

Theory of Disordered Ternary Alloys. I. The Linear Approximation*†

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A Green's-function formulation of the statistical mechanics of ternary systems, with arbitrary composition and pairwise interatomic potentials of arbitrary range, is given. Exact formal expressions for the relevant correlation parameters are derived. The linear approximation is worked out in detail, and expressions for the correlation parameters are derived in a form analogous to the results of self-consistent-mean-field theories. The usefulness of this representation lies in its qualitative validity even in the vicinity of the transition points. The transition temperatures are estimated through the condition of macroscopic increase in the range of the appropriate correlation parameters at the onset of spatial ordering. The relevance of the given expressions for inferring the ground-state orderings, i.e., the actual configurations that might obtain when the ordering sets in, is indicated. In the limit that the atomic composition of one of the components of the ternary system approaches zero, our results smoothly reduce to the corresponding self-consistent, linear-approximation results for binary systems derived by Clapp and Moss.

I. INTRODUCTION

THE central problem in the study of ternary alloys is the derivation of the statistical correlation functions. These are related to the conditional probabilities of the occurrence of an atom of type A , B , or C , in arbitrary spatial location when a particular type of atom is known to be present on a particular lattice position. The familiar notions of short- and long-range order parameters are special features of this general problem.

The experimental analysis of scattered diffuse x-ray or neutron intensities, produced by the statistical correlations existing in the disordered ternary alloys, can be related to the inverse-lattice Fourier transforms of a total of three linearly independent correlation parameters: $\alpha^{AB}(ij)$, $\alpha^{BC}(ij)$, and $\alpha^{AC}(ij)$.¹ In this paper, a statistical formulation designed for the computation of these correlation parameters, as functions of the system temperature and the interatomic potentials, is presented. In view of the remarkable success of the Clapp-Moss² calculation for the corresponding correlation parameter for a disordered binary alloy—there is only one such parameter for a binary system—in the present paper we shall, for convenience, restrict ourselves to those simple considerations which suffice to yield the correlation parameters for ternary systems to the same degree of rigor and accuracy as that of the results of Refs. 2–4 for binaries. Further improvements and generalizations of these considerations, in regard both to the accuracy of the mathematical approximations involved and of the features of the physical model being considered, remain future projects.

Section II deals with the description, and an appro-

appropriate spin representation, of the rather simplified model to be considered in the present paper. Section III contains the essentials of the mathematical solution of the problem. While this solution is exact, it is highly formal. In order to do calculations with this solution, a series expansion scheme has to be evolved. Section IV deals with the first-order evaluation of the correlation functions. This consists in retaining only those terms exactly which lead to the dominant temperature dependence. However, the nature of the solution is such that it retains a subset of terms in all higher orders of temperature. This feature is similar to that possessed by self-consistent mean field theory solutions and therefore leads to an approximate, but meaningful, solution even in the neighborhood of the phase transition. In this manner, expressions for the transition temperatures are derived.

The results are discussed and conclusions are presented in Sec. V.

II. FORMULATION

Consider a disordered ternary alloy with a total of N atoms of which N^A , N^B , and N^C are of types A , B , and C , respectively. Assume that these atoms are distributed on a regular, isotropic, and rigid lattice consisting of N sites. Further, postulate that the system—which has only its configurational degrees of freedom—can be described by a configurational interaction which is the sum only of two-body (i.e., pairwise) interactions, i.e.,

$$H(\text{config}) = H^{AA} + H^{BB} + H^{CC} + H^{AB} + H^{AC} + H^{BC}, \quad (2.1a)$$

where

$$H^{\lambda\lambda} = \frac{1}{2} \sum_{i,j} V^{\lambda\lambda}(ij) \sigma_i^\lambda \sigma_j^\lambda, \quad (2.1b)$$

$$H^{\lambda\nu} = \frac{1}{2} \sum_{\substack{\lambda \neq \nu \\ i,j}} V^{\lambda\nu}(ij) [\sigma_i^\lambda \sigma_j^\nu + \sigma_i^\nu \sigma_j^\lambda], \quad (2.1c)$$

$$V^{\lambda\nu}(ij) = V^{\nu\lambda}(ij) = V^{\nu\lambda}(ji) = V^{\lambda\nu}(ji), \quad (2.1d)$$

$$V^{\lambda\nu}(ii) = V^{\lambda\lambda}(ii) \equiv 0; \quad \lambda, \nu \equiv A, B, C, \quad (2.1e)$$

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¹ B. E. Warren, B. L. Averbach, and B. W. Roberts, J. Appl. Phys. **22**, 1493 (1951); L. Muldrew, Technical Report No. 2, Temple University, 1953 (unpublished).

² P. C. Clapp and S. C. Moss, Phys. Rev. **142**, 418 (1966).

³ P. C. Clapp and S. C. Moss (unpublished).

⁴ S. C. Moss and P. C. Clapp (unpublished).

and where the occupation operators σ_i^λ are defined as follows.

$$\begin{aligned} \sigma_i^\lambda &= +1, \text{ if the } i\text{th lattice position is occupied by an} \\ &\quad \text{atom of variety } \lambda \\ &= 0, \text{ otherwise.} \end{aligned} \quad (2.1f)$$

To study the statistical mechanics of the system, it is convenient to introduce a pseudospin representation which will transform the set of Eqs. (2.1) into a generalized Ising model.⁵ As any particular lattice site is allowed to be occupied by only one of the three atomic species A , B , and C , the appropriate representation is within the subspace of spin 1 (in Dirac's units, where $\hbar=1$). The appropriate choice for the occupation operators are, therefore,

$$\sigma_i^\lambda = \frac{1}{2}[(S_i^z)^2 + S_i^z], \quad (2.2a)$$

$$\sigma_i^{\lambda'} = 1 - (S_i^z)^2, \quad (2.2b)$$

$$\sigma_i^{\lambda''} = \frac{1}{2}[(S_i^z)^2 - S_i^z], \quad (2.2c)$$

where the set $(\lambda, \lambda', \lambda'')$ is the same as the set (A, B, C) . For the sake of definiteness, in Eqs. (2.2) above, we shall henceforth make the choice that $\lambda \equiv A$, $\lambda' \equiv B$, and $\lambda'' \equiv C$. (Note that any of the other five choices would do equally well as long as we stick to it once it is made).

The configurational interaction, $H(\text{config})$, can now readily be written in terms of the S^z operators. However, rather than displaying $H(\text{config})$ in this new representation, it is in order first to give some thought to the actual procedure whereby the statistical mechanics of the system should be computed. In common with the study of macroscopic systems with given amounts of various constituents, the grand canonical averaging procedure is the most convenient to use here. To this end, we need to introduce an appropriate set of chemical potentials. The choice of the size of these chemical potentials would then enable us to preserve the requirement of statistical consistency at any given temperature T such that the average number of A , B , and C atoms is identical to the actual composition of our system.

In view of the assumption that the alloy does not contain vacancies, etc., which is implicit in Eqs. (2.1) and (2.2), the total number N of the atoms is equal to the sum of the A , B , and C atoms, i.e.,

$$N = N^A + N^B + N^C. \quad (2.3)$$

Therefore, the amounts of only two of the three components of the alloy can be considered to be independent thermodynamic variables and as such we need a total of only two chemical potentials, say, μ and ρ .

⁵ Note that the term "generalized Ising model" for the set of Eqs. (2.5) is probably not in common use in the literature. However, it is our feeling that due to the dependence of the interaction only on the z components of spins, the resultant statistical mechanics of the system has similarities with that of the usual Ising model well known in the study of binary systems.

The appropriate transformation of the configuration interaction can now be made and the operation of statistical averaging defined; the thermodynamic average of a set of operators Ω is

$$\langle \Omega \rangle = \frac{\text{Tr}[\exp(-\beta \mathfrak{H}) \Omega]}{\text{Tr}[\exp(-\beta \mathfrak{H})]}, \quad (2.4)$$

where

$$\begin{aligned} \mathfrak{H} = & -\frac{1}{2} \sum_{i,j} [I_1(ij) S_i^z S_j^z + I_2(ij) (S_i^z)^2 (S_j^z)^2 \\ & + I_3(ij) (S_i^z)^2 S_j^z] - \mu \sum_i S_i^z - \rho \sum_i (S_i^z)^2, \end{aligned} \quad (2.5a)$$

$$I_1(ij) = \frac{1}{4} [2V^{AC}(ij) - V^{CC}(ij) - V^{AA}(ij)], \quad (2.5b)$$

$$\begin{aligned} I_2(ij) = & V^{AB}(ij) + V^{BC}(ij) - V^{BB}(ij) \\ & - \frac{1}{4} [V^{AA}(ij) + V^{CC}(ij) + 2V^{AC}(ij)], \end{aligned} \quad (2.5c)$$

$$\begin{aligned} I_3(ij) = & V^{AB}(ij) - V^{BC}(ij) \\ & + \frac{1}{2} [V^{CC}(ij) - V^{AA}(ij)], \end{aligned} \quad (2.5d)$$

$$I_\delta(ii) = I_\delta(jj) = 0; \quad \delta = 1, 2, 3. \quad (2.5e)$$

The chemical potentials μ and ρ are computed from the relations:

$$\langle N^\lambda \rangle = N^\lambda. \quad (2.6)$$

In terms of the spin operators, Eqs. (2.6) reduce to

$$\langle S_i^z \rangle \equiv m = m^A - m^C, \quad (2.7a)$$

$$\langle (S_i^z)^2 \rangle \equiv M = m^A + m^C, \quad (2.7b)$$

where

$$m^\lambda = N^\lambda / N. \quad (2.7c)$$

III. FORMAL SOLUTION

The formalism of thermodynamic Green's functions is particularly convenient for the present calculation. This method is in common use⁶ and is amply described in the literature. For the present purposes it suffices to note that if a double-time, retarded Green's function is defined as

$$\begin{aligned} -i\Theta(t-t') \langle a_g(t) b_p(t') + b_p(t') a_g(t) \rangle & \equiv \langle \langle a_g(t); b_p(t') \rangle \rangle \\ & = \int_{-\infty}^{+\infty} \langle \langle a_g; b_p \rangle \rangle_{(E)} \exp[-iE(t-t')] dE, \end{aligned} \quad (3.1)$$

where $\Theta(x)$ is the unit step function which is zero for $x < 0$ and is +1 for $x > 0$, and where $a_g(t)$ is an operator referring to spatial location g and time t such that

$$a_g(t) = \exp(i\mathfrak{H}t) a_g(0) \exp(-i\mathfrak{H}t). \quad (3.2)$$

The correlation function $\langle a_g(t) b_p(t) \rangle$ is simply related to the imaginary part of the energy Fourier transform

⁶ See, for example, the references cited in R. A. Tahir-Kheli and D. ter Haar, Phys. Rev. **127**, 88 (1962).

of the Green's function through the relation

$$\langle a_g(t)b_p(t) \rangle = \lim_{\epsilon \rightarrow +0} -2 \int_{-\infty}^{+\infty} \frac{d\omega \operatorname{Im}[\langle\langle a_g; b_p \rangle\rangle_{(\omega+i\epsilon)}]}{[1+\exp(-\beta\omega)]} \quad (3.3)$$

(lim $\epsilon \rightarrow +0$)

For the spin 1 system under consideration it is sufficient to study the properties of two families of Green's functions⁷:

$$\langle\langle [\dots] S_{\sigma}^+(t); S_{\sigma}^-(t') \rangle\rangle$$

and

$$\langle\langle [\dots] S_{\sigma}^z(t) S_{\sigma}^+(t); S_{\sigma}^-(t') \rangle\rangle.$$

The notation $[\dots]$ refers to any set of S^z operators not pertaining to the lattice position g .

The relevant Eqs. of motion of these Green's functions are readily found to be:

$$E \langle\langle [\dots] S_{\sigma}^+; S_{\sigma}^- \rangle\rangle_{(B)} = \frac{1}{2\pi} \langle\langle [\dots] [4 - 2(S_{\sigma}^z)^2] \rangle\rangle + \langle\langle [\dots] E^{(1)}(g) S_{\sigma}^+; S_{\sigma}^- \rangle\rangle_{(B)} + \langle\langle [\dots] E^{(2)}(g) S_{\sigma}^z S_{\sigma}^+; S_{\sigma}^- \rangle\rangle_{(B)}, \quad (3.4)$$

$$E \langle\langle [\dots] S_{\sigma}^z S_{\sigma}^+; S_{\sigma}^- \rangle\rangle_{(B)} = \frac{1}{2\pi} \langle\langle [\dots] [2 + S_{\sigma}^z - (S_{\sigma}^z)^2] \rangle\rangle + \langle\langle [\dots] E^{(3)}(g) S_{\sigma}^z S_{\sigma}^+; S_{\sigma}^- \rangle\rangle_{(B)}, \quad (3.5)$$

where

$$E^{(1)}(g) = \mu - \rho + \frac{1}{2} \sum_f [2I_1(gf) - I_3(gf)] S_f^z + \frac{1}{2} \sum_f [I_3(gf) - 2I_2(gf)] (S_f^z)^2, \quad (3.6)$$

$$E^{(2)}(g) = 2\rho + \sum_f [I_3(gf) S_f^z + 2I_2(gf) (S_f^z)^2], \quad (3.7)$$

$$E^{(3)}(g) = E^{(1)}(g) + E^{(2)}(g). \quad (3.8)$$

$$\langle\langle [\dots] S_{\sigma}^+; S_{\sigma}^- \rangle\rangle_{(B)} = \frac{1}{2\pi} \left\langle [\dots] \frac{4 - 2(S_{\sigma}^z)^2 + \{ [2 + S_{\sigma}^z - (S_{\sigma}^z)^2] E^{(2)}(g) / [E - E^{(3)}(g)] \}}{E - E^{(1)}(g)} \right\rangle. \quad (3.14)$$

It might be mentioned here that in the above discussion the Ising-like structure of our system has been implicitly invoked. Specifically, the absence of the spin flip terms in \mathcal{H} has dictated the ignoring of any consideration of averages of the form $\langle\langle [\dots] S_{\sigma}^+ S_{\sigma}^- \rangle\rangle$ when $g \neq p$. In view of the fact that the set of operators $[\dots]$ have always been assumed to be composed of S^z , rather than of S^+ , operators, such averages can be shown to be identically vanishing.⁸

⁷ Note that the Green's function $\langle\langle [\dots] (S_{\sigma}^z)^2 S_{\sigma}^+; S_{\sigma}^- \rangle\rangle$ is redundant here.

⁸ This can be self-consistently verified by starting with Green's functions of the form $\langle\langle [\dots] S_{\sigma}^+; S_{\sigma}^- \rangle\rangle$ and $\langle\langle [\dots] S_{\sigma}^z S_{\sigma}^+; S_{\sigma}^- \rangle\rangle$ instead of those used in the text.

Equations (3.4) and (3.5) form a coupled, infinite set. It turns out that one can write down exact, formal solutions for these. To see how this might be done, substitute in Eq. (3.5)

$$[\dots] = [E^{(3)}(g)]^n, \quad n = 0, 1, 2, \dots, \infty \quad (3.9)$$

and notice that the resultant set of equations forms a geometric set with the solution

$$\langle\langle S_{\sigma}^z S_{\sigma}^+; S_{\sigma}^- \rangle\rangle_{(B)} = \frac{1}{2\pi} \left\langle \frac{2 + S_{\sigma}^z - (S_{\sigma}^z)^2}{E - E^{(3)}(g)} \right\rangle, \quad (3.10)$$

and therefore,

$$\langle\langle [\dots] S_{\sigma}^z S_{\sigma}^+; S_{\sigma}^- \rangle\rangle_{(B)} = \frac{1}{2\pi} \left\langle \frac{[2 + S_{\sigma}^z - (S_{\sigma}^z)^2] [\dots]}{E - E^{(3)}(g)} \right\rangle. \quad (3.11)$$

We remind ourselves that the operator $[\dots]$ is arbitrary except for the restriction that it is not allowed to contain any spin operators referring to lattice position g .

Having found the above solutions, we now turn to the set of Eqs. (3.4). Here we combine the first and the last terms on the right-hand side and write

$$E \langle\langle [\dots] S_{\sigma}^+; S_{\sigma}^- \rangle\rangle_{(B)} = \frac{1}{2\pi} \left\langle [\dots] \left\{ 4 - 2(S_{\sigma}^z)^2 + \frac{[2 + S_{\sigma}^z - (S_{\sigma}^z)^2] E^{(2)}(g)}{E - E^{(3)}(g)} \right\} \right\rangle + \langle\langle [\dots] E^{(1)}(g) S_{\sigma}^+; S_{\sigma}^- \rangle\rangle_{(B)}. \quad (3.12)$$

The set of Eqs. (3.12) is, therefore, also a geometric one and the substitutions

$$[\dots] \equiv [E^{(1)}(g)]^n, \quad n = 0, 1, 2, \dots, \infty \quad (3.13)$$

readily lead to the formal solution

Equations (3.11) and (3.14) have next to be transformed into appropriate correlation functions. Using Eq. (3.3), this can be readily accomplished and we get

$$\langle\langle [\dots] [S_{\sigma}^z + (S_{\sigma}^z)^2] \rangle\rangle = \langle\langle [\dots] \Phi(3) [2 + S_{\sigma}^z - (S_{\sigma}^z)^2] \rangle\rangle, \quad (3.15)$$

and

$$\langle\langle [1 - \Phi(1) - \Phi(3)] [2 - (S_{\sigma}^z)^2] [\dots] \rangle\rangle = \langle\langle [\Phi(3) - \Phi(1) - 1] S_{\sigma}^z [\dots] \rangle\rangle, \quad (3.16)$$

where

$$[\Phi(n)]^{-1} = \exp[-\beta E^{(n)}(g)] + 1, \quad n = 1, 3. \quad (3.17)$$

For future convenience we shall use the notation

$$\begin{aligned}\bar{E}^{(1)}(g) &= E^{(1)}(g) - \mu + \rho, \\ \bar{E}^{(3)}(g) &= E^{(3)}(g) - \mu - \rho.\end{aligned}\quad (3.18)$$

IV. LINEAR APPROXIMATION

As already noted, the solution contained in Eqs. (3.15)–(3.17) is rather formal. It turns out, however, that starting from these equations a convergent series expansion for the correlation parameters, in powers of what essentially amounts to the ratio of the appropriate ordering temperature to that of the system temperature, can be readily generated. In the present section we shall initially be concerned with the salient features of the mechanics of the generation of such a power series expansion. We shall find that while both the procedure, as well as the resulting algebra, is straightforward, the details of the computation become rapidly cumbersome as higher powers in this series expansion are calculated. This feature, of course, is common to all the power expansion schemes used in the study of the interacting many-body problem, whether they be perturbation expansions, virial expansions, or temperature expansions. The attractive aspect of the present formulation lies principally in its versatility, which enables one quite naturally to calculate the correlation parameters for arbitrary composition as well as arbitrary range of the interparticle interaction in a straightforward manner.

Let us first look at the functions $\Phi(1)$ and $\Phi(3)$ given in Eqs. (3.17) and (3.18). The appropriate high-temperature power expansions are

$$\begin{aligned}\Phi(1) &= X(0) + \beta X(1)\bar{E}^{(1)}(g) \\ &\quad + \sum_{n=2}^{\infty} X(n)[\beta\bar{E}^{(1)}(g)]^n,\end{aligned}\quad (4.1)$$

$$\begin{aligned}\Phi(3) &= Y(0) + \beta Y(1)\bar{E}^{(3)}(g) \\ &\quad + \sum_{n=2}^{\infty} Y(n)[\beta\bar{E}^{(3)}(g)]^n,\end{aligned}\quad (4.2)$$

where $X(n)$ and $Y(n)$ are functions only of $X(0)$ and $Y(0)$ and where

$$[X(0)]^{-1} = 1 + \exp[-\beta(\mu - \rho)], \quad (4.3)$$

$$[Y(0)]^{-1} = 1 + \exp[-\beta(\mu - \rho)], \quad (4.4)$$

$$\begin{aligned}X(1) &= X(0)[1 - X(0)], \\ Y(1) &= Y(0)[1 - Y(0)], \text{ etc.}\end{aligned}\quad (4.5)$$

Note that in the above we have carefully avoided making any statement about the magnitude of $\beta\mu$ and $\beta\rho$ and have not expanded the exponentials containing these factors. This ensures the validity of the resultant expansions for arbitrary compositions which, of course, include those situations when these factors, rather than being small compared to unity,—as they would be for stoichiometric compositions—are of the same order of magnitude as unity.

The next step is to insert the expansions, Eqs. (4.1)–(4.5), into Eqs. (3.15) and (3.16). Let us first choose the operator $[\dots]$ to be simply unity. This leads to a set of expressions for the averages m and M as functions of $X(0)$, $Y(0)$ and of two, three, and higher particle correlation parameters. Now, in view of the fact that all correlation parameters are bounded in magnitude between 0 and 1, i.e.,

$$0 \leq |\langle (S_1^z)^{n_1} (S_2^z)^{n_2}, \dots, (S_i^z)^{n_i} \rangle| \leq 1, \quad (4.6)$$

where $1, 2, \dots, i$ are arbitrary spatial locations and where n_1, n_2, \dots, n_i are arbitrary positive integers or zero. The terms involving the correlation parameters are smaller than those involving just $X(0)$ and $Y(0)$ by at least a factor of order (T_c/T) , where T_c is of the order of magnitude of a transition temperature. Therefore, we get

$$X(0) = 2[1 - M]/[2 - m - M] + o(T_c/T), \quad (4.7)$$

$$Y(0) = [m + M]/[2 + m - M] + o(T_c/T). \quad (4.8)$$

Having derived the zeroth approximation to $X(0)$ and $Y(0)$, we proceed to the derivation of an equivalent approximation for the correlation functions $\langle S_g^z S_p^z \rangle$, $\langle (S_g^z)^2 (S_p^z)^2 \rangle$, and $\langle S_g^z (S_p^z)^2 \rangle$. This can be done by respectively inserting in the expanded versions of Eqs. (3.15) and (3.16) the following choices for the operator $[\dots]$:

$$[\dots] = S_p^z; \quad [\dots] = (S_p^z)^2; \quad p \neq g. \quad (4.9)$$

We find that the left-hand side, as well as the right-hand side, of these equations contain the correlation functions under study. Once again, we ignore the terms proportional to β , knowing that they will always contribute in the order (T_c/T) lower than the terms retained. This procedure rapidly leads to what turns out to be the simple mean field theory result:

$$\langle S_1^z S_2^z \rangle = m^2 + \delta_{1,2}[M - m^2] + o(T_c/T), \quad (4.10a)$$

$$\langle (S_1^z)^2 (S_2^z)^2 \rangle = M^2 + \delta_{1,2}[M - M^2] + o(T_c/T), \quad (4.10b)$$

$$\langle (S_1^z) (S_2^z)^2 \rangle = Mm + \delta_{1,2}[m - Mm] + o(T_c/T). \quad (4.10c)$$

The stage is now set for finding the next-order approximation. This consists in retaining the dominant temperature-dependent terms exactly and ignoring the consideration of all those terms which will contribute in the order $(T_c/T)^n$ for $n > 2$. However, before this can be done we need to know the following three particle correlation functions correct to the zeroth order:

$$\begin{aligned}\langle S_1^z S_2^z S_3^z \rangle; \quad \langle S_1^z S_2^z (S_3^z)^2 \rangle; \quad \langle S_1^z (S_2^z)^2 (S_3^z)^2 \rangle; \\ \langle (S_1^z)^2 (S_2^z)^2 (S_3^z)^2 \rangle.\end{aligned}\quad (4.11)$$

The obvious procedure for their computation would be as follows. In the expanded versions of Eqs. (3.15)–(3.16), successively introduce the following substitutions for $[\dots]$:

$$[\dots] = S_1^z S_2^z; \quad S_1^z (S_2^z)^2; \quad (S_1^z)^2 (S_2^z)^2; \quad 1, 2 \neq g \quad (4.12)$$

and retain only the zeroth-order terms in the (T_c/T) power expansion. The resultant equations are now readily solved. It turns out that the zeroth-order result for these correlation functions is identical to the corresponding mean field theory result,⁹ i.e.,

$$\begin{aligned} \langle S_1^z S_2^z S_3^z \rangle &= m^3 + [\delta_{1,2} + \delta_{1,3} + \delta_{2,3}] [Mm - m^3] + \delta_{1,2}\delta_{1,3} \\ &\quad \times [2m^3 + m - 3Mm] + o(T_c/T), \quad (4.13a) \end{aligned}$$

$$\begin{aligned} \langle S_1^z S_2^z (S_3^z)^2 \rangle &= m^2 M + [\delta_{1,3} + \delta_{2,3}] [m^2 - m^2 M] + \delta_{1,2} [M^2 - Mm^2] \\ &\quad + \delta_{1,2}\delta_{1,3} [M - M^2 - 2m^2 + 2m^2 M] \\ &\quad + o(T_c/T), \quad (4.13b) \end{aligned}$$

$$\begin{aligned} \langle S_1^z (S_2^z)^2 (S_3^z)^2 \rangle &= mM^2 + [mM - m^2 M^2] (\delta_{1,2} + \delta_{1,3} + \delta_{2,3}) + \delta_{1,2}\delta_{1,3} \\ &\quad \times [m - 3mM + 2mM^2] + o(T_c/T), \quad (4.13c) \end{aligned}$$

$$\begin{aligned} \langle (S_1^z)^2 (S_2^z)^2 (S_3^z)^2 \rangle &= M^3 + [\delta_{1,2} + \delta_{1,3} + \delta_{2,3}] [M^2 - M^3] + \delta_{1,2}\delta_{1,3} \\ &\quad \times [M - 3M^2 + 2M^3] + o(T_c/T). \quad (4.13d) \end{aligned}$$

The calculation of the first-order terms can now be carried out. After some straightforward but tedious algebra we find

$$\begin{aligned} \langle S_p^z S_q^z \rangle &= m^2 + \delta_{p,q} [M - m^2] + \beta I_1(gp) [M - m^2]^2 + \beta I_2(gp) m^2 \\ &\quad \times [1 - M]^2 + \beta I_3(gp) m(1 - M)(M - m^2) \\ &\quad + (1 - \delta_{p,q}) o(T_c/T)^2, \quad (4.14a) \end{aligned}$$

$$\begin{aligned} \langle (S_p^z)^2 (S_q^z)^2 \rangle &= M^2 + \delta_{p,q} M [1 - M] + \beta [1 - M]^2 [I_1(gp) m^2 \\ &\quad + I_2(gp) M^2 + I_3(gp) mM] + [1 - \delta_{p,q}] \\ &\quad \times o(T_c/T)^2, \quad (4.14b) \end{aligned}$$

$$\begin{aligned} \langle S_p^z (S_q^z)^2 \rangle &= \langle (S_p^z)^2 S_q^z \rangle \\ &= mM + \delta_{p,q} m [1 - M] + \beta m [1 - M] \\ &\quad \times \{ I_1(gp) [M - m^2] + I_2(gp) [M - M^2] \} \\ &\quad + \frac{1}{2} \beta I_3(gp) [1 - M] [m^2 + M^2 - 2m^2 M] \\ &\quad + [1 - \delta_{p,q}] o(T_c/T)^2. \quad (4.14c) \end{aligned}$$

The correlation parameters $\alpha^{AC}_{(qp)}$, $\alpha^{BC}_{(qp)}$, and $\alpha^{AB}_{(qp)}$ are now readily evaluated from Eqs. (4.14). However, before we present the results for these correlation parameters, we pause briefly to consider the salient features of their physical significance. Inasmuch as these parameters will represent the normalized statistical probability of finding a given type of atom at a given lattice site when a certain type of atom is known to be present at, say, the origin, the spatial range of these correlation parameters must approach the limit zero when the system temperature becomes infinitely large. In this limit, the disordering effect of

⁹ An obvious extension of the results (4.10) and (4.13) is now readily derived by induction. This states that the mean-field decoupling limit of all correlation functions of the type given in Eq. (4.6) is the correct zeroth-order term in a consistent high-temperature power-series expansion.

the temperature far outweighs any ordering tendency inherent in the system due to the interplay of the atomic potentials I_1 , I_2 , and I_3 . Now, as the system temperature is reduced to finite values, the range of these correlations is expected to increase. When the temperature approaches one of the transition temperatures, the ordering sets in and the range of the appropriate correlation parameter becomes macroscopically long. With this view point, and in the same spirit as the recent Padé approximant scheme,¹⁰ the appropriate form of the results is as follows.

$$\begin{aligned} \alpha^{AB}(K) &= D(AB) [1 - \beta U^{AB}(K) (2m^A m^B + m^C) \\ &\quad - \beta U^{AC}(K) m^C (2m^A - 1) \\ &\quad - \beta U^{BC}(K) m^C (2m^B - 1)]^{-1}, \quad (4.15) \end{aligned}$$

where

$$U^{AB}(K) = V^{AB}(K) - \frac{1}{2} [V^{AA}(K) + V^{BB}(K)], \quad (4.16a)$$

$$\langle \sigma_p^A \sigma_p^B \rangle = m^A m^B [1 - \alpha^{AB}(gp)], \quad (4.16b)$$

$$\alpha^{AB}(gp) = (1/N) \sum_K \alpha^{AB}(K) \exp[iK \cdot (g - p)]. \quad (4.16c)$$

The results for α^{AC} are obtained merely by exchanging the superscripts $B \leftrightarrow C$ in Eq. (4.15) and those for α^{BC} by exchanging the superscripts $A \leftrightarrow C$ in (4.15). The constants $D(\lambda\nu)$ are to be determined from the sum rules

$$(1/N) \sum_K \alpha^{\lambda\nu}(K) = 1, \quad (4.17)$$

and in the above equations the inverse lattice K sums extend over the N allowed wave vectors within the first Brillouin zone.

The foregoing expressions for the correlation parameters are exact only to the linear order in ratio (T_c/T) . However, much like the self-consistent field theory results, they do retain a subset of terms in all orders in (T_c/T) . This feature makes the extrapolation of these results to the region $T \sim T_c$ qualitatively permissible, although it is clear that in this region the detailed predictions of our linear theory results must be grossly in error. It is therefore reasonable to treat the estimated magnitude of the ordering temperatures T_c only as order-of-magnitude results. These estimates are readily arrived at by locating the smallest values of β for which the denominators of Eqs. (4.15) approach zero, i.e.,

$$\begin{aligned} (kT_c)^{AB} &= \lim_{K=K(AB)} U^{AB}(K) (2m^A m^B + m^C) + U^{AC}(K) \\ &\quad \times (2m^A - 1) m^C + U^{BC}(K) (2m^B - 1) m^C. \quad (4.18) \end{aligned}$$

As before, the corresponding expressions for $(kT_c)^{AC}$ and $(kT_c)^{BC}$ are derived from Eq. (4.18) by exchanging $B \leftrightarrow C$ and $A \leftrightarrow C$, respectively.

The inverse lattice vectors $K(\lambda\nu)$ are chosen such that for given values of m^λ and m^ν , the ordering tem-

¹⁰ G. A. Baker, Jr., Phys. Rev. **124**, 768 (1961); A. Bienenstock and J. Lewis, *ibid.* **160**, 393 (1967).

perature $(kT_c)^{\lambda\nu}$ is a maximum. Indeed, in analogy with the work of Tahir-Kheli, Callen, and Jarrett,¹¹ the wave vectors $K(\lambda\nu)$ can be expected to be related to the actual ordering configurations of the system.¹²

V. DISCUSSION

It is clear that strictly speaking the linear approximation of the preceding section would be expected to be accurate only at infinitely elevated temperatures. It is, however, a well-known feature of the self-consistent, mean field theory solutions—of which Eq. (4.15) are an example—that they are the more accurate, the larger the density or longer the range of the effective interparticle interaction. Thus, for the most unfavorable case of nearest neighbor interactions, the results of the preceding section can be expected to be reasonable for temperatures $T \sim 1.5T_c$ or greater.¹³ In practice, however, the range of interactions is likely to be rather longer than the nearest-neighbor distances and therefore the present results should be useful even for temperatures somewhat lower than $1.5T_c$.

In spite of the approximate nature of the linear-approximation results given in Eq. (4.15), they possess several important redeeming features. The most important of these is the extreme simplicity of their functional dependence on the Fourier transforms of the appropriate combinations of the interatomic potentials, i.e., Λ , $U^{AB}(K)$, $U^{AC}(K)$, and $U^{BC}(K)$. First, it was precisely the analogous feature of the Clapp-Moss² solution for the corresponding correlation parameter for binary systems which made the experimental analysis of the diffuse x-ray scattering data so convenient.^{3,4} Secondly, the form of Eq. (4.15) is such that it qualitatively approximates the gross features of the correlation parameters even in the critical region where the power series expansion is expected to converge exceedingly slowly. It is this feature which enabled us to infer the order-of-magnitude of the appropriate transition temperatures.

The possibility of the occurrence of a maximum of three transition temperatures has the following significance: The components λ and ν can exhibit a mutual ordering below a temperature of the order of magnitude of $(T_c)^{\lambda\nu}$. Of course, it is clear that the cases where there are a total of only two different ordering temperatures, or where there is only one T_c at which all three components order with respect to each other, are just special cases of this general situation.

A few words might also be said about how we expect the results for the transition temperatures to be modified in a more realistic approximation than is constituted by our linearized, mean-field approximation used in

the preceding section. First, we can expect the actual magnitude, for given composition and interparticle potentials, of these transition temperatures to be altered. Secondly, we expect that the inclusion of those additional correlation effects, which we have implicitly ignored in the present discussion, will alter the ordering conditions radically in the following general way: For given interatomic potentials, the possibility of the existence of an ordered region will critically depend on the system composition. And, as such, for certain ranges of compositions, certain orderings can be expected to be thermodynamically disallowed. Our present results do not, of course, display this behavior.

Let us next briefly examine an application of the present theory to some predictions regarding the actual atomic configurations into which the system may be expected to order as the temperature is reduced below the appropriate transition temperature. The inverse lattice vectors $K(\lambda\nu)$ corresponding to which the correlation parameters $\alpha^{\lambda\nu}(K)$ are a maximum, correspond to the peaks in the diffuse scattered intensity of the x ray or of the neutrons. If it is assumed that the effective interparticle potentials do not change as ordering sets in, a possible statement might be that the superlattice spots—in the intensity spectrum corresponding to the appropriately ordered phase—can be expected to coincide with some of the positions of the diffuse maxima observed in the disordered phase. It turns out, that this is only a part of the full story. To see this more clearly, let us display the configurational energy, $\langle H(\text{config}) \rangle$, as follows:

$$\langle H(\text{config}) \rangle = \text{const} + \sum_K [\alpha^{AB}(K)W^{AB}(K) + \alpha^{BC}(K)W^{BC}(K) + \alpha^{AC}(K)W^{AC}(K)], \quad (5.1)$$

where

$$W^{\lambda\nu}(K) = -m^\lambda m^\nu U^{\lambda\nu}(K), \quad (5.2)$$

and where the constant is a function only of the composition, rather than that of the configuration, and as such is irrelevant to the discussion of the ordering. In the limit of zero temperature, Eq. (5.1) represents the true free energy of the system and its minimization should thus locate the actual ordering. We notice that the minima of $\langle H(\text{config}) \rangle$ for a given composition would be achieved through an interplay of the correlation parameters $\alpha^{\lambda\nu}(K)$ and of the Fourier transforms $W^{\lambda\nu}(K)$ of the reduced potentials. Therefore, the conditions

$$W^{\lambda\nu}(K) = \text{a minimum}; \quad \alpha^{\lambda\nu}(K) = \text{a maximum}, \quad (5.3)$$

although sufficient for describing the ordering, are somewhat restrictive. It might be mentioned that the recent work of Philhours and Hall¹² and of Clapp and Moss^{3,4} is based on the corresponding representation of Eq. (5.3) for binary systems. However, the apparent simplicity of their task is owed primarily to the condition that the maxima of $\alpha^{\lambda\nu}(K)$ coincide with the minima of $W^{\lambda\nu}(K)$.

¹¹ R. A. Tahir-Kheli, H. B. Callen, and H. S. Jarrett, *J. Phys. Chem. Solids* **27**, 23 (1966).

¹² J. Philhours and G. L. Hall, *Phys. Rev.* **163**, 460 (1967); **163**, 463 (1967).

¹³ R. Brout, *Phase Transitions* (W. A. Benjamin, Inc., New York, 1965), p. 15.

It is a simple matter to show from Eq. (5.3) that for binary systems this simplification indeed obtains. For the more general case of ternary systems, the solution of Eqs. (5.3) is more complicated.

In conclusion, we might add a few words about the general direction along which the results of the present paper should be extended. Firstly, the formal solution for the correlation parameters given in Eqs. (3.15)–(3.18) should be explicitly evaluated to a higher order in the expansion parameter (T_c/T) than presently carried out. Secondly, the system interactions responsible for the order-disorder phenomena are not fully

represented by the given form of the $H(\text{config})$. The system Hamiltonian needs to be extended to include the static strain energies, as well as the dynamical lattice effects such as phonons. In the same spirit the inclusion of higher-body potentials than the two-body ones used presently is also indicated.

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Lattice-Dynamic Calculation for Alkali Metals*

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We present a model calculation of lattice dynamics for alkali metals. The lattice potential consists of the electrostatic energy and the screened electron-ion interaction. The screened potential is formed by linearly screening a Heine-Abarenkov-type ion potential, and the Hartree dielectric function is modified to include approximately exchange and correlation effects. The model parameters are determined according to the experimental elastic constants. Expressions for elastic constants are derived by taking the long-wave limit of the secular equation. From our results in lattice dynamics, we find that the shear waves are dominated by the electrostatic potential, but for the longitudinal waves the contributions from both potentials are comparable and opposite in size. The agreement between the calculated and the observed dispersion curves is good for Na and K where neutron-scattering data are available. We have also calculated the effective ion-ion potential for the alkali metals. All of these potentials exhibit a minimum near the equilibrium position and some long-range oscillations caused by electron-ion interaction.

I. INTRODUCTION

SINCE the inelastic neutron scattering technique was applied for direct measurement of dispersion curves, it becomes apparent that the Born-von Kármán rigid-ion model is inadequate in treating lattice dynamics. This is especially so for metals where the problem comes from the conduction electrons. The electron-ion interaction is a many-body interaction characterized by the long-range screening of ions by electrons. This long-range force shows up for alkali metals. In a Born-von Kármán analysis of the observed dispersion curves, force constants up to the fifth neighbors for Na¹ and K² have to be included.

Clearly a proper lattice-dynamic calculation for metals must take into account the effective electron-ion interaction. Toya³ first attempted such a calculation for monovalent metals by extending the Hartree-Fock calculation for the electron-phonon interactions. For

simple metals the electron-ion interaction can be treated by the method of pseudopotentials, an effective electron-ion potential first derived by Phillips and Kleinman⁴ in an orthogonalized-plane-wave (OPW) expansion for the conduction electrons. The pseudopotential model has been applied quite successfully in calculating atomic and electronic properties.^{5,6} There are many lattice-dynamic calculations for alkali metals, notably that of Harrison,⁵ Sham,⁷ and Vosko *et al.*⁸ Their good results establish the validity of using the pseudopotentials for alkali metals. The pseudopotential can be obtained from *a priori* calculation or from measured metal properties such as the atomic energy levels⁶ and the liquid metal resistivities.⁹ In this paper, we study the lattice

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⁵ W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

⁶ V. Heine and I. Abarenkov, *Phil. Mag.* **9**, 451 (1964); A. O. E. Animalu and V. Heine, *ibid.* **12**, 1249 (1965).

⁷ L. J. Sham, *Proc. Roy. Soc. (London)* **A283**, 33 (1965).

⁸ S. H. Vosko, R. Taylor, and G. H. Keech, *Can. J. Phys.* **43**, 1187 (1965).

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² R. A. Cowley, A. D. B. Woods, and G. Dolling, *Phys. Rev.* **150**, 487 (1966).

³ T. Toya, *J. Res. Inst. Catalysis, Hokkaido Univ.* **6**, 161 (1958); **6**, 183 (1958).