The properties of the B_{jk} are

$$B_{jk}=0,\ k>j\,;\ \ B_{jj}=2^j\,;\ \ B_{j0}=2,\ j\neq 0\,;$$

$$B_{j,j-n}=\sum_{t=0}^{j\text{-}n}\binom{j\text{-}n}{t}\sum_{n=0}^{u}\binom{t}{u}B_{nu}\,. \qquad (32)$$

Table 2 shows some B_{jk}.

Table 2. *The elements* B_{jk}

j k	0	1	2	3	4	5	6
0	1						
1	2	2					
2	2	6	4				
3	2	10	16	8			
4	2	14	36	40	16		
5	2	18	64	112	96	32	
6	2	22	100	240	320	224	64 .
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮ ⋮

Equation (32) permits a recursive calculation of further B_{jk}.

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References

BRINK, D. M. & SATCHLER, G. R. (1968). *Angular Momentum,* in *Oxford Library of Physical Sciences,* 2nd ed. Oxford: Clarendon Press.

DEBYE, P. (1915). *Ann. Physik*, **46**, 809.

DEBYE, P. & BÜCHE, A. M. (1949). *J. Appl. Phys.* **20**, 518.

EL-BAZ, E. & LAFOUCRIÈRE, J. (1965). *C. R. Acad. Sci. Paris*, **261**, 4641.

HOSEMANN, R. & BAGCHI, S. N. (1962). *Direct Analysis of Diffraction by Matter.* Amsterdam: North-Holland.

MASSOT, J. N., EL-BAZ, E. & LAFOUCRIÈRE, J. (1967). *Rev. Mod. Phys.* **39**, 288.

POROD, G. (1951). *Kolloid-Z.* **124**, 83.

SNEDDON, I. N. (1956). *Functional Analysis,* in *Handbuch der Physik, Math. Meth.* II. Berlin, Göttingen, Heidelberg: Springer Verlag.

TRICOMI, F. G. (1955). *Vorlesungen über Orthogonalreihen.* Berlin, Göttingen, Heidelberg: Springer Verlag.

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The Structure of Short-Range Ordered Alloys. I. Clustering of Ordered Cells*

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A statistical theory for the X-ray diffuse scattering from disordered binary alloys is developed. It conveys the probability of finding ordered cells as a function of the distance from a given cell. These probabilities are related to the Warren short-range-order parameters. It is also shown that if part of the volume of the crystal is completely disordered, then its size can be calculated from the usual diffuse-scattering measurements. Comparison with experiment shows clustering of ordered cells in disordered CuAu. For alloys which obey the Ornstein–Zernike pair correlation function just above T_c, such as β-brass, there is a clustering of ordered cells, but not an anti-phase domain structure.

Introduction

Binary alloys which undergo an order-disorder transition exhibit short-range order above the transition temperature. The actual substructures of such alloys influence many of their physical properties. Consequently the exact atomic correlation of short-range-ordered alloys has been a subject for many investigations (Gehlen & Cohen, 1965), but the situation is far from being clear.

X-ray diffuse scattering studies from short-range-ordered alloys convey the probabilities for the existence of a given type of atom in each shell of neighbours (Warren & Averbach, 1953). These are statistical results and may be compatible with different models of solid solution, *e.g.* with a liquid-like character of the distribution of each kind of neighbour or with a model of nucleation of the long-range-ordered phase, *i.e.* on the assumption that the alloy contains ordered nuclei in an otherwise disordered matrix.

On the other hand, in the parallel case of clustering in pre-precipitation alloys, it has been known for some time that these alloys contain zones of one kind of atom, such as the well-known Guinier–Preston zones in Al–Zn, *etc.* (Guinier, 1959).

We develop here a new diffraction theory for the diffuse scattering of X-rays from short-range-ordered alloys. This theory converts the treatment of short-range order between atoms to a treatment of 'local

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order' between ordered cells. This is a statistical theory which may show whether in a given alloy there is a clustering of ordered cells or some kind of 'short-range order' between the ordered cells. In extreme cases it may show if there is long-range order between anti-phase domains. In an accompanying paper (Greenholz & Kidron, 1970) we develop a non-statistical theory of diffraction for the case of alloys containing ordered zones in a disordered matrix.

As a relatively simple but important case we take an equiatomic binary alloy like Cu–Zn, where there can be only two kinds of ordered cell that are in anti-phase relative to each other, and write down the necessary diffraction equations. The crystal is taken as being made up partly of ordered unit cells and partly of disordered cells.

Theory of diffraction

The structure factor of an ordered unit cell can be written quite generally as $F=F_1+F_2$. F_1 is the structure factor of the 'average' unit cell, in which each atom is an average atom (*i.e.* made up of half Cu and half Zn in CuZn). F_2 is the order-dependent part of the structure factor of the cell.

When there are two types of ordered cells in anti-phase relative to each other, as in our case, the structure factor of each ordered unit cell is either

$$F_a=F_1+F_2 \quad \text{or} \quad F_b=F_1-F_2 \tag{1}$$

depending on whether the unit cell is in phase with the unit cell at the origin or in anti-phase with it. We also designate by F_r the structure factor of the unit cells in the disordered volume. F_r is different from F_1 because in the disordered volume the two types of atom are distributed at random whereas in a cell with the structure factor F_1 we have the same average atom at each atomic site.

The intensity diffracted by the whole crystal will be given by

$$I=\sum_m \sum_n F_m F_n \exp\,[2\pi i\mathbf{k}\,.\,(\mathbf{R}_m-\mathbf{R}_n)] \tag{2}$$

where the double sum is over the whole crystal and F_m, F_n are either F_r or F_a or F_b.

Writing down the different sums in (2) explicitly:

$$I=I_1+I_2+I_3+I_4$$

where

$$\begin{aligned}
I_1&=\sum_{r'} \sum_r |F_r|^2 \exp\,[2\pi i\mathbf{k}\,.\,(\mathbf{R}_{r'}-\mathbf{R}_r)]\\
I_2&=\sum_r \sum_a F_r F_a \exp\,[2\pi i\mathbf{k}\,.\,(\mathbf{R}_r-\mathbf{R}_a)]\\
I_3&=\sum_r \sum_b F_r F_b \exp\,[2\pi i\mathbf{k}\,.\,(\mathbf{R}_r-\mathbf{R}_b)]\\
I_4&=\sum_a \sum_b F_a F_b \exp\,[2\pi i\mathbf{k}\,.\,(\mathbf{R}_a-\mathbf{R}_b)]\,.
\end{aligned} \tag{3}$$

In the sums, the subscript (r) denotes unit cells in the disordered volume, (a) denotes unit cells which are in-phase with the cell at the origin, and (b) denotes the same for anti-phase cells.

Taking

$$F_r=F_1+(F_r-F_1)\,, \tag{4}$$

I_1 is evaluated as follows:

$$\begin{aligned}
I_1&=\sum_{r'} \sum_r |F_r|^2 \exp\,[2\pi i\mathbf{k}\,.\,(\mathbf{R}_{r'}-\mathbf{R}_r)]\\
&=\sum_{r'} \sum_r |F_1|^2 \exp\,[2\pi i\mathbf{k}\,.\,(\mathbf{R}_{r'}-\mathbf{R}_r)]\\
&+\sum_{r'} \sum_r (F_{r'}-F_1)\,(F_r-F_1) \exp\,[2\pi i\mathbf{k}\,.\,(\mathbf{R}_{r'}-\mathbf{R}_r)]\\
&+\sum_{r'} \sum_r F_1\,.\,(F_r-F_1) \exp\,[2\pi i\mathbf{k}\,.\,(\mathbf{R}_{r'}-\mathbf{R}_r)]\,.
\end{aligned}$$

The first term of I_1 is part of the intensity of the fundamental lines, and denoted by $I^{(1)}_{\text{fund}}$. The second term of I_1 gives the well-known Laue monotonic scattering, but only for the disordered volume of the crystal:

$$\begin{aligned}
I^{(\text{dis})}_{LM}&=\sum_{r'} \sum_r (F_{r'}-F_1)\,(F_r-F_1)\\
&\quad\times \exp\,[2\pi i\mathbf{k}\,.\,(\mathbf{R}_{r'}-\mathbf{R}_r)]\\
&=\sum_r \overline{F_r^2}-|F_1|^2\\
&=n_r[(m_A f_A^2+m_B f_B^2)-(m_A f_A+m_B f_B)^2]\\
&=n_r m_A m_B (f_A-f_B)^2\,,
\end{aligned}$$

where n_r is the number of *atoms* in the disordered volume. f_A, f_B are the scattering factors of the two types of *atoms* in the alloy, and m_A, m_B are the atomic fraction of the two types of atoms. A bar over a quantity denotes its mean value.

The third term in I_1 is equal to zero because $\bar{F}_r=F_1$. Summing the three parts of I_1 it is seen that

$$I_1=I^{(1)}_{\text{fund}}+I^{(\text{dis})}_{LM}\,. \tag{5}$$

The term I_2 in (3) is evaluated as follows, using (1) and (4):

$$\begin{aligned}
I_2&=\sum_r \sum_a F_r F_a \exp\,[2\pi i\mathbf{k}\,.\,(\mathbf{R}_r-\mathbf{R}_a)]\\
&=\sum_r \sum_a |F_1|^2 \exp\,[2\pi i\mathbf{k}\,.\,(\mathbf{R}_r-\mathbf{R}_a)]\\
&+\sum_r \sum_a F_1 F_2 \exp\,[2\pi i\mathbf{k}\,.\,(\mathbf{R}_r-\mathbf{R}_a)]\\
&+\sum_r \sum_a (F_r-F_1) F_1 \exp\,[2\pi i\mathbf{k}\,.\,(\mathbf{R}_r-\mathbf{R}_a)]\\
&+\sum_r \sum_a (F_r-F_1) F_2 \exp\,[2\pi i\mathbf{k}\,.\,(\mathbf{R}_r-\mathbf{R}_a)]\,.
\end{aligned}$$

The first term in I_2 is part of the intensity of the fundamental lines and will be denoted by $I^{(2)}_{\text{fund}}$. The second term is zero except under the fundamental lines, which do not interest us here. We include it in $I^{(2)}_{\text{fund}}$. The third term and the fourth term of I_2 are also equal to zero because $\bar{F}_r=F_1$. We have then

$$I_2=I^{(2)}_{\text{fund}}\,. \tag{6}$$

I_3 is evaluated similarly, and consequently

$$I_3=I^{(3)}_{\text{fund}}\,. \tag{7}$$

Now we evaluate

$$I_4=\sum_a\sum_b F_aF_b \exp\left[2\pi i\mathbf{k}\,.\,(\mathbf{R}_a-\mathbf{R}_b)\right].$$

For this purpose we denote by X_a the percentage of (a)-type cells among *all the ordered cells* and by X_b the same for (b)-type cells, so that $X_a+X_b=1$. If N_c is the number of ordered cells in the crystal, then the number of aa pairs in I_4 is N_cX_a and for them $R_a-R_b=0$. Similarly, the number of bb pairs in I_4 is N_cX_b, and for them $R_a-R_b=0$. Consequently

$$\begin{aligned}I_4&=N_c(X_aF^2_a+X_bF^2_b)\\&+\sum_{a\neq b}\sum F_aF_b \exp\left[2\pi i\mathbf{k}\,.\,(\mathbf{R}_a-\mathbf{R}_b)\right].\end{aligned} \tag{8}$$

The total intensity I will be given by:

$$I=I_1+I_2+I_3+I_4$$

which by the relations (5), (6), (7) and (8) will be

$$\begin{aligned}I&=I^{(1)}_{\text{fund}}+I^{(2)}_{\text{fund}}+I^{(3)}_{\text{fund}}+I^{(\text{dis})}_{LM}\\&+N_c(X_aF^2_a+X_bF^2_b)\\&+\sum_{a\neq b}\sum F_aF_b \exp\left[2\pi i\mathbf{k}\,.\,(\mathbf{R}_a-\mathbf{R}_b)\right].\end{aligned}$$

Now, the diffuse scattering alone is

$$I_D=I-I_{\text{fund}}\,,$$

where I_{fund} is the intensity of the fundamental lines. But

$$I_{\text{fund}}=I^{(1)}_{\text{fund}}+I^{(2)}_{\text{fund}}+I^{(3)}_{\text{fund}}+I^{(4)}_{\text{fund}}$$

where

$$\begin{aligned}I^{(4)}_{\text{fund}}&=N_c(X_aF_a+X_bF_b)^2\\&+\sum_{a\neq b}\sum (X_aF_a+X_bF_b)^2 \exp\left[2\pi i\mathbf{k}\,.\,(\mathbf{R}_a-\mathbf{R}_b)\right]\end{aligned}$$

is part of the intensity of the fundamental lines and is included in I_4. Accordingly

$$\begin{aligned}I_D=I-I_{\text{fund}}&=I^{(\text{dis})}_{LM}+N_c(X_aF^2_a+X_bF^2_b)\\&+\sum_{a\neq b}\sum F_aF_b \exp\left[2\pi i\mathbf{k}\,.\,(\mathbf{R}_a-\mathbf{R}_b)\right]\\&-N_c(X_aF_a+X_bF_b)^2\\&-\sum_{a\neq b}\sum (X_aF_a+X_bF_b)^2 \exp\left[2\pi i\mathbf{k}\,.\,(\mathbf{R}_a-\mathbf{R}_b)\right].\end{aligned}$$

$$\begin{aligned}I_D&=I^{(\text{dis})}_{LM}+N_cX_aX_b(F_a-F_b)^2\\&+\sum_{a\neq b}\sum F_aF_b \exp\left[2\pi i\mathbf{k}\,.\,(\mathbf{R}_a-\mathbf{R}_b)\right]\\&-\sum_{a\neq b}\sum (X_aF_a+X_bF_b)^2 \exp\left[2\pi i\mathbf{k}\,.\,(\mathbf{R}_a-\mathbf{R}_b)\right].\end{aligned} \tag{9}$$

We now define the parameters $A_{mn}=1-\dfrac{p^{ab}_{mn}}{X_a}$, where p^{ab}_{mn} is the probability of finding an (a)-type cell at the distance $(\mathbf{R}_m-\mathbf{R}_n)$ from a (b)-type cell at the origin.

At this stage we can use exactly the same type of calculation as given by Cowley (1950) for the normal short range order parameters. The result is that equation (9) takes the general form:

$$\begin{aligned}I_D=I^{(\text{dis})}_{LM}+\sum_a\sum_b X_aX_b(F_a-F_b)^2A_{mn}\\\times\exp\left[2\pi i\mathbf{k}\,.\,(\mathbf{R}_m-\mathbf{R}_n)\right]\end{aligned}$$

or the particular form for an f.c.c. or b.c.c. crystal,

$$\begin{aligned}I_D&=I^{(\text{dis})}_{LM}+N_cX_aX_b(F_a-F_b)^2\\&\times\sum_l\sum_m\sum_n A_{lmn}\\&\times\exp\left[2\pi i(2h_1l+2h_2m+2h_3n)\right].\end{aligned} \tag{10}$$

The parameters A_{lmn} are defined here by

$$A_{lmn}=1-\frac{p^{ab}_{lmn}}{X_a} \tag{11}$$

where p^{ab}_{lmn} is the probability of finding an (a)-type cell at the lattice site $l\mathbf{a}_1+m\mathbf{a}_2+n\mathbf{a}_3$ after first having found a (b)-type cell at the origin; $\mathbf{a}_1,\mathbf{a}_2,\mathbf{a}_3$ are the crystallographic vectors.

According to (1), equation (10) takes the form

$$\begin{aligned}I_D&=I^{(\text{dis})}_{LM}+4N_cX_aX_bF^2_2\\&\times\sum_l\sum_m\sum_n A_{lmn}\exp\left[2\pi i(2h_1l+2h_2m+2h_3n)\right]\end{aligned}$$

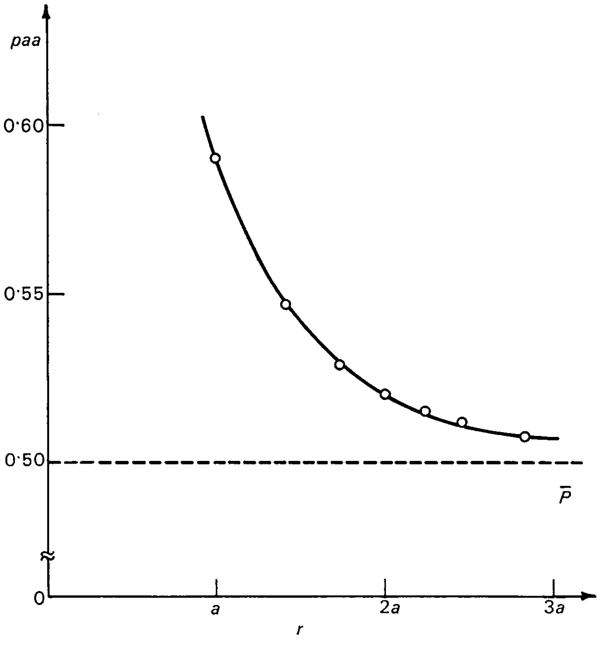

Fig. 1. The probability of finding an ordered cell, in-phase with the cell at the origin, as a function of the distance from the origin, for β-brass at $T=T_c+75°$. a is the lattice parameter.

or more explicitly

$$I_D = n_r m_A m_B (f_A - f_B)^2 + 4N_c X_a X_b F_2^2 \sum_l \sum_m \sum_n A_{lmn} \times \exp\,[2\pi i(2h_1 l + 2h_2 m + 2h_3 n)]\,. \tag{12}$$

Equation (12) can be written as

$$\frac{I_D}{n m_A m_B (f_A - f_B)^2} = \frac{n_r}{n} + \frac{4N_c X_a X_b F_2^2}{n m_A m_B (f_A - f_B)^2} \sum_l \sum_m \sum_n A_{lmn} \times \exp\,[2\pi i(2h_1 l + 2h_2 m + 2h_3 n)] \tag{13}$$

where n is the number of atoms in the irradiated volume of the crystal. The right side of this equation gives a modulation of the quantity $\frac{4N_c X_a X_b F_2^2}{n m_A m_2 (f_A - f_B)^2}$. There is also an unmodulated part, *i.e.* $\frac{n_r}{n}$, which can be calculated. From $\frac{n_r}{n}$ one can also calculate $\frac{N_c}{n}$. Putting the values of $\frac{n_r}{n}$ and $\frac{N_c}{n}$ back in (13) one calculates the parameters A_{lmn} from the Fourier transform of the left side of this equation.

If in a disordered alloy the Warren short-range-order parameters α_{lmn} (Cowley, 1950) have already been calculated from the experimental intensity, one can derive the parameters A_{lmn} directly from them in the following way:

The Fourier coefficients of the transform of the left side of the equation (13) are α_{lmn} by definition.

On the right side of (13) we have a constant factor $\frac{4N_c X_a X_b}{n m_A m_B}$. Besides this factor there are two functions. The first one is $\frac{F_2^2}{(f_A - f_B)^2}$. We designate the Fourier coefficients of this function by $F_{l'm'n'}$. The second function is the triple sum whose Fourier coefficients are A_{lmn}. The Fourier coefficients of the product of these two functions will be given by the convolution theorem by $\sum_{l'm'n'} F_{l'm'n'} A_{lmn-l'm'n'}$. We will then have

$$\alpha'_{lmn} = \frac{4N_c X_a X_b}{n m_a m_b} \sum_{l'} \sum_{m'} \sum_{n'} F_{l'm'n'} \,.\, A_{lmn-l'm'n'} \tag{14}$$

where

$$\alpha'_{000} = \alpha_{000} - \frac{n_r}{n} = 1 - \frac{n_r}{n} \cdot (\alpha_{000} = 1 \text{ by definition})$$

and

$$\alpha'_{lmn} = \alpha_{lmn} \text{ for } (lmn) \neq (000)\,.$$

Now $F_{l'm'n'}$ is given from the structure of the ordered alloy and is usually known. Then from α'_{lmn} we can calculate A_{lmn}, which gives $\frac{p^{AB}}{lmn}$ according to (11).

The treatment given above can be extended to other types of lattices, and to the cases where more than two kinds of anti-phase domain occur. Also in the most frequent f.c.c. lattices the ordered phase is usually f.c. tetragonal, and the c axis may be (at least in principle) along the different crystallographic axes. But the α_{lmn} given in the literature are usually average values over all orientations, and for them equation (14) can be used as it is.

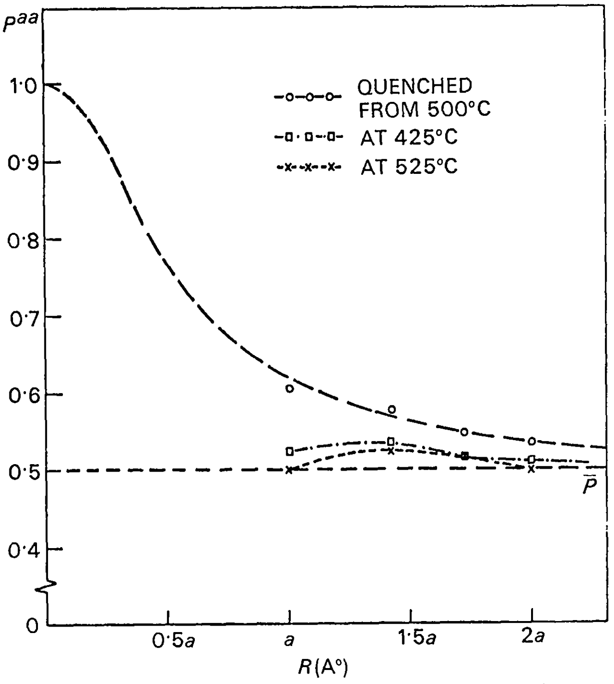

Fig. 2. The probability of finding an ordered cell, in-phase with the cell at the origin, as a function of the distance from the origin, for Cu–Au above T_c. a is the lattice parameter.

Comparison with experiment

The theory has been applied to a 50 at.% CuZn alloy. For this alloy there are critical neutron scattering measurements (Walker & Keating, 1963; Als-Nielsen & Dietrich, 1967) giving the pair correlation function, $p(\mathbf{r})$, for occupation of lattice sites. It is shown that $|p(\mathbf{r})| \propto [\exp(-K_1 r)]/r^{1+\eta}$, *i.e.* $p(\mathbf{r})$ is given by the Ornstein–Zernike pair correlation function (Elliott & Marshall, 1958), except for the small correction $\eta = \frac{1}{18}$. The measurements were performed just above T_c – the critical temperature for ordering, and it is shown that K_1 is linear with $(T - T_c)/T_c$.

The parameters A_{lmn} were calculated from the experimental values of $p(\mathbf{r})$ using equation (14). In Fig. 1 we give $p_{lmn}^{aa} = 1 - p_{lmn}^{ab}$, *i.e.* the probability of finding an ordered cell in phase with the cell at the origin as a function of the distance from the origin. This plot is similar to the plots of the probability of finding like atoms in the pre-precipitation stage of several binary alloys (Guinier, 1959). We have then a clustering of ordered cells in β-brass above T_c. A calculation of α'_{000} yielded $\alpha'=0{\cdot}66$, *i.e.* about $\frac{2}{3}$ of the crystal is in ordered form in this particular alloy ($T=T_c+75°$).

From Fig. 1 we see that the state of order (or rather 'disorder') in β-brass above T_c cannot be explained by assuming the existence of anti-phase domains, because in this case p^{aa}_{lmn} should oscillate with r and the resulting $|p(r)|\,.\,r$ (through α_{lmn}) would not decrease exponentially.

This discussion applies also to any equiatomic alloy which obeys the Ornstein–Zernike pair correlation function. Such an alloy will exhibit clustering of ordered cells, but not an anti-phase domain structure, above the critical temperature.

We took the experimental α_{lmn} given in the literature for CuAu (Roberts, 1954). From these values we calculated A_{lmn}, using equations (14) and assuming $n_r=0$. These give p^{ab}_{lmn} from the relation (11). In Fig. 2 we give $p^{aa}_{lmn}=1-p^{ab}_{lmn}$, *i.e.* the probability of finding an ordered cell in phase with the cell at the origin as a function of the distance from the origin. Curve (1) is for the specimen which was quenched to room temperature from 500°C. We see that up to a distance of more than two unit cells p^{aa} is higher than the average value P. The actual model of the solid solution may then well be that of ordered zones (with a statistical distribution of their sizes) in an otherwise disordered alloy, *i.e.* one of a pre-precipitation of the ordered phase.

Curves (2) and (3) in Fig. 2 are from the results of measurements at 425°C and 525°C respectively. They show a clustering of like cells which as expected is higher at the lower temperature. But the fact that the first point (at $r=a$ Å) is lower than the second one (at $r=\sqrt{2}a$ Å) is hard to explain. However, the diffuse scattering at high temperatures contains an appreciable amount of temperature diffuse scattering which is hard to calculate independently. This may also account for the fact that for the specimen measured at 425°C the α_{lmn} that Roberts found are smaller than those that he found for the specimen quenched from 500°C.

To sum up, we have clustering of ordered cells in the CuAu system above the transition temperature for ordering. In order to check if this is compatible with a model of ordered zones in a disordered matrix, we must write down the equation of scattering for such a model and compare the results with the experimental scattering curve. This has been done (Greenholz & Kidron, 1970). We find that the magnitude of α_{lmn} and their ratios to one another are such that they fit the model of zones. The sizes of the ordered zones have a distribution, but the mean radius is about 1·5 unit cells, and this is in accordance with the results of the present work.

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References

ALS-NIELSEN, J. & DIETRICH, O. W. (1967). *Phys. Rev.* **153**, 706.

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

ELLIOTT, R. J. & MARSHALL, W. (1958). *Rev. Mod. Phys.* **30**, 75.

GEHLEN, P. C. & COHEN, J. B. (1965). *Phys. Rev.* **139** (3A) 844.

GREENHOLZ, M. & KIDRON, A. (1970). *Acta Cryst.* A**26**, 000.

GUINIER, A. (1959), *Solid State Phys.* **9**, 323.

ROBERTS, B. W. (1954). *Acta Met.* **2**, 598.

WALKER, C. B. & KEATING, D. T. (1963). *Phys. Rev.* **130**, 1726.

WARREN, B. E. & AVERBACH, B. L. (1953). *Modern Research Techniques in Physical Metallurgy*, p. 95. Cleveland, Ohio: American Society for Metals.