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Correlation Functions of Disordered Binary Alloys. II

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It has been previously established on the basis of an Ising model of alloy ordering (part I of this series) that the observed maxima of short-range-order diffuse scattering in disordered alloys mark the positions of the minima of $V(\mathbf{k})$, the Fourier transform of the pairwise interatomic potential $V(r)$. It was suggested in I that the superlattice spots of the ordered state should occur at these same positions. This would establish a consistency requirement connecting the ordered and disordered configurations. We prove here that this is a sufficient but not a necessary condition, and we derive the full set of necessary conditions. We also show that for most of the diffuse maxima locations observed in bcc and fcc alloys, it is possible to establish the ordered configuration required by the disordered phase, or conversely to use a knowledge of the ordered configuration to restrict the possible choices of $V(r)$ in fitting the disordered-phase scattering data. The linear approximation for correlation functions in binary alloys presented by the authors in I is compared quantitatively with the more exact but less general formula of Fisher and Burford. Except at temperatures very close to T_c, it is found that the theoretical shape of the short-range order diffuse scattering is in agreement but the temperature dependencies differ. We note also that all the currently known approximate calculations of $\alpha(\mathbf{k})$ for arbitrary $V(r)$ can be represented in the same functional form, $\alpha(\mathbf{k})=G_2(T)/[1+G_1(T)V(\mathbf{k})]$, where the temperature-dependent factors G_1 and G_2 vary according to the method of calculation used, but that $V(\mathbf{k})$, the Fourier transform of $V(r)$, is the same for all. This leads to the conclusion that the ratios $V(r_{n+1})/V(r_n)$ determined by fitting the theoretical form to experimental data are insensitive to the particular choice of G_1 and G_2, but that the magnitudes of the $V(r_n)$ so determined vary according to this choice. As a consequence, the values obtained for $V(r_{n+1})/V(r_n)$ are to be regarded as more accurate than those for $V(r_n)$.

1. INTRODUCTION

In a previous paper[1] (hereafter referred to as I), the authors derived an expression for the diffuse x-ray or neutron scattering intensity produced by the short-range order present in an alloy above its ordering temperature T_c. The equation [Eq. (34) of I] relates the scattering intensity $\alpha(\mathbf{k})$ to the Fourier transform of the pairwise interatomic potential $V(\mathbf{k})$, the fraction of A and B atoms in the alloy m_A, m_B and the Boltzmann temperature factor β (or $1/kT$). It is written as

$$\alpha(\mathbf{k})=C/[1+2m_Am_B\beta V(\mathbf{k})], \tag{1.1}$$

where C is a normalization constant whose value is determined by the condition that the integral of $\alpha(\mathbf{k})$ over a unit cell of the reciprocal lattice be unity. An explicit expression for C is given by Eq. (34b) of I.

This part has been written to supplement the theoretical exposition of I in two principal areas. Section 2 is devoted to a more quantitative analysis of the approximations inherent in Eq. (1.1). Section 3 offers a partial analysis of the problem of predicting the ordered configuration of an alloy from a knowledge of the pairwise interatomic potential, and defines the region of values of the interatomic potential in which a given ordered configuration is the ground state of the system.

Since writing I, we have become aware of several derivations by other authors of equations closely related to our Eq. (1.1). deGennes and Friedel[2] and Brout[3] derive equations for magnetic spin-spin correlations (which are analogous to atomic pair correlations in AB alloys) that differ from our equation in the choice of C and the restriction that $m_A=m_B=\frac{1}{2}$. Brout's derivation is particularly informative, since it shows that the expression can be derived by either a random-phase approximation (RPA) or an extension of the molecular-field concept to correlations. Krivoglaz's[4] derivation is for alloy systems and is not restricted to the case $m_A=m_B$. He obtains a different value for C, however, which is the infinite-temperature limit, namely, 1.0.

Equation (1.1) has several advantages as a tool for analyzing diffuse scattering data. It can be used to fit the corrected data directly, rather than fitting to Fourier coefficients of the scattering intensity (as is necessary with Cowley's[5] equations) so that no experimental information is wasted. Furthermore, fits can be made to data that do not cover all three directions in reciprocal space, although it is necessary to have measurements in the regions of reciprocal space that are most sensitive to variations of $V(\mathbf{k})$ in order to establish $V(\mathbf{k})$ within reasonably narrow limits.

One of the most useful aspects of Eq. (1.1) is that it is easy to obtain a graphic picture of the effect that inclusion of second, third, or even higher-neighbor interactions have on the shape of the diffuse intensity.

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[1] P. C. Clapp and S. C. Moss, Phys. Rev. 142, 418 (1966).

[2] P. G. DeGennes and J. Friedel, J. Phys. Chem. Solids 4, 71 (1958).

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

[4] M. A. Krivoglas and A. A. Smirnov, *The Theory of Order-Disorder in Alloys* (MacDonald & Co., Ltd., London, 1964), p. 345.

[5] J. M. Cowley, Phys. Rev. 77, 669 (1950).

For instance, the disklike intensities observed in Cu_3Au by Cowley[5] and Moss,[6] the almost-spherical peak shapes observed by Roberts[7] in CuAu, and the egglike contours seen by Batterman[8] for $CuAu_3$ can all be obtained by suitably adjusting the strengths of V_2 and V_3 relative to V_1, so that it is possible to get a rough idea of the importance of higher-neighbor interactions by looking at contour plots of the diffuse intensity. These points will be covered in detail in the following paper (paper III).

Another quite useful aspect of Eq. (1.1) is that it is possible to put sharp limits on the range of values for V_2/V_1, V_3/V_1, etc., that will produce maxima of the diffuse intensity at the correct locations in reciprocal space. This may be seen from the fact that the maxima of $\alpha(\mathbf{k})$ occur at the minima of $V(\mathbf{k})$, and so the values of the V_n's must be chosen to locate correctly the minima of $V(\mathbf{k})$. This statement will be expanded upon in Sec. 3.

2. THEORY AND NATURE OF THE APPROXIMATIONS

In this section, two essentially different aspects of the theoretical background of Eq. (1.1) are discussed. The first concerns the validity of the Ising model itself in describing the configuration energy of a real alloy system. The second deals with the mathematical accuracy of the approximations used to derive Eq. (1.1) from an Ising model formulation.

In I it was assumed that the configurational energy of an alloy could be written as a standard Ising model Hamiltonian modified for unequal atom fractions:

$$H=\tfrac{1}{4}\sum_{i,j}^{N} V_{ij}\bar{\sigma}_i\bar{\sigma}_j\,, \tag{2.1}$$

where $\bar{\sigma}_i=(2m_B,\ -2m_A)$ if an (A,B) atom is at site i and (m_A,m_B) are the fractions of (A,B) atoms in the alloy. V_{ij} is the familiar combination $\frac{1}{2}(V_{ij}^{AA}+V_{ij}^{BB}-2V_{ij}^{AB})$, which is assumed to depend only on the neighbor distance between i and j and not on direction or location in the crystal. The V_{ij}'s may be assumed to be nonzero for an arbitrary range of neighbor distances, and they are the adjustable parameters of the theory. Very little success has been achieved in attempting to calculate the V_{ij}'s from first principles, and a basic motivation of this work is to establish their values for a number of real-alloy systems from available experimental data.

The pairwise interactions are thought to arise from the overlap of neighboring atomic-core orbitals (which would not be expected to have much effect beyond nearest neighbors) and in some cases from the interaction of incompletely screened ion cores (leading to a long-range oscillatory potential decaying as $1/r^3$).

Historically, two other major ideas have competed with the pairwise interaction model to describe ordering. The first is the well-known Brillouin-zone–Fermi-surface interaction model originally proposed by Jones to explain the Hume-Rothery phases and most recently applied by Sato and Toth[9] to long-period superlattices. This model provides a mechanism for lowering the energy of a particular ordered state, relative to the ensemble of disordered states, but it does not cause different disordered states to have different energies. Consequently, it cannot be used to explain changes in the short-range order of the disordered phase, nor the configuration of the short-range order, which is the principal concern here.

If it is correct to say that the short-range forces postulated for the Ising model are responsible for the local order in the disordered phase, these forces will produce an ordered phase at some lower temperature. It is possible that this process will be interrupted by the appearance of a different ordered phase caused by the Jones mechanism, and Sato and Toth suggest that this explains the interruption in the ordering of the CuAu I phase by the onset of the CuAu II long-period ordered phase. The disappearance of the CuAu II phase at a lower temperature remains paradoxical.

The second concept of ordering, which has more relevance to the disordered phase, is that of strain ordering. Ordering in this model is caused by a reduction in the strain energy of an alloy composed of atoms of different size. A recent calculation based on this model is that of Rudman.[10] Apart from providing a basis for rough estimates of the nearest-neighbor ordering forces, the strain-ordering theories suggest that the energy per atom is not simply a sum of pairwise interactions, but is an n-body interaction, where n is the nearest-neighbor coordination number. Rudman could rewrite his elastic strain energy in terms of a pairwise nearest-neighbor interaction that was dependent on the nearest-neighbor short-range-order parameter α. Rudman states that this dependence on α was very weak, causing the interaction to change by less than 5% as α varied from 0 to -0.2 (roughly the range of α for the disordered phase). These approximations, however, appear to be less valid as the size disparity between atoms increases, and for cases where large shifts of atoms off the regular lattice sites occur, Rudman's theory predicts irreducible n-body forces.

Given then that we expect the Ising Hamiltonian to describe properly the configurational energy of an alloy (with the possible exception of the long-period superlattices and large size-effect alloys noted above), Eq. (1.1) is still limited by the fact that it is not an exact solution of the Ising model. The details of its derivation and a comparison with the approximations

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[6] S. C. Moss, J. Appl. Phys. **35**, 3547 (1964).

[7] B. W. Roberts, Acta Met. **2**, 597 (1954).

[8] B. W. Batterman, J. Appl. Phys. **28**, 556 (1957).

[9] H. Sato and R. S. Toth, in *Alloying Behavior and Effects in Concentrated Solid Solutions*, edited by T. B. Massalski (Gordon and Breach Science Publishers, Inc., New York, 1965), p. 295.

[10] P. S. Rudman, Acta Met. **13**, 387 (1965).

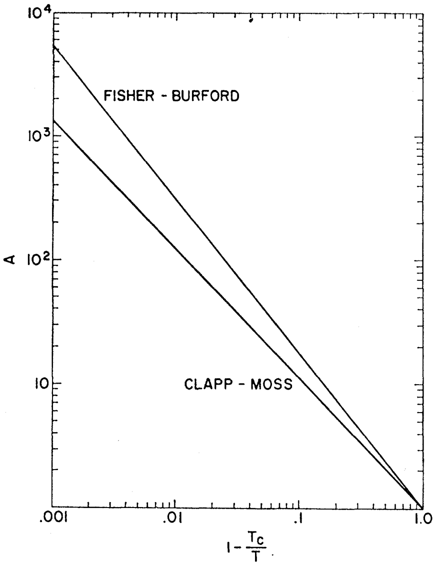

FIG. 1. Comparison of the maximum value of $\alpha(\mathbf{k})$ as predicted by Fisher and Burford (Ref. 11) and by our linear approximation for a fcc AB alloy with a negative nearest-neighbor interaction.

of Cowley and Zernike are the substance of I, and will not be repeated here. A rough estimate was made in I that Eq. (1.1) would be reasonably close to the exact Ising solution at temperatures greater than 10% above T_c, for bcc and fcc alloys. This estimate is in accordance with an estimate of Brout's[3] that the expression is accurate at temperatures above $(1+1/z)T_c$, where z is the nearest-neighbor coordination number of the lattice.

Fisher and Burford[11] have recently obtained a more accurate expression for $\alpha(\mathbf{k})$ in the case of nearest-neighbor interactions and an equiatomic alloy by applying the method of Padé approximants to exact high-temperature expansions. It is thus possible to compare Eq. (1.1) with a more accurate approximation for this special case.

With the exception of temperatures very close to T_c ($T/T_c<1.03$) our equation for $\alpha(\mathbf{k})$ and that of FB can be put in the same functional form[12]:

$$\alpha(\mathbf{k})=A(t)/[1+K^2(\mathbf{k})/K_1^2(t)], \tag{2.2}$$

where $t=T/T_c$ and the nearest-neighbor lattice separation is taken as unity. The temperature-dependent functions $A(t)$ and $K_1(t)$ in our case differ from that of the FB approximation but the k dependence of $\alpha(\mathbf{k})$ [contained in $K(\mathbf{k})$] is identical in the two cases, and has the form

$$K^2(\mathbf{k})=2d[1-V(\mathbf{k})/V(\mathbf{k}_M)],$$

where d is the dimension of the lattice and $\mathbf{k}_M$ is the position of minimum $V(\mathbf{k})$. For small departures of $\mathbf{k}$ from $\mathbf{k}_M$, $K^2(\mathbf{k})\cong(\mathbf{k}-\mathbf{k}_M)^2$, so that Eq. (2.2) represents a Lorentzian of amplitude $A(t)$ and half-width $K_1(t)$ in the neighborhood of the diffuse peak.

In Fig. 1, $A(t)$ is plotted for the two approximations for an fcc lattice with negative nearest-neighbor interactions (i.e., a clustering alloy). In our theory, $A(t)$ is given by $C(t)/(1-t^{-1})$, where $C(t)$ is the normalization constant previously defined. We have approximated the $A(t)$ of FB by $1/[r_1(t)K_1(t)]^{2-1/18}$, where $r_1(t)$ is a parameter plotted by FB in Ref. 11. Note that at a temperature 10% above T_c the peak height $A(t)$ given by our approximation is roughly $\frac{2}{3}$ that predicted by FB. Figure 2 has been taken directly from Fig. 5 of Ref. 11, and indicates that at 10% above T_c, the K_1 of FB is roughly $\frac{2}{3}$ smaller than our K_1 (the mean-field value).

Although this comparison indicates that Eq. (1.1) is not as accurate as might have been hoped, it does show that the k dependence of Eq. (1.1) for $T/T_c>1.03$ is essentially correct, and that it is the temperature-dependent parts of Eq. (1.1) that are in error. In fact, our expression for $\alpha(\mathbf{k})$ can very nearly be brought into

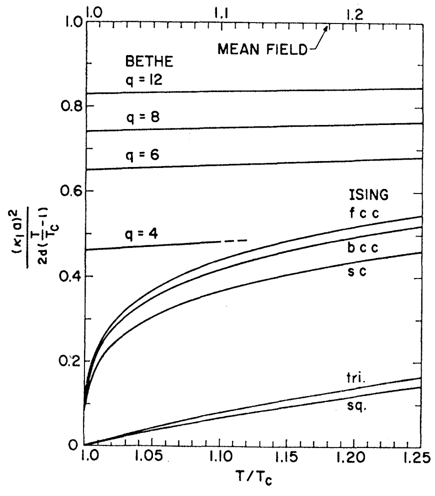

FIG. 2. Variation of the correlation-range parameter $K_1(t)$ for two- and three-dimensional AB alloys as given by the Bethe approximation (the curves labeled with coordination numbers q) the Fisher-Burford calculation (curves labeled by lattice type), and our approximation, which gives the same results for $K_1(t)$ as the mean-field approximation. Either positive or negative nearest-neighbor interactions may be assumed, except for the fcc lattice, where the positive case is special and must be considered separately. This figure is taken directly from Ref. 11.

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[11] M. E. Fisher and R. J. Burford, Phys. Rev. **156**, 583 (1967), referred to as FB.

[12] The complete FB expression for three dimensions is

$$\alpha(\mathbf{k})=\frac{A(t)}{1+\psi K^2(\mathbf{k})/K_1^2(t)}\left[\frac{1+\phi^2K^2(\mathbf{k})}{K_1^2(t)}\right]^{1/36}.$$

Here ψ and ϕ are essentially temperature-independent factors. ψ differs from unity by a negligible amount (less than three parts in 10 000). For values of $\mathbf{k}$ inside the half-width, $K^2(\mathbf{k})/K_1^2(t)<1$, the factor containing ϕ^2 is negligible at all temperatures, because it differs from unity by two parts in 10 000 at most. This factor is also insignificant for $T/T_c>1.03$ for all positions in k space (it differs from unity by less than 2%). However, in the temperature region $T/T_c<1.03$, and for values of k outside the half-width, this term does become appreciable and, as FB point out, this causes $\alpha(\mathbf{k})$ to fall off as $k^{-(2-1/18)}$ (rather than k^{-2}) at temperatures close to the critical point.

coincidence with FB by choosing a different value for T/T_c (i.e., for $T/T_c=1.10$, we find that an effective value of 1.05 is necessary in our expression to achieve agreement). This points up a general characteristic of all the approximate theoretical expressions for $\alpha(\mathbf{k})$ for arbitrary $V(r)$ known to us. These include the equations of deGennes and Friedel,[2] of Krivoglas,[4] the RPA,[3] our linear approximation, the spherical-model approximation,[3] the linked-cluster-expansion calculations of Brout[3] and of Horwitz and Callen,[13] and the Green's function calculation of Bell.[14] The results of all of these treatments can be written in the form given by Eq. (2.2) or, equivalently,

$$\alpha(\mathbf{k})=G_2(t)/[1+G_1(t)V(\mathbf{k})],$$

where the functions of temperature G_1 and G_2 depend upon the particular approximation employed. If this expression is normalized to satisfy the sum rule $\int\alpha(\mathbf{k})d^3k=1$, then $\alpha(\mathbf{k})$ can be written in terms of $G_1(t)$ and $V(\mathbf{k})$ alone, i.e.,

$$\alpha(\mathbf{k})=\frac{1}{1+G_1(t)V(\mathbf{k})}\bigg/\int\frac{1}{1+G_1(t)V(\mathbf{k})}d^3k.$$

In fitting this theoretical formula to experiment, the adjustable parameters are seen to be G_1V_1, G_1V_2, G_1V_3, etc., and as a consequence the absolute values of the V_i's will depend upon which theoretical method is used to provide the value of $G_1(t)$. However, the ratios of the V_i's will be model-independent and once they are determined for a particular system, the estimate of the absolute values of the V_i's can be improved as more accurate theoretical calculations of $G_1(t)$ become available. This, of course, assumes that higher-order calculations of $\alpha(\mathbf{k})$ will have the same functional dependence on $V(\mathbf{k})$. We have used our estimate of $G_1(t)$, namely, $2m_Am_B\,\beta$, to evaluate the V_i's for various alloys in III, because our principal interest here is to determine the range and relative importance of higher-neighbor interactions in real-alloy systems, and because most of the other estimates of G_1 are difficult to evaluate for $m_A\neq m_B$. To summarize then, we believe that the ratios of the V_i's determined in III can be accorded a reasonable degree of reliability, but that the values given for the magnitude of the V_i's should be taken with a grain of salt.

3. ORDERED STRUCTURES

We discuss here the theoretical problem of inferring the ground-state configuration of an alloy from $V(r)$, and the converse problem of obtaining restrictions on the possible form of $V(r)$ from a knowledge of the ordered-alloy configuration. The diffraction pattern of a disordered alloy is characterized by one or more diffuse peaks. Upon ordering, sharp peaks (or superlattice spots) appear which may or may not be located at the position of the former diffuse peaks. We have shown in I that Eq. (1.1) predicts that the location of the diffuse peaks should coincide with the minima of $V(\mathbf{k})$. We now consider the question of the relationship between $V(\mathbf{k})$ and the superlattice-diffraction spots, assuming that $V(r)$ does not change appreciably on passing through T_c, and that no radical distortions of the lattice occur. We assume also that the ordered phase appearing at T_c remains the stable phase down to zero temperature.[15] Under these circumstances, the ordered structure will be the atomic arrangement that minimizes the configuration energy.

The configurational energy of the lattice can be written directly in terms of the scattering intensity and $V(\mathbf{k})$, by Fourier transforming Eq. (2.1):

$$H=D\int d^3k\;V(\mathbf{k})\alpha(\mathbf{k}),\tag{3.1}$$

where $D=Nm_Am_B/(2\pi)^3$ and the integration is over the first Brillouin zone of the disordered lattice. As we show in the Appendix, $\alpha(\mathbf{k})$ for a perfectly ordered structure is a linear combination of δ functions, i.e.,

$$\alpha(\mathbf{k})=\sum_{\{\mathbf{K}_j\}}^{n}A_j\delta(\mathbf{k}-\mathbf{K}_j),\tag{3.2}$$

where the $\mathbf{K}_j$ are the positions of the superlattice spots. For convenience, we shall include the origin (000) as a superlattice point, although the weight factor A_0 will always turn out to be zero. There are n $\mathbf{K}_j$'s per unit cell of the disordered reciprocal lattice of volume v, and n is the ratio of the number of atoms per unit cell in the ordered and disordered phases. The weight factors A_j are proportional to the square of the structure factor for that reflection of the ordered lattice. They are never negative but may be zero, and they must satisfy the sum rule $\sum A_j=1$, in order that the condition $\alpha(r=0)=(1/v)\int' d^3k\,\alpha(\mathbf{k})=1$ be satisfied. Inserting Eq. (3.2) in Eq. (3.1) yields

$$H=D\sum_{\{\mathbf{K}_j\}}^{n}A_jV(\mathbf{K}_j),\tag{3.3}$$

and it is clear that Eq. (3.3) is minimized by that ordered structure for which the $\mathbf{K}_j$ are located only at minima of $V(\mathbf{k})$. If there were no other conditions on the A_j's, the prediction could be made that the superlattice spots of the ordered phase should occur precisely at the maxima of the diffuse peaks of the disordered phase (although not necessarily at all such positions).

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[13] G. Horwitz and H. B. Callen, Phys. Rev. **124**, 1757 (1961).

[14] R. L. Bell, Phys. Rev. **143**, 215 (1966).

[15] For the idealized case of $V(r)$ independent of temperature, Tahir-Kheli, Callen, and Jarrett (Ref. 20) have shown for the closely related problem of a Heisenberg antiferromagnet with second-neighbor interactions, that at all points in the phase diagram for the three cubic lattices the ordered phase that minimizes the configurational free energy at T_c does so at all lower temperatures, and thus minimizes the configurational energy at 0°K. They computed the configurational free energy at finite temperatures by the method of two-time Green's functions.

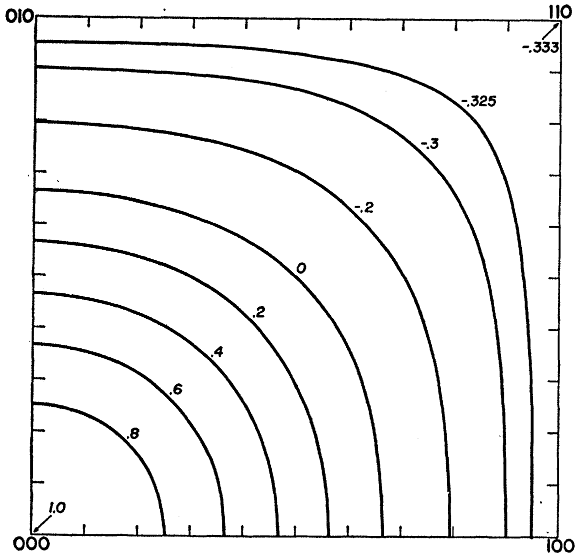

FIG. 3. $C_1(h_1h_20)$ for the fcc lattice.

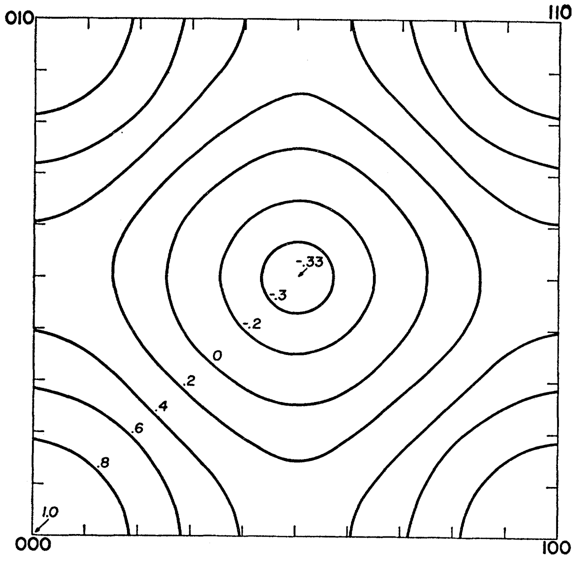

FIG. 4. $C_2(h_1h_20)$ for the fcc lattice.

This, then, is the proper theoretical basis for our suggestion in I that the superlattice spots of the ordered phase should occur at $V(\mathbf{k})$ minima, and it is clear that this conclusion is based entirely on the fundamental Ising Hamiltonian, and is independent of statistical approximations. It is, however, only a sufficient condition, and not a necessary one, because it is not always possible to find an ordered structure of the correct composition that satisfies this simple condition. This is so because there are additional restrictions on the A_j's that stem from the fact that each site of the ordered lattice must be occupied by either an A or a B atom, with fractional occupation prohibited. These necessary conditions are derived in the Appendix and are contained in Eqs. (A10) and (A12).

Luttinger[16] was apparently the first to consider this problem of finding the ground-state configuration of an antiferromagnetic Ising system for arbitrary $V(r)$. He could find no general solution, but suggested a procedure that is equivalent to initially relaxing the subsidiary conditions on the A_j's. This has come to be known as Luttinger's "weak condition," and the procedure is then to check whether any of the solutions generated with the weak condition also satisfy the necessary conditions. If one is lucky, at least one solution will, and the search is over.

This development has been continued by a number of other workers,[17–20] so that we now know the ground-state configurations for an AB alloy with first- and second-neighbor interactions in the three cubic lattices. Our approach here is different from that just cited, in that we treat compositions other than AB and use conditions based on the Fourier transform of the Ising Hamiltonian [i.e., Eq. (3.3)], which enables us to consider $V(r)$ of arbitrary range as long as the positions of $V(\mathbf{k})$ minima or, equivalently, the positions of diffuse maxima of $\alpha(\mathbf{k})$ are known.

Philhours and Hall[21] have recently published several investigations based upon our suggestion in I that the wave vectors (or superlattice spots) of the ordered phase should lie at the positions of $V(\mathbf{k})$ minima. They found independently that this is a sufficient but not a necessary condition for the ground state, and that it is dependent only upon the fundamental Ising Hamiltonian and not upon any statistical approximation.

The sufficient condition is satisfied for many of the familiar ordering systems, such as CuAu, $\mathrm{Cu_3Au}$, CuPt, CuZn, etc., but there are also exceptions, such as $\mathrm{Au_3Mn}$ [22] which are explicable only by including the subsidiary conditions on the A_j's. Before proceeding to a discussion of the full set of conditions, we shall examine the possible locations of the minima in $V(\mathbf{k})$ as determined by the strengths of near-neighbor interactions.

We first take the case of a fcc lattice. The vector from an atom to its (lmn) neighbor is expressed by

$$\mathbf{r}(lmn)=\tfrac{1}{2}l\,\mathbf{a}_1+\tfrac{1}{2}m\,\mathbf{a}_2+\tfrac{1}{2}n\,\mathbf{a}_3,$$

where $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are the three cubic axes; l, m, n are integers, and $l+m+n$ is even. The continuous vector $\mathbf{k}$ in reciprocal space is represented by the continuous variables h_1, h_2, h_3 and the three vectors $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$

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[16] J. M. Luttinger, Phys. Rev. **81**, 1015 (1951).

[17] J. S. Smart, Phys. Rev. **86**, 968 (1952).

[18] D. ter Haar and M. E. Lines, Phil. Trans. Roy. Soc. London **A254**, 521 (1962).

[19] D. H. Lyons and T. A. Kaplan, Phys. Rev. **120**, 1580 (1960).

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

[21] J. Philhours and G. L. Hall, Phys. Rev. **163**, 460 (1967).

[22] L. E. Tanner, Ledgemont Laboratory Internal Report No. TN-33, 1967 (unpublished).

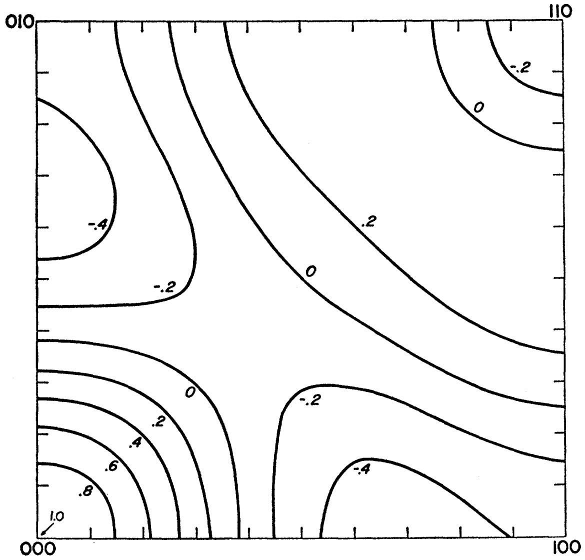


FIG. 5. $C_3(h_1h_20)$ for the fcc lattice.

reciprocal to the a_i's,

$$\mathbf{k}=h_1\mathbf{b}_1+h_2\mathbf{b}_2+h_3\mathbf{b}_3.$$

In this notation, the Bragg reflections occur at $(h_1h_2h_3)$ all odd or all even integers, i.e., (111), (200), etc. Writing out $V(\mathbf{k})$ explicitly for up to third-neighbor interactions, we have

$$\begin{aligned}V(\mathbf{k})&\equiv\sum_{lmn}V_{lmn}\cos\pi lh_1\cos\pi mh_2\cos\pi nh_3,\\&=\sum_i Z_iV_iC_i(h_1h_2h_3),\\&=12V_1[\tfrac{1}{3}(\cos\pi h_1\cos\pi h_2+\cos\pi h_2\cos\pi h_3\\&\quad+\cos\pi h_1\cos\pi h_3)]+6V_2[\tfrac{1}{3}(\cos2\pi h_1+\cos2\pi h_2\\&\quad+\cos2\pi h_3)]+24V_3[\tfrac{1}{3}(\cos2\pi h_1\cos\pi h_2\cos\pi h_3\\&\quad+\cos\pi h_1\cos2\pi h_2\cos\pi h_3\\&\quad+\cos\pi h_1\cos\pi h_2\cos2\pi h_3)],\end{aligned}\tag{3.4}$$

where Z_i is the coordination number of the i shell, V_i is the ith-neighbor interaction, and $C_i(h_1h_2h_3)$ is the appropriate sum of cosine terms, normalized such that $C_i(000)=1$. C_1, C_2, and C_3 have been plotted in the $h_3=0$ plane in Figs. 3–5. C_1 can never be greater than $+1$, nor less than -1, so that (000) is always a maximal point, but it may not be the only such point. The minimum value of C_1 is $-\frac{1}{3}$ and this occurs at all points of the line between (100) and $(1\ \frac{1}{2}\ 0)$ and all equivalent points (i.e., all points obtainable from these by applying the symmetry operations of the body-centered space group). Henceforth, the mention of a point $(h_1h_2h_3)$ will imply its equivalents as well.

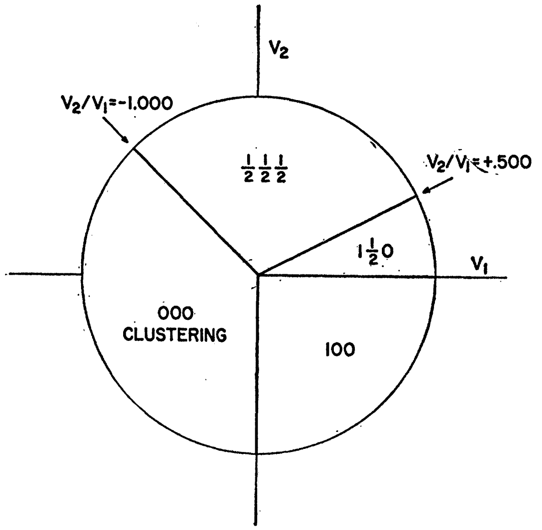


FIG. 6. Locations of the minima of $V(\mathbf{k})$ as a function of the ratio V_2/V_1 for the fcc lattice.

The maxima of C_2 occur at (100) as well as (000) and the minima occur at $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$ having a value of -1. The point $(\frac{1}{2}\ \frac{1}{2}\ 0)$ in Fig. 2 where C_2 is $-\frac{1}{3}$ is only a minimax. The maxima of C_3 occur only at (000) and C_3 takes on its lowest value $-\frac{1}{2}$ at $(\frac{2}{3}\ 0\ 0)$. (100) is a minimax.

Varying the strength of V_2 and V_3 relative to V_1 will obviously affect the location of the minima of $V(\mathbf{k})$. Figure 6 shows the position of the minima for the case when only V_1 and V_2 are nonzero. Figures 7 and 8 are similar plots for the case when V_3 is also nonzero. Where ordered structures are known that have superlattice spots at the given minima, their *Strukturbericht* symbols have been designated and a few examples indicated. Figure 9 illustrates the structures for AB and A_3B stoichiometric compositions. It is interesting that the AB analog of the DO_{22} structure has not yet been found in any system, and the only alloy known to be a possible candidate for the A_3B analog of the $L1_1$ structure is $CuPt_3$.

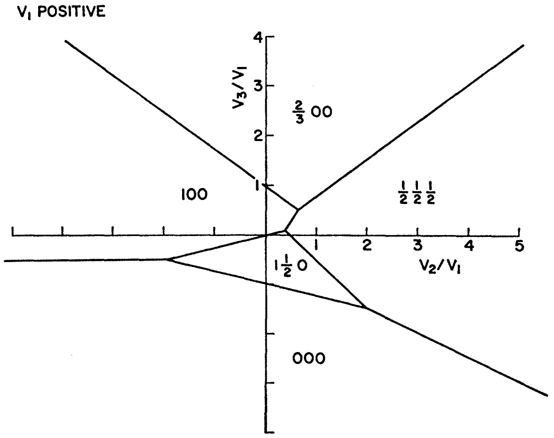


FIG. 7. Locations of the minima of $V(\mathbf{k})$ for V_1, V_2, and V_3 with V_1 positive in an fcc lattice.

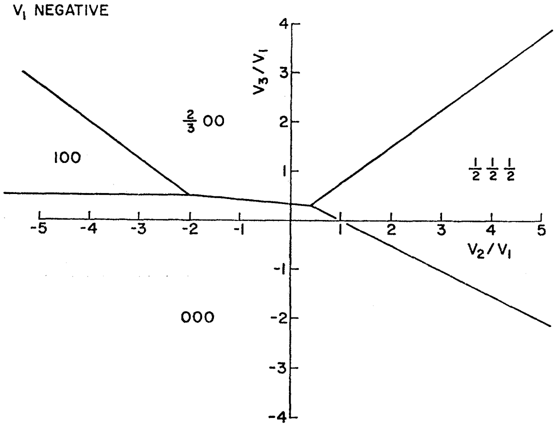


FIG. 8. Location of the minima of $V(\mathbf{k})$ for V_1, V_2, and V_3 with V_1 negative in an fcc lattice.

For a bcc lattice, a similar analysis is easily carried out. The atoms are again separated by the vector

$$\mathbf{r}(lmn)=\tfrac{1}{2}l\mathbf{a}_1+\tfrac{1}{2}m\mathbf{a}_2+\tfrac{1}{2}n\mathbf{a}_3\,,$$

where now l, m, n are all even or all odd, and the $\mathbf{k}$ vector has the same meaning as above, but with $h_1+h_2+h_3$ even for the Bragg reflections, namely, (110), (200), etc. A plot of the positions of $V(\mathbf{k})$ minima is given in Fig. 10 as a function of V_2 and V_1. $V(\mathbf{k})$ is now

$$\begin{aligned}V(\mathbf{k})=8V_1[\cos\pi h_1\cos\pi h_2\cos\pi h_3]+6V_2[\tfrac{1}{3}(\cos 2\pi h_1\\+\cos 2\pi h_2+\cos 2\pi h_3)]+12V_3[\tfrac{1}{3}(\cos 2\pi h_1\cos 2\pi h_2\\+\cos 2\pi h_2\cos 2\pi h_3+\cos 2\pi h_1\cos 2\pi h_3)]\,.\end{aligned}\qquad(3.5)$$

The two ordered structures of AB composition that have superlattice spots at the $V(\mathbf{k})$ minima are shown in Fig. 11. In both cases the diffuse short-range-order peaks of the disordered phase would be centered about the superlattice positions of the ordered phase.

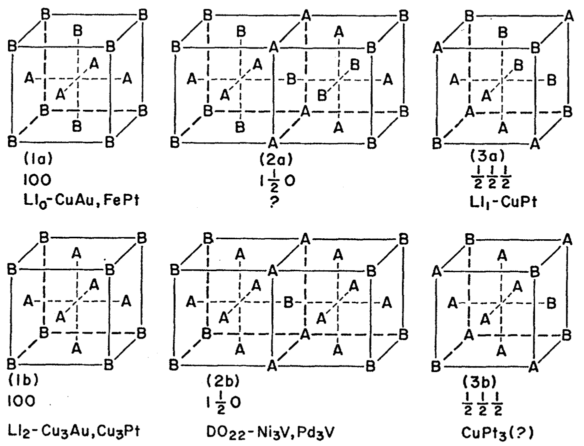


FIG. 9. Ordered structures on an fcc lattice showing location of superlattice spots and *Strukturbericht* symbols. The upper row is AB composition and the lower row is A_3B.

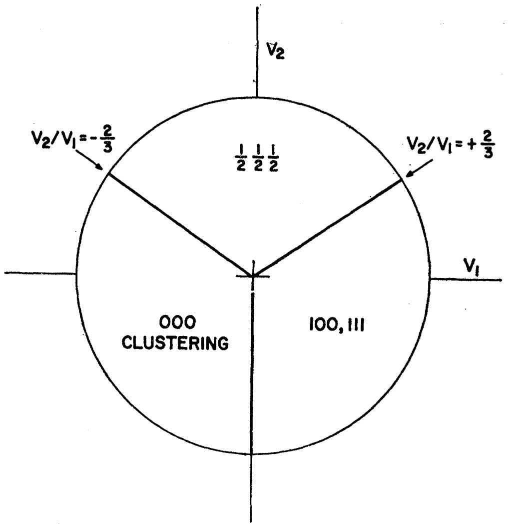


FIG. 10. Location of the minima of $V(\mathbf{k})$ as a function of the ratio V_2/V_1 for the bcc lattice.

We now return to the problem of predicting the configuration of the ordered phase from a knowledge of the positions of the $\alpha(\mathbf{k})$ diffuse maxima. As a first example, assume that the disordered lattice is fcc, that the composition is A_3B, and that the diffuse maxima are at (100) and (110) positions. Solving the necessary conditions for the ordered structure [Eqs. (A10)] requires two steps: (a) specifying the location of the superlattice spots (i.e., the set $\{\mathbf{K}_j\}$), and (b) solving Eqs. (A10) for the structure factors $F(\mathbf{K}_j)$, and hence the A_j's via Eqs. (A12). The set $\{\mathbf{K}_j\}$ can only be the four points 000, 100, 110, and 010 if the superlattice spots are to appear only at minima of $V(\mathbf{k})$. Equation (A10) then gives us four equations in the four unknown structure factors $F(000)$, $F(100)$, $F(110)$, and $F(010)$, which will be denoted as F_0, F_1, F_2, and F_3 in that order. The four equations are

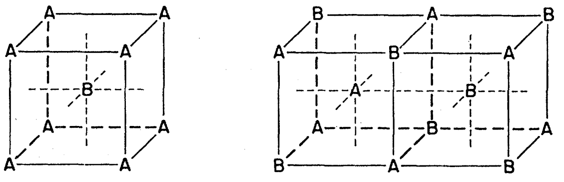
$$\begin{aligned}&F_0^2+F_1^2+F_2^2+F_3^2=1\,,\\&2F_1F_2+2F_3F_4=0\,,\\&2F_1F_3+2F_2F_4=0\,,\\&2F_1F_4+2F_2F_3=0\,.\end{aligned}\qquad(3.6)$$

The composition A_3B immediately fixes F_0 to be $\frac{1}{2}$ and by a process of eliminating variables the only solution is found to be

$$F_0^2=F_1^2=F_2^2=F_3^2=\tfrac{1}{4}\,.$$

Equations (A12) then give $A_0=0$, $A_1=A_2=A_3=\frac{1}{3}$. This obviously corresponds to the $L1_2$-ordered structure, and this proves it to be the unique solution for the ordered ground state.

For the composition AB and the diffuse maxima as above, one again obtains Eqs. (3.6), except that now $F_0=0$. This leads to a degeneracy of three solutions ($A_0=0$, $A_1=1$, $A_2=0$, $A_3=0$), ($A_0=0$, $A_1=0$, $A_2=1$, $A_3=0$), or ($A_0=0$, $A_1=0$, $A_2=0$, $A_3=1$), which corre-



(1a)

100, 111

$L2_0$ - CuZn, AgCd

(2a)

$\frac{1}{2}\frac{1}{2}\frac{1}{2}$

B32 - NaTl, LiZn

FIG. 11. Ordered structures on a bcc lattice for AB composition.

sponds to the well-known $L1_0$ structure with three possible directions for the tetragonal axis.

Finally we consider an example where all of the superlattice peaks cannot be located at the $V(\mathbf{k})$ minima, namely, when the diffuse peaks are at $(1\,\frac{1}{2}\,0)$ positions, as in Ni_3V and Au_3Mn. We begin with the AB case. The simplest starting assumption is that $\{\mathbf{K}_j\}$ consists of the two points (000) and $(1\,\frac{1}{2}\,0)$, implying an ordered structure with two atoms per unit cell. However, the set $\{\mathbf{K}_j\}$ must have the property that any integral multiple of a member also be a member of the set, since they form a lattice, and that any two points separated by a lattice spacing of the disordered reciprocal lattice are equivalent. These requirements make it necessary to include the point $(1\,\frac{3}{2}\,0)$, which is located at a minimum of $V(\mathbf{k})$, and the point (010), which is not. Figure 12 shows the proposed location of superlattice spots.

The second step of determining the A_j's may be done either by generating all possible values of the $F(\mathbf{K}_j)$'s from Eq. (A4b) by trying the various arrangements of atoms in a four-atom unit cell, or by finding the possible solutions to Eqs. (A10) by successively eliminating variables. By either method one finds a unique solution for both the AB and A_3B compositions as follows:

$$AB: A(000)=0,$$

$$A(1\,\tfrac{1}{2}\,0)=\tfrac{1}{2},\quad A(1\,\tfrac{3}{2}\,0)=\tfrac{1}{2},\quad A(010)=0,$$

$$A_3B: A(000)=0,$$

$$A(1\,\tfrac{1}{2}\,0)=\tfrac{1}{3},\quad A(1\,\tfrac{3}{2}\,0)=\tfrac{1}{3},\quad A(010)=\tfrac{1}{3}.$$

The AB solution corresponds to the (2a) structure of Fig. 9, and the fact that the A_j's are nonzero only at minima of $V(\mathbf{k})$ implies that this structure has the lowest possible configurational energy for this type of $V(r)$ as in the two cases above. It is perhaps puzzling that such a structure has never been observed in nature. The A_3B solution is the DO_{22} structure illustrated in Fig. 9, and, since $A(010)$ is now nonzero, we see that if this is indeed the arrangement of lowest configurational energy for A_3B composition, the subsidiary conditions for the A_j's force $\frac{1}{3}$ of the superlattice intensity in the ordered phase to appear at locations different from the diffuse maxima positions of the disordered phase.

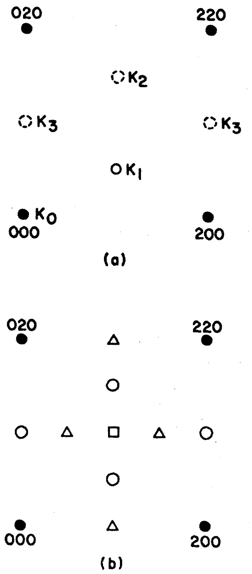


FIG. 12. (a) Minimum set $\{\mathbf{K}_j\}$ necessary to locate a superlattice peak at $(1\,\frac{1}{2}\,0)$. (b) Superlattice spots of the DO_{22} structure. Contributions from the three possible orientations of the tetragonal axis are labeled by separate symbols.

The question naturally arises, whether the diffuse intensity pattern anticipates this "anomalous" superlattice peak before the ordering temperature is actually reached, or if this peak emerges abruptly below T_c, as our theory would suggest. Tanner[22] has found from electron-diffraction measurements on thin films of Au_3Mn that, for this system at least, the latter suggestion fits the observations. Tanner's results will be discussed further in III.

Summarizing this discussion, we can say that we have provided a method for predicting the ordered configuration of an alloy by knowing only the location of the diffuse peaks in the disordered state in a number of simple cases. We do not claim to have completely solved the general problem of determining the ordered structure that is compatible with a given $V(\mathbf{k})$, and we have shown that, in at least one case (Au_3Mn), it is necessary to know more about $V(\mathbf{k})$ than just the location of its minima. It is clear that the stability of the DO_{22} structure, relative to others that may be imagined, will depend critically on the magnitude of $V(\mathbf{k})$ at the nonminimal (010) position.

4. SUMMARY AND CONCLUSION

The primary motivation of our first investigation (I) in this series was to provide a tractable method for determining the pairwise interaction strengths in alloys from an analysis of the short-range order diffuse scattering in the disordered state. In this paper, we have examined the accuracy of our method in greater detail to provide a better understanding of its limitations and its strengths. We have shown, by comparison with the recently published equation of Fisher and Burford for the special case of an AB alloy with nearest-neighbor interactions, that it has the same k dependence as ours but has a different temperature dependence. The two predictions become nearly identical if $(T-T_c)/T_c$ is reduced by roughly a factor of two in our equation in the neighborhood of $(T-T_c)/T_c=0.1$. For interactions beyond first neighbors, we have shown that the relative values of the V_i's can be determined with greater certainty than can their absolute values.

We have also shown that a study of the ordered state is valuable in determining the pairwise interactions in alloys, because the relative strengths of the pairwise interactions compatible with a given ordered structure are limited to a certain range. This is useful in narrowing down the field of interaction strengths that may be used to fit the diffuse short-range order scattering data of a particular alloy, assuming that the ordered structure is known and that it remains stable at lower temperatures. However, the actual values of the V_i ratios can be determined only from a detailed fit to the diffuse-scattering data. It should be realized that these consistency conditions do not depend in any way on the approximations used in I to derive our diffuse-scattering equation, but rely only upon the basic Ising model formulation of the configurational energy of an alloy.

We now have the theoretical framework necessary to provide a reasonably complete analysis of available diffuse short-range order scattering data in alloy systems. This is the subject of the following paper (III).

ACKNOWLEDGMENTS

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APPENDIX

For the purposes of describing ordered alloys, we shall use operators σ_i, which are given the value $(+1,\,-1)$ for an (A,B) atom at site i. The σ_i operators are related to the $\bar{\sigma}_i$ operators of I by the relation

$$\sigma_i=\bar{\sigma}_i+(m_A-m_B)\,, \qquad \text{(A1)}$$

and, recalling the relation between α_{ij} and $\langle\bar{\sigma}_i\bar{\sigma}_j\rangle$ given by Eq. (12) of I, i.e., $\langle\bar{\sigma}_i\rangle=0$, the result is as follows:

$$\langle\sigma_i\sigma_j\rangle=4m_Am_B\alpha_{ij}+(m_A-m_B)^2\,. \qquad \text{(A2)}$$

The N atoms of a disordered alloy are assumed to be on the points of a regular lattice located at endpoints of vectors $\mathbf{r}_j$, where $j=0,\ N-1$. $\mathbf{r}_0$ is taken to be the null vector; and $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$ are taken as the unit vectors of the unit cell. An analogous convention is to be understood for the other types of lattices which we shall consider. For the sake of simplicity we confine the discussion to disordered lattices having a single atom per unit cell (i.e., the Bravais lattices).

Upon ordering, a larger unit cell is formed containing, say, n atoms. Equivalent positions in the ordered structure form a superlattice whose points are now separated by vectors $\mathbf{R}_j$.

We define a "structure factor" $\sigma_{\mathbf{k}}$ for the ordered lattice of N sites, where N will ultimately become indefinitely large.

$$\sigma_{\mathbf{k}}\equiv\sum_{f=0}^{N-1}\sigma_f e^{i\mathbf{k}\cdot\mathbf{r}_f}\,, \qquad \text{(A3)}$$

which can be immediately factored into a unit-cell structure factor $F(\mathbf{k})$ and a superlattice structure factor $S(\mathbf{k})$ in the usual manner:

$$\sigma_{\mathbf{k}}=S(\mathbf{k})\times F(\mathbf{k})\,, \qquad \text{(A4a)}$$

with

$$F(\mathbf{k})\equiv\frac{1}{n}\sum_{f=0}^{n-1}\sigma_f e^{i\mathbf{k}\cdot\mathbf{r}_f} \qquad \text{(A4b)}$$

and

$$S(\mathbf{k})\equiv n\sum_{j=0}^{N'-1}e^{i\mathbf{k}\cdot\mathbf{R}_j}=\sum_{\{\mathbf{K}_j\}}\delta(\mathbf{k}-\mathbf{K}_j)\,, \qquad \text{(A4c)}$$

where $N'=N/n$ and $\delta(\mathbf{k}-\mathbf{K}_j)=N$ if $\mathbf{k}=\mathbf{K}_j$, and is zero otherwise. The set of points $\{\mathbf{K}_j\}$ are the points of the lattice reciprocal to the superlattice, and there will be n of them contained within a unit cell of the disordered reciprocal lattice. In the limit of N very large, $\delta(\mathbf{k}-\mathbf{k}')$ becomes a Dirac delta function and has the property

$$\frac{1}{v}\iiint G(\mathbf{k})\delta(\mathbf{k}-\mathbf{k}')d^3k=G(\mathbf{k}') \qquad \text{(A5)}$$

if $\mathbf{k}'$ is within the unit volume v of reciprocal space integrated over, and is zero otherwise. $G(\mathbf{k})$ is an arbitrary function of $\mathbf{k}$.

The inverse of Eq. (A3) is

$$\sigma_f=\frac{1}{v}\iiint\sigma_{\mathbf{k}}e^{-i\mathbf{k}\cdot\mathbf{r}_f}d^3k\,, \qquad \text{(A6)}$$

which becomes, on using Eq. (A4)

$$\sigma_f=\sum_{\{\mathbf{K}_j\}}F(\mathbf{K}_j)e^{-i\mathbf{K}_j\cdot\mathbf{r}_f}\,. \qquad \text{(A7)}$$

Since σ_f can only be $+1$ or -1, we have

$$\sigma_f{}^2=1=\sum_{\mathbf{K}_j}\sum_{\mathbf{K}_j'}F(\mathbf{K}_j)F(\mathbf{K}_j')e^{-i(\mathbf{K}_j+\mathbf{K}_j')\cdot\mathbf{r}_f}\,. \qquad \text{(A8)}$$

Using the variable change

$$\mathbf{K}_i=\mathbf{K}_j+\mathbf{K}_j' \quad\text{and}\quad H(\mathbf{K}_i)=\sum_{\mathbf{K}_j}F(\mathbf{K}_j)F(\mathbf{K}_i-\mathbf{K}_j)\,,$$

Eq. (A8) becomes

$$\sigma_f{}^2 = 1 = \sum_{\mathbf{K}_i} H(\mathbf{K}_i) e^{-i\mathbf{K}_i \cdot \mathbf{r}_f}. \tag{A9}$$

The left-hand side of Eq. (A9) is the same regardless of the choice of f, and in order that the right-hand side also be independent of f, the following conditions must hold:

$$H(\mathbf{K}_i) \equiv \sum_{\mathbf{K}_j} F(\mathbf{K}_j) F(\mathbf{K}_i - \mathbf{K}_j) = 0, \quad \text{if} \quad \mathbf{K}_i \neq 0 \tag{A10a}$$

and

$$H(0) \equiv \sum_{\mathbf{K}_j} F(\mathbf{K}_j) F(-\mathbf{K}_j) = 1. \tag{A10b}$$

These equations provide n interrelations among the n F's, so that in general there will only be a small limited set of F's that are allowable. In addition, $F(0)$ is fixed by the composition and is given by

$$F(0) \equiv \frac{1}{n} \sum_{f=0}^{n-1} \sigma_f = m_A - m_B. \tag{A11}$$

We shall now show that the A_j's of Eq. (3.2) are related to the $F(\mathbf{K}_j)$'s as follows:

$$A_0 = F^2(0) - (m_A - m_B)^2 = 0, \tag{A12a}$$

$$A_j = F(\mathbf{K}_j) F(-\mathbf{K}_j) / 4m_A m_B, \quad j \neq 0. \tag{A12b}$$

We have

$$\alpha(\mathbf{k}) \equiv \frac{1}{N} \sum_{f,g}^{N} \alpha_{fg} e^{i\mathbf{k} \cdot (\mathbf{r}_f - \mathbf{r}_g)},$$

and from (A2) and (A7) we get

$$\alpha(\mathbf{k}) = \frac{1}{4m_A m_B N} \sum_{f,g}^{N} \sum_{\{\mathbf{K}_j\}} \sum_{\{\mathbf{K}_j'\}} F(\mathbf{K}_j) F(\mathbf{K}_j') e^{i(\mathbf{k} - \mathbf{K}_j) \cdot \mathbf{r}_f} \times e^{-i(\mathbf{k} + \mathbf{K}_j) \cdot \mathbf{r}_g} - \frac{(m_A - m_B)^2}{4m_A m_B N} \sum_{f,g}^{N} e^{i\mathbf{k} \cdot (\mathbf{r}_f - \mathbf{r}_g)},$$

which becomes

$$\alpha(\mathbf{k}) = \frac{1}{4m_A m_B} \sum_{\{\mathbf{K}_j\}} F(\mathbf{K}_j) F(-\mathbf{K}_j) \delta(\mathbf{k} - \mathbf{K}_j) - \frac{(m_A - m_B)^2}{4m_A m_B} \delta(\mathbf{k}). \tag{A13}$$

By comparing (A13) with Eq. (3.2), i.e.,

$$\alpha(\mathbf{k}) = \sum_{\{\mathbf{K}_j\}}^{n} A_j \delta(\mathbf{k} - \mathbf{K}_j), \tag{3.2}$$

it is apparent that Eqs. (A12) are recovered when the relation given by (A11) is included.

In conclusion, the $F(\mathbf{K}_j)$'s are restricted by the n equations given above and the A_j's in turn are determined by the $F(\mathbf{K}_j)$'s. The n conditions (A10) cannot be written in terms of the A_j's directly, with the exception of (A10b), which converts to

$$\sum_{\{\mathbf{K}_j\}} A_j = 1.$$

This was mentioned in Sec. 3 as the condition necessary to ensure that $\alpha(r=0)=1$.