Acta Cryst. (1970). A**26**, 311

Structure of Short-Range Ordered Alloys. II. Ordered Zones in a Disordered Matrix*

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(*Received* 4 *August* 1969)

A diffraction theory is developed for the model of ordered zones embedded in an otherwise disordered binary alloy. Evaluation of the resulting lattice sums gives an equation for the diffuse scattering everywhere in reciprocal space except under the fundamental lines. From the experimental diffuse intensity one can calculate the relative volume of the ordered zones in the whole crystal, their mean sizes along each of the crystallographic axes, and the distribution of these sizes. A set of relations between the Warren short-range-order parameters α_{lmn} and the size of the ordered zones is also obtained.

Comparison with experimental α_{lmn} given in the literature show that a 50 at.% CuAu alloy quenched from 500°C contains ordered zones in a disordered matrix. Similar results were obtained for a 50 at.% CuPt alloy held at 890°C or quenched from 930°C. In a Cu_3Au alloy held at 450°C the calculations show the existence of ordered zones with a size of $(3\times3\times3)$ unit cells, in accordance with the results of computer simulation work published in the literature.

Introduction

Many of the physical properties of binary alloys depend on the exact correlation between the two types of atom. For a stoichiometric alloy which undergoes an order–disorder transformation, one of the possible models is that, high above the transition temperature, the solid solution includes ordered nuclei in an otherwise disordered matrix. This picture seems to have some support in studies of the kinetics of ordering in several binary alloys (Krivoglaz & Smirnov, 1964). When the temperature is lowered these nuclei grow and near the critical temperature they become big enough to touch each other and give the well-known anti-phase domains (Beeler, 1967).

We develop here an X-ray diffraction theory for alloys which include ordered zones embedded in a disordered matrix and compare this theory with the results of the diffuse scattering measurements in different systems. By a 'zone' we mean a precipitate coherent with the lattice of the matrix and without any distortions, similar to the Guinier–Preston zones in Al rich Ag–Al alloys in the very first stage of the precipitation of Ag (Guinier, 1959). The matrix is assumed to be completely disordered. On the other hand, the degree of order in each zone may be different for different zones and is taken as such. Also the zones are assumed to be distant enough from one another for interference effects between them to be negligible. Edge effects of the zones are also not included.

Theory of diffraction

The structure factor of a unit cell in an ordered zone can be written as:

$$F=F_1+SF_2 \tag{1}$$

where F_1 is the average structure factor of disordered unit cells, and S is the order parameter. The atoms in the disordered volume of the crystal are distributed randomly. We designate the structure factor of a unit cell in this disordered volume by F_r.

We assume in our treatment that each zone is fully ordered, the zones being embedded in a random matrix.

In this case the structure factor of the whole crystal takes the form:

$$F=\sum_m F_1 \exp\left(-2\pi i\mathbf{k}\,.\,\mathbf{R}_m\right)+\sum_s S_sF_2 \exp\left(-2\pi i\mathbf{k}\,.\,\mathbf{R}_s\right) + \sum_r (F_r-F_1)\exp\left(-2\pi i\mathbf{k}\,.\,\mathbf{R}_r\right)\,. \tag{2}$$

$\mathbf{k}$ is the wave vector with the absolute value $|k|=2\sin\theta/\lambda$, where θ is the Bragg angle, and λ the wavelength of the radiation. $\mathbf{R}_m$, $\mathbf{R}_s$ and $\mathbf{R}_r$ are vectors from the origin to the mth, sth and rth cell respectively.

The first term in (2) is a sum over all the unit cells of the crystal. The second term is a sum over all the ordered cells only, and the third term is a sum over all the disordered cells. This last term appears because in the first term we have an 'average' atom (*i.e.* made out of half gold and half copper in CuAu) at each site of the crystal, whereas in a disordered crystal there is either an A atom or a B atom at each site distributed at random.

We find the intensity of the diffracted beam by multiplying (2) with its complex conjugate. In this way, and by taking the second and the third terms together, we get:

$$I=I_1+I_2+I_3$$

where

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* This work represents part of the D.Sc. dissertation of M. Greenholz.

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\begin{aligned}
I_1 &= |F_1|^2 \sum_{m'} \sum_{m} \exp\,[2\pi i\mathbf{k}\,.\,(\mathbf{R}_{m'}-\mathbf{R}_m)] \\
I_2 &= 2 \sum_{m} \sum_{s} F_1 F_2^* S_s \exp\,[2\pi i\mathbf{k}\,.\,(\mathbf{R}_m-\mathbf{R}_s)] \\
&\quad + 2 \sum_{m} \sum_{r} F_1(F_r-F_1)^* \exp\,[2\pi i\mathbf{k}\,.\,(\mathbf{R}_m-\mathbf{R}_r)] \qquad (3) \\
I_3 &= |F_2|^2(\bar{S})^2 \sum_{s'} \sum_{s} \exp\,[2\pi i\mathbf{k}\,.\,(\mathbf{R}_{s'}-\mathbf{R}_s)] \\
&\quad + 2|F_2| \sum_{s} \sum_{r} S_s(F_r-F_1)^* \exp\,[2\pi i\mathbf{k}\,.\,(\mathbf{R}_s-\mathbf{R}_r)] \\
&\quad + \sum_{r'} \sum_{r} (F_r-F_1)\,(F_{r'}-F_1)^* \exp\,[2\pi i\mathbf{k}\,.\,(\mathbf{R}_{r'}-\mathbf{R}_r)]\,.
\end{aligned}
$$

Here $(\mathbf{R}_{m'}-\mathbf{R}_m)$ is the vector from the mth cell to the m'th cell, and likewise for the other similar expressions.

In (3) I_1 gives the fundamental reflexions. I_2 is zero everywhere in intensity space except under the fundamental lines. I_3 then gives the intensity of the diffuse scattering everywhere except under the fundamental lines.

In the expression for I_3 the second term is equal to zero because $\bar{F}_r = F_1$ and so $(\bar{F}_r - F_1) = 0$. The third term in I_3 gives the well-known Laue monotonic scattering for the disordered volume of the crystal, and is given by $I_{LM}(\text{dis}) = n_r(m_A m_B(f_A-f_B)^2$ (Greenholz & Kidron, 1970), where n_r is the number of atoms in the disordered volume, f_A, f_B are the scattering factors of A and B atoms respectively, and m_A, m_B are the atomic fraction of A and B atoms respectively.

The diffuse intensity I_3, now called I_D, can then be written as:

$$I_3 = I_D = I_{\text{order}} + n_r m_A m_B (f_A - f_B)^2$$

where

$$I_{\text{order}} = |F|^2(\bar{S})^2 \sum_{s'} \sum_{s} \exp\,[2\pi i\mathbf{k}\,.\,(\mathbf{R}_{s'}-\mathbf{R}_s)]\,. \qquad (4)$$

Let the ordered zones have the form of parallelepipeds with length of N_1, N_2 and N_3 unit cells each side. Then using the usual notation:

$$\mathbf{k} = h_1\mathbf{b}_1 + h_2\mathbf{b}_2 + h_3\mathbf{b}_3$$
$$\mathbf{R}_{s'} - \mathbf{R}_s = l\mathbf{a}_1 + m\mathbf{a}_2 + n\mathbf{a}_3$$

we can rewrite I_{order} as follows:

$$I_{\text{order}} = |F_2|^2(\bar{S})^2 \sum_{l=-(N-1)}^{N-1} \sum_{m} \sum_{n} (N_1-|l|)\,(N_2-|m|)\,(N_3-|n|) \exp\,[2\pi i(lh_1+mh_2+nh_3)]$$

where $(N_1-|1|)\,(N_2-|m|)\,(N_3-|n|)$ is the number of times that $(\mathbf{R}_{s'}-\mathbf{R}_s)$ appears in (4).

In an f.c.c. or b.c.c. crystal I_{order} is periodic in $(2h_1,\ 2h_2,\ 2h_3)$, and so we write the Fourier series in 'double' reciprocal space:

$$
\begin{aligned}
I_{\text{order}}(h_1', h_2', h_3') &= |F_2(h_1', h_2', h_3')|^2(\bar{S})^2 \\
&\quad \times \sum_{l} \sum_{m} \sum_{n} (N_1-|l|)\,(N_2-|m|)\,(N_3-|n|) \exp\,[2\pi i(lh_1'+mh_2'+nh_3')] \qquad (5)
\end{aligned}
$$

where h_1', h_2' and h_3' are equal to $2h_1$, $2h_2$ and $2h_3$ respectively.

It has been shown (Cowley, 1950) that the diffuse scattering due to short range order, for an f.c.c. or b.c.c. crystal, can be written as:

$$I_D = nm_A m_B (f_A-f_B)^2 \sum_{l} \sum_{m} \sum_{n} \alpha_{lmn} \exp\,[2\pi i(lh_1'+mh_2'+nh_3')] \qquad (6)$$

where the sum is over all the crystal; n is the total number of atoms and m_A, m_B are the atomic fraction of A type atoms and B type atoms respectively. α_{lmn} are the short range order parameters.

From (6) and by comparison with (4) we find that α_{lmn} are the Fourier coefficients of

$$\frac{I_D}{nm_A m_B(f_A-f_B)^2} = \frac{I_{\text{order}} + n_r m_A m_B (f_{\text{A}}-f_B)^2}{nm_A m_B(f_A-f_B)^2} = \frac{n_r}{n} + \frac{I_{\text{order}}}{nm_A m_B(f_A-f_B)^2}\,.$$

If we define

$$\alpha_{000}' = \alpha_{000} - \frac{n_r}{n}$$
$$\alpha_{lmn}' = \alpha_{lmn} \quad \text{for} \quad (lmn) \neq (000) \qquad (7)$$

then the Fourier coefficients of $\dfrac{I_{\text{order}}}{nm_A m_B(f_A-f_B)^2}$ will be the parameters α_{lmn}'. Since $\alpha_{000} = 1$ by definition we also have $1 - n_r/n = \alpha_{000}'$. This quantity gives the amount of atoms in the ordered zones.

We designate the Fourier coefficients of the function

$$\frac{F_2^2}{nm_A m_B(f_A-f_B)^2}$$

as $A_{l'm'n'}$ and the Fourier coefficients of the function

$$(\bar{S})^2 \sum_{l} \sum_{m} \sum_{n} (N_1-|l|)\,(N_2-|m|)\,(N_3-|n|) \exp 2\pi i(lh_1'+mh_2'+nh_3')]$$

as B_{2l2m2n}. Then from the convolution theorem we find that the Fourier coefficients of the product of the two functions, *i.e.* of

$$\frac{I_D}{nm_A m_B(f_A-f_B)^2}$$

will be the parameters

$$\alpha_{lmn}' = \sum_{l'} \sum_{m'} \sum_{n'} A_{l'm'n'}\,.\,B_{lmn-l'm'n'} \qquad (8)$$

where

$$B_{2l2m2n} = (\bar{S})^2 \sum_{l} \sum_{m} \sum_{n} (N_1-|l|)\,(N_2-|m|)\,(N_3-|n|)$$

and

$A_{l'm'n'}$ are the Fourier coefficients of

$$\frac{F_2^2}{nm_A m_B(f_A-f_B)^2}$$

Formula (8) gives the Warren short-range-order parameters from the size of the zones, the composition of the alloy, and the structure of the ordered phase, *i.e.* from the parameters of our model of the solid solution.

The ordered zones may have a distribution of their sizes. Here we assume a normal distribution for the size of the zones along each one of the crystallographic axes, *i.e.* for N_1, N_2 and N_3, and take them as independent random variables. Then from the definition of $B_{2l,2m,2n}$ in (8) we see that its expectation value will be given by the sum of the products of the expectation values of $(\bar{S})^2$, $(N_1-|l|)$, $(N_2-|m|)$ and $(N_3-|n|)$, *i.e.* by the products of their mean values:

$$\langle B_{2l,2m,2n}\rangle = (\bar{S})^2 \cdot \sum_l \sum_m \sum_n (\bar{N}_1-|l|)\,(N_2-|m|)\,(N_3-|n|)$$

where $\bar{N}_1$ is the mean value of N_1, *etc.*

As the Fourier coefficients $A_{l'm'n'}$ are given from calculated values, taken as precise, the expectation values of α'_{lmn} will be given once more by equation (8), except that this time we write $\langle B_{lmn-l'm'n'}\rangle$ instead of $B_{lmn-l'm'n'}$.

Discussion of the results

The equations (8) give certain relations between the α'_{lmn} themselves for the model of the ordered zones, *i.e.* from a given set of experimental α'_{lmn} we can say whether a model of ordered zones embedded in an otherwise disordered matrix is a realistic one for the given alloy and its heat treatment. From (8) we also see that α'_{lmn} are proportional to $(\bar{S})^2$, *i.e.* the amount of order inside the zones does not affect the relations between different α'_{lmn}.

If α_{lmn} are measured quite accurately then any three of them (except $\alpha_{000}=1$) will be enough to calculate N_1, N_2, N_3, *i.e.* the average size and shape of the ordered zones. From these values one can calculate n_r/n through α'_{000} in equations (7) and (8).

The theory has been applied to a few systems where α_{lmn} have been measured. Equation (8) shows that if one measures at least three α_{lmn} in different crystallographic directions (*e.g.* α_{100}, α_{010}, α_{001}) then it is possible to calculate N_1, N_2, N_3 independently. The experimental α_{lmn} given in the literature are values averaged over all the possible directions in space. The reason is that diffuse scattering measurements are very tedious, and consequently these measurements are carried out only for a small part of reciprocal space. The diffuse intensity in the whole reciprocal space is then obtained from symmetry considerations. But if there are ordered zones in the specimen which do not have the symmetry of the whole crystal (*e.g.* platetets in a cubic crystal) then the averaging of α_{lmn} for all the directions in space prevents the possibility of finding N_1, N_2, N_3 different from one another. For this reason we assumed in our calculations that $\bar{N}_1=\bar{N}_2=\bar{N}_3=\bar{N}$. To calculate $\bar{N}$ it is enough to know only one α_{lmn}. But using the different α_{lmn} given from the experiments we can find the distribution of $\bar{N}$, *i.e.* how many ordered zones there are with a volume of 1 unit cell, how many there are with a volume of $2\times2\times2=8$ unit cells, *etc.*

Comparison with experimental results

We took the experimental α_{lmn} given for CuAu (Roberts, 1954). In this work the diffuse scattering was measured from a specimen held at 425 and at 525°C, and also after the specimen was quenched from 500°C to room temperature. Equations (8) could not be solved consistently for the measurements at the two high temperatures, *i.e.* the back calculated α_{lmn} were very different from the experimental ones. It is concluded that in these two cases the simple model of ordered zones in a disordered matrix is not valid. Here there could be anti-phase domains which fill up almost all the volume of the crystal, or there could even be ordered zones which are very close to one another and which consequently should exhibit interference effects in the diffuse scattering.

On the other hand, using equations (8), we found that the α_i (*i* denotes the shell of neighbours) given for CuAu quenched from 500°C are representative of ordered zones in a disordered matrix. The results are given in Table 1. One sees that there is a good fit between the experimental α_i and the calculated values. The calculations also give $\alpha'_{000}=1-n_r/n=0{\cdot}32$, *i.e.* about one-third of the volume of the crystal is in the form of ordered zones. The mean size of the ordered zones is about $(3\times3\times3)$ unit cells. This result is similar to that found from the statistical theory of diffraction (Greenholz & Kidron, 1970).

Table 1. *Observed and calculated* α_i *for* CuAu

α_i	Experimental (Roberts, 1964)	Calculated
α_1	−0·158	−0·158
α_2	0·210	0·224
α_3	−0·048	−0·050
α_4	0·153	0·143
α_5	−0·050	−0·043
α_6	0·093	0·092
α_7	−0·035	−0·028
α_8	0·070	0·092

Similar calculations were carried out for CuPt. Here one has a set of α_i (Walker, 1952) for a specimen held at 890°C, and a set of α_i for a specimen quenched from 930°C. The results of the calculations are given in Table 2. There is a very good fit between the calculated and experimental α_i. For the quenched specimen the mean size of the ordered zones is 1·66 ordered unit cells, *i.e.* about 3·32 *a* where *a* is the lattice parameter of the disordered crystal. The total volume of the ordered zones is about 40% of the volume of the crystal.

For the specimen held at 890°C we find 1·10 ordered unit cells, *i.e.* about 2·2 *a* for the mean size of

Table 2. *Observed and calculated* α_i *for* CuPt

α_i	Experimental (Walker, 1952) Quenched 930°C	Calculated Quenched 930°C	Experimental (Walker, 1952) Held at 890°C	Calculated Held at 890°C
α_1	0·00	0·00	0·00	0·00
α_2	−0·28	−0·28	−0·20 ± 0·06	−0·20
α_3	0·00	0·00	0·00	0·00
α_4	0·20	0·23	0·12 ± 0·05	0·11
α_5	0·00	0·00	0·00	0·00
α_6	−0·14	−0·14	−0·06 ± 0·03	−0·06

the ordered zones. The relative volume consisting of the ordered zones is about 37%.

The diffuse scattering of disordered Cu_3Au has been measured (Cowley, 1950; Moss, 1964). Calculations were carried out on the results of Moss for a specimen held at 450°C. Table 3 gives the calculated α_i along with the experimental values. The fit for α_1 and α_2 is perfect, but not very good for the other α_i. The relative volume occupied by the ordered zones is found to be 77%. By a least-squares analysis, the distribution of the size of the ordered zones was calculated. It was found that about 60% of the ordered volume is made up of zones with a size of $(1 \times 1 \times 1)$ unit cells, and about 34% of it is in zones with a size of $(3 \times 3 \times 3)$ unit cells. There are no zones with a volume of $(2 \times 2 \times 2)$ unit cells.

Table 3. *Observed and calculated* α_i *for* Cu_3Au

α_i	Experimental (Moss, 1964)	Calculated
α_1	−0·195	−0·195
α_2	0·215	0·215
α_3	0·003	−0·019
α_4	0·077	0·114
α_5	−0·052	−0·040
α_6	0·028	0·076

Before discussing these interesting results we should mention that Moss calculated the parameters α_i twice. In his first calculation he finds for α_{000} the values of 1·14, 1·28 and 1·40 for the samples held at 450 and 405°C, and quenched from 800°C, respectively. Owing to the fact that α_{000} should be equal to 1, and assuming that he might have some parasitic scattering, Moss subtracted 0·14, 0·28 and 0·40 from each of the intensity values. In doing the calculations again he found new α_i, with absolute values somewhat higher than the first set of a_i. These new α_i are the values given in his paper.

Gehlen & Cohen (1965) have done some computer simulation work to find the substructure of disordered alloys. They took the experimental α_i given by Moss. In the case of Cu_3Au held at 450°C they found ordered zones in a disordered matrix, the zones having a dimension of about 12 Å, *i.e.* their size is about $3 \times 3 \times 3$ unit cells. This is exactly the size that we found here for the zones which make up a total of 34% of the ordered volume. The other part of the ordered volume is made up of zones with a volume of 1 unit cell. These are tiny ordered regions and seem to be smaller than the regions defined as 'ordered' by Gehlen & Cohen in their computer simulation work.

The authors wish to express their thanks to Professor H. Lipson, Dr D. T. Keating, Professor E. S. Machlin and Professor B. Post for interesting discussions.

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