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Structural Aspects of the Electrical Resistivity of Binary Alloys*

A. B. Bhatia and D. E. Thornton

Theoretical Physics Institute and Physics Department, University of Alberta, Edmonton, Canada

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Using the weak scattering approximation and the Van Hove correlation-function technique, it is shown that the scattering function for a binary alloy (solid or liquid) is quite generally expressible in terms of three structure factors $S_{NN}(\vec{q})$, $S_{NC}(\vec{q})$, and $S_{CC}(\vec{q})$ constructed from the Fourier transforms of the local number density and concentration in the alloy. These structure factors have the property that at temperatures above the Debye temperature and in the long-wavelength limit ($q \rightarrow 0$), $S_{NN}(0)$ and $S_{CC}(0)$ represent, respectively, the mean square thermal fluctuations in the particle number and concentration, and $S_{NC}(0)$ the correlation between these two fluctuations. Thermodynamic formulas for these fluctuations are given and their concentration and temperature dependence examined for various types of mixtures (regular, order-disorder type, athermal, etc.). It is concluded that the present formalism, because of its ready link with the thermodynamic properties of the alloy, can be helpful in interpreting the various experimental data and provides useful insight into the partial structure factors introduced in the Faber-Ziman theory of liquid alloys.

I. INTRODUCTION

In the current treatment of the problem of electrical conductivity of metals (liquid or solid), the relevant scattering function describing the scattering of electrons is given by the product of two factors: a structure factor which depends only on the relative positions of the ions in the metal, and the atom form factor or the pseudopotential matrix element which describes the scattering due to the individual ions in the metal.[1-5] The method depends on assuming that the total potential, responsible for scattering, in the metal may be written as the sum of the potentials due to individual ions in the metal and that it can be regarded as weak. Faber and Ziman[6] (FZ) have generalized this approach to discuss the electrical resistivity of liquid alloys. For a binary alloy the scattering function depends upon, in general, three independent partial structure factors which completely describe the structure of the alloy and the two form factors.

The transport properties of alloys have also been discussed on another, and seemingly unrelated, approach which is valid in the long-wavelength limit and which attributes the scattering of electrons – in analogy with the well-known theories[7,8] of light scattering in liquids and liquid mixtures – to the local thermal fluctuations in the density and concentration of the alloy. In particular, Krishnan and Bhatia[9] showed that the observed strong temperature dependence of the resistivity of an order-disorder type of alloy near its critical point may be attributed to the corresponding temperature dependence of the concentration fluctuations. A somewhat similar approach has been recently suggested by Takeuchi and Endo[10] for liquid alloys; see also Tomlinson and Lichter.[11]

The work of the present paper may, in a sense, be regarded as constituting a generalization of the above fluctuation approach so that it is applicable at shorter wavelengths and low temperatures. It is shown that in the aforementioned weak scattering approximation, the scattering function for a binary alloy (solid or liquid) is quite generally expressible in terms of three structure factors $S_{NN}(\vec{q})$, $S_{NC}(\vec{q})$, and $S_{CC}(\vec{q})$, which are derived from the Fourier transforms of the local number density and concentration of the alloy. For liquid alloys and for solids above the Debye temperature, these structure factors have the property that in the long-wavelength limit ($q \rightarrow 0$), $S_{NN}(0)$ and $S_{CC}(0)$ represent, respectively, the mean square fluctuations in the particle number and concentration, and $S_{NC}(0)$ the correlation between these two fluctuations. Since all these three quantities are readily calculated from the thermodynamic properties of the alloys, the present formalism provides useful insight into the various structure factors. This is illustrated in the text by consideration of various types of solutions, namely, ideal, order-disorder, athermal, etc.

Using the Van Hove correlation-function technique,[12] the general expressions (and their high-temperature limits) for the scattering function and the structure factors $S_{NN}(\vec{q})$, etc., are given in Sec. II. In the remainder of the paper we confine our discussion to the high-temperature case only. In Sec. III, we consider the long-wavelength limit and use the appropriate thermodynamic formulas to discuss the limiting forms of the structure factors $S_{NN}(\vec{q})$, etc., for various types of mixtures. Finally, a comparison between the partial structure factors of the FZ theory[6] and the structure factors introduced here is given in Sec. IV.

II. SCATTERING FUNCTION

In the weak scattering approximation, the function, here denoted by $\Gamma(\vec{q}, \omega)$, which determines the scattering of an electron from the initial wave-vector state $\vec{k}$ to the final wave-vector state $\vec{k}'$ in the alloy, is given by[12,13]

$$\Gamma(\vec{q}, \omega)=\frac{1}{2\pi N}\int e^{-i\omega t}\,dt\,\langle A^{\dagger}(\vec{q}, 0)A(\vec{q}, t)\rangle\ , \tag{1}$$

where

$$A(\vec{q}, t)=\sum\nolimits_j W_j(q)\,e^{\,i\vec{q}\cdot\vec{R}_j(t)}\ ,\qquad \vec{q}=\vec{k}-\vec{k}',\quad \hbar\omega=E_{\vec{k}}-E_{\vec{k}'} \tag{2}$$

$A^{\dagger}(\vec{q}, 0)$ is the conjugate of the operator $A(\vec{q}, 0)$, N is the total number of atoms in the crystal, $\vec{R}_j(t)$ the position operator of the atom j at time t, and $\langle\cdots\rangle$ denotes ensemble average in the equilibrium state of the alloy. Further, $W_j(q)$ is the pseudopotential matrix element of the ion j in the alloy, i.e., if $V_j(\vec{r}-\vec{R}_j)$ is the effective potential due to the jth ion centered at $\vec{R}_j$,

$$W_j(q)=\int e^{i\vec{q}\cdot(\vec{r}-\vec{R}_j)}\,V_j(\vec{r}-\vec{R}_j)\,d^3r\ .$$

We take, for convenience, $W_j(q)$ to be real and a function of $q\,(=|\vec{q}|)$ only. For a pure metal, all $W_j(q)$ are equal, and $\Gamma(\vec{q}, \omega)=|W(q)|^2 S(\vec{q}, \omega)$, where $S(\vec{q}, \omega)$ is the dynamical structure factor introduced by Van Hove.[12]

$\Gamma(\vec{q}, \omega)$ is related to the resistivity of the alloy in the same manner as it is for the case of a pure metal.[13–15] Remembering our definitions of $\vec{q}$ and ω, if we set

$$I(\vec{q})=\int_{-\infty}^{+\infty}\frac{\beta\omega}{e^{\beta\omega}-1}\,\Gamma(\vec{q}, \omega)\,d\omega,\quad \beta=\frac{\hbar}{k_B T} \tag{3}$$

where k_B is the Boltzmann constant and T the temperature, then the resistivity ρ is given by

$$\rho=\frac{12\pi(m^*)^2}{\hbar^3 e^2 k_F^2}\,\frac{N}{V}\int_0^1 I_{\mathrm{av}}(q)\,x^3\,dx\ , \tag{4}$$

where $x=q/2k_F$, k_F is the wave number of the electrons at the Fermi surface, m^* the electron effective mass, and V the volume of the system. In a solid, $I(\vec{q})$ depends, in general, on the direction of $\vec{q}$, and $I_{\mathrm{av}}(q)$ in (4) represents a suitable average of $I(\vec{q})$ (minus elastic Bragg scattering, if any) over all directions of $\vec{q}$.

Consider now a binary alloy having N_α, $\alpha=1, 2$, atoms of the type α, and let $\bar{n}_\alpha=N_\alpha/V$ be the mean number density of α ions. We define the average concentration c by

$$c=N_1/(N_1+N_2)=N_1/N=\bar{n}_1/(\bar{n}_1+\bar{n}_2)\ . \tag{5}$$

If $n_\alpha(\vec{r}, t)$ denote the number density operator at time t for the species α, then

$$\delta n_\alpha(\vec{r}, t)\equiv n_\alpha(\vec{r}, t)-\bar{n}_\alpha = -\bar{n}_\alpha+\sum\nolimits_j\delta(\vec{r}-\vec{R}_j^{\,\alpha}(t))\ . \tag{6}$$

Making the Fourier expansion

$$\delta n_\alpha(\vec{r}, t)=(1/V)\sum\nolimits_{\vec{q}} N_\alpha(\vec{q}, t)\,e^{-i\vec{q}\cdot\vec{r}}\ , \tag{7}$$

$$N_\alpha(\vec{q}, t)=\int e^{i\vec{q}\cdot\vec{r}}\,\delta n_\alpha(\vec{r}, t)\,d^3r =\sum\nolimits_j e^{i\vec{q}\cdot\vec{R}_j^{\,\alpha}(t)}-N_\alpha\delta_{\vec{q},0}\ . \tag{8}$$

The reality of $\delta n_\alpha(\vec{r}, t)$ requires that $N_\alpha^{\dagger}(\vec{q}, t)=N_\alpha(-\vec{q}, t)$. Similarly, if $N(\vec{q}, t)$ denotes the Fourier transform of the local deviation $\delta n(\vec{r}, t)$ in the total number density

$$n(\vec{r}, t)=n_1(\vec{r}, t)+n_2(\vec{r}, t)\ ,$$

then

$$N(\vec{q}, t)=\sum_{j,\alpha=1,2} e^{\,i\vec{q}\cdot\vec{R}_j^{\alpha}(t)}-N\delta_{\vec{q},0} =N_1(\vec{q}, t)+N_2(\vec{q}, t)\ . \tag{9}$$

We next define the local deviation from the mean concentration c by

$$\delta c(\vec{r}, t)=(V/N)\left[(1-c)\,\delta n_1(\vec{r}, t)-c\,\delta n_2(\vec{r}, t)\right]\ , \tag{10}$$

so that if δn_1 and δn_2 change in proportion to their respective mean concentration, namely, c and $(1-c)$, then $\delta c(\vec{r}, t)=0$, as it should. If we make the Fourier expansion

$$\delta c(\vec{r}, t) = \sum_{\vec{q}} C(\vec{q}, t) e^{-i\vec{q}\cdot\vec{r}}, \quad C^{\dagger}(\vec{q}, t) = C(-\vec{q}, t), \tag{11}$$

then

$$C(\vec{q}, t) = (1/V) \int \delta c(\vec{r}, t) e^{i\vec{q}\cdot\vec{r}} d^3r$$
$$= (N^{-1})[(1-c) N_1(\vec{q}, t) - c N_2(\vec{q}, t)] . \tag{12}$$

With the help of (8), (9), and (12), the expression (2) for $A(\vec{q}, t)$ may be written as

$$A(\vec{q}, t) = W_1 N_1(\vec{q}, t) + W_2 N_2(\vec{q}, t) , \tag{13}$$

or as

$$A(\vec{q}, t) = \overline{W} N(\vec{q}, t) + (W_1 - W_2) N C(\vec{q}, t) , \tag{14}$$

where

$$W_1 \equiv W_1(q), \text{ etc.},$$

and

$$\overline{W} = c W_1 + (1-c) W_2 .$$

In (13) and (14), we have ignored terms involving $\delta_{\vec{q},0}$, since they contribute to the scattering in the forward direction only, and their presence or absence does not affect the resistivity.

Substituting (14) into (1), we may write $\Gamma(\vec{q}, \omega)$ in the form

$$\Gamma(\vec{q}, \omega) = (\overline{W})^2 S_{NN}(\vec{q}, \omega) + (W_1 - W_2)^2 S_{CC}(\vec{q}, \omega)$$
$$+ 2\overline{W}(\overline{W}_1 - W_2) S_{NC}(\vec{q}, \omega) , \tag{15}$$

where

$$S_{NN}(\vec{q}, \omega) = (1/2\pi N) \int e^{-i\omega t} \, dt \langle N^{\dagger}(\vec{q}, 0) N(\vec{q}, t) \rangle ,$$
$$S_{CC}(\vec{q}, \omega) = (N/2\pi) \int e^{-i\omega t} dt \langle C^{\dagger}(\vec{q}, 0) C(\vec{q}, t) \rangle ,$$
$$2S_{NC}(\vec{q}, \omega) = (1/2\pi) \int e^{-i\omega t} dt \langle N^{\dagger}(\vec{q}, 0) C(\vec{q}, t)$$
$$+ C^{\dagger}(\vec{q}, 0) N(\vec{q}, t) \rangle . \tag{16}$$

The functions $S_{NN}(\vec{q}, \omega)$, etc., may be called the dynamical structure factors for the alloy. Of these $S_{NN}(\vec{q}, \omega)$ is similar to the $S(\vec{q}, \omega)$ for a pure metal since it is, like $S(\vec{q}, \omega)$, associated with the fluctuations in the number density of the ions.

If one now introduces

$$S_{NN}(\vec{q}) = \int [\beta\omega/(e^{\beta\omega} - 1)] S_{NN}(\vec{q}, \omega) d\omega , \tag{17}$$

with similar expressions for $S_{CC}(\vec{q})$ and $S_{NC}(\vec{q})$, the expression (3) for $I(\vec{q})$ becomes

$$I(\vec{q}) = (\overline{W})^2 S_{NN}(\vec{q}) + (W_1 - W_2)^2 S_{CC}(\vec{q})$$
$$+ 2\overline{W}(W_1 - W_2) S_{NC}(\vec{q}) . \tag{18}$$

This is the expression for $I(\vec{q})$ that we had wished to derive. It is valid at all temperatures and applicable to both solids and liquids. In accordance with the remarks made in Sec. I, we confine further discussion in this paper to the case of high temperatures only.

At temperatures above the Debye temperature, the scattering may be considered to be elastic, i.e., $\beta\omega (= \hbar\omega/k_B T) \ll 1$, for all ω for which $S_{NN}(\vec{q}, \omega)$, etc., are significantly different from zero. Then the factor $\beta\omega(e^{\beta\omega} - 1)^{-1}$ in (17) may be replaced by unity, and since

$$\int e^{-i\omega t} d\omega = 2\pi\delta(t) ,$$

we see from (16) and (17) that the structure factors $S_{NN}(\vec{q})$, etc., may be written as

$$S_{NN}(\vec{q}) = N^{-1} \langle N^*(\vec{q}) N(\vec{q}) \rangle ,$$
$$S_{CC}(\vec{q}) = N \langle C^*(\vec{q}) C(\vec{q}) \rangle , \tag{19}$$

and

$$S_{NC}(\vec{q}) = \mathrm{Re} \langle N^*(\vec{q}) C(\vec{q}) \rangle ,$$

where all the $N(\vec{q})$ and $C(\vec{q})$ now refer to the same time and hence need not be considered as quantum operators, and the asterisk represents the complex conjugate. For a liquid, from symmetry, all the structure factors $S_{NN}(\vec{q})$, etc., depend on the magnitude q of $\vec{q}$ only.

It is interesting to note that the structure factors defined in (19) obey certain sum rules. We have from (19) and (9)

$$S_{NN}(\vec{q}) = N^{-1} \langle | \sum_m e^{i\vec{q}\cdot\vec{R}_m} - N\delta_{\vec{q},0} |^2 \rangle$$
$$= N^{-1} \langle \sum_{m,n} e^{i\vec{q}\cdot(\vec{R}_m - \vec{R}_n)} \rangle - N\delta_{\vec{q},0}$$
$$= N^{-1} \int e^{i\vec{q}\cdot\vec{r}} \langle \sum_{m,n} \delta(\vec{r} - \vec{R}_m + \vec{R}_n) \rangle d^3r - N\delta_{\vec{q},0}$$
$$= 1 + N^{-1} \int e^{i\vec{q}\cdot\vec{r}} \langle \sum_{m \neq n} \delta(\vec{r} - \vec{R}_m + \vec{R}_n) \rangle d^3r - N\delta_{\vec{q},0} .$$

Hence,

$$\frac{1}{V} \sum_{\vec{q}} [S_{NN}(\vec{q}) - 1] = -\frac{N}{V} + \frac{1}{N} \int \delta(\vec{r})$$
$$\times \langle \sum_{m \neq n} \delta(\vec{r} - \vec{R}_m + \vec{R}_n) \rangle d^3r , \tag{20}$$

where we have used the relation

$$\frac{1}{V} \sum_{\vec{q}} e^{i\vec{q}\cdot(\vec{r}-\vec{r}\,')} = \frac{1}{(2\pi)^3} \int e^{i\vec{q}\cdot(\vec{r}-\vec{r}\,')} d^3q$$
$$= \delta(\vec{r} - \vec{r}\,') . \tag{21}$$

The integral on the right-hand side of (20) is obviously zero. Hence,

$$\frac{1}{V}\sum_{\vec{q}}[S_{NN}(\vec{q})-1]=\frac{1}{(2\pi)^3}\int[S_{NN}(\vec{q})-1)]\,d^3q=-\frac{N}{V}\ . \tag{22}$$

Similarly, one may show that

$$\int[S_{CC}(\vec{q})-c(1-c)]\,d^3q=0\ , \tag{23}$$

$$\int S_{NC}(\vec{q})\,d^3q=0\ . \tag{24}$$

III. LONG-WAVELENGTH LIMIT OF STRUCTURE FACTORS

From the definitions (9) and (12) of $N(\vec{q})$ and $C(\vec{q})$, respectively, it is easy to see that as $q\rightarrow 0$, the structure factors defined in (19) have simple physical meaning, namely,

$$S_{NN}(0)=\langle(\Delta N)^2\rangle/N\ ,\quad S_{CC}(0)=N\langle(\Delta c)^2\rangle\ ,$$

$$S_{NC}(0)=\langle\Delta N\Delta c\rangle\ . \tag{25}$$

In (25), $\langle(\Delta N)^2\rangle$ is the mean square fluctuation in the number of particles in the volume V of the medium, $\langle(\Delta c)^2\rangle$, the mean square fluctuation in the concentration, Δc being defined by

$$\Delta c=N^{-1}[(1-c)\,\Delta N_1-c\Delta N_2]\ ,$$

and $\langle\Delta N\Delta c\rangle$ is the correlation between the two fluctuations Δc and $\Delta N=\Delta N_1+\Delta N_2$.

The expressions for the fluctuations in any set of thermodynamic variables are readily derived from standard arguments in statistical thermodynamics.[16,17] For the right-hand sides of (25), one obtains (the derivation is outlined in the Appendix)

$$S_{CC}(0)=Nk_BT\Big/\left(\frac{\partial^2G}{\partial c^2}\right)_{T,P,N}\ , \tag{26}$$

$$S_{NN}(0)=(N/V)k_BT\kappa_T+\delta^2S_{CC}(0)\ , \tag{27}$$

$$S_{NC}(0)=-\,\delta S_{CC}(0)\ , \tag{28}$$

where κ_T is the isothermal compressibility, G is the Gibbs free energy, P is the pressure, and δ is a dilatation factor defined by

$$\delta=\frac{v_1-v_2}{cv_1+(1-c)v_2}=\frac{N}{V}(v_1-v_2)\ , \tag{29}$$

where v_1 and v_2 are the partial molar volumes per atom of the two species.

For $\delta=0$, Eqs. (26)–(28) reduce to those given by Krishnan and Bhatia[9] who assumed at the outset that in a solid solution the correlations between the fluctuations in particle number and concentration may be neglected ($S_{NC}=0$). As might be expected intuitively, we see from (29) that the condition for this is that the partial molar volumes v_1 and v_2 of the two species be equal. For a solid solution whose constituents are miscible in all proportions, δ is usually small so that $S_{NC}\simeq 0$ is a reasonable approximation for such solutions. It may be noted that when $\delta=0$, $S_{NN}(0)$ has the form corresponding to a pure metal, namely,

$$S_{NN}(0)=(N/V)k_BT\kappa_T\ .$$

We shall see later that when $\delta=0$, $S_{NC}(q)$ may be expected to be zero for all q; hence, for this case, only two independent structure factors are needed to describe the structure of the alloy completely.

Next it is instructive to examine the forms of $S_{CC}(0)$ on the basis of some simple theoretical expressions for G for different types of solutions. First we recall that for a solid or liquid solution G, to a good approximation (except, perhaps, near the critical point of a phase transition), may be written as[18]

$$G=N[c\mu_1^0(P,\,T)+(1-c)\,\mu_2^0(P,\,T)]+\Delta_mG\ , \tag{30}$$

where μ_1^0 and μ_2^0 are the chemical potentials of the two pure species and Δ_mG is the free energy of mixing (arising from the entropy and energy of mixing). Further, $\Delta_mG\simeq\Delta_mF$, where Δ_mF is the Helmoltz free energy due to mixing – which is the quantity that is usually evaluated theoretically. We note that the terms in the square brackets in (30) do not contribute to $S_{CC}(0)$.

First we consider the class of solutions known generally as regular solutions. A regular solution, by definition, is one in which δ is small [$|(v_2-v_1)/v_2|$ not more than 0.3 or 0.4]. For such a solution with no superlattice structure Δ_mF in the zeroth approximation is given by[18]

$$\Delta_mG\simeq\Delta_mF=Nk_BT[c\ln c+(1-c)\ln(1-c)]$$
$$-Nc(1-c)\,w\ , \tag{31}$$

where w is an interchange energy such that if we start with two pure metals A and B and exchange an interior A atom with an interior B atom, the total *decrease* in the energy of the metals is $2w$. (Note that our w is negative of the w defined in Chap. 3 of Ref. 18.) Using (30) and (31) in (26), one has

$$S_{CC}(0)=\frac{c(1-c)}{1+2c(1-c)\,w/(k_BT)}\ . \tag{32}$$

For an ideal solution ($w=0$), $S_{CC}(0)=c(1-c)$. This corresponds to random solutions and gives the resistivity due to alloying as proportional to $c(1-c)$ and independent of temperature (Nordheim's rule[19]).

If w is negative, the solution has a critical point of mixing, the critical temperature T_{cm} being given by $T_{cm}=\frac{1}{2}|w|/k_B$. Near this point $S_{CC}(0)$ and hence the fluctuations in concentration become very large. Although the expression (31) for free energy is too simple to adequately describe partially miscible liquids and the thermodynamic theory of fluctuations breaks down near the critical point, the above argument nonetheless suggests that the resistivity-versus-temperature curve should, in general, show a cusplike rise near T_{cm} in such alloys.

In a regular solution with superlattice structure (order-disorder type of alloy), the expressions for $\Delta_m F$ are more involved. For an AB type of superlattice (as in CuZn alloy), Krishnan and Bhatia[9] have given expressions for $S_{CC}(0)$ both in the zeroth and next higher (quasichemical) approximations. For illustration, we quote here two results. In the zeroth approximation, $S_{CC}(0)$ above the critical temperature is given by just (32). Below the critical temperature and for $c=\frac{1}{2}$, $S_{CC}(0)$, in the zeroth approximation, is

$$S_{CC}(0)=\frac{1}{4}\left(\frac{1}{1-\eta^2}+\frac{T_c}{T}\right)^{-1}, \qquad T_c=\frac{w}{2k_B} \tag{33}$$

where η is the usual long-range order parameter which is unity in the perfectly ordered state ($T \ll T_c$) and zero for $T > T_c$. The temperature variation of η is given by $\eta=\tanh(\eta T_c/T)$. One may then verify that $S_{CC}(0)=0$ for $T \ll T_c$. As the temperature rises, $S_{CC}(0)$ at first increases slowly and then sharply as T approaches T_c. Above T_c, $\eta=0$ and (33) reduces to (32) with $c=\frac{1}{2}$. As mentioned in Sec. I, this type of variation of resistivity with temperature is in qualitative agreement with experiment.

When the partial molar volumes v_1 and v_2 differ considerably from each other, a more valid approximation, in a similar vein to (31), is given by Flory's formula[20] (see also p. 229 of Ref. 18)

$$\Delta_m F = Nk_BT[c\ln\phi+(1-c)\ln(1-\phi)]+Ng(c)w\ , \tag{34}$$

where the last term is the energy of mixing whose concentration dependence we have not written explicitly and ϕ is the concentration by volume of species 1, i.e.,

$$\phi=\frac{cv_1}{cv_1+(1-c)v_2}=c+c(1-c)\delta\ . \tag{35}$$

From (34) and (26) we have

$$S_{CC}(0)=\frac{c(1-c)}{1+c(1-c)\delta^2+c(1-c)g''(c)w/k_BT}\ , \tag{36}$$

where a prime denotes differentiation with respect to the argument. We see from (36) that, unlike the case of regular solutions ($\delta \ll 1$), $S_{CC}(0)$ now also depends on δ. In particular, even when the interchange energy $w=0$, $S_{CC}(0)$ is not just equal to $c(1-c)$ as for a truly random (ideal) solution.

IV. COMPARISON WITH FABER-ZIMAN THEORY AND DISCUSSION

Starting from the high-temperature limit of the expression (3) for $I(\vec{q})$, namely,

$$I(\vec{q})=\frac{1}{N}\left\langle\sum_{i,j}W_iW_je^{i\vec{q}\cdot(\vec{R}_i-\vec{R}_j)}\right\rangle\ , \tag{37}$$

Faber and Ziman[6] show that for a liquid binary alloy, $I(q)$ may be written as

$$I(q)=c_1W_1^2+c_2W_2^2+c_1^2W_1^2(a_{11}-1)+c_2^2W_2^2(a_{22}-1)$$
$$+2c_1c_2W_1W_2(a_{12}-1)\ , \tag{38}$$

where, in terms of previous notation, $c_1\equiv c$, $c_2=1-c$, and $a_{\alpha\beta}[\equiv a_{\alpha\beta}(q)]$, the partial structure factor for the species α and β, (α, $\beta=1, 2$), is defined as follows:

Let $P_{\alpha\beta}(r)$ denote the pair distribution function defined as the probability of finding an α ion in a unit volume at a radius r from the center of a β ion, normalized in such a way that it tends to unity for large r. Then

$$a_{\alpha\beta}=1+\frac{N}{V}\int_0^\infty[P_{\alpha\beta}(r)-1]\frac{\sin qr}{qr}4\pi r^2dr\ . \tag{39}$$

We have $P_{\alpha\beta}(r)=P_{\beta\alpha}(r)$ and $a_{\alpha\beta}=a_{\beta\alpha}$.

The most straightforward way to obtain correspondence between the FZ formalism and the present work is to compare the coefficients of $W_\alpha W_\beta$ in the expressions (38) and (18) for $I(q)$. This shows that the $S_{NN}(q)$, etc., defined in (19), are related to $a_{\alpha\beta}$ by

$$\begin{aligned}S_{NN}(q)&=c_1^2a_{11}+c_2^2a_{22}+2c_1c_2a_{12}\ ,\\ S_{NC}(q)&=c_1c_2[c_1(a_{11}-a_{12})-c_2(a_{22}-a_{12})]\ ,\\ S_{CC}(q)&=c_1c_2[1+c_1c_2(a_{11}+a_{22}-2a_{12})]\ ,\end{aligned} \tag{40}$$

and, conversely,

$$\begin{aligned}c_1^2a_{11}&=c_1^2S_{NN}+2c_1S_{NC}+S_{CC}-c_1c_2\ ,\\ c_2^2a_{22}&=c_2^2S_{NN}-2c_2S_{NC}+S_{CC}-c_1c_2\ ,\\ c_1c_2a_{12}&=c_1c_2S_{NN}+(c_2-c_1)S_{NC}-S_{CC}+c_1c_2\ .\end{aligned} \tag{41}$$

It will be clear from the definition (39) that all the FZ structure factors $a_{\alpha\beta}$ would have more or less similar variation with q. This is not the case for the $S(q)$'s. For example, the simplest approximation in the FZ formalism is to take[6]

$$a_{11} = a_{22} = a_{12} = a(q) \,, \tag{42}$$

say, which gives

$$S_{NN}(q) = a(q), \quad S_{NC}(q) = 0, \quad S_{CC}(q) = c_1 c_2 \,. \tag{43}$$

Evidently (42) and (43) refer to ideal solutions with $\delta = 0$.

Again, if one integrates (39) over all $\vec{q}$, using (21) and the fact that $P_{\alpha\beta}(r) = 0$ at $r = 0$, one finds (Enderby *et al.*[21])

$$(2\pi)^{-3} \int [a_{\alpha\beta}(q) - 1]\, d^3q = -N/V \,, \tag{44}$$

for all the partial structure factors $a_{\alpha\beta}$. We recall that the sum rule (22) for $S_{NN}(q)$ is just the same as (44). In contrast, the sum rules (23) and (24) for $S_{CC}(q)$ and $S_{NC}(q)$, respectively, are different from that for $S_{NN}(q)$ or $a_{\alpha\beta}$. We note that for alloys in the liquid state the sum rules (22)–(24) can be obtained by using (44) in Eq. (40).

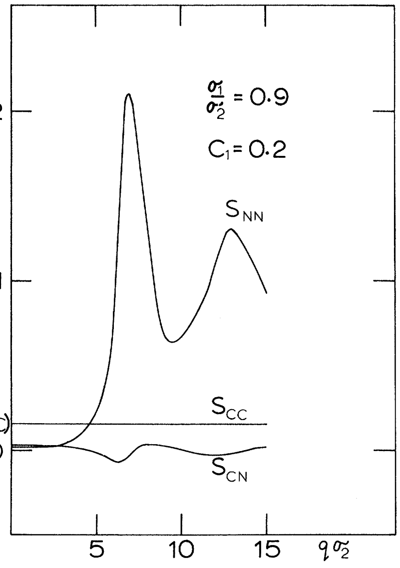

FIG. 1. Number-concentration structure factors [$S_{NN}(q)$, $S_{NC}(q)$, $S_{CC}(q)$], derived from the hard sphere Percus-Yevick model calculations (Ref. 22) with $c_1 = 0.2$ and $\sigma_1/\sigma_2 = 0.9$. Note that for this case $S_{CC}(q)$ has no significant variation with q. Further, the function $\theta(q)\,[= S_{NN}(q) - [S_{NC}(q)]^2/S_{CC}(q)]$ cannot be resolved from $S_{NN}(q)$ in this figure.

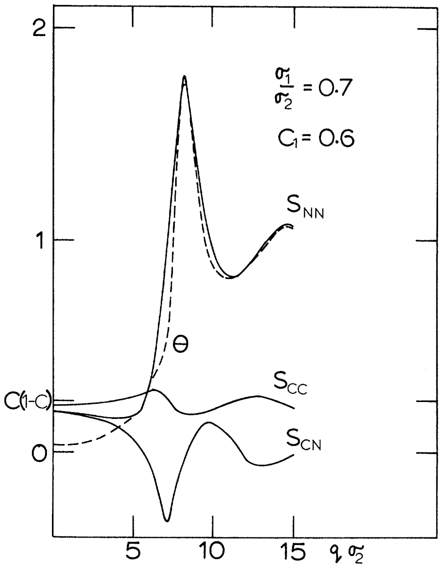

FIG. 2. Number-concentration structure factors derived from the hard sphere Percus-Yevick model calculations (Ref. 22) with $c_1 = 0.6$ and $\sigma_1/\sigma_2 = 0.7$. The function $\theta(q)$ is denoted by the broken curve.

A useful insight into the structure factor $S_{NC}(q)$, which describes N-C correlations, is obtained if we rewrite its expression from (40) making use of (39). We obtain

$$S_{NC}(q) = c_1 c_2 \frac{N}{V} \int [\mathcal{P}_{01}(r) - \mathcal{P}_{02}(r)] \frac{\sin qr}{qr}\, 4\pi r^2 dr \,, \tag{45}$$

where

$$\mathcal{P}_{0\beta} = c_\alpha P_{\alpha\beta} + c_\beta P_{\beta\beta} \,.$$

Clearly, $\mathcal{P}_{0\beta}$ ($\beta = 1, 2$) is the probability of finding any ion (α or β) in a unit volume at a distance r from the center of a β ion, normalized in such a way that it tends to unity at large r. If the two types of ions have the same volume ($v_1 = v_2$, $\delta = 0$) and are of similar shape, then one may expect that $\mathcal{P}_{01}(r) = \mathcal{P}_{02}(r)$ for all r. Hence, for this case, $S_{NC}(q) = 0$ for all q and, as mentioned earlier, only two structure factors are sufficient to describe the structure of the alloy completely. $S_{CC}(q)$ would, of course, be just $c_1 c_2$ only if the interchange energy w defined in Sec. III is also zero, as for an ideal solution.

In order to illustrate the variation of $S_{NN}(q)$, $S_{NC}(q)$, and $S_{CC}(q)$ with q, we have plotted these functions in Figs. 1 and 2 for two cases. They are constructed from the theoretical calculations of the structure factors $S_{\alpha\beta}(q)$, defined below, by Ashcroft and Langreth[22] for the hard sphere model in the Percus-Yevick approximation. $S_{\alpha\beta}$ are given by (α, $\beta = 1, 2$)

$$S_{\alpha\beta}(q)=(2N)^{-1}(c_\alpha c_\beta)^{-1/2}\langle N_\alpha^*(q)N_\beta(q)+N_\alpha(q)N_\beta^*(q)\rangle$$

$$=\delta_{\alpha\beta}+(c_\alpha c_\beta)^{1/2}(a_{\alpha\beta}-1)\ , \qquad (46)$$

which would have occurred in the expression of $I(q)$ if we had used (13) instead of (14) into (1). Figure 1 is for a smaller value of the dilatation factor δ than Fig. 2, as indicated by the ratio of the molecular diameters σ_1/σ_2 in the figures.

We first observe that, as expected, $S_{NN}(q)$ varies with q in a manner similar to the $S(q)$ for a single component liquid. However, $S_{NN}(0)$, unlike $S(0)$, is not just $(N/V)k_BT\kappa_T$. In particular, $S_{NN}(0)$ in Fig. 2 is considerably larger than in Fig. 1, which is to be expected from the long-wavelength limit formula (27) for $S_{NN}(0)$. $S_{CC}(q)$ and $S_{NC}(q)$ oscillate about the values c_1c_2 and zero, respectively. Again, due to the dilatation factor, the oscillations of $S_{NC}(q)$ are larger in Fig. 2 than in Fig. 1. A point to note is that the amplitude of oscillations in $S_{CC}(q)$ is quite small. From what we have said previously, one expects this result for solutions for which $(w/k_BT)c(1-c)$ and $\delta^2c(1-c)$ are both much less than unity.

As far as the authors are aware, the only experimentally determined partial structure factors $a_{\alpha\beta}$ which are available are those for liquid Cu_6Sn_5 (Enderby *et al.*[21,23]). $S_{NN}(q)$, etc., determined from these are given in Fig. 3. We see that $S_{NN}(q)$ and $S_{CC}(q)$ for all q and $S_{NC}(q)$ for $q \gtrsim 2.2$, behave roughly in the same manner as the corresponding functions in Fig. 2. For $q < 2.2$, however, $S_{NC}(q)$ dips down and gradually approaches nearly zero instead of tending to the value

$$S_{NC}(0)=-\delta S_{CC}(0)=0.8\,S_{CC}(0)\ ,$$

expected from (28) and the fact that for Cu_6Sn_5, $\delta \simeq -0.8$. We believe it not unlikely that this discrepancy is due to extreme difficulties in disentangling $a_{\alpha\beta}$ from the neutron scattering data, particularly at low values of q.

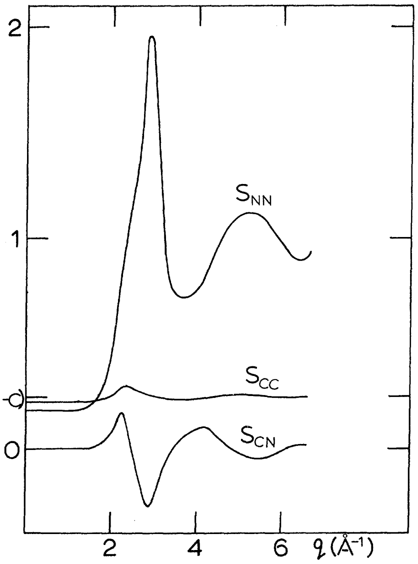

FIG. 3. Number-concentration structure factors derived from the experimentally determined FZ partial structure factors in $Cu_6\,Sn_5$ (Ref. 21).

To have some idea of the values of $a_{\alpha\beta}(0)$ expected thermodynamically, let us take, as an illustration, in expression (36) the quantity $c(1-c)g''(c)w/k_BT$ to be 0.5 (for $c=\frac{1}{2}$), a value not untypical for a 50-50 alloy which exhibits short-range order. Then from (36) and Eqs. (26)-(28), we obtain $S_{CC}(0) \simeq 0.16$, $S_{NC}(0)\simeq 0.13$, and $S_{NN}(0)\simeq 0.14$, where we have taken $\delta=-0.8$ and $(N/V)k_BT\kappa_T \simeq 0.04$. Hence, from (41), one obtains

$$a_{11}(0)\simeq 0.3,\quad a_{22}(0)\simeq -0.8,\quad \text{and}\quad a_{12}(0)\simeq 0.5\ ,$$

the index 1 referring to copper. If we take $w=0$, the corresponding values of $a_{\alpha\beta}(0)$ are

$$a_{11}(0)\simeq 0.7,\quad a_{22}(0)\simeq -0.7,\quad \text{and}\quad a_{12}(0)\simeq 0.3\ .$$

We note that δ and c for Cu_6Sn_5 are quite close to those for which $S_{NN}(q)$, etc., are given in Fig. 2 on the basis of the hard sphere model calculations by Ashcroft and Langreth.[22] The values of $S_{NN}(0)$, etc., in Fig. 2 imply

$$a_{11}(0)\simeq 0.7,\quad a_{22}(0)\simeq -0.8,\quad \text{and}\ a_{12}(0)\simeq 0.1\ .$$

The three sets of values of $a_{\alpha\beta}(0)$ given above may be contrasted with the experimental set in Ref. 21, namely,

$$a_{11}(0)\simeq 0.05,\ a_{22}(0)\simeq 0.0,\quad \text{and}\quad a_{12}(0)\simeq 0.35\ .$$

Finally, it is of interest to mention that the long-wavelength limit formulas (26)-(28) for $S_{NN}(0)$, etc., suggest the introduction of two related functions. Let

$$\Delta(\vec{q})=S_{NC}(\vec{q})/S_{CC}(\vec{q})\ , \qquad (47)$$

$$\theta(\vec{q})=S_{NN}(\vec{q})-[\Delta(\vec{q})]^2S_{CC}(\vec{q})\ . \qquad (48)$$

Since $\Delta(0)=-\delta$, $\Delta(\vec{q})$ may be called the dilatation function. $\theta(\vec{q})$ has the property that $\theta(0)=(N/V)\times k_BT\kappa_T$. We note that since by definition $S_{NN}(\vec{q})$ and $S_{CC}(\vec{q})$ are positive for all $\vec{q}$, and since $S_{NN}(\vec{q})S_{CC}(\vec{q})-[S_{NC}(\vec{q})]^2$ must be greater than or equal to zero if $I(\vec{q})$ is to be positive for all real values of W_1 and W_2, it follows that $\theta(\vec{q})\geqslant 0$ for all $\vec{q}$. The difference between $\theta(\vec{q})$ and $S_{NN}(\vec{q})$ is illustrated in Figs. 1 and 2.

In terms of $\theta(\vec{q})$ and $\Delta(\vec{q})$, the expression (18) for $I(\vec{q})$ may be written as

$$I(\vec{q}) = (\overline{W})^2\,\theta(\vec{q}) + (W_1' - W_2')^2 S_{CC}(\vec{q}) \ , \tag{49}$$

where

$$W_1' = W_1[1 + c\Delta(\vec{q})] \ , \quad W_2' = W_2[1 - (1-c)\Delta(\vec{q})] \ . \tag{50}$$

Such a form for $I(\vec{q})$ is reminiscent of the treatment given by FZ[6] for the case of low concentration. The function $\sigma(q)$ introduced there is such that

$$\sigma(0) = -\delta = -(v_1 - v_2)/v_2 \quad \text{for } c \ll 1$$

and is similar to the function $\Delta(\vec{q})$.

The form (49) for $I(\vec{q})$ may be useful in interpreting experimental data on the resisitivities in some alloys. This is because, first, δ and consequently $\Delta(\vec{q})$ and $W_1' - W_2'$ may be considered practically independent of temperature. Second, if the mixture is near ideal or athermal ($w \simeq 0$), $S_{CC}(\vec{q})$ will also be independent of temperature, so that all the temperature dependence of $I(\vec{q})$ would be concentrated in the single function $\theta(\vec{q})$.

V. CONCLUSION AND SUMMARY

In this paper, it has been shown that in the weak scattering approximation, the scattering function $I(\vec{q})$, occurring in the expression for the resistivity of a binary alloy, may be quite generally written in terms of three structure factors, $S_{NN}(\vec{q})$, $S_{NC}(\vec{q})$, and $S_{CC}(\vec{q})$, constructed from the Fourier transforms of the local number density and concentration of the alloy.

At temperatures above the Debye temperature, these structure factors have the property that in the long-wavelength limit ($q \to 0$), $S_{NN}(0)$, and $S_{CC}(0)$ represent, respectively, the mean square fluctuations in the ion number and their concentration, and $S_{NC}(0)$ describes the average of the correlations between these two fluctuations. Thermodynamic formulas for these averages and hence for $S_{NN}(0)$, $S_{NC}(0)$, and $S_{CC}(0)$ are given, and their concentration and temperature dependence are examined for different types of mixtures. For liquid alloys, the expression for $I(\vec{q})$ given here is, of course, formally equivalent to that of FZ, and the FZ partial structure factors are linear combinations of $S_{NN}(\vec{q})$, $S_{CC}(\vec{q})$, and $S_{NC}(\vec{q})$. Our work shows that the present formalism provides rather readily some additional information on the structure factors which can be useful in interpreting the various experimental data. This is desirable, particularly since both the theoretical and experimental (via neutron and x-ray scattering) techniques for determining the structure factors are, as yet, of limited applicability.

At low temperatures, where the inelastic nature of the scattering has to be considered, the evaluation of $S_{NN}(\vec{q})$, etc., requires the knowledge of the dynamical structure factors $S_{NN}(\vec{q}, \omega)$, etc., introduced in Eqs. (16). We may note that the expression for the inelastic scattering, per unit solid angle, per unit energy range, of thermal neutrons by the alloy may also be written in terms of $S_{NN}(\vec{q}, \omega)$, etc., it is essentially $\Gamma(\vec{q}, \omega)$, Eq. (15), with appropriate W's. Hence it is, in principle, possible to determine them experimentally. It is hoped that the low-temperature formalism given here may be useful in such problems as the calculation of electrical resistivity of alloys where the two types of ions have different[24] atomic radii, masses, and force constants.

APPENDIX

Let N_1 and N_2 denote the mean number of atoms of the two types in a given macroscopic volume V (in thermal bath with the rest of the medium) and let ΔN_1 and ΔN_2 denote the instantaneous deviations from the mean. The probability for these deviations is given by[16,17] ($i, j = 1, 2$)

$$w = w_0 \exp\left(-\sum_{i,j} \frac{F_{ij}\Delta N_i \Delta N_j}{2k_B T}\right) , \tag{A1}$$

where w_0 is the normalization constant and

$$F_{ij} = \left(\frac{\partial^2 F}{\partial N_i \partial N_j}\right)_{V,T} = \left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,V,N'} = \left(\frac{\partial \mu_j}{\partial N_i}\right)_{T,V,N'} = F_{ji} \ , \tag{A2}$$

$$\mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N'} = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N'} \ . \tag{A3}$$

In (A2) and (A3), F and G are, respectively, the Helmholtz and Gibbs free energies, μ_i is the chemical potential for the species i, and the subscript N' indicates that a N_i with respect to which differentiation is not being carried out is held constant. From the property of the Gaussian distributions, one has

$$\langle \Delta N_i \Delta N_j \rangle = k_B T (F^{-1})_{ij} \ , \tag{A4}$$

where $(F^{-1})_{ij}$ is the i-j element of the inverse matrix of F_{ij}.

Now

$$\left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,V,N'} = \left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,P,N'} + \frac{v_i v_j}{(V\kappa_T)} \ , \tag{A5}$$

where $v_i = (\partial V/\partial N_i)_{T,P,N'}$ is the partial molar volume, per atom (molecule), for the species i and $V=N_1v_1+N_2v_2$. Hence

$$\sum_{i,j} F_{ij}\,\Delta N_i\,\Delta N_j=\frac{1}{V\kappa_T}(v_1\Delta N_1+v_2\Delta N_2)^2 +\sum_{i,j}\left(\frac{\partial\mu_i}{\partial N_j}\right)_{T,P,N'}\Delta N_i\,\Delta N_j\;. \qquad \text{(A6)}$$

Using the Gibbs-Duhem relations

$$\sum_{i=1}^{2} N_i\left(\frac{\partial\mu_i}{\partial N_j}\right)_{T,P,N'}=0\;,\quad j=1,\,2$$

to simplify the sum in (A6) and remembering that $\Delta N=\Delta N_1+\Delta N_2$ and $N\Delta c=(1-c)\Delta N_1-c\Delta N_2$, one obtains

$$\sum_{i,j} F_{ij}\,\Delta N_i\,\Delta N_j=\left(\frac{V}{(\kappa_T N^2)}\right)[\Delta N+N(\Delta c)\delta]^2+B(\Delta c)^2\;, \qquad \text{(A7)}$$

where δ is given by (29) and

$$B=\left(\frac{N^4}{N_2^2}\right)\left(\frac{\partial\mu_1}{\partial N_1}\right)_{T,P,N'}=\left(\frac{\partial^2 G}{\partial c^2}\right)_{T,P,N}\;. \qquad \text{(A8)}$$

Substituting (A7) in (A1) and using expressions of the type (A4) for the averages, one immediately obtains the relations (26)–(28).

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[23] We would like to thank Dr. J. E. Enderby for kindly supplying us with the detailed table of $a_{\alpha\beta}$.

[24] The simple case, where these quantities are equal for the two types of ions and the ions are distributed at random, can be dealt with directly on the basis of Eqs. (1)–(3) without introducing the three structure factors; see Ref. 13.