Structural Aspects of the Electrical Resistivity of Binary Alloys. II. Long-Wavelength Limit of the Structure Factors for a Solid Alloy*

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(Received 25 January 1971)

Using the thermodynamic theory of fluctuations, the expressions for the long-wavelength (and high-temperature) limit of the three number-concentration structure factors (introduced in Paper I) of a binary solid alloy having arbitrary crystal symmetry are derived.

I. INTRODUCTION

In a previous paper[1] (hereafter referred to as I), the authors discussed some structural aspects of the electrical resistivity of binary alloys by expressing the scattering function in terms of three new structure factors $[S_{NN}(\vec{q}),\ S_{CC}(\vec{q}),\ \text{and}\ S_{NC}(\vec{q})]$ constructed from the Fourier transforms of the local number density and concentration of the ions. These "number-concentration" structure factors can be quite helpful in interpreting some of the experimental data,[1] since above the Debye temperature and in the long-wavelength limit $(q \to 0)$, they are simply related to the local thermal fluctuations in the number density and concentration of the ions and hence to the thermodynamic properties of the alloy.

Although the general formalism of I is applicable to both liquid and solid binary alloys, much of the attention in it was confined to molten alloys, and the simple expressions for $S_{NN}(\vec{q} \to 0)$, etc., given there are strictly true for fluid alloys and only approximately so for solids. The purpose of this paper is to apply the fluctuation theory to obtain expressions for the long-wavelength (and high-temperature) limit of the structure factors for a binary solid alloy, taking into account the full complement of the stress and strain variables (rather than just pressure and volume) which characterize a solid. The method, incidentally, provides an alternative derivation of the structure factor $S(\vec{q} \to 0)$ of a pure crystal which is customarily derived by expanding the displacement of the ions from their equilibrium positions in terms of the phonon coordinates.

II. THEORY

First we recall[2] that if W is the minimum work done (reversibly) to produce normal (small) fluctuations $\delta x_m\ (m = 1, 2, \dots)$ in the thermodynamic variables x_m from their respective equilibrium values, the probability for these fluctuations to occur is proportional to $e^{-W/k_B T}$. If x_m is a set of independent variables describing the state of the system, W can be written as (summation over repeated indices is implied throughout)

$$W = \tfrac{1}{2} D_{mn}\,\delta x_m \delta x_n \ , \tag{1}$$

where $D_{mn}\ (= D_{nm})$ are constants which depend on the thermodynamic equation of state for the system, and the averages are given by

$$\langle \delta x_m\,\delta x_n \rangle = k_B T\,(D^{-1})_{mn} \ , \tag{2}$$

where D^{-1} is the inverse matrix of D.

Consider now an element (volume V in the undeformed state) of the solid alloy. Let N_1 and N_2 be the number of the two types of atoms in this volume and let $N = N_1 + N_2$ and $c = N_1/N$. The rest of the medium (volume $\gg V$) is considered as an external medium which can exchange energy and atoms with this element. If we keep N constant and allow the concentration and other thermodynamic variables describing the element to fluctuate from their equilibrium values, W may be shown to be given by[3]

$$2W = \delta S \delta T + V \delta \sigma_{ij} \delta \epsilon_{ij} + \delta \mu_c \delta c \ , \tag{3}$$

where S is the entropy, $\sigma_{ij}\ (= \sigma_{ji})\ (i,j = 1, 2, 3)$ is the stress tensor, $\epsilon_{ij}\ (= \epsilon_{ji})$ is the strain tensor, and $\mu_c = N(\mu_1 - \mu_2)$, where μ_1 and μ_2 are the chemical potentials (per atom) of the two species of atoms in the alloy. At constant N, the expressions for the differential changes in the Helmholtz and Gibbs free energies A and G are, respectively,

$$\delta A = -S\delta T + V\sigma_{ij}\delta\epsilon_{ij} + \mu_c \delta c \ , \tag{4}$$

$$\delta G = -S\delta T - V\epsilon_{ij}\delta\sigma_{ij} + \mu_c \delta c \ . \tag{5}$$

Taking the independent variables in (3) to be ϵ_{ij}, c, and T, expanding the remainder in terms of them, and using the fact that δA and δG are perfect differentials, one may obtain after some algebra

$$2W = \left(\frac{\partial S}{\partial T}\right)_{\epsilon,c,N}(\delta T)^2 + V c_{ijkl}\,\delta\epsilon_{ij}\delta\epsilon_{kl}$$
$$- 2V c_{ijkl}\,e_{kl}\,\delta\epsilon_{ij}\delta c + D_{44}(\delta c)^2 \ , \tag{6}$$

where $c_{ijkl} = (\partial\sigma_{ij}/\partial\epsilon_{kl})_{e,c,T,N}$ are the isothermal elastic stiffness constants, $e_{kl} = (\partial\epsilon_{kl}/\partial c)_{T,\sigma,N}$,

and

$$D_{44} \equiv \left(\frac{\partial^2 G}{\partial c^2}\right)_{T,\sigma,N} + V c_{ijkl} e_{ij} e_{kl} \ . \tag{7}$$

In (6) and (7) a subscript like ϵ means that all the strain components are kept constant, while ϵ' indicates that all ϵ_{ij}, except the one with which differentiation is being performed, are kept constant. In (7) we have also used the relation

$$\left(\frac{\partial \mu_c}{\partial c}\right)_{T,\sigma,N} = \left(\frac{\partial^2 G}{\partial c^2}\right)_{T,\sigma,N} ,$$

which follows from (5). The reason for the notation D_{44} will become clear presently.

From (6) and (2) one sees that the fluctuations in temperature occur independently of those in c and ϵ_{ij}. The temperature fluctuations do not concern us here and the first term in (6) will be ignored in the following.

To evaluate the structure factors we have to consider $\delta \epsilon_{ij}$ and δc as smoothly varying functions of the position coordinates $\vec{r}$, for which case W may be written as[4]

$$W = \tfrac{1}{2} \int_V [c_{ijkl} \delta\epsilon_{ij}(\vec{r}) \delta\epsilon_{kl}(\vec{r}) - 2c_{ijkl} e_{kl} \delta\epsilon_{ij}(\vec{r}) \delta c(\vec{r})$$
$$+ V^{-1} D_{44} (\delta c(\vec{r}))^2] \, d^3r \ . \tag{8}$$

Now let $\vec{s}(\vec{r})$ denote the displacement of the ions at a point $\vec{r}$ and let (the term $\vec{q} \equiv 0$ being excluded from the sums)

$$\vec{s}(\vec{r}) = \sum_{\vec{q}} \vec{s}(\vec{q}) e^{-i\vec{q}\cdot\vec{r}} , \quad \vec{s}(\vec{q}) = \vec{s}^*(-\vec{q}) ,$$
$$\delta c(\vec{r}) = \sum_{\vec{q}} c(\vec{q}) e^{-i\vec{q}\cdot\vec{r}} , \quad c(\vec{q}) = c^*(-\vec{q}) \ . \tag{9}$$

Then, we have

$$\delta\epsilon_{ij}(\vec{r}) = \tfrac{1}{2}\left(\frac{\partial s_i(\vec{r})}{\partial x_j} + \frac{\partial s_j(\vec{r})}{\partial x_i}\right)$$

$$= -\tfrac{1}{2} i \sum_{\vec{q}} (s_i(\vec{q})q_j + s_j(\vec{q})q_i) e^{-i\vec{q}\cdot\vec{r}} \tag{10}$$

$$\equiv \sum_{\vec{q}} \epsilon_{ij}(\vec{q}) e^{-i\vec{q}\cdot\vec{r}} , \tag{11}$$

where the last identity defines $\epsilon_{ij}(\vec{q})$, the Fourier transform of $\delta\epsilon_{ij}(\vec{r})$. Substituting (9) and (10) in (8) and noting that $\int \exp[i(\vec{q}+\vec{q}')\cdot\vec{r}] d^3r = 0$, unless $\vec{q} = -\vec{q}'$, one obtains

$$W = \tfrac{1}{2}\sum_{\vec{q}} [D_{ik} s_i(-\vec{q}) s_k(\vec{q}) - 2D_{j4}(is_j(-\vec{q})c(\vec{q}))$$
$$+ D_{44} c(-\vec{q})c(\vec{q})] , \tag{12}$$

with $(i,j,k = 1, 2, 3)$

$$D_{ik} = D_{ki} = V c_{ijkl} q_j q_l , \quad D_{j4} = D_{4j} = V c_{ijkl} e_{kl} q_i ; \tag{13}$$

here we have used the usual symmetry properties of the elastic constants, $c_{ijkl} = c_{jikl}$, etc.

Next we note that since we have considered above the fluctuations in strain components or volume

keeping the total number of particles fixed, the deviation $\delta n(\vec{r})$ in the local number density of the particles for small fluctuations is $\delta n(\vec{r}) \simeq -(N/V) \times \delta\epsilon_{ii}(\vec{r})$. Denoting the Fourier transform of $\delta n(\vec{r})$ by $N(\vec{q})$ as in I, recalling the definitions of the structure factors [see Eqs. (7), (11), and (19) of I], and making use of (10) and (11), we may obtain

$$S_{NN}(\vec{q}) = N^{-1}\langle N(-\vec{q})N(\vec{q})\rangle = N q_i q_j \langle s_i(-\vec{q})s_j(\vec{q})\rangle , \tag{14}$$

$$S_{NC}(\vec{q}) = \mathrm{Re}\langle N(-\vec{q})c(\vec{q})\rangle = N \mathrm{Re} q_j \langle ic(-\vec{q})s_j(\vec{q})\rangle , \tag{15}$$

$$S_{CC}(\vec{q}) = N\langle c(-\vec{q})c(\vec{q})\rangle \ . \tag{16}$$

The averages in (14)–(16) are readily evaluated with the help of (12) and (2) by writing in (12)

$$s_j(\vec{q}) = s_j^{(1)} + is_j^{(2)}(\vec{q}), \quad c(\vec{q}) = c^{(1)}(\vec{q}) + ic^{(2)}(\vec{q}),$$

where $s_j^{(1)}$, $s_j^{(2)}$, $c^{(1)}$, and $c^{(2)}$ are all real, and calculating the averages of the various real binary products of $s_j^{(1)}$, $s_j^{(2)}$, $c^{(1)}$, and $c^{(2)}$ with each other. Denoting the inverse of the 4×4 matrix D, whose elements $D_{\alpha\beta}$ ($\alpha, \beta = 1, 2, 3, 4$) are given by (13) and (7), by D^{-1} and its elements by $(D^{-1})_{\alpha\beta}$, one obtains $(i, j = 1, 2, 3)$

$$S_{NN}(\vec{y}) = N k_B T (D^{-1})_{ij} q_i q_j , \tag{17}$$

$$S_{NC}(\vec{y}) = N k_B T (D^{-1})_{4j} q_j , \tag{18}$$

$$S_{CC}(\vec{y}) = N k_B T (D^{-1})_{44} , \tag{19}$$

where $\vec{y}$ is the unit vector along the direction of $\vec{q}$. In (17)–(19) we have written the argument of the structure factors as $\vec{y}$, rather than $\vec{q}$, (a) to signify that while the expressions (17)–(19) in general depend on the direction of $\vec{q}$, they are independent of the magnitude[5] of $\vec{q}$, and (b) to remind the reader that these expressions are the macroscopic or long-wavelength limit of the structure factors $S_{NN}(\vec{q})$, etc.

III. EVALUATION OF $(D^{-1})_{\alpha\beta}$ AND SPECIAL CASES

An instructive way to partially evaluate $(D^{-1})_{\alpha\beta}$ is as follows: Write the matrix D as

$$D = \begin{pmatrix} A & B \\ \tilde{B} & D_{44} \end{pmatrix} , \tag{20}$$

where A is the 3×3 matrix whose elements are D_{ij} $(i, j = 1, 2, 3)$, B is 3×1 (column matrix) with elements D_{j4}, and $\tilde{B}$ the transpose of B. If A^{-1} denotes the inverse matrix of A, then one may show that

$$(D^{-1})_{ij} = (A^{-1})_{ij} + (D^{-1})_{44}(A^{-1}B\tilde{B}A^{-1})_{ij} , \tag{21}$$

$$(D^{-1})_{j4} = -(D^{-1})_{44}(A^{-1}B)_j ,\qquad (22)$$

$$(D^{-1})_{44} = 1/(D_{44} - \tilde{B}A^{-1}B) .\qquad (23)$$

Now the elements of the matrix A may be seen to be just Vq^2 times the elements of the matrix which determines the velocities and polarization vectors of the three independent elastic waves propagating along the direction $\vec{y}$ ($\parallel \vec{q}$) in the crystal.[6] Hence, the elements of A^{-1} may be written as[7]

$$(A^{-1})_{ij} = \sum_{r=1}^{3} \frac{u_i^{(r)} u_j^{(r)}}{Vpq^2v_r^2} ,\qquad (24)$$

where $\vec{u}^{(r)} \equiv \vec{u}^{(r)}(\vec{y})$ is the unit polarization (displacement) vector associated with the particular elastic wave propagating along the y direction whose velocity is $v_r \equiv v_r(\vec{y})$, and ρ is the density of the medium. Note that v_r in (24), and hence also in subsequent expressions, refers to velocities calculated from isothermal (rather than adiabatic) elastic constants.

Noting the forms of (21) and (22) and using (18), (19), and (24), one sees that the expression (17) for $S_{NN}(\vec{y})$ may be written as

$$'S_{NN}(\vec{y}) = (N/V)k_B T\kappa(\vec{y}) + [S_{NC}(\vec{y})/S_{CC}(\vec{y})]^2 S_{CC}(\vec{y}) ,\qquad (25)$$

where

$$\kappa(\vec{y}) = \sum_{r=1}^{3} \frac{(\vec{u}^{(r)} \cdot \vec{y})^2}{\rho v_r^2} .\qquad (26)$$

If the second term in (25) is zero, $S_{NN}(\vec{y}) = (N/V)k_B T\kappa(\vec{y})$ which has the form of the well-known expression for the structure factor (in the limit under consideration) of a pure crystal.

For an alloy a specially simple case is that where the two types of atoms are of identical size and shape, i.e., $e_{ij} [= (\partial \epsilon_{ij}/\partial c)_{T,\sigma,N}] = 0$, for all i

and j. For this case all the elements D_{j4} of the matrix B in (20) are zero. Consequently $S_{NC}(\vec{y}) = 0$, so that fluctuations in number density and concentration are uncorrelated for this case, as might be expected intuitively. $S_{CC}(\vec{y})$ for this case is given by, using (7), (19), and (23),

$$S_{CC}(\vec{y}) = Nk_B T \bigg/ \left(\frac{\partial^2 G}{\partial c^2}\right)_{T,\sigma,N}\qquad (27)$$

and is independent of the direction $\vec{y}$.

For the general case of $e_{ij} \neq 0$ and a substance of arbitrary crystal symmetry, the expressions for $S_{NC}(\vec{y})$ and $S_{CC}(\vec{y})$ [and hence for $S_{NN}(\vec{y})$] may be written down using Eqs. (21)–(25). We may note that for crystals having orthorhombic symmetry or higher and no residual strains, considerable simplification occurs since the tensor e_{ij}, referred to crystal axes as coordinate axes, is diagonal, i.e., $e_{ij} = 0$ for $i \neq j$. Even so, the expressions are lengthy and we confine our attention here to the specific case of a crystal of cubic symmetry with no residual strains. Referring to cube edges as coordinate axes, one has for this case $e_{ij} = 0$ for $i \neq j$ and

$$e_{11} = e_{22} = e_{33} = \tfrac{1}{3}\delta ,\qquad (28)$$

say. δ is obviously the fractional change in volume per unit change in the concentration. Then using the symmetry characteristics of the elastic constants of a cubic crystal, one obtains

$$S_{NC}(\vec{y}) = -\delta B_T \kappa(\vec{y}) S_{CC}(\vec{y}) ,\qquad (29)$$

$$S_{CC}(\vec{y}) = \frac{Nk_B T}{(\partial^2 G/\partial c^2)_{T,\sigma,N} + V\delta^2 B_T(1 - B_T\kappa(\vec{y}))} ,\qquad (30)$$

where $B_T [= \tfrac{1}{3}(c_{11} + 2c_{12})]$ is the isothermal bulk modulus, and $\kappa(\vec{y})$ is as given in (26), which for a cubic crystal may be explicitly written as[7]

$$\kappa(\vec{y}) = \frac{1 + 2\eta(l^2 m^2 + m^2 n^2 + n^2 l^2) + 3\eta^2 l^2 m^2 n^2}{c_{11} + (c_{11} + c_{12})\eta(l^2 m^2 + m^2 n^2 + n^2 l^2) + (c_{11} + 2c_{12} + c_{44})\eta^2 l^2 m^2 n^2} ,\qquad (31)$$

where $\eta = (c_{11} - c_{12} - 2c_{44})/c_{44}$ is a measure of the elastic anisotropy and l, m, n are the direction cosines of $\vec{y}$. In (31) the elastic constants c_{ijkl} have been written in the two-suffix (Voigt) notation: $c_{ijkl} \equiv c_{pq}$, p, $q = 1, 2, 3, \ldots, 6$.

For an elastically isotropic solid, $\eta = 0$ and $\kappa(\vec{y}) = (c_{11})^{-1} = (B_T + \tfrac{4}{3}c_{44})^{-1}$. Hence $\kappa(\vec{y})$ and consequently all the structure factors $S_{NN}(\vec{y})$, etc., have no directional dependence. Further, if the shear modulus $c_{44} = 0$, as for a fluid, we have $\kappa(\vec{y}) = B_T^{-1}$. With this substitution in (29) and (30) and remembering that for a fluid $(\partial^2 G/\partial c^2)_{T,\sigma,N} \equiv (\partial^2 G/\partial c^2)_{T,P,N}$ (P, pressure), expressions (25), (29), and (30) for $S_{NN}(\vec{y})$, $S_{NC}(\vec{y})$, and $S_{CC}(\vec{y})$ become identical with

the corresponding expressions given in I.

Next we recall from I that the scattering function $I(\vec{q})$ may be written as

$$I(\vec{q}) = \theta(\vec{q})(\overline{W})^2 + [W_1 - W_2 + \overline{W}\Delta(\vec{q})]^2 S_{CC}(\vec{q}) ,\qquad (32)$$

where W_1 and W_2 are the pseudopotential matrix elements, $\overline{W} = cW_1 + (1 - c)W_2$, $\Delta(\vec{q}) = S_{NC}(\vec{q})/S_{CC}(\vec{q})$, and $\theta(\vec{q})$, by virtue of Eq. (48) of I and (25), is such that $\theta(\vec{y}) = (N/V)k_B T\kappa(\vec{y})$. Consider now the long-wavelength limit of (32) for a dilute ($c \ll 1$) isotropic solid alloy. Then $S_{CC} \simeq c$, $\Delta(\vec{y}) = -\delta B_T/c_{11}$, and, to linear terms in c, the temperature-independent part of $I(\vec{q})$ is $[W_1 - W_2 - \delta(B_T/c_{11})W_2]^2 c$.

This is equivalent to the result obtained by Blatt[8] from Friedel's sum rule considerations, the term involving δ in the square brackets being usually referred to as the dilatation effect.

In our treatment, as will be clear from Eq. (8), the origin of the term $\Delta(\vec{q})$ or $S_{NC}(\vec{q})$ may be ascribed to the fact that a fluctuation in concentration is always accompanied by a fluctuation in strain, unless the two types of atoms are of identical shape and size, i.e., $e_{ij} \equiv 0$, where $\Delta(\vec{q}) = 0$. At shorter wavelengths, in connection with x-ray scattering, the effect of these strain fluctuations has been considered by Huang[9] and Krivoglaz.[4] Although the formulations of these authors are different from ours, one may reasonably infer from them (see Sec. 18 of Ref. 4) that for a random solid solution $\Delta(\vec{q})$ is approximately of the form (assuming elastic isotropy and omitting a Debye-

Waller type of factor[9])

$$\Delta(\vec{q}) \sim \frac{\delta}{c_{11}} \frac{B_T}{\vec{q} \cdot (\vec{g}_n - \vec{q})}{|\vec{g}_n - \vec{q}|^2} \; , \tag{33}$$

where $\vec{g}_n$ is the "reciprocal-lattice vector" closest to $\vec{q}$.[10] We see that for a $\vec{g}_n \neq 0$, $\Delta(\vec{q})$ is singular at $\vec{q} = \vec{g}_n$ and the $[\Delta(\vec{q})]^2$ term in (32) gives a scattering near $\vec{q} = \vec{g}_n$, which is similar to the diffuse or umklapp scattering due to the thermal phonons.[9] Thus, the contribution from the $\Delta(\vec{q})$ terms in (32) to the scattering can be quite significant as compared to that arising from the difference $W_1 - W_2$ alone or even compared to that [e.g., if $\delta = 0.3$ and $S_{CC} \sim c(1 - c) = \frac{1}{4}$] from the $\theta(\vec{q})$ (thermal phonon) term at room temperature. In quantitative calculations of the resistivity it would, therefore, seem desirable to take these terms into account.

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[1]A. B. Bhatia and D. E. Thornton, Phys. Rev. B 2, 3004 (1970).

[2]See, e.g., L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, London, 1958).

[3]Equation (3) follows straightforwardly from similar arguments as given in Ref. 2 for deriving W for a fluid.

[4]We may note that expression (8) is formally similar to that used by Krivoglaz to calculate concentration fluctuations $S_{CC}(\vec{y})$ in our notation [M. A. Krivoglaz, *Theory of X-Ray and Thermal Neutron Scattering by Real Crystals* (Plenum, New York, 1969), Chap. III]. However, whereas in (8) the strain variables $\delta\epsilon_{ij}$ may vary independently of the changes in concentration, in his treatment $\delta\epsilon_{ij}(\vec{r})$ are functions of $\delta c(\vec{r})$. His final expression (9.4) is equivalent to our result for $S_{CC}(\vec{y})$.

[5]We may note that as $q \to 0$, $(D^{-1})_{ij}$ and $(D^{-1})_{4j}$ tend to

infinity. This divergence should not cast doubt on the validity of the results obtained here since the right-hand sides of Eqs. (17)–(19) each has the same finite value irrespective of whether $q \to 0$ or $q \neq 0$.

[6]See, for example, A. B. Bhatia, *Ultrasonic Absorption* (Oxford U. P., London, 1967), Chap. 3 or any book on elasticity theory.

[7]H. A. Jahn, Proc. Roy. Soc. (London) A179, 320 (1942).

[8]F. J. Blatt, Phys. Rev. 108, 285 (1957).

[9]K. Huang, Proc. Roy. Soc. (London) A190, 102 (1947).

[10]It may be noted that as $\vec{q}$ spans the reciprocal space, $\Delta(\vec{q})$ changes sign frequently, the first change occurring at $\vec{q} \sim \frac{1}{2}\vec{g}_0$, $\vec{g}_0$ the shortest nonzero "reciprocal-lattice vectors." In a liquid alloy, then, the first change in sign should occur roughly about midway between $q = 0$ and the value of q for which $|\Delta(q)|$ has its first peak. This is in qualitative agreement with the behavior of $S_{NC} = \Delta(q)S_{CC}$ ($S_{CC} > 0$ for all q) plotted in Figs. 1 and 2 of I.