# Equilibrium characteristics in the condensed state with nearest-neighbor interactions

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A review is given of results obtained by the author by applying a new approach developed by him to the Ising model and to the theory of magnetism, binary systems, and surface phenomena. The approach is based on the formalism of quantum-statistical Green's functions in the Bogolyubov-Tyablikov formulation.

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## INTRODUCTION

A large group of physical phenomena can be described very adequately in the framework of a very simple model. In this model, it is assumed that the "sites" of a regular one-, two-, or three-dimensional structure are associated with the variable $\sigma_f$ ($f$ is the site coordinate), which can take the two values ±1. It is also assumed that the total interaction energy is equal to the sum of the contributions of the states at all neighboring sites of the system, where the contribution from two nearest neighbors $f$ and $g$ in the same state (i.e., characterized by the same values of $\sigma_f$ and $\sigma_g$) appears in the sum with one sign $(+v)$, while the contribution of nearest neighbors in different states appears with the opposite sign $(-v)$. As we shall see, an important feature of this model is the assumption that "short-range interaction" plays the decisive role. This makes it possible to use the model in some simple variants of the theory of magnetic phenomena, in which $\sigma_f$ is associated with two orientations of the spin magnetic moment of the atom at site $f$ ($\sigma_f=+1$ along the field and $\sigma_f=-1$ opposite to the field), and $v$ is an exchange constant. This model played an important part in the theory of binary alloys and binary mixtures of the AB type ($\sigma_f=+1$ here corresponds to the presence of an atom of type B at site $f$ and $\sigma_f=-1$ to its absence, i.e., to the presence at site $f$ of an atom A); $v=v_{\mathrm{AB}}-(v_{\mathrm{AA}}+v_{\mathrm{BB}})/2$. It also proved effective in the theory of surface phenomena (adsorption of gases and metals on a surface and interaction processes between adatoms), in which $\sigma_f=1$ corresponds to the absence of an adatom at the adsorption center $f$, and $\sigma_f=-1$ to its presence, and $v$ is the effective interaction between neighboring adatoms. With certain reservations, this model can also be used in the theory of simple "classical" liquids.

Particular interest in this simple model also arises because it has proved possible in recent years to develop by means of it a theory of phase transitions of the second kind which is completely satisfactory in its main features. The actual possibility of describing phase transitions with very unusual behavior of the equilibrium quantities (logarithmic or power-law singularity of "branch-point type" of the specific heat, for example) was first demonstrated in the remarkable investigations of Onsager,[1] in the framework of the "magnetic" variant of the model. Quantitatively and qualitatively, Onsager's results differed strongly from the then currently adopted (1944–1949) variants of the van der Waals theory, which was regarded as the theory of phase transitions of the second kind. Almost 20 years were needed to demonstrate that the decisive factor in the phase transition is the interaction between fluctuations whose "size" as $T\to T_c$, the so-called correlation length, behaves as $|1-T/T_c|^{-v}, v>0$. This direction in the application of the model was in a certain sense summarized by the creation of the semiphenomenological theory of scaling[2] and the method of reduced description in the momentum space of Wilson.[3] In this paper, we shall not be concerned with the application of the Ising model[1)] in the theory of phase transitions, which has been developed intensively on a broad front in recent years, but instead we shall discuss the new possibilities of using the model to describe phenomena in magnetism, alloy formation and phase separation (stratification), surface phenomena, etc., that were discovered by a new approach to the Ising model developed by Tyablikov and the present author. This approach makes essential use of the method of retarded and advanced thermal Green's functions in the Bogolyubov–Tyablikov formulation.[4]

## 1. CORRELATION FUNCTIONS IN THE ISING MODEL

The Ising Hamiltonian is "derived" from the Heisenberg–Frenkel' Hamiltonian by ignoring in the latter the terms describing the "interaction" between the $x$ and $y$ components of the spin, which automatically rules out the possible existence of spin waves, and by restricting the summation to pairs of nearest neighbors[5]:

$$\hat{H}=-\mu H\sum_{f}\hat{S}_f^z-\frac{I}{2}\sum_{f_1\neq f_2}\hat{S}_{f_1}^z\hat{S}_{f_2}^z. \tag{1}$$

Here, $\mu$ is the magnetic moment of the atom at the lattice site, $H$ is an external magnetic field, and $I$ is the constant of the exchange interaction. It is assumed that eash site $f$ has $z$ nearest neighbors ($S_f^z=\pm\frac{1}{2}$). It is in this form that the Ising Hamiltonian is used in the traditional approaches due to Onsager, in which the partition function is calculated (exactly for $d=1$, $H\neq 0$, $z=2$; $d=2$, $H=0$, $z=3,4,6$ and approximately for $d=3$) as well as some correlation functions.[6]

However, in view of the questions with which we shall

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[1)] Historically, the name "Ising model" is used because the partition function for a one-dimensional system of spins in which only nearest neighbors interact was calculated by Ising, a student of the German scientist W. Lenz [E. Ising, Z. Phys. 31, 253 (1925)].

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be concerned in this review, it is more convenient to go over to the spin-deflection operators $\hat{n}_f$:

$$\hat{S}^z_f = 1/2 - \hat{n}_f,\ \hat{n}_f = \pm 1, \tag{2}$$

which makes it possible to regard $\hat{n}_f$ as occupation operators for site $f$ constructed with the Fermi operators $\hat{a}_f$:

$$\hat{n}_f = \hat{a}^+_f \hat{a}_f,\ \ \hat{a}_f \hat{a}^+_k + \hat{a}^+_k \hat{a}_f = \delta_{kf}. \tag{3}$$

The Hamiltonian (1) is then transformed to

$$\hat{H} = -N\left(\frac{\mu N}{2} + \frac{zI}{8}\right) + L\sum_f \hat{n}_f - \frac{I}{2}\sum_{f_1 \neq f_2} \hat{n}_{f_1}\hat{n}_{f_2},\ L = \mu H + \frac{zI}{2}. \tag{4}$$

The correlation effects are described by equilibrium mean values of the form

$$\left.\begin{array}{l} \Phi^{(h)}_{g_1,\ldots,g_k}(f) = \langle \hat{n}_f \prod\limits_{i=1}^{k} \hat{n}_{g_i} \prod\limits_{r=1}^{h} \hat{n}_{h_r} \rangle; \\ F^{\ h)}_{g_1,\ldots g_k} = \langle 1_f \prod\limits_{i=1}^{k} \hat{n}_{g_i} \prod\limits_{r=1}^{h} \hat{n}_{h_r} \rangle, \end{array}\right\} \tag{5}$$

where, as usual, the angular brackets denote the Gibbs mean value with the Hamiltonian (4); $g_i, r = 1, \ldots, z$ label the sites nearest site $f$, and $h_r \in f_1 g_i$.

The representation (3) and the explicit form of the Hamiltonian (4) make it possible to develop a standard Green's function approach[4] to the Ising model,[7,8] using here the anticommutator Green's functions

$$\langle\langle \hat{a}_f \mid \hat{O}_h \hat{a}^+_f \rangle\rangle = G^{(h)}_0;\ \hat{O}_h = \prod_{r=1}^{h} \hat{n}_{h_r};\ h_r \in f_1 g_i. \tag{6}$$

Since the derivation of the equations for the correlation functions (5) and (6) has been set forth in detail in Refs. 7 and 8, we shall treat this question here somewhat schematically, bearing in mind the aim of the present review.

The equations of motion for the operators $\hat{a}_f$,

$$i\dot{\hat{a}}_f = [\hat{a}_f, \hat{H}]_- = (L - I\hat{F}_1)\hat{a}_f; \tag{7}$$

$$\hat{F}_1 = \sum_{i=1}^{z} \hat{n}_{g_i},$$

the projection properties of $n_k$: $\hat{n}^2_k = \hat{n}_k$, and also the readily verified algebraic relations

$$\hat{F}^2_k = k\hat{F}_k + \hat{F}_{k+1};\ \hat{F}_{z+1} \equiv 0, \tag{8}$$

where

$$\hat{F}_k = \sum_{g_1 \neq \ldots \neq g_k} \prod_{i=1}^{k} \hat{n}_{g_i}$$

with summation over different permutations of $g_1, \ldots, g_k$ (in what follows, we shall denote it by the symbol $\sum_{\langle 1\ldots k\rangle}$), make it possible to write down exact equations for the correlation functions in a compact symmetrized form [see (11) and (12) below]. This is so because in the Ising model with the Hamiltonian (4) one can solve the system of equations for the Green's functions,

$$\langle\langle \hat{a}_f \sum_{\langle 1\ldots k\rangle} \prod_{1}^{k} \hat{n}_{g_i} \mid \hat{O}_h \hat{a}^+_f \rangle\rangle = G^{(h)}_k(f),\quad k = 0, 1, \ldots, z, \tag{9}$$

which arise in the hierarchy of equations generated in the usual manner if one proceeds from (6) and uses (7) and (8). (Here, it is decisive that the hierarchy of equations for $G^{(h)}_k(f)$ is automatically terminated at the equation for $G^{(h)}_z(f)$.[7,8]) This makes it possible to obtain (without any approximations) the following expressions for the spectral densities constructed from different symmetrized (and, if necessary, unsymmetrized) combinations of the operators $\hat{n}_k$ (see Refs. 7 and 8):

$$J^{(h)}_m(\omega) = \sum_{n=0}^{z-m} (-1)^n F^{(h)}_{m+n} \sum_{k=0}^{n} \frac{(-1)^k}{k!\,(n-k)!} \frac{\delta(\omega - E_{k+m})}{\exp(\beta E) + 1}, \tag{10}$$

where $E_p = L - pI$; $p = 0, 1, \ldots, z$; $m = 0, 1, \ldots, z$; $(h) \equiv \{h_1, \ldots, h_r \in f, g_i\}$. Equations (10) and the spectral theorems[4] for the correlation functions

$$\Phi^{(h)}_m = \langle n_f \sum_{\langle 1\ldots m\rangle} \prod_{i=1}^{m} n_{g_i} \rangle,\ F^{(h)}_k = \langle 1_f \sum_{\langle 1\ldots k\rangle} \prod_{p=1}^{k} n_p \rangle \tag{11}$$

lead to the system of exact algebraic equations

$$\Phi^{(h)}_m = \sum_{m=0}^{z-m} (-1)^n F^{(h)}_{m+n} \sum_{k=0}^{n} \frac{(-1)^k}{k!\,(n-k)!} \frac{1}{\exp(\beta E_{m+k}) + 1}. \tag{12}$$

It is worth emphasizing that the structure of Eqs. (12) is of one kind: It is completely independent of the choice of $\hat{O}_h = \Pi^h_{r=1} \hat{n}_{h_r}, h_r \in f_1 g_i$, i.e., the coefficients of the algebraic system of equations that determine the relation between mean values of the form $\langle \hat{n}_f \hat{n}_{g_i} \rangle$, $\langle \hat{n}_f \hat{n}_{g_i} \hat{n}_{g_k} \rangle, \ldots, \langle \hat{n}_f \hat{n}_{g_i}, \ldots, \hat{n}_{g_z} \rangle$ and the mean values $\langle \hat{n}_{g_k} \rangle$, $\langle \hat{n}_{g_k} \hat{n}_{g_p} \rangle, \ldots, \langle \hat{n}_{g_1}, \ldots, \hat{n}_{g_z} \rangle$ [they are given by the sum $\sum^n_{k=0}$ in (18)] are automatically reproduced for the system of algebraic equations that relate the mean values $\langle \hat{n}_j \hat{n}_{g_i} \hat{O}_h \rangle, \langle \hat{n}_f \hat{n}_{g_i} \hat{n}_{g_j} \hat{O}_h \rangle, \ldots, \langle \hat{n}_f \hat{n}_{g_1}, \ldots, \hat{n}_{g_z} \hat{O}_h \rangle$ to $\langle \hat{n}_{g_i} \hat{O}_h \rangle$, $\langle \hat{n}_{g_i} \hat{n}_{g_j} \hat{O} \rangle, \ldots, \langle n_{g_1}, \ldots, \hat{n}_{g_z} \hat{O}_h \rangle$.

The exact expressions (10) for $J^{(h)}_m(\omega)$ present a unique possibility of calculating in accordance with known formulas[4,9] the commutator Green's functions for $E = 0$ for any operators $\hat{A}$ and $\hat{B}$:

$$g_{\hat{A}\hat{B}}(0) = \frac{1}{2\pi} \int J_{\hat{A}\hat{B}}(\omega) \frac{\exp(\beta\omega) - 1}{\omega}\, d\omega, \tag{13}$$

and then obtaining useful inequalities for the correlation functions directly from Bogolyubov's canonical inequality[9]

$$\left.\begin{array}{l} g_{\hat{A}\hat{A}^+}(0)\, g_{\hat{B}\hat{B}^+}(0) \geqslant |g_{\hat{A}\hat{B}}(0)|^2; \\ g^*_{\hat{A}\hat{B}}(0) \overset{\text{det}}{=} g_{\hat{B}^+\hat{A}^+}(0). \end{array}\right\} \tag{14}$$

(Usually, a certain reduced form of (14) is employed.[9,10]) A number of useful inequalities was obtained in this manner in Ref. 11, which made it possible to give a comparatively simple classification of the possible types of phase transitions.[12]

Considering the system (12) for $\hat{O}_h \equiv 1 (h = 0)$, i.e., considering the system of equations that describe the correlation of states at neighboring sites, we can readily establish that we have at our disposal $z + 1$ equations [for $\Phi_k(f)$, $k = 0, 1, \ldots, z$, and $F_i(f)$, $i = 0, 1, \ldots, z$] for $2z + 2$ correlation functions. However, since $F_0(f) \equiv 1$ and $F_1(f) = \langle \sum^z_{i=1} \hat{n}_{g_i} \rangle = z\langle \hat{n}_f \rangle = z\Phi_0(f)$ by the translational invariance, there remain $2z$ unknown correlation functions: $\Phi_k(f)$, $k = 0, \ldots, z$, and $F_r(f)$, $r = 2, \ldots, z$. Thus, we need $z - 1$ equations to close the system. Choosing $\hat{O}_h$ in different ways, for example, taking $\hat{O}_h = \hat{n}_{h_i}, h_i \in f, g_i$, we formally complete our system, since the correlation functions of lower order in Eqs. (12) for $\hat{O}_h = 1$ are "coupled" to the correlation functions that describe the correlation of the states at the sites $f$ and $g_i$

with the states at the sites $h_i (h_i \in f, g_i)$. However, by analyzing the resulting system, one can show that the situation described above is preserved: we still lack $z-1$ equations (1 for $d=1$; 2 ($z=3$) or 3 ($z=4$) for $d=2$, etc.). In my opinion, one could attempt to construct the missing equations by using the invariance of definite structures under different symmetry transformations. It was in this way, by using the transitional invariance, that the system of equations was exactly solved in the one-dimensional case.[7,8] The single missing equation was obtained by taking into account the fact that $\langle \hat{n}_f \hat{n}_{g_2} \hat{n}_k \rangle = \langle \hat{n}_{g_1} \hat{n}_f \hat{n}_{k-1} \rangle$ ($g_2$ and $g_1$ are the right- and left-hand neighbors of site $f$; $k$ is a site separated from site $f$ by $k$ steps) and an effective rearrangement of the completed system of equations.[7,8] The finite-difference equation

$$\Phi_0^k + p\Phi_0^{(k-1)} + \Phi_0^{(k-2)} = q(\Phi_0); \quad \Phi_0^{(k)} = \langle \hat{n}_f \hat{n}_k \rangle \tag{15}$$

($p$ and $q(\Phi_0)$ are fairly cumbersome expressions[7,8]) obtained by this procedure can be readily solved, and this then gives the possibility of finding any correlation function for $z=2$ ($d=1$).

## 2. APPROXIMATIONS, POINT DEFECTS, AND LATTICE VIBRATIONS

*Approximations for the Correlation Functions.* It is clear that the assertion about the importance of symmetry and the possibility of actual implementation of the program in the case $d \geqslant 2$ are far from undisputed. But the fact that we have an exact system of algebraic equations for the equilibrium mean values opens up new possibilities for different approximations which are far better justified than the ones usually employed to decouple the higher Green's functions in terms of the lower ones. In our case, the approximations can be formulated in the language of decoupling of higher correlation functions in terms of lower ones (unary, binary, and other probabilities), i.e., in the language of approximations for quantities that have a clear physical meaning, whereas the usual decouplings involve assumptions about the analytic structure of functions of a complex variable—the Green's functions. Postulating a particular decoupling of the correlation functions, we can implement it in such a way that "on the whole" the complete system of equations (12) is satisfied. This makes it possible to obtain approximations in which allowance is made for short-range effects (i.e., to go beyond the lattice analog of the Hartree-Fock approximation; here, it is called the Bragg-Williams approximation).[2)] Note that the Bragg-Williams approximation can be formulated in the language of a single-particle Hamiltonian, which makes it possible to obtain concrete formulas for any higher correlation function. Approximations that to some extent describe short-range order were proposed and discussed in Refs. 8, 13–15. Thus, it was possible to prove rigorously that the well-known Bethe-Peierls-Guggenheim approximation is the lattice analog of Kirkwood's superposition decoupling.[17] Any higher correlation function must be decoupled in terms of binary correlation functions with allowance for the increase in the relative distance of the corresponding lattice site from the "initial" site,[8,15], i.e.,

$$\begin{gathered}\langle \hat{n}_f \hat{n}_{k_1} \hat{n}_{k_2} \ldots \hat{n}_{k_r} \rangle \\ \to \frac{\langle \hat{n}_f \hat{n}_{k_1} \rangle \langle \hat{n}_{k_1} \hat{n}_{k_2} \rangle \ldots \langle \hat{n}_{k_{r-1}} \hat{n}_{k_r} \rangle}{\langle \hat{n}_{k_1} \rangle \ldots \langle \hat{n}_{k_{r-1}} \rangle}, \\ |f-k_1| < |f-k_2| \ldots < |f-k_r|.\end{gathered} \tag{16}$$

The distance between sites $k_i$ and $f$ is measured simply in "steps" along the lattice, irrespective of the mutual geometrical disposition of $k_i$ and $f$. Satisfying the complete system of equations (12) by this decoupling (here $\hat{O}_h \equiv \hat{n}_h$, and $h$ is an arbitrary lattice site), we arrive at the well-known equation[17] for $\Phi_0 = \langle \hat{n}_f \rangle$ and the following formula[8,15] for $\Phi_0^k = \langle \hat{n}_f \hat{n}_k \rangle$:

$$\left.\begin{aligned}&\Phi_0^{(k)} = \Phi_0^2 + \Phi_0 (1-\Phi_0) \lambda^{|f-k|}; \quad \lambda = (r-1)/(r+1); \\ &r = \sqrt{\sigma^2 + y^2 (1-\sigma^2)}; \quad \sigma = 1 - 2\Phi_0; \\ &y = \exp(\beta I/2).\end{aligned}\right\} \tag{17}$$

In our earlier investigations, we also studied other approximations (polynomial decoupling,[13] an approximation for a regular hexagonal lattice on a plane[15]), which also led to concrete expressions for the higher correlation functions and made it possible to analyze the part played by short-range effects in alloys, magnets, and surface phenomena and to construct a completely satisfactory variant of the theory of diffraction of slow electrons by a surface on which there are adsorbed materials.

*Impurities in the Ising Model.* To calculate some equilibrium characteristics in the problems listed above it is sufficient to know the correlation functions of the first and second orders ($\langle n_f \rangle$ and $\langle n_f n_g \rangle$, respectively), but in the case of nonideal systems, which is important for applications, it is necessary to know the correlation functions of higher orders as well. By a nonideal system we here mean a system with $N_1$ point defects—an interstitial or substitutional impurity. For the magnetic variant of the Ising model, the characteristics of the state at the impurity site differ from those of the ordinary site of the structure:

$$S \to S'; \quad \mu \to \mu'; \quad I \to I'; \quad z \to z'. \tag{18}$$

Defects modify the equilibrium characteristics of the system in a definite manner, and, depending on the properties of the impurity atoms, this modification may be very important (see below). The Hamiltonian of a system of $N - N_1$ ideal atoms and $N_1$ impurities can be written as follows[8,18]:

$$\hat{H} = \hat{H}_0 + \delta\hat{H} + E, \quad \delta\hat{H} = \sum_{k=1}^{N_1} \delta\hat{H}(k), \tag{19}$$

where $\hat{H}_0$ is the Hamiltonian (1); $\delta\hat{H}(k)$ is the operator of the perturbation due to the presence at site $k$ of the impurity, this being given for a substitutional impurity by the expression

$$\delta\hat{H}(k) = L'\hat{N}_f - L\hat{n}_f + (S'I' - SI)\hat{F}_1 + (I\hat{n}_f - I'\hat{N}_f)\hat{F}_1, \tag{20}$$

where $E$ is the ground-state energy of the nonideal system:

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[2)] Incidentally, an equation for the order parameter was also obtained by Curie, Weiss, and Langevin, the ideas being due to van der Waals's investigations.

$$\left.\begin{array}{l} E=E_0+\delta E=-NS\,(\mu H+zSI/2)\\ +N_1H\,(\mu S-\mu'S')+zS\,(SI-S'I')\,N_1;\\ S=1/2;\quad N'=0,\ 1,\ \ldots,\ \ 2S';\quad z=z'. \end{array}\right\} \tag{21}$$

Since

$$[\hat{H}_0\delta\hat{H}\,(k)]_-=[\delta\hat{H}\,(k)\,\delta\hat{H}\,(k')]_-=0, \tag{22}$$

the density matrix of the nonideal system is written in the form

$$\left.\begin{array}{l} \hat{\rho}\equiv\exp\beta\,[F-\hat{H}]=\hat{\rho}_0\prod\limits_{k=1}^{N_1}\hat{V}\,(k)\exp\beta\,(F-F_0-\delta E);\\ \hat{V}\,(k)=\exp\,(-\beta\delta\hat{H}\,(k)), \end{array}\right\} \tag{23}$$

where $\hat{\rho}_0$ and $F_0$ are the density matrix and free energy of the ideal system. Equation (23) leads to the following expression for any equilibrium mean value of the nonideal system:

$$\mathrm{Sp}\,(\hat{\rho}\hat{A})=\langle\hat{A}\prod_{k=1}^{N_1}\hat{V}\,(k)\rangle_0/\langle\prod_{k=1}^{N_1}\hat{V}\,(k)\rangle_0, \tag{24}$$

where $\langle\ldots\rangle_0$ denotes an average with $\hat{\rho}_0$. Depending on the actual form of the operator $\hat{A}$ (it may be given by a sum of the operators $\hat{n}_i$, the sum of their products, their product, etc.), the expression (24) can be rewritten in a more concrete form. For example, if $\hat{A}\equiv\hat{A}_1=\sum_{k=1}^{N_1}\hat{A}(k)+\sum_{i\overline{\in}\{k\}}\hat{A}(i)$, then

$$\mathrm{Sp}\,(\hat{\rho}\,\hat{A}_1)=\sum_{i=1}^{N_1}\frac{\langle\hat{A}\,(k_i)\,\hat{V}\,(k_i)\prod\limits_{j\neq i}\hat{V}\,(k_j)\rangle_0}{\langle\prod\limits_{k=1}^{N_1}\hat{V}\,(k)\rangle_0}+\sum_{i\overline{\in}\{k\}}\frac{\langle\hat{A}\,(i)\prod\limits_{1}^{N_1}\hat{V}\,(k)\rangle_0}{\langle\prod\hat{V}\,(k)\rangle_0}. \tag{25}$$

The expression (25) already permits the use of approximations of the correlation decoupling type and reduces the problem of calculating the characteristics of a nonideal system to calculations that operate with the correlation functions of the ideal system (it is assumed that the impurities are distributed randomly over the lattice and that $c=N_1/N\ll 1$, which guarantees an appreciable distance between the impurities: $r_c\sim c^{-1/d}$, $d=1,2,3$). Note that in the Ising model the single-impurity problem can be solved exactly[18]: $\hat{V}(1)$ can be expressed in terms of (5) for $h$, $\Phi_{g_1,\ldots,g_k}(f)$, $F_{g_1,\ldots,g_k}(f)=0$ and in terms of the impurity parameters (or, more precisely, in terms of $\delta\mu=\mu'-\mu$ and $\delta I=I'-I$). For $S'=S=\frac{1}{2}$, for example

$$\left.\begin{array}{l} \hat{V}\,(1)=\sum\limits_{0}^{z}\frac{1}{k!}\,[(1+t_1)\,t_2^k\hat{\Phi}_k+t_3^k\,(\hat{F}_k-\hat{\Phi}_k)];\\ t_1=\exp\beta\,[\delta\mu H+(z/2)\,\delta I]-1;\\ t_2=\exp\beta\,(\delta I/2)-1;\quad t_3=\exp\,(\beta\delta I)-1. \end{array}\right\} \tag{26}$$

In the simplest case of complete decoupling of correlations between the impurity regions, (25) can be transformed to

$$\mathrm{Sp}\,(\hat{\rho}\hat{A}_1)=N_1\frac{\langle\hat{A}\,(1)\,\hat{V}\,(1)\rangle}{\langle\hat{V}\,(1)\rangle_0}+\sum_{i\neq k}\langle\hat{A}\,(i)\rangle_0. \tag{27}$$

Since $\hat{A}(1)$ is a combination of the operators $\hat{n}_k$ and $\hat{n}_k\hat{n}_{g_i}$, from which the operator $\hat{V}(1)$ is also "constructed", the mean values $\langle\hat{A}(1)\hat{V}(1)\rangle$ can be expressed in terms of $\Phi_{g_1,\ldots,g_k}(k)$ and $F_{g_1,\ldots,g_k}(k)$ (or, more precisely, in terms of sums of them with coefficients $t_i$, $i=1,2,3$). This then solves the problem of calculating $Tp(\hat{\rho}\hat{A}_1)$ if a particular approximation is used. With allowance for the correlation between the impurity atoms (which is important in problems in which one must find, for example, the influence of an impurity on a phase transition), it is necessary to calculate mean values of the type $\langle\hat{A}(k)\hat{V}(k)\rangle_0$ and $\langle\hat{V}(k_1)\hat{V}(k_2)\rangle_0$; for $\langle\hat{V}(k_1)\hat{V}(k_2)\rangle_0$ one can use an approximation of the scaling type.[2] Finally, it is absolutely necessary to know the actual asymptotic behavior of $\langle n_0n_p\rangle$, $p=0,1,\ldots,N$ and $\langle n_0n_pn_q\rangle$, $p,q=0,1,\ldots,N$, etc. [in the quasichemical approximation, it is described by Eqs. (16) and (17)] in a quantitative analysis of questions relating to the features of the diffraction picture formed by the diffraction of slow electrons by a surface on which there are adatoms (see below).

In Refs. 8, 14, 15, and 18, there has been a fairly detailed discussion of how one can use different approximations to calculate the characteristics of an ideal magnet, and therefore to illustrate the use of the approximation formulas in the investigation of nonideal systems we shall consider the evolution of the concentration of vacancies in a ferromagnet-paramagnet phase transition. Besides definite approximation formulas, we shall use the variational procedure proposed in Ref. 19.

Note that if the absence of correlations between impurity atoms is assumed, as in the derivation of (27), the results are valid when the mean distance between the impurities ($\sim c^{-1/d}$) is much greater than the correlation radius $R_c\sim\tau^{-\nu}$, $\tau=|1-\beta/\beta_c|$, which, as is well known, determines the asymptotic behavior of the binary correlation function in the paramagnetic region ($\beta_c>\beta$, $\beta\to\beta_c^-$). At the present time, the estimates made for $d\geqslant 2$ indicate that $\nu d\sim 2$.[2] Thus, conclusions about the behavior of the thermodynamic quantities obtained under the assumption of correlation decoupling are valid in the temperature range

$$|\,(\beta_c/\beta)-1\,|>\max\,(\sqrt[\nu d]{c}\approx\sqrt{c},\ z^{-1}). \tag{28}$$

It seems to us that the opposite assertion is also true: To make conclusions about the properties of a nonideal magnet in the region $\sqrt[\nu d]{c}<|(\beta_c/\beta)-1|<z^{-1}$ it is necessary to use approximations in which allowance is made for the correlations between the impurities (this is done below). In the region $\tau<\sqrt[\nu d]{c}$ a fundamentally new approach is necessary and the nature of the phase transition may change. For the time being we use the correlation functions of an ideal system at $R_c\approx 1$ (the Bragg-Williams approximation, polynomial decoupling, quasichemical approximation, etc.),[8,13,15] which essentially prevents us from determining the modifications in the properties of a magnet due to impurities that are associated with the presence of long-range correlations: the exact dependence of the spontaneous magnetization at $\beta=\beta_c$, the shift in the Curie point, etc.

*Evolution in the concentration of vacancies at the ferromagnet-paramagnet phase transition.*[19,20] Since $10^{-15}\lesssim c_v\lesssim 10^{-4}$, $c_v=N_v/N$, in the complete temperature range from room temperature to the melting point, we can use correlation decoupling everywhere except in the temperature region $|\beta_c/\beta-1|\lesssim 10^{-2}$ [see (28)]. In this case, $F$, the free energy of the nonideal system with $N_1(=N_v)$ impurities (vacancies), is given under the assumption of complete decoupling of the correlations between the impurities by (27), in which it is necessary to set

$$\left.\begin{array}{l}\mu'=I'=0;\ F=F_0+N_v\delta E_v-\beta^{-1}N_v\ln\langle\hat{\Gamma}(v)\rangle_0;\\ \delta E_v=-H\delta\mu/2-z\delta I/4\equiv\mu H/2+zI/4;\\ \langle\hat{V}(v)\rangle_0=\sum\frac{1}{k!}\left[(1+t_1^v)\,t_2^{v\,k}\Phi_k+t_2^{v\,k}(F_k-\Phi_k)\right];\\ t_1^v=\exp\beta(-\mu H-zI/2)-1;\\ t_2^v=\exp(-\beta I/2)-1;\\ t_3^v=\exp(-\rho I)-1.\end{array}\right\}\qquad(29)$$

Adding to $F$ the free energy $N_v$ of the noninteracting vacancies,

$$F_v=\varepsilon_vN_v-\beta^{-1}\ln\frac{N!}{N_v!\,(N-N_v)!},\quad\varepsilon_v\approx1\mathrm{eV},\qquad(30)$$

and minimizing $F_{\text{tot}}=F+F_v$ with respect to $N_v$, we obtain the following expression for $\eta=c_v/c_v^0$:

$$\begin{array}{l}\eta=V(v)\exp(-\beta\delta E_v),\\ \quad V(v)\equiv\langle\hat{U}(v)\rangle_0.\end{array}\qquad(31)$$

In the superposition approximation[8,15]

$$\left.\begin{array}{l}V(v)=x(1-\sigma)\,[y+(1-y)\,t]^z;\\ x=\exp(\beta\mu H);\quad \underset{\sim}{y}=\exp(\beta I/2);\\ x=[(r+\sigma)/(r-\sigma)]^{z/2}\,[(1-\sigma)/(1+\sigma)]^{(z-2)/2};\\ t=(r-\sigma)/(r+1).\end{array}\right\}\qquad(32)$$

Equations (32) can be obtained from (26) by using for $F_r$ and $\Phi_k$ the results of Ref. 8; $r$ and $\sigma$ are defined in (17).

Studying the evolution of the vacancy concentration when the spontaneous magnetization disappears or appears ($H=0$), we find that the behavior of

$$\left.\begin{array}{l}\eta(\chi,z)=V(\chi,z)\,[z/(z-2)]^{-z\chi/2};\\ \chi=\beta/\beta_c,\quad\beta_cI=2\ln[z/(z-2)]\end{array}\right\}\qquad(33)$$

is described by the curve shown in Fig. 1 (curve 1). We see that $\eta(\chi\lesssim1,z)\sim1$ and that on the appearance of the spontaneous magnetization $\eta(\chi,z)$ decreases smoothly:

$$\eta(2.17;\ z=4)=\eta(2.47;\ z=6)\approx0.1.\qquad(34)$$

Thus, an increase in temperature by a factor 2–2.5 (compared with the temperature at which the spontaneous magnetization appears) reduces $c_v$ by an order of magnitude compared with the vacancy concentration $c_v^0$ that should occur at the given temperature [$c_v^0=\exp(-\beta\varepsilon_v)$]. The numerical estimates may be slightly changed if different approximations are used for $F_r$ and $\Phi_k$ (in particular, for polynomial decoupling[11,1] the interval of rapid variation of $\eta$ from 1 to 0.1 becomes somewhat narrower).

As we noted above, as $\tau\to0$, beginning at a certain temperature, a situation arises which is such that for $\tau\lesssim1/z$ we are in the "critical" region, but for $R_c\lesssim c^{-1/d}$ the system "does not feel" the impurity. Here, it is necessary to carry out the correlation decoupling procedure more accurately and to take into account the correlation between the impurities.

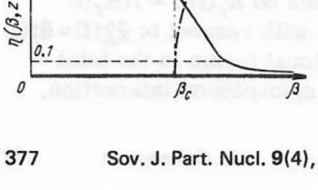

FIG. 1.

Note that at any fixed concentration (or concentration varying slowly with $T$) of the impurities one can always find temperatures fairly close to $T_c$ for which $R_c\gtrsim c^{-1/d}$. Here, the main parameter of the problem is the mean distance between the impurities, and this may change the nature of the phase transition (one of the second kind becoming actually one of the first kind). However, quantitatively the situation here is very obscure, and we shall restrict ourselves in the discussion below to the behavior of $c_v$ in the region

$$c^{1/d\nu}\leqslant\tau\leqslant z^{-1},\qquad(35)$$

using the basic ideas of superposition decoupling and the scaling formula to derive an equation for $c(\beta)$. In the given case, a natural generalization of (29) is

$$\delta F=-\theta\ln\left\langle\prod_{i=1}^{N}V(i)\right\rangle\to-\theta\ln\left[\langle V(v)\rangle_0^{N_1}\frac{\langle n_1n_2\rangle^{N_1-1}}{\bar{n}_1^{N_1-1}\bar{n}_2^{N_1-1}}\right],\qquad(36)$$

which can in some way be justified by "considering" the impurities nearest to each other and using the natural device

$$\begin{array}{l}\langle V(1)V(2)\ldots V(N_1)\rangle\equiv\langle\tilde{V}(1)\,\hat{n}_1^2\hat{n}_2^2\tilde{V}(2)\ldots\rangle\\ \quad\to\langle\tilde{V}(1)\,\hat{n}_{g_1}\rangle\,\langle\hat{n}_{g_1}(1)\,\hat{n}_{g_1}(2)\rangle\\ \quad\times\langle\hat{n}_2\tilde{V}(2)\ldots\rangle/\bar{n}_1\bar{n}_2\to\langle\hat{V}(1)\rangle\\ \quad\times\langle\hat{n}_1\hat{n}_2\rangle\,\langle\tilde{V}(2)\,\hat{n}_{g_2}(2)\rangle\,\langle\hat{n}_2\hat{n}_3\rangle\\ \quad\times\langle\hat{n}_{g_2}(3)\hat{V}(3)\ldots\rangle/\bar{n}_1\bar{n}_2\bar{n}_3.\end{array}\qquad(37)$$

Here, $\hat{n}_{gk}(k-1)$ is the occupation operator for the site of the $(k-1)$-th impurity nearest to impurity $k$. Since the vacancies are distributed randomly, and the distances between them are of the same order $r\sim c^{-1/3}$,

$$\langle\hat{n}_1\hat{n}_2\rangle=\langle\hat{n}_2\hat{n}_3\rangle=\ldots=\langle\hat{n}_k\hat{n}_{k+1}\rangle.\qquad(38)$$

These simple considerations lead to (36). Therefore, the total energy of the nonideal system is determined in the region (35), not by Eqs. (29) and (30), but by

$$\begin{array}{l}F_{\text{tot}}=F+F_v=F_0+\delta EN_v-\theta N_v\ln[N!/N_v!\,(N-N_v)!]+\varepsilon_vN_v\\ \quad-\theta N_v\ln\langle V_v\rangle_0-\theta(N_v-1)\ln\langle n_1n_2\rangle+2\theta(N_v-1)\ln\bar{n},\end{array}\qquad(39)$$

which reduces to (29) and (30) if we ignore the correlations between the impurities:

$$\langle\hat{n}_1\hat{n}_2\rangle\to\langle\hat{n}_1\rangle\langle\hat{n}_2\rangle=\langle\hat{n}_1\rangle^2.\qquad(40)$$

Minimizing (39) with respect to $N_v$ and ignoring terms of order o(1/$N$), o(1/$N_v$), o(1), we obtain the following equation for $c$:

$$\left.\begin{array}{l}c=\tilde{\eta}(\chi,z)\,(\langle n_1n_2\rangle_0/\bar{n}^2)\,c_0;\\ \tilde{\eta}(\chi,z)=\langle\hat{V}(v)\rangle_0\exp(-\beta\delta E_v);\quad c_0=\exp(-\beta\varepsilon_v).\end{array}\right\}\qquad(41)$$

If we remember that $\langle\hat{n}_f\rangle=1/2-\langle\hat{\sigma}_f\rangle$ and

$$\langle\hat{n}_f\hat{n}_k\rangle=1/4-\langle\hat{\sigma}_f\rangle+\langle\hat{\sigma}_f\sigma_k\rangle,$$

and use for $\langle\hat{\sigma}_f\rangle$, $\langle\hat{\sigma}_f\hat{\sigma}_k\rangle$ the scaling formulas for $h=0$ (Ref. 2):

$$\langle\hat{\sigma}_f\rangle\approx\tau^{\beta_0}f_1(0);\quad\langle\sigma_f\sigma_k\rangle\approx|f-k|^{-2x_\sigma}f_2(|f-g|/\tau^{-\nu}),\qquad(42)$$

then we can obtain the following expression for $c$ [the mean distance between vacancies is $r\approx(4\pi c/3)^{-1}$]:

$$c=\tilde{\eta}(\chi,z)\,c_0\,[1-\tau^{\beta_0}f_1(0)+(4\pi c/3)^{2x_\sigma/3}f_2(\tau^\nu c^{1/3})]\,[1/2-\tau^{\beta_0}f_1(0)].\qquad(43)$$

Note that $f_2(x) \sim 1$ for $x \leqslant 1$ and $f_2(x)$ decreases rapidly as $x \to \infty$; $f_1(0) \approx 1$; $2x_0 = 2/\nu d \approx 1$; $\beta_0 \approx 1/3$.

To calculate $\langle V(v)\rangle_0$ in the region (35) we must use $F_r(f)$ and $\Phi_k(f)$ calculated in the critical region, but these quantities are unknown, so that $\tilde{\eta}(\chi, z)$ differs from $\eta(\chi, z)$ in (33). However, these correlation functions are determined by the short-range correlations with range of the order of the lattice constant, and we can hope that the difference between $\eta(\chi, z)$ and $\tilde{\eta}(\chi, z)$ is small $[\langle n_f \prod_{i=1}^{k} n_{g_i}\rangle \sim (1/2)^{k+1} - (k+1)\tau^{\beta} f_1(0) + \ldots]$. Since $c \ll 1, c_0 \ll 1$ right up to the melting point, (43) can be reduced to the form

$$c\,[1 - 4\,(4\pi/3)^{1/3}\,c^{1/3}] = V(\chi, z)\,[z/(z-2)]^{-z\chi/2} c_0. \tag{44}$$

Specifying characteristic values of $c_0$, we can analyze this last expression on a computer. Qualitatively, it is clear that in the ferromagnetic phase $c/c_0 \approx 1$, and in the paraphase $c/c_0 \ll 1$ right up to $\tau \approx \sqrt{c}$, i.e., the temperature range of variation of $c/c_0$ from 1 to 0 is appreciably narrower than shown in Fig. 1. This conclusion that the vacancy concentration is "suppressed" when the spontaneous magnetization changes from its asymptotic value in the critical region ($\sigma \sim \tau^{\beta_0}$) to its asymptotic value in saturation ($\sigma \approx 1$) appears reasonable to the author. It seems that high Curie points $T_c$ and low energies $\varepsilon_v$ of vacancy formation should favor observation of this effect. Naturally, similar anomalies must be exhibited by the physical characteristics of a magnet that are related in some way to $c_v$ (for example, the coefficient of self-diffusion).

*Magnetization of a nonideal magnet.* As the operator $A$(24) we take the operator that describes the magnetization of a nonideal magnet:

$$\begin{aligned}\hat{\mathcal{M}} &= \mu' \sum_{k=1}^{N_1} \hat{S}_k + \mu \sum_{f \in \{H\}} \hat{S}_f \\ &\equiv \sum_f \Big(\mu' \hat{S}_f + \mu \sum_h \hat{S}_h\Big), \quad h \in G_{f,\,h} \neq f,\end{aligned} \tag{45}$$

where $G_f$ is a subregion of the lattice at whose center at site $f$ the impurity is situated ($N_1 G_f = N$). In such a case, assuming the absence of correlations between the impurities, we obtain from (27)

$$\begin{aligned}\bar{\mathcal{M}} &= \Big\{\sum_f \Big\langle \Big[\mu' S_f + \sum_{h \in G_f,\, f \neq h} \mu S_h\Big]\Big\rangle \\ &\times V_f \prod_{f' \neq f} V(f')\Big\}/\langle V(f)\rangle^{N_1} = [\langle \hat{\mathcal{M}} V(f)\rangle_0]/\langle V(f)\rangle_0; \\ &\Big\langle \prod_{f=1}^{N_1} V(f)\Big\rangle \to \prod_{f=1}^{N_1} \langle V(f)\rangle = \langle V(f)\rangle_0^{N_1}.\end{aligned} \tag{46}$$

Here, we have used the translational invariance of the ideal system; $V(f)$ is given by (26), and $\langle \hat{V}(f)\rangle_0$ by replacing in (26) the operators $\hat{F}_k$ and $\hat{\Phi}_r$ by the correlation functions $\langle \hat{F}_k\rangle = F_k$ and $\langle \hat{\Phi}_r\rangle = \Phi_r$. From (46) we obtain for $\sigma(c) = \bar{\mathcal{M}}/(\mu N/2)$:

$$\begin{aligned}\sigma(c) = \sigma(0) + c\,\Big\{&\frac{\mu'}{\mu}\frac{\langle \hat{\sigma}_f \hat{V}(f_1)\rangle}{\langle \hat{V}(f)\rangle} + \frac{\langle (z - 2\hat{F}_1)\,\hat{V}(f)\rangle}{\langle \hat{V}(f)\rangle} \\ &- (z+1)\,\sigma - \frac{1-\sigma^2}{2} \sum (z, \lambda)\Big\}.\end{aligned} \tag{47}$$

The last term in (47), $\sum(z, \lambda)$, is the contribution of long-range correlations of the type $\langle S(f) S(k)\rangle_0$; $|f - k| \sim c^{-1/d}$ is always small, and in the Bragg-Williams approximation, which we shall use because more realistic approximations[13-15] change the result little but lead to cumbersome expressions, we have $\sum(z, \lambda) = 0$. In this approximation, the spontaneous magnetization is

$$\begin{aligned}\sigma_0(c) = \sigma_0(0) + c\,\Big(&\frac{\mu'}{\mu}\frac{1-q^z}{1+q^z} - \sigma - \frac{z\rho\sigma\,(1-\sigma^2)}{1-\rho\sigma}\,\frac{1-q^{z-1}\exp(\beta z\sigma/2)}{1+q^z}\Big), \\ &q = [(1+\rho\sigma)/(1-\rho\sigma)]\exp(\beta I\sigma/2), \\ &\rho = -\operatorname{th}[\beta\delta I/2], \quad \sigma = \operatorname{th}(\beta z I\sigma/4).\end{aligned} \tag{48}$$

We can conclude from (48) that impurities have their maximal influence in the transitional range of variation of $\sigma$ when $\sigma$ varies from $\sigma \approx 1$ to $\sigma \approx [3\,|1 - \beta_c/\beta|\,]^{1/2}$.

If we assume that $\delta I/I \gg 1$, then the impurities modify $\sigma$ rather strongly:

$$\begin{aligned}\sigma_0(c) \approx \sigma + c\,\{&(\mu'/\mu + z)\operatorname{th}[\beta/\beta_c\,(z+1)\,\sigma] \\ &- (z+1)\operatorname{th}(\beta\sigma/\beta_c)\}, \quad \beta_c = zI/4\end{aligned} \tag{49}$$

[here we have taken into account $(t_i + 1) \approx 0$]. The greatest influence occurs in the region where the spontaneous magnetization disappears. Retaining in (49) the terms linear in $\sigma$, and assuming for simplicity $\mu' = \mu$, we obtain

$$\sigma_0(c) \approx \sigma\,[1 + cz\,(z+1)] + co\,(\sigma^2). \tag{50}$$

The modification of $\sigma$ in other approximations with $R_c \leqslant 1$ has approximately the same nature.[13-15] We emphasize that the question of the nature of the singularity of $\sigma_0(c)$ as $\beta \to \beta_c^+$ remains open: The fact that here the singularity of $\sigma_0(c)$ is the same as that of $\sigma$ is due to the use of the Bragg-Williams approximation. As one would expect, the vacancies do not modify $\sigma$ much:

$$\sigma_0^v(c) \approx \sigma\,(1-c) + o\,[c\,(d+1)/d]. \tag{51}$$

To conclude this section, we note that the approach developed in Ref. 18 has proved particularly effective when applied to impurity problems for systems with repulsion.[14,21,22,32,39] This has made it possible to explain, for example, a number of experimental data on physical and chemical adsorption under extreme conditions (high vacuum $p_0 \leqslant 10^{-11}$, very pure states, etc.) in the framework of ideas about the presence on a surface of topochemical impurities of low concentration interacting with adatoms.[21]

*Allowance for Lattice Vibrations.* Hitherto, we have assumed that the lattice is rigid. However, in a real physical situation it must be borne in mind that the "particles" placed at the sites of the periodic structure execute vibrations about these fixed positions, i.e., the value of the radius vector of a real particle (adatom, atom of an alloy, ion, spin carrier, etc.) at time $t$ in the neighborhood of site $f$ is a function of time of the form

$$\mathbf{R}_f^\alpha(t) = \langle \mathbf{R}_f^\alpha\rangle + \hat{\mathbf{u}}_f^\alpha(t), \quad \alpha = 1, 2, 3, \tag{52}$$

where $\langle \mathbf{R}_f^\alpha\rangle$ are certain equilibrium values determined by the external conditions and the interaction between the particles; $\hat{\mathbf{u}}_f^\alpha(t)$ are the deviations from these values. Allowance for the lattice vibrations renormalizes the "bare" Ising interaction [the exchange integral $I$, for example, in (1)], while the Ising interaction and the correlation effects renormalize the phonon frequencies. A general approach here is to introduce a dependence of the corresponding quantities on $R_f(t)\,[I \to I(R_f(t) - R_g(t))]$, and to expand them with respect to $\hat{\mathbf{x}}_{fg}^\alpha(t) = \hat{\mathbf{u}}_f^\alpha(t) - \hat{\mathbf{u}}_g^\alpha(t)$, which leads to additional terms in the total Hamiltonian of the type of a spin-phonon interaction, and then to use Bogolyubov's variational procedure with a minimization with respect to the parameters of the model Hamiltonian. If we consider the lattice vibrations in the pseudoharmonic approximation and if in the Ising Hamiltonian we take the interaction between the nearest neighbors as a variational parameter, this enables us to study explicitly the effects of the above renormalization.[23] Of course, it is necessary to know the dependence of the interaction energy on the distance between the particles, fixing, for example, $\langle R_f\rangle$ by specifying $T$ and the external pressure. We shall not here describe in detail the procedure, since it has been studied in detail in Refs. 23 and 24 in application to the Ising model. We also mention the review of Ref. 25, in which the approach was applied to a large class of models and was found to be very fruitful; this approach made it possible to analyze the change in the nature of the magnetic phase transition. The interaction parameter $I(r_0)$ is renormalized by $\langle\hat{S}_f\hat{S}_g\rangle_0$ as follows[23]:

$$\begin{aligned} I(r_0) &\to I(r_0) - 2v_0 p\eta_0 d/fr_0 z \\ &+ (\eta_0^2/f)\langle\hat{S}_f\hat{S}_g\rangle \equiv I(r_0, p)(1+\lambda\langle\hat{S}_f\hat{S}_g\rangle), \end{aligned} \tag{53}$$

where $r_0$ is the equilibrium distance between the centers of the rigid lattice for $p=0$, $v_0 \approx r_0^d$, $d=1, 2, 3$; $f$ is the harmonic constant, $p$ is the pressure, and $\eta_0 = (\partial I(r)/\partial r)\big|_{r=r_0}$.

If we use for $\langle\hat{S}_f\hat{S}_g\rangle_0$ any approximation of the molecular-field type (Bragg-Williams, polynomial, quasichemical, etc.), we can show that there always exists a range of variation of the parameter $\lambda = \eta_0^2/fI(r_0 p)$, $0<\lambda<\lambda_{\text{cr}}$, in which the nature of the transition is not changed but there is naturally a renormalization of $T_c$: $T_c \to T_c(\lambda)$. In a realistic approximation of the scaling type and for Onsager's exact solution ($d=2$) for all $\lambda>0$ the phase transition of the second kind is transformed into one of the first kind. A detailed discussion of these questions can be found in Refs. 23 and 24, in which concrete expressions are also given for $\lambda_{\text{cr}} T_c(\lambda)$, etc. In what follows, we shall only indicate how the various characteristics are modified when lattice vibrations are taken into account.

## 3. BINARY SYSTEMS (ALLOYS, MIXTURES)

*Model Hamiltonian.* The approach to binary systems was long ago grounded on the idea[3)] that the interaction between nearest neighbors plays a decisive role[26,27]: the interaction with "second" neighbors is 10–15% of this main interaction. It is also necessary to postulate the absence of long-range forces, which rules out, for example, ionic crystals, liquid metals, etc.

The generally adopted approach uses the canonical ensemble method: Helmholtz's free energy is constructed and then minimized with respect to the order parameter. This gives an equation for $S$ or an equation for the parameters of stratified mixtures.[29] An important point here is the approximation of the free energy, as a result of which it is impossible to take into account correlation effects.

In the present review, we briefly describe our approach to the theory of binary systems,[30-35] which is based essentially on the method of Green's functions and correlation functions in the Ising model.[7,8,14,15]

We shall assume that the atoms of a binary system are at the sites of a regular system of $d$ dimensions, each of the atoms having $z$ nearest neighbors ($d=1$, $z=2$; $d=2, z=3, 4, 6$; $d=3, z=4, 6, 8, \ldots$). A site of the lattice, which is approximated by a simple Bravais lattice, is always occupied by a particle of either species $A$ or $B$. Naturally, we need not fix the total number of particles in the system but assume that they are in equilibrium with the saturated vapor of "their" particles, whose chemical potentials are $\mu_0(P_A T)$ and $\mu_0(P_B T)$, respectively. It is necessary to use the grand canonical ensemble, introducing the chemical potentials $\mu_A$ and $\mu_B$ and setting them in equilibrium equal to $\mu_0(P_A T)$ and $\mu_0(P_B T)$, respectively.

We consider a binary system containing $N_A$ atoms of species $A$ and $N_B$ atoms of species $B$, with $N_A + N_B = N$. If their concentrations are $x_A$ and $x_B$, then $N_A = x_B N$, $N_B = x_B N$, $x_A + x_B = 1$. We introduce $\hat{n}_f(n_f = 0, 1)$, the occupation operator for site $f$, and postulate that the eigenvalues of the operator $n_f$ describe the presence or absence of a particle of species $A$ at site $f$; in such a case, $1 - \hat{n}_f$ describes the absence or presence of a particle of species $B$. Denoting the interaction energies of pairs of the atoms by $v_{ij}(i, j = A, B)$, we write the Hamiltonian of the system in the form

$$\begin{aligned} \hat{H} = &-\frac{v_{AA}}{2}\sum \hat{n}_{f_1}\hat{n}_{f_2} - \frac{v_{BB}}{2}\sum (1-\hat{n}_{f_1})(1-\hat{n}_{f_2}) \\ &-\frac{v_{AB}}{2}\sum \hat{n}_{f_1}(1-\hat{n}_{f_2}) - \frac{v_{BA}}{2}\sum (1-\hat{n}_{f_1})\hat{n}_{f_2} \\ &+\hat{h}_A \sum \hat{n}_f + \hat{h}_B \sum_f (1-\hat{n}_f), \end{aligned} \tag{54}$$

where the operators $\hat{h}_A$ and $\hat{h}_B$ describe the internal degrees of freedom of the atoms $A$ and $B$. If we take into account the interaction between only the nearest neighbors and average over the internal states of the atoms, we obtain

$$\left.\begin{aligned} \hat{H} &= E_0 - L\sum \hat{n}_f + v\sum_{fg_f} \hat{n}_f \hat{n}_g; \\ E_0 &= -\theta N \ln [j_B(0)\exp(zv_{BB}/2\theta)]; \\ L &= \theta \ln \{(j_A/j_B)\exp[z(v_{AB}-v_{BB})/\theta]\}; \\ v &= v_{AB} - (v_{AA}+v_{BB})/2; \\ j_i &= \mathrm{Sp}_{(i)} \exp(-\beta h_i). \end{aligned}\right\} \tag{55}$$

Depending on the relations between the $v_{ij}$, the Hamiltonian (54) describes stratified binary mixtures as well as ordered alloys. Since the phenomenon of unmixing into two phases below a certain $T_c$ consists of a tendency to segregation of the particles of one species, $v_{AB} < \frac{1}{2}(v_{AA}+v_{BB})$; and $v<0, L<0[j_A(\theta)\sim j_B(\theta)]$, and we arrive at the standard form of the Hamiltonian in the

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[3)] The approach to binary systems based on this hypothesis is set forth with great completeness and clarity in Chaps. VIII and XIII of Guggenheim's book.[26] Unfortunately, these chapters, whose material essentially provided the basis of all further investigations on binary systems and which contained an excellent exposition of Bethe's approach and its original variant given by Guggenheim, were omitted by the translator of the book, who asserted without proof that Bethe's work is erroneous [Translator's note: this apparently refers to a Russian translation].

Ising model "with the attraction" (1):

$$\hat{H}=E_0+L_m\sum\hat{n}_f-|v|\sum\hat{n}_f\hat{n}_g. \tag{56}$$

On the other hand, the phenomenon of ordering at low temperatures is characterized by the formation of regions in which the atoms of one species are surrounded preferentially by atoms of the other, i.e., $v>0, L>0$, which is reminiscent of the situation for systems with repulsion (see below).

It is convenient to introduce the operators

$$\left.\begin{aligned}&\hat{N}_A=\sum\hat{n}_f;\quad \hat{N}_B=\sum(1-\hat{n}_f);\ \hat{N}_{AA}=\frac{1}{2}\sum_{fg}\hat{n}_f\hat{n}_g;\\ &\hat{N}_{BB}=\frac{1}{2}\sum_{fg}(1-\hat{n}_f)(1-\hat{n}_g);\\ &N_{AB}=\sum_{fg}\hat{n}_f(1-\hat{n}_g);\quad N_{BA}=\sum_{fg}(1-\hat{n}_f)\hat{n}_g,\end{aligned}\right\} \tag{57}$$

which "count" the particles of species $A$ and $B$, and also the pairs $AA$, $BB$, $AB$, and $BA$, respectively; $f$ and $g$ label the nearest neighbors. The mean values of the operators (57) and of other operators constructed with the operators $\hat{n}_h (h\in f,g)$ calculated with the Hamiltonian (55) were defined above as the correlation functions of the problem.

*Stratified Binary Mixtures.*[31] We shall consider only $S$-regular or symmetric solutions,[29] whose molecules have approximately the same size and shape but whose configuration energy depends on the mutual positions of the molecules. In the grand canonical ensemble, the thermodynamic potential $\Omega$ is determined by the relation

$$\begin{aligned}&-\beta\Omega=\ln\mathrm{Sp}_{(i,\,n_f)}\exp\beta[\mu_AN_A+\mu_BN_B-\mathscr{H}]\\ &=-\beta\Omega'+\ln\mathrm{Sp}_{(n_f)}\exp\beta[-L_m\sum\hat{n}_f+w\sum\hat{n}_f\hat{n}_g],\ w=-v>0.\end{aligned} \tag{58}$$

One can see the complete formal analogy between such an approach to the theory of stratified mixtures and the problems of the theory of magnetism studied above on the basis of the Ising Hamiltonian (1), in which the parameter $L$ must be replaced by $L_m$ and $I/2$ by $w$. Using the different approximations described above, we arrive at the equations for the stratification curve, the critical temperature, and other thermodynamic characteristics of the binary system.[31] Since the system unmixes as $T\to 0$ into pure $A$ and $B$ phases, we can by means of (56) consider the situation only in the $B$ phase (assuming, to be specific, $x_A<x_B$). Then $\langle\sum_{f\in B}\hat{n}_f\rangle=N_B\bar{n}_B$ is the mean number of atoms of species $A$ in the $B$ phase and $\bar{n}_B=0$ at $T=0$; the summation in (56) is over the $N_B$ sites of the $B$ phase, which will not be specially stated below. Note that it is not necessary to introduce chemical potentials $\mu_A$ and $\mu_B$ of the components for the stratification problem: As parameters one can, as usual, consider $x_A$ and $x_B$ and study the behavior of the corresponding characteristics for $1/2\leqslant x_B\leqslant 1$. In the language of correlation functions, the condition of unmixing into two phases obviously has the form $f_1=\langle\hat{n}_B\rangle=\bar{x}_A$. In the widely used Bragg-Williams approximation[26]

$$f_1=\langle\hat{n}_f\rangle_{\{f\}\in B};\ f_1=[\exp\beta(L_m-2zf_1w)+1]^{-1}. \tag{59}$$

Substituting here $f_1=x_A$, we obtain

$$\theta\ln(x_A/x_B)=L_m-2zx_Aw. \tag{60}$$

For $\mu_A=\mu_B, j_A=j_B, v_{AA}=v_{BB}$, we arrive at the well-known equation of the stratification curve[29]:

$$zw(x_B-x_A)=\theta\ln(x_B/x_A) \tag{61}$$

and as $x_A\to\frac{1}{2}$, we obtain

$$zw\beta_c=2. \tag{62}$$

In the quasichemical approximation,[8,15] the equation for the stratification curve has the form

$$\left.\begin{aligned}&2w\beta=\ln\{(x_B-x_A)[x_A^{1/z}x_B^{(z-1)/z}-x_B^{1/z}x_A^{(z-1)/z}]^{-1}\};\\ &\beta_cw=\ln[z/(z-2)].\end{aligned}\right\} \tag{63}$$

In polynomial decoupling,[13] we obtain for the stratification curve

$$x_A=\sum_{k=0}^{z}\frac{z!}{k!\,(z-k)!}\frac{x_A^kx_B^{z-k}}{\exp(\beta E_k)+1},\quad E_k=L_m-2kw. \tag{64}$$

The temperature of critical mixing is here determined by the equation

$$2^{z-1}=y_c\sum_{k=0}^{z}\frac{z!}{k!\,(z-k)!}\left(\frac{1}{y_c+\exp(-2k\beta_cw)}\right),\ y_c=\exp(-z\beta_cw). \tag{65}$$

To find the thermodynamic characteristics of the systems, we also need to know the second correlation function $f_2=\langle\hat{n}_B\hat{n}_{gB}\rangle$, the probability that two $A$ atoms are next to each other in the $B$ phase. It is also necessary to take into account the constant additive quantity $\Omega'=-N_B(\nu_B+zv_{BB}/2)$, $v_B=\mu_B+\theta\ln j_B$, which is the thermodynamic potential of the pure $B$ phase. We give different expressions for $f_2$ on the stratification curve in the framework of the approximations listed above[31]:

$$\left.\begin{aligned}&f_2=x_A^2;\\ &f_2=x_A(r-x_B+x_A)/(1+r);\ r\\ &\quad=\sqrt{(x_B-x_A)^2+2\cdot 2x_Ax_B\exp(2\beta w)};\\ &f_2=\sum_{k=0}^{z}\frac{k}{z}\frac{z!}{k!\,(z-k)!}\frac{x_A^kx_B^{z-k}}{\exp\beta E_k+1}.\end{aligned}\right\} \tag{66}$$

If we are interested in questions relating to phase equilibrium, we must take into account the $A$ phase in the same way as we did the $B$ phase. The condition of thermodynamic equilibrium is the equality of the chemical potentials of the components in the $A$ and $B$ phases, which can be calculated using the Gibbs-Duhem relation. This makes it possible to find and analyze the melting diagrams of the system.

*Systems of Ordered Type.*[32] We divide the sites of the crystal lattice into two types $\alpha$ and $\beta$: $\{f\}=\{\alpha\},\{\beta\}$, and we assume that the nearest neighbors of the $\alpha$ sites are only $\beta$ sites and vice versa: $N_\alpha=N_\beta=N/2$. To be specific, we assume that $x_B>x_A$ and postulate that in the state of complete ordering ($T=0$) all the $A$ atoms are at $\alpha$ sites. Then all neighbors of the $A$ atoms are $B$ atoms and the $(x_B-x_A)$-th part of the $\alpha$ sites is occupied by atoms of species $B$. The Hamiltonian of the binary system for this splitting into two sublattices can be written in the form

$$\hat{H}=E_0-L\sum_\alpha\hat{n}_\alpha-L\sum_\beta\hat{n}_\beta+v\sum_{\alpha\beta}\hat{n}_\alpha\hat{n}_\beta+v\sum_{\beta\alpha}\hat{n}_\beta\hat{n}_\alpha. \tag{67}$$

If we are interested in transitions of the order-disorder type, the equilibrium properties of the system can be calculated by means of the density matrix

$$\begin{aligned}&\hat{\rho}=\exp[\beta(Fm-\hat{H})];\quad -\beta F_m=\ln[\mathrm{Sp}\exp(-\beta\hat{H}_0)]\\ &\qquad+zNv_{BB}/2\theta+N\ln[j_B(\theta)].\end{aligned} \tag{68}$$

With allowance for the splitting into the subsystems $\alpha$ and $\beta$, the "counting" operators (57) are

$$\hat{N}_A(\alpha)=\sum_{p\in\alpha}\hat{n}_p;\quad \hat{N}_A(\beta)=\sum_{q\in\beta}\hat{n}_q;\quad \hat{N}_A=\sum_f\hat{n}_f\equiv\sum_{f\in\alpha}\hat{n}_f+\sum_{f\in\beta}\hat{n}_f,\ \text{etc.}\tag{69}$$

In our case, it is expedient to define the parameter of long-range order by

$$S=(\langle\hat{N}_A(\alpha)\rangle-\langle\hat{N}_A(\beta)\rangle)/N_A=(\hat{n}_\alpha-\hat{n}_\beta)/(\hat{n}_\alpha+\hat{n}_\beta)=(\overline{n}_\alpha-\overline{n}_\beta)/2x_A.\tag{70}$$

We emphasize that (70) is obtained with allowance for the translational invariance (with twice the lattice constant) in the $\alpha$ and $\beta$ subsystems:

$$\langle\hat{O}_\alpha\hat{O}_{\alpha+2n}\rangle=f_\alpha(\ldots/2n),\quad \langle\hat{O}_\beta\hat{O}_{\beta+2k}\rangle=f_\beta(\ldots/2k)\tag{71}$$

and the circumstance that in accordance with (69)

$$\langle\hat{N}_A\rangle=\langle\hat{N}_A(\alpha)\rangle+\langle\hat{N}_A(\beta)\rangle=(N/2)(\overline{n}_\alpha+\overline{n}_\beta),\quad N\overline{n}_f=N\overline{n}.\tag{72}$$

It is natural to regard $\overline{n}_\alpha=\langle\hat{n}_f\rangle|_{f\in\alpha}$, $\overline{n}_\beta=\langle\hat{n}_f\rangle|_{f\in\beta}$ as the conditional probabilities for occupation of the sites of the $\alpha$ and $\beta$ subsystems by atoms of the species $A$. If $T=0$, then $\overline{n}_\beta=0, \overline{n}_\alpha=ax_A$; at $T=T_c$, we have $\overline{n}_\alpha=\overline{n}_\beta$, $S=0$. It is now easy to express $\overline{n}_\alpha$ and $\overline{n}_\beta$ in terms of $S$:

$$\overline{n}_\alpha=x_A(1+S),\quad \overline{n}_\beta=x_A(1-S).\tag{73}$$

For the correlation functions of the $\alpha$ and $\beta$ sublattices we arrive at a hierarchy of equations of the type (12). Using them to determine $\overline{n}_\alpha$ and $\overline{n}_\beta$, we can find an equation for the parameter $S$ of long-range order. The equations for the higher correlation functions discussed above provide a possibility for considering various correlation effects. Thus, for the symmetrized correlation functions that describe the correlation between nearest neighbors,

$$\left.\begin{aligned}\Phi_m(\alpha,\beta)&\equiv\langle\hat{n}_\alpha\hat{F}_m(\beta)\rangle\\&=\sum_{n=0}^{z-m}(-1)^nF_{n+m}(\beta)\sum_{k=0}^{z}\frac{(-1)^kN_{k+m}}{k!\,(n-k)!};\\ \Phi_m(\beta,\alpha)&\equiv\langle\hat{n}_\beta\hat{F}_m(\alpha)\rangle\\&=\sum_{n=0}^{z-m}(-1)^nF_{n+m}(\alpha)\sum_{k=0}^{z}\frac{(-1)^kN_{k+m}}{k!\,(n-k)!}.\end{aligned}\right\}\tag{74}$$

The equations for the order parameter $S$ in the Bragg-Williams, quasichemical, and polynomial approximations[32] are rather cumbersome (since $x_A$ and $x_B$ are arbitrary), and we shall not write them out here.

The formalism of correlation functions is entirely necessary to obtain higher correlation functions of the type $\langle\hat{n}_f\hat{O}_k(h)\rangle$, where $f=\alpha,\ \beta$, and $\hat{O}_k(h)$ is an operator defined on $k$ sites $h$, the $h$ sites not being nearest neighbors of site $f(h\notin g_f)$; $\hat{O}_k(h)=\Pi_{h_i\in\beta}\hat{n}_{h_i}$ is defined on the $k$ sites of the $\beta$ set that are at the distance $|h_i-f|$ from site $f$. In the Bragg-Williams approximation,

$$\langle\hat{n}_f\prod_{i=1}^{k}\hat{n}_{h_i}\rangle\to\langle\hat{n}_f\rangle\,\overline{n}_\beta^k,\quad f=\alpha,\ \beta.\tag{75}$$

In the case of polynomial decoupling, it is necessary to use the expressions derived in Ref. 13, remembering, however, to which set the neighbors of site $f$ belong. As is shown in Ref. 8, the quasichemical approximation is the lattice analog of Kirkwood decoupling: The higher correlation functions are decoupled in a definite manner in terms of the binary correlation functions [see Eqs. (16) and (17)]. After fairly cumbersome algebraic calculations, we obtain for the required binary correlation functions the expressions

$$\left.\begin{aligned}\langle\hat{n}_\alpha\hat{n}_{\alpha+2k+1}\rangle&=\langle\hat{n}_\beta\hat{n}_{\beta+2k+1}\rangle=\overline{n}_\alpha\overline{n}_\beta+\overline{n}_\beta(t_1-\overline{n}_\alpha)\lambda_0^{2k};\\ \langle\hat{n}_\alpha\hat{n}_{\alpha+2k}\rangle&=\overline{n}_\alpha^2+\overline{n}_\alpha(1-\overline{n}_\alpha)\lambda_0^{2k};\\ \langle\hat{n}_\beta\hat{n}_{\beta+2k}\rangle&=\overline{n}_\beta^2+\overline{n}_\beta(1-\overline{n}_\beta)\lambda_0^{2k},\end{aligned}\right\}\tag{76}$$

where $\overline{n}_\alpha$ and $\overline{n}_\beta$ are related to the order parameter $S$ by Eqs. (73), and the equations for the latter are obtained in Ref. 32; $t_1$ and $\lambda_0$ can be expressed in terms of $S$, $x_B$, $x_A$, $\beta$, and $v$ by means of the fairly cumbersome expressions given in Ref. 32.

Any higher correlation function is completely determined by Eq. (76) and also by specifying the sublattice containing the sites whose coordinates label the operators in it. For example, the analog of the decoupling (16) has the form

$$\begin{aligned}&\langle\hat{n}_\alpha\hat{n}_{\alpha+2k}\hat{n}_{\alpha+2k+2m+1}\rangle\\&\to\langle\hat{n}_\alpha\hat{n}_{\alpha+2k}\rangle\langle\hat{n}_{\alpha+2k}\hat{n}_{\alpha+2k+2m+1}\rangle/\langle\hat{n}_{\alpha+2k}\rangle\\&=(\overline{n}_\alpha+(1-\overline{n}_\alpha)\lambda_0^{2k})(\overline{n}_\alpha\overline{n}_\beta+\overline{n}_\beta(t_1-\overline{n}_\alpha)\lambda_0^{2m}).\end{aligned}\tag{77}$$

For binary stratified mixtures one can directly use the expressions obtained in Refs. 8 and 15.

*Short-Range Order in Ordered Alloys.* The equations given above enable us to treat quantitatively the correlation effects between two atoms in ordered alloys. We consider the $\alpha$ sublattice and the correlation between atoms of species $A$. The correlation functions can be of two types: $\langle\hat{n}_\alpha\hat{n}_{\alpha+2k}\rangle\equiv\langle\hat{n}_\alpha\hat{n}_{\alpha_{2k}}\rangle$ and $\langle\hat{n}_\alpha\hat{n}_{\alpha+2k+1}\rangle\equiv\langle\hat{n}_\alpha\hat{n}_{\beta_{2k+1}}\rangle$. Beginning to count from an $\alpha$ site, we arrive after an even number of steps at an $\alpha$ site, and after an odd number at a $\beta$ site. The binary correlation functions are conditional probabilities. For example, $\langle\hat{n}_\alpha\hat{n}_{\alpha+2k}\rangle$ is the conditional probability that if we are in the $\alpha$ subsystem and assume that at the original $\alpha$ site we have an atom $A$, we shall find an atom $A$ at a site separated from the original one by $2k$ steps ($\alpha$ site). Similarly, for the $\beta$ sublattice we can consider binary correlation functions of the type $\langle\hat{n}_\beta\hat{n}_{\beta+2k}\rangle$ and $\langle\hat{n}_\beta\hat{n}_{\beta+2k+1}\rangle$. It is easy to show that all the remaining binary correlation functions (between the pairs $AB, BA, BB$) can be expressed in terms of them and in terms of $\overline{n}_\alpha$, and $\overline{n}_\beta$. A correlation of this kind is the basis for the introduction of different kinds of parameters that characterize the short-range order in alloys. Widespread use is made of the Bethe parameter,[26-28,36] the correlation parameters $\epsilon_{LL'}^{jj'}$, and the disorder parameters.[37] We express them in terms of the correlation functions. The Bethe parameter is defined by

$$\sigma=(q-q_{\min})/(q_{\max}-q_{\min}),\tag{78}$$

where $q=Q_{AB}/Q$; $Q$ is the total number of pairs in the lattice, equal to $zN/2$; $Q_{AB}$ is the number of $AB$ pairs; $q_{\max}=q(T=0)$; $q_{\min}=q(T_c)$. From (78),

$$Q_{AB}=(zN/2)(2x_A-\langle\hat{n}_\alpha\hat{n}_\beta\rangle-\langle\hat{n}_\beta\hat{n}_\alpha\rangle).\tag{79}$$

Therefore

$$q=2(x_A-\langle\hat{n}_\alpha\hat{n}_\beta\rangle).\tag{80}$$

In the Bragg-Williams approximation $\langle\hat{n}_\alpha\hat{n}_\beta\rangle=\bar{n}_\alpha\bar{n}_\beta$, $q=2x_Ax_B+2x_A^2S^2$, $q_{\min}=2x_Ax_B$, $q_{\max}=2x_A$, and $\sigma=S^2$, i.e., the short-range order is entirely determined by the long-range order and $\sigma=0$ at $T=T_c$. In the quasichemical approximation,

$$\left.\begin{aligned}\langle\hat{n}_\alpha\hat{n}_\beta\rangle&=[2x_A(y^2-1)-y^2+R]/2(y^2-1);\quad q\\&=2x_A-[2x_A(y^2-1)-y^2+R]/(y^2-1);\\\sigma&=\frac{2x_A(zx_A-1)-[2x_A(y^2-1)-y^2+R](z-1)/(y^2-1)}{2x_A(zx_A-1)}.\end{aligned}\right\}\tag{81}$$

Finally, in polynomial decoupling

$$\sigma=\frac{2x_A(zx_A-x_B)-\sum\limits_0^z kC_z^kN_k[\bar{n}_\beta^k(1-\bar{n}_\beta)^{z-k}+\bar{n}_\alpha^k(1-\bar{n}_\alpha)^{z-k}]}{2x_A(zx_A-x_B)}.\tag{82}$$

It can be seen that (81) and (82) for $T\geqslant T_c$ and $S=0$ lead to $\sigma\neq0$.

The correlation parameters are defined as $\varepsilon_{LL'}^{jj'}=P_{LL'}^{jj'}-P_L^jP_{L'}^{j'}$, where $P_{LL'}^{jj'}$ is the probability that at a site of type $j$ there is an atom of the species $L$, and at a site of type $j'$ an atom of the species $L'$; $P_L^j(P_{L'}^{j'})$ is the probability that a site of type $j(j')$ is replaced by an atom $L(L')$. In terms of the binary correlation functions, we obtain

$$\varepsilon_{AB}^{f_1f_2}(\rho_i)=-\varepsilon_{AA}^{f_1f_2}(\rho_i)=-\varepsilon_{BB}^{f_1f_2}(\rho_i)=\bar{n}_{f_1}\bar{n}_{f_2}-\langle\hat{n}_{f_1}\hat{n}_{f_2}\rangle.\tag{83}$$

Here $f_1, f_2=\alpha,\beta$; $\rho_i$ is the distance between the corresponding sites; $\bar{n}_i$ in the different approximations can be expressed in terms of the order parameter $S$; $\langle\hat{n}_{f_1}\hat{n}_{f_2}\rangle$ in the quasichemical approximation was given above. In the Bragg-Williams approximation, all the correlation parameters are zero; in polynomial decoupling, they vanish for sites that are not nearest neighbors.

At temperatures above the critical temperature, the difference between the sublattices disappears and the short-range order in the alloys is characterized by means of the parameters

$$\alpha_i=1-P_{AB}(\rho_i)/x_Ax_B,\tag{84}$$

where $P_{AB}(\rho_i)$ is the probability that $A$ and $B$ atoms are at a distance $\rho_i$ from one another. It is obvious that

$$\left.\begin{aligned}P_{AB}(\rho_i)&=\langle\hat{n}_f(1-\hat{n}_{f+i})\rangle=\bar{n}_f-\langle\hat{n}_f\hat{n}_{f+i}\rangle=x_A-\langle\hat{n}_f\hat{n}_{f+i}\rangle;\\\alpha_i&=-(x_A^2-\langle\hat{n}_f\hat{n}_{f+i}\rangle)/x_Ax_B.\end{aligned}\right\}\tag{85}$$

In the Bragg-Williams approximation, $\alpha_i=0$ for all $i$; in polynomial decoupling,

$$\alpha_1=-\left(x_A^2-\sum\frac{k}{z}C_z^kN_kx_A^kx_B^{z-k}\right)/x_Ax_B;\ \alpha_i=0;\ i\geqslant2;\tag{86}$$

in the quasichemical approximation, using the expression for $\langle\hat{n}_f\hat{n}_{f+i}\rangle$, we obtain

$$\alpha_i=(-1)^i[(x_A-t)/x_B]^i,\tag{87}$$

where $t$ is determined by the expressions given in Ref. 32 for $S=0$.

*Point Defects and Allowance for Lattice Vibrations in Binary Systems.*$^{33-35}$ Referring the reader for details to Refs. 33-35, we briefly explain the possibility of the method developed here for quantitative allowance for the influence of point defects on the equilibrium properties of binary systems. We shall assume that an impurity modifies the parameters of a binary system as follows: $v_{ij}\to v'_{ij}$, $z\to z'$ [see (18) above].

To obtain the thermodynamic quantities of such a system, we must have recourse, as we mentioned above, to a procedure of decoupling the correlations between the impurity regions which can be assumed to be sufficiently justified at low defect concentration $c=N_1/N\ll1$ and at temperatures sufficiently far from $T_c$: $|1-T/T_c|\gtrsim z^{-1}$.

For simplicity, we consider substitutional impurities. If there are $N_1$ substitutional atoms in the system, then in this case the Hamiltonian of the system (19) is

$$\left.\begin{aligned}&\hat{H}'=\hat{H}_0+\sum_{i=1}^{N_1}\Delta E_0(i)+\sum_{i=1}^{N_1}\hat{H}(f_i);\ \Delta E_0=z(v_{BB}-v_{BC});\\&\hat{H}(f_i)=L_1\hat{n}_{f_i}+L_2\hat{F}_1(g_{f_i})+L_3\hat{\Phi}_1(f_i, g_{fi});\\&L_1=z(v_{AB}-v_{BB});\ L_2=v_{BC}-v_{AC}+v_{AB}-v_{BB};\ L_3=-2v.\end{aligned}\right\}\tag{88}$$

Under the assumption that there are no correlations between the impurity regions, $\langle\Pi\,\hat{U}(f_i)\rangle_0\to(\langle\hat{U}(f_i)\rangle_0)^{N_1}$, the contribution of the impurities to the free energy is ultimately determined by $\langle\hat{U}(f)\rangle_0$, the correlation functions of the ideal system. The mean value of any operator $A$ is found in accordance with Eq. (24), in which $\hat{H}(k)\to\hat{H}(f_i)$.

A certain care is needed when (24) is used in the theory of ordered systems$^7$: a site at which an impurity atom is localized may be either an $\alpha$ or a $\beta$ site. This leads to the following modification of $U(f_i)$:

$$\left.\begin{aligned}\hat{U}(\alpha)&=\sum_0^z\frac{\tau_2^k}{k!}\hat{F}_k(\beta)+\sum_0^z\frac{1}{k!}[(1+\tau_1)\tau^k-\tau_2^k]\hat{\Phi}_k(\alpha,\beta);\\\hat{U}(\beta)&=\sum_0^z\frac{\tau_2^k}{k!}\hat{F}_k(\alpha)+\sum_0^z\frac{1}{k!}[(1+\tau_1)\tau^k-\tau_2^k]\hat{\Phi}_k(\beta,\alpha).\end{aligned}\right\}\tag{89}$$

If the operator $\hat{A}$ is defined at the sites of both sublattices, then

$$\begin{aligned}\langle\hat{A}\rangle&=\operatorname{Sp}\hat{A}\exp(-\beta\delta\hat{H})/\operatorname{Sp}\exp(-\beta\delta H)\\&=\langle\hat{A}\hat{U}(\alpha)\hat{U}(\beta)\rangle_0/\langle\hat{U}(\alpha)\hat{U}(\beta)\rangle_0.\end{aligned}\tag{90}$$

Concrete results for the order parameters in the presence of interstitial and substitutional impurities—the expressions for $S(c)$ in Ref. 33—are very lengthy, but they make it possible to analyze the behavior of $S$ as $c$, $x_A$, $x_B$, and $T$ vary.

The arguments put forward in Sec. 3 concerning the region of applicability of results obtained in different approximations of the "molecular-field type" are also valid here: To analyze the properties of a nonideal alloy in the region $c^{1/dv}<|\beta_c/\beta-1|<z^{-1}$ it is necessary to use approximations that take into account the correlation between impurities.

To conclude this section, we consider the influence of disordering on the nature of the phonon spectrum of the lattice. If the instantaneous positions of the coordinates are represented as in (52),

$$\mathbf{R}_f^\nu(\alpha)=\langle\hat{R}_f^\nu(\alpha)\rangle+\mathbf{u}_f^\nu(\alpha,t);\ \mathbf{R}_f^\mu(\beta)=\langle R_f^\mu(\beta)\rangle+\mathbf{u}_f^\mu(\beta,t),\tag{91}$$

and for $T<T_c$ we introduce four phonon Green's functions

$$\langle\langle u_l^\nu(i)/u_m^\mu(j)\rangle\rangle,\ i,\ j=\alpha,\ \beta;\ l,\ m=1,\ 2,\ \ldots,\ N,\tag{92}$$

and for $T>T_c$, where there is no division into $\alpha$ and $\beta$, the single Green's function

$$\langle\langle u_l^{\nu}/u_m^{\mu}\rangle\rangle, \tag{93}$$

it is a simple matter in, say, an approximation of the Hartree-Fock type, to obtain for $T<T_c$ two modes of oscillation:

$$\omega_{1,2}^2 = z\tilde{\varphi}''(l)\,(\mathbf{e}_j\mathbf{l}/l^2)\,\Big\{x_A/M_A + x_B/M_B$$

$$\mp\Big[\frac{(M_A-M_B)^2}{M_A^2M_B^2}x_A^2S^2(1-\cos^2\mathbf{q}\mathbf{l}_g)+\Big(\frac{x_A}{M_A}+\frac{x_B}{M_B}\Big)^2\cos^2\mathbf{q}\mathbf{l}_g\Big]^{1/2}\Big\}. \tag{94}$$

Above $T_c(S=0)$ there remains only the single (acoustic) frequency

$$\omega_j^2(q) = (x_A/M_A + x_B/M_B)\,z\tilde{\varphi}''(l)\,(\mathbf{e}_j\mathbf{l}/l^2)\,(1-\cos\mathbf{q}\mathbf{l}_g) \tag{95}$$

($\varphi''(l)$ is the second derivative of the interaction potential calculated in the pseudoharmonic approximation[23,24,35]). This situation is confirmed qualitatively by the experiments made on $\beta$ brass.[38]

## 4. SURFACE PHENOMENA

*Adsorption on a Homogeneous Surface.* In this section, I give some of my results obtained using the approximation of nearest-neighbor interaction in the theory of surface phenomena.[22,39] Here, we have an "open system": Particles adsorbed by the surface (physically or chemically) are in equilibrium with the gas phase; in addition, the electron subsystem may contribute to the equilibrium properties of the system, and this can be simulated by a certain two-dimensional gas of interacting electrons.[40] The surface is simulated by a homogeneous two-dimensional periodic structure ($d=2, z=3, 4, 6$), which provides $N$ adsorption centers for the adatoms. The case of chemisorption is of greatest theoretical and practical interest, although physical adsorption, especially for systems with attraction in the adsorbate, also has its undoubted interest. An adatom can be bound (by covalent or ionic bonding) to an individual atom of the surface layer or to a group of atoms. The calculation of the energy $\varepsilon_0$ of binding of the adatom to the surface is a problem of quantum mechanics and is solved in the framework of either quantum-mechanical models (the most frequently used models are Anderson's and Hubbard's), or in the framework of semi-empirical quantum-chemical calculations. In either case the assumption about the type of bonding of the adatom to the surface is important. While this problem can be solved (in the Hartree-Fock approximation, the results of calculations of the energies of the binding of an atom to a surface are very far from the experimental data; when correlation effects are taken into account in the framework of Anderson's model, one can achieve qualitative agreement for chemisorption of metals on tungsten), the calculation of the effective interaction between adatoms in the case of chemisorption has so far defied quantitative treatment. The only thing that is clear here is that there is repulsion between the adatoms ($\varepsilon<0$). Greater success can be achieved in the calculation of the effective interaction in the case of physical adsorption.[41] Here one can assume (in a first approximation) that the particles "do not lose" their individuality and interact through forces of van der Waals type and also repulsive forces due to the overlapping of the electron shells (the surface "provides" an external field, in which the adatoms are situated at a distance 3–4 Å from the surface). Depending on the geometry of the surface and the positions of the active adsorption centers, the calculation[41] leads to both attractive ($\varepsilon>0$) and repulsive ($\varepsilon<0$) forces between the adatoms. In any case, postulating an interaction between neighboring adatoms of intensity $\varepsilon$ and assuming that the contribution of the electron subsystem (which is important for chemisorption) can be calculated separately and that it does not depend on the arrangement of the adatoms on the surface but only on their mean number $\overline{N}_a=\theta N$, $0\leqslant\theta\leqslant 1$ ($\theta$ in the theory of surface phenomena is called the surface coverage), we arrive at the effective adsorption Hamiltonian[22,39]:

$$\hat{H} = -\nu\sum_f \hat{n}_f - \frac{\varepsilon}{2}\sum_{f_1\neq f_2}\hat{n}_{f_1}\hat{n}_{f_2};\quad \nu=\beta^{-1}\ln(ap_0)^{1/n};$$

$$a=\beta j_a^n(\beta)\exp[\beta n\mu_e(\theta)]\exp(\beta\varepsilon_0)/j_0(\beta). \tag{96}$$

Here, $j_a(\beta)$ is the partition function of the adatom $j_0(\beta)$ is the partition function (per unit volume) of the atom in the gas phase, $p_0$ is the external pressure, and $\mu_e(\theta)$ is the chemical potential of the electron subsystem. To be specific, we consider the dissociative adsorption of an $n$-atom molecule from the gas phase: $A_n \rightleftharpoons n[A]$. Our approach can be readily extended to dissociative adsorption from a liquid or a solution, in which case it is merely necessary to use the corresponding activities.[22] Thus, we arrive at a variant of the Ising model by making the substitution $\nu\to -L$, $I\to\varepsilon$ in (1). Allowance for correlation effects is also very important in the case of repulsion. For example, for $\theta\leqslant 0.1$ in the quasichemical and polynomial approximations

$$\langle\hat{n}_f\hat{n}_g\rangle \approx \theta^2\exp(-\beta\varepsilon), \tag{97}$$

and since $\beta|\varepsilon|\approx 15$–$30$ for chemisorption, there is a strongly reduced probability of finding adatoms next to each other, which, in its turn, is reflected in the kinetic characteristics.[19,42] The parameter $\varepsilon$ can be determined from experimental data on the equilibrium heats of adsorption.[43] By definition, the heat of adsorption is the heat released when a monolayer is formed: $\Delta q = q(\theta=0)-q(\theta=1)$. It is easy to show that in our model

$$-N_A\frac{\partial\ln p}{\partial\beta}\Big|_\theta = q(\theta,\beta,z)$$

$$= nN_A\Big\{\frac{1}{n}\frac{\partial\ln a(\theta,\beta)}{\partial\beta}+\mu_e(\theta)+z\varepsilon\varphi(\varepsilon,\beta,\theta)\Big\}, \tag{98}$$

where $\varphi(\varepsilon,\beta,\theta)$ is a fairly complicated function of $\theta$, $\varepsilon$, and $\beta$[39,43]; $N_A$ is Avogadro's number. However, for the total heat of adsorption (56) simplified strongly and we obtain[43]

$$\Delta Q = -nN_A[z\varepsilon+\mu_e(1)-\mu_e(0)] \equiv nN_Az|\varepsilon| + nN_A[\mu_e(0)-\mu_e(1)]. \tag{99}$$

Naturally, a part of $\Delta Q$ is due to the change in the chemical potential of the electron subsystem, but the behavior of a number of equilibrium characteristics of chemisorption can be well explained under the assumption that $\mu_e(0)=\mu_e(1)$.[22] In any case, one can also use the experimental data on the heats of adsorption and determine $\varepsilon_{\text{eff}}$:

$$(\Delta Q)_{\text{exp}} = nzN_A|\varepsilon|_{\text{eff}};\quad |\varepsilon|_{\text{eff}} \doteq |\varepsilon| + (\mu_e(0)-\mu_e(1))/z, \tag{99'}$$

which for typical systems in the case of chemisorption gives $|\varepsilon|_{\text{eff}}\approx 0.1-0.2$ eV and $|\varepsilon|_{\text{eff}}\approx 0.01-0.02$ eV for physical adsorption.

Thus, $\varepsilon$ is renormalized by $\Delta\mu/z=[\mu_e(0)-\mu_e(1)]/z$, a quantity that must be calculated in a quantum-mechanical model. In a model of a two-dimensional gas of interacting electrons, it proved possible[40] to find $\mu_e(\theta)$, and for $\Delta\mu$ we obtain

$$\Delta\mu=-(\pi\sigma\hbar^2/m^*)\,[1-(m^*/2m_e)\,(1-\sqrt{8\pi a_0^2\sigma/9\pi})]. \qquad (100)$$

Here, $\sigma$ and $m^*=am_e$ are the density and effective mass of the electrons in the surface layer, and $a_0$ is the constant of the two-dimensional lattice of the adsorbent surface; the result is valid if $1\geqslant(m^*/2m_e)(1-\sqrt{8\pi a_0^2\sigma/9\pi})$. Combined analysis of the equilibrium and kinetic experimental data on K/W and B/W (Ref. 42) gave for $a$ a value $\gtrsim 2$; for adsorption of transition metals and gases, one can expect much larger values; $\sigma$ is a largely undetermined quantity,[40] but it is known that $\sigma<10^{15}$ electrons/cm$^2$. In such a case, for a large class of systems $\Delta\mu/z\lesssim 0.01$ eV. For chemisorption, (99) leads to $|\varepsilon|_{\text{eff}}\gtrsim 0.1$ eV, and we can therefore assume that $|\varepsilon|_{\text{eff}}\approx|\tilde{\varepsilon}|$. Note that $(\Delta Q)_{\text{exp}}$ is measured with an accuracy of 20%.

An important part is also played by the parameter of the effective interaction when one is analyzing the behavior of other equilibrium and kinetic characteristics of adsorption.[22,29,42,43] Thus, any attempt at the experimental or theoretical determination of this single parameter of the theory is of undoubted interest.

*Diffraction of Slow Electrons in the Presence of Adsorbed Materials on the Surface.* We now turn to our results on the diffraction of slow electrons ($E_e\approx 10-150$ eV) by a metal surface when there are adsorbed atoms on the latter.[45-50] Numerous experiments have established that in a definite range of pressures and temperatures for $\theta=1/2$ and $\theta=1/3$ in the case of scattering on the faces (100) and (110), respectively, there are, in addition to the Bragg spots, additional spots; the energy of the main and the additional maxima depends on the energy of the incident electrons, and for a large class of systems the additional maxima decrease in intensity and disappear as $T\to\infty$, though there are systems in which, remaining localized, they disappear at $T=T_c$. Below, we shall attempt to show how one can explain all these listed facts in the framework of the ideas about adsorption presented above.

Discovered in 1927 by Davisson and Germer, diffraction of slow electrons has become an indispensable method for investigating the surface properties of solids. This was recognized comparatively recently. In the middle of the sixties, there was a sudden increase in the number of experimental studies of different aspects of electron scattering by solids. This was due, on the one hand, to progress in vacuum technology and in the methods for obtaining a clean surface, and on the other to the increasing demands of technology. It is well known that surface phenomena play a very important role in the technology of semiconductor production, in catalysis, oxidation, and corrosion. The first experiments revealed a significant influence of adsorption of gases on the diffraction patterns; diffraction of slow electrons has in the meanwhile made it possible to establish a number of important facts concerning the properties of the adsorbate. Slow electrons, $E_e\approx 10-150$ eV, having a wavelength comparable with the lattice constants, penetrate a few atomic layers into a solid. The present review is devoted to our results on the diffraction of slow electrons with allowance for adsorption.[45-50] The majority of theoretical investigations into the diffraction of slow electrons is concerned with scattering by clean surfaces of solids; Refs. 51 and 52, in which the adsorbate is regarded as a one-dimensional system, are an exception.

The approach developed in Refs. 45–50 not only completely confirms that correlation effects are of primary importance in the appearance of the additional spots in the diffraction pattern when adsorbed atoms are present on the scattering surface, but also makes it possible to estimate the value of the parameter of the interaction between the adatoms from slow-electron diffraction experiments, which is an effective alternative to the calorimetric determination discussed above of this important parameter of the theory of surface phenomena.

We shall also consider some of the possibilities that the results of Refs. 45–50 offer for exploiting experimental information about the surface structures formed by an adsorbed gas on a homogeneous surface of a solid.

The derivations of Refs. 45–50 were based on the following general formula for the cross section of scattering of electrons on a rigid lattice:

$$\begin{aligned}\frac{d\sigma}{d\Omega}&=(2\pi)^4m^2\sum_{ff'}\langle\hat{t}_f\hat{t}^*_{f'}\rangle\exp[-i\mathbf{q}(\mathbf{R}_f-\mathbf{R}_{f'})]\\&\quad+(2\pi)^6m^3\sum_{f,\,f'\neq f''}\langle\hat{t}_f\hat{t}^*_{f'}\hat{t}^*_{f''}\rangle\\&\quad\times\exp[-i\mathbf{q}\mathbf{R}_f+i(\mathbf{p}'\mathbf{R}_{f'}-i\mathbf{p}\mathbf{R}_{f''})]\\&\quad\times\exp[-ip|\mathbf{R}_{f'}-\mathbf{R}_{f''}|]\,|\mathbf{R}_{f'}-\mathbf{R}_{f''}|^{-1}\\&\quad+(2\pi)^6m^3\sum_{f\neq f',\,f''}\langle\hat{t}_f\hat{t}_{f'}\hat{t}^*_{f''}\rangle\\&\quad\times\exp[i\mathbf{q}\mathbf{R}_{f''}-i(\mathbf{p}'\mathbf{R}_f-i\mathbf{p}\mathbf{R}_{f'})]\\&\quad\times\exp[ip|\mathbf{R}_f-\mathbf{R}_{f'}|]\,|\mathbf{R}_f-\mathbf{R}_{f''}|^{-1}+\ldots\end{aligned}\qquad (101)$$

Here, $\mathbf{R}_f$ is the coordinate of site $f$ of the lattice, $\mathbf{q}=\mathbf{p}'-\mathbf{p}$ is the momentum transfer of the scattered electrons, and $t_f$ is the $S$ matrix for the electron on center $f$:

$$\hat{t}_f=\alpha(\mathbf{p},\mathbf{p}')\,\hat{n}_f+\beta(\mathbf{p},\mathbf{p}')\,(1-\hat{n}_f), \qquad (102)$$

where $\alpha$ and $\beta$ are the scattering lengths of the occupied and free sites (a discussion and actual expressions are given in Refs. 45–47). The angular brackets in (101) denote the usual statistical averaging with the adsorption Hamiltonian (96), and the summation is over the lattice sites in the first term and over all nearest-neighbor pairs in the second. The importance of the contribution of lattice vibrations was analyzed in Ref. 47: They lead to the usual renormalization of the cross section through the Debye-Waller factor, but allowance for them does not alter the conclusions discussed below. Surface plasmons lead to a uniform background in the diffraction picture, and allowance for them also does not affect the results discussed below.[48]

For scattering of electrons by a one-dimensional periodic structure, the use of the exact results for the correlation functions in (101) derived in Refs. 7 and 8 with allowance for only single (in the terminology of Ref. 13) scattering [only the first term is retained in (101)] led to the conclusion that, besides the ordinary Bragg spots characterized by the index $n$, with $n=0, 1, 2, \ldots$, which also arise in the case of scattering by an ideal one-dimensional structure, there should be additional spots with index $n+\frac{1}{2}$. Their occurrence is due to the adsorbate. This result can be used to interpret the slow-electron diffraction experiments on quasi-one-dimensional systems (polymers).

In the case of a two-dimensional square lattice ($z=4$ nearest neighbors, $d=2$) there are in addition to the Bragg spots with indices $(m, n)$ additional spots in the diffraction pattern with coordinates $(m+\frac{1}{2}, n+\frac{1}{2})$ due to the presence on the surface of adsorbed substances. For a two-dimensional triangular lattice ($z=6, d=2$), in each region ($m<x<m+1$, $n<y<n+1$) there appear two additional spots with indices $(m+1/3, n+2/3)$ and $(m+2/3, n+1/3)$. In these last two cases, it was of course necessary to use the expressions for the correlation functions in (101) in the approximations discussed above. Note that all these conclusions are due to the appearance in (101) of additional terms of the type

$$\left.\begin{aligned} &d=1,\ z=2\colon\ \delta\sigma\sim-\theta^2[1-\exp(-\beta|\varepsilon|)]\cos\Phi;\\ &d=2,\ z=4\colon\ \delta\sigma\sim-\theta^2[1-\exp(-\beta|\varepsilon|)](\cos\Phi+\cos\Phi');\\ &d=2,\ z=6\colon\ \delta\sigma\sim-\theta^2[1-\exp(-\beta|\varepsilon|)]\\ &\qquad\qquad\times[\cos\Phi+\cos\Phi'+\cos(\Phi-\Phi')],\end{aligned}\right\}\tag{103}$$

whose adsorption origin is obvious.[45,46]

To determine what surface sturctures formed during adsorption correspond to the diffraction patterns considered above for the two types of lattice, we use the rule proposed in Ref. 54 (see also Ref. 55). According to these papers, one can introduce two matrices $\hat{A}$ and $\hat{G}$ related by

$$\hat{A}=\hat{G}^{-1},\tag{104}$$

and if the columns of the matrix $\hat{G}$ are taken to be the coordinates of the spots that have indices less than unity, the matrix $\hat{A}$ gives the coordinates of the basis vectors of the surface structure corresponding to the given diffraction pattern. In the case of a square lattice considered above, the complete diffraction pattern can be obtained by means of the vectors (1/2, 1/2) and (1/2, –1/2) and therefore the matrices $\hat{G}$ and $\hat{A}$ have the form

$$\hat{G}=\begin{vmatrix}1/2 & 1/2\\ 1/2 & -1/2\end{vmatrix};\quad \hat{A}=\begin{vmatrix}-1 & 1\\ 1 & 1\end{vmatrix}.$$

The matrix $\hat{A}$ can be constructed from the vectors $(\bar{1}\ 1)$ and (1 1), which are the basis translational vectors of the surface structure C $(2\times 2)$.

For a triangular lattice, the diffraction pattern can be obtained by means of the vectors (1 0) and (0 1/3). Here, the matrices $\hat{G}$ and $\hat{A}$ are given by

$$\hat{G}=\begin{vmatrix}1 & 0\\ 0 & 1/3\end{vmatrix};\quad \hat{A}=\begin{vmatrix}1 & 0\\ 0 & 3\end{vmatrix}.$$

The matrix $\hat{A}$ determines the translational vectors (1 0) and (0 3) of the $(3\times 1)$ surface structure.

The structure C $(2\times 2)$ on a square lattice is formed, for example, in the case of adsorption of H on W (100), N on W (100), CO on Ni (100), and Bi on Cu (100).[56]

The $(3\times 1)$ structure on a triangular lattice was observed, for example, in the case of adsorption of O on Nb (110) as early as the thirties. It should be noted that the Nb (110) surface differs somewhat from the lattice of regular triangles considred above. But it is easy to show that allowance for the anisotropy of the interaction leads to only a slight displacement of the additional spots.

We now turn to the problem of finding the parameter of the effective interaction between the adatoms from experimental slow-electron diffraction data. As was pointed out above, it is necessary here to distinguish two cases: 1) the intensity of an additional spot is spread out with increasing temperature and the spot disappears completely as $T\to\infty$; 2) the spot remains strictly localized in space but disappears at a temperature $T=T_c$ that is characteristic of the given adsorbate-adsorbent system.

In the first case, one can readily show that the effective interaction can be found from measurements of the intensities $M_1$ and $M_2$ of one of the additional spots at the temperatures $T_1$ and $T_2$, respectively:

$$\left.\begin{aligned} &d=2,\ z=4\colon\ (\beta_2-\beta_1)\varepsilon=\ln[M_1/M_2];\\ &d=2,\ v=6\colon\ 3[M_1\exp(\beta_2\varepsilon)-M_2\exp(\beta_1\varepsilon)]=5(M_1-M_2).\end{aligned}\right\}\tag{105}$$

The derivation of (105) used the fact that in a definite range of temperatures and pressures a stable diffraction pattern is formed for the structure C $(2\times 2)$ for $\theta=0.5$ and for $(3\times 1)$ for $\theta=1/3$.

The temperature dependence of the intensity of the additional spots in the case of adsorption on the square lattice given by Eq. (105) agrees well with the experimental data on the measured temperature dependence of the intensity of the spot $(\frac{1}{2}, \frac{1}{2})$ in the case of adsorption of Bi on Cu (100) (for this last case, see Ref. 56). For high temperatures, Eqs. (105) must be modified to take into account the renormalization of the scattering cross section by the Debye-Waller factor.[47]

A second case, which we have called critical scattering,[50] can be considered by means of a certain artificial device which modifies the binary correlation function in (1) and uses the analogy between a system with the adsorption Hamiltonian (2) for $\varepsilon<0$ and a system of antiferromagnetic type. This is achieved by the introduction of two sublattices, at $T=0$ one of them being completely occupied ($\theta=1$) and the other empty ($\theta=0$). Using for this modified system the exact results for the Onsager-Yang order parameter, and making some simple transformations, we obtain the following expression for the effective interaction in terms of the critical temperature:

$$|\varepsilon|=2\sinh^{-1}(\sqrt{2}+1)\beta_c^{-1},\ \beta^{-1}=k_BT.\tag{106}$$

Note in this connection that in both cases complete ordering (for $\theta=\frac{1}{2}$) is attained only at $T=0$. For this reason, we should, in our opinion, speak of the C $(2\times 2)$ diffraction picture and not the C $(2\times 2)$ diffraction structure. Using (106) to analyze adsorption of H on W (100) ($T_c = 550$°K; see Ref. 57), we obtained $|\varepsilon| \approx 0.145$ eV, which agrees excellently with the calorimetrically determined heat of adsorption difference $\Delta Q = 2z|\varepsilon|N_A \approx 26.7$ kcal/mole (Refs. 22 and 43) ($\Delta Q_{\text{exp}} \approx 26$ kcal/mole).

Allowance for second-order perturbation theory[47]—double scattering—made it possible to describe the energy dependence of the intensity of the diffraction spots of the scattered electrons observed in numerous experiments. In accordance with Ref. 47, for each given direction characterized by the coordinates $(x, y)$, the intensity of the diffraction as a function of the electron energy has, besides the usual maxima determined by the condition

$$pd_0/2\pi = (m^2+n^2)^{1/2} \tag{107}$$

(where $p$ is the momentum of the scattered electrons, $d_0$ is the lattice constant, and $m$ and $n$ are integers that are frequently interpreted in terms of the so-called Ewald construction and are also observed in the case of scattering by a clean surface), additional maxima at

$$pd_0/2\pi = [(x+m)^2+(y+n)^2]^{1/2}. \tag{108}$$

In deriving (107) and (108), we have for simplicity restricted ourselves to the case of normal incidence of the electrons. The generalization to an arbitrary angle of incidence is trivial and reduces to the substitution $x \to x - x_0$, $y \to y - y_0$.

The occurrence of additional spots in the diffraction pattern depending on the energy of the scattered electrons was already established by Rupp[58] in 1930 in an investigation of the effect of gases on a clean surface of metals. For the direction characterized, for example, by the indices $(\frac{1}{2}, 0)$, we find from (8) that the additional spots occur at

$$pd_0/2\pi = [(m+1/2)^2+n^2]^{1/2}. \tag{109}$$

This can explain the additional maxima of half-integral order observed in Ref. 58. Since we discuss the situation on a square lattice, and Rupp[58] investigated diffraction on the (111) plane, we cannot claim more than qualitative agreement, and this question requires additional experimental verification.

It can also be seen from (108) that the differential scattering cross section as a function of $x$ and $y$ becomes infinite on the circles

$$(pd_0/2\pi)^2 = (x+m)^2+(y+n)^2 \tag{110}$$

of radius $pd_0/2\pi$ with centers at the points of the Bragg maxima $(-m, -n)$. If $pd_0/2\pi > 1$, the circles can intersect. At the points of intersection, the diffraction intensity will be especially high, and it is natural to identify these points with the spots in the diffraction pattern. A change in the energy of the scattered electrons, which is equivalent to a change in the radius of the circles (110), produces a change in the number of such spots and their positions. An influence of a change in the electron energy on the form of the diffraction pattern was observed experimentally. Since the type of surface structure is obviously independent of the electron energy, this change in the diffraction pattern was not due to a change in the type of surface structure. The resulting contradiction with the rule formulated in Refs. 54 and 55 shows that the rule has limited applicability: It at least presupposes a fixed energy of the electrons. This, however, must not be a cause for pessimism: The majority of experiments are made under conditions when this rule can be used (see the review of Ref. 55).

In the quasichemical approximation for the correlation functions in (101), we have succeeded in analyzing the effects that arise in scattering when allowance is made for multiple scattering[49]; these terms are not included in (101). For the case of a square lattice and 50% surface coverage, $\theta = \frac{1}{2}$, and also low temperatures, it was found that adsorption leads to the appearance of spots of half-integral order associated with the main spots. This agrees with the slow-electron diffraction results for hydrogen on nickel, and also with the results of numerous other experiments in which the intensity of the main spots exhibited a fine structure.

Thus, as a result of the theory of the diffraction of slow electrons on a homogeneous surface containing adsorbed particles that was developed in Refs. 45–50 on the basis of a simple variant of the quantum-statistical theory of adsorption,[22,39] it has been possible to give a quantitative explanation of a number of experimentally established facts for diffraction of slow electrons and to determine for the first time the parameter of the interaction between adatoms at neighboring active centers—the most important parameter in the theory of surface phenomena.

[1] L. Onsager, Phys. Rev. **65**, 117 (1944); B. Kaufman and L. Onsager, Phys. Rev. **76**, 1244 (1949).

[2] A. Z. Patashinskiĭ and V. L. Pokrovskiĭ, Zh. Eksp. Teor. Fiz. **46**, 994 (1964) [Sov. Phys. JETP **19**, 677 (1964)]; B. Widom, J. Chem. Phys. **43**, 3892 (1965); L. Kadanoff, in: Kvantovaya teoriya polya i fizika fazovykh perekhodov (Quantum Field Theory and the Physics of Phase Transitions; Russian translation), Mir, Moscow (1975).

[3] K. G. Wilson and J. Kogut, Phys. Rep. C **12**, (1974) (Russian translation as book publ. by Mir, Moscow (1975)).

[4] N. N. Bogolyubov and S. V. Tyablikov, Dokl. Akad. Nauk SSSR, Ser. Fiz. **136**, 53 (1959).

[5] S. V. Tyablikov, Metody kvantivoĭ teorii magnetizma, Nauka, Moscow (1965) (English translation: Methods of Quantum Theory of Magnetism, Plenum Press, New York (1967)).

[6] G. F. Newell and E. W. Montroll, Rev. Mod. Phys. **25**, 353 (1953); H. S. Green and C. A. Hurst, Order Disorder Phenomena, Interscience, London (1964).

[7] S. V. Tyablikov and V. K. Fedyanin, Fiz. Met. Metalloved **23**, 193 (1967).

[8] V. K. Fedyanin, in: Statisticheskaya fizika i kvantovaya teoriya polya (Statistical Physics and Quantum Field Theory) (Ed. N. N. Bogolyubov), Nauka, Moscow (1973).

[9] N. N. Bogolyubov, Preprint D-781 [in Russian], JINR, Dubna (1961).

[10] B. I. Sadovnikov and V. K. Fedyanin, Teor. Mat. Fiz. **16**, 368 (1973).

[11] V. K. Fedyanin, Fiz. Met. Mettaloved. **28**, 217 (1969); Phys. Lett. A **29**, 40 (1969).

[12] V. K. Fedyanin, Teor. Mat. Fiz. **7**, 241 (1971); Phys. Lett. A **34**, 323 (1971).

[13] V. K. Fedyanin, Fiz. Met. Mettaloved. **26**, 968 (1968).

[14]V. K. Fedyanin, Metod korrelyatsionnykh funktsiĭ v modeli Izinga (Method of Correlation Functions in the Ising Model), Izd-vo Tartusskogo un-ta (1971).

[15]V. K. Fedyanin, in : Trudy Mezhdunarodnoĭ konferentsii po magnetizmu (Proc. Intern. Conf. on Magnetism), MKM-73, Vol. 2, Nauka, Moscow (1974), p. 1948.

[16]Yu. K. Tovbin and V. K. Fedyanin, Teor. Mat. Fiz. **24**, 129 (1975).

[17]T. L. Hill, Statistical Mechanics, McGraw-Hill, New York (1956) (Russian translation: Izd-vo inostr. lit. (1960)).

[18]S. V. Tyablikov and V. K. Fedyanin, Fiz. Met. Mettaloved. **23**, 999 (1967); **26**, 589 (1968).

[19]V. K. Fedyanin, Lecture at Fourth Conf. on Statistical Mechanics, L'vov (1972); Chem. Phys. Lett. **22**, 99 (1973); G. M. Morozova and V. K. Fedyanin, Preprint R17-10644 [in Russian], JINR, Dubna (1977).

[20]G. M. Gavrilenko, S. K. Morozova, and V. K. Fedyanin, Communication E17-10975, JINR, Dubna (1977).

[21]V. K. Fedyanin, Dokl. Akad. Nauk SSSR, Ser. Fiz. **191**, No. 6 (1971).

[22]V. K. Fedyanin, in: Trudy pervoĭ Vsesoyuznoĭ konferentsii po teorii zhidkosti (Proc. First All-Union Conf. on the Theory of Liquids), Izd-vo Leningradskogo un-ta, Leningrad (1972), p. 25.

[23]V. A. Zagrebnov and V. K. Fedyanin, Teor. Mat. Fiz. **10**, 127 (1972); Izv. Akad. Nauk SSSR, Ser. Fiz. **36**, 1390 (1972).

[24]V. A. Zagrebnov and V. K. Fedyanin, Preprint ITF-73-1578 [in Russian], Kiev (1973).

[25]M. D. Girardeau and R. M. Mazo, Adv. Chem. Phys. **24**, 188 (1973).

[26]R. H. Fowler and E. A. Guggenheim, Statistical Thermodynamics, Cambridge (1939), Chapters 8 and 13.

[27]E. A. Guggenheim, Mixtures, Clarendon Press, London (1952); E. A. Guggenheim, Applications of Statistical Mechanics, Clarendon Press, London (1966).

[28]T. Muto and Y. Takagi, Solid State Physics **1**, 194 (1955) (Russian translation as book published by Izd-vo inostr. lit., Moscow (1959)).

[29]A. G. Lesnik, Modeli mezhatomnogo vzaimodeĭstviya v statisticheskoĭ teorii splavov (Models of Interatomic Interaction in the Statistical Theory of Alloys), Fizmatgiz, Moscow (1962).

[30]V. K. Fedyanin, Fiz. Khim. Tverd. Tela (Physics and Chemistry of Solids), No. 1, 5 (1971).

[31]O. O. Sushkova and V. K. Fedyanin, Preprint R4-8952 [in Russian], JINR, Dubna (1975).

[32]O. O. Sushkova and V. K. Fedyanin, Preprint R4-8953 [in Russian], JINR, Dubna (1975).

[33]O. O. Sushkova and V. K. Fedyanin, Preprint R17-8359 [in Russian], JINR, Dubna (1975).

[34]O. O. Sushkova and V. K. Fedyanin, Preprint R17-9360 [in Russian], JINR, Dubna (1975).

[35]O. O. Sushkova and V. K. Fedyanin, Preprint R17-9361 [in Russian], JINR, Dubna (1975).

[36]M. A. Krivoglaz and A. A. Smirnov, Teoriya uporyadochivayushchikhsya splavov Fizmatgiz, Moscow (1958). (presumed English translation: The Theory of Order-Disorder in Alloys, Macdonald, London (1964)).

[37]J. M. Cowley, Phys. Rev. **77**, 669 (1950); **120**, 1648 (1960); Adv. High Temp. Chem. 3, 35 (1971).

[38]G. Gilat and G. Dolling, Phys. Rev. A **138**, 1053 (1965).

[39]V. K. Fedyanin, Zh. Fiz. Khim. **44**, 495 (1970); **45**, 2867 (1971); **46**, 119 (1972).

[40]S. F. Timashev and V. K. Fedyanin, Fiz. Met. Mettaloved. **30**, 713 (1970); Dokl. Akad. Nauk SSSR, Ser. Fiz. **191**, 1333 (1970); Fiz. Tverd. Tela (Leningrad) **13**, 1196 (1971) [Sov. Phys. Solid State **13**, 989 (1971)].

[41]V. K. Fedyanin, Zh. Fiz. Khim. **47**, 1287 (1973).

[42]Yu. K. Tovbin and V. K. Fedyanin, Fiz. Tverd. Tela (Leningrad) **17**, 1511 (1975) [Sov. Phys. Solid State **17**, 985 (1975)].

[43]V. K. Fedyanin, Kinet.Katal. **10**, 1391 (1969); **12**, 1353 (1971).

[45]A. E. Mozol'kov and V. K. Fedyanin, Dokl. Akad. Nauk SSSR, Ser. Fiz. **219**, 393 (1974).

[46]A. E. Mozol'kov and V. K. Fedyanin, Preprint R17-9530 [in Russian], JINR, Dubna (1976).

[47]A. E. Mozol'kov and V. K. Fedyanin, Preprint R17-9531 [in Russian], JINR, Dubna (1976).

[48]A. E. Mozol'kov and V. K. Fedyanin, Preprint R17-9532 [in Russian], JINR, Dubna (1976).

[49]A. E. Mozol'kov and V. K. Fedyanin, Preprint R17-9934 [in Russian], JINR, Dubna (1976).

[50]A. E. Mozol'kov and V. K. Fedyanin, Preprint R17-9935 [in Russian], JINR, Dubna (1976).

[51]C. E. Caroll, Surf. Sci. **32**, 119 (1972).

[52]C. B. Duke and A. Liebsch, Phys. Rev. B **9**, 1126, 1150 (1974).

[53]J. L. Beeby, J. Phys. C **1**, 82 (1968).

[54]R. L. Park and H. H. Madden, Jr., Surf. Sci. **11**, 188 (1968).

[55]G. A. Somorjai and H. H. Farrell, Adv. Chem. Phys. **20**, 215 (1971).

[56]P. J. Estrup and J. Anderson, J. Chem. Phys. **45**, 2254 (1966); **46**, 567 (1967); Surf. Sci. **8**, 101 (1967); M. Onchi and H. E. Farnsworth, Surf. Sci. **11**, 203 (1968); F. Delamare and G. E. Rhead, Surf. Sci. **35**, 172 (1973).

[57]A. G. Naumovets and A. G. Fedorus, Pis'ma Zh. Eksp. Teor. Fiz. **10**, 11 (1969) [JETP Lett. **10**, 6 (1969)]; L. D. Schmidt, in: Interaction on Metal Surfaces, Springer, Berlin (1975).

[58]E. Rupp, Z. Electrochem. **35**, 586 (1929); Ann. Phys. (Leipzig) **5**, 453 (1930).

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