It is significant that some compounds analogous to $(NH_4)_3FeF_6$, though closely related to it in crystal structure, are not cubic. In Na_3AlF_6 there is a framework of AlF_6 octahedra similar to that of the FeF_6 groups in $(NH)_3FeF_6$, but the octahedra are slightly rotated or displaced out of the highest symmetry orientation (Náray-Szabó & Sasvari, 1938). The true structure therefore becomes monoclinic and falls into space group $P2_1/m$.

It appears probable that similar displacements from symmetrical orientation, this time of the WO_6 octahedra, are responsible for the departures from the cubic system observed in R_3WO_6-type tungstates. Indeed, the form that the multiplicity of X-ray powder lines takes for, say, Ca_3WO_6 so closely resembles that in powder photographs of Na_3AlF_6 that the atomic arrangements may be in fact almost identical.

Nevertheless, it is improbable that all the structural deformations take exactly the same form. It is more likely that several different structure types occur, and in this connexion the relationship between members of the perovskite family may be recalled. Náray-Szabó (1943), in discussion of the perovskite group, has used the term 'sister-structures' to describe a family of structures that bear a very close likeness to one another and yet are not strictly isomorphous. The tungstates and molybdates appear to comprise another group of compounds for which the term 'sister-structures' is appropriate to emphasize the family resemblance. This group may also be regarded as embracing a number of fluorides of which $(NH)_3FeF_6$ is the prototype.

References

McKeag, A. H. & Ranby, P. W. (1939). British Patent No. 526,675.

Náray-Szabó, St.v. (1943). *Naturwissenschaften*, **31**, 466.

Náray-Szabó, St.v. & Sasvari, K. (1938). *Z. Krystallogr.* **99**, 27.

Rooksby, H. P. & Steward, E. G. (1946). *Nature, Lond.*, **157**, 548.

Rooksby, H. P. & Steward, E. G. (1951). *J. Appl. Phys.* **22**, 358.

Wyckoff, R. W. G. (1931). *The Structure of Crystals*, 2nd ed. New York: Reinhold.

Acta Cryst. (1951). **4**, 507

Diffuse Scattering by an Ordering Alloy*

By J. B. Newkirk† and R. Smoluchowski

Carnegie Institute of Technology, Pittsburgh, Pa., U.S.A.

and A. H. Geisler and D. L. Martin

General Electric Research Laboratory, Schenectady, N.Y., U.S.A.

(*Received* 24 *January* 1951)

At an early stage of the ordering reaction process in CoPt crystals, thin platelets of the ordered phase form on {110} planes of the disordered matrix phase. These platelets are coherent with the matrix. Since {110} planes of the two phases are not identical, when each is in an unstrained condition, they mutually strain each other, causing characteristic diffuse X-ray diffraction effects and the marked changes in physical properties previously reported.

Introduction

A report has recently been published concerning an experimental investigation of the order–disorder phenomena in cobalt–platinum alloys whose compositions lie near 50 atomic % (Newkirk, Geisler, Martin & Smoluchowski, 1950, 1951). In that report the nature of the ordering reaction was described, but only brief reference was made to a part of the investigation in which the state of a partially ordered crystal of CoPt produced diffuse X-ray diffraction effects. It is intended in the present paper to enlarge upon that part of the study, describing new techniques employed and discussing the analysis of the observed diffraction effects in detail.

The phase diagram (Fig. 1) shows that above 825° C., CoPt alloys form an unbroken series of solid solutions having a random face-centered cubic lattice. Below 825° C. alloys close to CoPt in composition become ordered, forming a tetragonal unit cell analogous to the ordered CuAu cell. Parameter measurements are reported elsewhere (Newkirk *et al.* 1950, 1951).

The disordered state of CoPt may be retained by quenching from above 825° C., and the progress of the ordering reaction may be followed by aging at lower temperatures. The time required to approach closely

* This work represents part of a Doctoral Dissertation submitted by the first-named author to the Department of Metallurgical Engineering, Carnegie Institute of Technology, in June 1950.

† Now studying under Fulbright grant at Cavendish Laboratory, Cambridge, England.

a state of equilibrium depends upon the composition and the temperature of aging. For wire specimens drawn from a 48 atomic % cobalt alloy, the following times were required to order the alloy completely and to give sharp resolution of all lines in Debye–Scherrer patterns:

Aging temperature (° C.)	Time (hr.)
400	> 936
500	> 402
600	> 251, < 792
700	> 25, < 120

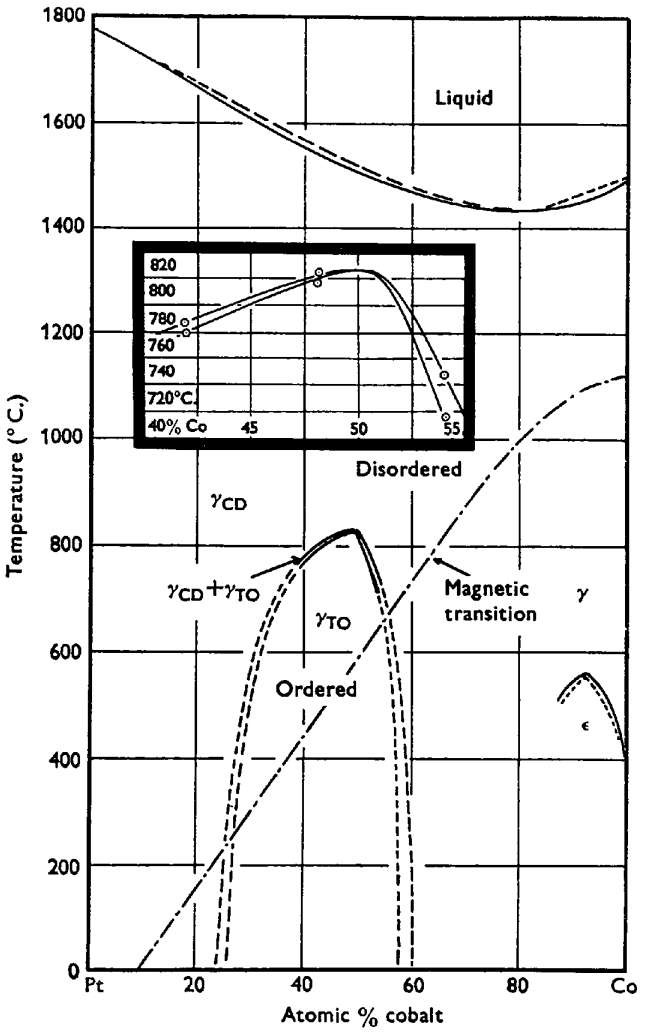

Fig. 1. Revised cobalt–platinum phase diagram.

Wires aged above 600° C. for comparatively short times gave Debye–Scherrer patterns in which the normal cubic lines were accompanied by diffuse side-bands (Newkirk *et al.* 1950, Fig. 3 (*b*)). When the partially ordered coarse-grained wire was exposed without rotation to the X-ray beam in a cylindrical camera, individual Laue spots were often associated with a square configuration of diffuse spots or were at the intersection of diffuse streaks in the shape of an 'X'. Such effects were never found with disordered or highly ordered wires. Since it was suspected that these effects were due to regular lattice strains resulting from the ordering reaction or to the formation of ordered particles on some characteristic habit plane of the disordered matrix, as often occurs in precipitation reactions, a systematic study of the diffuse scattering from a single crystal at an early stage of aging was undertaken. The aging treatment adopted was 12 min. at 600° C.

Experimental methods

Large crystals of CoPt were made by the method of slow freezing, under argon, in a crucible lined with alundum. The cobalt, in rondells, was obtained from the Reduction and Refining Company of Newark, New Jersey, and was reported to be 99·9 % cobalt. The platinum was bought in sheet form from the Vernon-Benshoff Company of Pittsburgh, Pennsylvania, who claimed purity of 99·99 %. The elements were mixed in proportions to give a 50 atomic % alloy. The ingot was homogenized by holding for 30 hr. at 1225° C. under static argon, after which it was quenched into water to retain the disordered state. A thin disc (*c.* 1 mm. thick) was cut from the large-grained ingot by means of a high-speed abrasive wheel. After the aging treatment (in argon) the disc was thinned by gently rubbing on metallographic polishing paper. The thickness was finally reduced from about 0·004 to 0·002 in. by etching in hot dilute aqua regia. The desired crystal was separated from the rest of those making up the thin disc, by coating the disc with beeswax, scratching around the desired crystal and immersing in aqua regia. The wax was then removed with warm carbon tetrachloride and the crystal was glued to a glass fiber for convenient handling. Since the diffraction effects to be studied were themselves quite indistinct, extreme care was necessary to avoid distorting the specimen mechanically. The crystal was cut so as to have a point at one end, thus allowing only a small part of the specimen to be exposed to the X-rays. In this way diffuse spots could be recognized which were only shapeless blurs when a larger area of crystal was exposed.

The method of determining the reciprocal lattice of the partially ordered crystal was based on the analysis of $K\alpha$ reflections in a series of stationary-crystal photographs for each reciprocal-lattice point as described in detail by Geisler & Hill (1948). All the X-ray photographs were made with a cylindrical camera of 5 cm. radius which takes a 5×12 in. film. Unfiltered cobalt radiation and a pinhole of 0·020 in. diameter were used throughout the investigation. Since accuracy of observation is much better and subsequent calculations are simplified if the reflection in question falls on the zero layer, the specimen crystal was oriented with either a [001] or a [101] direction vertical (see Fig. 2). In this way any point in the reciprocal lattice within the limiting sphere for Co $K\alpha$ could be made to reflect on the zero layer and could be conveniently observed and plotted.

Several methods for determining the orientation of the mounted crystal have been used. Since some of these are particularly suitable for this system, owing to the specimen about the vertical axis and observing the frequency and relative intensity of the reflections, any desired major direction could be brought to the vertical.

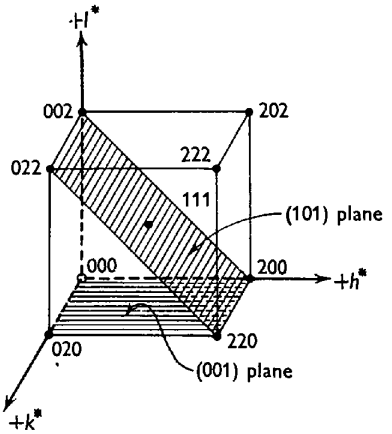

Fig. 2. Reciprocal lattice of reflecting planes in face-centered cubic space lattice.

(2) *Etch holes and surface ridges*

In very thin specimens, angular holes would occasionally be formed by the action of the acid. These were especially noticeable in specimens whose flat side was nearly parallel with a (100) plane of the crystal lattice, in which case the holes were square with sides parallel to <100> directions. In these specimens, bright ridges were often found which lay approximately parallel with the sides of the holes.

Results

The appearance of the reciprocal lattice at an early stage of aging is anticipated at this point in order to facilitate the presentation of the data. Fig. 3 shows the configurations of rods which were found to extend through points in the (101) plane of the reciprocal

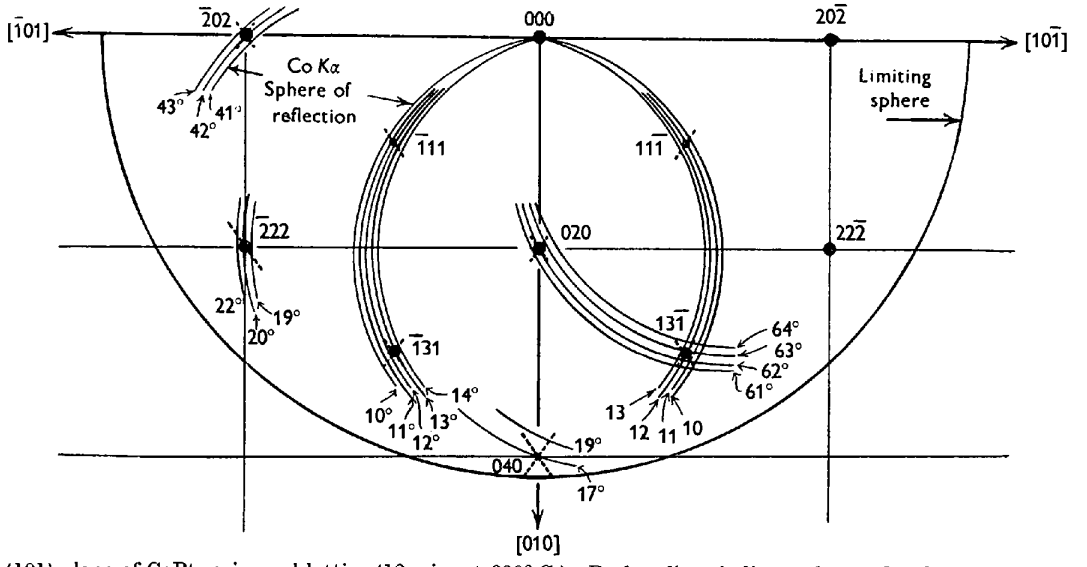

Fig. 3. (101) plane of CoPt reciprocal lattice (12 min. at 600° C.). Broken lines indicate observed rods at 30° to the plane; dots indicate observed rods perpendicular to the plane. For clarity rods are shown twice actual length.

the etching characteristics of Co–Pt alloys, they are described in some detail below. Final settings were made by Laue methods.

(1) *Etch pits*

The X-ray unit which was used for this study was equipped with a track on which could be fitted a goniometer-type specimen mount and also a telescope whose axis was coincident with the X-ray beam. By means of this arrangement and a glass slide between the telescope and the crystal, the specimen could be viewed with vertical illumination. Then, using the goniometer head on the specimen mount, the crystal could be oriented so as to reflect a maximum amount of light back into the telescope. It was determined that in this position a (100) plane was normal to the X-ray beam. By rotating

lattice. The following prominent features will be observed:

(*a*) Five rods in <110> directions pass through the (2̄02), (020), (1̄31) points. Four are at 30° to the (101) plane (their projections are plotted as dashed lines) and one is perpendicular to it.

(*b*) Three rods in <110> directions pass through the (1̄11), (111̄) and (2̄22) points. Two are at 30° to the (101) plane (dashed lines) and one is perpendicular.

(*c*) Only four <110> rods have been observed to pass through the (040) point, though one might expect to find them in the same five directions as were found at the (020) point. The rod normal to the (101) plane was not observed.

Enlarged views of two of these points are given in Figs. 4 and 5. In some cases evidence for a plane or web

between <110> rods has been found, as indicated in Fig. 4. No generality is apparent concerning the occurrence of these webbings, though by their geometry they must lie on a (111) plane.

In the paragraphs immediately following, the X-ray photographs from which Fig. 3 was constructed are briefly described. By comparing diffracted spots with the configuration of rods through the corresponding reciprocal-lattice point in Fig. 3, the qualitative relationship can in all cases be seen directly.

The series of enlargements in Fig. 6 show the diffraction spots resulting from the intersection of the Co $K\alpha$ sphere of reflection with the rods through the $(\bar{1}11)$ point.* There are three <110> rods at this point (see Fig. 3), all in the same plane and at an angle of 60°

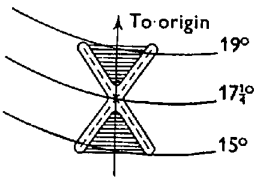

Fig. 4. Intersection of reflecting spheres with reciprocal-lattice point (040). ([101] vertical, [010] downwards, [10$\bar{1}$] to the right.)

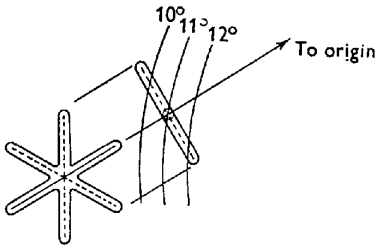

Fig. 5. Intersection of reflecting spheres with reciprocal-lattice point $(\bar{1}11)$. (Same orientation as Fig. 4.)

from each other. When the diameter of the sphere of reflection is 13° from the [010] direction, the surface of the sphere intersects the two <110> rods which lie at 30° to the plane. These intersections register as two diffuse spots, one slightly above and the other slightly below the zero layer, as is shown in the enlargement marked 13° in Fig. 6. When the crystal is set at 12°, the diffracted rays are sharper and closer together as shown in the strip marked 12°. At 11° the surface of the sphere precisely intersects the $(\bar{1}11)$ matrix point, and the [101] rod is registered directly as a vertical streak through the Laue spot (or in this case the Bragg spot). As the series of crystal settings is continued to 9°, the spots again separate, becoming more diffuse until they can no longer be seen. It is important to note that the angle at which the surface of the sphere cuts this figure is such that if other <110> rods, comparable in size to those observed, were present at that point, they would be clearly detected. A series of photographs wherein the sphere of reflection intersected the $(11\bar{1})$ reciprocal-lattice point gave spots similar to those in Fig. 6 and, when measured and plotted, fell on the appropriate dashed lines in Fig. 3, thus proving the expected rotational symmetry.

In Fig. 8 the surface of the sphere of reflection happens to pass across three major reciprocal-lattice points within a span of 6°, one on the zero layer and two on the first layer line. Though measurements were made only on the zero layer, the other two sequences of spots are presented for comparison with other series through the same point. From the contact print in Fig. 8 one may see the relative locations of the spots as they occur on the film. The strips showing the enlargements of the three spots are placed at an angle with the horizontal, equal to that made by a line from the corresponding spot to the nearest hole punched in the film. This preserves the original orientation of the diffraction spots with respect to the horizontal.

The upper central series of enlargements shows patterns which result from the configuration of rods through the $(\bar{2}02)$ reciprocal-lattice point on the zero layer and is much the same as that for the $(\bar{1}11)$ point, described above. However, at the $(\bar{2}02)$ point, five of the six possible <110> rods are present instead of only three. Three of these may be observed directly in the photograph made with the crystal set at 42°. The other two rods intersect the surface of the sphere at nearly 90° and are seen as elliptical spots on the film. The [101] rod (directed toward the origin) is not observed.* The most intense rod, [101], is vertical and the other two are both at 60° from it, furnishing further direct evidence that the rods lie in <110> directions. In Fig. 3 the surface of the sphere of reflection is seen to be almost coincident with a pair of <110> rods and also passes through the $(\bar{2}02)$ reciprocal-lattice point, consistent with the diffraction pattern obtained.

The diffraction spots from the $(\bar{1}13)$ plane, on the first layer for this series, are too diffuse for analyzing, but the (002) series is clearly consistent with that for the equivalent (020) point (see Fig. 7) when allowance is made for the oblique angle of the surface of the sphere at the first layer line and for the spherical symmetry of the reciprocal lattice about its origin. The series in Fig. 7 shows the patterns found when the crystal was oriented so as to place the surface of the sphere of reflection near the (020) point. At $61\frac{3}{4}$° the <110> rods cause lines on the film which lie at 60° from each other and from the vertical [101] direction.

* All the enlargements given here show the spots about twice their size on the original film. Actual sizes of the patterns may be judged from the contact print (reproduced half size) above the enlargements and from the scale at the bottom.

* One may object to this conclusion because the spot which would be caused by this rod would fall upon the Laue spot and, therefore, the [10$\bar{1}$] rod may actually be present. Such is probably not the case, however, because the Laue spot, like other Laue spots on the same film, is evidently much smaller and sharper than any of the non-Laue spots. This difference allows a Laue spot and a diffuse-scattering spot to be easily distinguished.

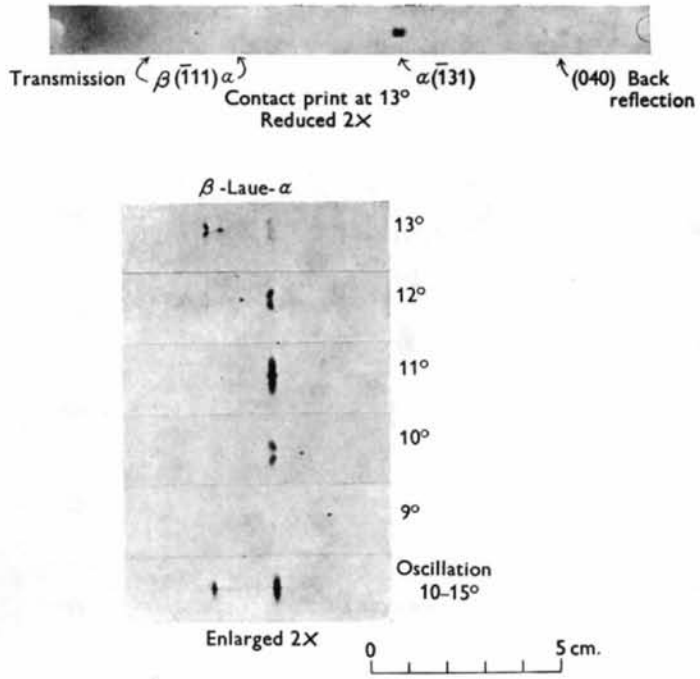

Fig. 6. Diffuse reflections about the (1̄11) reciprocal-lattice point of a small CoPt crystal aged 12 min. at 600° C. [101] is vertical; [010] is 9–13° from beam direction. Unfiltered Co radiation.

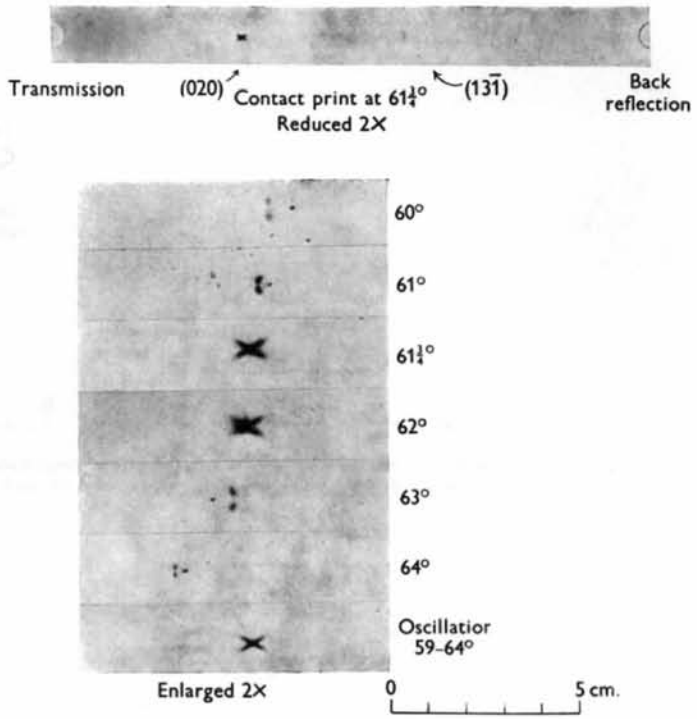

Fig. 7. Diffuse reflections about the (020) reciprocal-lattice point of a small crystal of CoPt aged 12 min. at 600° C. [101] is vertical and [010] is 60–64° from beam direction. Unfiltered Co radiation.

[*To face p.* 510

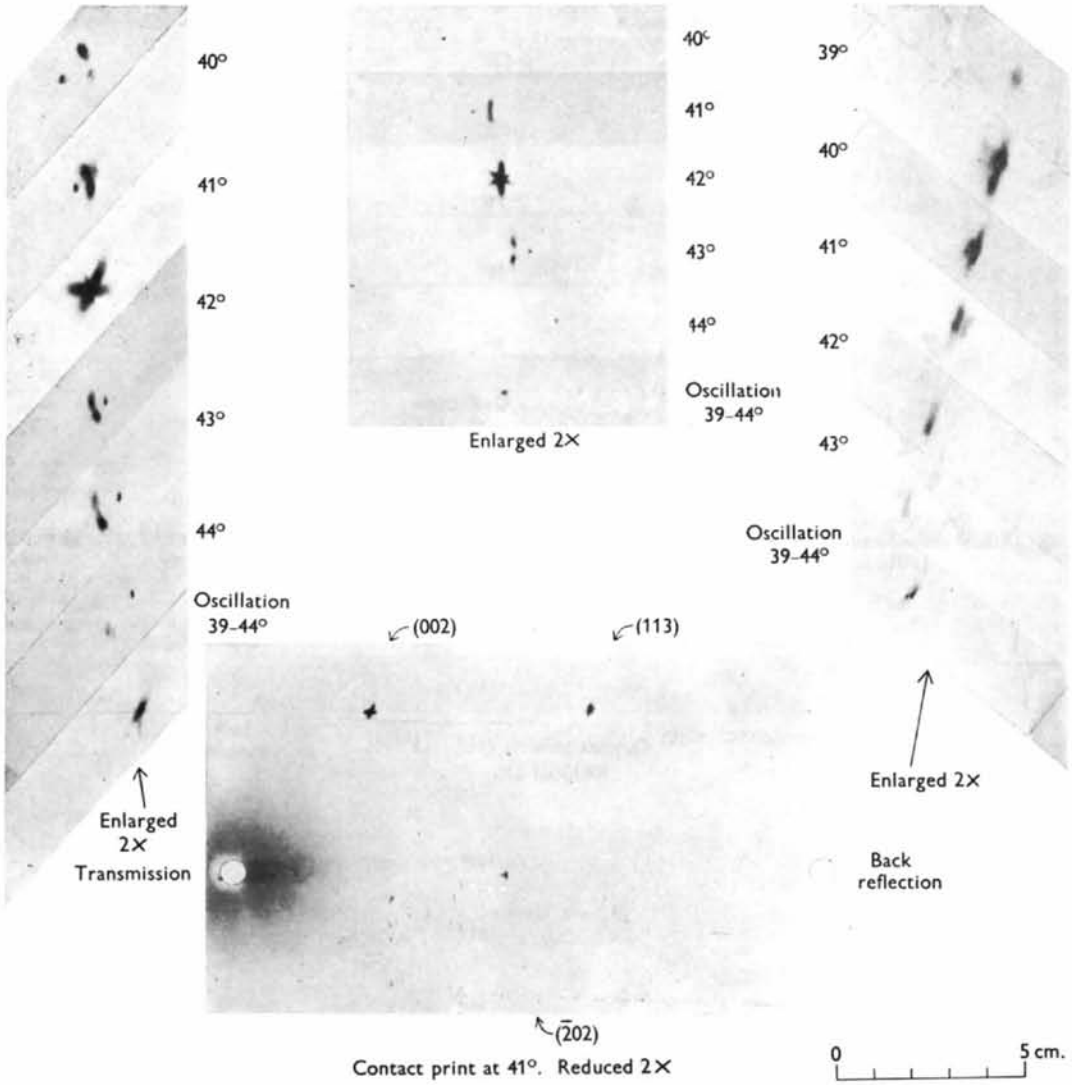

Fig. 8. Diffuse reflections about three reciprocal-lattice points of a small CoPt crystal aged 12 min. at 600° C. [101] is vertical and [010] is 38–44° from beam direction. Unfiltered Co radiation.

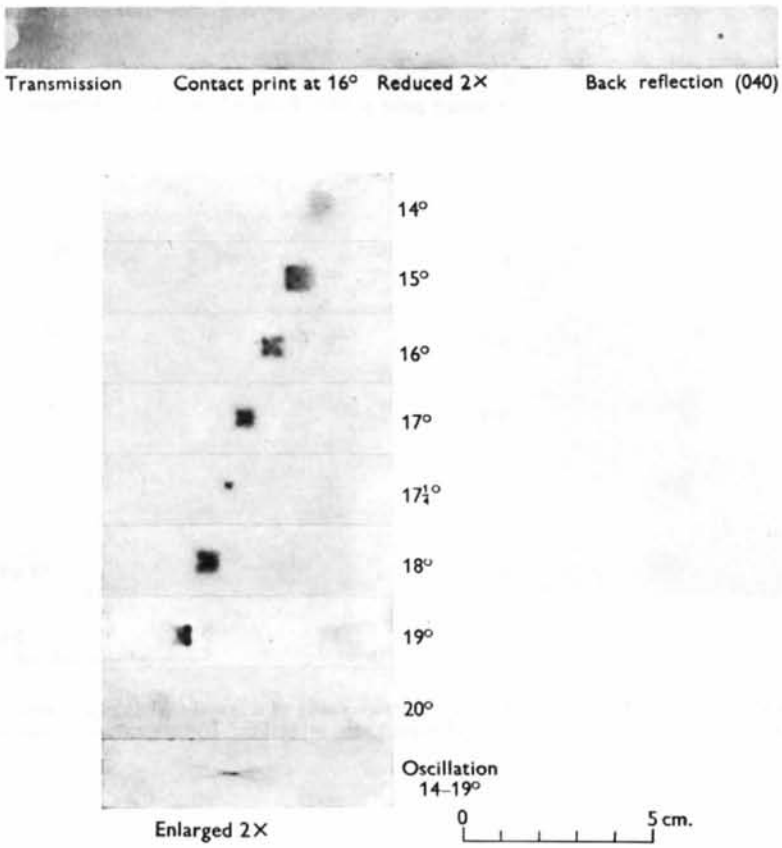

Fig. 9. Diffuse reflections about the (040) reciprocal-lattice point of a small CoPt crystal aged 12 min. at 600° C. [101] is vertical and [010] is 14–20° from beam direction. Unfiltered Co radiation.

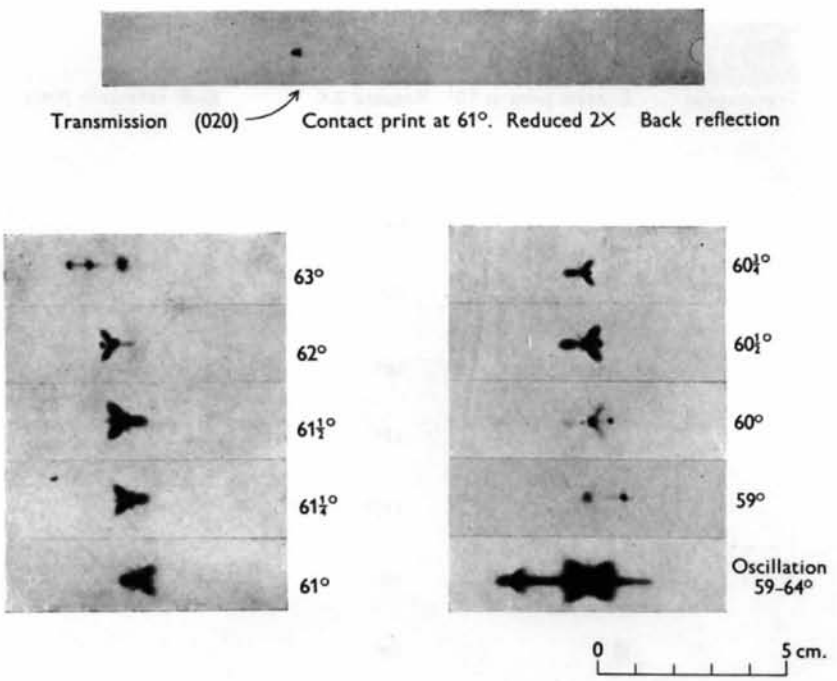

Fig. 10. Diffuse reflections about the (020) reciprocal-lattice point of a small CoPt crystal aged 12 min. at 600° C. [001] is vertical and [010] is 59–63° from beam direction. Unfiltered Co radiation.

Since the (040) reflection is merely a second-order reflection from (020) planes, one would expect to find the same configuration of rods about these two reciprocal-lattice points. The series of spots in Fig. 9, when related to Figs. 3 and 4, shows this to be true, though the [101] rod, known to be weak and diffuse at the (020) point, has become too diffuse to be registered clearly on the film. A webbing between the four points around the central Laue spot where the $<110>$ rods intersect the sphere of reflection is evident in this series.

were obtained while the specimen crystal was set with the [101] direction vertical, i.e. so that points in the (101) plane of Fig. 2 diffracted to the zero layer. By rotating the crystal 45° it was possible to make the (001) plane horizontal, thus bringing reflections of another group of reciprocal-lattice points to the zero layer line. The results of studies of this group of points are given in Fig. 11 which is a plot of the (001) plane of the reciprocal lattice. By comparing this with Fig. 3 one will observe that the number and position of rods through all equivalent points are symmetrical with respect to the

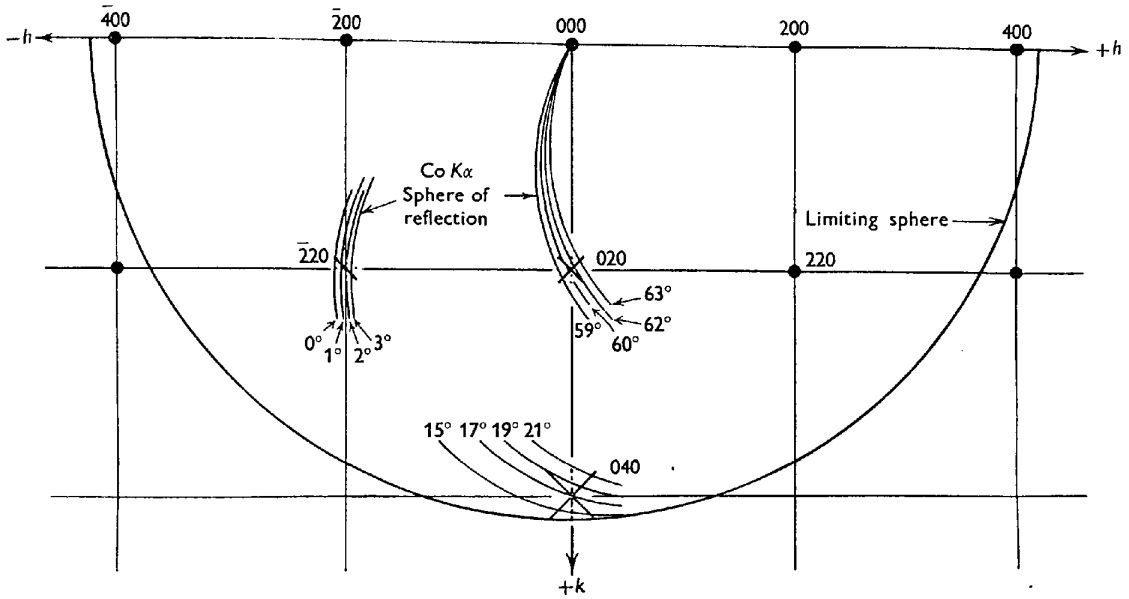

Fig. 11. (001) plane of CoPt reciprocal lattice (12 min. at 600° C.). Broken lines indicate observed rods at 45° to the plane; full lines indicate observed rods lying in the plane. For clarity rods are shown twice actual length.

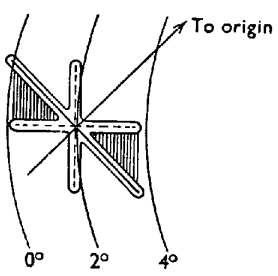

Fig. 12.

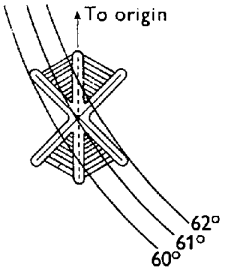

Fig. 13.

Fig. 12. Intersection of reflecting spheres with reciprocal lattice point ($\bar{2}20$). ([001] vertical, [010] downwards, [100] to the right.)

Fig. 13. Intersection of reflecting spheres with reciprocal-lattice point (020). (Same orientation as Fig. 11.)

The higher-order planes and those of low symmetry, including (131) and ($\bar{2}22$), give characteristically diffuse and indistinct reflections. Such information as can be obtained from them, however, is consistent with the former conclusion that a number of $<110>$ rods pass through their respective reciprocal-lattice points.

All of the diffuse diffraction effects described above

origin of the lattice. Enlarged views of two of the points on the (001) plane are given in Figs. 12 and 13.

By comparing Fig. 13 with the series of enlargements in Fig. 10 one may clearly see the relation between the reciprocal-lattice figure and the diffraction effects from which it was derived. At 63° there is a reflection (left spot), the Laue spot (middle), and the spot caused by the intersection of the [110] rod with the surface of the sphere of reflection. At 62° the Laue spot is closer to the rod group and, as shown in Fig. 11, the surface of the sphere intersects, at a small angle, two rods just off the zero layer. At a slightly greater reflection angle the sphere intersects, at nearly 90°, a rod on the zero layer. These intersections may be related by inspection to the group of spots for 62° in Fig. 10. In a similar manner one may closely correlate the remaining diffraction pattern with the reciprocal-lattice figure. The pattern found at 60° is of special interest since it shows evidence of the presence of a new type of rod which extends in the [100] direction. This evidence is given by the faint spot just to the left of the heaviest spot in the 60° pattern. Confirmatory evidence for the existence of this type of

rod has apparently been obscured by the more prominent <110> rods.

Summary and discussion

The diffuse diffraction effects described above are characteristic of CoPt crystals at an early stage of aging, before secondary reactions such as self-deformation and recrystallization have set in (Newkirk *et al.* 1950, 1951). They were not found in disordered or in highly ordered specimens. It is apparent that at an early stage of this ordering reaction, events occur which effectively cause the periodicity of the matrix lattice to be lowered in all of the six possible <110> directions. Among the various points in the reciprocal lattice which were studied, rods in every [110] direction have been found; however, the reason for the absence of certain <110> rods at a particular point is not yet apparent. The fact that the length of a rod increases with its distance from the origin of the reciprocal lattice indicates that the aperiodicities which cause the rods are in the form of atomic displacements rather than the segregation of solute atoms on preferred planes of a matrix. The effects observed here are similar to those described by Daniel & Lipson (1943, 1944) and by Jahn (1941–2) for a cubic crystal with a non-uniform stress.

All the prominent diffraction effects can be explained by assuming that the crystal contained internal lattice strains, of varying degree, in <110> directions, these strains being caused by thin platelets of the ordered tetragonal phase which are lying on, and are coherent with, {110} planes of the cubic matrix. Such a state of strain lowers the periodicity of the matrix lattice in the [110] direction and is manifest in a corresponding relaxation of the condition for Bragg reflection. This explanation is in accord with a previously drawn conclusion that coherency on the {110} matrix planes is the most probable on the basis of least coherency strain. It is also in agreement with microscopic evidence presented elsewhere (Newkirk *et al.* 1950, 1951) which shows a Widmanstätten pattern of plate-like particles parallel with {110} matrix planes. A rough estimate, based on the length of the rods, indicates that the average strain is in the neighborhood of 1 %.

Since the presence of ordered platelets lowers the periodicity of the matrix not only in the <110> directions but also (to a lesser extent) in others, one may expect to find less intense rods in other directions. The intensity of the other rods depends upon the atomic density of the reflecting planes and the angle which the platelets make with them. This might account for the weak [100] rod which was observed at the (020) point since in that direction the interplanar distance of the ordered lattice is much different from that of the disordered. In the <111> directions the change in interplanar distance is negligible and, therefore, no <111> rods nor rods of higher index would be expected.

An alternative explanation of the diffuse diffraction effects also can be developed on the basis of particle size. Platelets of the ordered phase on {110} matrix planes would account for the rods when the thickness is only 10–20 A. The analysis here has been confined to reflections for the disordered cubic matrix which later split into sharp main reflections for the ordered phase; however, the superlattice reflections are also diffuse when they first appear and undoubtedly would yield the same conclusion regarding the presence of an indefinite periodicity in <110> directions of the matrix crystal. Since superlattice reflections also are involved, one should probably associate the diffuse scattering with the ordered phase. Since the ordered phase forms by nucleation and growth of plate-like particles on {110} matrix planes, one might immediately suspect that particle size is the limiting factor in the early stage of ordering. While the platelets are mostly parallel to {110} matrix planes, the <100> rods and (111) webbing suggest slight tendencies, respectively, for platelets on {100} planes and needle-like particles along <111> directions if particle size is the cause of the diffuse scattering. A similar webbing was first observed for an aged Al–Mg–Si alloy (Geisler & Hill, 1948); it was interpreted as evidence for slim, needle-like particles along <100> directions, and this interpretation was later verified by electron microscopy by Castaing (see Geach, 1949).

The first-named author wishes to express his gratitude to the General Electric Company for a Fellowship which helped to make this work possible. The project was also supported in part by an AEC contract.

References

Daniel, V. & Lipson, H. (1943). *Proc. Roy. Soc.* A, **181**, 368.

Daniel, V. & Lipson, H. (1944). *Proc. Roy. Soc.* A, **182**, 378.

Geach, G. A. (1949). *Metallurgia*, **41**, 118.

Geisler, A. H. & Hill, J. K. (1948). *Acta Cryst.* **1**, 238.

Jahn, H. A. (1941–2). *Proc. Roy. Soc.* A, **179**, 320.

Newkirk, J. B., Geisler, A. H., Martin, D. L. & Smoluchowski, R. (1950). *J. Metals*, **188**, 1249.

Newkirk, J. B., Geisler, A. H., Martin, D. L. & Smoluchowski, R. (1951). *J. Appl. Phys.* **22**, 290.