The nearest tensors of higher symmetry may be read off from equations (13) or (15). In particular, the nearest isotropic tensor, c^0_{ijkl}, being an invariant, has the following matrix:

$$c^0_{IJ}=\begin{pmatrix} 10\cdot165 & 0\cdot601 & 0\cdot601 & 0 & 0 & 0 \\ 0\cdot601 & 10\cdot165 & 0\cdot601 & 0 & 0 & 0 \\ 0\cdot601 & 0\cdot601 & 10\cdot165 & 0 & 0 & 0 \\ 0 & 0 & 0 & 4\cdot782 & 0 & 0 \\ 0 & 0 & 0 & 0 & 4\cdot782 & 0 \\ 0 & 0 & 0 & 0 & 0 & 4\cdot782 \end{pmatrix} . \quad (16)$$

Define the number ε^0 by

$$\varepsilon^0 = \frac{||c|| - ||c^0||}{||c||}. \quad (17)$$

ε^0 is a scalar constant independent of the rotation of the axes. It is a measure of 'nearness' of the nearest isotropic tensor. The value of ε^0 for quartz at room-temperature is found to be 0·054. The use of ε^0 as a perturbation parameter is currently being investigated in a perturbation scheme of plane stress problems in anisotropic theory of elasticity.

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The Atomic Mechanism of the Body-Centred Cubic to σ-Phase Transformation

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An atomic mechanism for the body-centred cubic to σ-phase transformation is suggested. Atomic movements over small distances in the $[11\bar{1}]_{b.c.c.}$ direction take place leading to the formation of a new layer structure. The transformation is completed by rotation of alternate layers of hexagons within zones related to kagomé tile structures. The mechanism suggests that certain groups of atoms are more strongly bonded in the $[11\bar{1}]$ direction than others. The mechanism also suggests that the body-centred cubic phase exhibits partial long range order prior to the transformation. The ductility of β-uranium and the brittleness of FeCr and 2NbA1 alloys is discussed in terms of the ordering and coordination numbers of the atomic positions in the σ structure.

Introduction

The occurrence of the σ phase and its properties have been reviewed by Hall & Algie (1966). The σ phase always contains at least one transition group element. In alloys it is one of a series of phases occurring with the passage from the more open body-centred cubic structure to the closer packed hexagonal and face-
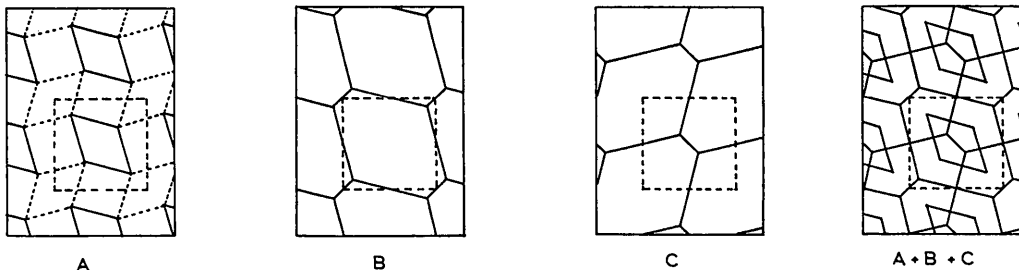

A   B   C   A + B + C

Fig. 1. The σ-phase structure described as a layer structure of kagomé tiles and diamond nets. The outline of the unit cell is also shown.

centred cubic structures as the alloy composition varies. Thus for example we get:

body-centred cubic→β-tungsten

$$(Cr_3O \text{ type})\rightarrow\sigma\rightarrow\genfrac{}{}{0pt}{}{\text{close-packed hexagonal}}{\text{face-centred cubic}}.$$

In a number of cases the body-centred cubic structure exists at higher temperatures and transforms as the temperature falls to the σ-phase structure.

Tucker (1951) has pointed out that the transformation of the body-centred cubic structure to the σ-phase structure can be accomplished by small atom motions. The close packed sheets of the σ-phase structure may be formed by atom movements in a direction equivalent to the [11$\bar{1}$] direction in the body-centred cubic structure. However, considerable motion of the sheets would be necessary to form the final σ-phase structure.

In this paper an attempt is made to describe the crystallographic features and paths followed by the atoms in a transformation process which results in the formation of a single domain of the σ-phase structure from

$$\circledcirc\; \tfrac{z}{c}=0 \qquad \bigcirc\; \tfrac{z}{c}=\tfrac{1}{3} \qquad \mathbf{O}\; \tfrac{z}{c}=\tfrac{2}{3}$$

Fig. 2. Three layers of the b.c.c structure telescoped together to form two layers of the σ-phase structure. The contribution from each b.c.c. layer is shown separately. The dashed atoms form the diamond nets of the σ-phase structure. Each hexagonal layer group of four kagomés is built up of the obverse groups C and B and the symmetrical group A [Fig. 3(c)]. Its neighbouring groups of four kagomés are similarly built up of these three groups in a different layer sequence. They must be so arranged as to make border atoms coincident. The larger groups of twelve kagomés are repeated throughout the structure. The tetragonal σ unit cell is shown in the lower section of the Figure. Its dimensions are $a'=\sqrt{26/3}\,a_0$, $c'=\sqrt{3}a_0$ where a_0 is the body-centred cubic lattice parameter. The angle between the faces differs from a right angle by 2° 12′.

the body-centred cubic structure. No attempt is made to ascribe the process to any particular metallurgical transformation mechanism. The relations described will be used to discuss the formation and some properties of the σ-phase structure.

Crystallographic relations

The structure of the β-uranium σ phase has been determined by Tucker (1951). Other σ phases have been shown to be similar save that in alloys partial long range order occurs. Tucker's work shows a tetragonal unit cell containing 30 atoms. The structure is best regarded as a simple layer structure of two hexagonal nets at right angles; each hexagonal net is supported on a diamond net which is the same throughout the structure. Tucker's structure shows minor deviations of atoms from true hexagonal nets in the [100]$_\sigma$ and [010]$_\sigma$ axial directions and also from the layers in the [001]$_\sigma$ axial direction. This is a secondary feature of the structure and in what follows these deviations will be ignored. It will also be assumed that the atoms within the layers in the [001]$_\sigma$ direction can be represented by spheres of equal size. The stacking sequence of the layers is *ABACABAC* where *A* signifies a diamond net layer and *B* and *C* hexagonal net layers.

The hexagonal nets may be described in terms of kagomé tiles as pointed out by Frank & Kasper (1958, 1959). The tiles form two nets at right angles whose centres are not coincident. A further feature of the structure is the intermediate layers of diamond nets. These consist of diamonds totally enclosed within a kagomé and a second set which join kagomés together. This is shown in Fig. 1.

The body-centred cubic structure may be regarded as a layer structure in the [11$\bar{1}$]$_{b.c.c.}$ direction, the stacking sequence being *ABCABC*. We can describe in such a structure the kagomé tile structure of the σ phase. It is produced by telescoping together three layers, *A, B, C*, of the body-centred cubic structure into one layer of the σ-phase structure and removing atoms at the centre of the hexagonal nets so formed to give the diamond nets of the *A* layer of the σ-phase structure, as shown in Fig. 2.

The crystallographic relations are:

$$(11\bar{1})_{b.c.c.} \parallel (001)_\sigma$$
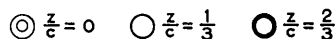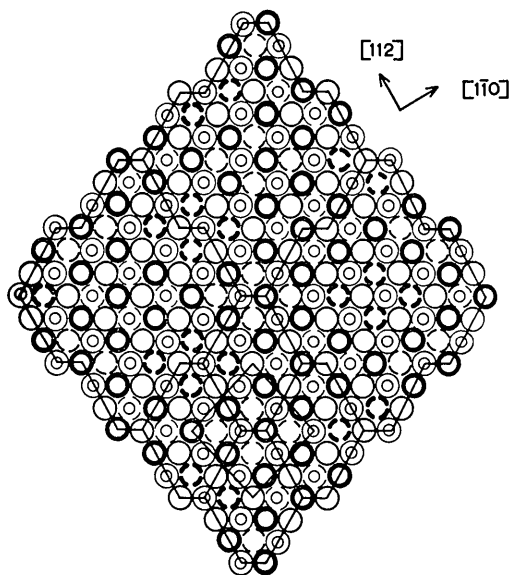$$[1\bar{1}0]_{b.c.c.} \parallel [\bar{1}40]_\sigma.$$

In order to complete the σ structure it is necessary to turn alternate hexagonal layers at right angles. Examination of a network of four kagomés formed from a sequence of *A*, *B* and *C* layers of the body-centred cubic structure shows three different groups of atoms removed from each layer, as in Fig. 3(*a*). *C* is the obverse of *B* and *A* is a symmetrical group formed of a half *C* and *B*. Three such kagomé groups, *i.e.* twelve kagomés, fit together so that their border atoms are coincident. The whole structure consists of such groups of twelve kagomés connected together as in Fig. 4. The

contribution from any one layer in the body-centred cubic structure, as in Fig. 3(*b*), shows that in each layer certain groups of four neighbouring atoms, the dashed atoms, associate together to form the diamond nets connecting kagomés, shown by the dashed nets of Fig. 1. Three layers below this there is a similar group of four atoms which are the nearest neighbour atoms in the body-centred cubic structure. In the disordered body-centred cubic structure this nearest neighbour distance is the sum of the respective atomic radii; on ordering in certain transition groups alloys it is reduced according to Beck & Philip (1957). In the σ phase this distance is also reduced compared with the sum of the radii.

This suggests that the formation of the σ phase commences with bonding between these four neighbouring atoms in the *A* layer and their nearest neighbours in the body-centred cubic structure within successive *A* layers, followed by their movement in the $[11\bar{1}]_{b.c.c.}$ direction. The transformation is completed by the remaining atoms in the body-centred cubic layers combining to form the kagomés of the *B* and *C* layers of the σ phase. In the case of the *B*-layer kagomés this only involves movements of atoms in the $[11\bar{1}]_{b.c.c.}$ direction, as pointed out by Tucker (1951). In the case of the *C*-layer kagomés the atoms must not only move in the $[11\bar{1}]_{b.c.c.}$ direction but also rotate to occupy the position of closest packing between the hexagons of the *B* layers.

The method of rotation and motion in the $[11\bar{1}]_{b.c.c.}$ direction in the body-centred cubic structure may be described by imagining lines of hexagons throughout the structure similar to the zones of Kronberg (1959), used to describe slip in β-uranium. The hexagons rotate within these zones as the atoms move in the $[11\bar{1}]_{b.c.c.}$ direction, atoms on opposite sides of a zone boundary moving in opposite directions. This rotation can only take place if one certain atom moves from one zone to the next as each kagomé at right angles is formed. This mechanism is shown in Figs. 5 and 6. In Kronberg's model a similar rotation of kagomés was brought about by the interchange of atoms from superposed hexagons. This was necessary since his mechanism described the transition from sigma to slipped sigma. In the present case it is not necessary since the atoms in the original body-centred cubic structure are already displaced perpendicular to the hexagons in the $[11\bar{1}]_{b.c.c.}$ direction, and the rotation takes place as they move from the positions of more open packing of the body-centred cubic structure to the closer hexagonal packing. Both mechanisms bring about the same rearrangement of atoms in the hexagonal planes.

Structural consequences of the transformation mechanism

Some selected examples of the occurrence of the σ-phase structure are shown in Table 1. The interesting facts here are the ductility of β-uranium compared with brittleness of the alloy σ-phase structure (in high alloy
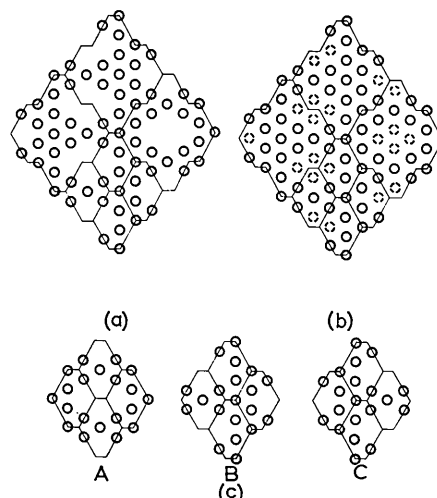

Fig. 3. (*a*) Contribution from a single layer of the b.c.c. structure to the kagomé tile layer of the σ-phase structure; derived from Fig. 2. (*b*) The same layer showing the dashed atoms which move out in groups of four to form the diamond nets of the σ-phase structure. (*c*) the obverse groups *C* and *B* and the symmetrical group *A* referred to in Fig. 2.

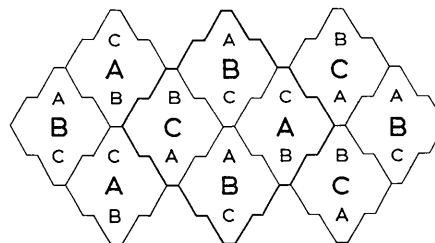Fig. 4. Planar and layer sequence of groups of four kagomés assembled from the b.c.c. structure to form the hexagonal layer of the σ-phase structure. The heavy letters correspond to the layer of Fig. 3(*a*) found at *z/c* = 2/3 in the b.c.c. structure. The upper light letters correspond to the layer at *z/c* = 1/3 and the lower light letters to that at *z/c* = 0 in the b.c.c. structure. A transformation domain is shown in heavy lines.
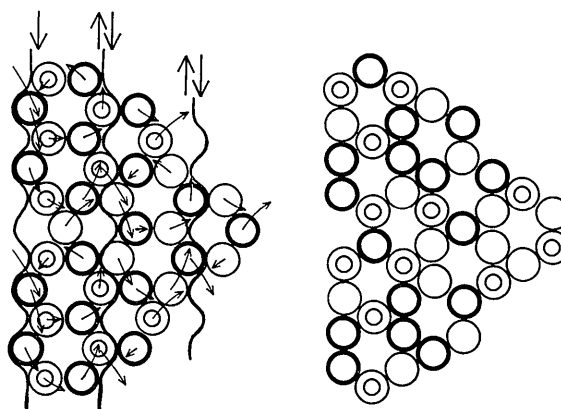

Fig. 5. Movements in zones which transform the kagomé nets through 90°. The small arrows show the direction in which the centres of the atoms move. Note that one atom in each kagomé jumps the boundary. Atoms on opposite sides of the boundary move in opposite directions. The atoms are also moving in the $[11\bar{1}]$ direction at the same time.

stainless steels the presence of FeCr σ phase is a possible source of failure), the absence of body-centred cubic structures at high temperatures in many systems forming σ phases and the formation of σ-phase structures in alloys containing only one transition group element. Kronberg has described a model for slip in β-uranium which will be considered with respect to FeCr and 2NbAl type alloy σ phases. These alloys show partial long range order characteristic of their composition. Fig. 7 is adapted from Kronberg's figure of slip in β-uranium. XY is the slip zone and the essential
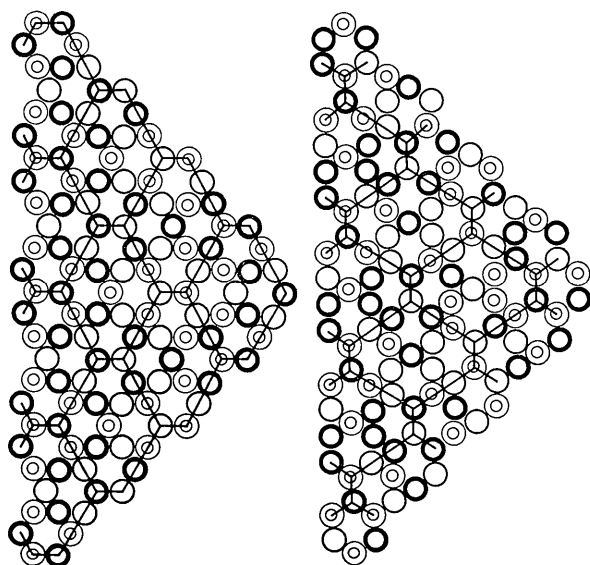

Fig. 6. Movements in groups of twelve kagomés relating the atom positions in the b.c.c. structure to those in the σ-phase structure based on the mechanism of Fig. 5. The circles refer to the different layers in which the atoms are found in the body-centred cubic structure. They form a single layer in the σ-phase structure after the transformation. The partial long range order in the b.c.c. structure just before transformation to the σ phase may be deduced from the partial long range order of the σ phase shown in Fig. 7.

requirement for slip is the rotation of hexagons within the slip zone. The atoms in the diamond nets play no part in the slip other than acting as central supports for the hexagons which rotate around them. This is in agreement with the suggested model in which these diamond net atoms are more strongly bonded than those in hexagonal nets. The position of the ordered atoms is shown together with their coordination numbers in Fig. 7. When slip takes place, in the case of β-uranium, rotation of the hexagons merely replaces uranium atoms with uranium atoms, uranium being present with all three coordination numbers, 12, 14 and 15, adopting the definition of coordination number of Frank & Kasper (1958). In the case of FeCr rotation leads to an incompatibility with respect to ordering since in the case of the atom replacement $B \rightarrow D$ an iron atom coordination number 12 is replacing a chromium atom coordination number 15; in other positions both atoms show coordination number 14. Similarly in the case of 2NbAl incompatibility occurs in the replacement $C \rightarrow D$ since aluminum atoms of coordination number 14 must be replaced by niobium atoms of coordination number 15. Here both atoms show coordination number 12 but aluminum does not show coordination number 15.

This suggests that uranium can exist in this structure in three different states characterized by the coordination numbers 12, 14 and 15. Similarly niobium has three states of C.N. 12, 14 and 15, iron two of C.N. 12 and 14, chromium two of C.N. 14 and 15 and aluminum two of C.N. 12 and 14. These states may be associated with slightly different outer electron structures. That iron may exist in two different electron states in alloys has been suggested by Mott & Stevens (1957) and Lomer & Marshall (1958) in order to explain certain magnetic properties of iron alloys.

The order present in alloy σ phases suggests that in those of the FeCr type, formed from body-centred cubic structures, partial long range order, as shown in Fig. 6, must exist in the body-centred cubic phase

Table 1. *Selected alloys in which σ phases occur and some of their properties together with lattice constants for the body-centred cubic structure, a_0, the σ-phase tetragonal cell in the body-centred cubic structure,*

$$a' = \sqrt{26}/3a_0, \quad c' = \sqrt{3}a_0, \text{ and the true } \sigma\text{-phase constants}$$

The figures in parentheses are the percentage expansion and contraction from the body-centred cubic constants, a' and c', to give the true σ-phase constants, a and c.

γ-uranium b.c.c. ductile ↓ β-uranium σ ductile ↓ α-uranium	α-Fe/V, Cr b.c.c. ductile ↓ σ brittle	CoV/NiV σ brittle	2NbAl σ brittle
γ-U b.c.c.	$a = 3\cdot474$ Å	$a' = 10\cdot227$ Å	$c' = 6\cdot017$ Å
β-U σ		$a = 10\cdot520$ Å (2·86%)	$c = 5\cdot570$ Å (7·43%)
α-FeCr b.c.c.	$a = 2\cdot874$ Å	$a' = 8\cdot461$ Å	$c' = 4\cdot978$ Å
FeCr σ		$a = 8\cdot799$ Å (3·99%)	$c = 4\cdot544$ Å (8·72%)
α-FeV b.c.c.	$a = 2\cdot920$ Å	$a' = 8\cdot596$ Å	$c' = 5\cdot057$ Å
FeV σ		$a = 8\cdot952$ Å (4·14%)	$c = 4\cdot622$ Å (8·60%)

X   Y

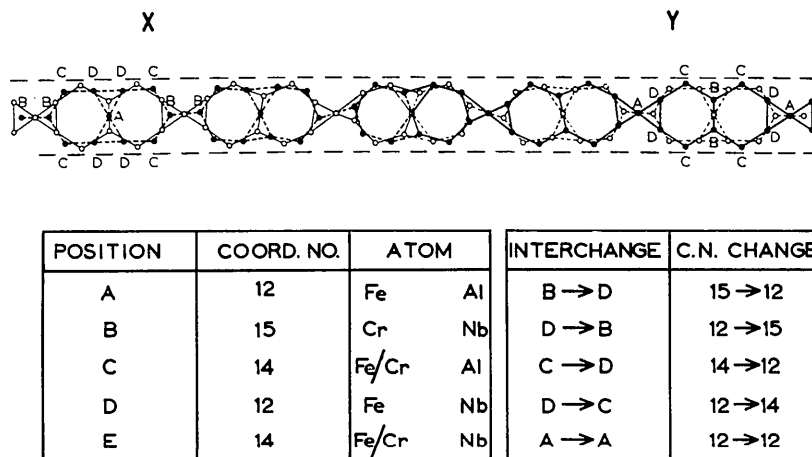| POSITION	COORD. NO.	ATOM		INTERCHANGE	C.N. CHANGE
A	12	Fe	Al	B → D	15 → 12
B	15	Cr	Nb	D → B	12 → 15
C	14	Fe/Cr	Al	C → D	14 → 12
D	12	Fe	Nb	D → C	12 → 14
E	14	Fe/Cr	Nb	A → A	12 → 12

Fig. 7. Order and coordination number in the σ-phase structure showing the atom interchange required if slip is to take place in accordance with Kronberg's model.

prior to the phase transformation, if the present model is accepted. Such a structure may or may not disorder at temperatures above that of the phase transformation. An ordered structure of the CsCl type has been reported on the basis of X-ray diffraction measurements in FeV by Beck & Philip (1957), and also in FeCr by Pomey (1954, 1955). Ordering of this type could bring about the association of the four nearest neighbour atoms of the diamond nets which form the A layer of the σ phase. According to the σ-phase ordering scheme these atoms are found at the corner and body-centred position in the CsCl structure. Beck reports a contraction in the bond length between such unlike atoms in the CsCl type phase of the transition group elements. This bond distance in the body-centred cubic structure corresponds to the d_{EE} bond distance in the σ structure which, as pointed out earlier, is much reduced compared with the sums of the relevant atomic radii and compared with the nearest neighbour distance in the disordered phase. The same argument cannot be related to the uranium or the 2NbAl σ phases in which the E type atoms are either all ura-

nium or all niobium. In these structures some other type of bonding must lead to this association of the four E type atoms.

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