This description of the structure of the graphitic carbons is the simplest which has been found to be consistent with all the experimental results. In any attempt to produce an alternative structure, the variation of the apparent inter-layer spacing with the degree of graphitization in the graphitic carbons and its constancy in both the non-graphitic graphitizing carbons and in graphite, the different breadths of the (002) and (004) lines, the shape (not merely the breadth) of the (11$\bar{2}$) lines, the similarity of the (101) and (103) lines, and the form of the relationship between the breadth of the (112) line and the apparent inter-layer spacing, must all be taken into account.

The author wishes to thank Monsieur J. Méring for his continued interest and frequent advice during the course of this work.

References

Bacon, G. E. (1950). *Acta Cryst.* **3**, 137.

Biscoe, J. & Warren, B. E. (1942). *J. Appl. Phys.* **13**, 364.

Franklin, R. E. (1950*a*). *Acta Cryst.* **3**, 107.

Franklin, R. E. (1950*b*). *Nature, Lond.*, **165**, 71.

Hendricks, S. B. & Teller, E. (1942). *J. Chem. Phys.* **10**, 147.

Lipson, H. & Stokes, A. R. (1942). *Proc. Roy. Soc.* A, **181**, 101.

Méring, J. (1949). *Acta Cryst.* **2**, 371.

Nelson, J. B. & Riley, D. P. (1945). *Proc. Phys. Soc. Lond.* **57**, 477.

Rooksby, H. P. (1942). *Elect. Times*, **102**, 19.

Warren, B. E. (1941). *Phys. Rev.* **9**, 693.

Wilson, A. J. C. (1949). *X-Ray Optics*. London: Methuen.

Acta Cryst. (1951). **4**, 261

Optical Methods in X-ray Analysis. I. The Study of Imperfect Structures

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The correspondence between the diffraction of X-rays by crystals and of light by gratings can be used to test hypotheses put forward to explain the X-ray diffraction patterns of imperfect structures. Two-dimensional gratings of holes in cardboard are made and their diffraction patterns observed in a specially constructed large spectrometer (the Bragg X-ray microscope). Illustrations are given of the application of the method to (*a*) the transition from the cubic to the hexagonal close-packed structure, and (*b*) the ordering process in the alloy $AuCu_3$. From the latter investigation it would appear that the X-ray diffraction effects observed can be accounted for entirely by changes in the degree of short-range order.

Some rules are given for guidance in the interpretation of the X-ray diffraction patterns of imperfect structures.

Introduction

It is well known that the fundamental difficulty in the study of matter by means of X-rays is the lack of a method both of focusing the radiation and of preserving the full resolving power. Because of this, direct images of crystal structures cannot be formed and processes of mathematical computation have to be used instead. For perfect structures the calculations are relatively simple, although they are limited in application to structures for which it is possible to derive, in one way or another, the relative phases in which the diffracted beams reach the image plane; but for imperfect structures, which give rise to diffuse reflexions and streaks on X-ray photographs, no general method of solution is known.

The usual way of solving such problems is one of trial-and-error: various types of fault are postulated in turn and their diffraction patterns are calculated and compared with those observed until agreement is reached. Certain general principles can be used as guides in making these postulations (James, 1948) and they have been used with success in connexion with, for example, the faults in graphite (Warren, 1941) and cobalt (Edwards & Lipson, 1942). Even so, the complete solutions demand considerable mathematical skill (Wilson, 1942) and can often be carried out only approximately. A rapid method of deciding which approach to a particular problem is likely to be most fruitful would therefore be desirable.

The basis of such a method has been described by Bragg & Lipson (1943) who made use of the correspondence between the diffraction of X-rays by crystals and the diffraction of light by ruled gratings. A large-scale optical system was constructed and used to examine the diffraction patterns of gratings which were coarse enough for various types of defect to be introduced deliberately.

While experiments of this type are adequate to con-

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firm general principles, the limitation imposed by the use of one-dimensional gratings is severe; extended to two dimensions, however, the method becomes much more powerful. The purpose of the present paper is to describe how this extended method has been applied to some known imperfect structures and to show how, in one case, the results give some indication of how the imperfections have developed.

The correspondence between the diffraction of X-rays and the diffraction of light can be applied to problems other than those involving structural defects, and it is hoped to produce further papers showing how the apparatus constructed can be used in other branches of X-ray analysis.

Optical system

A diagram of the apparatus is shown in Fig. 1. Light from a 250 watt 'compact source' mercury-vapour lamp *A* is directed by means of a lens and a prism on to a pinhole *B* which is at the focus of the lens *C*. The parallel beam so produced is brought to a focus at *F* by the lens *D* after reflexion at the optically flat mirror *E*. Any object placed at *O* will produce diffracted beams which are focused at different points in the plane of *F* to form an image—the Fraunhofer diffraction pattern—which may be either observed by means of the microscope or recorded photographically.

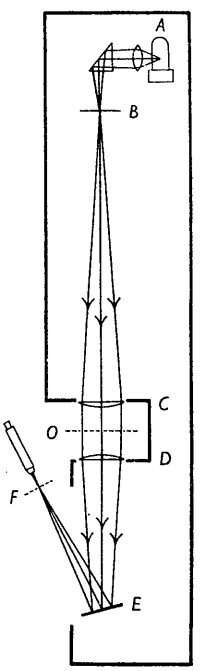

Fig. 1. Diagram of apparatus.

The yellow line of the mercury spectrum has been found most useful for both visual and photographic work and is isolated by inserting, immediately above the pinhole, two Ilford 'Mercury-Yellow' filters and a piece of Chance 'Signal-Green' glass 1 mm. thick. The latter absorbs the red light (from the continuum of the high-pressure discharge) which is passed by the yellow filters. For record purposes, short lengths of 35 mm. panchromatic film are used in a special holder and the resulting image is enlarged photographically. Exposures vary from a few seconds to 5 min. according to the type of grating in use.

With a pinhole 0·015 mm. in diameter, the apparatus is capable of resolving spectra separated by less than 4 sec. of arc, a separation given by a grating with a spacing of about 2 cm.

Construction of gratings

In the study of imperfect structures the two methods of constructing gratings that have so far proved most useful are as follows:

When several gratings are required with the same basic lattice, as in the study of the alloy $AuCu_3$ to be described later, it is convenient to drill one brass template and then, with this as a guide, to pierce five or six sheets of black paper simultaneously with a needle of appropriate size; individual holes may then be enlarged as required by piercing with a larger needle. The gratings for $AuCu_3$ covered an area 4 cm. square, the holes, of diameters 0·25 and 0·45 mm., being spaced 1 mm. apart.

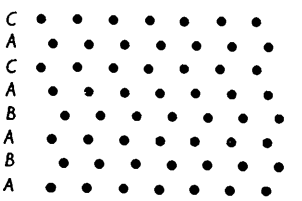

Fig. 2. Two-dimensional representation of the three types of plane in a close-packed structure.

On the other hand, where the imperfections are in the lattice itself, as in the transition from the face-centred cubic structure to the close-packed hexagonal structure to be described later, the most successful method is to impregnate thin black cardboard with paraffin wax and mount it on the surface of a wax block. Holes may then be pierced at the required places, a piece of graph paper being used as a guide. The wax block offers excellent support and prevents tearing; the impregnation counteracts any tendency for the holes to close up on account of the natural resilience of the fibres. The accuracy of the method is not, however, very great, and other methods of locating the holes are being considered.

Examples

1. *The cubic–hexagonal transition in metals*

Metallic cobalt can crystallize in either a close-packed hexagonal or a face-centred cubic arrangement. Some specimens give rise to a mixture of sharp reflexions and streaks on X-ray photographs and it has been shown by Edwards & Lipson (1942) that both forms are contributing to these photographs; the cubic structure

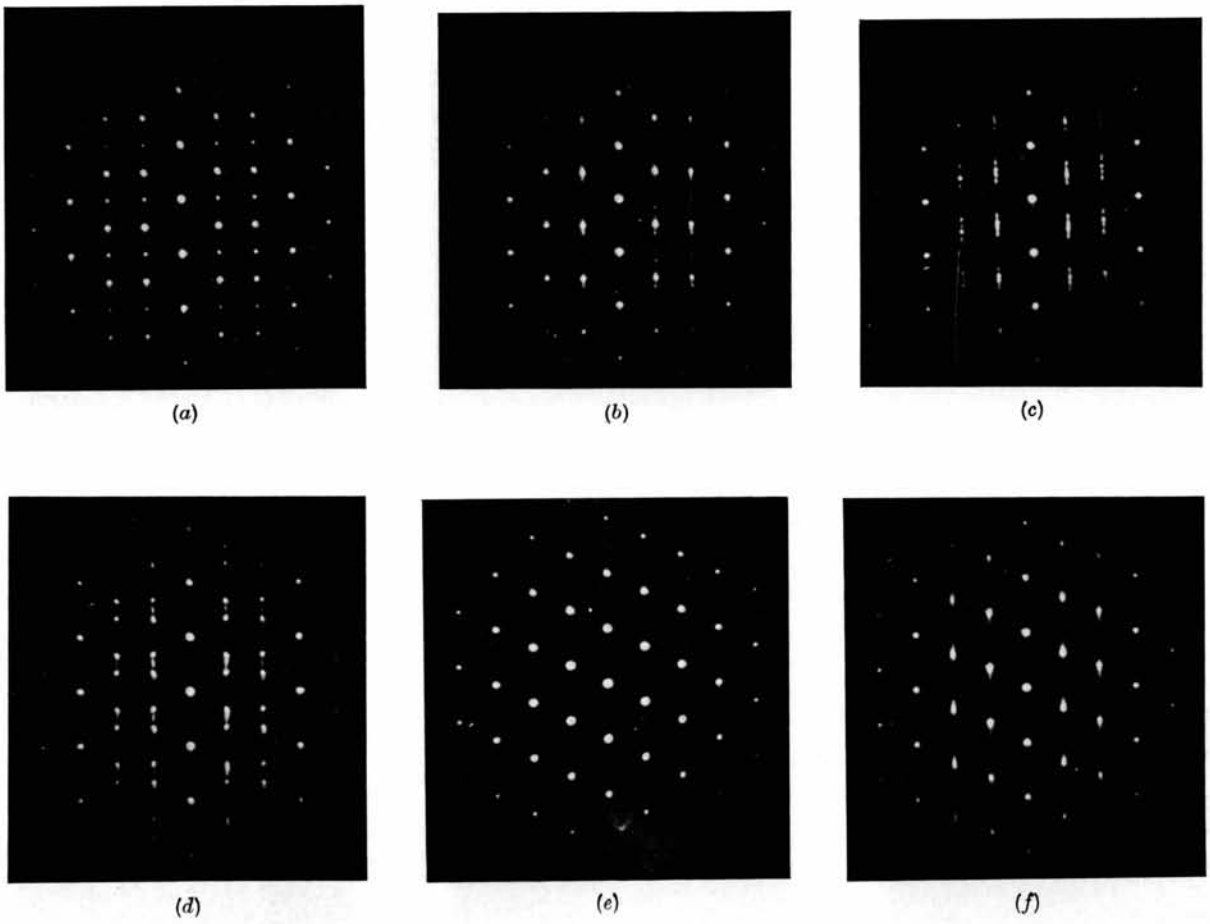

Fig. 3. Diffraction patterns of gratings representing different stages in the transition from hexagonal to cubic close-packed arrangements. (*a*) Perfect hexagonal. (*b*) Hexagonal predominating. (*c*) Random arrangement of planes. (*d*) Cubic predominating. (*e*) Perfect cubic. (*f*) Cubic predominating—faults of 'side-slip' type.

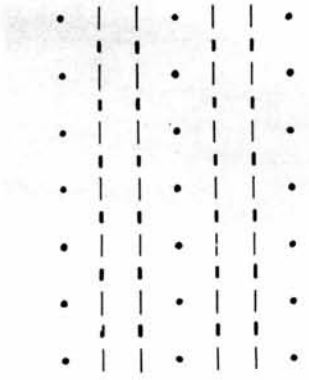

Fig. 4. Section of reciprocal lattice of cobalt derived from the results of Edwards & Lipson.

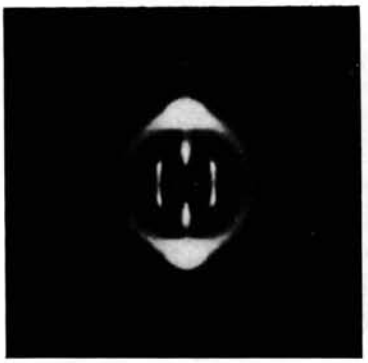

Fig. 5. X-ray fibre photograph of nylon.

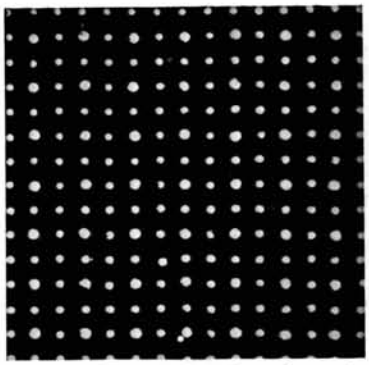

Fig. 6. Enlarged print of portion of grating representing perfectly ordered $AuCu_3$.

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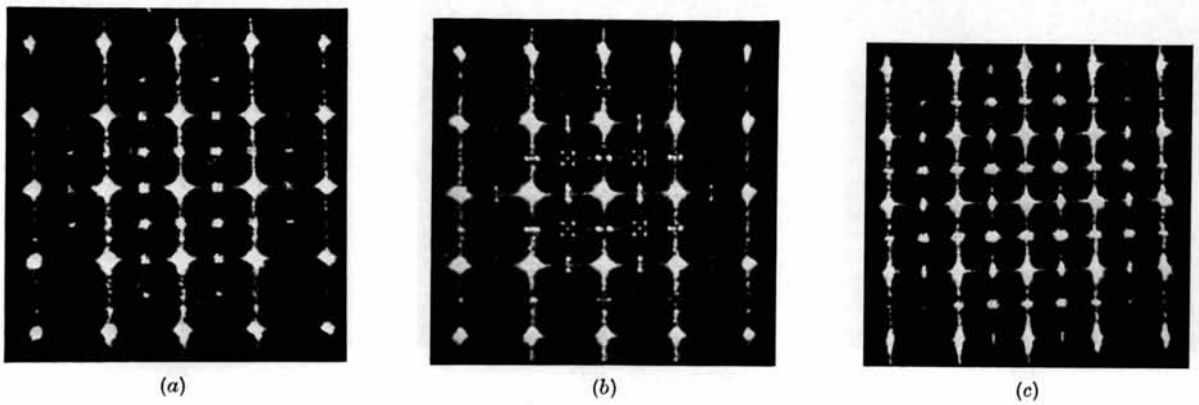
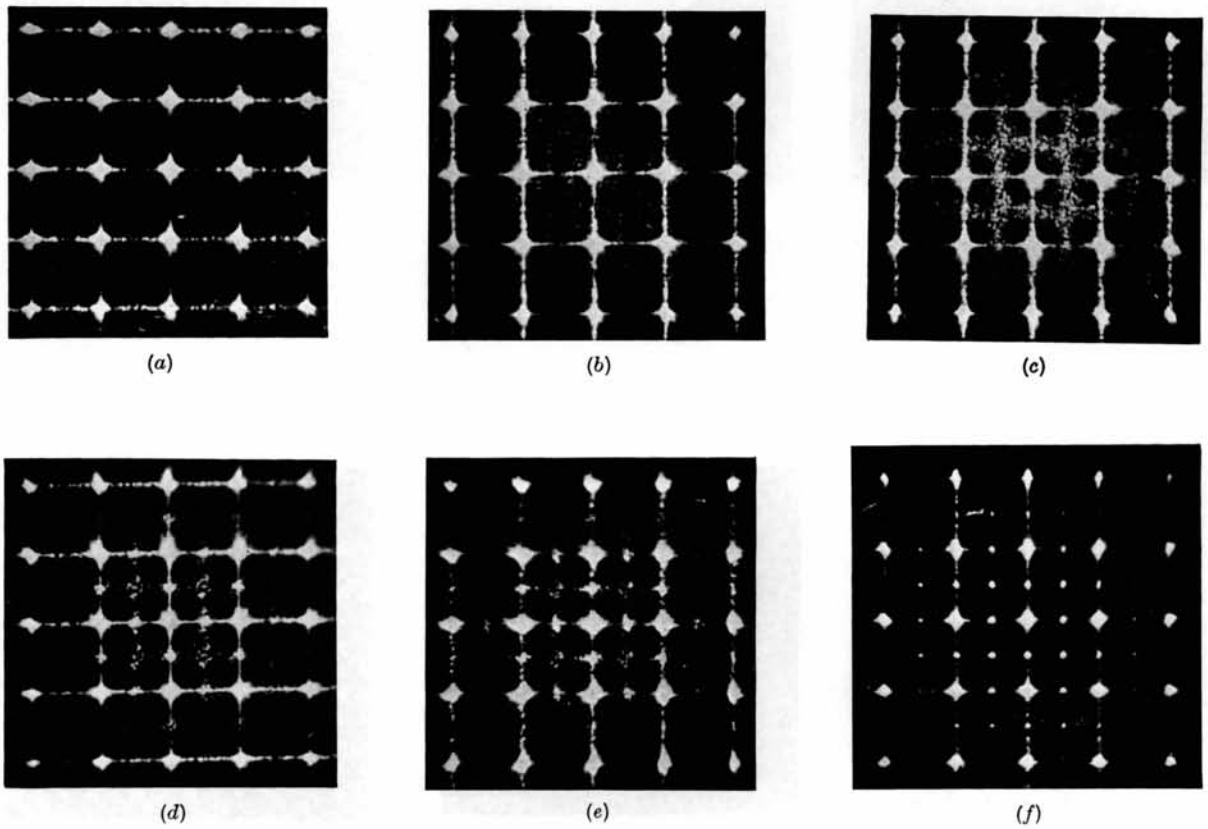


(a) (b) (c)

Fig. 7. Diffraction patterns of gratings representing three arrangements of domains in $AuCu_3$. In this figure and in Fig. 8 the secondary maxima, which form lines joining the main spots, should be disregarded.



(a) (b) (c)

(d) (e) (f)

Fig. 8. Diffraction patterns of gratings representing various stages in the ordering process of $AuCu_3$. (*a*) All copper. (*b*) Random arrangement of gold atoms in the alloy. (*c*) After the first stage of movement. (*d*) After the second stage. (*e*) After the third stage. (*f*) Perfect order.

gives only sharp reflexions, but the hexagonal structure gives a mixture of sharp and diffuse reflexions. This latter structure must therefore be imperfect and the type of imperfection postulated to explain the X-ray diffraction pattern is based upon the packing of close-packed layers of atoms.

Upon any one such layer of atoms, there are two situations in which the next layer can be placed to form a close-packed structure. Neither of these layers has atoms directly above those in the lower layer, and so, if we call the first layer *A*, we may call the other layers *B* and *C*. Any two of these layers can fit together and therefore any structure composed of these three layers, in which no two successive layers are alike, is a close-packed structure. The two most common are the hexagonal, in which alternate layers are similar, and the cubic, in which each layer is similar to that three layers below.

To simulate such structures in two dimensions, each layer is represented by a single row of equally spaced holes, and the three different layers are represented by displacements parallel to the rows. If one set of holes represents an *A* layer, the *B* layer can be represented by a set of holes displaced to the right by one-third of the spacing and the *C* layer by a set of holes displaced to the left by the same amount. Stacking of the layers is represented by punching these different rows of holes at equally spaced distances (Fig. 2). With suitable ratio of horizontal and vertical spacings, the gratings correspond to projections of the structures on prism faces (referred to hexagonal axes) and the diffraction patterns correspond to *h*0*l* sections of the corresponding reciprocal lattices.

Gratings have been constructed to represent a series of structures, some basically hexagonal and some basically cubic, with various arrangements of faults. Fig. 3 (*a*–*e*) shows the diffraction patterns of some of these gratings representing successive increases in the amount of cubic-type packing in a hexagonal-type structure. Fig. 3 (*b*) may be compared with Fig. 4, which is a representation of a section of the reciprocal lattice derived by Edwards & Lipson from their experimental results. Essentially similar effects are also given by the mineral chrysotile (Aruja, 1944), but complete details of the reciprocal lattice cannot be found experimentally because single crystals of the material cannot be obtained.

Another interesting point that emerges from these results is that two essentially different types of fault are possible in a basically cubic structure: there may be a change in the sequence of layers, represented by the sequence *ABCABCBACBA*..., or there may be a 'side-slip' represented by the sequence *ABCABABCA*.... The former may be regarded as an intimate twinning, and the diffraction pattern (Fig. 3 (*d*)) shows streaks joining spots due to the two components of the twin; the diffraction pattern of the latter (Fig. 3 (*f*)) shows reflexions from one structure only, but with some of the spots elongated. The former effect has been found in some forms of nylon (Fig. 5), suggesting that intimate twinning is present in these structures.

2. *Ordering in the alloy* $AuCu_3$

The alloy $AuCu_3$ crystallizes in the face-centred cubic arrangement and, according to its previous thermal history, may exhibit any degree of order ranging from a random arrangement of copper and gold atoms on the lattice sites to a completely ordered state in which the gold atoms may be considered to be at the corners of the unit cells and the copper atoms are at the centres of the faces. X-ray photographs of the perfectly ordered structure show sharp superlattice reflexions; but partially ordered structures show reflexions that are broadened in an unusual way (Edmunds, Hinde & Lipson, 1947). The relationship between the ordering process and the variations in shape and size of the superlattice reflexions provides a problem ideally suited to the optical method of attack.

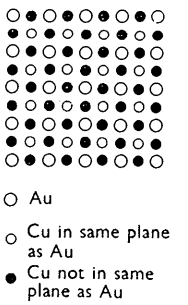


Fig. 9. Arrangement of atoms in two adjacent planes of $AuCu_3$.

The problem can be reduced to two dimensions fairly satisfactorily by considering only the atoms in two adjacent (100) planes projected on to a single plane; these two planes are separated by half a unit translation and no two atoms overlap in the projection. Thus in Fig. 9, which is a representation of a perfectly ordered arrangement, each atom may be considered as having eight nearest neighbours. An enlarged portion of a grating made to represent this structure is shown in Fig. 6, the holes representing gold atoms having three times the area of those representing copper atoms to correspond approximately with the relative scattering factors.

The problem is to find whether it is possible to produce a grating of which the diffraction pattern corresponds in certain essential features with the X-ray diffraction pattern of the $AuCu_3$ alloy at various stages of ordering. These features are as follows:

(1) The main-lattice reflexions are always sharp.

(2) The superlattice reflexions are broadened.

(3) In reciprocal space the superlattice reflexions are represented by approximately disk-like volumes of different orientations, the section in the (100) equatorial plane being represented by Fig. 10 (Edmunds, Hinde & Lipson, 1947).

There are two essentially different ways of looking at the problems. First, in any random arrangement there are bound to be accidental regions where the degree of order is high; when ordering begins, these regions may act as nuclei from which order may spread, and ordering will be complete when these ordered regions meet. There would presumably be a slower process of growth of these ordered regions, perhaps by the absorption of the smaller regions by the larger ones. Secondly, there may be merely an increase in the short-range order (Peierls, 1936) over the structure generally; when the short-range order parameter σ reaches unity, the long-range order parameter is also unity, and so the state of perfect order can also be attained in this way.

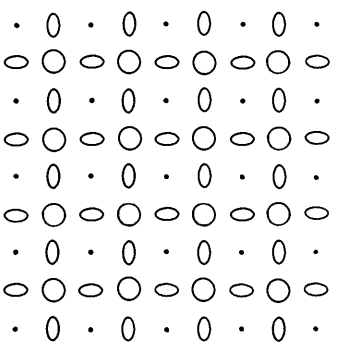


Fig. 10. Section of reciprocal lattice of $AuCu_3$ on the basis of Wilson's theory (derived by Edmunds, Hinde & Lipson).

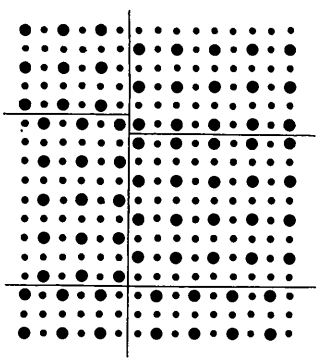


Fig. 11. Diagram showing part of the arrangement of holes giving the pattern of Fig. 7 (*a*).

The first possibility can be investigated by making a grating which has regions of perfect order (anti-phase domains) in which the larger holes have different relative positions, as shown in Fig. 11. The diffraction pattern (Fig. 7 (*a*)) shows sharp main spots and broadened superlattice spots, but the latter do not have the characteristic shapes shown in Fig. 10. Wilson (1943) has shown that these shapes would be produced if the domains met in such a way that the gold atoms tended to avoid each other; a grating in which this condition is rigidly obeyed gives the diffraction pattern shown in Fig. 7 (*b*), and it will be seen that the broadened reflexions are replaced by groups of spots whose dispositions follow the general outlines of Fig. 10. This result may have some significance in view of the findings of Guinier & Griffoul (1948), who state that, under certain conditions, the superlattice spots tend to split up into separate components; the spots shown in Fig. 7 (*b*), however, do not correspond to the type of splitting observed, but some modification of the grating might possibly lead to a greater measure of agreement.

A grating representing domains of different shapes and sizes, and with Wilson's condition not completely fulfilled, gives broadened reflexions (Fig. 7 (*c*)) corresponding with Fig. 10 fairly well. Nevertheless, it is difficult to see how a structure of this sort could come about from the process described; if two domains met with their gold atoms in contact, what type of process could cause their surface of junction to change so that it adopted the presumably more stable configuration with gold atoms avoiding each other? Difficulties of this

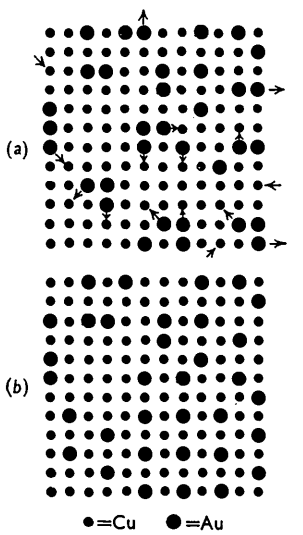


Fig. 12. Diagram to show the way in which gold atoms were moved to simulate the ordering process. (*a*) Before moving. Arrows indicate direction in which gold atom will be moved. (*b*) After movement.

sort do not arise if the anti-phase domains are considered as arising from an increase in short-range order. Hume-Rothery & Powell (1935) have suggested that order arises from the avoidance of similar atoms, and thus the avoidance of the gold atoms in $AuCu_3$ is introduced initially, and not as a secondary consequence at the boundaries of the domains.

These ideas were tested in the following way. A random two-dimensional structure was produced by associating the two types of atoms with cards in a well-shuffled pack of playing cards; when a diamond (the closest analogue to gold!) was turned up, a gold atom was drawn at the corresponding lattice point. In this way the arrangement, of which a portion is shown in Fig. 12 (*a*), was produced. The diffraction pattern (Fig. 8 (*b*)) of the corresponding grating has no superlattice spots, but there is a general background, due to the departure from strict periodicity, which is absent

from the diffraction pattern (Fig. 8 (*a*)) of the grating representing pure copper. The value of σ, found by counting the number of pairs of unlike holes, was 0·04; it should, of course, have been zero.

To increase the short-range order, the arrangement of atoms was altered by interchanging pairs of atoms in such a way that the number of gold atoms in contact decreased. Examples of the interchange are indicated by the arrows in Fig. 12 (*a*). The process is, of course, essentially subjective, but on the whole it was found that the required changes were often quite unambiguous, particularly in those regions where the gold atoms were outstandingly populous. In this way it was found possible to increase the short-range-order parameter to 0·51.

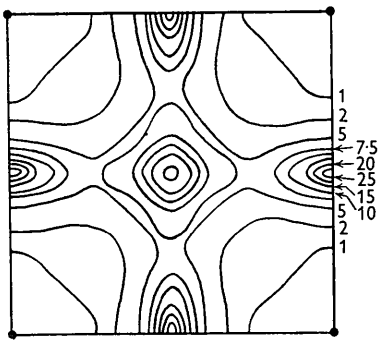


Fig. 13. Contours of constant scattering power in arbitrary units in a section of reciprocal space (after Cowley, 1950). The corners of the square are main-lattice points. (Reproduced by permission from the *Journal of Applied Physics*.)

The diffraction pattern (Fig. 8 (*c*)) of the corresponding grating showed considerable changes in the background. The regions around the main-lattice spots had become clearer, and the background had built up into a 'milky way' along the shortest lines joining the points which the superlattice spots would eventually occupy. This result is in excellent agreement with the measurements of Cowley (1950) who has investigated the X-ray diffraction pattern of an alloy annealed above the critical temperature. Fig. 13 shows a representation of Cowley's measurement of a section of the reciprocal space and this has a striking similarity to Fig. 8 (*c*).

The development of order in this way can be continued, and gratings were made with values of σ of 0·69, 0·78 and 0·80; after this it was almost impossible to make any simple changes that would increase the short-range order appreciably. (Presumably, the atoms in a real crystal would not meet the inhibitions set by the two-dimensional representation and by the condition that no atom should make more than one interchange of position until the others had had their turn.) Diffraction patterns of two of these gratings are shown in Fig. 8 (*d*, *e*). It will be seen that the background has become still more uneven, showing maxima at the positions of the superlattice reflexions; these maxima have shapes similar to those shown in Fig. 10.

The importance of these results is that they show that the observed X-ray diffraction patterns can be produced by postulating changes in short-range order only. Although the only condition postulated in the changes was that gold atoms should tend to separate from each other, it was found that domains of perfect order were produced and that these domains met in such a way that gold atoms tended to avoid each other (see Fig. 12). Thus it appears that the observations of Sykes & Jones (1938) are connected with the development of short-range order and not with an extra effect superimposed upon the formation of long-range order. With some extension of the theory of MacGillavry & Strijk (1946), it should be possible to derive the short-range order parameter from Sykes & Jones's measurements of the breadths of the superlattice lines on powder photographs.

Limitation of the method

Clearly, the extension of the method to two dimensions gives a great increase in its applicability, but there still remain problems which can probably only be solved by three-dimensional methods, and this constitutes the severest limitation. Even if the practical difficulties of making models could be overcome, the time required would probably be prohibitive; the time for making a grating with 40×40 holes—the number used for $AuCu_3$—was about 2 hr.

The gratings necessarily consist of small, finite numbers of holes, and this fact restricts the method in three ways. First, it makes the subsidiary maxima of the patterns appreciably strong, as can be clearly seen in Figs. 7 and 8; secondly, it prevents the quantitative evaluation of probabilities such as those introduced in the cobalt problem; and, thirdly, it tends to produce a spottiness in reflexions that should be completely diffuse.

It has not been found possible to illustrate problems involving small displacements of atoms from lattice points, such as those involved in the age-hardening of copper–aluminium alloys (Preston, 1938). Increase in accuracy in making the gratings would be necessary, and this may be possible if some improvement can be made in methods of producing them.

General principles

The experience gained from the optical experiments and from calculations published in connexion with other structures enables the following general rules to be laid down. They are not infallible, but they may be of help to others who may have to deal with similar problems.

(1) Streaks in reciprocal space correspond to faults in the crystal lying on planes perpendicular to the streaks, or to smallness of the crystal dimension parallel to the streaks.

(2) Disk-like diffusion in reciprocal space corresponds to faults in the structure lying along lines perpendicular to the disks, or to smallness of the crystal dimensions in the plane of the disk.

(3) If the properties of the streaks or diffusions vary with order of diffraction, they indicate displacements of the atoms from lattice sites. For example, in Cu_4FeNi_3 (Daniel & Lipson, 1943, 1944) the intensities of the side bands accompanying the main reflexions increase with order.

(4) If the properties of the streaks or diffusions, with respect to the reflexions they accompany or replace, are constant, then some form of imperfection not involving atomic displacements is indicated. $AuCu_3$ provides an example of this; all the unit cells of the reciprocal lattice contain the same distribution of scattered intensity, if the natural fall-off with angle is allowed for.

(5) If *all* the reflexions appear in the same degree of diffuseness, they are probably due to smallness of crystallite dimension, as given by rules (1) and (2); if, however, *some* of the reflexions remain sharp, the imperfections must be such that the atoms scatter in the same relative phases for the sharp reflexions, but not for the diffuse reflexions.

(6) Streaks joining spots usually imply submicroscopic twinning on planes perpendicular to the streaks. It is not necessary to postulate that the structure can assume all possible orientations between the two twins.

These rules are not adequate to explain all observed phenomena of the sort described, and should be regarded only as guiding principles. They do not, in themselves, account for all the details in the diffraction pattern of $AuCu_3$; since this pattern contains disks oriented in three different directions, rule (2) cannot apply. Problems of this sort must be treated individually, and there are several, such as that of ice (Owston, 1949), which still defy solution.

We wish to thank Mr W. Hughes, who constructed the apparatus and who showed great patience in drilling the template for the $AuCu_3$ gratings, and Mr C. W. Bunn who provided the photograph for Fig. 5. We also wish to acknowledge a maintenance grant for one of us (R. M. H.) from the British Iron and Steel Research Association, and a grant from the Department of Scientific and Industrial Research towards the cost of construction of the apparatus.

References

ARUJA, E. (1944). *Nature, Lond.*, **154**, 53.
BRAGG, W. L. & LIPSON, H. (1943). *J. Sci. Instrum.* **20**, 110.
COWLEY, J. M. (1950). *J. Appl. Phys.* **21**, 24.
DANIEL, V. & LIPSON, H. (1943). *Proc. Roy. Soc.* A, **181**, 368.
DANIEL, V. & LIPSON, H. (1944). *Proc. Roy. Soc.* A, **182**, 378.
EDMUNDS, I. G., HINDE, R. M. & LIPSON, H. (1947). *Nature, Lond.*, **160**, 304.
EDWARDS, O. S. & LIPSON, H. (1942). *Proc. Roy. Soc.* A, **180**, 268.
GUINIER, A. & GRIFFOUL, R. (1948). *Rev. Metall.* **45**, 387.
HUME-ROTHERY, W. & POWELL, H. M. (1935). *Z. Krystallogr.* **91**, 23.
JAMES, R. W. (1948). *Optical Principles of the Diffraction of X-rays.* London: Bell.
MACGILLAVRY, C. H. & STRIJK, B. (1946). *Physica, 's Grav.* **11**, 369.
OWSTON, P. G. (1949). *Acta Cryst.* **2**, 222.
PEIERLS, R. (1936). *Proc. Roy. Soc.* A, **154**, 207.
PRESTON, G. D. (1938). *Phil. Mag.* **26**, 855.
SYKES, C. & JONES, F. W. (1938). *Proc. Roy. Soc.* A, **166**, 376.
WARREN, B. E. (1941). *Phys. Rev.* **59**, 693.
WILSON, A. J. C. (1942). *Proc. Roy. Soc.* A, **180**, 277.
WILSON, A. J. C. (1943). *Proc. Roy. Soc.* A, **181**, 360.

Acta Cryst. (1951). **4**, 266

The Structure of Mercuric Amidochloride, $HgNH_2Cl$

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The structure of $HgNH_2Cl$ consists of infinite chains of alternating Hg and NH_2^+ with linear bonds about Hg and tetrahedral bonds about N. The unit cell is orthorhombic with $a = 5{\cdot}167$, $b = 4{\cdot}357$, $c = 6{\cdot}690$ A., and with Hg at 0, 0, 0 and 0, 0, $\frac{1}{2}$. The probable space group is C_{2v}^1–$P2mm$, and the Hg–N bond distance is $2{\cdot}05 \pm 0{\cdot}02$ A.

As a result of a study (Arora, Lipscomb & Sneed, 1951) of the products of reactions between ammonia and mercury (I) compounds, several samples of $HgNH_2Cl$ were prepared. The analysis of the crystal structure from the powder diagram has been carried out by the method employed in a study of Millon's base (Lipscomb, 1951). The mercury atoms have been located with certainty, and indications of the positions of the light