SOVIET PHYSICS JETP VOLUME 5, NUMBER 6 DECEMBER 15, 1957

Theory of Diffuse Scattering of X-Rays and Thermal Neutrons in Solid Solutions. II.

Microscopic Theory

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(Submitted to JETP editor May 13, 1956)
J. Exptl. Theoret. Phys. (U.S.S.R.) 32, 1368-1381 (June, 1957)

Diffuse scattering of x-rays and thermal neutrons by composition and order fluctuations in solid solutions is considered. For disordered solutions and ordered solutions of *AB* stoichiometric composition the calculations have been carried out taking into account interaction between atoms lying in coordinative spheres separated by arbitrarily large distances. A method is indicated for the determination of the ordering energy for various coordinative spheres from the experimental distribution of the background intensity. Anomalously high diffuse scattering near points of phase transition of the second order and near critical points on the decay curve is considered.

TWO TYPES OF APPROACH are possible in the investigation of scattering of x-rays and of slow neutrons by solid solutions. Usually in calculating the intensity of scattered radiation the interference pattern formed by secondary waves scattered by various atoms is first obtained for a given configuration of atoms at the various lattice points, and then an average is taken over the various possible configurations (see, for example, Refs. 1–8). In this approach the intensity of scattered radiation turns out to be expressed in terms of the correlation parameters for the occupancy of the different lattice points by atoms of a given kind. The formulae obtained in this way are convenient for calculating the intensity of scattered radiation when the distant order and the correlation parameters are known, and also for the solution of the inverse problem, that of determining the correlation parameters from the distribution of intensity of diffuse scattering as given by experiment. However, as a result of the fact that the calculation of correlation parameters for different coordinative spheres as functions of the temperature, of the composition of the solution, and of parameters characterizing the interaction energies of the crystal is, as a rule, difficult, this method of investigating the scattering is less convenient for the determination of the intensity of the scattered radiation as a function of the quantities enumerated above. The dependence of the intensity of diffuse scattering on the temperature and on the concentration has been found for a one-dimensional lattice. For a three-dimensional crystal a calculation of this type has been carried out in the nearest neighbor approximation only for the case of high temperatures when the correlation in the solution is not great. The very interesting case when the temperature of the solution is of the same order of magnitude as the temperature of transition into the ordered state was not considered.

Another method which was introduced by Einstein[9] for treating the problem of light scattering is considerably more convenient for the investigation of the dependence of the intensity of scattering on the temperature, on the composition and on the constants of the interatomic interaction. The crystal is regarded as a periodic structure consisting of effective atoms which is responsible for the appearance of lines (or spots) on an x-ray photograph. Fluctuations of composition and long range order which give rise to diffuse scattering of waves are superimposed on this periodic structure. The probability of fluctuations depends in an essential way on the temperature, on the composition and on the energy parameters and this permits one to relate these quantities in a simple manner to the intensity of diffuse scattering of x-rays or of neutrons. This method was applied for the first time to the scattering of x-rays by Landau[10] who considered scattering by fluctuations in the degree of long range order in crystals of molecular type near a point of phase transition of the second order. The scattering by solid solutions, which in addition to fluctuations of long range order also have fluctuations in composition with the correlation between these fluctuations being important, was investigated by the present author[11] (this paper will be referred to as I). In Refs. 10 and 22 scattering was considered to be due to fluctuations extending over a large number of lattice constants, which permits one to carry out a phenomenological investigation without making use of a concrete model for the crystal. However, in view of the fact that the x-ray wavelengths are of the same order as the lattice constants, the above large scale fluctuations are associated with diffuse scattering through angles close either to the directions of Bragg scattering or to the incident beam. In order to find the intensity of scattering at arbitrary angles it is necessary to consider fluctuations whose dimensions are of the same order as the lattice constant. The calculation of probabilities of such fluctuations can no longer be carried out by means of the thermodynamic theory of solutions and a concrete statistical model of the solution must be used which necessarily must contain a number of simplifying assumptions. At the same time the use of such a model makes it possible to relate the intensity of diffuse scattering to the constants of the atomic interaction.

In this paper the intensity of the scattered radiation is determined with the aid of the usual statistical model of a solid solution in which the energy of the crystal is represented as the sum of the interaction energies of different atom pairs. Just as in I, the background associated with the geometric (statistical and thermal) lattice distortions will not be considered, *i.e.*, only that part of the diffuse scattering will be investigated which is determined by the distribution (which is to some extent random) of the various kinds of atoms among the crystalline lattice points. The presentation will be given in terms of x-ray scattering. However, the results obtained will equally well apply to the scattering of thermal neutrons if in place of atomic factors for the scattering of x-rays one substitutes the neutron scattering factors averaged over the isotopes and takes into account the fact that in addition to the background considered here there exists in the case of neutron scattering a background associated with the random distribution of isotopes and with neutron scattering dependent on nuclear spins (see, for example, Ref. 8). Although the solution model used here is a very approximate one the method developed below may also be applied to more accurate models whenever they might be introduced.

1. GENERAL EXPRESSION FOR THE INTENSITY OF SCATTERING BY A SOLID SOLUTION

Almost all the known solid solutions of metals have in the disordered state crystalline lattices in which the elementary cell contains only one atom. A lattice of such type may be decomposed into n geometrically identical sublattices similarly situated with respect to each other (containing lattice points of a given kind) in such a way that each atom interacts only with the nearest atoms of other sublattices and does not interact with atoms at lattice points of its own sublattice. By choosing a sufficiently large n one can take into account the interaction with atoms situated in distant coordinative spheres.

The distribution of atoms among the lattice points of the binary solution $A-B$ may be characterized by the set of quantities p_{Ais} equal to unity or zero depending on whether the sth point of the ith sublattice is occupied by atom A or B respectively. Within the framework of the kinematic scattering theory the intensity of scattering of monochromatic x-rays by a single crystal with a given distribution of atoms may be written when expressed in electronic units in the form

$$I=\left|\sum_{i=1}^{n}\sum_{s=1}^{N_0}(f_A p_{Ais}+f_B p_{Bis})\exp(i\mathbf{q}\mathbf{R}_{is})\right|^2. \quad (1)$$

Here $N_0 = N/n$ is the number of atoms in a sublattice, $\mathbf{q} = \mathbf{k}_2 - \mathbf{k}_1$ is the difference between the propagation vectors of the scattered and incident waves, $\mathbf{R}_{is} = \mathbf{R}_i + \mathbf{R}_s$ is the vector drawn from the origin of coordinates to the sth lattice point of the ith sublattice, $p_{Bis} = 1 - p_{Ais}$, f_A and f_B are the atomic scattering factors of atoms A and B corresponding to the vector $\mathbf{q}$. The expression $f_A p_{Ais} + f_B p_{Bis}$, which changes in going over from one lattice point to another, can be written in the form of a sum of the term $f_A p_{Ai} + f_B p_{Bi}$ (p_{Ai} and p_{Bi} are the probabilities that the lattice points of the ith sublattice are occupied by atoms A and B) averaged over the lattice points of the given sublattice, and of the deviation $(p_{Ais} - p_{Ai})(f_A - f_B)$ from the average value. The square of the term corresponding to the purely periodic distribution of "average atoms"

$$I_1=\left|\sum_{i=1}^{n}(f_A p_{Ai}+f_B p_{Bi})\exp(i\mathbf{q}\mathbf{R}_i)\right|^2 \times\left|\sum_{s=1}^{N_0}\exp(i\mathbf{q}\,\mathbf{R}_s)\right|^2, \quad (2)$$

determines the intensity of the sharp lines (situated at $\mathbf{q} = 2\pi\mathbf{K}_n$ where $\mathbf{K}_n$ are the vectors of the reciprocal lattice) which will not be discussed below. The cross term disappears in the limit of an infinite crystal. The square of the second term is determined by the deviation of the actual distribution of the atoms among the lattice points from the average distribution and describes the diffuse scattering. The intensity of this scattering is equal to

$$I_2 = N_0^2 |f_A - f_B|^2 \left| \sum_{i=0}^{n} p_{\mathbf{q}i} \right|^2, \tag{3}$$

where

$$p_{\mathbf{q}i} = \frac{1}{N_0} \sum_{s=1}^{N_0} (p_{Ais} - p_{Ai}) \exp(i\,\mathbf{qR}_{is}) \tag{4}$$

and in the rest of this section we shall take **q** to be a reduced vector. We shall label the atomic planes perpendicular to the vector **q** by the index f. If **q** is not perpendicular to any system of atomic planes then the crystal may be divided into "infinitely thin" layers perpendicular to **q** which can also be labelled by the index f. The numbers of lattice points belonging to one of the sublattices are the same for the various parallel planes containing lattice points of this sublattice. We denote this number by ν. In summing over lattice points lying in one plane (layer) the exponential factor in (4) remains constant. Therefore in the summation (4) p_{Ais} may be replaced by the average density p^f_{Ai} of atoms A on the lattice points of the ith sublattice in the fth plane. Further, if the Z axis is chosen parallel to the vector **q**, then the expression (4) takes on the following form:

$$p_{\mathbf{q}i} = \frac{\nu}{N_0} \sum_{f_i=1}^{N_0/\nu} (p^f_{Ai} - p_{Ai}) \exp(iqZ_{if}). \tag{5}$$

Thus, in accordance with (3) and (5) the background intensity is determined by the deviation of the densities p^f_{Ai} in the various planes from the average density, *i.e.*, by the distribution of the fluctuations in the distribution of atoms A among the lattice points of the various sublattices. The probability of a given distribution of fluctuation is proportional to $\exp(-R/kT)$ where the minimun work R required to produce such a fluctuation is equal to

$$\begin{aligned} R = {} & \frac{1}{2} \sum_i \sum_f \frac{\partial^2 \varphi}{\partial p^{f2}_{Ai}} (p^f_{Ai} - p_{Ai})^2 \\ & + \sum_{i<j} \sum_{f,g} \frac{\partial^2 \varphi}{\partial p^f_{Ai} \partial p^g_{Aj}} (p^f_{Ai} - p_{Ai})(p^g_{Aj} - p_{Aj}) \\ & + \sum_i \sum_{f<g} \frac{\partial^2 \varphi}{\partial p^f_{Ai} \partial p^g_{Ai}} (p^f_{Ai} - p^g_{Ai})(p^g_{Ai} - p_{Ai}). \end{aligned} \tag{6}$$

Here φ is the thermodynamic potential of the crystal. The second derivatives of the thermodynamic potential with respect to the densities of atoms A in planes not containing lattice points the interaction between which is being taken into account are equal to zero. As a result of this the last term in (6) disappears when the crystal is broken up into sublattices as indicated, while in the second term only those terms are retained which correspond to planes the atoms of which interact with each other. The derivatives with respect to concentrations in atomic planes appearing in (6) are related to the derivatives with respect to the usual concentrations referring to the whole crystal by the expressions

$$\frac{\partial^2 \varphi}{\partial p^{f2}_{Ai}} = \frac{\nu}{N_0} \frac{\partial^2 \varphi}{\partial p^2_{Ai}}; \quad \frac{\partial^2 \varphi}{\partial p^f_{Ai} \partial p^g_{Aj}} = \frac{\nu}{N_0} \frac{z'}{z} \frac{\partial^2 \varphi}{\partial p_{Ai} \partial p_{Aj}}, \tag{7}$$

where z is the total number of lattice points of the jth sublattice closest to the given lattice point of the ith sublattice situated in the fth plane, while z' is the number of such points of the jth sublattice contained in the gth plane.

In accordance with (3) and (5), to determine the background intensity one must know not the spatial distribution of the quantities p^f_{Ai}, but the Fourier components of this distribution. Therefore it is more convenient to calculate directly the average values of the squares and the products of the Fourier components of the quantities p^f_{Ai}, p^g_{Aj}. The expansion into a Fourier series of the difference $p^f_{Ai} - p_{Ai}$ has the form

$$p^f_{Ai} - p_{Ai} = \sum_k [r_{ik} \exp(ikZ_{if}) + r^*_{ik} \exp(-ikZ_{if})], \tag{8}$$

with $0 < k < 2\pi/\Delta Z$ where ΔZ is the distance between adjacent atomic planes (layers). Substituting (8) and (7) into (6) and taking it into account that $k(Z_{ig} - Z_{if}) = \mathbf{ka}_{\xi ij}$, where the vector **k** is directed along the Z axis, $\mathbf{a}_{\xi ij}$ is the vector drawn from a lattice point of the ith sublattice situated in the fth plane to one of the nearest lattice points of the jth sublattice in the gth plane, we obtain

$$\begin{aligned} R = {} & \sum_i \frac{\partial^2 \varphi}{\partial p^2_{Ai}} \sum_{\mathbf{k}} r_{i\mathbf{k}} r^*_{i\mathbf{k}} \\ & + \frac{1}{z} \sum_{i<j} \frac{\partial^2 \varphi}{\partial p_{Ai} \partial p_{Aj}} \sum_{\xi=1}^{z} \sum_{\mathbf{k}} \cos \mathbf{a}_{\xi ij} \mathbf{k} \, (r_{i\mathbf{k}} r^*_{j\mathbf{k}} + r^*_{i\mathbf{k}} r_{j\mathbf{k}}). \end{aligned} \tag{9}$$

Thus the expression for the minimum work breaks up into terms $R_{\mathbf{k}}$ corresponding to different **k**. Therefore the expression for the distribution of the probabilities for the Fourier components of the fluctuations will correspondingly break up into a product of factors corresponding to the individual components. The distribution of the probabilities of fluctuations in the qth Fourier component which, in accordance with (3) and (5), determines the background intensity has the form

$$w \sim \exp\left(-\frac{R_{\mathbf{q}}}{kT}\right) = \exp\left\{-\sum_{i=1}^{n} a_{ii}\left(r'^{2}_{i\mathbf{q}} + r''^{2}_{i\mathbf{q}}\right) - \sum_{i\neq j=1}^{n} a_{ij}\left(r'_{i\mathbf{q}}r'_{j\mathbf{q}} + r''_{i\mathbf{q}}r''_{j\mathbf{q}}\right)\right\}, \tag{10}$$

where

$$a_{ii} = \frac{1}{kT}\frac{\partial^2\varphi}{\partial p^2_{Ai}}; \qquad a_{ij} = \frac{1}{zkT}\frac{\partial^2\varphi}{\partial p_{Ai}\partial p_{Aj}}\sum_{\xi=1}^{z}\cos \mathbf{a}_{\xi ij}\mathbf{q} \quad (i \neq j), \tag{11}$$

while $r'_{i\mathbf{q}}$ and $r''_{i\mathbf{q}}$ denote the real and the imaginary parts of the complex quantity $r_{i\mathbf{q}}$. With the aid of formula (10) one may determine the average values of the squares and of the products of Fourier components belonging to different sublattices

$$\frac{1}{2}\overline{\left(r_{i\mathbf{q}}r^{*}_{j\mathbf{q}} + r^{*}_{i\mathbf{q}}r_{j\mathbf{q}}\right)} = \bar{b}_{ij}. \tag{12}$$

Here the quantites b_{ij} form a matrix inverse to the matrix a_{ij} which is determined by formula (11), and (12) is applicable both for $i \neq j$ and for $i = j$. It follows from (3), (5), (8) and (12) that the intensity of diffuse scattering may be expressed in terms of the quantities b_{ij} in the following manner:

$$I_2 = N_0^2 \left| f_A - f_B \right|^2 \sum_{i,j=1}^{n} b_{ij}. \tag{13}$$

Thus, in order to determine the background intensity it is necessary to know the thermodynamic potential of the solution as a function of the variables p_{Ai} to calculate the matrix a_{ij} with the aid of formulas (11), and then to find the sum of all the matrix elements of the inverse matrix b_{ij}.

The sum $\sum_{i,j=1}^{n} b_{ij}$ may be obtained in a number of cases without carrying out the inversion of the matrix a_{ij}, but by directly finding the sum of the matrix elements of the inverse matrix. Assume that the sum of the matrix elements of each row of the matrix a_{ij} does not depend on the row index and is equal to A:

$$\sum_{i=1}^{n} a_{si} = A. \tag{14}$$

Then the sum of all the matrix elements of the inverse matrix will be equal to

$$\sum_{i,k=1}^{n} b_{ik} = n / A. \tag{15}$$

2. SCATTERING BY DISORDERED SOLID SOLUTIONS

Let us determine the intensity of diffuse scattering by a disordered solution with a crystalline lattice in which the elementary cell contains only one atom, taking into account interactions between pairs of atoms separated by arbitrary distances. For this purpose we pick out within the crystal a polyhedron containing a sufficiently large number of elementary cells to allow us to neglect the interaction of an atom at the center of the polyhedron with atoms outside its boundaries. We shall consider that each lattice point within this polyhedron belongs to its own sublattice, so that the number of sublattices is equal to the number n of lattice points within the polyhedron. Each atom will not interact with the atoms of its own sublattice and will interact with one atom of each of the other sublattices. Therefore for the calculation of the background intensity we can use the method described in the preceding section, and we shall have in the summation (11) for a_{ij} $(i \neq j)$ only one term corresponding to the given i and j $(z = 1)$. In a crystalline lattice whose elementary cell contains only one lattice point all the lattice points are equivalent, and the systems of vectors drawn from a given lattice point to all the other lattice points are the same independently of which lattice point is chosen as the initial one. Further, in a disordered solution the derivatives $\partial^2\varphi/\partial p_{Ai}\partial p_{Aj}$ depend only on the distance between the nearest lattice points of the ith and the jth sublattices (and also on the direction of the vector joining them) but do not depend on the nature of these sublattices. Therefore the same matrix elements appear in the different rows of the matrix a_{ij}, although they may occur in a different order. Therefore, formula (15) may be used for the calculation of the sum of the matrix elements of the inverse matrix, and in accordance with (13)–(15) and (11) the intensity of the diffuse scattering from a disordered solution is

$$I_2 = N\,|f_A - f_B|^2\left[x_0 + \sum_{l=1}^{\infty} x_l \sum_{\varkappa_l=1}^{z_l} \cos \mathbf{a}_{\varkappa l}\mathbf{q}\right]^{-1}. \quad (16)$$

Here l is the index of the coordinative sphere,* $\varkappa_l$ are indices of the lattice points of this sphere, z_l is the coordination number corresponding to the lth sphere, $\mathbf{a}_{\varkappa l}$ is a vector drawn from the central lattice point to the lattice point with the index $\varkappa_l$ in the lth coordinative sphere, and

$$x_0 = \frac{1}{N_0 kT}\,\frac{\partial^2 \varphi}{\partial p_{A1}^2}; \quad x_l = \frac{1}{N_0 kT}\,\frac{\partial^2 \varphi}{\partial p_{A1}\partial p_{Ail}}. \quad (17)$$

In order to be able to use formula (16) we must know the thermodynamic potential of the solution as a function of the variables p_{Ail}. In the model of the solution which we have adopted at high temperatures when correlation in the solution is not important we have

$$\begin{aligned}\varphi = -\frac{N_0}{2}\sum_{j=1}\sum_{\substack{i_l=1\\(i_l\neq j)}}^{n} \{&p_{Aj}p_{Ail}v_{AAl}\\ &+[p_{Aj}(1-p_{Ail})+p_{Ail}(1-p_{Aj})]\,v_{ABl}\\ &+(1-p_{Aj})(1-p_{Ail})\,v_{BBl}\}\\ +N_0kT\sum_{i_l=1}^{n}&[p_{Ail}\ln p_{Ail}+(1-p_{Ail})\ln(1-p_{Ail})],\end{aligned} \quad (18)$$

where v_{AAl}, v_{ABl} and v_{BBl} are the interaction energies taken with reversed sign for the atom pairs AA, AB and BB when one of the atoms is at some lattice point j while the other atom of the crystal is at the lattice point $\varkappa_l$ at a distance equal to the radius of the lth coordinative sphere. It follows from (17) and (18) that at high temperatures

$$\begin{aligned} x_0 &= 1/c(1-c); \quad x_l = w_l/kT,\\ w_l &= 2v_{ABl} - v_{AAl} - v_{BBl},\end{aligned} \quad (19)$$

where c is the concentration of atoms A in solution, while w_l is the energy of ordering for the lth coordinative sphere.

Expression (18) is valid only at high temperatures if $l|w_l|/kT \ll 1$ for all l. In the case of arbitrary temperature one may obtain an expression for φ if the concentration of one of the components of the solution is sufficiently small ($c \ll 1$). According to Ref. 12, we have in this case

$$\begin{aligned}\varphi = -\tfrac{1}{2}N\sum_{i_l=2}^{n} v_{BBl} - N_0\sum_{j=1}^{n} p_{Aj}\sum_{i_l=1}^{n}(v_{ABl}-v_{BBl})&\\ +kTN_0\sum_{i=1}^{n}[p_{Ail}\ln p_{Ail}&\\ +(1-p_{Ail})\ln(1-p_{Ail})]&\\ -N_0kT\sum_{j<i_l=1}^{n} p_{Aj}p_{Ail}\left[\exp\left(-\frac{w_l}{kT}\right)-1\right].&\end{aligned} \quad (20)$$

In the above

$$x_0 = 1/c(1-c); \quad x_l = 1-\exp(-w_l/kT). \quad (21)$$

It follows from (16), (19) and (21) that according to I, both when the temperature is increased and when the concentration of one of the components of the solution is made to approach zero, when the solution becomes ideal or weak, the distribution of background approaches the uniform Laue background $I_2 = N|f_A - f_B|^2 c(1-c)$.

If only the interaction with the same atoms of the first coordinative sphere ($w_1 = w$; $w_l = 0$ for $l \neq 1$) is important, then for a decaying solution ($w < 0$) the maxima of the ratio $I_2/|f_A - f_B|^2$ lie near the reflections corresponding to the principal lines and to the incident beam (where the sum $\Sigma \cos \mathbf{a}_\varkappa \cdot \mathbf{q} = z$), while the minima lie near reflections corresponding to superstructure lines (where the above sum is negative). Conversely, for a solution undergoing ordering ($w > 0$) the maxima of the ratio $I_2/|f_A - f_B|^2$ lie near reflections corresponding to superstructure lines, while the minima lie near the principal lines. In the nearest neighbor approximation it also follows from (16) and (21) that at low concentration of one of the components the inhomogeneity of the background is more sharply pronounced for decaying solutions (for the same $|w|/kT$).

The quantities x_l occuring in (16) may be found from experiment if the experimental distribution of the background intensity is known for different $\mathbf{q}$. Indeed, by taking the components of the vectors $\mathbf{a}_{\varkappa l}$ and $\mathbf{q}$ respectively along the basic vectors of the crystalline lattice and along the vectors $\mathbf{b}_\alpha$ of the reciprocal lattice

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*For the same distance between the central and the $\varkappa_l$th lattice points the quantities x_l may, generally speaking, be different. In such a case we shall take the coordinative sphere to be subdivided into several coordinative spheres of the same radius for which the x_l are the same, while z_l denote the coordination numbers for such coordinative spheres.

$$\mathbf{a}_{\varkappa l} = \sum_{\alpha=1}^{3} \mathbf{d}_\alpha n_{\varkappa l \alpha}; \quad \mathbf{q} = \sum_{\alpha=1}^{3} \mathbf{b}_\alpha k_\alpha$$

it is possible to write the above ratio in the form of a three-dimensional Fourier series

$$\frac{N\,|f_A - f_B|^2}{I_2} = x_0 + \sum_{n_{\varkappa l\alpha}=-\infty}^{\infty} x_l \exp\left(i \sum_{\alpha=1}^{3} n_{\varkappa l\alpha} k_\alpha\right), \tag{22}$$

where $n_{\varkappa l\alpha}$ take on all the integral values from $-\infty$ to ∞ for each α. Carrying out the Fourier transformation we obtain

$$x_0 = \frac{1}{8\pi^3} \int_0^{2\pi}\!\int_0^{2\pi}\!\int_0^{2\pi} \frac{N\,|f_A - f_B|^2}{I_2}\, dk_1 dk_2 dk_3;$$

$$x_l = \frac{1}{8\pi^3} \int_0^{2\pi}\!\int_0^{2\pi}\!\int_0^{2\pi} \frac{N\,|f_A - f_B|^2}{I_2} \cos\left(\sum_{\alpha=1}^{3} n_{\varkappa l\alpha} k_\alpha\right) dk_1 dk_2 dk_3, \tag{23}$$

where the numbers $n_{\varkappa l\alpha}$, $\alpha = 1, 2, 3$ correspond to some lattice point in the lth coordinative sphere.* In using formulas (23) it should be kept in mind that other parts of diffuse scattering which are not considered here (associated with thermal vibrations, geometric distortions, *etc.*) must be excluded, and do not enter into I_2. The method for the experimental determination of the functions $I_2(k_1, k_2, k_3)$ is given in Cowley's paper.[6]

Thus with the aid of formulas (23), (19) and (21) it is possible to calculate the energies of ordering w_e for different coordinative spheres from the experimental values of the background intensity for various crystal orientations and for various scattering angles (various k_α) obtained in the case of scattering by a solution at high temperature or having a low concentration of one of the components. The use of solutions with a low concentration of one of the components is more convenient in the case of negative w_e since in this case the quantities $|x_l|$ are sufficiently large at low temperatures.

The case when the correlation in solution is not small can be investigated by means of the approximation in which only the interaction with neighboring atoms is taken into account. It should be emphasized that in this case, as before, the correlation in all the coordinative spheres is taken into account, and not only in the occupancy of neighboring lattice points. We shall consider first solutions whose crystalline lattices may be broken up into two sublattices with the same number of lattice points in such a way that each lattice point is surrounded only by lattice points of the other sublattice (for example solutions with a body-centered cubic lattice, or with a simple cubic lattice). After denoting the concentrations of atoms A in these two sublattices by $p_A^{(1)}$ and $p_A^{(2)}$ we shall find that in the nearest neighbor approximation formula (16) for the intensity of diffuse scattering from a disordered crystal takes on the form

$$I_2 = N\,|f_A - f_B|^2 \left[a_1 + a_2 \sum_{\varkappa=1}^{z} \cos \mathbf{a}_\varkappa \mathbf{q}\right]^{-1}. \tag{24}$$

Here

$$a_1 = \frac{2}{NkT} \frac{\partial^2 \varphi}{\partial p_A^{(1)^2}}, \qquad a_2 = \frac{2}{zNkT} \frac{\partial^2 \varphi}{\partial p_A^{(1)} \partial p_A^{(2)}},$$

z is the coordination number of the first coordinative sphere, while $\mathbf{a}_\varkappa$ are vectors drawn from the central lattice point to the lattice points of this sphere. The quantities a_1 and a_2 may be calculated in the nearest neighbor approximation if use is made of the expression for the thermodynamic potential in the form of an expansion in powers of w/kT where w is the energy of ordering for the first coordinative sphere. Expansions for structures of the type under consideration have been obtained by Chang.[13] By differentiating the series obtained by him for the thermodynamic potential we shall obtain the following expansions for a_1 and a_2 in the case of disordered solutions:

$$a_1 = \frac{1}{f} + zf\left(\frac{w}{kT}\right)^2 - zf(1-4f)\left(\frac{w}{kT}\right)^3 - f\left[-\frac{z}{12}(7 - 72f + 180f^2) + \frac{y}{2} f(1-6f)\right]\left(\frac{w}{kT}\right)^4 + \cdots \tag{25}$$

$$a_2 = \frac{w}{kT} - \frac{1}{2}(1-4f)\left(\frac{w}{kT}\right)^2 + \frac{1}{6}(1-6f)^2\left(\frac{w}{kT}\right)^3 - (1-4f)\left[\frac{1}{24}(1-12f)^2 + \left(\frac{y}{z} - 1\right) f^2\right]\left(\frac{w}{kT}\right)^4 + \cdots. \tag{26}$$

Here $f = c(1-c)$, $y = 24$ for the simple cubic lattice and $y = 96$ for the body centered cubic lattice. The terms proportional to $(w/kT)^5$ and $(w/kT)^6$ give small corrections to the expansions (25) and (26).

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*The integration in (23) is carried out over the volume of an elementary cell in the space of the reciprocal lattice. This integration obviously can be taken over the volume of any arbitrary cell.

In the case of high temperatures formulae (24), (25 and (26) lead to the following expression for the back ground intensity:

$$I_2 = N\,|f_A - f_B|^2\, c(1-c)\Big[1 + \frac{w}{kT}\, c(1-c) \sum_{\varkappa=1}^{z} \cos \mathbf{a}_\varkappa \mathbf{q}\Big]^{-1}. \tag{27}$$

Up to quadratic terms this expression coincides with the expression for I_2 obtained by Lifshitz[9] (for a simple cubic lattice).

In the structures under consideration sharp Bragg reflections corresponding to principal lines occur at values of the quantity $\mathbf{k}_1 - \mathbf{k}_2$ for which the conditions $\mathbf{q}\cdot\mathbf{a}_\varkappa = 2\pi m_\varkappa$ are satisfied, where $m_\varkappa$ are integers. The conditions $\mathbf{q}\cdot\mathbf{a}_\varkappa = \pi(2m_\varkappa + 1)$ correspond to the superstructure lines. Near these values of the vector $\mathbf{q}$ one can expand $\cos \mathbf{a}_\varkappa\cdot\mathbf{q}$ in powers of the vector $\mathbf{q}'$ which represents the amount that must be added to $\mathbf{q}$ to obtain the value for which a given principal or superstructure Bragg reflection occurs If we limit ourselves to quadratic terms we obtain:

$$I_2 = N\,|f_A - f_B|^2 \Big[a_1 + z a_2 \mp \frac{a_2}{2} \sum_{\varkappa=1}^{z} (\mathbf{a}_\varkappa \mathbf{q}')^2\Big]^{-1}, \tag{28}$$

where the upper sign corresponds to a principal line and the lower to a superstructure line.

It was shown in I [see formulae (15) and (21) of Ref. I] that at temperatures somewhat greater than the temperature of ordering (in solutions undergoing ordering) or the temperature of decay (in decaying solutions) the background intensity near superstructure or principal lines respectively is anomalously large. If the composition of the solution corresponds to the maximum temperature of ordering or decay, then for cubic crystals the expression for the background intensity has the form

$$I_2 = N\,|f_A - f_B|^2 \beta \Big[\frac{T - T_0}{T_0} + \gamma q'^2\Big]^{-1}, \tag{29}$$

where T_0 is the temperature of ordering or decay respectively.

Expressions of the same type for solutions of stoichiometric composition are obtained in the statistical theory from formulae (25), (26) and (28) if one takes into account the fact that according to Chang[13] the temperature T_0 of such a solution is determined by the relation

$$\frac{w}{kT_0} = \pm \frac{4}{z}\Big[1 + \frac{1}{z} + \frac{4}{3}\frac{1}{z^2} + \Big(\frac{y}{z} + 2\Big)\frac{1}{z^3} + \cdots\Big]$$

(the plus sign corresponds to the ordering and the minus sign to the decaying solution) and if one expands $a_1 \pm z a_2$ in powers of $1/z$. Moreover the statistical theory permits one to calculate the quantities β and γ which appeared in the thermodynamic theory as parameters. Expansions of these quantities in powers of $1/z$ have the form

$$\beta = \frac{1}{4}\Big[1 + \frac{1}{z} + \frac{5}{3}\frac{1}{z^2} + 3\Big(\frac{y}{z} + 1\Big)\frac{1}{z^3} + \cdots\Big];$$
$$\gamma = \frac{1}{6}\Big[1 + \frac{2}{z} + \frac{14}{3}\frac{1}{z^2} + \Big(4\frac{y}{z} + \frac{32}{3}\Big)\frac{1}{z^3} + \cdots\Big]a^2, \tag{30}$$

where $a = |\mathbf{a}_\varkappa|$. Thus the parameter γ is of order $a^2/4$ and $\beta \sim 1/3$.*

In order to discuss in the nearest neighbor approximation solutions with a face-centered cubic lattice, one should break up this lattice into four simple sublattices each of which contains one of the lattice points of the elementary cell of the original lattice. In this case the given lattice point has for its nearest neighbors only lattice points of other sublattices, so that the formulas given above may be utilized. The intensity of diffuse scattering by a disordered crystal is given, as before, by formula (24), but the expressions for the quantities a_1 and a_2 appearing in this formula have a somewhat different form. Making use of the expression for the thermodynamic potential of the solution with a face-centered cubic lattice[12] in the for of an expansion in powers of w/kT we obtain

$$a_1 = 1/f + 12f\,(w/kT)^2 - 12f\,(w/kT)^3 + \cdots, \tag{31}$$

$$a_2 = w/kT - {}^1/_2\,(1 - 4f)\,(w/kT)^2 + {}^1/_6\,(1 + 12f - 60f^2)\,(w/kT)^3 + \cdots. \tag{32}$$

These expansions can be used at temperatures considerably higher than the temperature of ordering of a solution with a face-centered cubic lattice (in a

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*In Ref. 5 a conclusion is reached that at a phase transition of the second order the background intensity has only a weak maximum and anomalously large scattering should not be observed. This erroneous conclusion is connected with the unjustified extension to a three-dimensional crystal of the formula derived by Obraztsov[5] for a linear chain (where, as is well known, there is no phase transition to the ordered state).

decaying solution with $c \sim \frac{1}{2}$ formulae (31) and (32) are approximately valid right up to the temperature of decay).

3. SCATTERING BY ORDERED SOLID SOLUTIONS

In the case of an ordered solution of arbitrary composition the sums of the matrix elements belonging to the various rows of the matrix (11) are, generally speaking, not the same, so that one cannot use formula (15) for the determination of the sum $\sum_{i,j=1}^{n} b_{ij}$, but one must invert the matrix a_{ij}. If in an ordered solution there is the same number of lattice points of the first and the second kind, and if each of the lattice points is surrounded only by lattice points of the other kind, then in the nearest neighbor approximation one should choose lattice points of the first and second kinds for sublattices into which the crystal must be broken up in order to be able to apply the formulas of Sec. 1. By inverting the second order matrix a_{ij} determined by formulae (11) we shall obtain from (13) the following expression for the background intensity:

$$I_2 = N\,|f_A - f_B|^2\Big[a_1 + a_2 \sum_{\varkappa=1}^{z} \cos \mathbf{a}_\varkappa \mathbf{q} - M\Big]^{-1}, \tag{33}$$

where

$$a_1 = \frac{1}{NkT}\left(\frac{\partial^2\varphi}{\partial p_A^{(1)^2}} + \frac{\partial^2\varphi}{\partial p_A^{(2)^2}}\right); \qquad a_2 = \frac{2}{zNkT}\,\frac{\partial^2\varphi}{\partial p_A^{(1)}\partial p_A^{(2)}};$$

$$M = \frac{1}{(NkT)^2}\left(\frac{\partial^2\varphi}{\partial p_A^{(1)^2}} - \frac{\partial^2\varphi}{\partial p_A^{(2)^2}}\right)^2 \Big/ \Big[a_1 - a_2 \sum_{\varkappa=1}^{z} \cos \mathbf{a}_\varkappa \mathbf{q}\Big]. \tag{34}$$

Thus, in the nearest neighbor approximation the dependence of I_2 on the direction of the beam, on the angle of scattering, and on the wavelength is determined by the sum $\sum \cos \mathbf{a}_\varkappa \cdot \mathbf{q}$. If the coordinate axes in the cubic crystal are directed along the cubic axes, then this sum for a simple cubic lattice is given by $2(\cos aq_x + \cos aq_y + \cos aq_z)$ while for a body centered cubic lattice

$$4 \cos \frac{\sqrt{3}}{3} aq_x \cdot \cos \frac{\sqrt{3}}{3} aq_y \cdot \cos \frac{\sqrt{3}}{3} aq_z.$$

Expressions for a_1, a_2, and for the numerator in M may be written in the form of an expansion in powers of w/kT if one starts out with Chang's[13] expansion for φ. On carrying out a differentiation we obtain

$$\begin{aligned} a_1 = {} & \frac{v}{2u} + \frac{z}{2} v \left(\frac{w}{kT}\right)^2 - \frac{z}{2} vs \left(\frac{w}{kT}\right)^3 \\ & + \Big[\frac{z}{24}(7v - 36v^2 + 180vu) \\ & - \frac{y}{4}(v^2 - 2u - 6uv)\Big]\left(\frac{w}{kT}\right)^4 + \cdots, \end{aligned} \tag{35}$$

$$\begin{aligned} a_2 = {} & \frac{w}{kT} - \frac{1}{2} s \left(\frac{w}{kT}\right)^2 + \frac{1}{6}(1 - 6v + 36u)\left(\frac{w}{kT}\right)^3 \\ & - \Big[\frac{1}{24}(1 - 12v + 120u) + \frac{y}{z} u\Big] s \left(\frac{w}{kT}\right)^4 + \cdots, \end{aligned} \tag{36}$$

$$\begin{aligned} & \frac{1}{NkT}\left(\frac{\partial^2\varphi}{\partial p_A^{(1)^2}} - \frac{\partial^2\varphi}{\partial p_A^{(2)^2}}\right) = \\ & -\frac{t}{2}\Big\{\frac{1}{u} + z\left(\frac{w}{kT}\right)^2 - zs\left(\frac{w}{kT}\right)^3 \\ & + \Big[\frac{z}{12}(7 - 36v + 180u) \\ & + \frac{y}{2}(-v + 6u)\Big]\left(\frac{w}{kT}\right)^4 + \cdots\Big\}. \end{aligned} \tag{37}$$

Here

$$\left.\begin{aligned} v &= p_A^{(1)}(1 - p_A^{(1)}) + p_A^{(2)}(1 - p_A^{(2)}) \\ &= 2c(1 - c) - \frac{\eta^2}{2}; \\ u &= p_A^{(1)} p_A^{(2)} (1 - p_A^{(1)})(1 - p_A^{(2)}) \\ &= \left(c^2 - \frac{\eta^2}{4}\right)\left[(1 - c)^2 - \frac{\eta^2}{4}\right]; \\ s &= (1 - 2p_A^{(1)})(1 - 2p_A^{(2)}) = (1 - 2c)^2 - \eta^2; \\ t &= p_A^{(1)}(1 - p_A^{(1)}) - p_A^{(2)}(1 - p_A^{(2)}) = (1 - 2c)\,\eta, \end{aligned}\right\} \tag{38}$$

where η is the degree of long range order defined by the relations

$$p_A^{(1)} = c + {}^1\!/_2\,\eta; \quad p_A^{(2)} = c - {}^1\!/_2\,\eta.$$

The quantity t becomes zero for a solution of stoichiometric composition $c = \frac{1}{2}$ and for a disordered solution. In this case according to (37) $M = 0$ (within the framework of the model adopted this conclusion is valid not only in the nearest neighbor approximation, but also taking into account the interaction with more distant atoms) and formula (33) for the background intensity becomes considerably simpler. We note that in this case the expansions (35) and (36) coincide with the expansions (25) and (26) for a disordered solution if in the latter one replaces $f \to p_A^{(1)}(1 - p_A^{(1)})$; $w/kT \to -w/kT$; $\alpha_2 \to -\alpha_2$.

In agreement with I near the temperature of ordering the intensity of diffuse scattering becomes anomalously large close to the superstructure lines. For $c = \frac{1}{2}$ the expression for I_2 is found to be the same as (29) if in this formula $(T - T_0)/T_0$ is replaced by $2(T_0 - T)/T_0$.

In solutions of stoichiometric composition AB in which lattice points of the first kind are surrounded by lattice points of the second and first kinds in the same way in which lattice points of the second kind are surrounded by lattice points of the first and second kinds (crystals of the type of NaCl, β-brass, AuCu etc.) one can investigate the scattering without making use of the nearest neighbor approximation. In order to do this one must break up the crystal into n sublattices as was done in the preceding section for disordered lattices. When this is done $n/2$ sublattices will consist of lattice points of the first kind and the same number of sublattices will consit of lattice points of the second kind. In the case of solutions of stoichoimetric composition AB the derivatives $\partial^2\varphi/\partial p_{Ai}^2$ are the same for different i, and for the structures under consideration the sum of the matrix elements belonging to any given row of the matrix (11) does not depend on the row index. Therefore the sum of all the b_{ij} may be computed by means of formula (15). Thus, in the case under consideration, just as in the case of disordered solutions, the intensity of diffuse scattering is given by formula (16). However, in this formula one must now regard lattice points of different kinds, even if they are situated at the same distance, as belonging to different coordinative spheres, so that z_e is equal to the number of lattice points of a given kind situated at a definite distance from the central lattice point (see also the first footnote of this article).

The quantities x_0 and x_l appearing in formula (16) may be found in the case of low temperatures, considerably lower than the temperature of ordering, if the solution is in an almost completely ordered state. In this case according to Krivoglaz[12] the thermodynamic potential is equal to

$$\varphi = \varphi' + kTN_0 \sum_{i=1}^{n} [p_{Ai} \ln p_{Ai} + (1 - p_{Ai}) \ln (1 - p_{Ai})] - kTN_0 \Bigg[\sum_{i_l < j = 1}^{n|2} (1 - p_{Ail})(1 - p_{Aj})(e^{-w_l | kT} - 1)$$

$$+ \sum_{i_l < j = n|2+1}^{n} p_{Ail} p_{Aj} (e^{-w_l | kT} - 1) + \sum_{i_l = 1}^{n|2} \sum_{j = n|2+1}^{n} (1 - p_{Ail}) p_{Aj} (e^{w_l | kT} - 1) \Bigg]. \qquad (39)$$

Here φ' depends linearly on p_{Ai}, and the energies w_l correspond, as before, to a given pair of lattice points of sublattices i and j. Taking the first sublattice to consist of lattice points of the first kind, and taking into account the fact that for $c = \frac{1}{2}$ $p_{Ai} = \frac{1}{2}(1 + \eta)$ we obtain

$$x_0 = 1 / p_{A1}(1 - p_{A1}) = 4/(1 - \eta^2), \qquad (40)$$

$$x_l = 1 - \exp(-w_l / kT), \qquad (41)$$

if the lth coordinative sphere about a lattice point of the first sublattice consists of lattice points of the first kind, and

$$x_l = \exp(w_l / kT) - 1, \qquad (42)$$

if the lth coordinative sphere consists of lattice points of the second kind.* Formulas (23), (41) and (42) enable us to determine the energies of ordering for different coordinative spheres in an almost completely ordered solution from data on the distribution of background intensity.

In the case of solutions AB in which each lattice point is surrounded only by lattice points of the other kind (of the type of NaCl, or β-brass) it follows from (16), (40) and (42) that in the nearest neighbor approximation the background intensity at low temperatures is equal to

$$I_2 = \frac{1}{4} N |f_A - f_B|^2 (1 - \eta^2)$$

$$\times \left[1 + \frac{1 - \eta^2}{4} (e^{w | kT} - 1) \sum_{\varkappa=1}^{z} \cos \mathbf{a}_\varkappa \mathbf{q} \right]^{-1}. \qquad (43)$$

As $T \to 0$, η approaches unity exponentially:[12] $1 - \eta \approx 2 \exp(-zw/kT)$. Therefore the second term in the denominator of (43), which is associated with correlation and which leads to an increase in the background near the superstructure lines, decreases exponentially as $\exp[-(z - 2)w/kT]$ as the

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*Here we consider lattice points of different kinds, corresponding to the same value of ρ_l, as belonging to different coordinative spheres.

temperature is reduced and the inhomogeneity of the background disappears in agreement with I. The quantity I_2 itself also decreases exponentially like $\exp(-zw/2kT)$ (in a completely ordered crystal the intensity of diffuse scattering of the type under consideration is evidently equal to zero). It can be easily shown that for solutions having a structure of the type under consideration whose composition differs somewhat from the stoichiometric composition with $c = \frac{1}{2}$ the value of I_2 at very low temperatures is equal to

$$I_2 = N\,|f_A - f_B|^2 \Big\{c(1-c) - \frac{\eta^2}{4} - \Big(c^2 - \frac{\eta^2}{4}\Big)\Big[(1-c)^2 - \frac{\eta^2}{4}\Big] \times (e^{w/kT} - 1)\sum_{\varkappa=1}^{z}{}' \cos \mathbf{a}_\varkappa \mathbf{q}\Big\}. \tag{44}$$

In the case of almost completely ordered solutions with a face centered crystal lattice having a layered structure of the type of AuCu and of stoichiometric composition it follows from (16), (40), (41) and (42) that in the nearest neighbor approximation

$$I_2 = \frac{1}{4} N\,|f_A - f_B|^2 \Big\{1 + \frac{1-\eta^2}{4}\Big[(1 - e^{-w/kT})\sum_{\varkappa=1}^{4} \cos \mathbf{a}_{\varkappa_1} \mathbf{q} + (e^{w/kT} - 1)\sum_{\varkappa_2=1}^{8} \cos \mathbf{a}_{\varkappa_2} \mathbf{q}\Big]\Big\}^{-1}(1-\eta^2), \tag{45}$$

where the index $\varkappa_1$ labels vectors drawn between lattice points of the same kind while $\varkappa_2$ labels those drawn between lattice points of different kinds. It may be seen from formula (45) that even if one neglects the usually small tetragonality of crystals of the symmetry type under consideration (a difference in the length of the vectors $\mathbf{a}_{\varkappa_1}$ and $\mathbf{a}_{\varkappa_2}$), nevertheless the directions (100) perpendicular to the planes containing lattice points of one kind, and the directions (010) and (001) which lie in these planes turn out not to be equivalent with respect to x-ray scattering.

For solutions of the type AuCu whose composition differs slightly from a stoichiometric one it is easy to carry out at low temperatures the inversion of the matrix a_{ij} making use of the fact that in this case the non-diagonal matrix elements are considerably smaller than the diagonal ones. As a result of this we shall obtain from (11), (13) and (39)

$$I_2 = N\,|f_A - f_B|^2 \Big\{c(1-c) - \frac{\eta^2}{4} - \Big[1 - \exp\Big(-\frac{w}{kT}\Big)\Big]\Big[\Big(c(1-c) - \frac{\eta^2}{4}\Big)^2 + (1 - 4c(1-c))\frac{\eta^2}{4}\Big] \cdot \sum_{\varkappa_1=1}^{4}{}' \cos \mathbf{a}_{\varkappa_1} \mathbf{q} - \Big[\exp\Big(\frac{w}{kT}\Big) - 1\Big]\Big(c^2 - \frac{\eta^2}{4}\Big)\Big[(1-c)^2 - \frac{\eta^2}{4}\Big] \times \sum_{\varkappa_2=1}^{8} \cos \mathbf{a}_{\varkappa_2} \mathbf{q}\Big\} \tag{46}$$

In an analogous manner it is possible to obtain the intensity of diffuse scattering from almost completely ordered solutions with a face centered cubic lattice of the type $AuCu_3$

$$I_2 = N\,|f_A - f_B|^2 \Big\{c(1-c) - \frac{3}{16}\eta^2 - \frac{1}{2}\Big(c - \frac{\eta}{4}\Big)\Big(1 - c + \frac{\eta}{4}\Big)\Big[\Big(c + \frac{3}{4}\eta\Big) \times \Big(1 - c - \frac{3}{4}\eta\Big)(e^{w/kT} - 1) + \Big(c - \frac{\eta}{4}\Big)\Big(1 - c + \frac{\eta}{4}\Big)(1 - e^{-w/kT})\Big]\sum_{\varkappa=1}^{1} \cos \mathbf{a}_\varkappa \mathbf{q}\Big\}. \tag{47}$$

We note that formulas (45) – (47) which have been derived for almost completely ordered solutions hold over a considerable range of the existence of an ordered phase in solutions of the type of AuCu and $AuCu_3$, since in these solutions the phase transition into the ordered state must necessarily be a phase transition of the first order,[14] and the degree of long range order usually increases as a result of the transition to a value close to unity.

I take this opportunity to express my gratitude to A. A. Smirnov for his interest in this work and for discussion of results.

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Translated by G. M. Volkoff
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SOVIET PHYSICS JETP VOLUME 5, NUMBER 6 DECEMBER 15, 1957

Interaction between Current Carriers and *F*-centers and the Acoustic Vibrations of the Lattice in Ionic Crystals

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(Submitted to JETP editor July 7, 1956)
J. Exptl. Theoret. Phys. (U.S.S.R.) 32, 1382-1392 (June, 1957)

Interaction between an "excess" electron in an ionic crystal with optical and acoustical vibrations of the lattice is considered. Account of interaction with acoustical vibrations leads to a reduction of the energy of the system and to a change in the effective mass of the current carrier in comparison with the polaron. The wave functions, the energies of the ground and excited states of the *F*-centers and the parameters of the *F*-absorption band are computed with account of the "condenson" interaction. A comparison of the polaron and condenson effects in ionic crystals is given.

THE INTERACTION of the "excess" electron with optical vibrations in an ionic dielectric leads to the appearance of "polaron" states.[1] The effective mass of the current carrier in such crystals – the polarons – can differ appreciably from the effective mass of the "band" electron. In polaron theory the interaction with acoustical vibrations was not excluded in the zeroth approximation, but was considered as a reason for the scattering of polaron waves.[2] As an excitation potential, use was made of the micropotential assumed by Bloch, Brillouin and Bethe.[3] Such a consideration is valid for those crystals in which the corrections to the energy (as a result of consideration of the interaction with the acoustical vibrations of the lattice) are significantly smaller than the spacing of the energy levels of the polaron. However, the effect of the interaction with acoustical vibrations of the lattice is not small in a whole series of ionic crystals with strong homopolar coupling. Hence, consideration of this interaction in the zeroth approximation of the theory is a necessity.

Such a consideration is given below. We chose a potential of the deformation type as the interaction potential for the electron with the acoustical vibrations of the lattice. This potential was hypothesized by Pekar and one of the authors of this paper,[4] and is the condenson potential.* The energy terms and wave functions of the system were computed by the variational method and by an adiabatic approximation. The effective mass of the current carrier was computed; it differs from the effective mass of the polaron. In this same approximation, the quantum states of the *F*-center were considered and the parameters of the *F*-absorption band were obtained. A comparison of the magnitude of the condenson and polaron effects in ionic crystals is given.

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* This potential was proposed independently by Bardeen and Shockley.[10]