting the above terms is justified by the observation that for most solutions (for example AuCu) v changes considerably less as a result of ordering than of going over from component A to B. However, cases are possible when taking into account terms containing $b_\mathbf{q}$ would improve the expression for I_ϕ.

For sufficiently small q one may neglect terms on the order of q^2 compared to φ'_{cc}, $\varphi'_{\eta c}$ and

$\varphi'_{\eta\eta}$. In this case the following expression appears in the denominator of formula (35)

$$\varphi'_{cc} - \varphi'^{2}_{\eta c} / \varphi'_{\eta\eta} = \varphi_{cc} = \frac{kT}{(1-c)\,\Delta}\,\frac{d \ln a_{\mathrm{A}}}{dc},$$

where in the evaluation of the derivative d/dc (in contrast to $\partial/\partial c$) the dependence of η on c is taken into account. At the temperature T_0 of the phase transition of the second kind into the ordered state, I_ϕ varies sharply in the vicinity of structural reflections, but remains finite. The dependence of I_ϕ on $\mathbf{q}$ in the vicinity of superstructural reflections close to the temperature T_0 differs essentially from the corresponding dependence near structural reflections. While near structural reflections I_ϕ always contains a term proportional to q^{-2}, near points of the reciprocal lattice corresponding to superstructural reflections for $T > T_0$ $(\eta = 0)$ such a term is missing entirely, while for $T < T_0$ it is proportional to η^4 $(\varphi'_{\eta\eta}/\varphi'_{cc} \sim \eta^2,\ \varphi'_{\eta c}/\varphi'_{cc} \sim \eta)$ and begins to play an essential role only for very small q, when $q/q_1 \sim a_{\mathbf{q}}\eta^2$. For $T > T_0$, the expression for I_ϕ turns out to be the same as in the absence of geometrical distortions [see formula (10) in I]. Since at $T = T_0$ $\varphi'_{\eta\eta} = 0$ and $\varphi'_{\eta c} = 0$, in the neighborhood of this temperature the first term in (36) determines the anomalously large scattering in the neighborhood of superstructural reflection which was discussed in Ref. 18 for single component crystals and in I for solid solutions.

At the critical point at which the curve of phase transitions of the second kind goes over into the decay curve (point 0 in Fig. 1 of I) the condition[19] $\varphi'_{cc}\varphi'_{\eta\eta} = \varphi'^{2}_{\eta c}$ is fulfilled in the ordered phase. Therefore, as is evident from (35), in the neighborhood of this point, I_ϕ in the ordered phase becomes especially large not only near superstructural reflections, but also near structural reflections where the terms $\sim q^{-2}$ are also anomalously large. In the disordered phase, $\varphi'_{\eta c} \equiv 0$ and I_ϕ must be considerably smaller in the vicinity of structural reflections.

The expression for I_ϕ assumes a simple form also in the case of almost completely ordered solutions $(T \ll T_0)$. In this case, as shown by the author,[20] one may neglect $\epsilon_\gamma(\rho)$ in comparison with the products $\bar{c}_\gamma(1-\bar{c}_\gamma)$ (also small). Therefore in the general formula (32) one may neglect terms containing $\epsilon_\gamma(\rho)$, so that I_ϕ turns out to be expressed only in terms of the parameters $\bar{c}_\gamma$, which characterize the long-range order. In the special case of structures considered above, which are characterized by a single long range order parameter, we shall obtain from (32)

$$I_\Phi = N\,[c\,(1-c) - \eta^2/4]\,\{[a_{\mathbf{q}}\bar{f}\,(\mathbf{q}_1\mathbf{q}')/q^2 - f_{\mathrm{A}} + f_{\mathrm{B}}]^2 + (f_{\mathrm{A}} - f_{\mathrm{B}})^2\,a^2_{\mathbf{q}'}\,(\mathbf{q}_1\mathbf{q}'_s)^2/q'^4\}, \tag{37}$$

where $\mathbf{q}/2\pi$ and $\mathbf{q}_s/2\pi$ characterize distances to lattice points corresponding to structural and superstructural reflections. For $\eta \approx 1$, as was shown by the author,[20] $c(1-c) - \eta^2/4$, and consequently also I_ϕ, decrease exponentially as the temperature is lowered.

The formulas obtained above have been derived for binary substitution solutions. They may also be applied to the determination of I_ϕ in the vicinity of regular reflections by occlusion solutions in which atoms are occluded between the lattice points of the crystalline lattice of the pure metal. By means of the method developed above it is not difficult to obtain formulas for I_ϕ in such solutions, valid for arbitrary $\mathbf{q}$. We note that with the aid of formula (21) it is also possible to determine the intensity of scattering by vacancies (or by complexes of vacancies) if c is interpreted as their concentration (equilibrium or non-equilibrium). The method developed above may also be used for the investigation of scattering by more complicated defects, for example by precipitations formed on aging or by dislocations.

In conclusion we note that the method used here, in which the geometrical distortions are related to fluctuations of composition or of internal parameters, may also be employed for the solution of other problems related to geometrical distortions in solution, for example for the determination of its electrical resistance, of the elastic energy of the distortions, of the mean squared displacements of the atoms, etc.

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29