

Short- and Long-Range Order Parameters in Disordered Solid Solutions

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For a crystalline solid made up of a partially ordered array of structural units of more than one type it is shown that the state of order may be described and defined in terms of the self-convolution, or Patterson, function of the structure. The peak heights of the Patterson function are proportional to the short-range order parameters, α_i . The periodic component is described by the long-range order parameters, defined as the limiting values of the α_i at large distances from the origin. The limitations of previous definitions of long-range order parameters are discussed.

The interpretation of the Patterson function as a vector distribution function forms a basis for the calculation of configurational free energy and hence the derivation of equations giving the order parameters as functions of temperature. Some

numerical results are obtained for short- and long-range order parameters for the alloys Cu_3Au and $\beta\text{-CuZn}$.

For Cu_3Au , and for most other binary alloys, it is shown that two long-range order parameters, s_1 and s_2 , are required to specify the state of long-range order, rather than the single parameter previously used. The fact that these two parameters are not simply related is interpreted as evidence for nonrandom fluctuations in the composition of the alloy, probably associated with the presence of out-of-phase domain boundaries which may be rich in one or other of the component types of atoms. It is suggested that a regular superlattice of out-of-phase domains may be present under equilibrium conditions for most alloys.

1. INTRODUCTION

IN a previous publication,¹ the author developed an approximate method for deriving short-range-order (s.r.o.) parameters in disordered alloys and obtained values of these order parameters in excellent agreement with those obtained experimentally by analysis of the diffuse scattering of x rays from single crystals of the alloy Cu_3Au .²⁻⁴ Equations were also derived giving the long-range order (l.r.o.) parameters as a function of temperature and, in spite of the fact that the assumptions and approximations of the method seemed even worse in this case, these equations gave agreement with experimental results⁵⁻⁷ to within the probable experimental error.

A recent reappraisal of this theory has shown that the derivation of useful equations from it must be considered as completely fortuitous. Not only is the assumption that the order parameters are independent gross and unjustifiable, but there are also serious fallacies in the arguments used to derive the expressions for the configurational entropy and energy. However, the equations which were deduced remain the most convenient and accurate means available for calculating the values of order parameters to be expected under any given experimental conditions. In view of the increased interest which has recently been shown in the calculation and measurement of such parameters, it was considered worthwhile to reformulate the problem and attempt a more satisfactory development of the theory and justification of these equations.

The basis for a reformulation of the problem became evident in the course of calculations of x ray and

electron diffraction intensities given by disordered systems. It was previously shown^{1,2} that it is possible to define short-range order (s.r.o.) coefficients, α_i , which could be used to specify the state of order of the system and also to calculate diffraction intensities.^{7a} The diffraction intensities are given, in fact, by summing a Fourier series with the α_i as coefficients. The α_i therefore correspond to the weights of peaks in the (nonperiodic) Patterson function, which is the Fourier transform of the intensity distribution. It is well known that the Patterson function can be interpreted in terms of the interatomic vectors in the crystal lattice. The maxima in the Patterson function indicate the magnitude and direction and the frequency of occurrence of each type of interatomic vector. The Patterson function therefore contains all the information concerning the average surroundings of an atom which is normally of interest in discussing the physical properties of an imperfectly ordered system. It can be used not only to specify the state of order of a system but also as a basis for the calculation of configurational energy and entropy and hence of the equilibrium state of order as a function of temperature.

In general the Patterson function as described above will be nonperiodic, but if long-range order exists in the crystal lattice it will have a periodic component and appreciable deviations from periodicity will occur only in the neighborhood of the origin point. The periodic component may then be described by one or more l.r.o. parameters which may be regarded as the limiting values of the s.r.o. parameters.

2. PATTERSON FUNCTION AND SHORT-RANGE ORDER PARAMETERS

It is possible to deduce from the observed intensities in x-ray, electron-, or neutron-diffraction experiments

^{7a} These, we suggest, should be called the "Warren s.r.o. parameters" in honor of their originator, Professor B. E. Warren of M. I. T.

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

² J. M. Cowley, *J. Appl. Phys.* **21**, 24 (1950).

³ B. W. Roberts and G. H. Vineyard, *J. Appl. Phys.* **27**, 203 (1956).

⁴ D. R. Chipman, *J. Appl. Phys.* **27**, 739 (1956).

⁵ D. Chipman and B. E. Warren, *J. Appl. Phys.* **21**, 696 (1950).

⁶ D. T. Keating and B. E. Warren, *J. Appl. Phys.* **22**, 286 (1951).

⁷ L. Muldrew, *J. Appl. Phys.* **22**, 663 (1951).

a quantity expressed, in x-ray diffraction terminology, as $|F(u,v,w)|^2$, where $F(u,v,w)$ is the Fourier transform of the electron density distribution, $\rho(x,y,z)$; thus,

$$F(u,v,w) = \mathcal{F}\rho(x,y,z) \equiv \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \rho(x,y,z) \times \exp\{2\pi i(ux+vy+wz)\} dx dy dz.$$

The Patterson function is then given by the inverse Fourier transform,

$$P(x,y,z) = \mathcal{F}^{-1}\{F(u,v,w) \cdot F^*(u,v,w)\} = \rho(x,y,z) * \rho(-x, -y, -z),$$

where the $*$ sign signifies a convolution, i.e.,

$$P(x,y,z) = \int \int \int \rho(X,Y,Z) \cdot \rho(x+X, y+Y, z+Z) \cdot dX \cdot dY \cdot dZ.$$

Thus, in the language of statistics $P(x,y,z)$ can be called an autocorrelation function or, in optical terms, a coherence function.

For simplicity we consider a crystal made up of only two different kinds of structural unit, designated A and B , with electron density distributions, referred to arbitrary origins, $\rho_A(x,y,z)$ and $\rho_B(x,y,z)$ or $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$. Relative to some arbitrary origin, the origins of the A and B units are defined by the vectors $\mathbf{r}_{A,j}$ and $\mathbf{r}_{B,k}$. Then

$$\rho(\mathbf{r}) = \rho_A(\mathbf{r}) * \sum_j \delta(\mathbf{r} - \mathbf{r}_{A,j}) + \rho_B(\mathbf{r}) * \sum_k \delta(\mathbf{r} - \mathbf{r}_{B,k}).$$

Hence

$$\begin{aligned} P(x,y,z) &= \rho(\mathbf{r}) * \rho(-\mathbf{r}) \\ &= \rho_A(\mathbf{r}) * \rho_A(-\mathbf{r}) * \sum_j \sum_J \delta(\mathbf{r} - \mathbf{r}_{A,j} + \mathbf{r}_{A,J}) \\ &\quad + \rho_B(\mathbf{r}) * \rho_B(-\mathbf{r}) * \sum_k \sum_K \delta(\mathbf{r} - \mathbf{r}_{B,k} + \mathbf{r}_{B,K}) \\ &\quad + \rho_A(\mathbf{r}) * \rho_B(-\mathbf{r}) * \sum_j \sum_K \delta(\mathbf{r} - \mathbf{r}_{A,j} + \mathbf{r}_{B,K}) \\ &\quad + \rho_B(\mathbf{r}) * \rho_A(-\mathbf{r}) * \sum_k \sum_J \delta(\mathbf{r} - \mathbf{r}_{B,k} + \mathbf{r}_{A,J}). \end{aligned}$$

Let N be the total number of structural units of which Nm_A are A and Nm_B are B .

If we assume that the surroundings of all A units and of all B units are equivalent, i.e., if we ignore the

effects at crystal boundaries, we can say that relative to each of the Nm_A A units, other A units can occur at positions given by the set of vectors $\mathbf{r}_{AA,i}$ and B units can occur at positions given by a set of vectors $\mathbf{r}_{AB,i}$ such that $\mathbf{r}_{AA,i}$ contains all vectors $\mathbf{r}_{A,j} - \mathbf{r}_{A,J}$ and $\mathbf{r}_{AB,i}$ contains all vectors $\mathbf{r}_{A,j} - \mathbf{r}_{B,k}$. Similarly we can define vector sets $\mathbf{r}_{BB,i}$ and $\mathbf{r}_{BA,i}$. Then

$$\begin{aligned} P(\mathbf{r}) &= Nm_A \{ \rho_A(\mathbf{r}) * \rho_A(-\mathbf{r}) * \sum_i p_{AA,i} \cdot \delta(\mathbf{r} - \mathbf{r}_{AA,i}) \\ &\quad + \rho_A(\mathbf{r}) * \rho_B(-\mathbf{r}) * \sum_i p_{AB,i} \cdot \delta(\mathbf{r} - \mathbf{r}_{AB,i}) \} \\ &\quad + Nm_B \{ \rho_B(\mathbf{r}) * \rho_B(-\mathbf{r}) * \sum_i p_{BB,i} \cdot \delta(\mathbf{r} - \mathbf{r}_{BB,i}) \\ &\quad + \rho_B(\mathbf{r}) * \rho_A(-\mathbf{r}) * \sum_i p_{BA,i} \cdot \delta(\mathbf{r} - \mathbf{r}_{BA,i}) \}, \quad (1) \end{aligned}$$

where $p_{AA,i}$ is the probability that an A unit should be separated by the vector $\mathbf{r}_{AA,i}$ from another A unit, and $p_{AB,i}$, $p_{BA,i}$ and $p_{BB,i}$ are defined in an analogous way.

If the numbers i are assigned in a consistent manner to denote the various members of the vector sets $\mathbf{r}_{AA,i}$, $\mathbf{r}_{BA,i}$, etc., it is possible to define a set of order parameters α_i by which the probabilities $p_{AA,i}$, $p_{BA,i}$, etc., can be specified. Thus we put

$$p_{BA,i} = m_A(1 - \alpha_i). \quad (2a)$$

Then, since the number of AB vectors is the same as the number of BA vectors,

$$p_{AB,i} = m_B(1 - \alpha_i), \quad (2b)$$

and since the probability for an A plus the probability for a B must be unity at all points,

$$p_{AA,i} = m_A + m_B \alpha_i, \quad (2c)$$

and

$$p_{BB,i} = m_B + m_A \alpha_i. \quad (2d)$$

Substitution of (2) in (1) thus gives the Patterson function in terms of the s.r.o. coefficients.

A further simplification of (1) is possible if the A and B units are located on a set of fixed positions, such as the lattice points of a regular one-, two-, or three-dimensional lattice. Then the various vector sets $\mathbf{r}_{AA,i}$, $\mathbf{r}_{AB,i}$, $\mathbf{r}_{BA,i}$, and $\mathbf{r}_{BB,i}$ are identical and may be denoted by \mathbf{r}_i . This is the case, for example, in binary alloy solid solutions such as Cu_3Au or CuZn if the differences in size of the constituent atoms are ignored. Then (1) reduces to

$$\begin{aligned} P(\mathbf{r}) &= N \{ [m_A \rho_A(\mathbf{r}) + m_B \rho_B(\mathbf{r})] * [m_A \rho_A(-\mathbf{r}) + m_B \rho_B(-\mathbf{r})] * \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \} \\ &\quad + Nm_A m_B \{ [\rho_A(\mathbf{r}) - \rho_B(\mathbf{r})] * [\rho_A(-\mathbf{r}) - \rho_B(-\mathbf{r})] * \sum_i \alpha_i \cdot \delta(\mathbf{r} - \mathbf{r}_i) \}. \quad (3) \end{aligned}$$

Taking the Fourier transform gives the expression for the diffraction intensity:

$$\begin{aligned} I(\mathbf{h}) &\propto F(\mathbf{h}) \cdot F^*(\mathbf{h}) \\ &= N [m_A F_A(\mathbf{h}) + m_B F_B(\mathbf{h})]^2 \sum_i \exp\{-2\pi i(\mathbf{h} \cdot \mathbf{r}_i)\} \\ &\quad + Nm_A m_B [F_A(\mathbf{h}) - F_B(\mathbf{h})]^2 \sum_i \alpha_i \\ &\quad \times \exp\{-2\pi i(\mathbf{h} \cdot \mathbf{r}_i)\}, \quad (4) \end{aligned}$$

where \mathbf{h} is the reciprocal lattice vector with components u, v, w .

For both Eq. (3) and Eq. (4) the first term is independent of the α_i and corresponds to the state of complete disorder.

3. LONG-RANGE ORDER PARAMETERS

A state of long-range order may be said to exist if the second, order-dependent, part of Eq. (3) or, more generally, the corresponding part of Eq. (1), has a periodic component, i.e., if the values of α_i become

spatially periodic for very large magnitudes of the vectors \mathbf{r}_i . If the periodic component has a unit cell containing a number, m , of the end points of vectors \mathbf{r}_i , then we may define l.r.o. parameters $s_1, s_2 \dots s_m$, corresponding to the limiting value of the m sets of s.r.o. parameters, α_i .

It has been assumed in the past that all the l.r.o. coefficients s_1 to s_m will be either identical or directly proportional to one another, so that a single l.r.o. parameter, say s , can be used to describe the state of l.r.o. completely. It is shown below that this is not necessarily the case.

The l.r.o. parameter, S , defined by Bragg and Williams⁸ and subsequently used almost universally, is defined in relation to the ordered lattice itself and not to the Patterson function. Since only the Patterson function, and not the lattice, is observable, the definition of S involves an arbitrary assumption. For example, in the case of an AB alloy of the body-centered cubic CuZn type, the lattice can be considered as made up of two interpenetrating simple cubic lattices, designated α and β . Then the α sites are arbitrarily chosen as the "right" sites for A atoms, so that for perfect order all A atoms are on α sites and all B atoms are on β sites.

Then

$$S = \frac{1}{2} \left(\frac{u_\alpha - m_A}{1 - m_A} \right) + \frac{1}{2} \left(\frac{u_\beta - m_B}{1 - m_B} \right), \quad (5)$$

where u_α is the fraction of α sights rightly occupied (by A atoms) and u_β is the fraction of β sights rightly occupied.

By summing the number of A and B atoms we derive from (5)

$$u_\alpha = m_A + 2m_A m_B S; \quad u_\beta = m_B + 2m_A m_B S. \quad (6)$$

The periodic part of the Patterson function has two types of peaks, one occupying the corner positions of the unit cells and corresponding to $\alpha \rightarrow \alpha$ and $\beta \rightarrow \beta$ vectors, and the other occupying body-centered positions and corresponding to $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ vectors.

For the unit cell corner sites we can find the probability that both ends of the vector are occupied by A atoms. If we assume deviations from perfect order to be completely random, we get

$$m_A p_{AA,i} = u_\alpha u_{\alpha/2} + (1 - u_\beta)(1 - u_\beta)/2,$$

or

$$p_{AA,i} = m_A + 4m_A m_B^2 S^2.$$

Similarly

$$p_{AB,i} = m_B - 4m_A m_B^2 S^2,$$

$$p_{BA,i} = m_A - 4m_A^2 m_B S^2,$$

$$p_{BB,i} = m_B + 4m_A^2 m_B S^2.$$

Comparing these equations with (2) above, we see that for these sites the limiting of α_i is equal to $4m_A m_B S^2$.

⁸ W. L. Bragg and E. J. Williams, Proc. Roy. Soc. (London) **A145**, 699 (1934).

Hence, for unit cell corner sites,

$$s_1 = 4m_A m_B S^2.$$

Similarly it can be shown that if \mathbf{r}_i corresponds to a body-centered site, and the assumption of complete randomness of ordering defects is made,

$$s_2 = -4m_A m_B S^2 = -s_1.$$

It is therefore evident that the state of long-range order is properly characterized by a quantity, such as s , proportional to S^2 , rather than by S . An ambiguity is thereby removed since, from (5), S and $-S$ refer to exactly the same state of order, the minus sign appearing if A atoms are concentrated on β rather than α sites.

Similar considerations apply in the case of alloys of near A_3B composition with the face-centered cubic Cu₃Au-type ordered lattice. The lattice is then composed of three simple cubic sublattices of α sites and one simple cubic sublattice of β sites. Then

$$S = \frac{3}{4} \left(\frac{u_\alpha - m_A}{1 - m_A} \right) + \frac{1}{4} \left(\frac{u_\beta - m_B}{1 - m_B} \right).$$

As was demonstrated previously,¹ we have for a unit cell corner site

$$\alpha_i \rightarrow s_1 = 16m_A m_B S^2/3,$$

and for a face-centered site, if we make the assumption, which is later shown to be probably invalid, that there is complete randomness in the deviations from perfect order,

$$s_2 = -16m_A m_B S^2/9 = -s_1/3.$$

4. THE EQUILIBRIUM STATE

The configurational free energy of a crystal is given by

$$F = -kT \ln \sum_n \exp(-U_n/kT),$$

where the summation is over the index n , enumerating the configurations of the system for which the order parameters have the values α_i . The information required for the enumeration of the states and evaluation of the energy terms is contained in the Patterson function if we can associate a particular contribution to the energy with each type of interatomic vector. However, a general solution to the problem of evaluating this free energy has not yet been found. We therefore make plausible simplifying assumptions.

For equilibrium conditions a definite relation exists between all the order parameters, α_i . Given the value of one order parameter, the values of all other order parameters may, in principle, be determined. If changes of temperature are considered, the variations of the order parameters may be specified by expressing all order parameters as functions of any one particular order parameter. The assumption we make is that for small isothermal deviations from equilibrium the

functional relationship between order parameters is the same as for small temperature changes, i.e., that $\partial\alpha_j/\partial\alpha_i$ for T constant is equal to $(\partial\alpha_j/\partial T)(\partial T/\partial\alpha_i)$.

Near the equilibrium state, then, we need consider only the free energy term associated with one particular order parameter. The number of configurations of the system is given by the number of configurations for which the order parameter associated with the i th Patterson function peak is α_i , and the energy for each configuration is the energy associated with the fact that this order parameter has the value α_i . The equilibrium state is determined by minimizing the free energy so calculated with respect to this one order parameter.

We assume that an energy $V_{AA,i}$ is associated with a pair of A atoms separated by the vector $\mathbf{r}_{AA,i}$, and we define similarly $V_{AB,i}$ ($=V_{BA,i}$) and $V_{BB,i}$. Considering each A and B atom in turn as origin, the total number of vectors of each type and hence the total energy associated with these origin atoms is found, using Eqs. (1) and (2), as

$$\begin{aligned} U &= \frac{1}{2}Nm_A^2 \sum_i V_{AA,i} + \frac{1}{2}Nm_B^2 \sum_i V_{BB,i} \\ &\quad + Nm_Am_B \sum_i V_{AB,i} + \frac{1}{2}Nm_Am_B \\ &\quad \times \sum_i \alpha_i (V_{AA,i} + V_{BB,i} - 2V_{AB,i}) \\ &= V_0 + Nm_Am_B \sum_i \alpha_i V_i, \end{aligned} \quad (7)$$

where V_i is half the average energy required to replace two A - B atom pairs separated by vectors $\mathbf{r}_{AB,i}$ by a pair of A atoms separated by $\mathbf{r}_{AA,i}$ and a pair of B atoms separated by $\mathbf{r}_{BB,i}$. Equation (7) thus gives the energy associated with taking each atom in turn as origin and saying that it is definitely either an A atom or a B atom. Hence, this may be considered as the energy associated with the origin peak of the Patterson function. However, what we require is the energy associated with the fact that an order parameter α_i is assigned to the peaks of the Patterson function corresponding to the vectors \mathbf{r}_i . This is given by considering the average interaction energy of all atoms with the atoms at the sites separated from the chosen origin sites by \mathbf{r}_i for which the probability of being an A or a B is given by the coefficient α_i . It is readily shown that the average energy associated with a pair of sites with order parameters α_i and α_j is $m_Am_B\alpha_i\alpha_j V_{ij}$ plus a constant term, where V_{ij} is the analog of V_i for vectors $\mathbf{r}_i - \mathbf{r}_j$. The total energy associated with the \mathbf{r}_i peaks of the Patterson function is therefore

$$U_i = U_{0,i} + Nm_Am_B \sum_j \alpha_i \alpha_j V_{ij}. \quad (8)$$

We now assume that

$$\sum_n \exp(-U_n/kT) = W_i \exp(-U_i/kT),$$

where W_i is the number of configurations with the value α_i for the i th order parameter, i.e., that we may take an average value of $\sum_j \alpha_j V_{ij}$ for all of these configurations, equal to the equilibrium value.

From Eq. (2) it follows that the $N \mathbf{r}_i$ vectors are divided as follows:

$$\begin{aligned} \text{number of } A\text{-}A \text{ vectors: } N_{AA} &= Nm_A(m_A + m_B\alpha_i), \\ \text{number of } A\text{-}B \text{ vectors: } N_{AB} &= Nm_Am_B(1 - \alpha_i), \\ \text{number of } B\text{-}A \text{ vectors: } N_{BA} &= Nm_Bm_A(1 - \alpha_i), \\ \text{number of } B\text{-}B \text{ vectors: } N_{BB} &= Nm_B(m_B + m_A\alpha_i). \end{aligned}$$

These can be arranged in a number of ways given approximately by

$$W_i = N! / N_{AA}! N_{BB}! (N_{AB})^2.$$

Using Stirling's approximation for the logarithm of a factorial,

$$\begin{aligned} +k \ln W_i &= -N [m_A(m_A + m_B\alpha_i) \ln \{m_A(m_A + m_B\alpha_i)\} \\ &\quad + m_B(m_B + m_A\alpha_i) \ln \{m_B(m_B + m_A\alpha_i)\} \\ &\quad + 2m_Am_B(1 - \alpha_i) \ln \{m_Am_B(1 - \alpha_i)\}]. \end{aligned}$$

The free energy term associated with the \mathbf{r}_i vectors is thus

$$F = U_i - kT \ln W_i,$$

and minimizing this with respect to α_i by putting $\partial F / \partial \alpha_i = 0$ for constant T gives,

$$\begin{aligned} \sum_j \alpha_j V_{ij} + \alpha_i \sum_j \frac{\partial \alpha_j}{\partial \alpha_i} V_{ij} \\ + kT \ln \left\{ \frac{(m_A + m_B\alpha_i)(m_B + m_A\alpha_i)}{m_Am_B(1 - \alpha_i)^2} \right\} = 0. \end{aligned} \quad (9)$$

There is one such equation for each value of i , giving α_i in terms of the other order parameters and the temperature T . This simultaneous set of equations can, in principle, be solved to give all order parameters and so specify completely the state of order at any temperature.

It may be noted that Eq. (9) is identical with Eq. (1) of the previous paper¹ except for the second term. The earlier result may thus be considered a good approximation if the second term can be shown to be either very small compared to the first term or else very nearly equal to it. In the calculations reported below it was found that, at least for the particular cases considered, this seems to be the case. The second term approximates to the first for low temperatures when there is considerable long-range order and is small for temperatures much greater than the critical temperature.

When the vectors \mathbf{r}_i define the points of a regular lattice, as is the case, for example, for alloys such as CuZn or Cu₃Au if the differences in atom size are ignored, it may be possible and convenient to group them into sets of vectors which are all of the same length and are symmetrically equivalent. The sites defined by such a set of vectors have a common order parameter, α_n , and may be referred to collectively as

an n th nearest neighbor shell, the shells being numbered according to the magnitude of the vectors. Equation (9) can then be written

$$\sum_n V_n \sum_{j^{i,n}} \left(\alpha_j + \alpha_i \frac{\partial \alpha_j}{\partial \alpha_i} \right) + kT \ln f(\alpha_i) = 0, \quad (10)$$

where

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

and $\sum_{j^{i,n}}$ is a summation over j for sites which are n th nearest neighbors of the i th site. In general, the value of the V_n will decrease very rapidly with increasing n and only the first one or two values need be considered.

The solution of the simultaneous set of Eqs. (9) or (10) is a matter of considerable difficulty. An approximate method of solution, which could be made iterative has, however, been found. Integrating Eq. (10) gives

$$\alpha_i \sum_n V_n \sum_{j^{i,n}} \alpha_j + kTH(\alpha_i) = C,$$

where

$$H(\alpha_i) = \int f(\alpha_i) d\alpha_i.$$

This may be written in the form

$$\sum_n V_n \sum_{j^{i,n}} \alpha_j + b_i \alpha_i = 0, \quad (11)$$

where

$$b_i = \alpha_i^{-2} \{ kTH(\alpha_i) + C \}.$$

The constant, C , is independent of α_i , and so of all order parameters, for constant T . The value of C may thus be obtained by taking the limiting value of α_i for very large r_i . Above the critical temperature, α_i tends to zero and $C = kTH(0)$. Below the critical temperature the α_i values tend to the l.r.o. parameters, s_m , and substituting the values of s_m for the α_i in Eq. (10) leads to a set of m equations which may be soluble by trial and error methods if m is a small number.

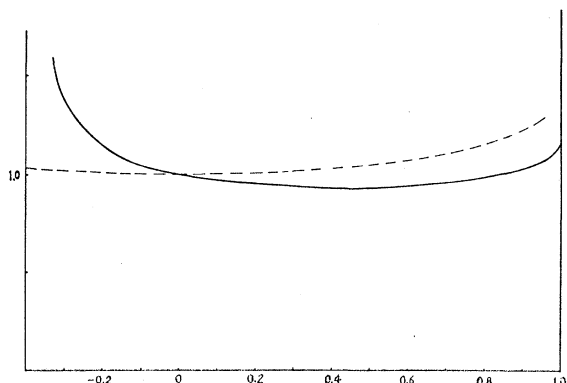


FIG. 1. The function $\alpha_i^{-2}[H(\alpha_i) - H(0)]$ plotted against α_i for Cu_3Au and $\beta\text{-CuZn}$ type alloys. The ordinates have been adjusted to make the values for $\alpha_i = 0$ equal. The dashed line refers to CuZn ; the solid line to Cu_3Au .

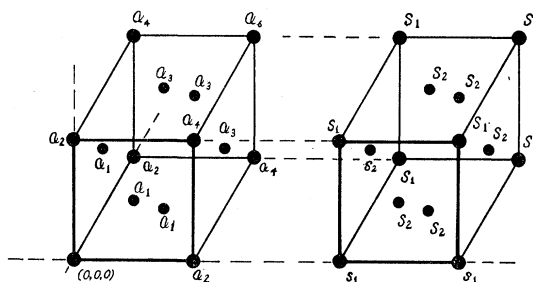


FIG. 2. A portion of the Patterson function for Cu_3Au showing the assignment of s.r.o. and l.r.o. parameters to the peaks of one unit cell including the origin and one unit cell far from the origin.

The function $\alpha_i^{-2}[H(\alpha_i) - H(0)]$ is plotted in Fig. 1 for the alloys, CuZn and Cu_3Au . It does not vary a great deal over the range of α_i values and is, in fact, very nearly constant for small values of α_i , for which $f(\alpha_i)$ is nearly linear. Hence, approximate values for α_i give fairly accurate values of b_i . For temperatures above the critical temperature, if we assume that only a finite number of order parameters are different from zero, we get from (11) a set of linear equations for the α_i which may be solved by standard methods. The first, approximate values of α_i can be obtained either by assuming all the b_i to be equal for a given temperature, or else by using the results of the previous paper.¹ For temperatures below the critical temperature the problem is not quite so easily solved but a limited number of order parameters can be found without great difficulty.

5. Cu_3Au —LONG-RANGE ORDER

Equations for the l.r.o. parameters are obtained by substituting in Eq. (9) or (10) the limiting values, for large distances from the origin, of the order parameters α_i . For the face-centered cubic Cu_3Au lattice the periodic component of the Patterson function has a unit cell containing four peaks, one at the cube corner and three at face-centered positions as shown in Fig. 2. We let the limiting value of α_i for unit cell corner position be s_1 , and since the face-centered positions are equivalent we assign them a common order parameter, s_2 , which varies from zero for no long-range order to $-\frac{1}{3}$ for perfect order. From Eq. (10), taking into account only the nearest neighbor energy term V_1 , we get the two equations

$$\begin{aligned} s_2 + s_1 \frac{\partial s_2}{\partial s_1} &= -\frac{kT}{12V_1} f(s_1), \\ s_1 + 4s_2 + s_2 \frac{\partial s_1}{\partial s_2} &= -\frac{kT}{4V_1} f(s_2). \end{aligned} \quad (12)$$

These simultaneous equations have no unique solution. Some further assumptions as to the behavior of s_1 and s_2 must be made so that a solution may be obtained. Approximate solutions were obtained firstly

by using the limiting form of Eq. (11) with the value of the constant C appropriate to $T=0$ and secondly by assuming $\partial s_2/\partial s_1$ to be a constant, which seemed from the first method to be approximately true. Both of these methods gave values of s_1 and $-3s_2$ differing by a maximum of about ten percent, and predicted a critical temperature of about $T=1.5V_1/k$ at which the long-range order parameters dropped discontinuously to zero. This is also the value for the critical temperature found in the previous paper.¹

A more exact solution was obtained by assuming near-linear relationships between s_1 and s_2 to calculate the differentials and using these to solve Eqs. (12) numerically at various temperatures. From the solutions a new relationship between s_1 and s_2 was found and used to correct the initial assumption.

Several stages of such refinement gave finally a set of parameter values consistent with (12). The variation of s_1 and $-3s_2$ with temperature is shown in Fig. 3.

If it is assumed that both s_1 and $-3s_2$ tend to unity for $T=0$ the only solution found was approximately represented by $\delta s_2/\delta s_1 = -0.267$ which gives $-3s_2 > s_1$ for $T > 0$. This is a physically impossible solution. Hence it was necessary to admit the possibility that s_1 or $-3s_2$ might deviate from unity for $T=0$. The solution illustrated in Fig. 2 is approximately represented by $-3s_2 = -0.015 + 0.960 s_1$ for $s_1 > 0.2$, so that for $T=0$, $-3s_2 = 0.945$. This solution is the one with $-3s_2 \leq s_1$ which seemed to be indicated by the approximate solutions mentioned above. It is not necessarily the only solution, but no other reasonable solution was found. The solution $-3s_2 = s_1$ was definitely excluded.

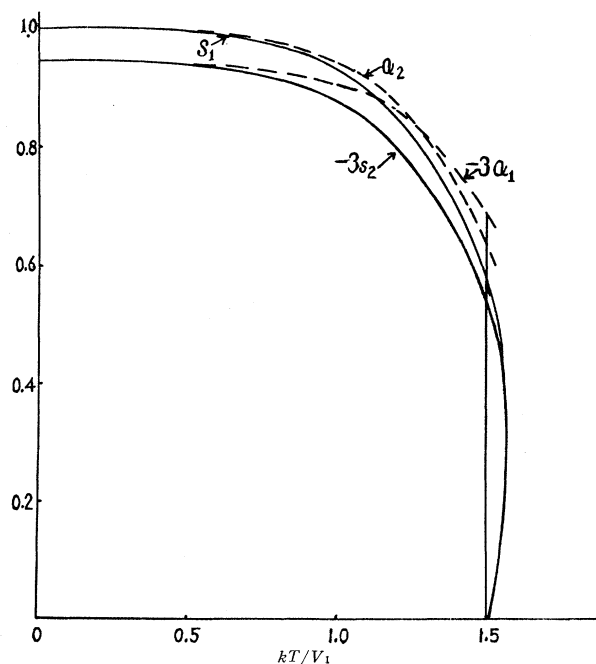


FIG. 3. The variation of the order parameters s_1 , $-3s_2$, $-3\alpha_1$, and α_2 with temperature for Cu_3Au .

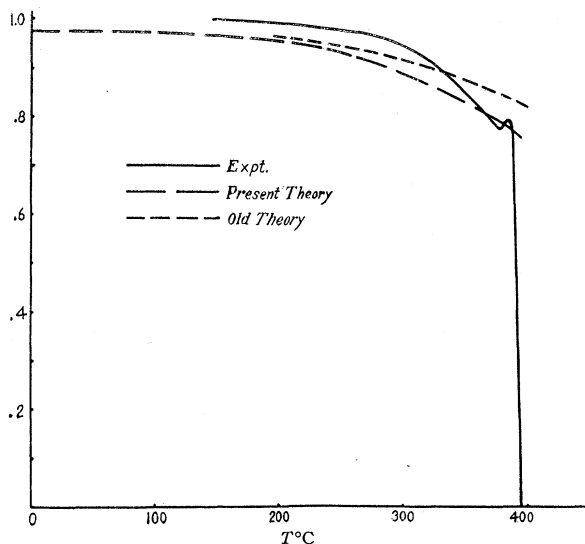


FIG. 4. Comparison of the experimental values⁶ of the l.r.o. parameter, S , for Cu_3Au with theoretical values from the previous¹ and present treatments.

It is seen that $-3s_2$ is consistently about 5% lower than s_1 up to the critical temperature given by $T_c = 1.5 V_1/k$. At T_c the order parameters drop discontinuously to zero from the values $s_1 = 0.576$, $-3s_2 = 0.540$, both of which are lower than the previous value, $S^2 = 0.685$, obtained¹ by making the assumption $s_1 = -3s_2$ and considering unit cell corner vectors only.

The intensities of x-ray reflections are given by the Fourier transform of the Patterson function. It is evident from Fig. 2 that superlattice reflections such as, for example, the (100), will have an intensity proportional to $(s_1 - s_2)$ instead of $\frac{4}{3}S^2$. Hence, the value of the long-range order parameter S deduced from x-ray diffraction intensities should be slightly lower than predicted in the previous paper.¹ Figure 4 shows that the agreement with experimental results⁶ is now very good at temperatures near T_c but not quite so good at lower temperatures. Our present results are thus in excellent agreement with the Monte Carlo calculations of Fosdick.⁹

The significance of the difference between the values of s_1 and $-3s_2$ is probably best seen by considering the diffraction intensities. The so-called "fundamental reflections" are normally considered to be independent of the state of order since for them all atoms scatter in phase and the intensity is proportional to the square of the sum of atomic scattering factors for the average unit cell contents, i.e., to $(f_{\text{Au}} + 3f_{\text{Cu}})^2$. However, for $s_1 > -3s_2$ it is evident from Fig. 2 that fundamental reflections [the (200) for example] will show an increase in intensity proportional to $3s_2 + s_1$. This is not possible if deviations from the average unit cell contents in the lattice are completely random. To explain the increase in the intensity of the fundamental reflections, we must

⁹ L. D. Fosdick, Phys. Rev. **116**, 565 (1959).

assume that the deviations from the average unit cell content are not random, i.e., that gold-rich and copper-rich regions exist in the equilibrium alloy, so that regions with increased and decreased scattering power per unit cell are present.

For a regular modulation of the scattering power, with a periodicity many times that of the unit cell, the fundamental reflections will be accompanied by very close satellite reflections. For irregular modulation the fundamental reflections will be broadened. In our theoretical treatment the satellite intensities in either case will be added to those of the fundamental reflections, giving the effect of an increase in the intensity of the latter. Let us suppose, for example, that the average scattering power of the unit cell is modulated by multiplying by a function

$$Q(x, y, z) = 1 + \epsilon(\cos 2\pi Ax + \cos 2\pi By + \cos 2\pi Cz),$$

which has periodicities $1/A$, $1/B$, and $1/C$, assumed to be much larger than the unit cell. Then we have

$$\iiint Q^2(x, y, z) dx dy dz = 1 + 3\epsilon^2/2,$$

where the integration is taken over one repeat distance of the function in each direction. Applying Parseval's theorem, we deduce that the intensity of the fundamental reflections will also be increased by a factor of $1 + 3\epsilon^2/2$.

From Eq. (4) we then obtain

$$1 + 3\epsilon^2/2 = [\frac{1}{4}(3f_{\text{Cu}} + f_{\text{Au}})^2 + \frac{3}{16}(f_{\text{Au}} - f_{\text{Cu}})^2(s_1 + 3s_2)] / \frac{1}{4}(3f_{\text{Cu}} + f_{\text{Au}})^2,$$

or

$$\epsilon = (f_{\text{Au}} - f_{\text{Cu}})(3f_{\text{Cu}} + f_{\text{Au}})^{-1} \left(\frac{s_1 + 3s_2}{2} \right)^{\frac{1}{2}}.$$

This value is seen to be independent of periodicity of the modulation of average scattering power in the lattice. From Fig. 3 we have $s_1 + 3s_2 \approx 1/20$, from which it follows that the fluctuation in the sum of the scattering factors is of the order of $\frac{1}{6}(f_{\text{Au}} - f_{\text{Cu}})$ per unit cell in each direction.

Our result therefore implies that at all temperatures below the critical temperature, the equilibrium state of order in the alloy Cu_3Au is one in which there is a fluctuation in average composition to the extent that one gold atom is replaced by a copper atom or vice versa for each six or seven unit cells distance in each direction. Such a fluctuation could be the result of the occurrence of the out-of-phase domain structure, which is well known to occur in this and many other alloys. If the lattice is considered to consist of four interpenetrating simple-cubic sublattices, out-of-phase domain boundaries occur where the preferred sites for gold atoms shift from one of these sublattices to another. The inter-domain boundaries may then be gold-rich or copper-rich. To explain our result, such boundaries

would have to occur at intervals of about six or seven unit cells.

A regular arrangement of such out-of-phase domain boundaries could result in a superlattice unit cell with repeat distances many unit cells in each direction, the minimum repeat distance being about 12 or 13 unit cells. Superlattices of this sort are well known. The most commonly quoted and the most studied is in the alloy CuAu II , but such superlattices have also been observed in the Cu_3Au -type alloys Cu_3Pd ,^{10,11} Ag_3Mg ,¹² and Au_3Mn .¹³ For CuAu_3 Hirabayashi¹⁴ observed such a superlattice formation, with periodicity 11 times the fundamental unit cell, by x-ray diffraction and Raether,¹⁵ using electron diffraction methods, observed a superlattice periodicity of 7 to 10 times the unit cell dimensions for Cu_3Au . It is interesting to speculate that an out-of-phase domain superlattice may in fact be the true equilibrium state for the alloy Cu_3Au and that it is only under the conditions of intense electron bombardment present in electron diffraction experiments that the equilibrium state may be achieved since the ordering time would normally be too long for convenient observation.

It may be significant, in this connection, that Fosdick⁹ found that "out-of-phase planes" appeared in stable configurations of the set of 500 atoms which he considered, especially if he assumed, as we have, that $V_2 = 0$.

6. Cu_3Au ; SHORT-RANGE ORDER ACCOMPANYING LONG-RANGE ORDER

A limited number of s.r.o. parameters for Cu_3Au may be calculated in the region $T < T_c$ using Eq. (11) with the value of the constant C given by taking the limiting values of the s.r.o. parameters to be the l.r.o. parameters found in the previous section.

For example, if we assume that only V_1 is appreciable so that the other V_n may be neglected, Eq. (11) becomes

$$\alpha_i \sum_j s_j^{i,1} \alpha_j + \frac{kT}{V_1} \{H(\alpha_i) - H(s_i)\} - s_i \sum_j s_j^{s_i,1} \alpha_j = 0. \quad (13)$$

If we then assume that all α_i except α_1 and α_2 have the limiting values s_1 or s_2 , we get two equations for α_1 and α_2 , by using the relations, derived from Eq. (14) below:

$$\begin{aligned} \sum_j s_j^{1,1} \alpha_j &= 1 + 4\alpha_1 + 2\alpha_2 + s_1 + 4s_2, \\ \sum_j s_j^{2,1} \alpha_j &= 4\alpha_1 + 8s_2, \\ \sum_j s_j^{s_1,1} \alpha_j &= 12s_2, \\ \sum_j s_j^{s_2,1} \alpha_j &= 4s_1 + 8s_2. \end{aligned}$$

¹⁰ D. Watanabe and S. Ogawa, J. Phys. Soc. (Japan) **11**, 226 (1956).

¹¹ M. Hirabayashi and S. Ogawa, J. Phys. Soc. (Japan) **12**, 259 (1957).

¹² K. Fujiwara, M. Hirabayashi, D. Watanabe, and S. Ogawa, J. Phys. Soc. (Japan) **13**, 167 (1958).

¹³ D. Watanabe, J. Phys. Soc. (Japan) **13**, 535 (1958).

¹⁴ M. Hirabayashi, J. Phys. Soc. (Japan) **14**, 262 (1959).

¹⁵ H. Raether, Z. angew. Phys. **4**, 53 (1952).

TABLE I. Comparison of theoretical and experimental values^a of the first ten s.r.o. parameters for Cu₃Au. The coordinates in column two refer to unit distances of half the unit cell dimensions.

Shell numbers	Coordinates	Perfect order $T=0^\circ\text{K}$	$T=405^\circ\text{C}$		$T=460^\circ\text{C}$		$T=550^\circ\text{C}$	
			Expt.	Theor.	Expt.	Theor.	Expt.	Theor.
1	1,1,0	-0.315	-0.152	-0.201	-0.148	-0.178	-0.131	-0.154
2	2,0,0	1.000	0.186	0.260	0.172	0.192	0.105	0.135
3	2,1,1	-0.315	0.009	0.037	0.019	0.038	0.026	0.034
4	2,2,0	1.000	0.095	0.067	0.068	0.043	0.045	0.026
5	3,1,0	-0.315	-0.053	-0.091	-0.049	-0.064	-0.032	-0.040
6	2,2,2	1.000	0.025	-0.028	0.007	-0.023	-0.009	-0.017
7	3,2,1	-0.315	-0.016	-0.003	-0.008	-0.004	-0.003	-0.004
8	4,0,0	1.000	0.048	0.086	0.042	0.053	0.019	0.029
9	3,3,0	-0.315	-0.026	-0.030	-0.022	-0.015	-0.011	-0.007
10	4,1,1	-0.315	0.011	0.010	0.020	0.009	0.007	0.007
	4,2,0	1.000	0.026	0.034	0.025	0.022	0.007	0.013

^a See reference 2.

These two equations were solved by trial and error methods at a number of temperatures to give the variation of $-3\alpha_1$ and α_2 with temperature which is shown in Fig. 3. At $T=0$, $\alpha_1=s_2$ and $\alpha_2=s_1=1$. For $T=T_c$, $\alpha_1=-0.229$, $\alpha_2=0.637$.

7. Cu₃Au; SHORT-RANGE ORDER ABOVE T_c

To evaluate the s.r.o. parameters for Cu₃Au at temperatures above the critical temperature, Eq. (11) has been used in the manner suggested in the paragraph following that equation. From the geometry of the lattice we see that if only $V_1 \neq 0$, Eq. (11) gives the set of equations:

$$\begin{aligned}
 -b_1\alpha_{1,1,0} &= -b_1\alpha_1 = 1 + 4\alpha_1 + 2\alpha_2 + 4\alpha_3 + \alpha_4, \\
 -b_2\alpha_{2,0,0} &= -b_2\alpha_2 = 4\alpha_1 + 4\alpha_3 + 4\alpha_5, \\
 -b_3\alpha_{2,1,1} &= -b_3\alpha_3 = 2\alpha_1 + \alpha_2 + 2\alpha_3 + 2\alpha_4 + 2\alpha_5 + \alpha_6 + 2\alpha_7, \\
 -b_4\alpha_{2,2,0} &= -b_4\alpha_4 = \alpha_1 + 4\alpha_3 + 2\alpha_5 + 4\alpha_7 + \alpha_9, \\
 \text{etc.}
 \end{aligned} \quad (14)$$

Here the subscripts of the α 's in the first term of each line refer to the coordinates, in terms of half the unit cell dimensions, of a typical point of a shell of atoms, and the subscripts in the rest of each line refer to shell numbers.

If we assume that all $\alpha_i=0$ for $i>m$, where m is some integer, we can use the first m of Eqs. (14) to obtain the m values of the nonzero order parameters. Previous results¹ have shown that only α_1 and α_2 are liable to exceed the value of 0.1 for $T>T_c$. It is seen from Fig. 1 that, with possible exceptions in the case of the first two b_i values, it should be a good approximation to assume that all the b_i values in Eqs. (14) have the value appropriate to $\alpha_i=0$. The set of equations is then linear and can be solved readily.

Assuming $b_i=b_0$ and $\alpha_i=0$ for $i>12$, the set of twelve linear equations derived from (14) was solved for a number of b_0 values by use of the digital computer SILLIAC. The temperature corresponding to each b_0 value was found from the expression for b_i given with Eq. (11), taking $i>2$. The values of α_1 and α_2 were

subsequently refined by iterative solution of the first two equations of (14) using values of b_1 and b_2 from Eq. (11) with the temperature and α_i values obtained from the previous solution. The maximum change on refinement was about ten percent. The values of the first five order parameters are plotted as functions of temperature in Fig. 5. The experimental values² are added for comparison. In Table I the theoretical and experimental values of the first ten order parameters are compared for the temperatures at which the measurements were made.

The agreement of the calculated values with the experimental results is about as good as can be expected. Since the experimental values were obtained it has been shown^{16,17} that the difference in atomic size for the Au and Cu atoms will give rise to appreciable diffuse scattering, and this will in general make the values of the s.r.o. parameters, deduced on the assumption that all diffuse scattering is due to short-range order, too low by an appreciable amount.¹⁷ A reappraisal of the

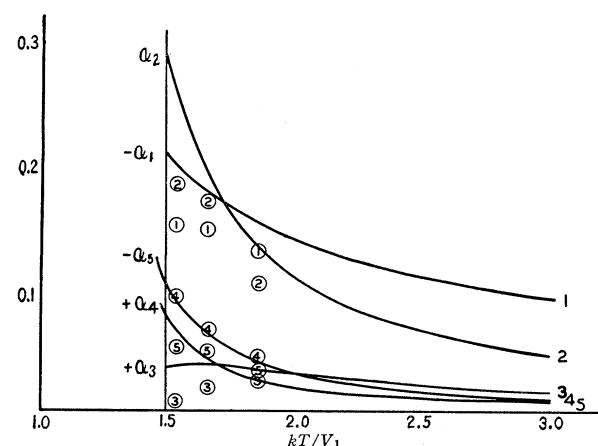


FIG. 5. Values of the first five s.r.o. parameters for Cu₃Au plotted against temperature and compared with experimental values² of α_i , indicated by an encircled i .

¹⁶ B. E. Warren, B. L. Averbach, and B. W. Roberts, J. Appl. Phys. **22**, 1493 (1951).

¹⁷ B. Borie, Acta Cryst. **10**, 89 (1957).

experimental data should therefore lead to better agreement of the experimental values of the first two order parameters in particular with the theoretical values. Also the results of Fosdick⁹ indicate that the magnitudes of α_1 and α_2 calculated for $V_2=0$ may be greater than those calculated for $V_2 \neq 0$. Hence, the agreement with experiment would probably be improved further by modifying Eqs. (14) to include the effects of a finite V_2 .

From both the experimental results² and the previous theoretical results,¹ it was deduced that above the critical temperature the values of the order parameters were more nearly dependent on the radial distance from the origin than on the preferred occupancy of the lattice site for the state of long-range order, i.e., that there is a "liquid-like" state of order in which the occupancy of a site by Cu or Au atoms is governed by a radial distribution function such as applies to the density of atoms in a liquid. As a consequence, some of the order parameters, including α_3 , α_6 , and the part of α_9 referring to coordinates 4,1,1, tend to have the sign opposite to that appropriate to the state of perfect order. The present theoretical results confirm that this effect occurs and, in fact, predict that the effect should be even more marked than the experimental results indicate. The theoretical value of α_6 , for example, is negative for all $T > T_c$, whereas experimentally α_6 was found to be negative only for $T > 500^\circ\text{C}$.

8. β -CuZn STRUCTURE—LONG-RANGE ORDER AND SHORT-RANGE ORDER

The ordered lattice of the β -brass structure is body-centered cubic. The periodic component of the Patterson function has two distinguishable types of vector peaks, those at cube corner positions and those at cube-centered positions. If we let the l.r.o. parameters associated with these two sets of peaks be s_2 and s_1 , respectively, then for perfect order $s_2 = -s_1 = 1$. Assuming that only V_1 is important, Eq. (10) gives

$$\begin{aligned} s_2 + s_1 \frac{\partial s_2}{\partial s_1} &= -\frac{kT}{8V_1} f(s_1), \\ s_1 + s_2 \frac{\partial s_1}{\partial s_2} &= -\frac{kT}{8V_1} f(s_2). \end{aligned} \quad (15)$$

From Eq. (10) also,

$$f(s_1) = \ln(1+s_1)^2 / (1-s_1)^2 = 2 \ln(1+s_1) / (1-s_1)$$

if the two types of atoms are present in equal amounts. Then $f(s_1) = -f(-s_1)$ and the two equations (15) are symmetrical in s_1 and s_2 . One solution, although not necessarily the only solution, is given by putting $-s_1 = s_2 = s$. This is consistent with the reasonable condition that $-s_1 = s_2 = 0$ for T large. It gives

$$s = -(kT/16V_1) f(s). \quad (16)$$

Since $s = S^2$ for this structure, Eq. (16) is identical with that derived previously,¹ and has already been shown^{5,7} to give excellent agreement with x-ray diffraction measurements. The variation of s with temperature is shown in Fig. 6. The order parameter falls smoothly to zero at a critical temperature T_c equal to $4 V_1/k$.

As in the case of Cu_3Au , the first two s.r.o. parameters were calculated in the range $T < T_c$ by using Eq. (13). The appropriate sums of nearest neighbor s.r.o. parameters are:

$$\begin{aligned} \sum_j^{1,1} \alpha_j &= 1 + 3\alpha_2 + 4s, \\ \sum_j^{2,1} \alpha_j &= 4\alpha_1 - 4s, \\ \sum_j^{8,1} \alpha_j &= -8s. \end{aligned}$$

The values for $-\alpha_1$ and α_2 so derived are shown in Fig. 6.

For temperatures above T_c , values of the s.r.o. parameters were found in the same way as for Cu_3Au . The set of equations analogous to (14) is

$$\begin{aligned} -b_1\alpha_{1,1,1} &= -b_1\alpha_1 = 1 + 3\alpha_2 + 3\alpha_3 + \alpha_5, \\ -b_2\alpha_{2,0,0} &= -b_2\alpha_2 = 4\alpha_1 + 4\alpha_4, \\ -b_3\alpha_{2,2,0} &= -b_3\alpha_3 = 2\alpha_1 + 4\alpha_4 + 2\alpha_7, \\ -b_4\alpha_{3,1,1} &= -b_4\alpha_4 = \alpha_2 + 2\alpha_3 + \alpha_5 + \alpha_6 + 2\alpha_8 + \alpha_9, \end{aligned}$$

etc.,

where the coordinates in the subscripts of the first term in each line refer to half the unit cell dimensions.

As can be seen from Fig. 1, the approximation of assuming $[H(\alpha_i) - H(0)]/\alpha_i^2$ to be a constant is even better in this case than for Cu_3Au . We therefore put $b_i = b_0$, the value for $\alpha_i = 0$, for all i values and solve the resultant set of linear equations, assuming α_i to be zero for i greater than some integer m . For $m=11$ the set of equations was solved using the digital computer SILLIAC. The values of the first two order parameters so found are plotted against kT/V_1 in Fig. 6, and in Table II the values of the first eight s.r.o. parameters are given for $kT/V_1 = 4.1, 4.4$, and 5.0 .

The values for $kT/V_1 = 4.4$ are compared with the only available experimental measurements, those of

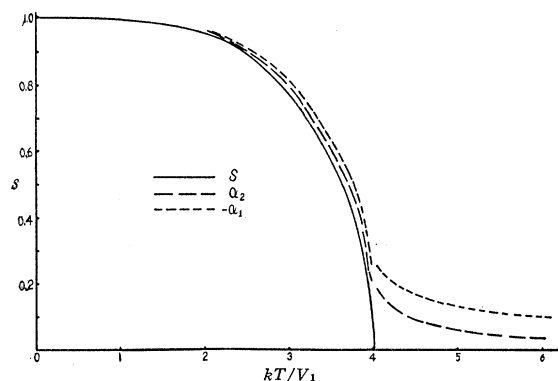


FIG. 6. Theoretical values of the l.r.o. parameter, s , and the first two s.r.o. parameters, $-\alpha_1$ and α_2 , at temperatures above and below the critical temperature for β -CuZn.

TABLE II. Theoretical values for the first eight s.r.o. parameters for β -CuZn type lattices at several temperatures: compared with experimental values^a for β -AgZn at $kT/V_1=4.40$ ($T=330^\circ\text{C}$).

Shell number	Coordinates	$T=0^\circ\text{K}$	$kT/V_1=4.1$	$kT/V_1=4.4$		$kT/V_1=5.0$
			Theor.	Theor.	Expt.	Theor.
1	1,1,1	-1.00	-0.271	-0.176	-0.31	-0.131
2	2,0,0	1.00	0.199	0.100	0.27	0.060
3	2,2,0	1.00	0.162	0.066	0.14	0.035
4	3,1,1	-1.00	-0.137	-0.044	-0.08	-0.018
5	2,2,2	1.00	0.140	0.047	0.06	0.022
6	4,0,0	1.00	0.120	0.030		0.009
7	3,3,1	-1.00	-0.119	-0.029		-0.009
8	4,2,0	1.00	0.115	0.026		0.007

^a See reference 17.

Suoninen and Warren¹⁸ for β -AgZn at 330°C ($T_c=272^\circ\text{C}$), for which no great accuracy is claimed. The theoretical and experimental values differ by a factor of about 2, but the relative values of the different s.r.o. parameters show fair agreement.

9. CONCLUSION

The use of the self-convolution of the structure, or Patterson function, as a basis for a description of the state of order in a system has proved fruitful. The ambiguity and limitations inherent in the definition of the Bragg-Williams l.r.o. parameter, S , have been clearly shown and it has been demonstrated that at least in the case of Cu_3Au -type alloys a single parameter is not sufficient to describe the state of l.r.o., i.e., the periodic component of the Patterson function.

This conclusion may be generalized. It seems that more than one l.r.o. parameter is required when the two kinds of atoms are not present in equal numbers, so that $m_A \neq m_B$ and the function $f(\alpha_i)$ defined after Eq. (10) is not antisymmetric about $\alpha_i=0$. For example, for β -CuZn type alloys it follows from Eqs. (15) that $\partial s_1/\partial s_2 = f(s_2)/f(s_1)$. If at some temperature $s_1 = -s_2$, then $f(s_1) \neq -f(s_2)$ and $\partial s_1/\partial s_2 \neq -1$, so that $\partial s_1/\partial T \neq -\partial s_2/\partial T$ and at neighboring temperatures $s_1 \neq -s_2$. Hence, with the possible exception of a limited number of temperatures, two order parameters will be required to specify the long-range order since no simple relationship exists between s_1 and s_2 .

For the special case $m_A = m_B$, it is sometimes possible to obtain a solution of the equations for which the s_i values are simply related, as in the case of β -CuZn, and this solution seems to be in excellent agreement with

experimental results. In other cases, such as the CuAu structure, this is not necessarily so since one direction, the c axis, is uniquely defined in the ordered structure and it is necessary to distinguish between peaks in the Patterson map corresponding to vectors not equally inclined to this unique direction.

When more than one l.r.o. parameter is needed, the contributions to the intensities of the fundamental diffraction maxima due to the state of order will not cancel out. The fundamental reflections will show an increase in intensity corresponding to a modulation of the diffracting power of the lattice which, presumably, corresponds to the existence of out-of-phase domains with boundaries rich in one or other type of atom, or else corresponds to a segregation of the atoms of the alloy to form two phases of slightly differing composition. The considerable number of observations of out-of-phase domain superlattices, which have recently been reported in the literature, suggests that such superlattices may occur much more widely than was previously supposed and may, in fact, represent the true equilibrium state of ordered alloys for which there are two or more unequal l.r.o. parameters, s_m .

Finally, it may be noted that, although this theoretical treatment has here been applied to only the simplest of order-disorder systems, it is equally applicable to other more complicated systems including those with unequal size of the ordering units, those with nonstoichiometric composition and those with more than two types of structural unit.

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¹⁸ E. Suoninen and B. E. Warren, *Acta Metallurgica* **6**, 172 (1958).