

EFFECT OF INHOMOGENEITIES OF THE CRYSTAL LATTICE ON THE THERMODYNAMICS OF A GAS OF QUASI PARTICLES IN THE CRYSTAL

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Submitted to JETP editor March 28, 1957

J. Exptl. Theoret. Phys. (U.S.S.R.) **34**, 355-370 (February, 1958)

Various types of quasi particles interacting among themselves or with static inhomogeneities of the crystal are considered. General formulas for the thermodynamic potential, valid for any type of particle and for an arbitrary law of interaction, are obtained by perturbation theory methods under the assumption that the interaction energy is not large. As an example an almost-degenerate Fermi gas of quasi particles (metal electrons) interacting with the crystal defects is considered. Interaction of the conductivity electrons with composition fluctuations leads in the case of alloys to a dependence of the electron part of the free energy, the electron chemical potential, the thermoelectron emission current, etc. on the long and short range order parameters. The ordering energies associated with the electron part of the free energy are of the same order of magnitude as the experimentally observed ordering energies. The vibrational part of the free energy has been determined for solid solutions in which both the masses of the atoms and their interaction energies are different.

AS is well known (see, for example, Landau and Lifshitz¹) the weakly excited states of a solid may be regarded as a superposition of elementary excitations which form a "gas" of weakly interacting quasi particles. The existence in the crystal of various inhomogeneities alters the properties of the elementary excitations (for example, their energy spectrum). The introduction of elementary excitations in a system which does not have translational symmetry is a much more complicated problem than their introduction in the case of an ideal crystal. Therefore for the investigation of a non-ideal crystal if the degree of inhomogeneity occurring in it is not great, it often turns out to be more convenient to introduce elementary excitations in an ideal crystal which serves as a "zero-order approximation" for the inhomogeneous crystal under discussion, and to take into account the effect of the inhomogeneities by means of a potential energy acting on them. In this case the problem of finding the partition function for the crystal is reduced to the problem of finding the partition function for the gas of quasi particles moving in an external potential field.

The inhomogeneities of the crystal are often practically stationary. Static inhomogeneities of such a type occur, for example, in solid solutions where they are associated with composition fluctuations, in piezoelectric crystals where they are associated with polarization fluctuations, etc. The

potential energy of the quasi particles in such cases depends on the magnitude of the corresponding fluctuations. In other cases fields produced by the inhomogeneities of the lattice vary rapidly in time and it is necessary to take their dynamic character into account explicitly. Dynamic inhomogeneities occur, for example, as a result of vibrations of the atoms of the lattice, or as a result of the excitation of spin waves in ferromagnetics. The effect of such inhomogeneities on the quasi particles could be described in a number of cases by considering the action of a variable field on a system of particles. However, since in such cases time averaging must be performed, and often the reaction of the quasi particles on the inhomogeneities is important, such a method of treatment is usually inconvenient. It is much more convenient to consider that to each type of dynamic inhomogeneities there corresponds its own kind of quasi particles (phonons, ferromagnons, etc.) and their effect on the thermodynamics of the system of quasi particles under discussion can be determined by evaluating the partition function for the interacting quasi particles of different kinds.

Thus, in order to determine the effect of the inhomogeneities of the lattice on the thermodynamic quantities it is necessary to obtain the partition function for the gas of quasi particles subjected to the field of the static fluctuation inhomogeneities of the crystal, or interacting with another

system of quasi particles. In practice, it is more convenient to evaluate not the ordinary but the grand partition function which, as is well known, may be represented in the form

$$Z = \sum_{\dots N_{\alpha} \dots} \exp \left(\lambda \sum_{\alpha} \mu_{\alpha} N_{\alpha} \right) \text{Sp } e^{-\lambda H}. \quad (1)$$

Here $\lambda = 1/kT$, N_{α} is the number of particles of type α , μ_{α} is their chemical potential, $H = H_0 + H_1$ is the Hamiltonian of the system (dependent on N_{α}), H_0 is the Hamiltonian of the system in the absence of static inhomogeneities and of interactions between the quasi particles, and H_1 is the interaction Hamiltonian. In the evaluation of the trace the summation is taken over the complete system of functions possessing the required symmetry (depending on the type of quasi particles). If the interaction energy is not great, one can use for the evaluation of Z the thermodynamic perturbation theory treating H_1 as a small perturbation. In so doing it is convenient to make use of Schwinger's expansion² for the trace of the exponential operator:

$$\begin{aligned} \text{Sp } \exp [-\lambda (H_0 + H_1)] &= \text{Sp } e^{-\lambda H_0} - \lambda \text{Sp } H_1 e^{-\lambda H_0} \\ &+ \frac{\lambda^2}{2} \int_0^1 du \text{Sp } H_1 e^{-\lambda H_0 u} H_1 e^{-\lambda H_0 (1-u)} + \dots \end{aligned} \quad (2)$$

Formula (2) has been used previously for the determination of the partition function of conduction electrons interacting with lattice vibrations³ or with static inhomogeneities⁴ in semiconductors. In the present paper we shall determine with the aid of formulas (1) and (2) the grand partition function (and the thermodynamic potential corresponding to it) for a system which is described by a Hamiltonian of quite a general form.

As an example we shall consider the interaction of metal conduction electrons with static inhomogeneities arising as a result of composition fluctuations in solid solutions or of fluctuations in magnetization of ferromagnetics near the Curie point. As a second example we shall consider the interaction of lattice vibrations with composition fluctuations.

1. GENERAL EXPRESSION FOR THE THERMODYNAMIC POTENTIAL

For the zero-order Hamiltonian H_0 we shall take the Hamiltonian of non-interacting particles consisting of the sum of terms corresponding to the individual particles. Then $H_1 = H - H_0$ will describe the interaction between the particles and

also their interaction with the static inhomogeneities. It is convenient to solve the above many-body problem by making use of the second quantization representation obtained with the aid of single particle functions which are eigenfunctions of the Hamiltonians of the individual particles. In this representation the energy operator H_0 (defined up to a constant term) has the form

$$H_0 = \sum_{\alpha} \sum_k \epsilon_{\alpha k} a_{\alpha k}^+ a_{\alpha k}, \quad (3)$$

where α denotes the kind of particles, k is the set of quantum numbers characterizing the states of the individual particles, $\epsilon_{\alpha k}$ is the energy of the particle in the k -th state, and $a_{\alpha k}^+$ and $a_{\alpha k}$ are the particle creation and annihilation operators. These operators satisfy the commutation relation

$$a_{\alpha k} a_{\alpha' k'}^+ \pm a_{\alpha k}^+ a_{\alpha' k'} = \delta_{\alpha \alpha'} \delta_{k k'}. \quad (4)$$

Both here and below the upper sign should be taken in the case of Fermi statistics, and the lower sign in the case of Bose statistics.

The perturbation energy operator H_1 in the case of particles interacting with static inhomogeneities, or of particles of one kind interacting among themselves, may be written in the form

$$\begin{aligned} H_1 &= \sum_{\alpha k} \sum_{i=1}^l [V_{\alpha k i} a_{\alpha k_1}^+ \dots a_{\alpha k_i}^+ a_{\alpha k_{i+1}} \dots a_{\alpha k_l} \\ &+ V_{\alpha k i}^* a_{\alpha k_1} \dots a_{\alpha k_i} a_{\alpha k_{i+1}}^+ \dots a_{\alpha k_l}], \end{aligned} \quad (5)$$

where the constants $V_{\mathbf{k} \ell i} = V_{\alpha k_1 \dots k_{\ell} i}$ are determined by the nature of the quasi particles and of the static inhomogeneities and satisfy the conditions

$$V_{\alpha \dots k_a \dots k_b \dots i} = V_{\alpha \dots k_b \dots k_a \dots i}^* \quad \text{for } 1 \leq a \leq i, \quad i < b \leq l.$$

The summation over αk is taken over all $k_1 \dots k_{\ell}$ and over all α . In special cases expressions (5) may be considerably simplified since the $V_{\alpha k i}$ differ from zero only for special values of i satisfying certain conditions. In a number of cases H_1 may be a sum of expressions (5) corresponding to different ℓ . However, since in the evaluation of Z up to the second order inclusively the individual terms of H_1 enter additively, we shall restrict ourselves to a consideration of H_1 of type (5) [or (6)], bearing in mind that corrections corresponding to terms with different ℓ may be simply added.

In the case of interaction of quasi particles of different kinds with each other (and also in the case of interaction with static inhomogeneities if

quasi particles of one kind can transform into quasi particles of a different kind), H_1 has the form

$$H_1 = \sum_{\alpha < \beta} \sum_{k\kappa} \sum_{i=1}^l \sum_{j=1}^m [V_{\alpha k i \beta \kappa j} a_{\alpha k i}^+ \dots a_{\alpha k i}^+ a_{\alpha k i+1} \dots a_{\alpha k l} a_{\beta \kappa i}^+ \dots a_{\beta \kappa j}^+ a_{\beta \kappa j+1} \dots a_{\beta \kappa m}^+ + V_{\alpha k i \beta \kappa j}^* a_{\alpha k i} \dots a_{\alpha k i} a_{\alpha k i+1}^+ \dots a_{\alpha k l}^+ a_{\beta \kappa i} \dots a_{\beta \kappa j} a_{\beta \kappa j+1}^+ \dots a_{\beta \kappa m}^*] \quad (6)$$

where κ_a denote quantum numbers of quasi particles of type β

$$V_{\alpha k i \beta \kappa j} = V_{\alpha k i \dots k_l i, \beta \kappa i \dots \kappa_m j},$$

$$V_{\alpha \dots h_a \dots h_b \dots i, \beta \dots \kappa_c \dots \kappa_d \dots j} = V_{\alpha \dots h_b \dots h_a \dots i, \beta \dots \kappa_d \dots \kappa_c \dots j}$$

with $1 \leq a \leq i$, $i < b \leq l$, $1 \leq c \leq j$, $j < d \leq m$. Summation over $k\kappa$ is taken over all $k_1 \dots k_l$, $\kappa_1 \dots \kappa_m$.

Let us now evaluate by means of formulas (1) and (2) the grand partition function up to the second order perturbation theory terms inclusively, and also the corresponding thermodynamic potential

$$\Omega = \Omega_0 + \Omega_1 + \Omega_2 + \dots = -kT \ln Z = -kT \ln Z^{(0)} - kT \frac{Z^{(1)}}{Z^{(0)}} - kT \left[\frac{Z^{(2)}}{Z^{(0)}} - \frac{1}{2} \left(\frac{Z^{(1)}}{Z^{(0)}} \right)^2 \right] - \dots \quad (7)$$

In carrying out the above calculation we shall evaluate the traces with the aid of the complete system of eigenfunctions of the operator H_0 in the second quantization representation. These functions are specified by the occupation numbers

$$n_{\alpha k} = a_{\alpha k}^+ a_{\alpha k}, \quad N_{\alpha} = \sum_k n_{\alpha k}. \quad (8)$$

It is convenient to use the grand partition function and the second quantization representation because in this case the evaluation of the trace in (1) and the summation over N_{α} reduces to an elementary summation over all possible values of $n_{\alpha k}$. Thus for $Z^{(0)}$ one immediately obtains from (1), (3), and (8) the well-known expression (see, for example, Landau and Lifshitz¹):

$$Z^{(0)} = \prod_{\alpha} \prod_k [1 \pm \exp \lambda (\mu_{\alpha} - \varepsilon_{\alpha k})]^{\pm 1}. \quad (9)$$

In evaluating the first order corrections in the case of interaction with static inhomogeneities, it should be taken into account that the diagonal matrix elements in (5) differ from zero only if to each annihilation operator there corresponds a creation operator with the same α and k , i.e.,

only those terms are important for which $i = l/2$ (l should be even), and which have the same sets of numbers $k_1 \dots k_l$ and $k_{i+1} \dots k_l$. Evaluating Ω_1 by means of formulas (7), (1) – (3), (5), and (8) we obtain

$$\Omega_{1st} = -kT \frac{Z_{st}^{(1)}}{Z^{(0)}} = \frac{1}{Z^{(0)}} \times \sum_{\dots N_{\alpha} \dots} \exp \left(\lambda \sum_{\alpha} \mu_{\alpha} N_{\alpha} \right) \text{Sp} [H_1 \exp(-\lambda H_0)] \quad (10) = i! \sum_{\alpha k} V'_{\alpha k i} [\bar{n}_{\alpha k_1} \dots \bar{n}_{\alpha k_i} + (1 \mp \bar{n}_{\alpha k_1}) \dots (1 \mp \bar{n}_{\alpha k_i})],$$

where $i = l/2$, $V'_{\alpha k l} = V_{\alpha k_1 \dots k_l k_1 \dots k_l}$ and $\bar{n}_{\alpha k}$ are the mean occupation numbers

$$\bar{n}_{\alpha k} = [\exp \lambda (\varepsilon_{\alpha k} - \mu_{\alpha}) \pm 1]^{-1}. \quad (11)$$

If H_1 is given by formula (6) then Ω_1 is determined in a similar manner:

$$\Omega_{1d} = i! j! \sum_{\alpha < \beta} \sum_{k\kappa} V'_{\alpha k i \beta \kappa j} [\bar{n}_{\alpha k_1} \dots \bar{n}_{\alpha k_i} \bar{n}_{\beta \kappa_1} \dots \bar{n}_{\beta \kappa_j} + (1 \mp \bar{n}_{\alpha k_1}) \dots (1 \mp \bar{n}_{\alpha k_i}) (1 \mp \bar{n}_{\beta \kappa_1}) \dots (1 \mp \bar{n}_{\beta \kappa_j})], \quad (12)$$

where

$$i = l/2, \quad j = m/2, \quad V'_{\alpha k i \beta \kappa j} = V_{\alpha k_1 \dots k_i k_{i+1} \dots k_l i, \beta \kappa_1 \dots \kappa_j \kappa_{j+1} \dots \kappa_m j}.$$

Determining further on the correction Ω_2 to the operators (5) and (6) we obtain

$$\Omega_{2st} = -\lambda \sum_{\alpha k} \sum_{i=1}^l (1 + \delta_{i, l/2}) i! (l-i)! |V_{\alpha k i}|^2 \times \int_0^1 du (1 \mp \bar{n}_{\alpha k_i}) \dots (1 \mp \bar{n}_{\alpha k_l}) \times \bar{n}_{\alpha k_{i+1}} \dots \bar{n}_{\alpha k_l} \exp [-\lambda (\varepsilon_{\alpha k_i} + \dots + \varepsilon_{\alpha k_i} - \varepsilon_{\alpha k_{i+1}} - \dots - \varepsilon_{\alpha k_l}) u]; \quad (13)$$

$$\Omega_{2st} = -\lambda \sum_{\alpha < \beta} \sum_{k\kappa} \sum_{i=1}^l \sum_{j=1}^m (1 + \delta_{i, l/2}) (1 + \delta_{j, m/2}) i! (l-i)! j! (m-j)! \times |V_{\alpha k i \beta \kappa j}|^2 \int_0^1 du (1 \mp \bar{n}_{\alpha k_i}) \dots (1 \mp \bar{n}_{\alpha k_l}) \bar{n}_{\alpha k_{i+1}} \dots \bar{n}_{\alpha k_l} (1 \mp \bar{n}_{\beta \kappa_1}) \dots \dots (1 \mp \bar{n}_{\beta \kappa_j}) \bar{n}_{\beta \kappa_{j+1}} \dots \bar{n}_{\beta \kappa_m} \exp [-\lambda (\varepsilon_{\alpha k_i} + \dots + \varepsilon_{\alpha k_i} - \varepsilon_{\alpha k_{i+1}} - \dots - \varepsilon_{\alpha k_l} + \varepsilon_{\beta \kappa_1} + \dots + \varepsilon_{\beta \kappa_j} - \varepsilon_{\beta \kappa_{j+1}} - \dots - \varepsilon_{\beta \kappa_m}) u]. \quad (14)$$

In summing over $\dots k_a \dots k_b \dots$ ($1 \leq a \leq i$, $i < b \leq \ell$) in formulas (13) and (14), the terms with $k_a = k_b$ (or $\kappa_a = \kappa_b$) should be excluded.

The above general formulas for the corrections to Ω will be applied below to various physical systems. In addition to the examples considered below they may be employed for the investigation of the effect on the thermodynamics of spin waves in ferromagnetics of their interaction with fluctuations in composition and in order parameters, with conduction electrons and with lattice vibrations. They can also be used for the investigation of the effect of anharmonicity on the thermodynamics of the phonon gas, for the determination of corrections to the thermodynamic potential associated with the interaction of atoms in a mixture of different gases (for example, $\text{He}^3\text{-He}^4$), etc.

2. INTERACTION OF A STRONGLY DEGENERATE GAS OF FERMI QUASI PARTICLES WITH CRYSTAL INHOMOGENEITIES

As the first example, we consider a system of Fermi quasi particles interacting with static crystal inhomogeneities. We suppose that the interaction of the particles with each other may be neglected and that the gas is in a nearly completely degenerate state. The results obtained on solving such a problem may be applied to the investigation of the effect on the thermodynamics of the crystal of the interaction of metal conduction electrons with static inhomogeneities. In this case one can consider either the conduction electrons in a single-electron approximation, or (more accurately) the Fermi quasi particles obtained after eliminating the Coulomb interaction between the electrons. The screened Coulomb interaction of such particles with one another, and their interaction with the collective oscillations of the electron plasma, are both small and their effect on the thermodynamics of the electrons may be taken into account separately by means of formulas (13) and (14).

We expand the potential energy of interaction of a particle with the static inhomogeneities into a Fourier series:

$$V(r) = \sum_{\kappa} (V_{\kappa} e^{i\kappa r} + V_{\kappa}^* e^{-i\kappa r}); \quad V_{-\kappa} = V_{\kappa}^*, \quad (15)$$

where the vector κ takes on values determined by the conditions at the crystal boundary. (Terms corresponding to κ and to $-\kappa$ are obviously the same.) We shall choose the potential energy in the zero-order approximation in such a way that $V_{\kappa} = 0$ for $\kappa = 0$. Going over to the second-quantization representation we find that the Hamiltonian of the system in the case under discussion has the form

$$H = H_0 + H_1 = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} \bar{a}_{\mathbf{k}} a_{\mathbf{k}} + \sum_{\kappa} \sum_{\mathbf{k}} [V_{\kappa \mathbf{k}} a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}-\kappa} + V_{\kappa \mathbf{k}}^* a_{\mathbf{k}} a_{\mathbf{k}-\kappa}^{\dagger}]. \quad (16)$$

Here \mathbf{k} is the propagation vector (not in reduced form) of the quasi particle; $\epsilon_{\mathbf{k}}$ is its energy; $V_{\kappa \mathbf{k}} = V_{\kappa} p_{\kappa \mathbf{k}}$ where $p_{\kappa \mathbf{k}}$ is the matrix element of the function $\exp(i\kappa \cdot \mathbf{r})$ formed using the single-particle wave functions corresponding to the propagation vectors \mathbf{k} and $\mathbf{k} - \kappa'$ ($p_{\kappa \mathbf{k}} \sim 1$), $\kappa' = \kappa - 2\pi \mathbf{K}_{\delta}$ where the reciprocal lattice vector \mathbf{K}_{δ} is chosen in such a way as to make the vectors \mathbf{k} and $\mathbf{k} - \kappa'$ lie in one cell. For the sake of simplicity in the Hamiltonian (16) terms are omitted which correspond to virtual transitions between different energy zones. This approximation holds if the separation between the zones is considerably larger than the Fermi energy. We note that taking into account the terms mentioned above does not alter the qualitative conclusions reached below.

Since for $\kappa = 0$, $V_{\kappa} = 0$ and $V_{\kappa \mathbf{k}} = 0$ (i.e., in the notation of the preceding section, $V_{\alpha \mathbf{k}_1 \mathbf{k}_2} = 0$), then it follows from (10) that the first order correction Ω_1 reduces to zero. Evaluating the second order correction by means of formulas (13), (16) and taking into account the fact that in the new notation $\mathbf{k}_1 \rightarrow \mathbf{k}$, $\mathbf{k}_2 \rightarrow \mathbf{k} - \kappa'$, $V_{\alpha \mathbf{k}_1 \mathbf{k}_2} \rightarrow V_{\kappa \mathbf{k}}$ we obtain

$$\Omega \approx \Omega_0 + \Omega_2 = \Omega_0 - 2g\lambda \sum_{\kappa} \sum_{\mathbf{k}} |V_{\kappa \mathbf{k}}|^2 \bar{n}_{\mathbf{k}} (1 - \bar{n}_{\mathbf{k}-\kappa'}) \times \int_0^1 \exp[\lambda(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\kappa'})u] du. \quad (17)$$

Here Ω_0 is the thermodynamic potential (expressed in terms of the variables v , T , μ) of the system of Fermi quasi particles in an ideal crystal, while the factor g takes into account the spin of the particles and in the case of electrons is equal to 2. The sum over \mathbf{k} in the second term of formula (17) may be replaced by integration over $(v/8\pi^3) d\mathbf{k}$, where v is the volume of the crystal, and similarly in the case of the summation over κ . The integration over \mathbf{k} may be carried out in the limiting cases of weak and strong degeneracy of the Fermi gas. In the case of weak degeneracy one gets a result which had been obtained earlier by Krivoglaз and Rybak.⁴ In the case of almost complete degeneracy when $\mu/kT \gg 1$ in the evaluation of the sum over \mathbf{k} and of the integral over u

$$J(\kappa) = \lambda \sum_{\mathbf{k}} |p_{\kappa \mathbf{k}}|^2 \bar{n}_{\mathbf{k}} (1 - \bar{n}_{\mathbf{k}-\kappa'}) \int_0^1 \exp[\lambda(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\kappa'})u] du = \frac{v}{8\pi^3} \int d\mathbf{k} |p_{\kappa \mathbf{k}}|^2 \frac{\bar{n}_{\mathbf{k}} - \bar{n}_{\mathbf{k}-\kappa'}}{\epsilon_{\mathbf{k}-\kappa'} - \epsilon_{\mathbf{k}}} \quad (18)$$

one may expand asymptotically in powers of kT/μ and limit oneself to the first non-vanishing term of the expansion.

It is not difficult to obtain an explicit expression for $J(\kappa)$ in the case when the dependence of $|p_{\kappa\mathbf{k}}|^2$ on \mathbf{k} may be neglected ($|p_{\kappa\mathbf{k}}|^2 = |p_{\kappa\mathbf{k}}|^2$) and when, moreover, $\epsilon_{\mathbf{k}}$ depends quadratically on \mathbf{k} : $\epsilon_{\mathbf{k}} = \hbar^2 k^2/2m$ where m is the effective mass of the Fermi quasi particles. Carrying out a simple calculation, we find that in this case

$$J(\kappa) = \frac{v}{4\pi^2} \frac{mk_0}{\hbar^2} |p_{\kappa}|^2 \left(1 + \frac{4k_0^2 - \kappa'^2}{4k_0\kappa'} \ln \frac{2k_0 + \kappa'}{|2k_0 - \kappa'|} \right), \quad (19)$$

$$k_0 = \sqrt{2\mu m} / \hbar = \sqrt{6\pi^2 N_e / gv};$$

k_0 is the boundary propagation vector of the degenerate Fermi gas, N_e is the number of Fermi quasi particles. The derivative of the function (19) with respect to κ has a discontinuity at the point $\kappa = 2k_0$. This singularity, as well as the singularity of the function $\bar{n}_{\mathbf{k}}$ at absolute zero, is associated with the asymptotic nature of the expression obtained above and disappears in the exact expression.

In the general case of arbitrary dependence of $\epsilon_{\mathbf{k}}$ on \mathbf{k} it is impossible to carry out the evaluation of $J(\kappa)$ for arbitrary κ . One can only note that in the adopted approximation $J(\kappa)$ does not depend on λ , and one can also find the expression in the limiting case of small $|\kappa'|$:

$$J(\kappa) = \frac{v}{8\pi^3} S(\mu) \overline{|p_{\kappa\mathbf{k}}|^2}. \quad (20)$$

Here $S(\epsilon) = d\omega(\epsilon)/d\epsilon$ where $\omega(\epsilon)$ is the volume of \mathbf{k} space contained inside the surface $\epsilon_{\mathbf{k}} = \epsilon$ while the bar denotes averaging over the surface $\epsilon_{\mathbf{k}} = \mu$.

As is well known, small changes in the thermodynamic potentials, expressed in appropriate variables, are all the same (see, for example, Landau and Lifshitz¹). This means that the correction Ω_2 expressed in terms of the variables T , v , and μ_{α} coincides with the correction to the free energy F_2 expressed in terms of the variables T , v , N_{α} . Therefore, it follows from formulas (17) and (18) that the expression for the free energy may be written in the form

$$F_{\phi} \approx F_0 + F_2 = F_0 - (gv/4\pi^3) \int J(\kappa) |V_{\kappa}|^2 d\kappa. \quad (21)$$

Here one should replace $|V_{\kappa}|^2$ in (21) by its average over the statistical ensemble.

Static inhomogeneities should play an essential role in alloys. In this case the inhomogeneities are caused by fluctuations in the concentrations of the components of the alloy. Let us consider a bi-

nary alloy AB which in the general case may be in an ordered state. Let us suppose that the atomic sizes are almost the same so that the geometric distortions of the crystal lattice can be neglected. It is convenient to choose for the zero-order approximation the completely ordered alloy composed of effective atoms whose potential energy of interaction with the Fermi quasi particles is equal to the average potential energy of interaction of atoms situated at lattice points of a given kind. Then the potential energy of the perturbation associated with the inhomogeneities of concentrations may be written in the following form:

$$V(\mathbf{r}) = \sum_{s=1}^{N/v} \sum_{\gamma=1}^v [c_{s\gamma} V_A(\mathbf{r} - \mathbf{R}_{s\gamma}) + (1 - c_{s\gamma}) V_B(\mathbf{r} - \mathbf{R}_{s\gamma}) - \bar{c}_{\gamma} V_A(\mathbf{r} - \mathbf{R}_{s\gamma}) - (1 - \bar{c}_{\gamma}) V_B(\mathbf{r} - \mathbf{R}_{s\gamma})]. \quad (22)$$

Here s is the index of the crystal cell; γ is the index of the lattice point in the cell; N is the number of atoms in the crystal, v is the number of lattice points in the cell; $\mathbf{R}_{s\gamma}$ is the vector drawn from the origin to the lattice point γ in the s -th cell; $c_{s\gamma} = 1$ if an atom A is situated at the lattice point $s\gamma$, and $c_{s\gamma} = 0$ if an atom B is situated there; \bar{c}_{γ} and $1 - \bar{c}_{\gamma}$ are atomic concentrations of atoms A and B at lattice points of type γ ; V_A and V_B are potential energies of interaction with atoms A and B respectively.

It follows from (22) that the Fourier component of the potential energy V_{κ} is equal to

$$V_{\kappa} = \frac{1}{2v} \int V(\mathbf{r}) \exp(-i\kappa\mathbf{r}) d\mathbf{r} = \frac{1}{v_a} (f_A - f_B) c_{\kappa}, \quad (23)$$

where

$$c_{\kappa} = c_{\kappa'} = \frac{1}{2N} \sum_s \sum_{\gamma} (c_{s\gamma} - \bar{c}_{\gamma}) \exp(-i\kappa'\mathbf{R}_{s\gamma}); \quad c_{s\gamma} - \bar{c}_{\gamma} = \sum_{\kappa'} [c_{\kappa'} \exp(i\kappa'\mathbf{R}_{s\gamma}) + c_{\kappa'}^* \exp(-i\kappa'\mathbf{R}_{s\gamma})]; \quad (24)$$

$$f_A = \int V_A(\mathbf{r}) \exp(-i\kappa\mathbf{r}) d\mathbf{r}; \quad f_B = \int V_B(\mathbf{r}) \exp(-i\kappa\mathbf{r}) d\mathbf{r}, \quad (25)$$

$v_a = v/N$ is the atomic volume. The quantities c_{κ} obviously satisfy the condition

$$\sum_{\kappa'} |c_{\kappa}|^2 = \frac{1}{4N} \sum_s \sum_{\gamma} (c_{s\gamma} - \bar{c}_{\gamma})^2 = \frac{1}{4v} \sum_{\gamma=1}^v \bar{c}_{\gamma} (1 - \bar{c}_{\gamma}). \quad (26)$$

It may be seen from formulas (21) and (23) that the correction to the free energy is determined by the magnitude of the mean values of the squares of the Fourier components of the concentration fluctuations. Multiplying the expression (24) for c_{κ} by the complex conjugate expression we obtain

$$|\overline{c_{\mathbf{x}}}|^2 = \frac{1}{4vN} \sum_{\gamma=1}^v \overline{c_{\gamma}} (1 - \overline{c_{\gamma}}) - \frac{1}{4N} \sum_{\rho \neq 0} \cos(\mathbf{x}' \cdot \boldsymbol{\rho}) \varepsilon(\boldsymbol{\rho}), \quad (27)$$

where the vectors $\boldsymbol{\rho} = \mathbf{R}_{\mathbf{S}'\gamma'} - \mathbf{R}_{\mathbf{S}\gamma}$ take on the values of all the radius vectors of the lattice points and

$$\varepsilon(\boldsymbol{\rho}) = -\frac{1}{v} \sum_{\gamma=1}^v \overline{(c_{\mathbf{S}\gamma} c_{\mathbf{S}'\gamma'} - \overline{c_{\gamma}} \overline{c_{\gamma'}})}. \quad (28)$$

The quantities $\varepsilon(\boldsymbol{\rho})$ are the parameters of correlation between the occupancy by atoms A of lattice points separated from one another by a distance $\boldsymbol{\rho}$ (more accurately they are the average values of these parameters over different kinds of lattice points separated by a distance $\boldsymbol{\rho}$). These quantities may be determined on the basis of x-ray or neutron data.⁵ We note that if we can neglect the scattering associated with geometric distortions of the lattice and with thermal vibrations then the quantity $|\overline{c_{\mathbf{x}}}|^2$ is proportional to the intensity of diffuse scattering of x-rays or of neutrons divided by the square of the difference between the atomic scattering factors for atoms A and B.

Substituting (23) into (27) and (21) we find that the electron part of the free energy of the alloy up to the second order perturbation theory terms may be written in the form

$$F_{\phi} = F_0 - a_0 \frac{1}{v} \sum_{\gamma=1}^v \overline{c_{\gamma}} (1 - \overline{c_{\gamma}}) + \sum_{\rho \neq 0} a_{\rho} \varepsilon(\boldsymbol{\rho}), \quad (29)$$

where

$$a_0 = \frac{g}{16\pi^3 v_a} \int |f_A - f_B|^2 J(\mathbf{x}) d\mathbf{x};$$

$$a_{\rho} = \frac{g}{16\pi^3 v_a} \int |f_A - f_B|^2 J(\mathbf{x}) \cos \mathbf{x}' \cdot \boldsymbol{\rho} d\mathbf{x}. \quad (30)$$

The electron part of the zero-order free energy F_0 is defined as the free energy of the electron gas in an ideal periodic crystal made up of effective atoms, and depends only on the long-range parameters (on the quantities $\overline{c_{\gamma}}$), but not on the correlation parameters. In the case of absence of long-range order (disordered alloys), F_0 may be considered to be independent of the temperature (if one neglects a small term proportional to T^2 which provides a linear term in the heat capacity of the metal). However, in this case the last term in (29) still depends on the temperature due to the correlation parameters $\varepsilon(\boldsymbol{\rho})$. For the same reason the electron chemical potential $\mu = dF/dN_e$ also depends on the temperature (in defining F and μ , we adopt as zero energy the energy of the electron at the bottom of the conduction band of a

disordered crystal composed of effective atoms). The dependence of μ on the correlation parameters must lead to a change in alloy properties such as contact potential, thermoelectron emission current, etc., when the short-range order is changed. Thus, the magnitude of the thermoelectron emission current J from a metal is given, as is well known,⁶ by the formula

$$J = D \frac{m_e k^2 |e|}{2\pi^2 \hbar^3} T^2 \exp \frac{\mu - \chi}{kT}. \quad (31)$$

Here m_e is the electron mass (in vacuo), D is the transmission coefficient of electrons from vacuum into the metal, χ is the energy difference between an electron at rest in vacuo and at the bottom of the conduction band.

In order to estimate the change in J when short-range order is established, one may set $|\partial F'/\partial N_e| \sim |F/N_e|$ and evaluate the constants a_0 and a_{ρ} by making use of data on the residual electrical resistance of alloys. Thus, for example, by utilizing the estimate of the matrix element of the perturbing energy for Au Ag alloys (see Bethe and Sommerfeld,⁷ §43) we shall find that $|f_A - f_B|^2 \sim 10^{-2} \mu^2 v_a^2$ for $\kappa \sim k_0$. Carrying out the integration in formula (30) for a_0 over the volume of the first cell of the reciprocal lattice (this will give an underestimate of the result), and utilizing expression (19) for $J(\kappa)$, we obtain $a_0 \sim 10^{-2} \mu N_e$, i.e., $a_0/N_e \sim 0.1$ ev. Because of the factors $\cos(\boldsymbol{\kappa} \cdot \boldsymbol{\rho})$ in the integrand of formula (30), the quantities a_{ρ} must be somewhat smaller and may be negative. For a number of disordered alloys the correlation parameters $\varepsilon(\boldsymbol{\rho})$ for the first few coordinative spheres are $\sim 10^{-12}$. Since $kT \sim 0.1$ ev, and the coordination number is ~ 10 , it can be seen from (31) that, if the change in $\varepsilon(\boldsymbol{\rho})$ is of the same order as $\varepsilon(\boldsymbol{\rho})$ itself, the change in J , in establishing or destroying short-range order in the solution, may amount to $\sim 0.1J$. The change in the contact potential, which is equal to the change in the chemical potential, may in this case amount to $\sim 10^{-2}$ ev. For the same change in $\varepsilon(\boldsymbol{\rho})$, greater effects can be expected, generally speaking, in the case of alloys with a large residual resistance. A particularly large change in μ in disordered solutions can be expected during the early stages of decay (during aging) when large regions appear in the crystal with a very high degree of short-range order.

In the commonly employed theory of alloys, which is based on the approximation of pair interactions, and which does not take into account collective degrees of freedom, the coefficient $Nz w/2$, (where w is the energy of ordering and z is the

coordination number), appears in the expression for the total energy in front of the correlation parameter for the first coordinative sphere. For the majority of alloys $w \sim 0.01 - 0.1$ eV, i.e., zw is of the same order of magnitude as the corresponding coefficient $z\alpha\rho_1/N_e$ in the electron part of the free energy. Thus, contrary to the rather widely held opinion,⁶ the change in the electron part of the free energy may play a very essential role in the appearance of short-range (and also of long-range) order in the alloy.

The change in the long-range order in the alloy may affect the electron part of the free energy and the properties of the alloy discussed above considerably more than a change in the short-range order. In this case the concentrations are different for lattice points of different kinds, and the potential energy of the electrons in the zero-order approximation, and consequently also F_0 , depend on the degree of long-range order. In the approximation of strongly-bound and weakly-bound electrons, the dependence of the energy spectrum of the zero-order approximation on the degree of long-range order (which enables us to determine F_0) has been obtained by Smirnov.⁸ The terms in F_0 containing the degree of long-range order are proportional to the square of the difference $V_A - V_B$ (and not to the difference itself), so that in order to investigate the effect of order, even for small $V_A - V_B$, it is necessary to take into account not only F_0 , but also the second term in (29).

A particularly sharp change in the electron part of the free energy can be expected near the temperature of the transition of the second kind into the ordered state, and also near the critical point on the decay curve. In such cases the second derivatives of the free energy with respect to the degree of long-range order, or with respect to the concentration, vanish, and anomalously large fluctuations occur in the degree of long-range order or in the composition, respectively.^{9,10} For the sake of simplicity let us consider a binary solid solution undergoing ordering, which contains in an elementary cell of the ordered crystal one lattice point of the first kind and one of the second kind (for example, crystals of the type NaCl or of the type of β -brass). In this case the quantities $c_{S\gamma}$ can be written in the form $c_{S1} = c_S + \eta_S/2$, $c_{S2} = c_S - \eta_S/2$. The average values of the quantities c_S and η_S , taken over a large number of cells, evidently coincide with the concentration of atoms A and with the long-range order η , which are related to the concentrations \bar{c}_γ by the equations: $\bar{c}_1 = c + \eta/2$, $\bar{c}_2 = c - \eta/2$. For small $\kappa' = \kappa - 2\pi \times \mathbf{K}_\delta$ (\mathbf{K}_δ is a vector of the reciprocal lattice of

the disordered alloy) the quantities $c_{S\gamma}$ in formula (24) for c_κ can be approximately replaced by the quantities c_S , since $\exp(-i\kappa' \cdot \mathbf{R}_{S\gamma})$ changes appreciably only over distances which extend over a large number of lattice constants, while the quantities $\pm \eta_S/2$ mutually cancel within the boundaries of a cell. On the other hand, for values of κ close to $2\pi\mathbf{K}'_\delta$ (\mathbf{K}'_δ is the vector of the reciprocal lattice which appears in the ordered alloy), the quantities c_S compensate each other [since the factors $\exp(-2\pi i\mathbf{K}'_\delta \cdot \mathbf{R}_{S\gamma})$ have different signs for lattice points of different kinds in a cell], and one must substitute $\eta_S/2$ in place of $c_{S\gamma}$ in (24). Thus, for small $\kappa' = \kappa - 2\pi\mathbf{K}_\delta$ or $\kappa'' = \kappa - 2\pi\mathbf{K}'_\delta$, the average values of $|c_\kappa|^2$ can be evaluated as average values of the squares of the moduli of the Fourier components of the fluctuations in the composition or in the degree of long-range order. The latter have been evaluated by the author¹⁰ for solid solutions in connection with the problem of the diffuse scattering of x-rays or of neutrons. Making use of the results given in that paper we find that in the case of cubic crystals in the neighborhood of a point of phase transition of the second kind for $|\kappa''| \ll 1/d_0$:

$$\overline{|c_\kappa|^2} = 1/4 \overline{|\eta_\kappa|^2} = (kT/16v) [\varphi_{\eta\eta} - \varphi_{c\eta}^2/\varphi_{cc} + \alpha\kappa''^2]^{-1}; \quad (32)$$

where φ_{cc} , $\varphi_{\eta\eta}$, and $\varphi_{c\eta}$ are the second derivatives of the free energy (and not only of its electron part) per unit volume with respect to c and η ; α may be taken as constant in the neighborhood of the transition point and on the order of⁹ $N_0 k T_0 d_0^2$, where N_0 is Avogadro's number, T_0 is the temperature of ordering, and d_0 is the lattice constant. The derivative $\varphi_{c\eta}$ is always equal to zero for disordered solutions, and vanishes near the point at which ordering occurs for ordered solutions whose composition corresponds to the maximum temperature of ordering. Similarly, for $|\kappa'| \ll 1/d_0$, one can obtain for disordered solutions

$$\overline{|c_\kappa|^2} = (kT/4v) [\varphi_{cc} + \beta\kappa'^2]^{-1}, \quad (33)$$

where β is a constant of the same order of magnitude as α .

At the point of phase transition of the second kind, $\varphi_{\eta\eta}$ and $\varphi_{c\eta}$ vanish and $\overline{|c_\kappa|^2} \rightarrow \infty$ as $\kappa'' \rightarrow 0$. As a result of this, the electron part of the free energy must vary sharply near the temperature T_0 . We consider first the case when $\varphi_{c\eta} = 0$. In order to separate out that term in F_Φ which depends most strongly on the temperature, we separate in the integral (21), in the neighborhood of the points $\kappa = 2\pi\mathbf{K}'_\delta$ (in which $\overline{|c_\kappa|^2}$ reaches a maximum), spheres of small radius

$R \ll 1/d_0$ and carry out a change of variables $\kappa = \mathbf{x}\sqrt{\varphi_{\eta\eta}/\alpha}$. In accordance with (21), (23), and

(22) integration over these spheres will lead to the appearance in F_{Φ} of the term

$$-g \frac{kT}{16\pi^2 v_a^2} \frac{V_{\varphi_{\eta\eta}}}{\alpha^{3/2}} \int_0^{\sqrt{\varphi_{\eta\eta}} R} \frac{x^2 + 1 - 1}{x^2 + 1} dx \sum_{\delta} J(2\pi\mathbf{K}'_{\delta}) |f_{A\delta} - f_{B\delta}|^2 = -g \frac{kT}{16\pi^2 v_a^2} R \sum_{\delta} J(2\pi\mathbf{K}'_{\delta}) |f_{A\delta} - f_{B\delta}|^2 + g \frac{kT}{32\pi v_a^2} \frac{V_{\varphi_{\eta\eta}}}{\alpha^{3/2}} \sum_{\delta} J(2\pi\mathbf{K}'_{\delta}) |f_{A\delta} - f_{B\delta}|^2, \quad (34)$$

where $f_{A\delta}$ and $f_{B\delta}$ are the values of the functions f_A and f_B at the points $\kappa = 2\pi\mathbf{K}_{\delta}$.

The last term in (34) proportional to $\sqrt{\varphi_{\eta\eta}}$ leads to the most pronounced dependence of F_{Φ} on the temperature in the neighborhood of the temperature T_0 . However, one should keep in mind that the integration in the integral (21) over the remainder of κ -space outside the selected spheres also contains a term proportional to $\sqrt{\varphi_{\eta\eta}}$ which, however, cannot be evaluated without making use of a specific model of the alloy which permits one to evaluate the correlation parameters $\epsilon(\rho)$. We shall therefore take these terms into account by means of the factors L_{δ} (where $L_{\delta} \lesssim 1$) under the summation sign in formula (34). Thus, near the point of phase transition of the second kind, the expression for the electron part of the free energy may be written in the form

$$F_{\Phi} = F_0 + F'_2 + A' V_{\varphi_{\eta\eta}}, \quad (35)$$

where

$$A' = (gkT_0/32\pi v_a^2 \alpha^{3/2}) \sum_{\delta} L_{\delta} J(2\pi\mathbf{K}'_{\delta}) |f_{A\delta} - f_{B\delta}|^2, \quad (36)$$

while F'_2 contains higher powers of $\varphi_{\eta\eta}$ (for example, the first). For small η , F_0 contains a term $\sim \eta^2$ which leads to a less pronounced temperature dependence of F_{Φ} near T_0 than the term with $\sqrt{\varphi_{\eta\eta}}$. In the general case when for a given composition the temperature T_0 is not a maximum and in the ordered state $\varphi_{C\eta} \neq 0$, one should replace $\varphi_{\eta\eta}$ in (35) by the expression $\varphi_{\eta\eta} - \varphi_{C\eta}^2/\varphi_{CC}$ (which also vanishes when $T = T_0$).

Similarly, near the critical point on the decay curve in which φ_{CC} vanishes,

$$F_{\Phi} = F_0 + F''_2 + A'' V_{\varphi_{CC}}, \quad (37)$$

where A'' differs from A' by the replacement of α by β and by summation over the points $2\pi\mathbf{K}_{\delta}$, which correspond to vectors of the reciprocal lattice of the disordered alloy.

One can similarly determine the form of the expression for the electron part of the free energy near the point of phase transition into the ferromagnetic state in pure metals (the Curie point).

In this case an interaction, associated with exchange interaction,¹¹ takes place between the conduction electrons and the fluctuations of magnetization. The Hamiltonian of such an interaction has the form

$$H_1 = Cs\Delta\mathfrak{M}(\mathbf{r}), \quad (38)$$

where s is the spin operator of a conduction electron, $\Delta\mathfrak{M}(\mathbf{r})$ is the fluctuation change in the distribution of magnetic moments at the point \mathbf{r} [$\mathfrak{M}(\mathbf{r})$ is a periodic function with the periods of the lattice], while C is a constant. Since near the Curie point the relaxation processes become extremely slow, the fluctuations may be regarded as static ones (see, for example, Krivoglaz and Rybak⁴). Since in the case under consideration the electron energy in the zero-order approximation depends on the spin direction (in the ferromagnetic state), taking the spin into account does not reduce simply to multiplication by g , and the expression for $J(\kappa)$ will be somewhat altered. However, near the Curie temperature, when the terms proportional to the square of the magnetization M^2 are negligibly small (see Krivoglaz and Rybak⁴), one may, as before, use formulas (21) and (18) in the calculation of F_0 , after replacing $|V_{\kappa\mathbf{k}}|^2$ by

$$1/2 \sum_{\sigma, \sigma'} |V_{\kappa\sigma\sigma'}|^2 = 1/4 C^2 |p_{\kappa\mathbf{k}}|^2 |f_{\kappa}|^2 |\overline{M_{\kappa}}|^2. \quad (39)$$

Here σ and σ' are the spin components ($\pm 1/2$), \mathbf{M}_{κ} are the Fourier components of the magnetization vector, while f_{κ} is a factor which appears in the transition from the Fourier component of a rapidly oscillating function $\mathfrak{M}(\mathbf{r})$ to the smooth function $\mathbf{M}(\mathbf{r})$ ($f_{\kappa} < 1$ and $f_{\kappa} \rightarrow 1$ as $\kappa \rightarrow 0$). Applying the same considerations to the case of a cubic ferromagnetic in which the spontaneous magnetization is directed along the cubic axis (z axis), as in the case of solid solutions, and utilizing the expressions for $|\overline{M_{\kappa i}}|^2$ ($i = x, y, z$) given by Krivoglaz and Rybak,⁴ we find that near the Curie point the expression for the electron part of the free energy has the form

$$F = F_0 + F''_2 + A''' [2\sqrt{\partial^2\varphi/\partial M_x^2} + \sqrt{\partial^2\varphi/\partial M_z^2}], \quad (40)$$

where A''' is a constant, while the derivatives of φ vanish at the Curie point.

One can make a rough estimate of the constants A' , A'' , A''' . Assuming, as we have done before on the basis of data on the residual resistance of alloys, that $|f_A - f_B|^2 \sim 10^{-2} \mu^2 v_a^2$, we obtain with the aid of formulas (36) and (19)

$$\sqrt{N_0 k T_0 A'} / N_e \sim \sqrt{N_0 k T_0 A''} / N_e \sim 10^{-3} \text{ ev.}$$

In order to evaluate the constant A''' , we set $CM_S \sim kT_0 \sim 10^{-3} \mu$, where M_S is the saturation magnetization. Then

$$\sqrt{N_0 k T_0 A'''} / N_e M_S \sim 10^{-5} \text{ ev.}$$

It should be noted that the expressions for the free energy given above cease to be valid at the transition point itself, since on approaching it the higher order terms in the expansion in powers of the interaction constant of the quasi particles with the inhomogeneities of the crystal lattice begin to play an ever increasing role.

The interaction between the electrons and the lattice vibrations may be treated with the aid of formula (14) in the same way as was done above in the case of the interaction of electrons with static inhomogeneities. Such an interaction leads to a renormalization of the velocities of propagation of elastic vibrations and to the appearance of a certain correction to the electron part of the free energy. The solution of this problem has already been obtained¹³ by means of perturbation theory.*

*We note the free energy must contain terms associated with the interaction not only for superconductivity, but also for certain other phenomena. Thus, the term in the free energy of the conduction electrons (proportional to T), which appears because of frequency renormalization at high temperatures ($T \gg \theta$, where θ is the Debye temperature), must lead to the appearance of a term proportional to T in the contact potential of the metal, and also to appearance of an additional factor in front the exponential in the thermoelectron emission current [see formula (31)]. An additional factor in front of the exponential also appears owing to thermal expansion, but this effect may be separated out by studying the dependence of J on the pressure. The interaction of conduction electrons with lattice vibrations leads to the dependence of the chemical potential of the conduction electrons on the isotopic composition. This means that the contact potential difference, the thermoelectromotive force, the factor in front of the exponential in the thermo-electron emission current (but not the work function) etc., must also depend on the isotopic composition. From this it follows, in particular, that a contact potential difference (which is almost independent of T at low temperatures and is proportional to T at high temperatures) and a thermoelectromotive force (smaller by 2 or 3 orders of magnitude than in the case of different elements) must arise between different isotopes of the same metal. The isotope effects noted above must occur not only in metals but also in semiconductors, where they are a consequence of the "polaron" or the "condenson" effect.¹⁴

3. INTERACTION OF LATTICE VIBRATIONS WITH INHOMOGENEITIES OF COMPOSITION

In the investigation of the vibrations of the crystal lattice the inhomogeneities may consist either of a difference in the atomic masses or of a difference in the potential energy of interaction of different atoms. In the case when only the masses are different (solution of isotopes) the lattice vibrations have been treated in a number of papers.¹⁵ In the present article we shall investigate with the aid of the perturbation theory formulas derived above (on the assumption that no local vibrations appear) the more general case of a binary solid solution of atoms of different kinds in which not only the masses of the atoms, but also their interaction energies, are different. The solution may be either in a disordered state with one atom per unit cell, or in an ordered state.

The Hamiltonian of the lattice vibrations has in the harmonic approximation the form

$$H = -\frac{\hbar^2}{2} \sum_{s\gamma} \sum_{i=1}^3 \frac{1}{m_{s\gamma}} \frac{\partial^2}{\partial r_{s\gamma i}^2} + \frac{1}{2} \sum_{s\gamma} \sum_{s'\gamma'} \sum_{i,j=1}^3 V_{s\gamma s'\gamma'}^{ij} r_{s\gamma i} r_{s'\gamma' j}. \quad (41)$$

Here i and j are indices of the Cartesian coordinates, and $r_{s\gamma i}$ is the deflection of the atom situated at the lattice point γ of the s -th cell from its equilibrium position (in a solid solution these positions do not form an ideal lattice). The atomic masses $m_{s\gamma}$ may take on two values, m_1 and m_2 , depending on whether atom A or B occupies the lattice point $s\gamma$.

We suppose that the coefficients V in (41) depend only on the kind of atoms situated at the lattice points $s\gamma$ and $s'\gamma'$, and do not depend on the kind of neighboring atoms. Then for the pairs AA, AB, and BB these quantities may take on respectively the values

$$V(1,1), V(1,2), V(2,2).$$

For the zero-order Hamiltonian we choose the Hamiltonian for the vibrations of an ideal ordered crystal with masses \bar{m}_γ and constants \bar{V} which are the average values of the corresponding quantities

$$\bar{m}_\gamma = \bar{c}_\gamma m_1 + (1 - \bar{c}_\gamma) m_2, \\ \bar{V}_{s\gamma s'\gamma'}^{ij} = p_{s\gamma s'\gamma'}(1,1) V_{s\gamma s'\gamma'}^{ij}(1,1) + [p_{s\gamma s'\gamma'}(1,2) + p_{s\gamma s'\gamma'}(2,1)] V_{s\gamma s'\gamma'}^{ij}(1,2) + p_{s\gamma s'\gamma'}(2,2) V_{s\gamma s'\gamma'}^{ij}(2,2). \quad (42)$$

Here, for example, $p_{s\gamma s'\gamma'}(1,2)$ is the probability that the lattice point $s\gamma$ is occupied by atom A, while the lattice point $s'\gamma'$, separated from it

by the distance $\mathbf{R}_{S'\gamma} - \mathbf{R}_{S\gamma}$, is occupied by atom B. Then the Hamiltonian (41) takes on the form

$$H = H_0 + H_1 = -\frac{\hbar^2}{2} \sum_{\gamma} \frac{1}{m_{\gamma}} \sum_s \sum_{i=1}^3 \frac{\partial^2}{\partial r_{s\gamma i}^2} + \frac{1}{2} \sum_{s\gamma s'\gamma'} \sum_{i,j=1}^3 \overline{V}_{s\gamma s'\gamma'}^{ij} r_{s\gamma i} r_{s'\gamma' j} - \frac{\hbar^2}{2} \sum_{\gamma} \frac{1}{m_{\gamma}} \sum_s \sum_{i=1}^3 \mu_{s\gamma} \frac{\partial^2}{\partial r_{s\gamma i}^2} + \frac{1}{2} \sum_{s\gamma s'\gamma'} \sum_{i,j=1}^3 \Delta V_{s\gamma s'\gamma'}^{ij} r_{s\gamma i} r_{s'\gamma' j}, \quad (43)$$

where

$$\mu_{s\gamma} = (\overline{m}_{\gamma} - m_{s\gamma}) / m_{s\gamma}; \quad \Delta V = V - \overline{V}. \quad (44)$$

We express the coordinates of the atomic deflections in terms of creation and annihilation operators for Bose particles corresponding to different normal coordinates:

$$\mathbf{r}_{s\gamma} = \sum_{\mathbf{k}t} (\hbar / 2N\overline{m}_{\gamma}\omega_{\mathbf{k}t})^{1/2} \mathbf{e}_{\mathbf{k}t\gamma} (\cos \mathbf{k}\mathbf{R}_{s\gamma} - \sin \mathbf{k}\mathbf{R}_{s\gamma}) (a_{\mathbf{k}t} + a_{\mathbf{k}t}^{\dagger}), \quad (45)$$

$$\partial / \partial \mathbf{r}_{s\gamma} = \frac{1}{2N} \sum_{\mathbf{k}t} (2N\overline{m}_{\gamma}\omega_{\mathbf{k}t} / \hbar)^{1/2} \frac{\mathbf{e}_{\mathbf{k}t\gamma}}{|\mathbf{e}_{\mathbf{k}t\gamma}|^2} (\cos \mathbf{k}\mathbf{R}_{s\gamma} - \sin \mathbf{k}\mathbf{R}_{s\gamma}) (a_{\mathbf{k}t} - a_{\mathbf{k}t}^{\dagger}).$$

Here t indicates the branches of the vibration frequencies, $\omega_{\mathbf{k}t}$ are the eigen-frequencies in the zero-order approximation, $\mathbf{e}_{\mathbf{k}t\gamma}$ are the polarization vectors satisfying the condition

$$\sum_{\gamma=1}^v |\mathbf{e}_{\mathbf{k}t\gamma}|^2 \overline{m}_{\gamma} = \sum_{\gamma=1}^v \overline{m}_{\gamma}.$$

Substituting (45) into (44) we shall find the expression for H in the second-quantization representation:

$$H = H_0 + H_1 = \sum_{\mathbf{k}t} \hbar\omega_{\mathbf{k}t} (a_{\mathbf{k}t}^{\dagger} a_{\mathbf{k}t} + \frac{1}{2}) + \frac{1}{4} \sum_{\mathbf{k}t} \sum_{\mathbf{k}'t'} \hbar \sqrt{\omega_{\mathbf{k}t}\omega_{\mathbf{k}'t'}} (V'_{\mathbf{k}t\mathbf{k}'t'} + V''_{-\mathbf{k}t\mathbf{k}'t'}) - \mu'_{\mathbf{k}t\mathbf{k}'t'} + \mu''_{-\mathbf{k}t\mathbf{k}'t'} (a_{\mathbf{k}t} a_{\mathbf{k}'t'} + a_{\mathbf{k}t}^{\dagger} a_{\mathbf{k}'t'}^{\dagger} + a_{\mathbf{k}t} a_{\mathbf{k}'t'}^{\dagger} + a_{\mathbf{k}t}^{\dagger} a_{\mathbf{k}'t'}), \quad (46)$$

where

$$\mu_{\mathbf{k}t\mathbf{k}'t'} = \frac{1}{N} \sum_{s\gamma} \mu_{s\gamma} (\mathbf{e}_{\mathbf{k}t\gamma} \mathbf{e}_{\mathbf{k}'t'\gamma}) \exp [i(\mathbf{k} - \mathbf{k}', \mathbf{R}_{s\gamma})],$$

$$V_{\mathbf{k}t\mathbf{k}'t'} = \frac{1}{N\omega_{\mathbf{k}t}\omega_{\mathbf{k}'t'}} \sum_{i,j=1}^3 \sum_{ss'\gamma\gamma'} (\overline{m}_{\gamma}\overline{m}_{\gamma'})^{-1/2} \Delta V_{s\gamma s'\gamma'}^{ij} e_{\mathbf{k}t\gamma i} e_{\mathbf{k}'t'\gamma' j} \times \exp [i(\mathbf{k}\mathbf{R}_{s\gamma} - \mathbf{k}'\mathbf{R}_{s'\gamma'})], \quad (47)$$

while ' and '' denote the real and the imaginary parts of the quantities μ and V .

We note that for $\mathbf{k} = \mathbf{k}'$, $t = t'$ in accordance with (47), (44), and (42)

$$V_{\mathbf{k}t\mathbf{k}t} = 0, \quad \mu_{\mathbf{k}t\mathbf{k}t} = \frac{1}{N} \sum_{s\gamma} \mu_{s\gamma} = \frac{(m_1 - m_2)^2}{m_1 m_2} \frac{1}{v} \sum_{\gamma=1}^v \overline{c}_{\gamma} (1 - \overline{c}_{\gamma}). \quad (48)$$

The quantities $\mu_{\mathbf{k}t\mathbf{k}'t'}$ and $V_{\mathbf{k}t\mathbf{k}'t'}$ may be expressed in terms of $c_{\mathbf{k}}$ [see (24)] and of the Fourier components of $p_{\mathbf{q}}(\rho)$ defined by the formula

$$p_{\mathbf{q}}(\rho) = \frac{1}{2N} \sum_{s\gamma} (c_{s\gamma} c_{s'\gamma'} - \overline{c_{s\gamma} c_{s'\gamma'}}) \exp \left(-\frac{1}{2} i\mathbf{q}, \mathbf{R}_{s\gamma} + \mathbf{R}_{s'\gamma'} \right), \quad (49)$$

where the summation is carried out keeping $\mathbf{R}_{S'\gamma'} = \mathbf{R}_{S\gamma} + \rho$. The free energy may then be calculated up to the second order inclusively with the aid of formulae (12) and (14) (in which one should set $l = 2$). Taking into account (48) and (26) and the fact that a small change in Ω is equivalent to a small change in F expressed in terms of appropriate variables we obtain

$$F_{\mathbf{k}} = F_0 + \frac{2(m_1 - m_2)^2}{m_1 m_2} \sum_{\mathbf{k}t} \sum_{\mathbf{k}'t'} \varphi_{\mathbf{k}t\mathbf{k}'t'} (e_{\mathbf{k}t} e_{\mathbf{k}'t'})^2 |\overline{c_{\mathbf{k}-\mathbf{k}'}}|^2 - 2 \sum_{\mathbf{k}t} \sum_{\mathbf{k}'t'} \left[\hbar\omega_{\mathbf{k}t} \left(\overline{n}_{\mathbf{k}t} + \frac{1}{2} \right) - \varphi_{\mathbf{k}t\mathbf{k}'t'} \right] \times \left| \sum_{\rho \neq 0} u_{\mathbf{k}t\mathbf{k}'t'}(\rho) c_{\mathbf{k}-\mathbf{k}'} - \omega_{\mathbf{k}t\mathbf{k}'t'}(\rho) p_{\mathbf{k}-\mathbf{k}'}(\rho) \right|^2, \quad (50)$$

where F_0 is the free energy of the vibrations of a completely ordered crystal consisting of effective atoms corresponding to the zero-order approximation, and

$$u_{\mathbf{k}t\mathbf{k}'t'}(\rho) = \frac{4}{m\omega_{\mathbf{k}t}\omega_{\mathbf{k}'t'}} \sin \frac{\mathbf{k}\rho}{2} \sin \frac{\mathbf{k}'\rho}{2} \cos \frac{\mathbf{k}-\mathbf{k}'}{2} \rho$$

$$\times \sum_{i,j=1}^3 e_{\mathbf{k}t i} e_{\mathbf{k}'t' j} [\Delta V_{\rho}^{ij}(1,2) - \Delta V_{\rho}^{ij}(2,2)],$$

$$\omega_{\mathbf{k}t\mathbf{k}'t'}(\rho) = \frac{2}{m\omega_{\mathbf{k}t}\omega_{\mathbf{k}'t'}} \sin \frac{\mathbf{k}\rho}{2} \sin \frac{\mathbf{k}'\rho}{2} \sum_{i,j=1}^3 e_{\mathbf{k}t i} e_{\mathbf{k}'t' j} [2\Delta V_{\rho}^{ij}(1,2) - \Delta V_{\rho}^{ij}(1,1) - \Delta V_{\rho}^{ij}(2,2)]; \quad (51)$$

$$\varphi_{\mathbf{k}t\mathbf{k}'t'} = \hbar [\omega_{\mathbf{k}t}^3 (\overline{n}_{\mathbf{k}t} + 1/2),$$

$$- \omega_{\mathbf{k}'t'}^3 (\overline{n}_{\mathbf{k}'t'} + 1/2)] / 2 (\omega_{\mathbf{k}t}^2 - \omega_{\mathbf{k}'t'}^2). \quad (52)$$

For ideal solutions in which all the lattice points are equivalent and there is no correlation the expression for F_K simplifies to

$$\begin{aligned}
 F_K = F_0 + \frac{(m_1 - m_2)^2}{2Nm_1m_2} c(1-c) \sum_{kt} \sum_{k't'} \varphi_{ktk't'} (\mathbf{e}_{kt} \mathbf{e}_{k't'})^2 \\
 - \frac{c(1-c)}{2N} \sum_{kt} \sum_{k't'} \left[\hbar \omega_{kt} \left(\bar{n}_{kt} + \frac{1}{2} \right) - \varphi_{ktk't'} \right] \left\{ 2c(1-c) \sum_{\rho \neq 0} \omega_{ktk't'}^2(\rho) \right. \\
 \left. + \left[\sum_{\rho \neq 0} \left(u_{ktk't'}(\rho) - 2c \cos\left(\frac{\mathbf{k}-\mathbf{k}'}{2} \cdot \rho\right) \omega_{ktk't'}(\rho) \right) \right]^2 \right\}. \quad (53)
 \end{aligned}$$

Formulas (50) and (53) enable us to compute F_K without determining the frequency spectrum of the vibrations of the solution, but using only the frequency spectrum of the ideal crystal corresponding to the zero-order approximation and the values of the constants u and w for different ρ .

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Translated by G. Volkoff