slight spread, but there would not be spherical smoothing to the same extent as in the 5 and 10 Å reflexions, which are more numerous and at lower angles. The 1·5 Å reflexion is, therefore, of considerable significance in deciding between a chain structure and a three-dimensional net, and it is more profitable to study the diffraction pattern at high angles rather than the near-origin regions of the Patterson function. If, for example, there are found to be several areas of high intensity on the surface of the 1·5 Å sphere in reciprocal space, there is a strong presumption that the structure contains chains parallel to the directions joining these areas to the origin.

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The Determination of the Crystal Structure of the σ Phase in the Iron–Chromium and Iron–Molybdenum Systems*

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The crystal structure of the σ phase in the iron–chromium system at 46·5 atomic % chromium was determined by the application of powder and single-crystal X-ray diffraction methods. The crystal structure of this phase in the iron–molybdenum system was also determined by the use of powder and single-crystal methods, and found to be essentially the same as that for the iron–chromium phase. Reliable information regarding the distribution of iron and chromium among the various positions could not be obtained directly for σ-FeCr. However, reasonably reliable information regarding the distribution of iron and molybdenum in σ-FeMo was obtained, and probably the chromium atoms in σ-FeCr occupy substantially the same positions as the molybdenum atoms in σ-FeMo.

The iron–chromium σ-phase structure has space group D_{4h}^{14}–$P4_2/mnm$, with $a_0 = 8{\cdot}800$ Å and $c_0 = 4{\cdot}544$ Å. The iron–molybdenum presumably has the same space group, and has $a_0 = 9{\cdot}188$ Å and $c_0 = 4{\cdot}812$ Å. There are 30 atoms in the unit cell. The positions of the atoms are at the points of two pseudo-hexagonal nets normal to **c** at $z = 0$ and $z = \frac{1}{2}$. Eight of the 30 atoms are displaced parallel to **c** by approximately the distance $\frac{1}{4}c_0$, so that there are four atoms at $z \approx \frac{1}{4}$ and four at $z \approx \frac{3}{4}$. The structure is nearly identical with that found independently by Tucker for β-uranium.

1. Introduction

The σ phase is a brittle phase of complex structure which occurs in a number of binary and ternary systems involving transition-group elements, in particular vanadium through nickel in the first long period and molybdenum in the second. Systems in which the σ phase has been found to occur, with compositions as determined after annealing at elevated temperatures, are listed in Table 1 (Duwez & Baen, 1950; Greenfield & Beck, 1954).

The σ phase has a characteristic powder diffraction pattern. It contains a group of about eight strong lines with spacings close to 2 Å, only a few very weak lines at larger spacings, and only a few weak lines with spacings in the range 1·8–1·3 Å. These general features are not unique to the σ phase; other phases, such as the μ phase (Fe_7W_6 and Fe_7Mo_6, Arnfelt & Westgren, 1935; Co_7W_6, Magneli & Westgren, 1938; Co_7Mo_6, Henglein & Kohsok, 1949), and the phases designated δ, *P*, and *R* (in the respective systems Ni–Mo, Cr–Ni–Mo, and Cr–Co–Mo; Rideout *et al.*, 1951) give similar powder diffraction patterns. The σ phase has often been described as non-magnetic, but it has been found to be ferromagnetic with a low Curie temperature (about −113° C.; Beck, 1952). The σ phase in the iron–chromium system is of some technological importance in connection with stainless steels.

Previous attempts to determine the crystal structure of the σ phase have been unsuccessful for the

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Table 1. *Compositions of known σ phases*

System	Composition range (% second constituent)	Temperature (°C.)	References*	
			Discovery and characterization	Composition range
Mn–V	13·4–24·5	1000	*c, d*	*b*
Fe–V	39 –54·5	1075	*e*	*e, b*
Co–V	44·4–55·3	1200	*a*	*b*
Ni–V	55 –68·5	1200	*a, f*	*f, b*
Mn–Cr	16 –24	1000	*c, g, h*	*g, h, b*
Fe–Cr	43 –49	600	*i, j*	*j*
Co–Cr	58·6–63	1200	*k, l*	*l*
Mn–Mo	—	—	*m*	—
Fe–Mo	50 (< ½% wide)	1300	*n, o, p*	*b*
Co–Mo	60·5 (< ½% wide)	1300	*q, c*	*b*
FeW	—	—	*q*	—
CoW	—	—	*q*	—
Co–Cr–Fe	—	—	*r*	—
Co–Cr–Ni	—	—	*r*	—
Fe–Cr–Mo	—	—	*a*	—

*References:

a:	Duwez & Baen, 1950
b:	Greenfield & Beck, 1954
c:	Dickins & Douglas, 1951
d:	Pearson, Christian & Hume-Rothery, 1951
e:	Wever & Jellinghaus, 1930
f:	Pearson & Hume-Rothery, 1952
g:	Zwicker, 1951
h:	Pearson & Hume-Rothery, 1953
i:	Bradley & Goldschmidt, 1941
j:	Cook & Jones, 1943
k:	Elsea, Westerman & Manning, 1949
l:	Rideout, Manly, Kamen, Lement & Beck, 1951
m:	Kasper, Decker & Belanger, 1951
n:	Goldschmidt, 1949
o:	Duwez & Pietrokowsky, 1951
p:	Bergman, 1951
q:	Goldschmidt, 1951
r:	Beck & Manly, 1949

following reasons: (1) the great weakness of reflections from planes with large spacings and the closeness of bunching of powder lines at the largest spacings observed rendered the powder pattern extremely difficult to interpret in terms of a unit cell, and (2) for a long time all the σ phases known were of a type formed through a solid-state transition only, making it difficult to obtain single crystals of a size convenient for single-crystal X-ray photography. The sample used in this investigation fortunately contained a relatively large number of single-crystal fragments of suitable size.

In the first report of the elucidation of the structure of the σ phase (Shoemaker & Bergman, 1950) the unit cell (tetragonal, $a_0 = 8{\cdot}799$ Å, $c_0 = 4{\cdot}546$ Å), tentative space group (D_{4h}^{14}–$P4_2/mnm$), and approximate atomic positions were given for σ-FeCr (46·5 atomic% Cr). After finishing this preliminary work we learned that the structure of β-uranium had been determined shortly before by Tucker (1950*a*, *b*). This structure is very closely similar to the structure we found for the σ phase, differing from it principally in the assignment to β-uranium of a space group of lower symmetry (C_{4v}^4). Shortly afterward there was published a report of an independent determination of the structure of σ-CoCr (Dickins, Douglas, & Taylor, 1951*a*, *b*) based in part on a comparison of the powder diagram of this phase with that of β-uranium. This work was subsequently confirmed by Kasper *et al.* (1951).

In our continued work we found additional evidence confirming the tentative space group (D_{4h}^{14}) of σ-FeCr, and we predicted that β-uranium and σ-CoCr would very likely prove eventually to have this same space group and similarly flat atomic layers (Bergman & Shoemaker, 1951*a*; Bergman, 1951). Through the work of Tucker & Senio (1953) evidence was produced supporting the space group D_{4h}^{14} for β-uranium, rather than C_{4v}^4 as originally reported by Tucker (1950*a*, *b*). Recently Thewlis & Steeple (1954) have, however, done some additional work on the β-uranium structure with results favoring the non-centrosymmetric space group.

2. σ-FeCr

Experimental

The sample of σ-FeCr used in this investigation was provided by Prof. Pol Duwez of this Institute. Powdered chromium and iron in the atomic proportion 1:1 were mixed and compressed to a pellet, which was sintered in vacuum at 650° C. for 10 days and allowed to cool. The pellet was then crushed to a powder, which was annealed at 650° C. for 1 hr. An analysis of the powder gave 46·5 atomic% chromium; this composition falls not far from the center of the composition range for stable Fe–Cr σ phase at room temperature, and corresponds closely to the formula Fe_8Cr_7.

A powder photograph showed such pronounced graininess that the possibility of doing single-crystal work suggested itself. Tiny particles, roughly 0·1 mm. (or smaller) in size, were therefore selected from the original material under a binocular microscope and mounted on very fine pyrex fibers for Laue photography. Among several such particles two satisfactory single crystals were found and oriented.

The Laue symmetry of the crystals was found to be D_{4h}. A tracing of a Laue photograph taken with the beam parallel to the fourfold axis is given in Fig. 1 ($\lambda_{\text{min.}} = 0{\cdot}24$ Å). The photograph reveals a strong pseudo-hexagonality.

Rotation and Weissenberg photographs (Cu $K\alpha$) showed that the lattice is primitive, and gave approximate values for the lattice constants which enabled a powder photograph (114·59 mm. camera, Straumanis arrangement, Cu $K\alpha$) to be indexed. A least-squares refinement of the lattice constants, based on powder data, gave the following results (λ for Cu $K\alpha = 1{\cdot}5418$ Å):

$$a_0 = 8{\cdot}7995 \pm 0{\cdot}0004,\ c_0 = 4{\cdot}5442 \pm 0{\cdot}0020 \text{ Å}.$$

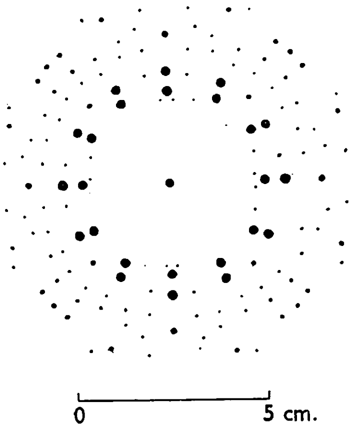

Fig. 1. Laue pattern for σ phase (traced from photograph). X-ray beam parallel to [001]. Horizontal and vertical axes of pattern parallel to [110] and [$\bar{1}$10]. Crystal-to-film distance 5 cm. $\lambda_{\text{min.}} = 0{\cdot}24$ Å. Intensity indicated approximately by size of spot.

The uncertainties given are probable errors, as determined by statistical treatment of the powder data. The density of a specimen of very nearly the same composition had been earlier found by Duwez & Baen to be 7·600 g.cm.$^{-3}$; this corresponds to 30 atoms per unit cell (29·80 calculated).

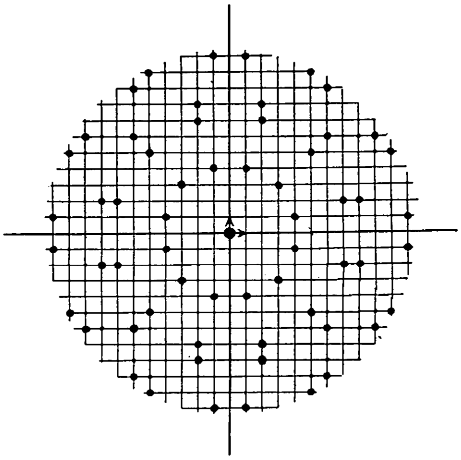

Fig. 2. The reciprocal lattice net $\zeta = 0$.

Derivation of the approximate structure.

It turned out to be possible to interpret the peculiar distribution of intensities in reciprocal space in such a way as to make the derivation of the correct trial structure unexpectedly straightforward and simple. It was noticed that in the ($hk0$) zone, except for the reflexions (410), (330), (550), (720), (820), (660), (960), (11,1,0), and (10,5,0) and their symmetrical equivalents, all of which were strong and (aside from normal decline) of about equal intensity, only a few very weak reflections were found (see Fig. 2). The general appearance of the layer was suggestive of twinning, and accordingly attempts were made to decompose the $hk0$ reciprocal-lattice net into two or more nets with larger reciprocal cells. It was found possible to account for all of the above-mentioned strong reflections with two slightly distorted hexagonal nets with a relative orientation of 90°, as shown in Fig. 3.

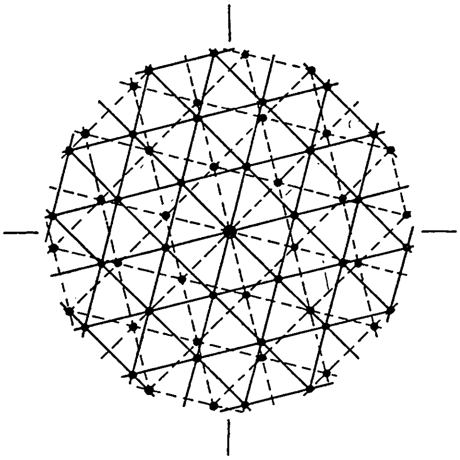

Fig. 3. The reciprocal lattice net $\zeta = 0$ with the strong planes fitted to two pseudo-hexagonal nets at 90° to one another.

It was apparent from inspection of the reciprocal-lattice net that the scattering of the two pseudo-hexagonal nets is essentially independent (the combined scattering from one net always vanishing when that from the other has a finite value) except for reflections of the type ($15m,15n,l$) (which lie outside the range of Cu $K\alpha$ radiation), at which the two pseudo-hexagonal reciprocal nets coincide.

The relationship between one pseudo-hexagonal net (with primed axes) and the true tetragonal net (with unprimed axes) may be taken as follows:

$$\begin{aligned} \mathbf{a}' &= 4\mathbf{a}/15 - \mathbf{b}/15\,, \\ \mathbf{b}' &= -\mathbf{a}/15 + 4\mathbf{b}/15\,, \\ \mathbf{a}' + \mathbf{b}' &= \mathbf{a}/5 + \mathbf{b}/5\,. \end{aligned}$$

The ratio $|\mathbf{a}'+\mathbf{b}'| \div |a'|$, which is unity in a true hexagonal net, is here $3\sqrt{2}/\sqrt{17} = 1{\cdot}029$.

The length of the **c** axis (4·54 Å) is such that the unit cell can accommodate two pseudo-hexagonal layers of atoms, half the unit cell apart. Two arrangements of these layers appeared compatible with the observed D_{4h} Laue symmetry: one (with space group D_{4h}^{10}) with a vertical *c* glide, atoms from both layers lying on 4_2 screw axes, the other (with space group D_{4h}^{14}) with a vertical *n* glide, no atoms lying on 4_2 screw axes. In order to decide between the two, the reflections $(0,15,l)$, with $l = 0$ and 1, were examined with Mo $K\alpha$ radiation. The reflection with $l = 1$ was found to be very strong, and that with $l = 0$ was found to be absent, thereby enabling the first arrangement to be ruled out and confirming the second. Subsequent examination of $(0kl)$ reflections with Weissenberg photography (Cu $K\alpha$) showed many reflections consistent with an *n* glide and none inconsistent with it. This observation, too, agrees with the choice of the second arrangement, and confines the space groups requiring consideration to three, D_{4h}^{14}–$P4_2/mnm$, C_{4v}^{4}–$P4_2nm$, and D_{2d}^{8}–$P\bar{4}n2$.

If the second arrangement were correct, with the layers truly planar and $\frac{1}{2}c_0$ apart, for all reflections (hkl) except those of kind $(15m,15n,l)$ the intensity should be independent of l (aside from normal decline). It was apparent from oscillation and Weissenberg photographs that this is not the case. To correct the structure it was necessary to move some of the atoms out of the plane layers, in directions parallel to **c**, without appreciably changing their x and y coordinates. Since the reciprocal lattice layer $(hk1)$ is superficially similar to $(hk0)$, most of the atoms should remain unshifted. Eight of the thirty atoms in the unit cell (the ones at $\frac{1}{5}, \frac{1}{5}, 0$; $\frac{1}{6}, \frac{1}{6}, \frac{1}{2}$; and symmetrical equivalents) can be shifted without disrupting the pseudo-hexagonality of the layers in projection on (001), since each such atom had above it and below it an atom of very nearly the same x and y coordinates which would be shifted with it. If these atoms (designated *E*) are shifted to positions half-way between the main layers and then shifted slightly so that they have the same x and y coordinates ($\frac{11}{60}$, being the mean of $\frac{1}{5}$ and $\frac{1}{6}$) a structure with space group D_{4h}^{14} is obtained.

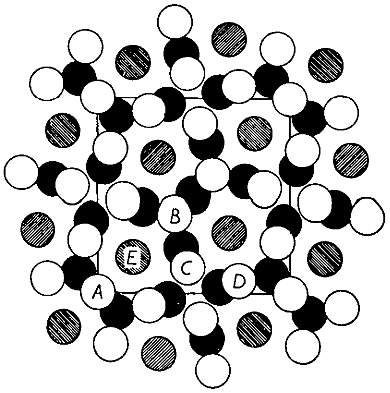

Fig. 4. The structure of the σ phase, in projection on (001). Open circles: atoms in the planes $z = 0, 1, \ldots$; filled circles: atoms in the planes $z = \frac{1}{2}, \ldots$; shaded circles: each represents two atoms per unit cell with z coordinates equal to approximately $\frac{1}{4}$ and $\frac{3}{4}, \ldots$.

The resulting structure (Fig. 4) is the one which proved to be correct. With the notation of the *International Tables* (1952), the following positions in space group D_{4h}^{14}–$P4_2/mnm$ are occupied:

2 atoms *A* in 2(*a*)	$0, 0, 0$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	—
4 atoms *B* in 4(*f*)	$x_B, x_B, 0$; ...	$x_B = \frac{2}{5}$
8 atoms *C* in 8(i_C)	$x_C, y_C, 0$; ...	$x_C = \frac{7}{15}$
		$y_C = \frac{2}{15}$
8 atoms *D* in 8(i_D)	$x_D, y_D, 0$; ...	$x_D = \frac{11}{15}$
		$y_D = \frac{1}{15}$
8 atoms *E* in 8(*j*)	x_E, x_E, z_E	$x_E = \frac{11}{60}$
		$z_E = \frac{1}{4}$

Because of the similar scattering powers of iron and chromium, no attempt was made until later in the work to distinguish among the atoms with regard to kind.

Confirmation of the space group

It is seen that the structure contains atoms confined to planes $\frac{1}{4}c_0$ apart, if the parameter z_E is close to $\frac{1}{4}$. A consequence is that the intensities of planes (hkl) with given h and k and with $l = l_0$ mod 4 should be the same as the intensity of the plane with $l = l_0$, aside from normal decline, and that the intensities of planes with l odd should be independent of l, aside from normal decline. A test of such intensity relationships constitutes a test of the flatness of the layers and of their proximity to planes exactly $\frac{1}{4}c_0$ apart. Such a test was carried out by means of Weissenberg photography of the layers $(0kl)$ and $(2kl)$ with Mo $K\alpha$ radiation. Within the limitations of visual semi-quantitative comparisons the above relationship was found to hold throughout these reciprocal-lattice layers. It could therefore be concluded that the atoms are closely confined to planes $\frac{1}{4}c_0$ apart. This conclusion makes the space group D_{4h}^{14} by far the most likely one as it requires that all of the atoms, except the eight displaced atoms *E*, be confined rigorously to the planes $z = 0$ and $z = \frac{1}{2}$, and that vertical rows containing the eight displaced atoms be straight rather than staggered. Confirmation of this space group is provided by the excellent agreement between observed and calculated structure factors, reported below.

Refinement of parameters

Intensity data for refining positional parameters were obtained by equi-inclination Weissenberg photography for all planes accessible to (nickel-filtered) Cu $K\alpha$ radiation. Photographs were taken of reciprocal lattice layers $l = 0, 1, 2$, and 3 with one crystal and $h = 0, 1, 2, 3, 4$, and 5 with another. The multiple-film technique due to de Lange, Robertson & Woodward (1939) and Robertson (1943) was used. Exposures of the order of 100 hr. were required. Intensities were estimated visually, on a logarithmic scale, by use of intensity strips. Scale and temperature factors were determined by a least-squares method. The temperature factor was found to be approximately isotropic, but the average figure obtained for B was negative ($-1{\cdot}1$ Å^2). This is possibly a result of extinction effects; no separate correction was made for extinction in the strong planes of low scattering angles.

Because of the regularity among intensities that is mentioned in the previous section, the possibility presented itself of simplifying the refinement calculations by considering similar reciprocal-lattice layers together ($l = 4$ with $l = 0$; $l = 5$ and $l = 3$ with $l = 1$; only $l = 2$ by itself). In order to make this possible, form factors and temperature factors were divided out of all observed structure factors, giving quantities ($\hat{F}$) representing the geometrical parts of the structure factors.

The refinement was carried out by the method of least squares, following essentially the procedure of Hughes (1941), except with regard to weighting. In addition to the seven positional parameters, parameters representing the effective 'atomic numbers' were also included, in an attempt to obtain some information about the distribution of iron and chromium atoms. The parameter z_E was refined separately from the other positional parameters, for it was possible to write one-parameter observational equations making use of the differences between observed and calculated values of $\hat{F}$ for ($hk1$), ($hk3$), and ($hk5$). For the refinement of the other parameters z_E was assumed to be exactly $\frac{1}{4}$, and it was therefore possible to combine essentially equivalent reciprocal-lattice nets (as outlined above) for the purpose of reducing the number of observational equations. This procedure is equivalent to the complete least-squares treatment if off-diagonal matrix elements connecting z_E with the other parameters are neglected. The weights of observations were determined by a procedure similar to that employed by Shoemaker, Donohue, Schomaker & Corey (1950); standard errors were estimated for individual reflections by examination of differences between independent intensity observations, and a smooth empirical curve relating relative standard error to intensity was used in calculating weights. Weights were also calculated for the null observations ($\hat{F} < \hat{F}_{\text{min.}}$), but since these weights proved to be small these observations were omitted from the least-squares calculations. A total of 92 different reflections remained to be used in the least-squares calculation, after rejection of those of very small weight.

The refinement of the x and y positional parameters and the atomic-number parameters was carried out by means of punched cards and IBM machines. All off-diagonal matrix elements except those involving z_E were calculated. The normal equations were solved by iteration to yield the final values of the positional and atomic-number parameters. For the purpose of obtaining the most reliable values of the positional parameters the off-diagonal matrix elements connecting them with the atomic-number parameters were neglected, because of uncertainty regarding the validity of the atomic-number parameters. The values obtained for all parameters are listed in Table 2.

A comparison of observed and calculated structure factors ($\hat{F}$) is given in Table 3. The agreement is everywhere satisfactory; the reliability factor R has the value 0·11.

The atomic-number parameters given in Table 2 are normalized to the weighted average 25·07 of the atomic numbers of iron and chromium; as originally calculated, the weighted average came out to be 24·5, presumably as an effect of a residual error in the scale factor and temperature factor. The atomic-number parameters appear at first sight to differ sufficiently to permit interpretation in terms of ordering of the atoms, but confidence in the figures is shaken by the high value obtained for the atomic number of atoms A, which exceeds 26 (the nominal value for iron) by nearly three times the probable error.

3. σ-FeMo

A specimen of a σ-phase iron–molybdenum alloy was made available to us by Prof. Pol Duwez of this Institute. The alloy had been prepared as follows. Powdered iron and molybdenum were mixed in the atomic proportion 1:1 and compressed to a pellet under a pressure of 72,500 lb. in.$^{-2}$. The pellet was then heated at 1430° C. for 4 hr. and then was crushed. The coarse powder was annealed at 1430° C. and then quenched in a stream of cold helium gas. The material gave powder photographs (Cu $K\alpha$) which were similar to those obtained for σ-FeCr, though the lines were only moderately sharp. The photographs could be indexed on the basis of a tetragonal cell, and the fol-

Table 2. *Results of least-squares parameter refinement*

Kind of atom	Position	Initial	Final	Probable error	Atomic number	Probable error
A	2(a)	—	—	—	28·1	0·8
B	4(f)	x_B = 0·4000	0·3981	0·0006	23·8	0·5
C	8(i_C)	x_C = 0·4667	0·4632	0·0007	25·8	0·4
		y_C = 0·1333	0·1316	0·0006	—	—
D	8(i_D)	x_D = 0·7333	0·7376	0·0006	25·8	0·4
		y_D = 0·0667	0·0653	0·0006	—	—
E	8(j)	x_E = 0·1833	0·1823	0·0006	23·3	0·4
		z_E = 0·2500	0·2524	0·0006	—	—

Table 3. *Observed and calculated structure factors for σ-FeCr*

hkl	$\hat{F}_o$	$\hat{F}_c$
000	—	30·0
4	30·0	30·0
2	14·8	14·8
101	*	1·4
3	*	1·6
5	*	1·2
110	< 1·0	0·0
4	< 1·0	0·0
1	< 1·0	0·4
3	< 1·0	0·0
5	< 1·0	0·8
2	2·0	−0·6
200	< 1·0	−0·2
4	< 1·0	−0·2
2	11·1	10·4
210	< 1·0	−0·1
4	< 1·0	−0·1
1	< 1·3	0·1
3	< 1·3	−0·1
5	< 1·3	0·2
2	11·8	10·9
220	< 1·0	−0·2
4	< 1·0	−0·2
1	< 1·6	−1·0
3	< 1·6	−1·3
5	< 1·6	−0·7
2	9·7	−7·2
301	< 1·6	−0·5
3	< 1·6	−0·9
5	< 1·6	0·0
310	< 1·0	−0·5
4	< 1·0	−0·5
1	2·7	−2·5
3	2·6	−2·3
5	2·6	−2·6
2	5·8	5·8
320	< 1·4	1·5
4	< 1·4	1·5
1	< 1·6	−0·9
3	< 1·6	−0·6
5	< 1·6	−1·2
2	3·4	−2·1
400	< 1·0	−0·4
4	< 1·0	−0·4
2	2·2	1·6
410	14·4	15·6
4	16·1	15·6
1	12·8	13·6
3	13·1	13·6
5	12·4	13·6
2	2·9	1·1
330	13·8	15·3
4	16·2	15·3
1	14·7	−13·9
3	14·8	−13·9
5	13·9	−13·9
2	< 1·7	0·7
420	< 1·5	0·9
4	< 1·5	0·9
1	< 2·2	1·0
3	< 2·2	1·3
5	< 2·2	0·6
2	< 1·5	−0·5
501	< 1·7	−2·1
3	< 1·7	−1·7
5	< 1·7	−2·5
430	< 1·0	−0·6
4	< 1·0	−0·6
1	3·8	3·2
3	3·8	3·2
5	3·1	3·1
2	4·4	4·1
510	< 1·5	1·3
4	< 1·5	1·3
1	3·3	3·2
3	3·6	3·4
5	3·0	3·0
2	3·7	−4·4
520	< 1·0	−0·2
4	< 1·0	−0·2
1	2·9	2·0
3	3·0	1·8
5	2·8	2·3
2	6·9	−6·5
440	< 1·5	−0·3
4	< 1·5	−0·3
1	< 2·5	0·4
3	< 2·5	−0·1
2	< 2·0	−0·6
530	< 1·5	−1·2
4	< 1·5	−1·2
1	< 2·5	0·2
3	< 2·5	0·2
2	13·4	11·9
600	1·5	0·7
4	< 1·5	0·7
2	12·4	−12·6
610	< 1·5	1·0
4	< 1·5	1·0
1	< 2·0	0·9
3	< 2·0	1·0
2	7·3	9·1
620	< 1·7	−1·6
4	< 1·7	−1·6
1	3·4	3·0
3	†	2·8
2	7·9	−7·5
540	< 1·7	−1·6
4	< 1·7	−1·6
1	3·2	−2·7
3	3·2	−2·1
2	7·6	6·8
630	< 1·7	−0·7
4	< 1·7	−0·7
1	< 2·2	−2·2
3	< 2·2	−2·6
2	3·3	−3·3
701	4·4	4·9
3	4·4	4·8
710	< 1·7	−0·3
4	< 1·7	−0·3
1	< 2·5	−0·4
3	< 2·5	−0·8
2	< 2·5	0·8
550	11·8	15·0
4	15·3	15·0
1	13·4	12·9
3	14·3	12·8
2	3·9	3·4
640	< 1·8	0·9
4	< 1·8	0·9
1	3·5	−3·2
3	4·0	−4·1
2	2·9	2·6
720	16·7	−17·3
4	15·2	−17·3
1	11·8	10·5
3	10·3	10·6
2	6·5	−5·4
730	< 1·8	0·6
4	< 1·8	0·6
1	< 2·3	−2·0
3	< 2·3	−1·8
2	< 2·0	−2·0
650	3·4	3·5
4	3·6	3·5
1	< 2·0	0·9
3	< 2·0	1·3
2	< 2·0	−1·3
800	1·8	−2·2
4	< 1·8	−2·2
2	13·1	13·4
810	< 1·8	−1·1
4	< 1·8	−1·1
1	< 1·9	−0·3
3	< 1·9	−0·5
2	< 2·1	2·6
740	< 2·0	1·7
4	< 2·0	1·7
1	< 1·8	−0·8
3	< 1·8	−0·8
2	13·5	−13·9
820	16·5	17·2
1	10·5	9·9
3	8·1	9·8
2	7·9	7·0
660	14·8	15·8
1	9·7	−11·7
3	11·2	−11·9
2	4·5	4·8
830	< 2·0	1·5
1	< 1·7	0·6
3	< 1·7	1·1
2	< 2·0	0·3
750	< 2·0	0·8
1	2·6	2·8
3	3·3	3·0
2	3·4	3·1
840	< 2·0	1·0
1	4·6	4·7
3	4·4	4·8
2	< 1·9	0·7
901	3·2	−3·7
3	3·6	−4·0
910	< 2·1	0·9
1	3·5	−3·2
3	2·5	−2·8
2	4·3	4·4
920	3·1	3·6
1	4·2	3·8
3	3·9	4·0
2	5·9	−5·9
760	2·1	−2·2
1	4·3	3·8
3	3·9	3·8
2	5·2	6·3
850	2·1	−1·6
1	†	2·7
3	†	2·3
2	4·3	−3·6
930	< 2·1	1·0
1	3·3	−2·2
3	2·4	−2·3
2	6·5	−8·7
940	< 2·1	−1·2
1	< 1·6	0·8
2	10·9	11·2
770	< 2·0	−1·5
1	< 1·7	−1·4
2	< 1·8	−1·9
10,0,0	< 1·9	0·0
2	6·3	−7·2

Table 3 (*cont.*)

hkl	$\hat{F}_o$	$\hat{F}_c$	*hkl*	$\hat{F}_o$	$\hat{F}_c$	*hkl*	$\hat{F}_o$	$\hat{F}_c$
860	3·4	− 4·2	1	2·4	2·3	1	3·1	− 3·8
1	3·6	− 3·0	2	4·2	4·6	960	10·4	15·0
2	5·4	8·6	950	3·9	− 5·0	1	8·3	10·8
10,1,0	3·0	3·8	1	$<$ 1·7	0·3	11,1,0	12·5	15·5
1	3·6	− 3·9	10,3,0	$<$ 1·9	− 1·6	1	6·5	− 8·6
2	7·8	− 9·2	1	4·3	5·3	10,5,0	10·8	−15·3
10,2,0	$<$ 1·9	− 0·1	870	$<$ 1·8	− 0·4			

* Geometry of camera prevented observation.

† Reflexion observed but intensity difficult to measure.

lowing values of the lattice constants were obtained by analysis of powder data (λ for Cu $K\alpha$ = 1·5418 Å):

$$a_0 = 9{\cdot}188\pm0{\cdot}002,\ c_0 = 4{\cdot}812\pm0{\cdot}002\ \text{Å}\ .$$

Attempts to isolate satisfactory single-crystal specimens for diffraction work were not so successful as in the case of σ-FeCr. Two very small crystals (of the order of 30 microns in size) were found, and with long-exposed Laue photographs it was possible to establish that the material is a σ phase. Only fifteen powder lines were suitable for intensity measurement. Of these, ten which were rather close together (in the range of interplanar spacings 2·5–1·8 Å) were used; the remaining five, corresponding to much smaller spacings, were not used because of the infeasibility of estimating and applying a temperature factor and absorption correction for lines of widely different scattering angle. Intensities were estimated by the multiple-film technique.

For the purpose of determining atomic-number parameters the assumptions were made that this alloy has the same space group as σ-FeCr, and that the atomic positional parameters have the same values as those in σ-FeCr. On these assumptions and the assumption that the form factors for iron and molybdenum have a constant ratio, the five atomic-number parameters were determined by least squares. The results of the calculations, normalized so as to give the correct weighed average of 34, are as follows:

Kind of atom:	*A*	*B*	*C*	*D*	*E*
Atomic number:	47	54	18	28	43

The calculated probable error is about 7. It is apparent that atoms *B* must be mainly molybdenum, and the same is probably true of atoms *A* and *E*. Atoms *C*, on the other hand, must be mainly iron, and atoms *D* may be iron or may be a mixture.

The axial ratio c_0/a_0 for σ-FeCr is 0·5164, and that for σ-FeMo is 0·5237. This may be taken as additional evidence that the positions *E* are occupied predominantly by molybdenum, for replacement of chromium in those positions by molybdenum should be expected to have a larger effect upon c_0 than upon a_0, while with the other positions the effects should be approximately the same.

4. Discussion

The structure represented by the σ phase and β-uranium is an interesting one in several respects. The most striking feature is its pseudo-hexagonality, and the manner in which a hexagonal close-packed net can be fitted into a tetragonal cell with only a small distortion. Another interesting feature is the displacement of certain atoms from the otherwise close-packed hexagonal net, to positions intermediate between the layers, leading to improved overall packing, but to rather short distances along the vertical rows containing these atoms. These atoms presumably key the hexagonal layers together, preventing slip and thereby contributing to the considerable brittleness of the material.

The ligancy of the atoms in the σ phase varies from 12 to 15, as seen in Table 4, in which near-neighbor interatomic distances are given. Atoms of kind *A* and *D* have ligancy 12, and the atoms surrounding them lie approximately at the vertices of a regular icosahedron. Atoms of kind *C* and *E* have ligancy 14, and atoms of kind *B* have ligancy 15.

Table 4. *Interatomic distances in* σ-FeCr

(All values in Ångström units)

A–B	4	2·603	B–A	2	2·603	C–B	1	2·414
A–D	4	2·380	B–B	1	2·536	C–C	1	2·404
A–E	4	2·542	B–C	2	2·414	C–C	4	2·838
	12		B–D	4	2·695	C–D	1	2·483
			B–E	4	2·833	C–D	1	2·476
			B–E	2	2·920	C–D	2	2·470
				15		C–E	2	2·763
						C–E	2	2·768
							14	

D–A	1	2·380	E–A	1	2·542
D–B	2	2·695	E–B	1	2·920
D–C	1	2·483	E–B	2	2·833
D–C	1	2·476	E–C	2	2·763
D–C	2	2·470	E–C	2	2·768
D–D	1	2·453	E–D	2	2·538
D–E	2	2·538	E–D	2	2·562
D–E	2	2·562	E–E	1	2·253
	12		E–E	1	2·294
				14	

Near-neighbor interatomic distances, listed in Table 4, are distributed from 2·253 Å to 2·920 Å. By use of Pauling's equation (1947)

$$D(n) = D(1) - 0{\cdot}600 \log_{10} n$$

it can be calculated that the shortest bond is approximately a $\frac{3}{2}$ bond and that the longest is about a $\frac{1}{10}$ bond. Because of uncertainty regarding the occupancy of the atomic positions by iron and chromium, and because their single-bond radii (1·165 and 1·176 Å, respectively) are close together, an average single-bond radius may be assumed. Summation of the bond numbers for bonds around each kind of atom, as calculated with Pauling's equation, gives the following metallic valences:

A, 6·76; *B*, 4·55; *C*, 5·34; *D*, 6·23; *E*, 6·07.

The weighted average valence is 5·76, which is substantially identical to the usual first-row transition-element valence of about 5·78. The low valence of 4·55 obtained for atoms *B* suggests that these atoms are quadrivalent chromium; otherwise the figures are compatible with either iron or chromium with valences of 5·78 or 6.

Layers rather similar to the σ-phase atomic layers —layers obtained by removing certain atoms from hexagonal close-packed layers so as to leave hexagonal holes, other atoms being above and below the holes— exist in two other structures represented by phases related to the σ phase: the rhombohedral μ phase, Fe_7W_6 (Arnfelt & Westgren, 1935) and the structurally isomorphous compounds Fe_7Mo_6 (Arnfelt & Westgren, 1935), Co_7W_6 (Magneli & Westgren, 1938), and Co_7Mo_6 (Henglein & Kohsok, 1949); and the hexagonal phase Fe_2W, of simpler structure (Arnfelt & Westgren, 1935).

It has also been demonstrated by single-crystal work that the δ phase MoNi has a close structural relationship to the σ phase, with marked pseudo-hexagonality in a tetragonal structure (with, however, pseudo-hexagonal axes perpendicular to the fourfold axis instead of parallel to it); however, not all structural details have been worked out (Shoemaker, Fox & Brink, 1953).

It is apparent that no reliable conclusions regarding the distribution of iron and chromium among the various positions in σ-FeCr can be drawn from the values obtained by least squares for the atomic-number parameters. The same uncertainty affects the results obtained for σ-FeMo, although to a smaller extent. However, the fact that the results obtained for the two phases with respect to ordering are in agreement, except for the positions of kind *A*, very likely has some significance. There seems to be at least a strong tendency toward ordering, with the iron atoms occupying essentially the same positions in the two phases.

However, the facts that most binary σ phases have composition ranges 5–15% wide and that binary atom ratios deviate as far from equality as 13:2 (manganese to vanadium) suggest that most positions are subject to statistical occupancy. Aside from the manganese–vanadium σ phase with the limiting composition $Mn_{13}V_2$ (13·33 atom% vanadium calculated, 13·4 observed), there is apparently no case in which a *limiting* composition is one which can be explained without statistical occupancy.

There is also evidence to indicate that the σ phase is a sort of electron compound, based perhaps on the filling of a Brillouin zone. Among published interpretations along these lines are those of Sully (1952); Rideout *et al.* (1951); Bloom & Grant (1953); and Greenfield & Beck (1954). Rideout *et al.*, on the assumption that there is a preferred concentration of 3*d* vacancies amounting to about 3·61 per atom, have derived an expression by which the mean compositions of all known binary σ phases can be predicted with a standard deviation of only 2·8 on the percentage composition scale. The treatment of Bloom & Grant is based on the assumption that the σ-phase compositions are largely determined by a preferred electron number of 210 electrons per unit cell, or seven per atom, and indeed Greenfield & Beck have pointed out that an average electron number of 6·93 per atom (beyond the rare-gas shell) can be obtained from the mean compositions of all known binary σ phases, and that with this value the mean compositions of the binary σ phases can be predicted with a standard deviation of 9·1 on the percentage composition scale.

In wave-number space there are two polyhedra bounded by planes of crystallographic forms with large structure factors, which may be connected with Brillouin zones (Jones, 1934*a*, *b*; Pauling & Ewing, 1948). The smaller polyhedron has a volume sufficient to accommodate about 1·72 electrons per atom (Douglas, 1951). The larger polyhedron (Bergman, 1951), which is bounded by nine forms (720, 550, 721, 551, 602, 532, 413, 333, and 004) and shows a high degree of sphericity (see Fig. 5), accommodates 6·97 electrons per atom. However, it seems doubtful that the average valence of the metal atoms in the σ phase can be as high as 6·97; it is probable that the actual average valence is closer to 5·76 (the value obtained by treatment of the interatomic distances) than it is to 7, and that the large polyhedron remains incompletely filled. The simple Brillouin zone treatment therefore does not

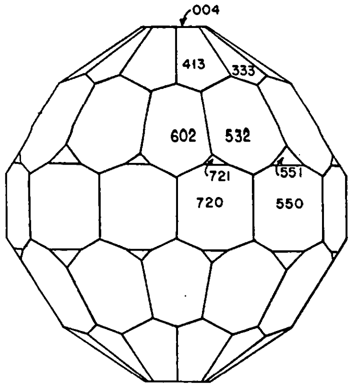

Fig. 5. The polyhedron of the second strong Brillouin zone in σ-FeCr.

provide a satisfactory explanation of the stability of the various σ phases.

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