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The Formation of Order in the Alloy $CdMg_3$

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An X-ray analysis of the order–disorder transformation in the close-packed-hexagonal alloy $CdMg_3$ is described. The distribution of intensity in the principal sections of the diffuse superlattice reflexions is determined from moving-film photographs obtained at one stage of the ordering process. It is shown that the intensity at any point in a diffuse reflexion having indices $hkil$ with l odd is given by the Fourier summation

$$I(u, v, w) = \sum_x \sum_y \sum_z K \exp\left[-(\alpha x^2+\beta y^2+\gamma z^2-\delta xy)\right] \exp\left[2\pi i(ux+vy+wz)\right],$$

where the constants α, β, γ and δ tend to zero as complete order is approached.

Qualitative results obtained in optical-diffraction experiments, with punched cardboard masks simulating the structure of the alloy, indicate that ordering progresses by the interchange of nearest-neighbour atoms in such a way that cadmium atoms avoid each other. At a sufficiently advanced state of order antiphase domains appear, but the boundaries of these domains do not coincide with any preferred crystallographic planes.

1. Introduction

It is well known that, at the appropriate temperatures and compositions, a number of binary and ternary alloys undergo an order–disorder transformation. Further, those alloys whose structures are such that at least four different unit cells can be outlined on the same lattice may, possibly, possess varying degrees of short-range order (Bragg, 1940) which can be retained on quenching. Hitherto, however, the X-ray diffraction phenomena associated with short-range order have been observed only with certain compositions of the copper–palladium system (Jones & Sykes, 1939), CuPt (Walker, 1952), AuCu (Roberts, 1954), $CdMg_3$ (Steeple & Lipson, 1951) and with $AuCu_3$. Quantitative studies of the diffuse superlattice reflexions which result from imperfect order have been limited, principally, to $AuCu_3$, and among the many workers who have been attracted to the problem are Sykes & Jones (1936, 1938), Guinier & Griffoul (1947, 1948), Strijk & MacGillavry (1946), Cowley (1950), Taylor, Hinde & Lipson (1951), and Edmunds & Hinde (1952).

Sykes & Jones interpreted the presence of diffuse superlattice lines on their powder photographs in terms of antiphase domains, which they assumed grew from nuclei until the boundaries of the domains touched. From a purely theoretical standpoint, Wilson (1943, 1949) calculated the diffraction effects to be expected from a number of models in which the antiphase domains came into contact in various ways, and the theoretical predictions from one of his models were in fair agreement with the powder data of Sykes & Jones. The results derived by Wilson for a partially ordered single crystal were in qualitative, but not in quantitative, agreement with the published single-crystal data.

An alternative view of the kinetics of the order–disorder transformation in $AuCu_3$ has been proposed by Edmunds & Hinde. They believe that the experimental evidence suggests that order develops throughout the crystal by the interchange of nearest-neighbour atoms so that gold atoms tend to avoid each other, and that, in consequence, antiphase domains are formed. The present investigation was undertaken in order to obtain further experimental data which might help to clarify the position both in regard to the kinetics of the transformation and to the theoretically derived results of Wilson.

2. Experimental details

2·1. *Growth of single crystals of* $CdMg_3$

The materials used in the preparation of the alloy were cadmium and magnesium of 99·98% and 99·95% purity respectively. These constituents were melted under flux in an iron crucible at a temperature of approximately 560° C. and, after being cast in a thick copper mould, the alloy was homogenized by heat-treatment for 60 hr. at 450° C. in an evacuated silica tube. From an analysis of the alloy it was found that the atomic percentage of magnesium was 75·4.

Single crystals were obtained by slow-cooling finely divided pieces of $CdMg_3$ from the melt at the rate of 1° C. per minute. Since magnesium is readily attacked by both silica and air at temperatures of this order, the pieces of alloy were packed into an iron container which was then sealed off in a silica tube under low-pressure argon. Although many of the specimens were

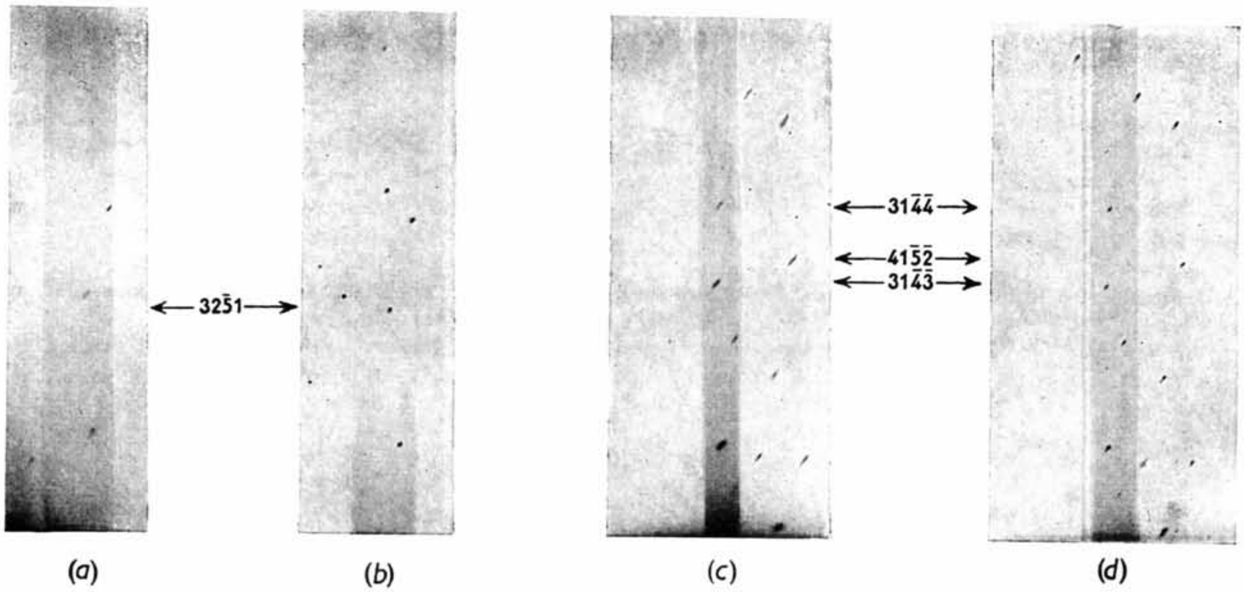

Fig. 1. Moving-film photographs of the diffuse and sharp reflexions. (*a*) Oscillation about [0001], diffuse. (*b*) Oscillation about [0001], sharp. (*c*) Oscillation about $[01\bar{1}0]$, diffuse. (*d*) Oscillation about $[01\bar{1}0]$, sharp.

attacked by the residual gases in the container, a number remained unaffected; these formed shiny spherical pellets ranging in diameter from 0·1 mm. to 0·2 mm. which X-ray examination showed to be single crystals of $CdMg_3$.

2·2. *X-ray technique*

The specimen was attached, by means of a thin film of adhesive, to the inside wall of an evacuated thin-walled capillary tube of pyrex glass. With other than a thin film the crystal was distorted, on heat-treatment, by the differential expansion between the alloy and the adhesive. As the structure of $CdMg_3$ is hexagonal (Dehlinger, 1930), the X-ray data were obtained by irradiating the alloy (with Cu $K\alpha$ radiation) with the $[10\bar{1}0]$ and [0001] directions set in turn along the axis of rotation. Use was made of the moving-film technique developed by Edmunds & Hinde (1952) in which the screen of the Weissenberg goniometer was an accurately uniform aperture of approximate width 0·1 mm.; thus, from a photograph obtained with an oscillating single crystal, the intensity distribution in a thin section of reciprocal space perpendicular to the axis of rotation could be deduced.

The X-ray intensities were measured on a deflection microphotometer, intensity readings of the diffuse reflexions being taken at intervals of 0·075 mm. in two perpendicular directions whilst those of the corresponding sharp reflexions were obtained at intervals of 0·05 mm.; observations were continued well into the general background and the intensity distribution in each spot was determined relative to this background. Over the angular range covered by a reflexion the temperature, absorption, and polarization and Lorentz factors could be assumed constant.

2·3. *Choice of reflexions and the method of heat treatment*

The critical temperature for $CdMg_3$ was found to be 160° C. Above this temperature the alloy has a disordered close-packed hexagonal structure while at room temperature ordering proceeds slowly (Hume-Rothery & Raynor, 1940). The structure amplitude of a superlattice reflexion from a fully ordered crystal depends upon the indices of that reflexion; with l odd it is proportional to $\pm\sqrt{3}(f_{Cd}-f_{Mg})$, while for l even the value is proportional to $\pm 2(f_{Cd}-f_{Mg})$ or to $\pm(f_{Cd}-f_{Mg})$ according as $(h-k)$ is or is not a multiple of 3, f being the atomic scattering factor.

Owing to the geometry of the apparatus, it was possible to pass only first-layer-line reflexions through the modified screen of the Weissenberg goniometer. Thus when the crystal was oscillating about the [0001] direction only reflexions with l odd were recorded, but all three types of superlattice reflexion could be examined when the oscillation was about the $[10\bar{1}0]$ direction. Reflexions $32\bar{5}1$, $41\bar{5}\bar{2}$, $31\bar{4}\bar{3}$ and $31\bar{4}\bar{4}$ were selected because they occurred at a Bragg angle of approximately 45°, in which angular region the effects of both instrumental broadening and white radiation were small.

Once the crystal had been correctly orientated on the goniometer it remained untouched, heat-treatments being carried out *in situ* by directing a stream of hot air on to the specimen. In this way the alloy was disordered by subjecting it to a 15 min. anneal at 200° C., after which an effective quench was obtained by cutting off abruptly the supply of hot air. When ordering had been allowed to progress for 15 days at 16° C. the process was virtually arrested by lowering the temperature of the crystal to 5° C. by means of a stream of cold, dry air; the diffuse reflexions were

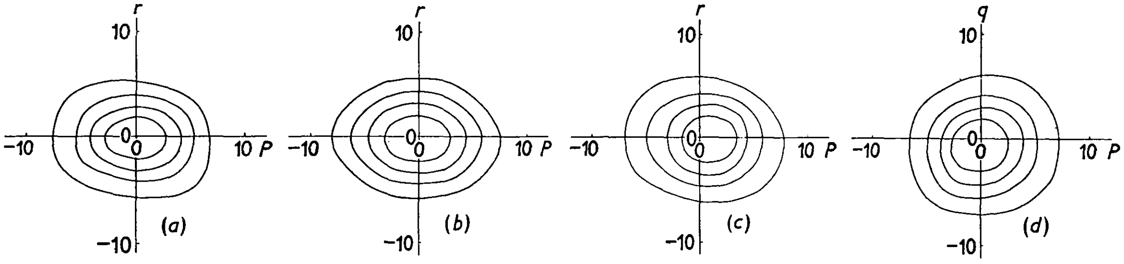

Fig. 2. Distribution of intensity in principal sections of reciprocal space. (a) Reflexion $41\bar{5}\bar{2}$. (b) Reflexion $41\bar{5}\bar{2}$, two-dimensional correction. (c) Reflexion $31\bar{4}\bar{3}$. (d) Reflexion $32\bar{5}1$.
$I/I_{\text{max.}}$ = 0·8, 0·6, 0·4, 0·2.

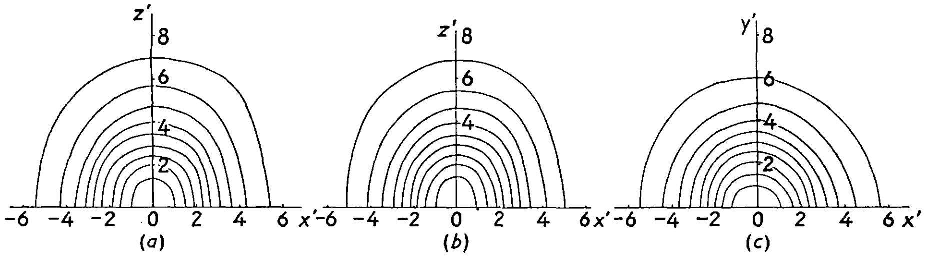

Fig. 3. Variation of the values of the Fourier transform K. (a) Reflexion $41\bar{5}\bar{2}$. (b) Reflexion $31\bar{4}\bar{3}$. (c) Reflexion $32\bar{5}1$.
$K_{x'y'}/K_{00} = K_{x'z'}/K_{00}$ = 0·9, 0·8, 0·7, 0·6, 0·5, 0·4, 0·3, 0·2, 0·1.

then recorded. The corresponding sharp reflexions were photographed after the alloy had been cooled from 200° C. to room temperature in 8 hr.

The diffuse and sharp spots are shown in Fig. 1. It was clear that the intensity of the diffuse $31\bar{4}\bar{4}$ reflexion relative to the background was too weak to be reliable, and work on this reflexion was therefore abandoned.

3. Analysis of the experimental data

3·1. *Corrected intensity distributions in reciprocal space*

Superimposed on the broadening due to imperfect order was an instrumental broadening which occurs to a greater or less degree on all types of X-ray-diffraction photograph. The linear correction for the instrumental broadening of a line (Stokes, 1948) is not strictly applicable to the intensity distribution in the principal section of a spot, and a two-dimensional modification of Stokes' treatment was applied by Edmunds & Hinde. However, this involves considerable arithmetical labour, and therefore the diffuse reflexions from $CdMg_3$ were corrected by the one-dimensional method since it was considered that the attendant loss in accuracy could be tolerated. The linear correction was made in six different directions across each spot when the latter was both diffuse and sharp, and the corrected intensity at the point (ϱ) in each direction was expressed as a Fourier summation of the form

$$I(\varrho) = \Sigma F_R \exp\,[2\pi i \varrho R]\,, \qquad (1)$$

where the values of R and ϱ were the computational coordinates, and the coefficients F_R were the quotients of the corresponding Fourier coefficients for the observed diffuse and sharp reflexions.

Contours of constant intensity are drawn in Fig. 2(*a*), (*c*) and (*d*) for the principal sections in reciprocal space of the $41\bar{5}\bar{2}$, $31\bar{4}\bar{3}$ and $32\bar{5}1$ reflexions respectively. For the purposes of comparison, the distribution of intensity in the $41\bar{5}\bar{2}$ reflexion resulting from a two-dimensional correction—evaluated on the Manchester computer—is shown in Fig. 2(*b*). It will be seen that the agreement with Fig. 2(*a*) is quite satisfactory.

The shapes of the contours in the principal section

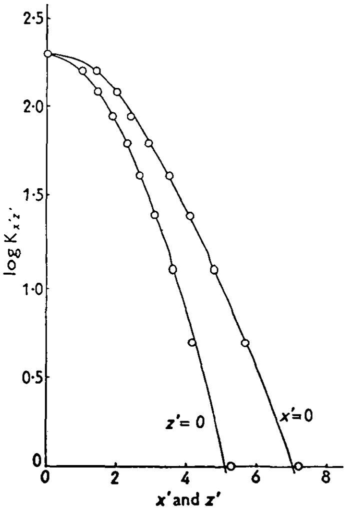

Fig. 4. Logarithmic variation of the values of $K_{x'z'}$ along Ox' and Oz' for the $41\bar{5}\bar{2}$ reflexion.

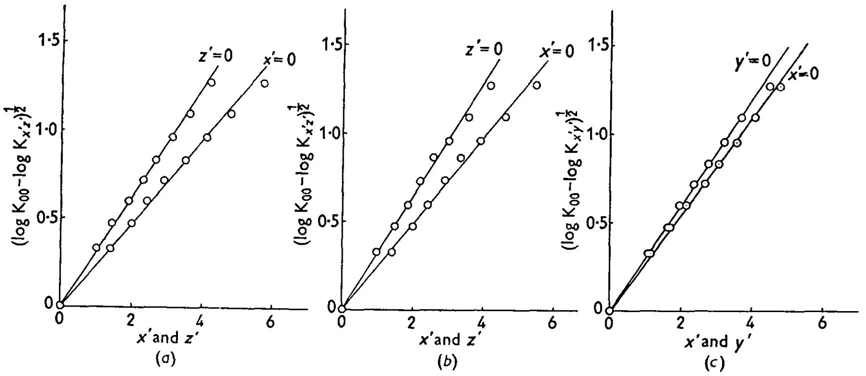

Fig. 5. Variation of expressions of the type $(\log_e K_{00}-\log_e K_{x'0})^{\frac{1}{2}}$ with x', y' and z'. (a) Reflexion $41\overline{5}\overline{2}$. (b) Reflexion $31\overline{4}\overline{3}$. (c) Reflexion $32\overline{5}1$.

of reciprocal space which is parallel to the a^*c^* plane are roughly elliptical, as are the contours parallel to the a^*b^* plane, although the latter are very nearly circular. Distances along the orthogonal axes $(0pqr)$ are measured in reciprocal-length units, and the intensity at the point (p, r) is given by the Fourier summation

$$I(p, r) = \Sigma\Sigma F_{x'z'} \exp\,[2\pi i(px'+rz')]\,, \qquad (2)$$

where the axes $(0x'y'z')$ in the crystal space are parallel to $(0pqr)$.

Each corrected intensity distribution was found to be centrosymmetrical, but for the reflexions considered the origins of p and q, and of p and r, did not fall exactly at the centres of symmetry. The origins were therefore transferred to the appropriate centres, the new Fourier coefficients being real.

3·2. *Relationship between the Fourier coefficients and the coordinates in crystal space*

The Fourier transform of the two-dimensional distribution of intensity $I(p, q)$ round a reciprocal-lattice point will be a function of x' and y', say $K_{x'y'}$. It follows that the Fourier coefficients $F_{x'y'}$ of the summation for the intensity distribution as derived above will be the values of this transform at regularly spaced points, and therefore the coefficients may be utilized to plot the continuous variations of the function $K_{x'y'}$. Similarly for other sections.

The variations of $K_{x'z'}$ in the $x'z'$ plane for reflexions $41\overline{5}\overline{2}$ and $31\overline{4}\overline{3}$ are shown respectively in Fig. 3(*a*) and (*b*), while the variation of $K_{x'y'}$ in the $x'y'$ plane for reflexion $32\overline{5}1$ is given in Fig. 3(*c*); in Fig. 4 are plotted the logarithmic variations of $K_{x'z'}$ along the x' and z' directions for the $41\overline{5}\overline{2}$ reflexion. Within the limits of experimental error the latter curves are parabolic—as are similar graphs for the $31\overline{4}\overline{3}$ and the $32\overline{5}1$ reflexions—a conclusion which is verified by the fact that graphs of the type $(\log K_{00}-\log K_{x'0})^{\frac{1}{2}}$ against x' are all straight lines through the origin (Fig. 5(*a*), (*b*) and (*c*)). It follows from the straight-line relationships that

$$K_{x'0} = K_{00} \exp\,(-\alpha' x'^2)\,, \qquad (3a)$$

$$K_{0y'} = K_{00} \exp\,(-\beta' y'^2)\,, \qquad (3b)$$

$$K_{0z'} = K_{00} \exp\,(-\gamma' z'^2)\,, \qquad (3c)$$

where $(\alpha')^{\frac{1}{2}}$, $(\beta')^{\frac{1}{2}}$ and $(\gamma')^{\frac{1}{2}}$ are the slopes of the respective lines. The values of the coefficients α', β' and γ' for the three reflexions considered are shown in Table 1.

Table 1. *The values of the coefficients α', β' and γ'*

Reflexion	α' (x' axis)	β' (y' axis)	γ' (z' axis)
$41\overline{5}\overline{2}$	0·098	—	0·056
$31\overline{4}\overline{3}$	0·105	—	0·060
$32\overline{5}1$	0·092	0·076	—

On examination, the contours of Fig. 3 appear to be elliptical or, in Fig. 3(*c*), possibly circular. If this conclusion is correct, then the straight-line graphs of Fig. 5 show that these families of ellipses will be represented by the expressions

$$K_{x'y'} = K_{00} \exp\,[-(\alpha' x'^2+\beta' y'^2)] \qquad (4a)$$

and

$$K_{x'z'} = K_{00} \exp\,[-(\alpha' x'^2+\gamma' z'^2)]\,, \qquad (4b)$$

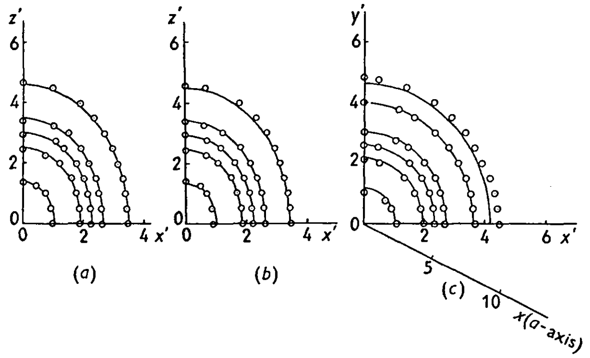

Fig. 6. Contours of constant $K_{x'y'}$ and $K_{x'z'}$, derived from expressions (4a) and (4b). (a) Reflexion $41\overline{5}\overline{2}$. (b) Reflexion $31\overline{4}\overline{3}$. (c) Reflexion $32\overline{5}1$.

$K_{x'y'}/K_{00} = K_{x'z'}/K_{00} = 0{\cdot}9$, 0·7, 0·6, 0·5, 0·3 and (Fig. 6(*c*) only) 0·2.

○: Mean values of the experimental coefficients.

where α', β' and γ' have the values given in Table 1.

The full lines shown in Fig. 6(*a*), (*b*) and (*c*) are contours of constant K calculated from the expressions (4*a*) and (4*b*), and on the same graphs the mean values of the experimental coefficients derived from the left and right quadrants of Fig. 3 are plotted. Agreement between the experimental points and the full lines is so satisfactory as to justify the conclusion that the function K is, in fact, given by the equations (4*a*) and (4*b*). The agreement for values of K/K_{00} less than 0·3 is less satisfactory; one such contour is shown in Fig. 6(*c*), and the discrepancies arise because at these low values the effect of experimental error is more marked.

As already stated, the structure amplitude associated with a given sharp superlattice reflexion from $CdMg_3$ is the same, except for changes in sign, for all reflexions of the same type. It can be shown also that for diffuse reflexions of the same type the distribution of intensity round the corresponding reciprocal-lattice point is the same. Thus, from consideration of the data for the $31\bar{4}3$ and $32\bar{5}1$ reflexions, it may be deduced that for any diffuse spot for which l is odd the distribution of intensity in the three principal sections may be expressed as a Fourier summation whose coefficients are given by the function K, where

$$K_{x'z'} = K_{00} \exp\left[-(\alpha' x'^2+\gamma' z'^2)\right], \qquad (5a)$$

$$K_{z'y'} = K_{00} \exp\left[-(\gamma' z'^2+\beta' y'^2)\right], \qquad (5b)$$

$$K_{y'x'} = K_{00} \exp\left[-(\beta' y'^2+\alpha' x'^2)\right]. \qquad (5c)$$

Examination of the intensities at points common to any two sections shows that K_{00} and the coefficients α', β' and γ' have the same values in each of these expressions; allowing for experimental error, the measured values of α' given in Table 1 confirm this.

For superlattice reflexions of the type $h-k = 3n$ with l even it was possible to determine the intensity distribution only in the a^*c^* section, no data being available for the other sections. This distribution can be expressed as a Fourier summation whose coefficients are given by equation (5*a*).

It was pointed out earlier that reflexions of the type $h-k \neq 3n$ with l even were too weak to be recorded satisfactorily.

Wilson (1949) has shown that the intensity of reflexion, as a function of position in reciprocal space, for a crystal whose unit cells are not all alike may be expressed as an integral, or a summation

$$I(u,v,w) = U^{-1} \sum_{x=-\infty}^{\infty} \sum_{y} \sum_{z} V(x,y,z) J(x,y,z) \times \exp\left[2\pi i(ux+vy+wz)\right]. \qquad (6)$$

In this expression, $J(x,y,z)$ is the mean value of $F_j F_{j'}^*$ for two cells j and j' separated by lattice translations xa, yb and zc, and the quantities ua^*, vb^* and wc^* are distances measured from the reciprocal-lattice point. The volume U of a unit cell is constant and $V(x,y,z)$ can also be assumed constant over displacements xa, yb and zc which are small compared with the size of the crystal.

The function $U^{-1}V(x,y,z)J(x,y,z)$, where x, y and z are now regarded as continuously variable, is the Fourier transform of the distribution of intensity $I(u,v,w)$ round a reciprocal-lattice point. For comparison with the experimental results for $CdMg_3$ the intensity distribution may be referred to the orthogonal axes $(0pqr)$ used above, in which case U, V and J will be referred to the axes $(0x'y'z')$ and expression (6) becomes

$$I(p,q,r) = U^{-1} \sum_{x'=-\infty}^{\infty} \sum_{y'} \sum_{z'} V(x',y',z') J(x',y',z') \times \exp\left[2\pi i(px'+qy'+rz')\right]. \qquad (7)$$

Substitution of the summation for an integral is valid when referred to the transformed axes, as the argument $2\pi i(px'+qy'+rz')$ only varies slowly with integral changes of $x'y'z'$ when p, q and r are small.

Over the principal section for which r is zero, we have

$$I(p,q,0) = \sum_{x'} \sum_{y'} U^{-1} \sum_{z'} V(x',y',z') J(x',y',z') \times \exp\left[2\pi i(px'+qy')\right]. \qquad (8)$$

The coefficients $U^{-1}\sum_{z'} V(x',y',z')J(x',y',z')$, or in practice $\sum_{z'} J(x',y',z')$ since $U^{-1}V(x',y',z')$ is virtually constant, will be directly comparable with the function $K_{x'y'}$ which has been plotted from the experimental values of the Fourier coefficients obtained from the measured distribution $I(p,q,r)$. Similarly the functions $K_{y'z'}$ and $K_{x'y'}$ will be directly comparable with $\sum_{x'} J(x',y',z')$ and $\sum_{z'} J(x',y',z')$ respectively. Consequently, for superlattice reflexions with l odd (the only type for which data in three dimensions were available) the probable solution for the function $J(x',y',z')$ is

$$J(x',y',z') = K \exp\left[-(\alpha' x'^2+\beta' y'^2+\gamma' z'^2)\right], \qquad (9)$$

giving

$$I(p,q,r) = \sum_{x'} \sum_{y'} \sum_{z'} K \exp\left[-(\alpha' x'^2+\beta' y'^2+\gamma' z'^2)\right] \times \exp\left[2\pi i(px'+qy'+rz')\right]. \qquad (10)$$

The intensity distribution in the pr plane for reflexions of the type $h-k = 3n$ with l even is given by a relation of the form

$$I(p,0,r) = \sum_{x'} \sum_{z'} K \exp\left[-(\alpha' x'^2+\gamma' z'^2)\right] \times \exp\left[2\pi i(px'+rz')\right], \qquad (11)$$

where α' and γ' have the same values as for the first type of reflexion (l odd) within experimental error. As the values of α', β' and γ' tend to zero the alloy approaches the state of perfect order, and as the values tend to infinity the system tends to complete disorder. Since the values of α', β' and γ' were of the order of 0·1 it is evident that the experimental data refer to a high degree of order.

To express J as a function of (x, y, z) it is necessary to apply the transformation equations

$$x = 2{\cdot}308x', \tag{12a}$$

$$\begin{aligned} y &= (2{\cdot}308 \cos 60).x' + (2{\cdot}308 \sin 60).y' \\ &= 1{\cdot}154x' + 1{\cdot}999y', \end{aligned} \tag{12b}$$

$$z = 2{\cdot}508z', \tag{12c}$$

leading to

$$J(x, y, z) = K \exp\left[-(\alpha x^2 + \beta y^2 + \gamma z^2 - \delta xy)\right], \tag{13}$$

where

$$\alpha = \frac{(3\alpha' + \beta')}{3 \times 2{\cdot}308^2}, \quad \beta = \frac{4\beta'}{3 \times 2{\cdot}308^2},$$

$$\gamma = \frac{\gamma'}{2{\cdot}508^2}, \quad \delta = \frac{4\beta'}{3 \times 2{\cdot}308^2};$$

the values of which, for l odd, are given in Table 2.

Table 2. *The values of the coefficients α, β, γ and δ for l odd*

α (x axis)	β (y axis)	γ (z axis)	δ
0·024	0·019	0·0032	0·024

This is the value of J, i.e. the mean of $F_j F_{j'}^*$, for two cells j and j' separated by lattice translations xa, yb and zc parallel to the crystallographic axes.

For the section with $w = 0$, the intensity distribution for l odd is given by

$$\begin{aligned} I(u, v, 0) = \sum_{x=-\infty}^{\infty} \sum_{y} K \exp\left[-(\alpha x^2 + \beta y^2 - \delta xy)\right] \\ \times \exp\left[2\pi i(ux + vy)\right], \end{aligned} \tag{14a}$$

where $\alpha = \beta = \delta$ if the section has circular contours, i.e. if $\alpha' = \beta'$. Similarly, we have

$$\begin{aligned} I(0, v, w) = \sum_{y=-\infty}^{\infty} \sum_{z} K \exp\left[-(\beta y^2 + \gamma z^2)\right] \\ \times \exp\left[2\pi i(vy + wz)\right]. \end{aligned} \tag{14b}$$

4. The accuracy of the experimental data

The theoretical treatment by Wilson (1949) of the problem of diffraction by a crystal containing mistakes leads to an expression for the variation of the Fourier coefficients along an axis which is given by the expression

$$K_{x'0} = K_{00} \exp(-\varepsilon x'). \tag{15}$$

However, according to the experimental results obtained with $CdMg_3$ the variation is given by equation (3a), and this is in agreement with the conclusions of Edmunds & Hinde (1952) for $AuCu_3$. One of the ways in which the curve of $K_{x'0}$ derived from equation (3a) differs from that predicted by Wilson is that the former has a rounded peak at the origin whereas the latter has a sharply pointed cusp. It has been suggested by Wilson that the expression (15) represents the true variation of K with x' and that the cumulative effect of several factors makes this curve conform to the expression (3a); these factors include experimental errors and the finite extent of the diffuse reflexions in reciprocal space. An estimate was therefore made of their effect on the variation of K with x', and for this purpose the data for the $41\overline{5}\overline{2}$ reflexion were utilized. The experimental curve is drawn as a full line in Fig. 7, and at various values of $K_{x'0}$ are shown the standard deviations as calculated from the expression given by Stokes (1948). It was then assumed that the true variation of K was according to equation (15) and the values of $K_{x'0}$ were calculated from the integral

$$K_{x'0} = 2\varepsilon K_{00} \int_{-A}^{A} \frac{\exp(-2\pi i x' p)\, dp}{\varepsilon^2 + 4\pi^2 p^2}, \tag{16}$$

the experimental value of A being finite (Eastabrook & Wilson, 1952) and equal to $\frac{1}{8}$.

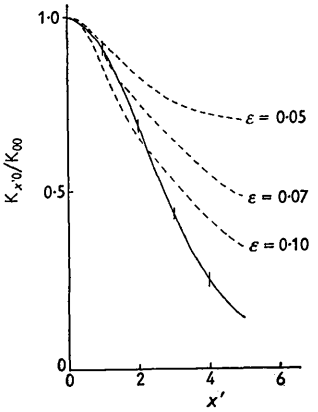

Fig. 7. Variation of $K_{x'0}/K_{00}$ with x'. The full line and the broken lines are derived from expressions (3a) and (16) respectively.

The curves for different values of ε are shown by the broken lines (Fig. 7), and it is clear that although the cusp at the origin has been converted into a rounded peak there is no value of ε which will bring a calculated curve into satisfactory agreement with the experimental curve.

Some error will arise from the spread of the sharp reflexion (from the fully ordered crystal) in a direction normal to the reciprocal-lattice section under consideration, and also from the finite width of the screen aperture; these two errors may be considered together.

If $g(p, q, r)$ is the true distribution of intensity for the sharp spot, then the observed sharp spot will be broadened slightly, giving an intensity distribution

$$\underset{\text{sharp}}{h(q, r)} \propto \int_{-b}^{b} g(p, q + \lambda p, r + \mu p)\, dp = \psi(0, q, r), \tag{17}$$

where $2b$ is the width of the reciprocal-lattice section corresponding to the slot width, and λ and μ are constants. The intensity at the point (q, r) of the diffuse spot is

$$\underset{\text{diffuse}}{h(q,r)} = \iint_{-\infty}^{\infty} dq'dr' \int_{p'=-\infty}^{\infty} I(p',q',r')\psi(-p',q-q',r-r')dp', \tag{18}$$

where

$$\psi(-p',q-q',r-r') = \int_{-b}^{b} g(p-p',q-q',(r-r')dp \, .$$

For any fixed value of $q-q'$, $r-r'$ the function $\psi(-p',q-q',r-r')$ may be written in the form $f(p')\psi(0,q-q',r-r')$, where $f(p')$ gives the intensity variation with p' of the broadened sharp spot for these particular $q-q'$, $r-r'$ coordinates. Unfortunately, the value of $f(p')$ will differ for different values of $q-q'$, $r-r'$, but it should be possible to choose a mean value of the function $f(p')$ which gives a fairly close representation of its variation with p' when $q-q'$, $r-r'$ are small, i.e. for values of $q-q'$, $r-r'$ which make $\psi(-p',q-q',r-r')$ of appreciable magnitude. If this be done, the intensity distribution in the diffuse reflexion may be written as

$$\begin{aligned}\underset{\text{diffuse}}{h(q,r)} &= \int_{q'=-\infty}^{\infty}\int_{r'} dq'dr'\psi(0,q-q',r-r') \\ &\quad \times \int_{p'=-\infty}^{\infty} I(p',q',r')f(p')dp' \\ &= \int_{q'=-\infty}^{\infty}\int_{r'} dq'dr'\psi(0,q-q',r-r')\varphi(0,q',r') \, .\end{aligned} \tag{19}$$

Stokes' analysis of the diffuse and sharp spots then gives the coefficients of a Fourier summation for

$$\varphi(0,q,r) = \int_{-\infty}^{\infty} I(p,q,r)f(p)dp \, . \tag{20}$$

Thus, instead of $I(0,q,r)$ for any chosen q, r coordinates, a mean of the values of $I(p,q,r)$ is obtained for points on either side of the section $0, q, r$ weighted according to the spread $f(p)$ of the sharp spot in the direction p. Since $f(p)$ refers to the sharp spot, its value falls to zero quickly as p departs from zero so that the values of $I(p,q,r)$ averaged will not vary much from $I(0,q,r)$. For a function such as that given by equation (10) above, the variables p, q and q, r are separable and we have

$$I(p,q,r) = I(0,q,r)\xi(p) \tag{21}$$

exactly. It follows that for such a function

$$\varphi(0,q,r) = I(0,q,r)\int_{-\infty}^{\infty} \xi(p)f(p)dp \propto I(0,q,r); \tag{22}$$

the only error arises from a failure of $f(p)$ to represent each section accurately.

5. Optical-diffraction data

There is a formal analogy between two-dimensional optical-diffraction patterns and two-dimensional X-ray diffraction patterns. Therefore the distribution of intensity in a section of the reciprocal lattice may be compared with the optical-diffraction pattern of a two-dimensional array of holes, the latter representing the projection, along the corresponding zone axis, of the atomic arrangement in a single crystal. Steeple & Lipson (1955) exploited this analogy and they produced gratings which simulated the projections of the $CdMg_3$ structure along the $[01\bar{1}0]$ and $[0001]$ directions respectively. After commencing with disordered gratings, order was gradually introduced by interchanging nearest-neighbour atoms in such a way that cadmium atoms tended to avoid each other. As order progressed, the general background of the diffraction pattern began to collect into well-defined regions of diffuse intensity until finally the distribution of intensity in the optical pattern was similar to that in reciprocal space obtained from the X-ray data. Further, although the only condition imposed on the interchanges was that cadmium atoms should avoid each other, it was found that antiphase domains appeared and that these domains increased in size as order increased. This result is in agreement with that obtained by Taylor *et al.* (1951) with $AuCu_3$, but with the difference that the domain boundaries in the $CdMg_3$ model do not lie along any preferred crystallographic planes. The observations give support to the suggestion of Edmunds & Hinde that ordering progresses through the interchange of nearest-neighbour atoms so that like atoms tend to avoid each other. It is unlikely, however, that the avoidance results in a reduction of strain energy because the atomic radii of cadmium and magnesium atoms are almost identical. There is the possibility, nevertheless, that in the alloy the cadmium and magnesium ions may differ appreciably in radius.

6. Conclusion

Analysis of the distribution of intensity in the diffuse reflexions of the type with l-index odd leads to values of the function $J(x,y,z)$, the average of $F_jF_j^*$ for cells separated by translations xa, yb, zc, which vary inversely as the exponential of a quadratic function of x, y and z. This is in agreement with the conclusions of Edmunds & Hinde for the face-centred cubic structure of $AuCu_3$, although the expression for $J(x,y,z)$ is more complex for $CdMg_3$ owing to the lower symmetry. There are a number of possible sources of error, but after examining these carefully it is concluded that the suggested expression for $J(x,y,z)$ is sensibly of the correct form for the rather high degree of order present in the specimens examined. On the other hand, the Laplacian type of expression for $J(x,y,z)$ proposed by Wilson does not agree with the observations within the estimated experimental error.

Comparison of the results obtained by both optical-diffraction and X-ray-diffraction methods lends support to the suggestion made by Edmunds & Hinde, in connection with $AuCu_3$, that ordering progresses through the general interchange of nearest-neighbour atoms so that like atoms tend to avoid each other. However, it seems unlikely that reduction in strain energy contributes to the ordering forces in $CdMg_3$ as the atoms of Cd and Mg have almost identical radii, although there remains the possibility that the constituent ions of the alloy may differ appreciably in radii.

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Scattering of X-rays by Defect Structures. II. An Extension of the Theory

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An earlier theory of the scattering of X-rays by a crystal containing defects is extended to the case where atoms are displaced by comparatively large amounts from their mean positions. It is assumed that a displaced atom is influenced to about the same extent by a number of defects.

In an earlier paper (Cochran, 1956; referred to here as Part I) it was shown that the intensity of X-ray scattering from a crystal containing defects depends in a simple way on the Fourier transforms of the defects considered separately. The theory given in that paper is believed to be accurate, no matter how large the displacements of the atoms from their positions in the corresponding perfect crystal, in the situation where each atom is affected by no more than one defect. The theory also applies to the more important case where each atom is influenced by a large number of defects, provided that the displacement $\mathbf{u}$ of an atom is small enough for the approximation

$$\exp[2\pi i\mathbf{u}\cdot\mathbf{S}]-1 = 2\pi i\mathbf{u}\cdot\mathbf{S}$$

to apply, $\mathbf{S}$ being a vector in reciprocal space, as defined in Part I. Taking $S = 1{\cdot}3$ Å^{-1} (the limit of Cu $K\alpha$ radiation) requires $\mathbf{u}$ to be less than about 0·02 Å, a very restrictive condition. In applying this theory to the problem of the scattering of X-rays by a structure containing interstitial atoms, considerably larger displacements are encountered. We have therefore extended the theory to the situation where the displacements may be large, and are brought about by the simultaneous operation of a large number of defects, randomly distributed throughout the crystal. The theory of Part I took account of possible changes, by replacement, of the scattering factors of atoms; the present theory is restricted to defects made up of atomic displacements.

The intensity from the crystal containing defects will be

$$|T_{C+\Delta}(\mathbf{S})|^2 = \sum_p \sum_q f_p f_q \exp[2\pi i(\mathbf{R}_p-\mathbf{R}_q)\cdot\mathbf{S}] \times \exp[2\pi i(\mathbf{u}_p-\mathbf{u}_q)\cdot\mathbf{S}] . \qquad (1)$$