

Short-Range Order and Long-Range Order Parameters

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The equations for the short-range order parameters relating to ordering in binary solid solutions, as previously derived by the author, have been rederived in a more satisfactory manner. Applying the equations to situations with long-range order, a more complete analysis of predictions regarding multiple long-range order parameters has been made. It is shown that long-range order parameters may be redefined in such a way that they provide a reasonable description of the state of order in situations involving finite crystal size, finite out-of-phase domain size, and fluctuations in composition.

1. INTRODUCTION

IN previous papers^{1,2} the author has calculated short-range order coefficients using sets of equations derived from elementary thermodynamic arguments. Comments on the derivation of these equations by Hall and others^{3,4} have suggested that they cannot reasonably be derived from considerations of pair correlations only. This is probably true. It therefore seems useful to rederive the equations in such a way as to emphasize that they are generated by consideration not of pair correlations but of extended correlation functions.

While the application of the short-range order (s.r.o.) equations to situations involving long-range order (l.r.o.) may be considered as scarcely justifiable, it has been shown to give values for the l.r.o. parameters in reasonable agreement with experiment,¹ and also has served to introduce the concept of multiple l.r.o. parameters. Reconsideration of the preliminary results on this latter subject² has shown that some modifications of the concept are necessary, and at the same time has led to a proposal for the redefinition of l.r.o. parameters, whether single or multiple, which can take into account the presence of antiphase domains, finite crystal size or fluctuations in composition. These subjects are treated in the later sections of this paper.

2. DERIVATION OF SHORT-RANGE ORDER EQUATIONS

For an alloy with fractions m_A and m_B of A and B atoms the short-range order parameters α_i , as introduced by Warren (see footnote of above Ref. 2), have been shown to represent the contributions due to ordering to the peaks of the Patterson, or autocorrelation, function of the array of atoms.² The indices i refer here to particular interatomic vectors rather than to shells of atoms. A standard interpretation of the Patterson function for N equal atoms, readily proved, is that it represents N times the average environment of an atom. Similarly, given that Nm_A and Nm_B are the numbers of A and B atoms present, the Patterson function, or the set of α_i parameters, defines the average environment of an A or a B atom.

In calculating the free-energy contribution due to ordering, $F = U - TS$, the energy term U is assumed to

be equal to Nm_A times the energy of the average configuration of atoms about an A atom plus Nm_B times the energy of the average configuration about a B atom.

If, for example, an A atom is chosen as origin the probabilities for occupation of all other sites are established by the full set of parameters α_i . Because the occupancy of the i site is nonrandom there will be an energy term corresponding to interaction of atoms at this site with the origin atom. Similarly for the j site. It is these energy terms which Christy and Hall,³ include as the only energy terms involved in their energy expression. However, because the choice of the A atom as origin establishes nonrandom occupancies for both the i and j sites simultaneously, additional energy terms corresponding to i - j interactions must be included. Christy and Hall derive an "exact" energy expression, but this is not relevant to these order-parameter calculations since it refers to specified configurations of atoms and not to a system with *correlations* between atomic positions specified by order parameters.

In the average configuration about an A atom, the site defined by the i vector contains a fraction $m_A + m_B\alpha_i$ of A atoms and a fraction $m_B(1 - \alpha_i)$ of B atoms and the site defined by the j vector has similar fractional occupancy with α_j replacing α_i . If the interaction energies of pairs of atoms on the i and j sites are given by $V_{AA,ij}$, $V_{AB,ij}$, etc., the contribution to the energy due to the occupancy of these sites in the average configuration will be made up of terms such as

$$\dots + m_B(1 - \alpha_i)(m_A + m_B\alpha_j)V_{AB,ij} + \dots$$

If we then sum all such terms arising from Nm_A average configurations about A atoms and Nm_B average configurations about B atoms we obtain:

$$\begin{aligned} U &= \frac{1}{2}Nm_A \sum_i \sum_j [m_B^2(1 - \alpha_i)(1 - \alpha_j)V_{BB,ij} \\ &\quad + (m_A + m_B\alpha_i)(m_A + m_B\alpha_j)V_{AA,ij} \\ &\quad + \{m_B(1 - \alpha_i)(m_A + m_B\alpha_j) \\ &\quad + m_B(1 - \alpha_j)(m_A + m_B\alpha_i)\}V_{AB,ij}] \\ &\quad + \frac{1}{2}Nm_B \sum_i \sum_j [m_A^2(1 - \alpha_i)(1 - \alpha_j)V_{AA,ij} \\ &\quad + (m_B + m_A\alpha_i)(m_B + m_A\alpha_j)V_{BB,ij} \\ &\quad + \{m_A(1 - \alpha_i)(m_B + m_A\alpha_j) \\ &\quad + m_A(1 - \alpha_j)(m_B + m_A\alpha_i)\}V_{AB,ij}] \quad (1) \\ &= \frac{1}{2}N \sum_i \sum_j \{ (m_A^2V_{AA,ij} + 2m_Am_BV_{AB,ij} \\ &\quad + m_B^2V_{BB,ij}) + m_Am_B\alpha_i\alpha_j \\ &\quad \times (V_{AA,ij} + V_{BB,ij} - 2V_{AB,ij}) \} \\ &\equiv U_0 + Nm_Am_B \sum_i \sum_j \alpha_i\alpha_j V_{ij}. \end{aligned}$$

¹J. M. Cowley, Phys. Rev. **77**, 669 (1950).

²J. M. Cowley, Phys. Rev. **120**, 1648 (1960).

³D. O. Christy and G. L. Hall, Phys. Rev. **132**, 1958 (1963).

⁴G. L. Hall and J. Philhous (to be published).

The factor $\frac{1}{2}$ is introduced on the right-hand side so that each interaction energy will not be counted twice.

In calculating the entropy, we consider the number of ways of dividing the Nm_A vectors from A atoms chosen as origin to atoms on the i site in such a way as to give an order parameter α_i , i.e., so that there are $Nm_A(m_A+m_B\alpha_i)$ vectors AA and $Nm_Am_B(1-\alpha_i)$ vectors AB , and similarly for the Nm_B vectors from B atoms. The total entropy term obtained by using Stirling's approximation is then

$$S-S_0 = -Nk \sum_i \{ m_A(m_A+m_B\alpha_i) \ln(m_A+m_B\alpha_i) \\ + m_B(m_B+m_A\alpha_i) \ln(m_B+m_A\alpha_i) \\ + m_Am_B(1-\alpha_i) \ln m_Am_B(1-\alpha_i)^2 \}.$$

If we take the equilibrium condition to be $\delta F/\delta\alpha_i=0$ for all α_j with $j \neq i$ and T constant, we obtain the equations previously found¹:

$$2 \sum_j \alpha_j V_{ij} + kT f(\alpha_i) = 0,$$

where

$$f(\alpha_i) = \ln \left\{ \frac{(m_A/m_B + \alpha_i)(m_B/m_A + \alpha_i)}{(1-\alpha_i)^2} \right\}. \quad (2)$$

The factor 2 reappears before the summation in the course of the differentiation.

In both the energy and the entropy terms we have considered N average configurations, each of N interatomic vector peaks. Since treatment of the interactions of these configurations presents considerable difficulties, we have assumed the N configurations to be independent, and relating to vector sets for separate sets of N atoms. Above the critical temperature, when the s.r.o. parameters are different from zero for only a small number of interatomic vectors, we get the order-dependent parts of the energy and entropy terms given by N times the contribution from the localized modification of the average configuration. However, the part of the configuration of N vectors which does not depend on order is the same for each of the N configurations. Hence the order-independent terms U_0 and S_0 are both of the order of N^2 . The over determination of these terms does not, of course, affect the derivation of Eq. (2).

When we apply the s.r.o. equations to the case where l.r.o. exists, in each configuration there are N vectors for which the order parameter has the limiting value s_i . Then both the energy and entropy terms contain factors N^2 for the order-dependent part as well as for the order-independent part. Thus the free-energy contribution is N times overestimated. However, on putting the derivative of the free energy equal to zero the factors N^2 cancel out, and equations analogous to (2) are obtained.

3. EQUATIONS FOR LONG-RANGE ORDER PARAMETERS

It was previously suggested² that long-range order may not be uniquely defined by a single l.r.o. parameter. The l.r.o. parameter or parameters are defined as the

limiting values of the s.r.o. parameters for large distances from the Patterson origin. In the case of the Cu_3Au -type lattice it is necessary to distinguish between the limiting values s_1 corresponding to unit cell corners and s_2 corresponding to face-centers in the unit cell of the Patterson function. The assumption that the composition of the alloy is everywhere the same leads to the relation $s_1 = -3s_2$.

Before we can derive an equation equivalent to (2) for l.r.o. parameters, it is necessary to decide whether the free energy is to be minimized with respect to one parameter, or independently with respect to two parameters. For the Cu_3Au -type lattice, for example, the energy term (1) becomes

$$U = U_0 + Nm_Am_B \\ \times \sum_i \left[\left\{ \frac{1}{4} 12s_1s_2 + \frac{3}{4}s_2(4s_1+8s_2) \right\} V_1 \right. \\ \left. + \left\{ \frac{1}{4} 6s_1^2 + \frac{3}{4} 6s_2^2 \right\} V_2 + \dots \right].$$

Then if we assume that $s_1 = -3s_2$, differentiating the free-energy term with respect to s_1 gives

$$-\frac{8}{3}s_1(V_1-V_2) + \frac{kT}{4} \left[f(s_1) - f\left(\frac{-s_1}{3}\right) \right] = 0, \quad (3)$$

and taking the limit $s_1 \rightarrow 0$ gives the critical temperature as

$$T_c = \frac{3}{2}(V_1-V_2)/k, \quad (4)$$

where we have assumed that the only nonzero energy terms are V_1 and V_2 , relating to nearest and next-nearest neighbor pairs, respectively.

If instead we do not assume $s_1 = -3s_2$, but consider s_1 and s_2 as independent parameters, differentiation with respect to s_1 and s_2 gives the pair of equations;

$$3s_2V_1 + \frac{3}{2}s_1V_2 = -\frac{1}{8}kTf(s_1), \\ (s_1+2s_2)V_1 + \frac{3}{2}s_2V_2 = -\frac{1}{8}kTf(s_2).$$

Rearranging these equations we obtain

$$8s_1(V_1 - \frac{3}{2}V_2) - kTf(s_1) = 8s_2(V_1 - \frac{3}{2}V_2) - kTf(s_2) \\ = 8(s_1+3s_2)V_1. \quad (5)$$

From the form of the function $f(x)$, as defined by (2), it follows that there is no solution of (5) for which $s_1+3s_2=0$ except for the limiting cases $s_1=s_2=0$ or $T=0$.

From the limiting case $s_1=s_2=0$, we find the critical temperature as

$$T_c = \frac{3}{2}(V_1 - \frac{3}{2}V_2)/k, \quad (6)$$

which differs slightly from (4). Disregarding this difference, the values of the l.r.o. parameters calculated from Eqs. (3) and (5) are plotted in Fig. 1, as functions of T/T_c . The values of s_1 and $-3s_2$ calculated from (5) are seen to differ by a maximum of about 5%, and bracket the value of s_1 calculated from (3).

The previous result² that $s_1+3s_2 \neq 0$ for $T=0$ was obtained because the iteration method then used became unreliable in that region. However by solving

(5) graphically it is evident that $s_1 + 3s_2$ goes to zero for $T=0$. Further, this can be proved by putting $s_1 = 1 - \epsilon_1$ and $s_2 = (-s_1/3) + \epsilon_2$ in (5) and considering the limiting cases for the equations in s_1 and s_2 successively.

It was pointed out previously that the assumption $s_1 + 3s_2 = 0$ corresponds to the assumption of a uniform composition whereas any departure from this relation must involve a separation of the alloy into regions of different composition, the minimum size for such regions being dependent on the basis for the definition of long-range order, as discussed below. For the Cu_3Au -type alloy, there are only small differences in the values of experimentally observable quantities predicted for the two cases of either one only or two l.r.o. parameters. Any resolution of a difference seems unlikely at the moment. Also calculations of the free energy for the two cases indicates no difference sufficient to allow one or the other to be clearly preferred on the basis of this simple theory.

For the CuAu composition there is no ambiguity since only one solution, that with a single l.r.o. parameter, can exist.

However, at other than these simple stoichiometric compositions large differences appear between the possible solutions. In each case free-energy calculations favor the solution with multiple l.r.o. parameters.

For the composition A_4B , for example, if only one independent parameter, s_1 is assumed, the limiting value

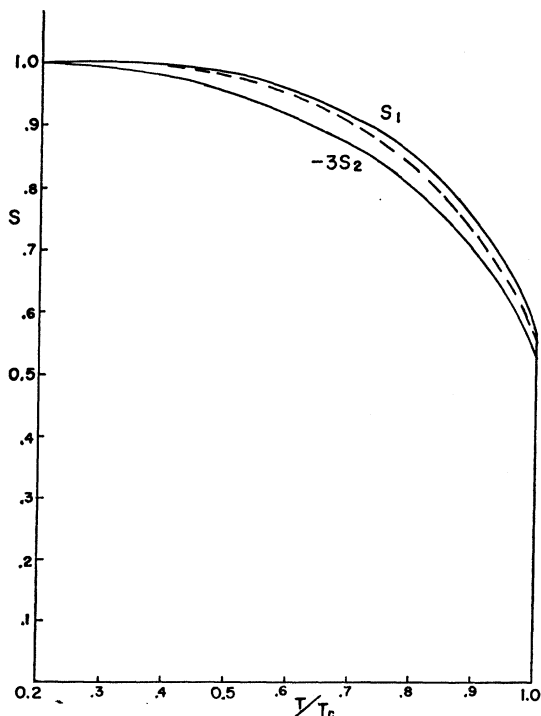


FIG. 1. Values of l.r.o. parameters calculated for a Cu_3Au -type alloy. Dashed line: values of s_1 calculated on the assumption that $s_1 + 3s_2 = 0$. Full lines: values of s_1 and $-3s_2$ calculated without this assumption.

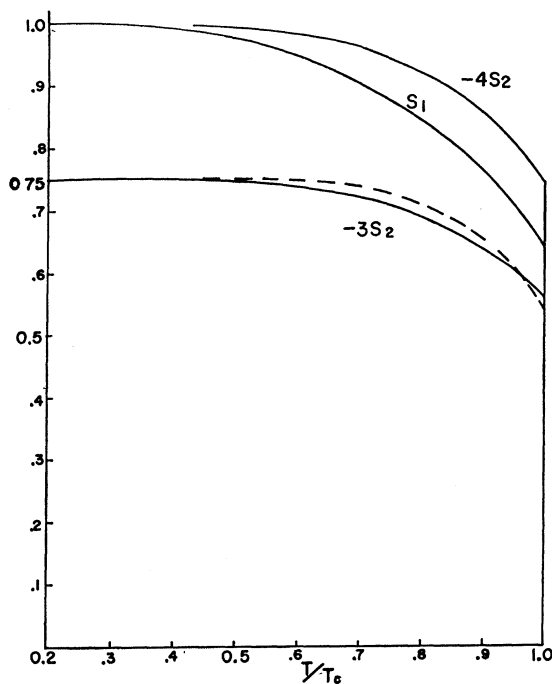


FIG. 2. Values of l.r.o. parameters for composition A_4B . Dashed line: values of s_1 calculated on the assumption that $s_1 + 3s_2 = 0$. Full lines: values of s_1 , $-3s_2$ and $-4s_2$ calculated without this assumption.

for low temperatures is $s_1 = 0.75$, corresponding to a random distribution of the excess A atoms and all the B atoms on one sublattice of the unit cell. For two independent parameters, the limiting values are $s_1 = 1.0$ and $-3s_2 = 0.75$ and the variation with temperatures is as shown in Fig. 2. Thus for low temperatures, $s_1 + 4s_2 \approx 0$, and the equilibrium state corresponds to a separation of the alloy into pure A and an A_3B alloy.

Similarly, for an A_2B alloy the assumption $s_1 + 3s_2 = 0$ leads to $s_1 = 1$ at $T=0$, with an equilibrium state in which the B atoms in excess compared to the A_3B alloy are distributed at random over the sites of A atoms. The assumption of two independent order parameters leads to the relationship $s_1 + 2s_2 \approx 0$ at low temperatures. However, for such alloys it seems reasonable to suppose that the arrangement of the excess B atoms will not be random. The number of nearest-neighbor B - B pairs will be reduced if the excess B atoms are arranged preferentially on one of the A sublattices, as suggested in Fig. 3(b). There is, in fact, a tendency for a CuAu -type ordering into planes of A and B atoms. Then the three face-center lattice sites in the Patterson function are no longer equivalent, and a minimum of three l.r.o. parameters is necessary. In place of Eq. (5) we then have

$$\begin{aligned} 8s_1(V_1 - \frac{3}{2}V_2) - kTf(s_1) &= 8s_2(V_1 - \frac{3}{2}V_2) - kTf(s_2) \\ &= 8s_3(V_1 - \frac{3}{2}V_2) - kTf(s_3) \quad (7) \\ &= 8(s_1 + 2s_2 + s_3) \cdot V_1. \end{aligned}$$

The graphical solution of this equation gives the

values for the l.r.o. parameters shown in Fig. 4. Above $T/T_c \approx 0.60$, the only solutions possible are with $s_3 = s_2$, so that the ordering is similar to that of an A_3B alloy, with $s_1 + 3s_2$ small. For lower temperatures, such solutions are no longer possible. Then s_3 is small and negative while $-s_2$ increases suddenly so that $s_1 + 2s_2$ is small. In this region, then, the ordering tends to that for the AB alloy.

From the form of the curves it is clear that only three roots of the equations $c_1x - f(x) = c_2$ are possible. Therefore, no more than three different l.r.o. parameters can be derived from sets of equations such as (7) for binary alloys based on a face-central cubic disordered structure.

For other compositions in the range between the A_3B and the AB alloys it is to be expected that the temperature of the change-over from the A_3B -type ordering to the AB type will increase as the AB composition is approached.

The simplicity of the assumptions on which the above calculations are based appears to ensure that no direct comparison with any real alloy system is possible and more complete calculations of the variation of l.r.o. parameters with composition on this basis, although readily performed, seem to have limited value. For example, it may be pointed out that the equations such as (5) and (7) lead to a critical temperature which varies with composition according to the simple hyperbolic law

$$T_c = 8(V_1 - \frac{3}{2}V_2) / 8 \left(2 + \frac{m_A}{m_B} + \frac{m_B}{m_A} \right). \quad (8)$$

Previously¹ it was shown that the variation of T_c for the Cu-Au alloys could be reasonably reproduced by modifying the function $f(x)$ in such a way as to give special significance to the stoichiometric compositions, but a logical development for this modified form is difficult to find. It seems evident that in order to account for the details of the Au-Cu phase diagram it will be necessary to take into account additional factors, such as the difference in size of the atoms and, probably, the electronic energy states.⁵

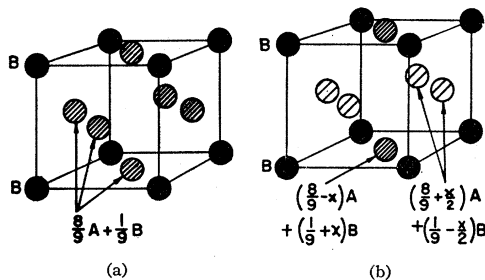


FIG. 3. Average unit cell for a fully ordered A_2B alloy, (a) with random arrangement of excess B atoms, and (b) with excess B atoms arranged preferentially on one A sublattice.

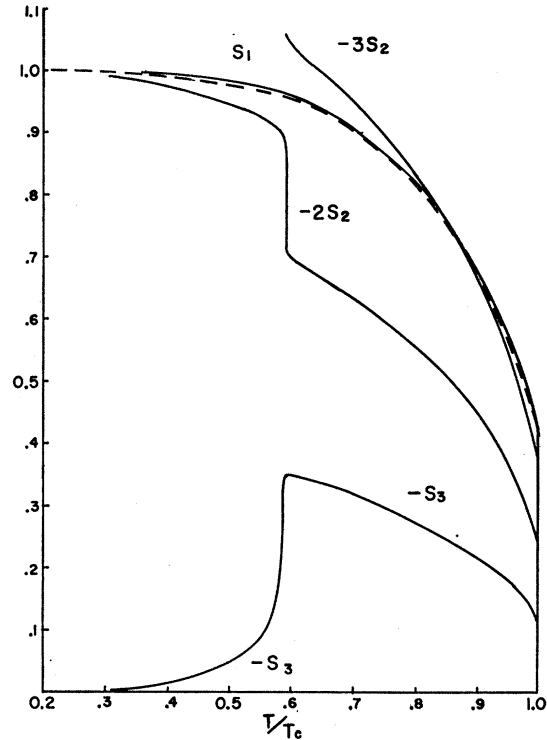


FIG. 4. Values of l.r.o. parameters for composition A_2B . Dashed line: values of s_1 calculated on the assumption that $s_1 + 3s_2 = 0$. Full lines: values of s_1 , $-2s_2$, $-3s_2$ and $-s_3$ calculated without this assumption.

4. DEFINITIONS OF LONG-RANGE ORDER PARAMETERS

There are obvious inconsistencies between the definitions of l.r.o. parameters in terms of periodic, and therefore infinite, structures and the practical realities of antiphase domains and finite crystal size. The definitions of the parameters in terms of infinite lattices may be used for many purposes without leading to serious error or misunderstanding because "reasonable" interpretations of infinity are taken in both theoretical and experimental work. However, when cases are considered involving relatively small out-of-phase domains or possible regions of varying composition, it is necessary to consider the basis for such interpretations in detail.

For simplicity we will consider limitations of periodicity in one dimension only for a simple AB alloy perfectly ordered except for the limitation imposed.

Firstly, if the crystal is of finite size, limited to N unit cells of dimension a , the value of the Bragg and Williams order parameter S is unaffected because of its definition in terms of the proportion of sites "correctly" occupied. However, the values of the order parameters defined in the same way as the s.r.o. parameters above decrease linearly from $(N-1)/N$ for α_1 to become zero for interatomic vectors of length Na as in Fig. 5(a).

For the case discussed by Guttman,⁶ where there is a

⁵ H. Sato and R. S. Toth, Phys. Rev. **127**, 469 (1962).

⁶ L. Guttman, Solid State Phys. **3**, 174 (1956).

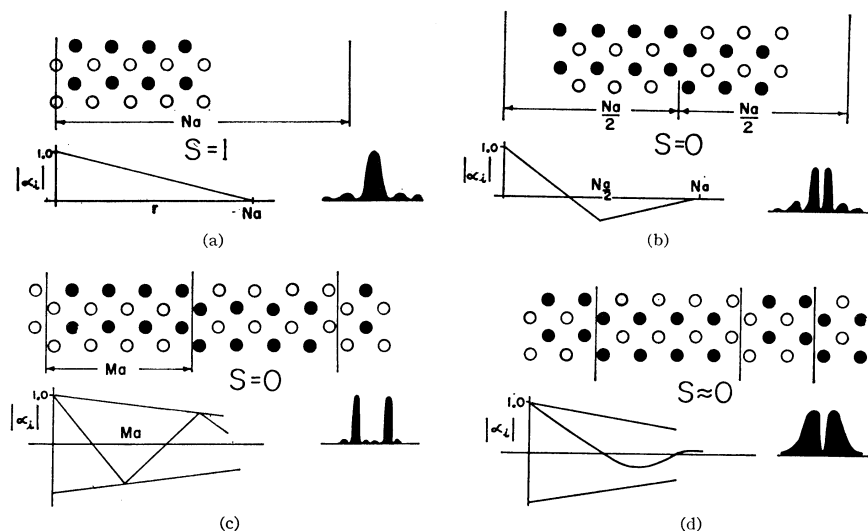


FIG. 5. Diagrams suggesting the limitations of the lattice, the variation of order parameter with vector length and the form of the reciprocal lattice peak for (a) a finite crystal, (b) a finite crystal with one domain boundary, (c) a crystal with regularly spaced domain boundaries, (d) a crystal with irregularly spaced domain boundaries.

single out-of-phase boundary in the middle of the crystal, as in Fig. 5(b), we find $S=0$. The s.r.o.-type parameters, starting from a value $(N-2)/N$ decrease to a value of approximately $-\frac{1}{2}$ for vector lengths $Na/2$ and then increase to zero for vectors of length Na .

If there are regular out-of-phase boundaries separated by M unit cells, then $S=0$ again, and the s.r.o. parameters now start from a value of $(M-1)/M$ and oscillate from positive to negative values gradually decreasing to zero for vector length Na , as in Fig. 5(c). However because we now have a periodic superlattice we should redefine the l.r.o. and s.r.o. parameters in terms of the greater unit cell. Redefining the "correct" positions for atoms, $S=1$, and the s.r.o. parameters corresponding to multiples of unit-cell edge vectors, decrease uniformly to zero as in Fig. 5(a).

If the out-of-phase domain structure is not completely regular, of course, we cannot make this redefinition of order parameters in terms of a new unit cell. Then, again $S=0$; the variation of the s.r.o. parameters with vector length then shows damped oscillations as in Fig. 5(d).

For these four cases, represented by Figs. 5(a)–(d), we can consider the experimental data from which a value for a l.r.o. parameter may most conveniently be derived, namely the form and magnitude of the superlattice reflections found in x-ray diffraction patterns, such as the (100) reflection for the example of Fig. 5. In order to avoid complications of the description due to experimental details we deal with the form of the distribution of scattering power in reciprocal space rather than with measured intensities.

The distribution of scattering power is normally said to contain a sharp peak due to l.r.o. superimposed on the diffuse scattering-power maximum due to s.r.o. The integrated strength of this sharp peak is then taken as a measure of the l.r.o. parameter, the assumption being made that the sharp peak may be clearly separated from the diffuse s.r.o. maximum. The form of the sharp

peak is given by the Fourier transform of the order-dependent parts of the Patterson function, i.e., the Fourier transform of the functions giving the variation of s.r.o. parameters with vector length, as plotted in the Figs. 5. For the finite-crystal case of Fig. 5(a), the peak has the familiar $\sin^2 x/x^2$ form. The integrated intensity appropriately scaled is given by the intercept of the $|\alpha_i|$ curve on the $r=0$ axis. Thus the l.r.o. parameter measured in this way has the value 1.

For the other cases illustrated, the value of the scattering power exactly at the superlattice reciprocal lattice point is zero. The Bragg and Williams order parameter S corresponds to this value and is likewise zero. However, unless the distance between domain boundaries is only a few unit cells the details of the profile of the peak are not resolved under normal experimental conditions. Only the integrated strength of the peak is recorded and the measure of l.r.o. is taken as this integrated value. In each case the integrated value is given by the intercept of the $|\alpha_i|$ curve on the $r=0$ axis.

It is therefore consistent with the experimental procedures of x-ray diffraction and with reasonable theoretical approximations to take this intercept as a measure of l.r.o. This is also consistent with the result of Chipman and Warren⁷ that the integrated intensity measures the long-range order within the domains.

The examples we have discussed above have referred to situations in which the order within the domains is "perfect." Relative to the concept of an infinite lattice it is known that for partial l.r.o. the values of the s.r.o. parameters for short interatomic vectors may differ appreciably from the limiting values for large interatomic vectors, so that in the plot of $|\alpha_i|$ against r the value of $|\alpha_i|$ oscillates about the limiting value as in Fig. 6(a). The definition of l.r.o. parameters s_i , which we

⁷ D. Chipman and B. E. Warren, J. Appl. Phys. **21**, 696 (1950).

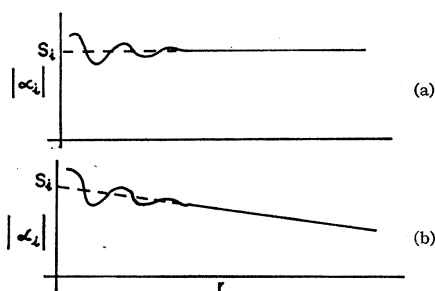


FIG. 6. The variation of order parameters with vector length for (a) an infinite crystal, and (b) a limited crystal.

have used in the previous sections of this paper, is in terms of this limiting value.

When the effects of finite crystallite or domain size are superimposed on the curve of 6(a) we get a curve as in Fig. 6(b), where instead of oscillating about a limiting value, the $|\alpha_i|$ values oscillate about the beginnings of a curve such as shown in one of the sections of Fig. 5.

Hence the values of the l.r.o. parameters s_i must be redefined as the values given by the intercept on the $r=0$ axis of the curve of α_i against r established at moderately large values of r and extrapolated through the oscillations of the curve for small r values.

It is evident that such a definition cannot give unique values for l.r.o. parameters when the crystallite or domain size is so small that no clear distinction can be made between the oscillations of the curve at small r due to s.r.o. variations and the further complications of the curve introduced by limitations of the size of regions with long-range order. This is consistent with the experimental difficulty in such cases of distinguishing the greatly broadened "sharp" superlattice reflections from the s.r.o. diffuse scattering in diffraction experiments. Under such circumstances it is necessary both experimentally and theoretically to make special assumptions in order to define what is meant by long-range order for the particular system under discussion.

It seems clear that while special reference has been made here to x-ray or other diffraction methods of measuring long-range order, similar considerations must apply in reference to other experimental techniques, and the redefinition of l.r.o. parameters suggested will be equally valid and useful for other approaches to the problem.

5. LONG-RANGE ORDER AND FLUCTUATIONS IN COMPOSITION

While the concept of the segregation of an alloy into regions of differing composition, as implied by the results of the simple theory given above, is not subject to direct experimental verification, it is of interest to show that the definitions of l.r.o. parameters given in the previous section are sufficient for the description of such effects, should they exist.

Previously, it was shown that, for the case of an infinite crystal, uniform composition is consistent with $\sum_i s_i = 0$ where the sum is taken over all peaks of the

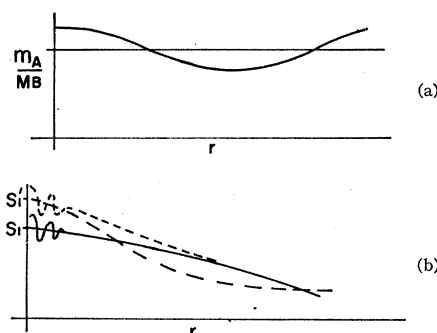


FIG. 7. (a) Variation of composition with distance and (b) its influence on the variation of order parameter with vector length.

unit cell of the periodic part of the Patterson function. This holds likewise for finite crystals when the new definitions of the s_i are used.

As a simple example of a case of nonuniform composition, we consider the case of Fig. 7(a) where there are periodic fluctuations in the ratio m_A/m_B . If we now consider the interatomic vectors corresponding to unit cell corners of the Patterson function, the peak heights will be modulated with the same periodicity. Instead of the full-line curve of 7(b) which extrapolates to the value s_1 at $r=0$, we now get the dashed line which extrapolates to a higher value s_1^1 at $r=0$.

If, instead of the regular fluctuations of Fig. 7(a), there are irregular fluctuations, there will be no oscillations of the order parameter curve in 7(b). We will get a curve such as the dotted one extrapolating to s_1^1 , and this is indistinguishable from that for a sample with uniform composition, an l.r.o. parameter s_1^1 , and a somewhat smaller crystallite size.

Similar considerations hold for the l.r.o. parameter corresponding to other peaks of the Patterson unit cell. The modification of the full-line curve for 7(b) will be different, giving curves extrapolating to other values of s_1^1 at $r=0$ so that we obtain on this basis values of the l.r.o. parameters for which $\sum_i s_i \neq 0$ as in the case of l.r.o. parameters previously defined in terms of an infinite lattice.

It thus appears that the new definition of l.r.o. parameters allows us to describe ordering in situations of varying composition in a consistent and experimentally useful manner.

Note added in proof. A recent paper by P. Clapp [Phys. Letters 13, 305 (1964)], gives a more exact statement of the approximations involved in deriving the equations of Cowley and those of Christy and Hall. I thank D. T. Keating for bringing this paper to my attention.

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