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The Structure of the ζ Phase in the Silver–Zinc System

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The structure of a silver–zinc ζ-phase alloy of 50 atomic % silver has been determined from X-ray powder photographs, using a modified form of the method of steepest descents. The high-temperature (β-phase) form of the same alloy was taken as the starting point for the analysis, but, owing to the high symmetry of this structure, the residual, R, was found to have a stationary value so that the method of steepest descents failed at this stage. The difficulty was overcome by a systematic use of absent reflexions, and the first approximation to the ζ structure thus obtained was subsequently refined by the steepest-descent method, including the use of order parameters.

The ζ-phase alloy has a centro-symmetrical hexagonal unit cell containing nine atoms; the lattice parameters for the 50 atomic % alloy are $a=7{\cdot}6360$, $c=2{\cdot}8197$ A. The fractional co-ordinates are as follows: the three positions (0, 0, 0), ($\frac{2}{3}$, $\frac{1}{3}$, 0·250), ($\frac{1}{3}$, $\frac{2}{3}$, 0·750) occupied almost exclusively by zinc atoms; the six positions derived by symmetry operations from the position (0·350, 0·032, 0·750) occupied at random by the remaining atoms (about 75% silver and 25% zinc). The space group is $C\bar{3}$. The zinc atom at the origin has an abnormally high thermal vibration parallel to the crystallographic axis.

The study of silver–zinc alloys of about 50 atomic % silver is of interest because of the structural transformations which take place on subjecting them to different heat treatments. In common with the corresponding alloys in the gold–zinc and copper–zinc systems (β-brass), the silver–zinc alloys have a body-centred cubic structure at high temperatures. Unlike these alloys, however, the silver–zinc alloys possess a low-temperature modification with a hexagonal structure—the ζ phase—which is stable below about 280° C. A further point of interest is that while the β-phase alloys develop a superlattice on quenching, high-temperature X-ray photographs show no trace of superlattice reflexions, even within a few degrees of the $\beta\rightleftharpoons\zeta$ transformation temperature (Owen & Edmunds, 1938*a*). The present investigation seeks to determine the nature of these changes, and this paper gives an account of the first stage, the determination of the crystal structure of the ζ phase. The first section of the paper explains the approach to the problem and describes the experimental technique, including the correction for absorption. In § 2 we develop the mathematical methods to be used in the next two sections, in which the structure is derived. The final structure is discussed in § 5.

1. Introduction and experimental methods

1·1. *Introduction*

Straumanis & Weerts (1931) studied the $\beta\rightleftharpoons\zeta$ transformation, showing that the ζ phase possesses trigonal symmetry and proposing a unit cell containing nine atoms. Owen & Edmunds (1938*b*, *c*), using X-ray powder methods, have determined the extent of the ζ phase and also the accurate lattice parameter over a range of compositions. An analysis of their experimental results shows that the unit cell contains nine atoms, and that, for an alloy of 50 atomic % silver, its dimensions at 20° C. are

$$a=7{\cdot}6360,\quad c=2{\cdot}8197\text{ A.};\quad c/a=0{\cdot}3692_6. \tag{1}$$

A starting point for the present investigation of the ζ-phase structure was provided by the observation that the body-centred-cubic β structure can be described in terms of a hexagonal unit cell, also containing nine atoms, and having its axis along the cube diagonal (Fig. 1). For the 50 atomic % alloy the dimensions of this cell are

$$a=\surd 6\,a_0=7{\cdot}7299\text{ A.},\quad c=\tfrac{1}{2}\surd 3\,a_0=2{\cdot}7329\text{ A.}, \tag{2}$$

where a_0 is the cubic lattice parameter. A comparison of the values (1) and (2) shows agreement of the parameters to within about 3% and therefore suggests that the β-phase and ζ-phase structures are closely related. The intensities of the reflexions to be expected from the β-phase structure can be calculated, and, when indexed with reference to the hexagonal cell given above, may be compared with the intensities observed from the ζ-phase alloys. Such a comparison is shown later in Table 6 and indicates the points of difference between the two structures. (The transformation from cubic indices (pqr) to hexagonal indices ($hkil$) is given by the relations $l=\frac{1}{2}(p+q+r)$, $h=(2p-q-r)$, etc.) It is seen that there is reasonable agreement between the two sets of intensities for low indices. The $hki0$ reflexions show fair agreement up to almost the highest indices, but the $000l$ reflexions, on the other hand, give poor agreement even for $l=2$. These facts suggest that

(1) the β-phase structure is a good enough approxi-

mation to the ζ-phase structure to serve as a starting point for its determination, and

(2) only small movements of the atoms from the special positions in the β structure are needed parallel to the basal plane of the hexagonal cell, while considerably larger displacements are needed in the axial direction.

The ζ-phase intensity measurements were made on powder photographs. It was not found possible to prepare a single crystal of the alloy; moreover, owing to the high linear absorption coefficient, it would be very difficult to make accurate corrections for absorption with a single crystal. There remains the chief drawback of the powder method, namely, the overlapping of reflexions, but the following structure analysis shows clearly how this difficulty may be overcome by the method of steepest descents.

1·2. *Experimental details*

Alloy ingots, about 10 g. in weight, were prepared by melting weighed amounts of spectroscopically pure silver and zinc in evacuated silica tubes. The melt was maintained at about 1000° C. for half an hour, thorough mixing being ensured by means of a mechanical shaker. After cooling the alloy to 850° C. while still being shaken, it was plunged into cold water. The ingots were annealed at 500° C. for a week in evacuated Pyrex tubes.

The ingots were not analysed chemically, but filings from different parts of one ingot were quenched from the β phase, and their lattice parameters were accurately measured. These parameters were compared with β-phase parameters determined by Owen & Edmunds, and found to correspond to a composition of $50{\cdot}0 \pm 0{\cdot}1$ atomic %. The intended composition was 50·0 atomic %.

The filings, prepared with a very fine file, were annealed in evacuated Pyrex tubes, a few days' annealing at 250° C. proving adequate for the ζ-phase specimens. Powder photographs were taken on a 19 cm. camera with Cu $K\alpha$ radiation; the usual precautions were observed in processing the films for intensity work. The intensities of the reflexions were measured with a deflexion microphotometer incorporating a barrier-layer photo-cell, readings being taken at intervals of 0·1 mm. along the film. The instrument was calibrated by means of a standard X-ray exposure wedge. The mean values of the intensities measured on three ζ-phase films were used in the calculations.

1·3. *Absorption correction*

Owing to the very high coefficient of absorption of the alloys ($\mu \doteqdot 1500$ cm.$^{-1}$), it is not possible to assume that the ζ-phase powder specimens have a perfectly cylindrical surface. It was therefore decided to obtain the absorption correction by direct comparison with β-phase specimens of comparable dimensions. This is possible as the atomic compositions of the two phases are the same, and their densities differ by 0·6 % only. The intensities of reflexions from two β-phase specimens, of radii 0·43 and 0·27 mm., were measured and used, together with the calculated β-phase values of $|F|^2$, to plot curves of the relative absorption factor

$$A'(\theta)\,[=A(\theta)/A(90^\circ)]$$

against the Bragg angle, θ. To plot these curves, a value for the constant B in the temperature factor, $\exp[-B(\sin\theta/\lambda)^2]$, must be assumed. The curves for radii 0·41 and 0·32 mm. (radii of the ζ-phase specimens) were obtained by interpolation. These curves, taken in conjunction with the temperature correction, would apply accurately to the ζ-phase specimens if the value of B were the same for both phases. This was the assumption made initially, the value of B taken, about $0{\cdot}8 \times 10^{-16}$ cm.^{2}, being based on the Debye characteristic temperatures of silver (215° K.) and of zinc (235° K.). At a later stage, a more exact correction for temperature and absorption was obtained by plotting $\log[\sum_1 |F_c|^2/\sum_1 |F_o|^2]$ against $(\sin\theta/\lambda)^2$, where $\sum_1$ denotes summation over a small range of θ. From the slope of this graph, B was estimated to be

$$0{\cdot}95 \times 10^{-16}\ \text{cm.}^2.$$

To place the intensities on an absolute scale, the approximate relation

$$\sum_{hkil}(|F_o|^2)_\zeta = \sum_{hkil}(|F|^2)_\beta \tag{3}$$

was first used; later, the more accurate relation

$$\sum_{hkil}(|F_o|^2)_\zeta = \sum_{hkil}(|F_c|^2)_\zeta \tag{4}$$

was used, but it was found to make no significant difference.

2. Mathematical methods of analysis

2·1. *Method of steepest descents*

The steepest-descents formula used in the initial stages was

$$-\epsilon_j \simeq \frac{2R\dfrac{\partial R}{\partial u_j}}{\sum_j\left(\dfrac{\partial R}{\partial u_j}\right)^2} \quad \text{(Booth, 1947, 1949),} \tag{5}$$

where R is either

$$\sum_{hkil}(|F_o|^2-|F_c|^2)^2 \quad \text{or} \quad \sum_{hkil}(|F_o|-|F_c|)^2,$$

and ϵ_j is the correction required in the co-ordinate u_j. Here, and in what follows, the suffix o denotes the observed value of any quantity while c denotes the value of a quantity calculated with the parameters of an assumed structure.

In the course of the analysis it became apparent that the above formula gave values of ϵ_j strongly dependent on the scale of representation of the different parameters. A study of this point led to the formula

$$\epsilon_j \simeq \frac{\sum\limits_{hkil} W^2(\phi_o-\phi_c)\dfrac{\partial\phi_c}{\partial u_j}}{\sum\limits_{hkil} W^2\left(\dfrac{\partial\phi_c}{\partial u_j}\right)^2} \quad \text{(Qurashi, 1949)}, \tag{6}$$

where ϕ is some suitable function of the atomic parameters (usually $|F|$) and the W's are weights allotted to the values of $(\phi_o-\phi_c)$. It can be shown that with $\phi \equiv |F|$ the weights may be put in the form

$$W^2_{hkil} = 1/(K^2+\psi^2hkil), \tag{7}$$

where K is constant for any given value of $\sum\limits_j \epsilon_j^2$, and ψ_{hkil} is the root-mean-square error of the observed F value. In the initial stages, when the ϵ_j's are large, the term ψ^2_{hkil} can be neglected and we can take the W's as equal. In powder work, $|F|$ must be replaced by $F_p = +\sqrt{(\Sigma\,|F|^2)}$, the summation extending to all overlapping reflexions.

2·2. *Method of irregular absences*

It was found at the outset that the steepest-descents formulae could not be applied with the β-phase structure as a starting point, since for this structure all the $(\partial R/\partial u_j)$'s become identically zero if

$$R = \sum_{hkil}(|F_o|^2-|F_c|^2)^2,$$

while if

$$R = \sum_{hkil}(|F_o|-|F_c|)^2$$

the signs of the $(\partial R/\partial u_j)$'s are indeterminate. This is because the residual, R, has a stationary (maximum) value at the highly symmetrical β structure. The following method has been developed to meet this difficulty.

For any particular $hkil$ reflexion, we may write

$$|F|^2 = |F(u_1\ldots u_j\ldots u_n)|^2 = A^2(u_1\ldots u_j\ldots u_n) + B^2(u_1\ldots u_j\ldots u_n), \tag{8}$$

where A is the sum of terms of the form of

$$f\cos 2\pi(hx+ky+lz)$$

and B the sum of the corresponding sine terms. Expanding A_o and B_o in a Taylor series in $\epsilon_j\ (=\delta u_j)$ gives as a first approximation

$$\left.\begin{aligned} A_o &= A_c + \sum_j \frac{\partial A_c}{\partial u_j}\epsilon_j, \\ B_o &= B_c + \sum_j \frac{\partial B}{\partial u_j}\epsilon_j. \end{aligned}\right\} \tag{9}$$

If the reflexion is absent in the assumed approximation (in our case, the β structure), we have $A_c = B_c = 0$, and it then follows from (8) and (9) that

$$|F_o|^2 = \left(\sum_j \frac{\partial A_c}{\partial u_j}\epsilon_j\right)^2 + \left(\sum_j \frac{\partial B}{\partial u_j}\epsilon_j\right)^2. \tag{10}$$

If, in addition, the reflexion is absent in the observed structure (the ζ structure) we have

$$\sum_j \frac{\partial A_c}{\partial u_j}\epsilon_j = 0, \quad \sum_j \frac{\partial B_c}{\partial u_j}\epsilon_j = 0. \tag{11}$$

Similar equations hold for each reflexion absent in both assumed and observed structures. As the coefficients $\partial A_c/\partial u_j$ and $\partial B_c/\partial u_j$ can all be calculated, we obtain a set of simultaneous equations linear in the ϵ_j's which can be solved for the ratios $\epsilon_1 : \epsilon_2 : \ldots : \epsilon_n$ by the method of least squares.

If, as in a disordered alloy, all the atoms may be considered as having the same scattering factor, this factor may be omitted in equations (11), giving

$$\sum_j \frac{\partial A'_c}{\partial u_j}\epsilon_j = 0, \quad \sum_j \frac{\partial B'_c}{\partial u_j}\epsilon_j = 0, \tag{12}$$

where $A'_c = \sum\limits_{hkil} \cos 2\pi(hx+ky+lz)$

and $B'_c = \sum\limits_{hkil} \sin 2\pi(hx+ky+lz)$.

It is of interest to note that Booth (1949) has recently suggested the use of absent reflexions for structure determination.

3. Examination of structure assuming complete disorder

3·1. *Specification of co-ordinates*

As the ζ-phase photographs show no systematic absences, only threefold symmetry axes can be assumed. If we try to form the ζ-phase unit by modifying the β-phase cell, subject to this symmetry condition, the nine atoms in the unit cell may be considered in three different sets as follows:

(*a*) One atom, *a*, on a triad axis, which we may consider to be at the origin (0, 0, 0).

(*b*) Two atoms, *b* and *b'*, at $(\frac{2}{3}, \frac{1}{3}, z_3)$ and $(\frac{1}{3}, \frac{2}{3}, z_4)$ with freedom of movement along triad axes only.

(*c*) Two independent groups of three atoms, *c* and *c'*, which may be derived respectively from the atoms at $(\frac{1}{3}+x_1, y_1, \frac{2}{3}+z_1)$ and $(\frac{2}{3}+x_2, y_2, \frac{1}{3}+z_2)$ by operation about triad axes.

The expressions for A' and B' take a simpler form in terms of new parameters defined as follows:

$$\left.\begin{aligned} &X=\tfrac{1}{2}(x_1+x_2), \quad Y=\tfrac{1}{2}(y_1+y_2), \quad Z=\tfrac{1}{2}(z_1+z_2), \\ &\qquad\qquad\qquad\qquad\qquad\qquad\quad \beta=\tfrac{1}{2}(z_3+z_4), \\ &x=\tfrac{1}{2}(x_1-x_2), \quad y=\tfrac{1}{2}(y_1-y_2), \quad z=\tfrac{1}{2}(z_1-z_2), \\ &\qquad\qquad\qquad\qquad\qquad\qquad\quad \gamma=\tfrac{1}{2}(z_3-z_4). \end{aligned}\right\} \tag{13}$$

It can then be shown that

$$\begin{aligned} A'_c = 1 &+ 2\cos 2\pi l\beta \cos 2\pi\{\tfrac{1}{3}(k-h)+l\gamma\} \\ &+ 2\sum_3 \cos 2\pi(hX+kY+lZ)\cos 2\pi\{\tfrac{1}{3}(h-l) \\ &+ hx+ky+lz\} \end{aligned} \tag{14}$$

and

$$\begin{aligned} B'_c = 2\sin 2\pi l\beta \cos 2\pi\{\tfrac{1}{3}(k-l)+l\gamma\} \\ + 2\sum_3 \sin 2\pi(hX+kY+lZ)\cos 2\pi\{\tfrac{1}{3}(h-l) \\ + hx+ky+lz\}, \end{aligned}$$

where $\sum_3$ denotes cyclic permutation of h, k and i. If the ζ structure has a centre of symmetry, X, Y, Z and β will be zero. The β structure is obtained by making *all* the variable parameters equal to zero, i.e. all $u_{jc}=0$, so that the corrections, ϵ_j, will be equal to the parameters $x, y, \ldots, Z, \beta, \gamma$.

3·2. *Application of method of irregular absences*

The coefficients $\partial A'_c/\partial u_j$ and $\partial B'_c/\partial u_j$ in equations (12) are obtained by differentiating (14) with respect to β, γ, etc., and writing $\cos 2\pi l\beta \doteqdot 1$ and $\sin 2\pi l\beta \doteqdot 2\pi l\beta$, etc., as the co-ordinates are small. The equations give

$$\left.\begin{aligned} &l\gamma \sin 2\pi\tfrac{1}{3}(k-h) + x\sum_3 h \sin 2\pi\tfrac{1}{3}(h-l) \\ &\quad + y\sum_3 k \sin 2\pi\tfrac{1}{3}(h-l) + z\sum_3 l \sin 2\pi\tfrac{1}{3}(h-l) = 0, \\ &l\beta \cos 2\pi\tfrac{1}{3}(k-h) + X\sum_3 h \cos 2\pi\tfrac{1}{3}(h-l) \\ &\quad + Y\sum_3 k \cos 2\pi\tfrac{1}{3}(h-l) + Z\sum_3 l \cos 2\pi\tfrac{1}{3}(h-l) = 0. \end{aligned}\right\} \quad (15)$$

Some of the low-angle reflexions yielded the following equations:

$hkil$	$\Sigma \dfrac{\partial A'_c}{\partial u_j}\epsilon_j=0$	$\Sigma \dfrac{\partial B'_c}{\partial u_j}\epsilon_j=0$	Multiplicity factor
$20\bar{2}0$	$2x-y=0$	$Y=0$	6
0001	$z=0$	$Z=0$	2
$\{31\bar{4}1\}$	$-\gamma+7x-2y=0$	$-\beta+3X-12Y=0$	6
	$\gamma+7x-5y=0$	$-\beta+3X+9Y=0$	6
	$\gamma-2x-5y=0$	$\beta-12X+9Y=0$	6
	$-\gamma-2x+7y=0$	$\beta-12X+3Y=0$	6

For the complete solution, only those reflexions were used for which $l<2$ and $\sin\theta/\lambda<0{\cdot}5$; the normal equations for these give:

$$\left.\begin{array}{ll} X/\beta = 0{\cdot}078 \pm 0{\cdot}018, & x/\gamma = 0{\cdot}092 \pm 0{\cdot}020, \\ Y/\beta = -0{\cdot}002 \pm 0{\cdot}013, & y/\gamma = 0{\cdot}178 \pm 0{\cdot}026, \\ Z/\beta = 0{\cdot}67 \pm 0{\cdot}13, & z/\gamma = 0{\cdot}00 \pm 0{\cdot}20. \end{array}\right\} \quad (16)$$

In forming the normal equations, the individual equations were allotted weights proportional to the multiplicity factor and to the interplanar spacings, d_{hkil}. This is desirable, as the approximations

$$\cos 2\pi l\beta = 1, \quad \sin 2\pi l\beta = 2\pi l\beta, \text{ etc.},$$

become progressively less reliable for reflexions with higher indices. The uncertainties quoted are only rough estimates from the deviations obtained on substituting the parameters in the original equations.

To determine the absolute values of the parameters, we apply equation (10) to reflexions absent in the β-phase but present in the ζ-phase photographs. Using the expressions for $\partial A'_c/\partial u_j$ and $\partial B'_c/\partial u_j$ as given in (15), together with the ratios (16), equation (10) takes the form

$$\phi = \Sigma \frac{|F_o|^2}{f^2_{\text{mean}}} = K_\gamma \gamma^2 + K_\beta \beta^2, \quad (17)$$

where K_γ and K_β are numerical constants which can be evaluated, and the summation extends to all overlapping reflexions. The equations obtained from (17) for some of the low-angle reflexions, and suitably weighted, are given below; since the equations are now quadratic, the weighting function has been altered to

$$W' = W/\sqrt{\phi} \doteqdot d_{hkil}/\sqrt{\phi}.$$

$\sin\theta/\lambda$	$hkil$	$w'(K_\gamma\gamma^2+K_\beta\beta^2)=w'\phi$
0·200	$21\bar{3}0$	$0{\cdot}49\gamma^2+0{\cdot}13\beta^2=0{\cdot}020$
0·273	$31\bar{4}0$	$0{\cdot}36\gamma^2+0{\cdot}10\beta^2=0{\cdot}014$
0·330	$32\bar{5}0$	$0{\cdot}30\gamma^2+0{\cdot}08\beta^2=0{\cdot}011$
0·400	$42\bar{6}0$	$0{\cdot}48\gamma^2+0{\cdot}14\beta^2=0{\cdot}020$

Solution:

$$\gamma^2 + (0{\cdot}278 \pm 0{\cdot}001)\,\beta^2 = 0{\cdot}0399 \pm 0{\cdot}0010 = (0{\cdot}200 \pm 0{\cdot}002)^2 \quad (18)$$

$\sin\theta/\lambda$	$hkil$	$w'(K_\gamma\gamma^2+K_\beta\beta^2)=w'\phi$
0·193	$10\bar{1}1$	$0{\cdot}64\gamma^2+0{\cdot}23\beta^2=0{\cdot}003$
0·233	$20\bar{2}1$	$1{\cdot}13\gamma^2+0{\cdot}36\beta^2=0{\cdot}017$
0·267	$21\bar{3}1$	$0{\cdot}77\gamma^2+0{\cdot}25\beta^2=0{\cdot}015$
0·374	$32\bar{5}1$	$0{\cdot}94\gamma^2+0{\cdot}28\beta^2=0{\cdot}025$

Solution:

$$\gamma^2 + (0{\cdot}322 \pm 0{\cdot}007)\,\beta^2 = 0{\cdot}0172 \pm 0{\cdot}0030 = (0{\cdot}131 \pm 0{\cdot}011)^2$$

The equations split into two distinct sets for $l=0$ and $l=1$, and two significant facts emerge:

(1) For each set of equations the ratio K_γ/K_β is substantially constant, thus making it impossible to solve separately for β^2 and γ^2. All that can be obtained is the value of $\chi^2=(\gamma^2+0{\cdot}3\beta^2)$.

(2) The value of χ appears to depend largely on l. Thus $\chi=0{\cdot}20$ for $l=0$ and $\chi=0{\cdot}13$ for $l=1$. The difference is considerably greater than the mean deviation of either of the sets of equations. This strongly suggests the presence of some other parameters which are effectively correlated with the value of l. As all position co-ordinates have already been considered, the pro-

Table 1. *Comparison of observed F_p's with the values calculated for various β and γ*

($F_p = V\Sigma F$ for all overlapping reflexions)

$hkil$	$(F_p)_o$	$(F_p)_c$		
		$\gamma=0{\cdot}21$	$\gamma=0{\cdot}16$	$\gamma=0{\cdot}00$
$30\bar{3}0$	199	209	209	210
$22\bar{4}0$	23	0	0	0
$31\bar{4}0$	61	56	51	51
$50\bar{5}0$	<31	18	18	18
$33\bar{6}0$	112	118	119	121
$42\bar{6}0$	86	76	76	74
$60\bar{6}0$	86	97	99	100
$62\bar{8}0$	49	44	42	42
$63\bar{9}0$	76	72	75	79
$72\bar{9}0$	45	54	53	53
0001	0	0	0	0
$11\bar{2}1$	202	191	191	191
$22\bar{4}1$	140	136	137	137
$40\bar{4}1$	19	19	27	27
0002	83	73	75	78
$11\bar{2}2$	<31	53	59	56
$41\bar{5}1$	147	143	145	146
0003	0	13	25	31
$60\bar{6}2$	81	64	62	61
$44\bar{8}2$	0	10	20	28

bable variables are ordering parameters; these will be considered in § 4.

Following the failure to solve equations (18) for β^2 and γ^2, detailed calculations of the F_p values were made, first for the $000l$ reflexions and then for a number of reflexions of general indices. Comparison with the experimental values gave $Z=\frac{2}{3}\beta$ and the more reliable value of 0·07 for z, but, as shown in Table 1, no significant variation of the F_p's could be detected when β and γ were varied subject to the relation $\gamma^2+0{\cdot}3\beta^2=(0{\cdot}21)^2$. (The value of $\chi^2=\gamma^2+0{\cdot}3\beta^2$ was changed from 0·17 (mean of equations (18)) to 0·21 by an analysis of these reflexions by steepest descents.)

3·3. *Examination of atomic packing*

An independent line of approach, the consideration of interatomic distances, proves equally inconclusive in resolving the above difficulty. The interatomic distances in the range of structures possible under the condition $\gamma^2+0{\cdot}3\beta^2=0{\cdot}21^2$ were calculated, and are listed in Table 2, together with the metallic radii of silver and zinc for comparison. It is seen that the agreement is equally good for the distances obtained from all the possible structures. It would appear, then, that not only do the structures in this range all give rise to very nearly the same X-ray diffraction intensities, but that they are all equally possible on the grounds of atomic packing. It is of interest to note that if the β structure be considered as an arrangement of identical spherical atoms, a distortion of the structure keeping the same atoms in contact, and preserving trigonal symmetry, gives rise to the same set of equations (16) as has been obtained above from quite independent considerations.

Table 2. *Interatomic distances in various structures subject to* $\gamma^2+0{\cdot}3\beta^2=(0{\cdot}21)^2$

		Calculated distances (A.)			
β	γ	a–c a–c'	b–c b'–c'	b–c' b'–c	c–c'
0·000	0·210	2·662 2·662	2·688 2·688	2·769 2·769	2·917 2·885
0·100	0·203	2·674 2·662	2·706 2·671	2·787 2·744	2·914 2·895
0·250	0·157	2·718 2·690	2·699 2·647	2·784 2·694	2·898 2·909
0·362	0·070	2·767 2·712	2·688 2·664	2·738 2·666	2·879 2·912
0·383	0·000	2·778 2·681	2·675 2·695	2·695 2·675	2·874 2·902

Standard distances (A.)		
Ag–Ag (In pure Ag)	Ag–Zn (In b.-c.c. β-structure)	Zn–Zn (In pure Zn)
2·88	2·73	2·66

Table 3 lists the atomic co-ordinates for three of the structures possible under the condition $\gamma^2+0{\cdot}3\beta^2=0{\cdot}21^2$. (Only positive values of β and γ are considered, since it can be shown that $|F_{hkil}|^2$ depends only on $|\beta|$ and $|\gamma|$, when, as given in equations (16), $y/x=2$.) The co-ordinates are referred to a new origin displaced parallel to the z axis and chosen so that the mean fractional z co-ordinates of the two groups of atoms c and c' in Fig. 1 is always $\frac{1}{2}$. The variation in position of the six atoms comprising c and c' is less than 0·35 A. over the whole range of structures from $\beta=0$ to $\gamma=0$. The x and y co-ordinates of the remaining atoms are fixed; their z co-ordinates vary by amounts of the order of 0·6 A., with a maximum of 0·94 A. Thus there is not much variation in the atomic positions throughout these possible structures. In view of these findings, it was considered that the most profitable course at this stage would be to choose any one structure and, with the inclusion of order parameters, to refine it to give the best agreement with the observed data. The structure for $\beta=0$ was selected, since it has a centre of symmetry which simplifies the calculations; the need for examining other possible structures is considered later.

4. Examination of structure, introducing order parameters

4·1. *Positional co-ordinates and order parameters*

The dependence of $\chi^2=\gamma^2+0{\cdot}3\beta^2$ on l was confirmed by detailed calculations of the intensities for the groups of reflexions $hki0$, $hki1$ and $hki2$. The choice of $\chi=0{\cdot}18$, $\chi=0{\cdot}12$ and $\chi=0{\cdot}25$ respectively for these groups gave good agreement between calculated and observed intensities, but no single choice of χ for all groups gave such agreement.

With the introduction of a centre of symmetry, only three order parameters, p, q and r, are required, one for each of the independent positions a, b and c respectively. The order parameter may be defined as f/f_m, where f is the effective scattering factor for the position considered, and f_m is the mean scattering factor, $\frac{1}{2}(f_{\mathrm{Ag}}+f_{\mathrm{Zn}})$; as the variations of f_{Ag} and f_{Zn} with $(\sin\theta/\lambda)$ are very similar, p, q and r depend only slightly on the indices

Table 3. *Atomic positions in various structures subject to* $\gamma^2+0{\cdot}3\beta^2=(0{\cdot}21)^2$

(Values in Ångström units)

Atom	$\beta=0$, $\gamma=0{\cdot}21$	$\beta=0{\cdot}25$, $\gamma=0{\cdot}15_7$	$\beta=0{\cdot}38_3$, $\gamma=0$
a	(0·00, 0·00, 0·00)	(0·00, 0·00, −0·47)	(0·00, 0·00, −0·70)
b	(5·08, 2·54, 0·59) (2·54, 5·08, −0·59)	(5·08, 2·54, 0·67) (2·54, 5·08, −0·21)	(5·08, 2·54, 0·35) (2·54, 5·08, 0·35)
c	(2·68, 0·29, 2·07) (4·94, −0·29, 0·74)	(2·80, 0·22, 2·07) (5·12, −0·22, 0·74)	(2·77, 0·00, 2·07) (5·31, 0·00, 0·74)

(*hkil*). The expression for the structure factor now becomes

$$F = f_m[p + 2q\cos 2\pi\{\tfrac{1}{3}(k-h) + l\gamma\} + 2r\sum_{3}\cos 2\pi\{\tfrac{1}{3}(h-l) + hx + ky + lz\}]. \quad (19)$$

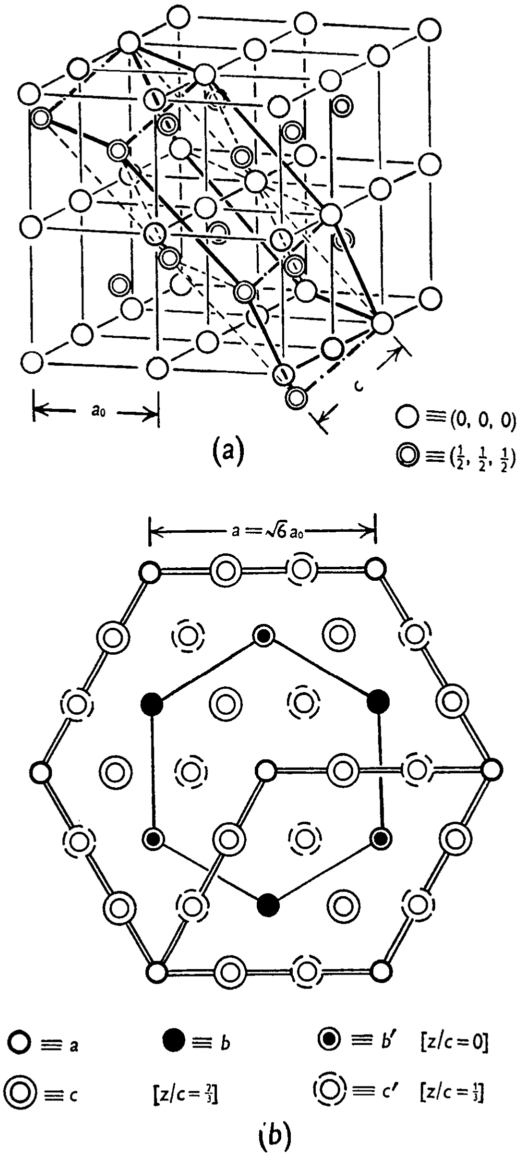

Fig. 1. Description of the β-structure in terms of the hexagonal cell, and the different atomic positions in the ζ-phase cell.

A fair estimate for p, q and r was obtained from a small number of reflexions by setting up equations, linear in these parameters, and solving them by least squares; the values obtained were

$$p = 0{\cdot}62_6, \quad q = 0{\cdot}69_5, \quad r = 1{\cdot}16_4.$$

As the average value of f_{Zn}/f_m is about 0·70, these values suggest that positions a and b are occupied entirely by zinc atoms, while the silver and remaining zinc atoms are distributed at random amongst the six equivalent positions c. On this assumption, i.e. making $p = q = 0{\cdot}70$ and $r = 1{\cdot}15$, the co-ordinates x and y were amended in a preliminary calculation by the steepest-descents formula (5); an earlier calculation had changed γ and z from the values 0·21 and 0·07, giving us the new co-ordinates

$$\left.\begin{array}{l} x = 0{\cdot}022, \quad y = 0{\cdot}034, \quad z = 0{\cdot}083, \quad \gamma = 0{\cdot}250, \\ (X = Y = Z = \beta = 0 \text{ by hypothesis}). \end{array}\right\} \quad (20)$$

The structure thus obtained was considered to be a suitable approximation to form the starting point of a complete analysis, using all reflexions, by the method of steepest descents. To this end, accurate values of p, q and r were determined, allowing for the small variation of these parameters with $(\sin\theta/\lambda)$, after which the intensities of all reflexions possible with Cu $K\alpha$ radiation were calculated.

It was at this stage that the modified steepest-descents formula (6), involving the weighting factor W (equation (7)) was derived. For the present application, the value of W was estimated as approximately

$$W = 1 \text{ for } F_p > 25, \quad W = \tfrac{1}{4} \text{ for } F_p \leqslant 25.$$

The corrections, ϵ_j, together with the corrected parameters, are shown in Table 4. The probabilities of silver or of zinc atoms occupying the positions a, b and c are also given; these are derived from the values of p, q and r and the known scattering factors of silver and zinc. The value of p is lower than required for 100 % Zn in position a and is taken to indicate a zinc atom with an abnormally high temperature factor.

On calculating the values of F_p with the above parameters, the *hki*0 and *hki*1 reflexions agreed well with the observed values, but the agreement was poor for the *hki*2 reflexions, showing that the parameters γ and z were not satisfactory. A steepest-descent calculation showed that both these parameters needed altering towards the initial values used for the previous descent. It was then realized that the corrections to γ and z derived in that descent were unreliable, since many of the F_p values were stationary with respect to these variables at $\gamma = 0{\cdot}25$, $z = 0{\cdot}083$, owing to the overlap of the $hkil$ and $hki\bar{l}$ reflexions. Trials with various values of γ and z gave the best agreement (for all values of l) with $\gamma = 0{\cdot}25$ and $z = 0{\cdot}083$. Considerations of packing support this conclusion, as in this case the b, b', c and c' atoms all lie exactly half-way between two groups of c (or c') atoms.

4·2. *Anisotropic thermal vibration of the zinc atom at the origin*

To investigate the thermal vibration of the atoms, the dependence of the corrections ϵ_p, ϵ_q and ϵ_r on $(\sin\theta/\lambda)$ was examined; the corrections were calculated separately from groups of reflexions each extending over a small range of θ. The curves obtained are shown in Fig. 2; their slopes give a measure of the extra temperature correction required in each case. It appears that a large extra correction is needed for the zinc atom a (corresponding to ϵ_p), while the corrections already applied are adequate for the remaining atoms.

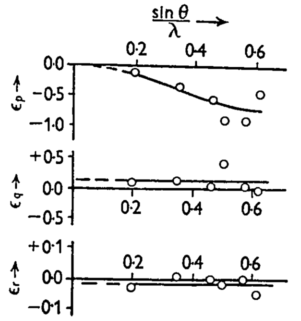

Fig. 2. Curves for the effective scattering factor in the three atomic positions, a, b and c.

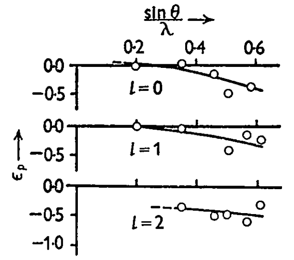

Fig. 3. Curves for effective scattering factor for the zinc atom in position a (at the cell-corner).

Furthermore, reflexions of different l indices gave different curves for ϵ_p, as shown in Fig. 3 (but not for ϵ_q or ϵ_r), indicating a progressive decrease in scattering factor for a given θ with a decrease in the angle, ψ, between the reflecting and basal planes. This may be attributed to a preferred thermal vibration of the atom a parallel to the axis. A similar effect was noted by Brindley (1936) in his work on pure zinc, while the effect has been considered mathematically by Zenner.

With these considerations in mind, the temperature factor for the atom a was written as

$$\exp\{-(X+Y\cos^2\psi)(\sin\theta/\lambda)^2\}$$

and the best values of X and Y were found by least squares. The values obtained were $X=0{\cdot}8$ and $Y=2{\cdot}7$, but trial calculations showed a continued improvement in F_p values as Y was increased to about 7·0. This value implies a vibration parallel to the axis of an amplitude about 0·2 A., i.e. about three times the normal amplitude. A preferred vibration of about this amplitude is consistent with the interatomic distances of the structure. Each a atom touches three c and three c' atoms (predominantly silver) at a distance of 2·66 A. in a direction inclined at 15° to the basal plane, while its only other near neighbours are a (zinc) atoms distant 2·82 A. along the axis. It therefore seems reasonable to expect considerably greater freedom of movement for the a atoms parallel to the axis than in a perpendicular direction. The change in X to 0·8 makes no appreciable difference to the F_p values, so that this parameter cannot be determined very precisely.

5. Conclusions

A further steepest-descents calculation, with all reflexions, gave a small change in the x and y parameters. The values of parameters finally accepted are given in Table 5; they do not differ greatly from the values obtained in the first approximation, which are also given for comparison. The values of F_p calculated with these parameters agree satisfactorily with the observed values, as shown in Table 6. The mean deviation, expressed in this case by $\sum_{hkil} |(F_p)_o-(F_p)_c| \div \sum_{hkil} (F_p)_c$ is given separately for reflexions of different l indices in Table 7, the average value being 0·116.

In view of the good agreement shown in these tables and of the values of the observational errors quoted, the possible non-centro-symmetrical structures mentioned earlier were not examined in detail. Even if a slightly improved agreement between observed and calculated intensities were obtained, this would not be really significant. Thus, although other structures subject to the relation $\gamma^2+0{\cdot}3\beta^2=\text{constant}$ ($\div 0{\cdot}25$) are not completely ruled out, they are considered to be most improbable, particularly in view of the more plausible

Table 4. *Calculation of the corrections ϵ_j to the parameters u_j*

u_j	x	y	z	γ	p	q	r
$\sum_{hkil} W^2\left(\frac{\partial F_p}{\partial u_j}\right)^2$	$58{\cdot}9\times10^6$	$99{\cdot}2\times10^6$	470×10^3	107×10^3	$9{\cdot}08\times10^3$	$46{\cdot}0\times10^3$	277×10^3
$\sum_{hkil} W^2[(F_p)_o-(F_p)_c]\frac{\partial F_p}{\partial u_j}$	-262×10^3	-241×10^3	$-5{\cdot}02\times10^3$	$-5{\cdot}26\times10^3$	$-4{\cdot}48\times10^3$	$+2{\cdot}35\times10^3$	$-5{\cdot}36\times10^3$
ϵ_j	−0·0044	−0·0024	−0·011	−0·049	−0·493	+0·051	−0·019
Initial u_j	0·022	0·034	0·083	0·250	0·70	0·70	1·15
Corrected u_j	$0{\cdot}017_6$	$0{\cdot}031_6$	$0{\cdot}07_2$	$0{\cdot}20_1$	$0{\cdot}20_7$	$0{\cdot}75_1$	$1{\cdot}13_1$
Corrected parameters	$0{\cdot}13_4$ A.	$0{\cdot}23_7$ A.	$0{\cdot}20_3$ A.	$0{\cdot}56_7$ A.	100 % Zn	90 % Zn	28 % Zn

Table 5. *Comparison of the first approximation with the final structures*

u_j	x	y	z	γ	p	q	r
First approximation	$0{\cdot}11_4$ A.	$0{\cdot}22_9$ A.	$0{\cdot}00_0$ A.	$0{\cdot}47_8$ A.	50 % Zn	50 % Zn	50 % Ag
Final u_j	$0{\cdot}017_1$	$0{\cdot}031_6$	0·083	0·250	—	—	—
Final parameters	$0{\cdot}13_1$ A.	$0{\cdot}23_7$ A.	$0{\cdot}23_4$ A.	$0{\cdot}70_5$ A.	100 % Zn	90 % Zn	28 % Zn

Table 6. *Comparison of the calculated and observed values of F_p for the final ζ-phase structure. The corresponding values for the β-phase structure are also included for comparison*

hkil	(F_p)	$(F_p)_o$	$(F_p)_c$
0000	330	—	330
$10\bar{1}0$	—	—	—
$11\bar{2}0$	0	35	27
$20\bar{2}0$	0	0	2
$21\bar{3}0$	0	66	65
$30\bar{3}0$	232	191	212
$22\bar{4}0$	0	14	17
$31\bar{4}0$	0	56	52
$40\bar{4}0$	0	0	14
$32\bar{5}0$	0	47	47
$41\bar{5}0$	0	0	14
$50\bar{5}0$	0	45	52
1122	157		
$33\bar{6}0$	157	126	125
$42\bar{6}0$	0	85	74
$51\bar{6}0$	0	191	184
$30\bar{3}2$	0		
$60\bar{6}0$	138	101	104
$43\bar{7}0$	0	0	35
$52\bar{7}0$	0	0	6
$61\bar{7}0$	0	62	67
$41\bar{5}2$	174		
$44\bar{8}0$	0	0	4
$53\bar{8}0$	0	130	119
$70\bar{7}0$	0		
$33\bar{6}2$	0		
$62\bar{8}0$	0	53	50
$71\bar{8}0$	0	0	14
5490	0	66	67
$52\bar{7}2$	141		
$63\bar{9}0$	141	75	77
$80\bar{8}0$	0	0	15
$72\bar{9}0$	0	53	56
0001	0	0	9
$10\bar{1}1$	0	28	35
$11\bar{2}1$	232	193	207
$20\bar{2}1$	0	104	94
$21\bar{3}1$	0	84	81
$30\bar{3}1$	0	0	18
$22\bar{4}1$	186	152	152
$31\bar{4}1$	0	0	28
$40\bar{4}1$	0	32	36
$32\bar{5}1$	0	130	126
$41\bar{5}1$	222	167	166
$50\bar{5}1$	0	104	95
$33\bar{6}1$	0	0	12
$42\bar{6}1$	0	0	30
$51\bar{6}1$	0	79	78
$60\bar{6}1$	0	0	14
$43\bar{7}1$	0	52	58
$52\bar{7}1$	174	105	104
$61\bar{7}1$	0	41	36
$44\bar{8}1$	110	90	74
$20\bar{2}3$	0		
$53\bar{8}1$	0	121	122
$70\bar{7}1$	0		
$62\bar{8}1$	0	97	97
$71\bar{8}1$	141	70	69
$31\bar{4}3$	0		
$54\bar{9}1$	0	30	22
$63\bar{9}1$	0	70	71
$32\bar{5}3$	0		
$80\bar{8}1$	0	76	70
0002	0	95	87
$10\bar{1}2$	0	0	29
$11\bar{2}2$	157	45	52
$50\bar{5}0$	0		
$20\bar{2}2$	0	0	27
$21\bar{3}2$	0	67	62
$30\bar{3}2$	0	191	184
$51\bar{6}0$	0		
$22\bar{4}2$	138	0	39
$31\bar{4}2$	0	49	59
$40\bar{4}2$	0	0	33
$32\bar{5}2$	0	41	56
$41\bar{5}2$	174	62	67
$61\bar{7}0$	0		
$50\bar{5}2$	0	0	29
$33\bar{6}2$	0	130	119
$53\bar{8}0$	0		
$70\bar{7}0$	0		
$42\bar{6}2$	0	82	75
$51\bar{6}2$	0	119	124
$11\bar{2}3$	0		
$60\bar{6}2$	0	102	93
$43\bar{7}2$	0	32	52
$52\bar{7}2$	141	66	67
$54\bar{9}0$	0		
$61\bar{7}2$	0	60	60
$44\bar{8}2$	90	0	10
$70\bar{7}2$	0	42	57
$53\bar{8}2$	0		
0003	63	0	1
$10\bar{1}3$	0	0	11
$11\bar{2}3$	0	119	124
$51\bar{6}2$	0		
$20\bar{2}3$	0	90	74
$44\bar{8}1$	110		
$21\bar{3}3$	0	42	37
$30\bar{3}3$	141	0	2
$22\bar{4}3$	0	79	81
$31\bar{4}3$	0	70	69
$71\bar{8}1$	141		
$40\bar{4}3$	0	0	19
$32\bar{5}3$	0	70	71
$63\bar{9}1$	0		
$41\bar{5}3$	0	92	95

Table 7. *Reliability factors, $\Sigma \mid (F_p)_o - (F_p)_c \mid \div \Sigma (F_p)_c$ for different sets of reflexions*

	$l=0$	$l=1$	$l=2$	$l=3$	Weighted mean	Estimated observational error
All reflexions included	0·154	0·114	0·240	0·110	0·156	0·090
Reflexions with $(F_p)_o = 0$ excluded	0·063	0·057	0·116	0·039	0·072	0·033

packing arrangement in the centro-symmetrical structure derived above.

We conclude, therefore, that the structure of the elementary hexagonal cell of the ζ-phase alloy is as follows: three positions *a* (0, 0, 0) and *b* $(\frac{2}{3}, \frac{1}{3}, 0{\cdot}250)$ $(\frac{1}{3}, \frac{2}{3}, 0{\cdot}750)$ occupied almost exclusively by zinc atoms; and six positions derived by symmetry operations from the position *c* (0·350, 0·032, 0·750) occupied at random by the remaining atoms, very nearly 75 % silver. The space group is $C\bar{3}$. The zinc atom at the origin has an abnormally high temperature vibration parallel to the hexagonal axis; our analysis gives the amplitude in this direction as approximately 0·2 A., i.e. about three times the normal amplitude. The positions of the atoms in the final structure are shown in Fig. 4 (*a*); Fig. 4 (*b*) gives a clinographic view of the unit cell.

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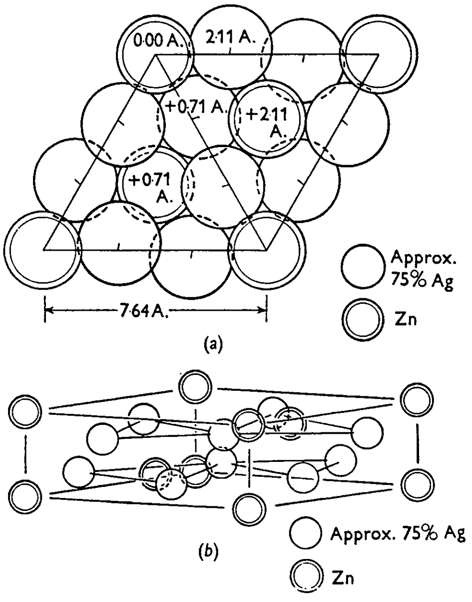

Fig. 4. The ζ-phase structure. (*a*) Projection on the 0001 plane, (*b*) clinographic view.

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The Crystal Structure of the β Phase of Uranium

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The crystal structure of the β phase of metallic uranium (stable between 660 and 760° C.) has been deduced from X-ray diffraction measurements made on single crystals of the phase retained in an alloy containing 1·4 atomic % chromium and rapidly cooled from 720° C. The diffraction data and other measurements show that the unit cell of the β phase is tetragonal, with $a_0 = 10{\cdot}52$, $c_0 = 5{\cdot}57$ A., and contains 30 atoms. Of the three possible space groups (*P*4/*mnm*, *P*4*nm* and *P*$\bar{4}$*n*2), *P*4/*mnm* appears definitely excluded, while of the remaining two, *P*4*nm* appears to account adequately for the diffraction intensities. Positions of the 30 atoms in the unit cell have been deduced using the Patterson and Patterson–Harker F^2 syntheses and the Fourier electron-density synthesis.

The β phase has a layer structure with the layers parallel to the a_0b_0 plane of the unit cell at $\frac{1}{4}c_0$ and $\frac{3}{4}c_0$. Midway between the layers are atoms which are linked to those in the adjacent layers but not to each other. The layers are quite closely related to the basal planes of the familiar hexagonal close-packed structure, except that atoms at the centers of certain hexagons are displaced normal to the layers to form the set of atoms found midway between the layers. A structure essentially the same as that of β uranium is being found by other investigators for the σ phase of the Fe–Cr and other systems.

The low symmetry and complexity of the structure accounts for the rather hard, brittle nature of the phase. The interrelations between the α, β and γ phases of the metal are clear from the β-phase crystal structure, but the precise mechanism of the transformations has not yet been studied.

Introduction

It is now well known that the element uranium exhibits three crystalline modifications. The α phase is stable from ordinary temperatures up to 660° C., the β phase from 660 to 760° C., and the γ phase from 760° C. to the melting-point.

The crystal structure of the α phase was determined by Jacob & Warren (1937) and that of the γ phase was first published in the unclassified literature by Wilson & Rundle (1949). The α phase is orthorhombic having lattice parameters $a_0 = 2{\cdot}852$, $b_0 = 5{\cdot}865$ and $c_0 = 4{\cdot}945$ A. The γ phase is body-centered cubic with $a_0 = 3{\cdot}474$ A. at room temperature.

Some work on the β phase was carried on at Iowa State College and at the Battelle Memorial Institute during the past ten years. The work consisted of obtaining powder patterns of the metal at high temperatures and of the phase retained at room temperature in alloys quenched from the β region and containing several atomic % chromium or molybdenum. The powder patterns so obtained did not yield to analysis owing to their complexity. Similar work was carried on at the Knolls Atomic Power Laboratory by the present author (Tucker, 1950*a*), and similar results were obtained.

Unit cell and space group of the β phase

More recently single crystals of the β phase have been made by lowering a uranium wire containing 1·36 atomic % chromium through a thermal gradient into the β region and quenching in water. Laue, rotation and Weissenberg patterns of such a single crystal established that the unit cell was tetragonal. Refinement of the unit-cell dimensions, using powder and single-crystal pattern data, gave the values

$$a_0 = 10{\cdot}52, \quad c_0 = 5{\cdot}57 \text{ A.}$$

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