The Immanent Chaotization of Crystal Structures and the Resulting Diffuse Scattering. I. Mathematical Scheme and Physical Models

By F. A. Kassan-Ogly and V. E. Naish

Institute of Metal Physics of the Ural Scientific Centre, ul. S. Kovalevskoi 18, GSP-170, Sverdlovsk, USSR

Abstract

This series of papers is devoted to the development of the theory of X-ray diffuse scattering observed by the mono-Laue method in some ionic crystals. The ultimate cause of such diffuse scattering is revealed. It does not depend upon disordering, impurities, structural defects and the like, but inevitably exists in ideal crystals owing to the immanent loose packing of the crystal structure itself. The cause is rather general and such diffuse scattering should take place in many classes of crystals. This paper develops the necessary mathematical scheme for simple physical models and in the following papers the theory is applied to concrete ionic crystals with wide discussion of up-to-date experimental data.

Introduction

Considering hereafter both Bragg and diffuse scattering we shall keep in mind X-ray scattering (although much is also valid for neutron scattering). While Bragg scattering does not need any explanation as it is well known and understood unambiguously the notion 'diffuse scattering' (DS) is not so well understood. Various authors using such a notion imply different experimental phenomena. It is obvious that in a wide sense any non-Bragg scattering should be called diffuse (or anomalous) scattering. At present, hundreds of papers are published on various types of diffuse scattering in different materials. In any event all of these papers deal with intensities I_{DS}, of scattered particles which are rather weak in comparison with the intensities of the Bragg reflections, I_{Br}, whereas the distribution of any $I_{DS}(\varkappa)$ in reciprocal space (relspace) differs markedly from that of $I_{Br}(\varkappa)$ ($\varkappa$ is the scattering vector with components hkl). Among the causes of the appearance of DS the following are usually considered: (*a*) thermal chaotic motion of atoms, (*b*) chemical disordering in an alloy or in a compound, (*c*) chemical inhomogeneity in an alloy and inhomogeneity of lattice constants induced by it, (*d*) random structural distortions of the lattice, (*e*) random distribution and orientation of various defects in the crystal, (*f*) crystal ageing with formation of different phases, *etc.* In general, one may conclude that DS occurs as a result of various types of imperfections.

At present most papers on DS are concerned with alloys where DS is caused, for example, by the concentrational decomposition of the initially homogeneous solid solution and the precipitation of a new phase in submicroscopic regions. For this reason the notion DS is often used with just this narrow meaning. It should be pointed out that we shall not consider the diffuse scattering induced by imperfections at all, but *the diffuse scattering under our consideration and the cause of its appearance are to be universal for any crystal.*

DS should be subdivided into two types: (1) a more or less homogeneous type continuously distributed in relspace (diffuse background); (2) a sharply inhomogeneous type displaying a specific symmetrical pattern of curves or points. Henceforth we shall deal mainly with the inhomogeneous type and later on we shall see that such scattering has to occur in the completely ideal crystal. *The loose packing of almost all real crystals appears to be the universal microscopical cause of the inhomogeneous diffuse scattering under consideration.* The atoms or ions forming the crystal structure are not completely fixed in their positions but posses either one, two or three degrees of freedom. The vibrational phonon modes corresponding to these degrees of freedom create the more or less symmetrical pattern of DS which will be investigated together with its temperature evolution.

The study of such DS is not considered as the main goal, but as a sensitive method for the extraction of information on the crystal structure and its temperature behaviour. *From the physical point of view the cause of such DS, namely, the intrinsic immanent chaotization of the crystal structure of highly symmetrical ideal crystals, and its microscopical mechanism are the main interest.*

In this connection the observation of DS in the so-called *mono-Laue* (or fixed-beam–fixed-crystal) experiment appears to be the most informative source. Strictly speaking it is the X-ray diffraction experiment performed on a fixed single crystal, with the use of the monochromatic focused beam described, for example, in the review by Dornier & Comes (1977). In the whole history of the diffraction technique rather

few such experiments have been carried out. The first experiments with this method apparently belong to Laval (1939, 1941) on a KCl single crystal, to Preston (1942) on KCl, and to Harada & Honjo (1967) on $BaTiO_3$. Later on we shall try to analyse most of the experimental data on DS in the mono-Laue method. Among them a very special place belongs to the paper by Comes, Lambert & Guinier (1970) on $KNbO_3$ and one of our papers will be devoted especially to this crystal. We shall analyse the immanent chaotization in all perovskites studied, in binary compounds and in monoatomic crystals.

Comes, Lambert & Guinier (1970) proposed a model of rigid atomic chains moving relative to one another and a very clear explanation of the DS observed in $KNbO_3$ and $BaTiO_3$ has been made by them, but no theoretical studies in this direction have so far been performed and therefore *the detailed elaboration of the mathematical description of such immanent chaotization in crystals and the resulting DS turned out to be our main task.*

Such chaotization and its temperature evolution are often capable of leading to structural phase transitions (as, for example, in $KNbO_3$) and in our papers the ability or inability of a crystal to undergo such transitions or even a cascade of transitions, the temperature dependence of DS and the features of the phase transitions will be studied in detail.

Finally, it should be remarked that although the special vibrational phonon modes frozen below the corresponding phase transition appear to be responsible for the phase transition and DS the main features of the whole phenomenon are revealed in the elastic scattering and therefore *we shall deal only with the elastic scattering.*

The results obtained by us make up a series of five papers. Let us briefly survey their contents. Paper I is devoted to the development of a special mathematical description of immanent chaotization and diffuse scattering, their temperature evolution and the consequent structural phase transitions.

In paper II the main attention is paid to the microscopical nature of chaotization, namely, to the quantitative description of the loose packing of different structures and their ability to chaotize and to the phase transitions.

Papers III and IV are concerned with the most striking examples of cubic perovskites of $KNbO_3$ and $KMnF_3$ types and the method of their description possesses, in fact, far wider applicability.

Paper V deals with binary systems and with the very interesting and important question of immanent chaotization of a second kind.

In the future for an adequate and balanced development of the theory it will be necessary to consider all the other crystals with experimentally observed DS in the mono-Laue method [$LiNbO_3$ (Zhdanov, Ivanov, Kolontsova & Korneev, 1978),

$NaNO_2$ (Canut & Hosemann, 1964), and $NaNbO_3$ (Denoyer, Comes & Lambert, 1971; Ishida & Honjo, 1972) are of main interest] and then to expand the theory to metals and alloys.

I. Chaotization of a one-dimensional crystal. Ising model

To show just the possibility for the appearance of DS in the ideal crystal and to develop gradually the mathematical scheme it is convenient to begin with the simplest tasks, complicating them one by one. The problem of scattering for a one-dimensional monoatomic crystal (linear chain) may serve as the first task. It should be reiterated that only elastic scattering will be calculated and only the diffuse scattering revealed in the mono-Laue experiment is to be considered.

Linear chain without chaotization

As is known, the linear chain with translation a (Fig. 1a) under irradiation produces the set of Bragg peaks* in the relpoints $\varkappa = (2\pi/a)m$. We shall first show how this result is obtained for a finite chain and we shall then extend the number of atoms N to infinity.

The elastic-scattering amplitude for such a chain of N atoms is as follows (the atomic form factor f is

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* We assume that atoms occupy just the equilibrium positions, *i.e.* we do not take into account the usual thermal vibrations of atoms in a single-well potential. As is well known, such thermal motion leads to diffuse background and to the reduction of the Bragg peaks described by the Debye–Waller factor.
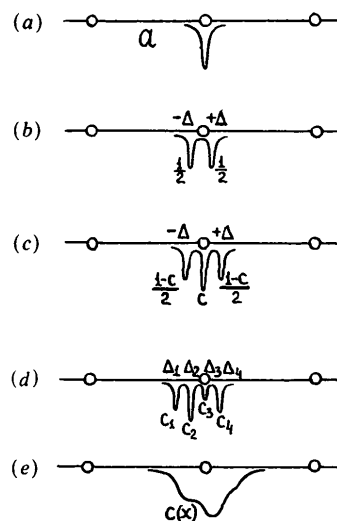

Fig. 1. Various possible examples of chaotization of a linear chain [(a) is the ideal chain without chaotization].

the same for all atoms, and is omitted here):

$$F(\varkappa) = \exp[-i\varkappa 0] + \exp[-i\varkappa a] + \exp[-i\varkappa 2a] + \dots$$
$$+ \exp[-i\varkappa(N-1)a] \qquad (1)$$

and the scattering intensity (per atom) is

$$I(\varkappa) = F(\varkappa)F^*(\varkappa). \qquad (2)$$

Using (1), (2) and the formula of geometric progression one obtains the known result:

$$I(\varkappa) = \frac{1}{N} \frac{\sin^2[\varkappa(Na/2)]}{\sin^2[\varkappa(a/2)]}, \qquad (3)$$

which is called the Laue function.

Only at $N \to \infty$ does the Laue function transfer to the set of δ functions in the relpoints $\varkappa = (2\pi/a)m$, while at finite values of N the Bragg peaks possess finite width and height. The Laue function, its gradual transformation into the set of δ functions and the dependence upon N (or length of a chain) are described in detail by Guinier (1956). Henceforth we shall write down all the results in the limit $N \to \infty$, and the Bragg scattering with δ functions and the DS without δ functions will be written keeping in mind the Laue function.

Linear chain with dichotomic chaotization without interaction. Ising operators

Now let the potential well for any atom n of a chain not have a minimum at point na but have two equal narrow minima (infinitely narrow) in two symmetrical positions $na \pm \Delta(\Delta < a/2)$, see Fig. 1(b). In such a problem of symmetrical double-well potentials the occupation probabilities at the right and left positions are equal to one-half. It should be noted that the chain possesses the same translational symmetry as a chain without chaotization (Fig. 1a), i.e. once again the ideal crystal is considered.

Now let the right and left positions be occupied quite randomly. Then for a chain of N atoms we obtain 2^N configurations, the statistical weights of which are the same and equal to $1/2^N$.

Let us now introduce Ising operators σ_n on each atom with eigenvalues $+1$ and -1. Then any displacement of any atom n relative to its equilibrium position na may be written as $\Delta\sigma_n$. With the assumption that the time of interaction of a single quantum X with the system is far less than the time of atom displacement the scattering intensity may be written as the sum of separate scattering acts on the ensemble of all atomic configurations.

$$I(\varkappa) = \frac{1}{N2^N} \sum_{\sigma_1 \dots \sigma_N} \sum_{nn'} \exp\{-i\varkappa[(na + \Delta\sigma_n)$$
$$- (n'a + \Delta\sigma_{n'})]\}.$$

Henceforth we shall use a simple contrivance:

$$\sum_{nn'}(\dots) = \sum_{nn'}(\dots)(1 - \delta_{nn'}) + \sum_{nn'}(\dots)\delta_{nn'}. \qquad (4)$$

Then in the first term of (4) n and n' are different and σ_n and $\sigma_{n'}$ are independent, while in the second term the σ's are completely absent, and the exponent is equal to zero. For the scattering intensity one obtains:

$$I(\varkappa) = \frac{1}{N2^N} \left\{ \sum_{nn'} \exp[-i\varkappa(na - n'a)] \right.$$
$$\times \sum_{\sigma_1 \dots \sigma_N} \exp[-i\varkappa\Delta(\sigma_n - \sigma_{n'})](1 - \delta_{nn'})$$
$$\left. + \sum_{\sigma_1 \dots \sigma_N} N \right\}. \qquad (5)$$

Then, using the simple relations:

$$\sum_{\sigma_n} \exp[-i\varkappa\Delta\sigma_n] = \exp[-i\varkappa\Delta] + \exp[i\varkappa\Delta]$$
$$= 2\cos(\varkappa\Delta),$$

$$\sum_{\sigma_{n'}} \exp[i\varkappa\Delta\sigma_{n'}] = \exp[i\varkappa\Delta] + \exp[-i\varkappa\Delta] \qquad (6)$$
$$= 2\cos(\varkappa\Delta),$$

$$\sum_{\sigma_1 \dots \sigma_N} 1 = 2^N,$$

and

$$\sum_{\sigma_1 \dots \sigma_N} \exp[-i\varkappa\Delta(\sigma_n - \sigma_{n'})]$$
$$= \sum_{\sigma_n \sigma_{n'}} \exp[-i\varkappa\Delta(\sigma_n - \sigma_{n'})] \sum_{\sigma_1 \dots \sigma_N}'' 1$$
$$= 2^2 \cos^2(\varkappa\Delta) \times 2^{N-2}, \qquad (7)$$

where $\sum''$ denotes the sum over all operators except σ_n and $\sigma_{n'}$, one obtains:

$$I(\varkappa) = \left\{ \frac{1}{N} \sum_{nn'} \exp[-i\varkappa(na - n'a)] \right\} \cos^2(\varkappa\Delta)$$
$$- \frac{1}{N} \sum_{nn'} \delta_{nn'} \cos^2(\varkappa\Delta) + 1$$
$$= \frac{1}{N} \sum_{nn'} \exp[-i\varkappa(na - n'a)]$$
$$\times (1 - \delta_{nn'}) \cos^2(\varkappa\Delta) + 1. \qquad (8)$$

Making use of the usual relation:*

$$\frac{1}{N} \sum_{nn'} \exp[-i\varkappa a(n - n')] = \sum_{\mathbf{b}} \delta^{(1)}(\varkappa - \mathbf{b}), \qquad (9)$$

where $\mathbf{b} = (2\pi/a)m$ are the vectors of the reciprocal lattice for a one-dimensional chain (m integers), one

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* We use the notation $\delta^{(1)}(x) = (2\pi/a)\delta(x)$ where $\delta(x)$ is the usual Dirac function.

may write:

$$I(\mathbf{x}) = \cos^2 \mathbf{x}\Delta \sum_b \delta^{(1)}(\mathbf{x} - \mathbf{b}) + \sin^2 \mathbf{x}\Delta. \quad (10)$$

In the very simple model of dichotomic chaotization in a linear chain for the first time we have obtained the intensity of the elastic scattering as a sum of two terms: the first one in (10) contains the δ function and describes Bragg reflections modulated by the factor $\cos^2 \mathbf{x}\Delta$ which will be called henceforth *the Bragg-reducing factor*; the second term in (10), $\sin^2 \mathbf{x}\Delta$, does not contain the δ function and describes the diffuse scattering gradually varying in relspace. Henceforth $\sin^2 \mathbf{x}\Delta$ will be called the *typical DS factor*. In the limiting case $\Delta = 0$ one returns to the ideal crystal without chaotization in which DS is absent and there is only the system of equal Bragg peaks.* Fig. 2(a) illustrates the resulting intensity (10). The modulation wavelength depends upon Δ and at small values of Δ ($\Delta \ll a$) DS gradually varies over the relspace as a weak inhomogeneous background. Two particular cases should be noted here: $\Delta = a/2$ and $\Delta = a/4$ (see Fig. 2b and c).

Chaotization of linear chain with interaction

Let us consider a linear chain with the double-well potential shown in Fig. 1(b). The correlation ('interaction') of the atomic displacements ($+\Delta$ and $-\Delta$) of the neighbouring atoms can be described by the different probabilities of different configurations:

$$\exp\left[-\beta \mathcal{H}(\sigma_1, \sigma_2, \ldots, \sigma_N)\right],$$

where the Hamiltonian of the simplest conceivable model may be chosen as the Ising Hamiltonian with nearest neighbour 'exchange interaction' V:

$$\mathcal{H} = -V \sum_K \Delta\sigma_K \Delta\sigma_{K+1}. \quad (11)$$

Using the usual notation $J' = (V/KT)\Delta^2$ one obtains for the scattering intensity of a linear chain with correlated chaotization:

$$I(\mathbf{x}) = \left\{ \frac{1}{N} \sum_{nn'} \exp\left[-i\mathbf{x}a(n - n')\right] \right.$$

$$\times \sum_{\{\sigma\}} \exp\left[-i\mathbf{x}\Delta(\sigma_n - \sigma_{n'})\right]$$

$$\left. \times \exp\left[J'(\ldots + \sigma_{n-1}\sigma_n + \sigma_n\sigma_{n+1} + \ldots)\right]\right\}$$

$$\times \left\{ \sum_{\{\sigma\}} \exp\left[J'(\ldots + \sigma_{n-1}\sigma_n + \sigma_n\sigma_{n+1} + \ldots)\right]\right\}^{-1}. \quad (12)$$

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*The usual decrease of Bragg peaks in relspace is absent here for the usual angular decrease of the X-ray form factor $f(\mathbf{x})$ has not been taken into account.

Mean-field approximation

This approximation involves the simplification of the Ising Hamiltonian in the following way:

$$\mathcal{H} = -V\Delta^2 \sum_K \sigma_K \sigma_{K+1} \rightarrow -zV\Delta^2 \langle\sigma\rangle \sum_K \sigma_K, \quad (13)$$

where $z = 2$ is the number of nearest neighbours, and $\langle\sigma\rangle\Delta$ is the average thermodynamical value of the atomic displacement from the equilibrium position. For the sake of simplicity henceforth the notation $J \equiv zJ'$ will be used.

To calculate the scattering intensity (12) we make use of relation (4). Now, in the sum $\sum_{nn'} (1 - \delta_{nn'}) \ldots$ the operators σ_n and $\sigma_{n'}$ are independent and we may take the sums $\sum_{\sigma_n}$ and $\sum_{\sigma_{n'}}$ separately:

$$\sum_{\sigma_n} = \exp\left[-i\mathbf{x}\Delta\sigma_n\right] \exp\left[J\langle\sigma\rangle\sigma_n\right]$$

$$= 2 \cosh\left(J\langle\sigma\rangle - i\mathbf{x}\Delta\right) \quad (14)$$

$$\sum_{\sigma_{n'}} \exp\left[i\mathbf{x}\Delta\sigma_{n'}\right] \exp\left[J\langle\sigma\rangle\sigma_{n'}\right] = 2 \cosh\left(J\langle\sigma\rangle + i\mathbf{x}\Delta\right).$$

All the remaining $N - 2$ factors from $\sum_{\{\sigma\}}$ will cancel each other in the numerator and denominator of (12) and one obtains:

$$I(\mathbf{x}) = \left\{ 2^2 \cosh\left(J\langle\sigma\rangle - i\mathbf{x}\Delta\right) \cosh\left(J\langle\sigma\rangle + i\mathbf{x}\Delta\right) \right.$$

$$\times \left[\frac{1}{N} \sum_{nn'} \exp\left[-i\mathbf{x}a(n - n')\right]\right.$$

$$\left. - \frac{1}{N} \sum_{nn'} \exp\left[-i\mathbf{x}a(n - n')\right]\delta_{nn'}\right]$$

$$\left. + \frac{1}{N} \sum_n 2^2 \cosh\left(J\langle\sigma\rangle\right)\right\}\left[2^2 \cosh\left(J\langle\sigma\rangle\right)\right]^{-1}.$$

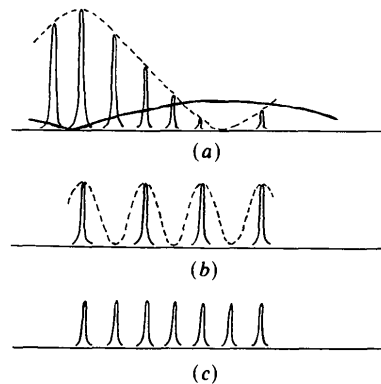After simple calculations one obtains the resulting expression for the scattering intensity in the mean-

Fig. 2. Modulated Bragg and diffuse-scattering intensities. (a) $\Delta \ll a$, (b)$\Delta = a/2$, (c) $\Delta = a/4$.

field approximation:

$$I(\varkappa) = \{1 - \sin^2(\varkappa\Delta)[1 - \tanh^2(J\langle\sigma\rangle)]\}$$

$$\times \sum_b \delta(\varkappa - \mathbf{b}) + \sin^2(\varkappa\Delta)\{1 - \tanh^2[J\langle\sigma\rangle]\}. \tag{15}$$

The limiting case $J = 0$ gives the previous result (10).

The interaction J has complicated the result (10) by a factor $1 - \tanh^2(J\langle\sigma\rangle)$. In such a way for the first time in the theory there appears the temperature dependence of the diffuse scattering.

For the final calculation of $I(\varkappa)$ by formula (15) one should know the $\langle\sigma\rangle$ values which are easily obtained from the usual mean-field equation:

$$\langle\sigma\rangle = \tanh J\langle\sigma\rangle. \tag{16}$$

It should be noted that the one-dimensional system differs from the two- or three-dimensional ones for although in the mean-field approximation there *exists* a transition temperature T_c at which the non-zero solution $\langle\sigma\rangle \neq 0$ of equation (16) appears nevertheless the exact solution of the one-dimensional problem *does not* give any T_c (absence of phase transition). Therefore expression (15) is not valid in the one-dimensional case, but our task has been to show for a very simple example the mathematical scheme of the intensity calculation in the mean-field approximation. Later on the intensity calculation in the real three-dimensional crystal and for more complicated problems will be carried out similarly but is far more cumbersome.

The exact solution of linear-chain chaotization

For a correct description of the linear-chain chaotization one should find the exact solution. Let us return to expression (12). To help the calculations one may use the usual Born–Karman boundary conditions: the $(N+1)$th atom is identified with the first one and hence $\sigma_{N+1} = \sigma_1$. One may make use of the well known result for the partition function of a one-dimensional chain under such cyclic conditions, which is $2^N(\cosh^N J + \sinh^N J)$.

The whole calculation treatment of the exact solution is very cumbersome and there is no need to give it at length. We shall confine ourselves only to a sketch.

First of all one should calculate the sum $X_{nn'}$ in the numerator of (12)

$$X_{nn'} = \sum_{\{\sigma\}} \exp[i\varkappa\Delta(\sigma_n - \sigma_{n'})] \exp\left[J\sum_k \sigma_k\sigma_{k+1}\right]$$

$$= \sum_{\sigma_1\ldots\sigma_n\ldots\sigma_N} \exp[-i\varkappa\Delta(\sigma_n - \sigma_{n'})]$$

$$\times \exp[J(\sigma_1\sigma_2 + \sigma_2\sigma_3 + \ldots + \sigma_{n-1}\sigma_n + \sigma_n\sigma_{n+1}$$

$$+ \ldots + \sigma_N\sigma_1)]. \tag{17}$$

At a fixed value of n the variable n' covers a series of N values:

$$n, n+1, n+2, \ldots, N, 1, 2, \ldots, n-1.$$

One should calculate $X_{nn'}$ for all these values one by one; the first two steps are peculiar and all the rest are similar to each other. One should take the sums over $\sigma_n, \sigma_{n+1}, \ldots$, then expand the hyperbolic cosines obtained with combined arguments into the terms with sines and cosines with simple arguments of $\sinh J\sigma_K$ and $\cosh J\sigma_K$ types. The successive summing over all $\{\sigma\}$ raises the powers of $\sinh J$ and $\cosh J$. During such a procedure one can easily see the natural regularities. At the end of the calculation one should take the limit $N \to \infty$, put $\sinh^N J = 0$ and obtain:

$$I(\varkappa) = \cos^2\varkappa\Delta \sum_b \delta(\varkappa - \mathbf{b}) + \sin^2\varkappa\Delta$$

$$\times[(1 - \tanh^2 J)/(1 - 2\tanh J\cos\varkappa a$$

$$+ \tanh^2 J)], \tag{18}$$

the exact solution for the scattering intensity.

In the limiting case of correlation absence $(J = 0)$ one returns again to formula (10). When $J \neq 0$ expression (18) describes two quite different cases depending upon the sign of J (or the sign of the 'exchange interaction' V where $J = V\Delta^2/KT \equiv T_0/T$).

Let us consider the temperature-dependent factor in (18):

$$L(T, \varkappa) \simeq (1 - \tanh^2 J)/(1 - 2\tanh J\cos\varkappa a$$

$$+ \tanh^2 J). \tag{19}$$

Fig. 3(a) shows $L(\varkappa)$ at different temperatures when V is positive. One can see in Fig. 3(a) that owing to L at high temperatures the DS [second term in (18)] is more or less uniform and diffuse peaks are growing at the points of the Bragg reflections [$\varkappa = (2\pi/a)m$]. At $T = 0$ only such diffuse peaks with the shape of the δ function modulated by a factor $\sin^2\varkappa\Delta$ are left out of the whole DS. As a result at $T = 0$ the whole scattering intensity turns to Bragg reflections without any modulation ($\cos^2\varkappa\Delta + \sin^2\varkappa\Delta = 1$).

When V is negative (Fig. 3b) the temperature dependence of $L(\varkappa)$ is similar to that for positive V; however, the diffuse peaks do not lie at the Bragg points but between them [$\varkappa = (\pi/a)(2m+1)$]. As a result as the temperature decreases a more or less uniform DS concentrates at diffuse peaks between the Bragg reflections. At $T \to 0$ the shape of these diffuse peaks becomes more and more of the δ-function type while the initial Bragg reflections remain reduced by the factor $\cos^2\varkappa\Delta$ and do not depend upon temperature.

II. Chaotization of a two-dimensional crystal. Ising model

Let us consider the two-dimensional crystal on the xy plane as a square lattice of atoms with translations $a_x = a_y = a$. Let us assume the simplest way of chaotization: each atom has a double well as in Fig. 1(b) along the x axis and a single well along the y axis. Then the Ising operators $\sigma_{n_x n_y}$ with eigenvalues $+1$ and -1 should be ascribed to each site of the lattice but the site numeration is now twofold: n_x is the number of 'a line', and n_y is the number of 'a column'. The displacements of atoms are one-dimensional as before: $\Delta\sigma_{n_x n_y}$, and accept the values $+\Delta$ or $-\Delta$ along the x axis.

Two-dimensional lattice without chaotization

Similarly to the linear-chain case it is not difficult to obtain the following result for scattering intensities:

$$I(\varkappa) = \delta(h - b^x)\delta(k - b^y) \equiv \delta^{(2)}(\varkappa - \mathbf{b}), \quad (20)$$

where h and k are the components of the scattering vector $\varkappa$, measured in $2\pi/a$ units, and b^x and b^y are the components of reciprocal-lattice vectors. The two-dimensional δ function $\delta^{(2)}(\varkappa - \mathbf{b})$ should be understood as the limit $N_x, N_y \to \infty$ of the corresponding Laue function [see (3)]

$$\frac{1}{N_x N_y} \frac{\sin^2\left(N_x \frac{ha}{2}\right)}{\sin^2\left(\frac{ha}{2}\right)} \frac{\sin^2\left(N_y \frac{ka}{2}\right)}{\sin^2\left(\frac{ka}{2}\right)}.$$
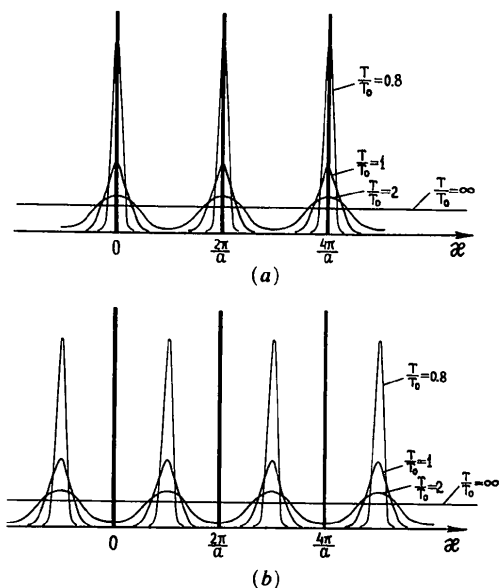

(a)

(b)

Fig. 3. Temperature dependence of diffuse scattering for the one-dimensional chain with correlation. (a) $J > 0$, (b) $J < 0$.

Chaotization of a two-dimensional lattice without correlation

Any possible distribution of $+$ and $-$ signs over the ideal lattice sites, where $+$ denotes the displacement $+\Delta$ of the corresponding atom along the x axis and $-$ denotes the displacement $-\Delta$, should now be called a configuration. The total number of configurations is equal to $2^{N_x} 2^{N_y}$ and the statistical weight of each is equal to $1/2^{N_x} 2^{N_y}$. One then obtains:

$$I(\varkappa) = \frac{1}{N_x N_y} \sum_{nn'} \sum_{\{\sigma\}} \frac{1}{2^{N_x} 2^{N_y}}$$

$$\times \exp\{-i\varkappa[(na + \Delta\sigma_n) - (n'a + \Delta\sigma_{n'})]\}. \quad (21)$$

The intensity calculation is similar to that in the linear chain. We shall not give this at length but note that at the first step of the calculation instead of (4) one should use the more complicated equality:

$$1 = (1 - \delta_{n_x n_x'})(1 - \delta_{n_y n_y'}) + \delta_{n_x n_x'}(1 - \delta_{n_y n_y'})$$

$$+ (1 - \delta_{n_x n_x'})\delta_{n_y n_y'} + \delta_{n_x n_x'}\delta_{n_y n_y'}. \quad (22)$$

Then one should take the sums over all $\sigma_{n_x n_y}$ separately for the four terms in (22).

Making use of the relations similar to (6) one obtains as a result:

$$I(\varkappa) = \cos^2 h\Delta \sum_{\mathbf{b}} \delta^{(2)}(\varkappa - \mathbf{b}) + \sin^2 h\Delta. \quad (23)$$

In the scalar product $\varkappa . \Delta$ we have $\varkappa^x\Delta^x = h\Delta$ as the only non-zero term since the displacements are directed only along the x axis. If the direction of the displacement is arbitrary then one obtains:

$$I(\varkappa) = \cos^2 \varkappa . \Delta \sum_{\mathbf{b}} \delta^{(2)}(\varkappa - \mathbf{b}) + \sin^2 \varkappa . \Delta. \quad (24)$$

Chaotization of a two-dimensional lattice with correlation

For the sake of simplicity let us assume the 'exchange' parameter V responsible for the correlation of the nearest atoms to be equal in both directions x and y: $V_x = V_y = V$. Then the Ising Hamiltonian is written as:

$$\mathcal{H} = -V \sum_{n_x n_y} \Delta\sigma_{n_x n_y}(\Delta\sigma_{n_x+1, n_y} + \Delta\sigma_{n_x, n_y+1}). \quad (25)$$

Mean-field approximation

In this approximation the Hamiltonian accepts the form:

$$\mathcal{H} = -zV\Delta^2\langle\sigma\rangle \sum_{n_x n_y} \sigma_{n_x n_y}, \quad (26)$$

where $z = 4$ is the number of nearest neighbours. The calculations similar to that for the linear chain with the help of relations (22) and (6) lead to the ultimate

result for the scattering intensity:

$$I(\varkappa) = [1 - \sin^2 \varkappa \cdot \Delta(1 - \tanh^2 J\langle\sigma\rangle)] \sum_{\mathbf{b}} \delta^{(2)}(\varkappa - \mathbf{b})$$

$$+ \sin^2 \varkappa \cdot \Delta(1 - \tanh^2 J\langle\sigma\rangle). \qquad (27)$$

To this expression should be added the mean-field equation (16), where $J = zV\Delta^2/KT$. At the critical temperature $T_c = zV\Delta^2/K$ (*i.e.* at $J = 1$) the second-order phase transition from the state with $\langle\sigma\rangle = 0$ into the state with $\langle\sigma\rangle \neq 0$ takes place.

Thus in accordance with the formula (27) one can say that in the mean-field approximation DS is constant above the critical temperature whereas below the critical temperature it gradually decreases to zero as temperature decreases while the reducing factor of the Bragg reflections which is constant above the transition increases to unity as the temperature decreases below the transition.

III. Rigid movable extended objects. Models

Model of chains

Let us consider the three-dimensional monoatomic crystal with simple cubic structure (a is the lattice parameter) consisting of parallel, atomic chains of infinite length which are rigid in one direction (z) and able to move relative to one another; let them be allowed to move only along their own directions (*i.e.* along the z axis) with $+\Delta$ and $-\Delta$ displacements from the equilibrium positions (Ising case, see Fig. 4a). In the two remaining directions, x and y directions, the atoms form the ideal square lattice (the projection of such a lattice onto the xy plane is shown in Fig. 4b). Fig. 4(b) shows one of the possible states (one configuration) of such a crystal where the chains shifted by $+\Delta$ or $-\Delta$ along the z axis are shown by $+$ or $-$ signs. One can easily see that this is the two-dimensional problem with Ising chaotization; however, Ising operators now describe the positions of the *chains* but not of the atoms. Initially the correlation will be omitted. Now let X-ray scattering take place on a crystal with such chaotization. The problem of the $I(\varkappa)$ calculation on such a crystal differs from the two-dimensional Ising problem described above. First, atomic displacements Δ are directed normally to the xy plane; hence $\cos^2 h\Delta$ and $\sin^2 h\Delta$ in (23) should be replaced by $\cos^2 l\Delta$ and $\sin^2 l\Delta$ (hkl are
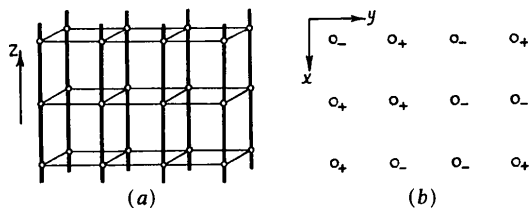
the components of the scattering vector $\varkappa$). Secondly, we now deal with the three-dimensional crystal and calculate the scattering intensity $I(\varkappa)$ distribution in the three-dimensional relspace. Therefore, the whole expression (23) should be multiplied by a factor $\delta(l - b^z)$. As a result, for the scattering intensity in the problem under consideration instead of (23) one obtains:

$$I(\varkappa) = \cos^2 l\Delta \sum_{\mathbf{b}} \delta^{(3)}(\varkappa - \mathbf{b}) + \sin^2 l\Delta \sum_{b^z} \delta^{(1)}(l - b^z).$$

$$(28)$$

Fig. 5 shows $I(\varkappa)$ where the Bragg reflections are depicted by solid points; the 'size' of a point corresponds to the intensity of the corresponding Bragg peak according to the factor $\cos^2 l\Delta$. The important new feature of the model considered now appears: DS as a whole consists of infinite (normal to the z axis) equidistant 'shining' relplanes the intensity of which is modulated by the factor $\sin^2 l\Delta$ while the Bragg reflections are reduced by the factor $\cos^2 l\Delta$. One can see in Fig. 5 the gradual pumping over of Bragg-scattering intensity into diffuse-scattering intensity. For the sake of clarity the pumping over is exaggerated in Fig. 5 while in reality it varies slowly with the varying plane number. The scattering intensity equals zero between the planes (saying nothing about the usual thermal background). It should be reiterated that the angular decrease of the form factor $f(\varkappa)$ has not been taken into account. It would slightly change the distribution of intensity along the pattern but the whole pattern would be the same.

If one were to take into account the exchange interaction J between the nearest-neighbour chains one would obtain in the mean-field approximation a result similar to (27) with the necessary corrections mentioned above:

$$I(\varkappa) = [1 - \sin^2 l\Delta(1 - \tanh^2 J\langle\sigma\rangle)] \sum_{\mathbf{b}} \delta^{(3)}(\varkappa - \mathbf{b})$$

$$+ \sin^2 l\Delta(1 - \tanh^2 J\langle\sigma\rangle) \sum_{b^z} \delta^{(1)}(l - b^z). \qquad (29)$$

Fig. 4. (a) Rigid chains in a three-dimensional crystal and (b) the chaotization of the chain displacements.
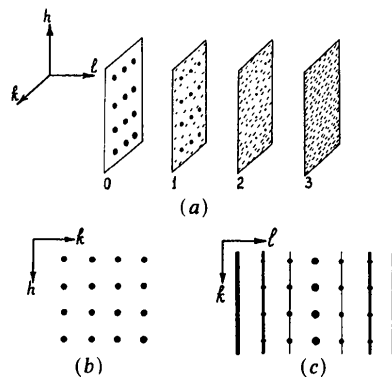

Fig. 5. Three projections of the intensity distribution of Bragg and diffuse scattering in relspace for a crystal with rigid chains.

Leaving aside the calculation details let us reproduce some results for other possible cases (without correlation).

(1) Rigid z chains in a three-dimensional crystal of simple cubic structure oscillating in a double well with arbitrary fixed direction $\mathbf{\Delta} = (\Delta_x, \Delta_y, \Delta_z)$ with amplitude $\Delta = |\mathbf{\Delta}|$:

$$I(\mathbf{\varkappa}) = \cos^2 \mathbf{\varkappa} . \Delta \sum_b \delta^{(3)}(\mathbf{\varkappa} - \mathbf{b})$$
$$+ \sin^2 \mathbf{\varkappa} . \Delta \sum_{b^z} \delta^{(1)}(l - b^z). \quad (30)$$

In the particular case when chains move along their own direction DS possesses two peculiar features: relplanes are uniform and the central plane passing through the relspace origin is absent.

(2) Rigid z planes in a three-dimensional crystal moving in a double well with arbitrary fixed direction:

$$I(\mathbf{\varkappa}) = \cos^2 \mathbf{\varkappa} . \Delta \sum_b \delta^{(3)}(\mathbf{\varkappa} - \mathbf{b})$$
$$+ \sin^2 \mathbf{\varkappa} . \Delta \sum_{b^x, b^y} \delta_{xy}^{(2)}(\mathbf{\varkappa} - \mathbf{b}), \quad (31)$$

where

$$\delta_{xy}^{(2)}(\mathbf{\varkappa} - \mathbf{b}) = \delta^{(1)}(h - b^x)\delta^{(1)}(k - b^y).$$

In this case the DS has the shape of shining equidistant relrods parallel to l. In the particular case when two-dimensional rigid objects move in their own planes DS possesses two peculiar features: relrods are uniform and the central relrod is absent.

(3) Finally, rigid movable objects may be of three dimensions, for example, sublattices. In such a case DS will have the shape of separate shining points in relspace – the diffuse reflections.

In all of these cases the accounting for correlation may be performed in the simplest mean-field approximation that will correct all results by a factor $1 - \tanh^2 J\langle\sigma\rangle$. A more adequate description of the scattering intensity (DS in particular) would be obtained in the corresponding exact solutions.

Rigid objects of various dimensions

Let us survey the results obtained. In the models where the chaotization of separate atoms has been considered DS had the shape of a smoothly varying $\sim\sin^2 \mathbf{\varkappa} . \Delta$ continuous background in relspace. In the model problems, where the existence of rigid chains has been taken for granted and chaotization of such chains has been regarded, DS had the shape of continuous shining relplanes (uniform or non-uniform). The models of rigid-planes chaotization have given DS as a family of relrods and finally the chaotization of sublattices has led to relpoints (diffuse reflections).

Thus one may consider the rigid extended 'objects' of $\nu = 0, 1, 2, 3$ dimensions and the corresponding shining reciprocal 'objects' of $\mu = 3 - \nu$ dimensions:

the background ($\mu = 3$), the relplanes ($\mu = 2$), the relrods ($\mu = 1$) and diffuse reflections ($\mu = 0$). The important question about the physical origin of the rigid objects will be discussed at length in the following papers and here it should be emphasized that the concepts of rigid extended objects developed and the diffuse scattering of various dimensions had been stated by Guinier (1956); later on the concept of rigid chains was elaborated to explain the diffuse picture in $KNbO_3$ by Comes, Lambert & Guinier (1970) and our theory is based on and appears to be a development of these ideas. Henceforth one will see that for the appearance of shining relplanes and the resulting diffuse streaks on an X-ray pattern in a mono-Laue experiment the existence of strictly rectilinear chains is not necessary. They may be of zigzag type, for example. The two-dimensional objects need not necessarily coincide with the crystal planes, and so on.

From the experimental point of view less interest is paid to zero-dimensional objects since the smoothly varying background in relspace generated by them is hardly suitable for quantitative analysis owing to the very weak intensity at a relpoint (at a fixed point of an X-ray pattern). More valuable information on the structure and dynamics of a crystal is contained in the diffuse reflections generated by the three-dimensional objects (sublattices), but first they are weak compared with Bragg reflections, and, second, they can only be observed in a mono-Laue experiment by chance. A special search should be performed to reveal such diffuse reflections. Therefore, the one-dimensional (chains) and two-dimensional (planes) objects generating correspondingly the diffuse streaks and points on an X-ray pattern appear to be the most useful and valuable objects for investigation. Both have already been observed in experiments by several authors in various crystals. Our main goals of the theory development are as follow: (1) to describe the whole geometric picture of DS observed in a mono-Laue experiment at an arbitrary orientation of a single crystal and to predict such a picture for any new crystal; (2) to describe the temperature evolution of diffuse scattering over the whole temperature region; (3) to describe the corresponding structural phase transitions owing to chaotization of rigid movable objects in such crystals; (4) to explain the physical microscopical origin of such rigid objects and their chaotization; (5) to predict the behaviour of various physical properties and characteristics of the crystal under investigation. Papers II-V of this series will be devoted to these questions.

IV. Non-Ising chaotization

Fig. 1(c) and (d) gives the simplest examples of non-Ising chaotization of a one-dimensional system. The first distinguishing feature of non-Ising chaotization is the number of local minima of δ shape near

to the initial lattice site, being more than one or two. Let this number be q and let them be denoted by vectors Δ_i showing the actual positions of an atom relative to the lattice site (for a one-dimensional crystal these magnitudes are merely scalars Δ_i). Consider the case where separate local δ-shape minima of the multi-well potential are equivalent, *i.e.* their occupation probabilities c_Δ are equal $(c_\Delta = 1/q)$; such a formal model has already been found in statistical physics and partially investigated. It is called the q-state Potts' model [see, for example, the review by Wu (1982)].

The second distinguishing feature of a non-Ising model is the non-equivalence of local minima, *i.e.* the occupation probabilities c_Δ are different (wells of different depth). Such models are far more complicated than even the Potts' model and had not been investigated practically. The scattering problem in such models had never been considered. Let us sketch the approach to such a problem in non-Ising models. Consider some examples of intensity calculations.

Occupation operators

Let us assume that the atomic potential has a multi-well shape as in Fig. 1(c) or (d). Let us introduce the operators $p_{n\Delta}$ at each local minimum with eigenvalues 0 and 1. The total number of all possible configurations of an N-atomic chain is equal to q^N and our task is to calculate the average scattering intensity $I(\varkappa)$ on the ensemble of all configurations. Such an averaging procedure will be denoted by a bar above the corresponding expressions.

Intensity calculation

In the absence of correlation

$I(\varkappa)$

$= \overline{\sum_{nn'} \sum_{\Delta\Delta'} \exp[-i\varkappa a(n-n')] \exp[-i\varkappa(\Delta-\Delta')]p_{n\Delta}p_{n'\Delta'}}$

$= \sum_{nn'} \exp[-i\varkappa a(n-n')]$

$\times \sum_{\Delta\Delta'} \exp[-i\varkappa(\Delta-\Delta')]\overline{p_{n\Delta}p_{n'\Delta'}}$,   (32)

where the sums $\sum_{\Delta\Delta'}$ run over all q states of each site. Once again making use of a relation similar to (4) one obtains:

$$p_{n\Delta}p_{n'\Delta'} = p_{n\Delta}p_{n'\Delta'}\cdot[(1-\delta_{nn'})(1-\delta_{\Delta\Delta'})$$
$$+ \delta_{nn'}(1-\delta_{\Delta\Delta'})+(1-\delta_{nn'})\delta_{\Delta\Delta'}+\delta_{nn'}\delta_{\Delta\Delta'}],$$
(33)

where the sum in (32) should be taken separately for all four terms in (33).

First term: $n \neq n'$, $\Delta \neq \Delta'$. The statistical independence of the atomic displacements in different sites

gives:

$$\overline{p_{n\Delta}p_{n'\Delta'}}(1-\delta_{nn'})(1-\delta_{\Delta\Delta'}) = c_\Delta c_{\Delta'}(1-\delta_{nn'})(1-\delta_{\Delta\Delta'}).$$
(34)

Second term: $n = n'$. In one and the same site there is no different displacement and thus:

$$\overline{p_{n\Delta}p_{n'\Delta'}\delta_{nn'}}(1-\delta_{\Delta\Delta'}) = 0.$$ (35)

Third term: $n \neq n'$, $\Delta = \Delta'$:

$$\overline{p_{n\Delta}p_{n'\Delta'}}(1-\delta_{nn'})\delta_{\Delta\Delta'} = c_\Delta^2(1-\delta_{nn'})\delta_{\Delta\Delta'}.$$ (36)

Fourth term: $n = n'$, $\Delta = \Delta'$. In such a case $p_{n\Delta}p_{n'\Delta'} = p_{n\Delta}^2$ and as long as the occupation operators possess the properties of projection operators $p^2 = p$, so:

$$\overline{p_{n\Delta}p_{n'\Delta'}\delta_{nn'}\delta_{\Delta\Delta'}} = \overline{p_{n\Delta}^2\delta_{nn'}\delta_{\Delta\Delta'}} = c_\Delta\delta_{nn'}\delta_{\Delta\Delta'}.$$ (37)

Let us return to the calculation of intensity (32) per atom

$$I(\varkappa) = \left[\sum_b \delta^{(1)}(\varkappa - b) - 1\right]$$
$$\times \left[\sum_{\Delta\Delta'} c_\Delta c_{\Delta'} \exp[-i\varkappa(\Delta - \Delta')]\right.$$
$$\left. \times (1-\delta_{\Delta\Delta'}) + \sum_\Delta c_\Delta^2\right] + 1.$$ (38)

Calculation of the second bracket gives:

$$\sum_{\Delta\Delta'} c_\Delta c_{\Delta'} \exp[-i\varkappa(\Delta - \Delta')]$$
$$= \sum_{\Delta\Delta'} c_\Delta c_{\Delta'}\left[1 - 2\sin^2\frac{\varkappa(\Delta-\Delta')}{2}\right]$$
$$= \left(\sum_\Delta c_\Delta\right)^2 - 2\sum_{\Delta\Delta'} c_\Delta c_{\Delta'}\sin^2\frac{\varkappa(\Delta-\Delta')}{2}$$
$$= 1 - 2\sum_{\Delta\Delta'} c_\Delta c_{\Delta'}\sin^2\frac{\varkappa(\Delta-\Delta')}{2}.$$ (39)

The final expression for intensity has the form:

$$I(\varkappa) = \sum_b \delta^{(1)}(\varkappa - b)$$
$$\times \left[1 - 2\sum_{\Delta\Delta'} c_\Delta c_{\Delta'}\sin^2\frac{\varkappa(\Delta-\Delta')}{2}\right]$$
$$+ 2\sum_{\Delta\Delta'} c_\Delta c_{\Delta'}\sin^2\frac{\varkappa(\Delta-\Delta')}{2}.$$ (40)

The first term in (40) describes the Bragg reflections reduced by the chaotization and the second term – the diffuse scattering. Again one can see that as far as the chaotization of just zero-dimensional objects (atoms) has been considered so DS was obtained in the shape of a modulated continuous background. If the one-dimensional objects (chains) were considered in a three-dimensional crystal the result would be analogous but in the Bragg term the δ function would be three-dimensional and in the DS term again the

one-dimensional δ function would appear corresponding to shining relplanes and so on. It should be noted that in such a calculation (the chains in the z direction) the sum in $I(\varkappa)$ has the form $\sum_{n_x n_y n'_x n'_y \Delta \Delta'}$ and instead of (33) a more complicated equality has to be used:

$$p_{n_x n_y \Delta} p_{n'_x n'_y \Delta'} = p_{n_x n_y \Delta} p_{n'_x n'_y \Delta'}[(1 - \delta_{n_x n'_x}) + \delta_{n_x n'_x}]$$

$$\times [(1 - \delta_{n_y n'_y}) + \delta_{n_y n'_y}][(1 - \delta_{\Delta \Delta'}) + \delta_{\Delta \Delta'}].$$

$$(41)$$

Using (41) and the procedure described above one obtains for scattering intensity a result similar to (40):

$$I(\varkappa) = \left[1 - 2 \sum_{\Delta \Delta'} c_\Delta c_{\Delta'} \sin^2 \frac{\varkappa(\Delta - \Delta')}{2} \right] \sum_b \delta^{(3)}(\varkappa - b)$$

$$+ 2 \sum_{\Delta \Delta'} c_\Delta c_{\Delta'} \sin^2 \frac{\varkappa(\Delta - \Delta')}{2} \sum_{b^z} \delta^{(1)}(l - b^z) \quad (42)$$

and the analogous result for the case of rigid planes differing from (40) only by the two-dimensional δ function in the DS term.

The results obtained yield the natural limit crossing to the Ising models. For example, let us consider (40) in detail. The particular case when $q = 2$ and two minima are equivalent $c_1 = c_2 = \frac{1}{2}$ coincides with the Ising model. Then $\Delta' = -\Delta$ or $|\Delta - \Delta'| = 2\Delta$ and instead of (40) one can obtain:

$$I(\varkappa) = [1 - \frac{1}{2}(0 + \sin^2 \varkappa \Delta + \sin^2 \varkappa \Delta + 0)] \sum_b \delta^{(1)}(\varkappa - b)$$

$$+ \frac{1}{2}(0 + \sin^2 \varkappa \Delta + \sin^2 \varkappa \Delta + 0)$$

$$= (1 - \sin^2 \varkappa \Delta) \sum_b \delta^{(1)}(\varkappa - b) + \sin^2 \varkappa \Delta,$$

which coincides with (10) and thus proves our statement. The similar crossing may be retraced from (42) to (28) and so on.

The continuous chaotization

Let us now make the number of local minima near to a lattice site infinity. Then for the occupation probability of an atom one would obtain the enveloped curve $c(x)$ of all local minima (Fig. 1e), the integral of which from $-a/2$ to $+a/2$ has to be equal to unity. This is a closer approximation to the real atomic potential well (not necessarily symmetrical).

Then instead of (40) one can write:

$$I(\varkappa) = \left[1 - 2 \int\int_{-a/2} c(x)c(x') \sin^2 \frac{\varkappa(x - x')}{2} \, dx \, dx' \right.$$

$$\times \sum_b \delta^{(1)}(\varkappa - b) + 2 \int\int_{-a/2}^{a/2} c(x)c(x')$$

$$\times \sin^2 \frac{\varkappa(x - x')}{2} \, dx \, dx'. \quad (43)$$

It is proper to change the variables $x - x' \to x$, $x' \to y$. Taking into account the fact that

$$\int_{-a/2}^{a/2} c(y) \, dy = 1$$

one obtains:

$$I(\varkappa) = \left[1 - \int_0^{a/2} c(x) \sin^2 \frac{\varkappa x}{2} \, dx \right] \sum_b \delta^{(1)}(\varkappa - b)$$

$$+ \int_0^{a/2} c(x) \sin^2 \frac{\varkappa x}{2} \, dx. \quad (44)$$

From the physical point of view it is obvious that $c(x) \sim \exp[-\beta U(x)]$, where $U(x)$ is the profile of the potential energy (harmonic or anharmonic) near to the lattice site.

It should be noted that the last model of continuous chaotization is the natural way to calculate the Debye–Waller factor for any anharmonic potential well and also to calculate the corresponding diffuse-scattering background.

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