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On the Crystal Structure of the ζ Phase in the Silver–Zinc System and the Mechanism of the β–ζ Transformation*

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The space group and approximate structure of the ζ phase in the silver–zinc system have been determined by the use of single-crystal and powder methods. The results are in agreement with those obtained by Edmunds & Qurashi through a rather lengthy procedure using powder data only.

The mechanism of the transformation from the cubic β phase to the structurally closely related hexagonal ζ phase has been clarified. The mechanism, which has 'oriented' character, consists of a displacement of the atoms in the β phase mainly in the [111] direction.

Introduction

A structure investigation of the ζ phase in the Ag–Zn system was first reported by Straumanis & Weerts (1931). By X-ray powder methods they found that the phase has a structure of hexagonal symmetry with $c_0/a_0 = 0{\cdot}367$ and with a unit cell containing nine atoms. A report on a complete structure determination was published by Edmunds & Qurashi (1951). They reported the lattice parameters

$$a_0 = 7{\cdot}6360,\ c_0 = 2{\cdot}8197\ \text{Å}\ ,$$

and an atomic arrangement closely related to that of the body-centered β phase. Their structure determination was based entirely on powder diffraction data.

Although the agreement between the observed and calculated intensities as given by Edmunds & Qurashi was relatively good and the structure therefore most likely correct, it was decided that an attempt be made to check the reported structure by single-crystal methods. This decision was made as crystal-structure determinations based on powder data only, in general, are less reliable than those based on single-crystal data. In this particular case the confirmation by single-crystal techniques of the space group proposed by Edmunds & Qurashi was of primary interest. It was also hoped that single-crystal work would give some information with respect to the mechanism of the transformation from the β phase to the structurally closely related ζ phase.

Experimental: space group and approximate structure

Since the ζ phase is formed through a solid-state transformation and, furthermore, since it is quite soft and malleable, considerable difficulties were anticipated in isolating single crystals. The procedure adopted was the following. An alloy containing 50 atomic % Ag and 50 atomic % Zn was prepared by melting the pure elements in an evacuated silica tube. Single crystals of the β phase were then made by lowering glass capillaries containing the molten alloy through a temperature gradient. Attempts to grow single crystals of the ζ phase were made by slow cooling and subsequent annealing of the thin rods obtained in this way. Ultimately a region of one of the rods was found to give Laue photographs which indicated the presence of a single-crystal domain of fairly large size (at least 4 mm. long). The Laue symmetry was found to be O_h; however, the diffraction maxima were

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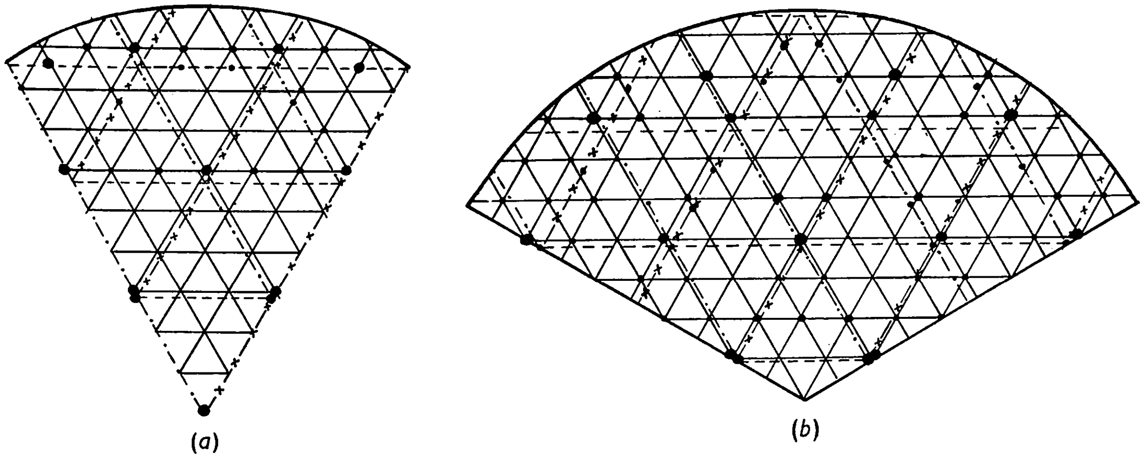

Fig. 1. Reciprocal-lattice plot (*a*) for $l = 0$, (*b*) for $l = 1$, as obtained from the positions of the diffraction maxima on Weissenberg photographs. The sets of lines marked – – –, —·—·— and — × — × — respectively are the lines of intersection of the planes of four different interpenetrating reciprocal lattices.

not well defined, which seemed to indicate the presence of many crystallites in almost the same orientation. Rotation photographs of this domain showed that it consisted of the ζ phase, as there was complete agreement between the Bragg angles for the various reflections on these photographs and the Bragg angles for the hexagonal ζ phase calculated on the basis of Edmunds & Qurashi's lattice constants. The same good agreement was also found with respect to the intensities of the different reflections.

The O_h Laue symmetry is not consistent with hexagonal symmetry, but this inconsistency could be satisfactorily explained by assuming the single-crystal domain to consist not of a single crystal of cubic symmetry but of a large number of single crystals of hexagonal symmetry occurring in four groups with the hexagonal axes of the crystals in each group parallel, or very nearly parallel, to one of the four body diagonals of a cube.

Weissenberg photographs (Cu $K\alpha$ radiation) taken with rotation around one of the hexagonal axes (one of the four cube diagonals) showed that the total Laue symmetry of each of the groups of crystals is D_{3d}. The photographs also provided evidence supporting the hypothesis of the existence of many hexagonal crystals with different orientation in the 'single crystal' domain, as developed above. This is shown in Fig. 1, showing plots of the reciprocal lattice layers $l = 0$ and $l = 1$. The interpenetration of four hexagonal reciprocal lattices with their hexagonal axes parallel to the four different body diagonals of a cube is indicated. The reciprocal-lattice points shown on the lines of intersection of the reciprocal-lattice planes belong to the inclined planes and are, of course, not exactly on those lines but only nearly so, as the ratio c_0/a_0 is a little different from that of the β phase.

Although the total Laue symmetry of each of the four groups of hexagonal crystals was D_{3d}, the actual Laue symmetry could be either D_{3d} or C_{3i}, since a three-dimensional pattern of D_{3d} symmetry can be considered as the superposition of two three-dimensional patterns of C_{3i} symmetry. Consequently, the true space group must be one of those compatible with Laue symmetry D_{3d} or C_{3i}. There are 25 space groups within this requirement, but as no systematic extinctions compatible with hexagonal Laue symmetry occurred, 17 of these could be eliminated. The remaining eight space groups were:

Laue symmetry D_{3d}: D^1_{3d}, D^3_{3d}, D^1_3, D^2_3, C^1_{3v}, C^2_{3v}
Laue symmetry C_{3i}: C^1_{3i}, C^1_3 .

As the following analysis shows, all but one of these could be eliminated through a sequence of arguments based on a few qualitative intensity observations. The zero-layer Weissenberg diagram showed the following characteristic features. Only reflections with $h = 3n$ and $k = 3m$ (n and m integers) occurred, with the exception of some high-order reflections. They were all strong and, apart from normal decline, of approximately the same intensity. It could therefore be concluded that in projection on the x–y plane, the structure possesses a pseudo unit cell of only one-ninth the area of the projection of the true unit cell. The pseudo cell can contain only one atom, and it immediately followed that the approximate x and y coordinates of the atoms in the true unit cell can, as a first approximation, all be taken as multiples of $\frac{1}{3}$. In projection on the x–y plane the ζ phase is therefore substantially the same as the cubic β phase, which, when indexed on the basis of the smallest possible hexagonal cell, has non-vanishing ($hki0$) reflections for $h = 3m$ and $k = 3n$ only, and in which the x and y coordinates of the atoms are all multiples of $\frac{1}{3}$.

The only strong reflections of type ($hkil$) were those with $h = 2+3m$ and $k = 2+3n$. Again these are the only non-vanishing ($hkil$) reflections of the β phase.

However, even at relatively small Bragg angles, a number of weak to medium-strong reflections were observed and it was therefore concluded that possibly a few of the atoms have z parameters substantially different in the two structures.

Powder photographs (Cu $K\alpha$ radiation) obtained with filings of an alloy sample (50 atomic % Ag) showed that while for the β phase the reflections (0001) and (0002) are absent and (0003) very strong (all atoms scattering in phase) the (0001) and (0003) reflections of the ζ phase are both unobservably weak, and the (0002) reflection very strong. The (0002) reflection was in fact found to have a structure factor considerably greater than that for the $(33\bar{6}0)$ reflection which occurs at very nearly the same Bragg angle (the structure factor ratio was 1·33).

As the $(33\bar{6}0)$ reflection is one of the non-vanishing reflections of the β phase (all atoms scattering in phase) and this phase and the ζ phase had already been shown to have substantially the same x–y projection, it appeared very likely that all the atoms in the ζ-phase structure are in planes perpendicular to the z axis and $c_0/2$ apart, with all atoms scattering in phase in the (0002) reflection. In view of the weakness of the (0001) and (0003) reflections it seemed likely that the number of atoms in the two layers is five and four respectively. This arrangement of atoms possesses a mirror plane at each of the two layers. Mirror planes perpendicular to the z axis are, however, not compatible with the Laue symmetry (D_{3d} or C_{3i}) and the arrangement was therefore not acceptable. The possibility of removing the horizontal mirror by small shifts of the atoms in the direction of the z axis seemed remote, as justification for assuming such small shifts with destruction of the higher symmetry would be difficult to find. It seemed far more likely that the horizontal mirror plane is destroyed by the displacement of one of the atoms to a position half way between the two layers. It seemed hardly possible that more than one of the atoms could be in such a displaced position in view of the great intensity of the (0002) reflection. Also the weakness of the (0001) and (0003) reflections made it necessary that four atoms occur in each of the two layers (with the ninth atom between the layers).

The problem of assigning the correct z coordinates to the nine pairs of approximate x and y coordinates (all multiples of $\frac{1}{3}$) was solved as follows. Because of the existence of at least a threefold symmetry axis it is necessary that six of the atoms form two groups of three, with the atoms in each group possessing the same z coordinates. The two z coordinates may or may not be related by a symmetry operation. Whether they are or not they must, in this particular case, differ by very nearly $\frac{1}{2}$. The six atoms therefore form a network of the type shown in Fig. 2.

From this figure it is also clearly seen that by far the most plausible positions of the three remaining atoms is either in or half way between the planes at $z = \frac{1}{4}$ and $z = -\frac{1}{4}$. As has been stated earlier, two of the three atoms must be in the planes, one in each of them, and the third half way between the planes. As is easily seen, the various combinations of z parameters subject to this condition correspond to one structure only. This structure has space group C_{3i}^1 and with the notation of the *International Tables for the Determination of Crystal Structures* (1935) the approximate positions of the atoms are:

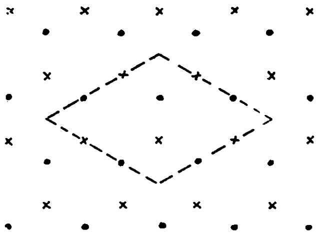

Fig. 2. The positions of six of the nine atoms in the unit cell. The x and y coordinates are approximately equal to multiples of $\frac{1}{3}$ and the z coordinates of the atoms marked × and • differ by very nearly $\frac{1}{2}$.

1: (a) 0, 0, 0.
2: (d) $\frac{1}{3}, \frac{2}{3}, z$; $\frac{2}{3}, \frac{1}{3}, \bar{z}$ with $z \approx \frac{1}{4}$.
6: (g) x, y, z; etc. with $x \approx \frac{1}{3}$, $y \approx 0$, $z \approx \frac{1}{4}$.

For comparison, the positions of the atoms in the β phase are given below (space group D_{3d}^1).

1: (a) 0, 0, 0.
2: (c) $\frac{1}{3}, \frac{2}{3}, 0$; $\frac{2}{3}, \frac{1}{3}, 0$.
6: (k) $x, 0, z$ with $x = \frac{1}{3}$ and $z = \frac{1}{3}$.

The atoms are in essentially the same position in the two structures except for those in the twofold positions, which have been displaced parallel to the z axis a distance approximately equal to $\frac{1}{4}c_0$.

This derivation of the space group and approximate structure of the ζ phase is, of course, valid also if the structure is assumed to be partially ordered.

The structure is the same as that reported by Edmunds & Qurashi. Since the agreement between observed and calculated structure factors as given by these authors is relatively good, further refinement of the structure, including the determination of order parameters, seemed unnecessary. It is very satisfying that a sequence of relatively few and entirely qualitative arguments sufficed for the determination of the space group as well as the approximate structure of the ζ phase with results in complete agreement with those obtained by Edmunds & Qurashi by a rather lengthy procedure.

The mechanism of the solid state transformation

The interesting fact that the hexagonal ζ-phase crystals in the investigated specimen were all oriented with their hexagonal axes parallel to one of the four body diagonals of a cube indicates that they were all formed from one larger single crystal of the body-centered cubic β phase by a transformation of 'oriented' character, as was observed already by Weerts (1932). Each hexagonal crystal is formed from the β-phase crystal by the displacement of the atoms mainly in the direction of one of the cube diagonals of the cubic structure. There are eight different sets of such displacements, two for each cube diagonal. They correspond to the transformation to hexagonal crystals having identical structures but different orientation in space. The transformation evidently takes place with equal utilization of the four different possibilities of spatial orientation (four body diagonals) with the result that one single crystal of the β phase yields a multitude of hexagonal crystals with an apparent cubic symmetry.

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Formation and Identification of Thallium Single Crystals

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A crucible is described in which a metal can be cooled from the melt while subjected to a strong temperature gradient. By this method single crystals of thallium were obtained when the gradient exceeded 20° C. cm.$^{-1}$. A simple X-ray method is described for determining whether the sample is a single crystal and for finding the hexagonal axis. In some samples a body-centered cubic phase was observed with a lattice constant 3% smaller than the value for the high-temperature phase.

Introduction

Certain nuclear experiments which have been on the way in this institution require single crystals of thallium in the shape of spheres approximately 6 mm. in diameter. A knowledge of the direction of the hexagonal axis is also necessary. Because of the short lifetime of the radioactivity induced in the material, it is essential that the single crystal be grown and its crystal orientation be determined in a matter of a few hours.

Upon cooling, thallium undergoes a martensitic transformation from b.c.c. to h.c.p. (Lipson & Stokes, 1941). In other similar cases it is generally accepted that, even if the high-temperature phase is in the form of a single crystal, polycrystalline material will result upon cooling. However, in the case of thallium it has been found (Dehlinger, 1932; Rao & Subramaniam, 1936) that a single crystal is obtained if the cooling is sufficiently slow. This method could not be used in the present case, because of the length of time involved in the treatment. The present paper reports on single crystals obtained from a melt cooled at a relatively large rate in a strong temperature gradient.

Method and results

A cylindrical carbon crucible was made of two halves lightly pressed together (Fig. 1). The thallium was filled into a cavity *b* in one of the pieces. A 2 mm. duct directed the melt into a spherical hollow *h*. The outer diameter of the crucible was considerably constricted in this region. The lower base of the crucible was seated on a metal disk *A*, which rested on a hot plate. A similar metal disk *D* rested upon the upper surface of the crucible. This disk was hard-soldered to a copper tube *E*, which could be heated with a heating coil. A brass tube *F* carrying a cooling coil was hard-soldered to the hot copper tube. The cooling coil could be soft-soldered to the brass tube at different distances from the joint so that the heat

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