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Computer study of the bcc \( \rightarrow \) fcc structure change by homogeneous deformations

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*(Reçu le 24 janvier 1983, révisé le 11 mai, accepté le 24 mai 1983)*

Résumé. — La transformation de Bain cc \( \rightarrow \) cfc peut être réalisée par les deux « cisaillements » homogènes E et E' proposés par Bogers et Burgers. Nous discutons tout d'abord les conditions pour que les potentiels d'interactions de paires assurent à la fois la stabilité mécanique des structures cc et cfc ; nous utilisons ensuite trois potentiels phénoménologiques de métaux pour calculer la densité d'énergie libre W du cristal dans les états de déformation \( \gamma E + \gamma' E' \) \((\gamma \text{ et } \gamma' \text{ vont de } -0,5 \text{ à } 1,5)\). Le chemin \( \gamma = \gamma' \), qui conserve au cristal une structure qua, brise le moins de symétries et s'avère être le chemin d'énergie minimum. Pour généraliser ce résultat nous avons considéré les coefficients élastiques B (module de compressibilité), \(1/2(C_{11} - C_{12})\), \(C_{44}\), \(C_{66}\) des structures qua intermédiaires : s'ils sont positifs le chemin \( \gamma = \gamma' \) demeure un chemin d'énergie minimum par rapport à l'axé de déformation. Les potentiels que nous avons utilisés répondent à ces conditions qui devraient, en général, être remplies pour la plupart des potentiels assurant la stabilité mécanique aux deux extrémités du chemin. On caractérise par \( \eta_1 = (\log c/a)/\log \sqrt{2} \) les structures qua intermédiaires. La densité d'énergie \( W(\eta_1) \) présente deux minima pour \( \eta_1 = 0 \) (cc) et \( \eta_1 = 1 \) (cfc) séparés par un maximum. La dérivée première \( dW/d\eta_1 \) est proportionnelle à la contrainte appliquée. Les points d'inflexion, où la dérivée seconde \( d^2W/d\eta_1^2 \) s'annule, définissent des déformations et des contraintes critiques pour le déclenchement de la transformation ; ces déformations sont de l'ordre de 1/4 de la distorsion totale de Bain et ces contraintes sont inférieures à la résistance théorique à la cission.

On a déterminé, en outre, des lignes critiques dans les cinq plans \((\eta_1, \eta_2)\) où \( \eta_2 \) est soit un des cisaillements \( \{110\} \), \(\{112\}, \{123\}, \{213\}, \{211\}\), soit une déformation isotrope. Lorsque \( \eta_1 \) est un cisaillement la ligne critique est perpendiculaire à l'axe \( \eta_1 \), même pour des déformations de quelques \( \% \) ; le cisaillement additionnel n'a donc pas d'influence sur le déclenchement de la transformation : seule l'amplitude de la distorsion quadratique mesurée par \( \eta_1 \) est importante. Lorsque \( \eta_1 \) est une déformation isotrope la ligne critique n'est pas perpendiculaire à l'axe \( \eta_1 \), mais il faudrait des pressions très élevées pour avoir un effet notable. Les déformations critiques obtenues ci-dessus sont de l'ordre des distorsions quadratiques moyennes mesurées par Foos, Frantz et Gantois pour des phénomènes pré-martensitiques dans Fe\(_3\)Pt.

Abstract. — The Bain transformation bcc \( \rightarrow \) fcc can be achieved by the two homogeneous « shears » E and E' proposed by Bogers and Burgers. We first discuss the conditions for pair potentials to ensure the mechanical stability of both bcc and fcc structures; then, three phenomenological potentials for metals are used to calculate the crystal free energy density \( W \) for the deformation states \( \eta E + \eta' E' \) \((\eta \text{ and } \eta' \text{ range from } -0.5 \text{ to } 1.5)\). The path \( \gamma = \gamma' \), which keeps the crystal in a bct structure, breaks the smallest number of symmetries and is found to be the minimum energy path. To generalize this result we have considered the elastic coefficients \( B \) (bulk modulus), \(1/2(C_{11} - C_{12})\), \(C_{44}\), \(C_{66}\) of the intermediate bct structures : if they are positive the path \( \gamma = \gamma' \) remains a minimum energy path with respect to any type of deformation. The potentials we have tried satisfy these conditions which, in general, are expected to be fulfilled for most potentials ensuring the mechanical stability at both ends of the path. The bct intermediate structures are characterized by \( \eta_1 = (\log c/a)/\log \sqrt{2} \). The energy density \( W(\eta_1) \) presents two minima at \( \eta_1 = 0 \) (bcc) and \( \eta_1 = 1 \) (fcc) separated by a maximum. The first derivative \( dW/d\eta_1 \) is proportional to the applied stress. The inflexion points, where the second derivative \( d^2W/d\eta_1^2 \) vanishes, define critical strains and stresses for the triggering of the transformation ; these strains are of the order of 1/4 of the full Bain distortion and these stresses are lower than the theoretical shear strength. Besides, critical lines have been determined in the five planes \((\eta_1, \eta_2)\) where \( \eta_2 \) is either one of the shears \( \{110\} \), \(\{112\}, \{123\}, \{213\}, \{211\}\), or an isotropic deformation. When \( \eta_1 \) is a shear, the critical line is perpendicular to the \( \eta_1 \) axis even for deformations of some \( \% \); thus, the additional shear does not play any part in the triggering of the transformation : only the amount of tetragonal distortion measured by \( \eta_1 \) is important. When \( \eta_1 \) is an isotropic strain, the critical line is not perpendicular to the \( \eta_1 \) axis, but only very high pressures could have a significant effect. The critical deformations found above are of the order of the mean tetragonal distortions measured by Foos, Frantz and Gantois for premartensitic phenomena in Fe\(_3\)Pt.

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Article published online by EDP Sciences and available at http://dx.doi.org/10.1051/jphys:019830044090111700
1. Introduction.

An important problem in martensite nucleation is that of the movement of atoms to form an embryo at the very early stage of the process. Perhaps because of its technological importance in steels, but more likely because of its relative simplicity, the bcc $\rightarrow$ fcc transformation has drawn the attention of a large number of authors. Bain [1] established a correspondence between the points of bcc and fcc lattices which shows that the transformation can be realized by homogeneous deformations. Jaswon and Wheeler [2] described the atomic displacements involved and derived the corresponding strains. A number of double shear mechanisms have been proposed, in particular by Kurdjumov and Sachs [3], Nishiyama [4, 5], Bogers and Burgers [6]. In general, one chooses the first shear in the initial phase because it seems intuitively easy to produce: it involves dense planes or usual twinning planes. The amplitude of the strain is increased until the initial phase is deformed into something which can reasonably be regarded as a distorted final structure. It is then assumed that the second shear which transforms the intermediate structure into the final one spontaneously occurs; for the mechanism to be reversible the second shear has to be « easy », that is a twinning or a dense plane shear. In the Bogers and Burgers (B. & B.) [6] model the shears are on dense planes and in the directions introducing the minimum volume increase of the hard-sphere lattice. These authors propose that the shears are produced by regularly spaced partial dislocations in both structures. Olson and Cohen [7] considered this process in their thermodynamic analysis of martensite nucleation and determination of critical sizes for embryos.

In this paper we present a calculation of the crystal energy when B. & B. deformations are applied in small steps. The crystal energy is calculated by pair interaction summation and several potentials have been used. B. & B. « shears » are applied in such a way that all combinations of applying partially the first « shear » and partially the second « shear » are examined. This allows a more general discussion than to consider simply the two B. & B. « shears » and it is possible to define a path of particular symmetry. The effect of any kind of deformation applied on the structures corresponding to this path is analysed by calculating the relevant elastic coefficients. Then the stresses involved in the transformation are derived, which allows discussion of instabilities; critical stresses and critical strains for the triggering of the transformation are determined.

2. Use of the same pair potential for two crystal structures.

Crystal energy is calculated by summation of interactions between pairs of atoms. The chosen interatomic potential must ensure stable equilibrium of both bcc and fcc phases. In general, this leads to two different atomic volumes for the two phases. Thus, pair potentials for simple metals derived from the pseudo-potential theory, which are determined for one particular volume, cannot be used. We have to choose a phenomenological potential from the literature; these potentials are usually determined for one particular structure. In the problem studied here, where two different structures are involved, the following procedure was used:

- for a given potential we determined, for each phase, the lattice parameters $a_{bcc}$ and $a_{fcc}$ which correspond to the minimum of the crystal energy $W$ with respect to the volume $v$, so that the following stability conditions are satisfied:

$$\frac{dW}{dv} = 0, \quad \frac{d^2W}{dv^2} > 0, \quad (1)$$

the second condition is equivalent, for cubic lattices, to $1/3(C_{11} + 2C_{12}) > 0$ and corresponds to stability with respect to variations in hydrostatic stress;

- then the mechanical stability of these two structures with respect to any other deformation has to be checked; for cubic structures this stability is realized if the introduction of shears such as $\{100\} <010>$ and $\{110\} <110>$ produces an increase of the energy; this is respectively equivalent to:

$$C_{44} > 0 \quad \text{and} \quad 1/2(C_{11} - C_{12}) > 0. \quad (2)$$

We have found potentials for which these conditions are not realized, for instance a vanadium potential [8] and the gold potential discussed below [9]; they cannot be used for this study.

Three polynomial pair potentials, shown on figure 1, were used for crystal energy calculation under B. & B. deformations:

- a potential for Cu developed by Englert, Tompa and Bullough [10], referred to as « potential I »,
- a Johnson potential for α-Fe [11], « potential II »,
- the radial part of a Johnson potential for Au [9], « potential III ».

![Fig. 1. — The three chosen phenomenological pair potentials.](image-url)
The first two were chosen to be examples for a fcc and a bcc metal. In fact, it will be seen that these potentials exhibit a similar behaviour: they predict a bcc structure more stable than fcc. We did not use the third potential in its full form, which includes an angular dependence, because this form could not stabilize a bcc lattice; the radial part alone was kept and led to a more stable fcc structure. No importance should be attached to the fact that these potentials have been designed to represent such or such metal; we do not pretend to calculate the energy variations of any particular metal, but we consider these potentials as reasonable force laws between atoms which can stabilize both bcc and fcc structures.


3.1 Bogers and Burgers' « shears ». — The bcc → fcc structure change is characterized by the transformation of the initial elementary tetrahedron, the faces of which are isosceles triangles with a 70° 32' angle lying on {110} planes of the bcc lattice, into the equilateral tetrahedron with faces on {111} planes of the fcc lattice. Consider the tetrahedron ABCD constituting the unit cell of a bcc lattice (Fig. 2); in the first B. & B. « shear » the atom A is displaced into A' by a rotation around the axis CD changing the angle \(\theta = \angle ACB \) (or ADB) from 70.53° to 60°. In this deformation the upper {110} plane containing A is mainly displaced by \(1/8 a_{\text{bcc}} \langle 110 \rangle\) with respect to the lower BCD plane; there is also a 3.2% compression. The A'BCD tetrahedron can be regarded as the unit cell of a deformed fcc lattice. This latter structure is obtained by applying the second B. & B. « shear » in which the atom D is rotated around the axis A'B so that the angle \(\theta' = \angle CA'D \) (or CBD) is changed from 70.53° to 60°. In the fcc structure this is a displacement of \(1/18 a_{\text{fcc}} \langle 112 \rangle\) of the {111} plane containing D with respect to the plane A'BC; in addition there is a 5.4% compression. Of course, this transformation can be reversed to change a fcc into a bcc lattice. If the first « shear » \(1/8 a_{\text{bcc}} \langle 110 \rangle\) in the bcc → fcc transformation, or \(1/18 a_{\text{fcc}} \langle 112 \rangle\) for the fcc → bcc transformation) is realized, for instance by a convenient array of dislocations or by some lattice wave, it is assumed that the second will spontaneously occur since the intermediate phase can be regarded as a distorted final structure. These « shears » seem easy to produce since they involve dense planes in both structures and they correspond to a minimum volume change of the hard-sphere lattice.

3.2 Energy surface \(W(y, y')\). — The crystal energy per atom \(W\) has been calculated as a function of the two variables:

\[
y = \frac{70.53 - \theta}{70.53 - 60} \quad \text{and} \quad y' = \frac{70.53 - \theta'}{70.53 - 60}.
\]

The bcc structure is represented by the point \((y, y') = (0, 0)\) and the fcc structure by \((y, y') = (1, 1)\). The points \((0, 0)\) and \((1, 1)\) correspond to the intermediate states that B. & B. described as a distorted bcc or fcc phase. A couple \((y, y')\) does not completely define a crystal deformation state: in the elementary tetrahedron the angles \(\theta\) and \(\theta'\) are unambiguously known, but not the size of this tetrahedron, i.e. the atomic volume. At each point \((y, y')\) this atomic volume was determined by minimizing the crystal energy per atom with respect to the atomic volume; it is the same procedure as that used to determine the lattice parameters \(a_{\text{bcc}}\) and \(a_{\text{fcc}}\).

Figure 3 shows the lines of equal energy spaced at 0.01 eV at \(-1\) of the surface \(W(y, y')\), calculated using the Cu potential (potential I), on a 100 × 100 grid (10,000 points) for \(y\) and \(y'\) ranging from \(-0.5\) to 1.5. For the other two potentials, similar surfaces are found. The values at remarkable points of these surfaces are shown in table I. The points \((0, 0)\) and \((1, 1)\), respectively bcc and fcc, are local minima. Potentials I and II give a lower energy to the bcc structure although they are supposed to represent Cu or \(\alpha\)-Fe which are, in fact, fcc and bcc respectively. This does not mean that these potentials are not good phenomenological potentials: they reproduce correct elastic constants for fcc Cu and bcc \(\alpha\)-Fe, that is, they give the right energy variations for small deformations of the stable structure. But here, when going from bcc to fcc (or from fcc to bcc) the deformations are larger than what the potential can account for, so that it cannot be
Table I. — *Volume changes and remarkable points of the surface $W(\gamma, \gamma')$ for potentials I, II, III.*

<table>
<thead>
<tr>
<th>Potential</th>
<th>$V_{\text{fcc}} / V_{\text{bce}}$</th>
<th>$W_{\text{bce}}$</th>
<th>$W_{\text{fcc}}$</th>
<th>Saddle point</th>
<th>$W(0,1)$ or $W(1,0)$</th>
<th>Maximum on B. &amp; B. path</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.043</td>
<td>-1.417</td>
<td>-1.382</td>
<td>0.48</td>
<td>-1.350</td>
<td>-1.287</td>
</tr>
<tr>
<td>II</td>
<td>1.082</td>
<td>-1.537</td>
<td>-1.510</td>
<td>0.61</td>
<td>-1.482</td>
<td>-1.409</td>
</tr>
<tr>
<td>III</td>
<td>1.199</td>
<td>-2.939</td>
<td>-3.340</td>
<td>0.25</td>
<td>-2.833</td>
<td>-2.816</td>
</tr>
</tbody>
</table>

said that the calculated values are the energies of what would be a bcc Cu or a fcc Fe. For potential III the fcc structure has a lower energy than the bcc and the potential was chosen for this reason.

The three potentials give a larger atomic volume for the fcc phase than for the bcc. The volume increase is 4.3% for potential I, 8.2% with potential II and about 20% for potential III.

3.3 MINIMUM ENERGY PATH ON THE SURFACE $W(\gamma, \gamma')$.

The energy surface is symmetric with respect to the diagonal plane $\gamma = \gamma'$:

$$W(\gamma, \gamma') = W(\gamma', \gamma).$$

This arises from the crystallographic equivalence of the angles $\theta$ and $\theta'$. Thus, the lowest point of the energy barrier is situated in this diagonal plane. The deformation discussed by B. & B., represented by the segments $(0,0)-(1,0)-(1,1)$ or $(0,0)-(0,1)-(1,1)$, reaches an energy value much higher than the saddle point energy. For potentials I and II the maximum energy point of the B. & B. paths is $(0,1)$ or $(1,0)$ which is the structure that B. & B. thought to be a natural intermediate between bcc and fcc. For potential III the minimum at the fcc point is much deeper than that at the bcc point and the energy barrier is displaced towards bcc; for this reason the maximum on the B. & B. path is around $(0,0.48)$ or $(0.48,0)$. The two B. & B. paths are not particularly special compared to others and no reason appears why they should play a particular part in the bcc $\Rightarrow$ fcc transformation. The only remarkable path is the line $\gamma = \gamma'$ since it is situated in the symmetry plane of the surface $W(\gamma, \gamma')$. Along this line $\theta$ equals $\theta'$ and consequently the opposite edges AB and CD of the tetrahedron are equal; it can be shown that they remain orthogonal since the other edges of the tetrahedron (AC, AD, BD) remain equal to each other. Such a tetrahedron is the unit cell of a body-centred-tetragonal structure (Fig. 4). The edges CD and AB in the tetrahedron are parallel and equal to the edges $a_3$ and $a_4$ of the tetragonal cell and the distance between AB and CD is half of the height $c$. The bcc lattice corresponds to $c/a = 1$ and the fcc to $c/a = \sqrt{2}$. The deformation bcc $\Rightarrow$ fcc defined by $\gamma = \gamma'$ consists of a lengthening of the edge $c$ of the initial body-centred cube, or of a shortening of $a_3$ and $a_4$ equally, or in a combination of these two deformations depending on the volume change, until the $c/a$ ratio is $\sqrt{2}$; this completes the Bain transformation.

Energy variations in the vicinity of the diagonal $\gamma = \gamma'$ can be characterized as follows: in the $(\gamma, \gamma')$ plane a new system of coordinates can be chosen in which the OX axis is parallel to the first diagonal and the OY axis to the second diagonal. The new coordinates $\Gamma$ and $\Gamma'$ are:

$$\Gamma = 1/2(\gamma + \gamma')$$ and $\Gamma' = 1/2(\gamma - \gamma')$.

The symmetry of the energy surface is expressed by:

$$W(\Gamma, \Gamma') = W(\Gamma', -\Gamma').$$

At a point $(\Gamma, d\Gamma')$ near the first diagonal the symmetry relation 6 allows one to write, up to second order:

$$W(\Gamma, d\Gamma') = W(\Gamma, 0) + 1/2 C(\Gamma) d\Gamma'^2.$$

The intersection of the energy surface with a plane perpendicular to the first diagonal at $\Gamma$ exhibits an extremum for $\Gamma = 0$. It is seen from figure 3 that this extremum is a minimum, so that the coefficient $C(\Gamma)$ is positive for any $\Gamma$ between 0 and 1. This expresses precisely the fact that the diagonal path $\gamma = \gamma'$ is the minimum energy path in the plane $(\gamma, \gamma')$. It is important to remark that, when one moves perpendicularly away from the line $\gamma = \gamma'$, the energy keeps increasing even for large deformations. Hence, over the whole range of values of $\gamma$ and $\gamma'$ shown on figure 3 there is no sign of the possible existence of any other minimum energy path joining the bcc and fcc structures.

The bct structure has tetragonal symmetry. The deformation of a cubic cell into a tetragonal cell is represented by only one order parameter $\eta_1$ in the Landau theory of phase transformations [12]. This order parameter is related to the $c/a$ ratio. The other
order parameters $\eta'$ associated with the deformations of a cubic lattice correspond to \{110\} $\langle 110 \rangle$ and \{100\} $\langle 001 \rangle$ types of shear; they do not affect the tetragonality ratio. If a deformation represented by one of the order parameters is given, the symmetry group of the obtained structure is a sub-group of that of the initial structure. No order parameter is attached to isotropic deformations because they do not modify the crystal structure. It is not possible to go from bcc to fcc without changing the $c/a$ ratio, thus $\eta_1$ has to be non-zero. The addition of a deformation related to another order parameter $\eta'$ would break more crystal symmetries. Thus, the path for which the crystal has the highest symmetry is that which keeps the tetragonal structure, that is the diagonal $\gamma = \gamma'$.

4. Energy variations around the bct intermediate structures.

In the above paragraph we have calculated the energy variations of a crystal submitted to the deformations produced by the variations of the angles $\theta$ and $\theta'$ in the tetrahedron. We have determined the minimum energy path to go from one phase to the other when only the deformations characterized by $\gamma$ and $\gamma'$ are considered. In this paragraph we want to examine if the line $\gamma = \gamma'$ remains or not the minimum energy path when other deformations are added to those considered above; for this, the energy variations of the bct structures with a $c/a$ ratio ranging from 1 to $\sqrt{2}$ have to be calculated.

A crystal is in equilibrium under the stress system $\sigma_{ij}$. The variation $\delta W$ of the energy per atom of the crystal when the applied stresses vary by $\delta \sigma_{ij}$ is equal to the work done by these stresses:

$$
\delta W = \sum_{ij} (\sigma_{ij} \delta \varepsilon_{ij} + 1/2 \delta \sigma_{ij} \delta \varepsilon_{ij}), \quad (8)
$$

where $\delta \varepsilon_{ij}$ is the deformation variation induced by $\delta \sigma_{ij}$. This becomes, after introducing the elastic constants $c_{ijkl}$ of the crystal in the considered deformation state (elastic constants which are different from those of the unstressed crystal):

$$
\delta W = \sum_{ij} \sigma_{ij} \delta \varepsilon_{ij} + 1/2 \sum_{ijkl} c_{ijkl} \delta \varepsilon_{ij} \delta \varepsilon_{kl}. \quad (9)
$$

We consider here a tetragonal crystal. Positions and displacements of the lattice points are referred to a system of orthonormal axes lying along the edges of the tetragonal cell. The matrix representing the quadratic form:

$$
\sum_{ijkl} c_{ijkl} \delta \varepsilon_{ij} \delta \varepsilon_{kl}
$$

of relation 9 is given, in Voigt notation, by:

$$
\begin{bmatrix}
C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\
C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\
C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & 2 C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & 2 C_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & 2 C_{66}
\end{bmatrix}.
$$

(11)

It differs from the matrix of elastic coefficients for a tetragonal structure [13] only by the factor two in front of the shear constants.

4.1 DEFINITION OF NEW DEFORMATION VARIABLES. —

A more simple form of matrix (11), and thus a simplified expression of the energy, will be obtained by characterizing the deformations of the tetragonal structures by the quantities $\eta_1$, $\eta_2$, $\eta_3$, $\varepsilon_{23}$, $\varepsilon_{13}$, $\varepsilon_{12}$ defined as follows: in an infinitesimal deformation $\delta \varepsilon_{ij}$ the deformation tensor can be written as:

$$
\begin{bmatrix}
\delta \varepsilon_{11} & \delta \varepsilon_{12} & \delta \varepsilon_{13} \\
\delta \varepsilon_{12} & \delta \varepsilon_{22} & \delta \varepsilon_{23} \\
\delta \varepsilon_{13} & \delta \varepsilon_{23} & \delta \varepsilon_{33}
\end{bmatrix} = \frac{k}{\sqrt{6}} \delta \eta_1 \begin{bmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 2
\end{bmatrix} + \frac{1}{\sqrt{3}} \delta \eta_2 \begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix} + \frac{1}{\sqrt{2}} \delta \eta_3 \begin{bmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 0
\end{bmatrix} + \begin{bmatrix}
\delta \varepsilon_{12} & \delta \varepsilon_{13} \\
\delta \varepsilon_{13} & \delta \varepsilon_{23} \\
0 & 0
\end{bmatrix},
$$

(12)
where \( k \) is a normalization factor which will be defined later. The first tensor:

\[
\begin{bmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 2
\end{bmatrix}
\]

represents an elongation along \( Oz \) and two compressions along \( Ox \) and \( Oy \) with an amplitude half of the \( Oz \) elongation; this deformation modifies the \( c/a \) ratio of the quadratic cell but leaves the volume unchanged. The tensor:

\[
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\]

is an isotropic dilatation which does not change the \( c/a \) ratio. The tensor:

\[
\begin{bmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 0
\end{bmatrix}
\]

is a \( \{110\} \langle 110 \rangle \) shear. Thus, the six deformations \( \sqrt{6} k \delta n_1, \sqrt{3} \delta n_2, \sqrt{2} \delta n_3, \delta e_{13}, \delta e_{12}, \delta e_{33} \) are independent. Equation 12 can be reversed to obtain \( k \delta n_1, \delta n_2, \delta n_3 \) from \( \delta e_{11}, \delta e_{22}, \delta e_{33} \):

\[
\begin{align*}
kd \delta n_1 &= \frac{1}{\sqrt{6}} (\delta e_{11} + \delta e_{22} - 2 \delta e_{33}) \\
kd \delta n_2 &= \frac{1}{\sqrt{3}} (\delta e_{11} + \delta e_{22} + \delta e_{33}) \\
kd \delta n_3 &= \frac{1}{\sqrt{2}} (\delta e_{11} - \delta e_{22}).
\end{align*}
\]

At each point of the diagonal \( \gamma = \gamma' \) is attached a \( c/a \) ratio between 1 and \( \sqrt{2} \); if we make:

\[
\eta_1 = \frac{\log c/a}{\log \sqrt{2}}.
\]

\( \eta_1 \) satisfies the relations 12 and 13 and constitutes a graduation of the diagonal which varies from 0 for bcc to 1 for fcc. The coefficient \( k \) necessary to normalize \( k\sqrt{6} \delta n_1 \) is then:

\[
k = \frac{\log 2}{\sqrt{6}}.
\]

Moreover, \( 1/\sqrt{3} \delta n_2 \) representing one third of the relative volume variation, \( \eta_2 \) can be defined by:

\[
\eta_2 = \frac{1}{\sqrt{3}} \log \frac{v}{v_0},
\]

where \( v \) is the atomic volume in the considered state of deformation and \( v_0 \) the atomic volume, in the absence of any hydrostatic pressure, of the quadratic structure corresponding to the value of \( \eta_1 \) chosen as reference state. Finally, \( \eta_3 \) is defined by:

\[
\eta_3 = \frac{1}{\sqrt{2}} (\epsilon_{11} - \epsilon_{22}).
\]

It can easily be seen that the parameter \( \eta_3 \), on one hand, and the parameter \( \Gamma' \) of the B. & B. deformations, on the other hand, represent the same type of deformation: in figure 3 a point close to the diagonal has the coordinates \( (\Gamma', d\Gamma') \) equivalent to \( (\gamma + d\gamma, \gamma - d\gamma) \) so that the angles of the elementary tetrahedron are \( \theta + d\theta \) and \( \theta - d\theta \) (relation 3). The edges AB and CD opposite to these angles, and consequently the edges \( a_1 \) and \( a_2 \) of the quadratic cell (Fig. 4), have the lengths \( a + da \) and \( a - da \). The corresponding deformation tensor is:

\[
\begin{bmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 0
\end{bmatrix}
\]

this is a \( \{110\} \langle 110 \rangle \) shear : \( d\Gamma' \) and \( d\eta_3 \) are proportional.

Fig. 4.—Body-centred-tetragonal cells and elementary tetrahedron (ABCD).
with

\[ K_1 = \frac{1}{3} (C_{11} + C_{12} - 4C_{13} + 2C_{33}) \]
\[ K_2 = \frac{\sqrt{2}}{3} (C_{11} + C_{12} - C_{13} - C_{33}) \]
\[ K_3 = 3B = \frac{1}{3} (2C_{11} + 2C_{12} + 4C_{13} + 2C_{33}) \]

Note that for the two cubic structures bcc and fcc:

\[ K_1 = C_{11} - C_{12}, \quad K_2 = 0, \quad K_3 = C_{11} + 2C_{12} \]

From the above definitions a bct structure \((\gamma = \gamma')\) for which the energy is minimum with respect to the atomic volume is represented by \(\eta = \eta'\) and \(\eta_2 = \eta_3 = \eta_{23} = \eta_{13} = \eta_{12} = 0\). The energy variation of a bct structure \((\eta_1, 0, 0, 0, 0, 0)\) deformed into \((\eta_1 + \delta \eta_1, \delta \eta_2, \delta \eta_3, \delta \eta_{23}, \delta \eta_{13}, \delta \eta_{12})\) is (relation 9):

\[
dW = W(\eta_1 + \delta \eta_1, \delta \eta_2, \delta \eta_3, \delta \eta_{23}, \delta \eta_{13}, \delta \eta_{12}) - W(\eta_1, 0, 0, 0, 0, 0) =
\]

\[
-\sigma_{11} + \sigma_{22} - \frac{2}{3} \sigma_{33} \frac{k}{\sqrt{6}} \delta \eta_1 + (\sigma_{11} + \sigma_{22} + \sigma_{33}) \frac{1}{\sqrt{3}} \delta \eta_2 + (\sigma_{11} - \sigma_{22}) \frac{1}{\sqrt{2}} \delta \eta_3 + \sum \sigma_{ij} \delta \epsilon_{ij}
\]

\[-\frac{1}{2} (\sigma_{11} + \sigma_{22} - 2 \sigma_{33}) \frac{k}{\sqrt{6}} \delta \eta_1 + \frac{1}{2} (\sigma_{11} + \sigma_{22} + \sigma_{33}) \frac{1}{\sqrt{3}} \delta \eta_2
\]

\[+ \frac{1}{2} (\sigma_{11} - \sigma_{22}) \frac{1}{\sqrt{2}} \delta \eta_3 + \frac{1}{2} \sum \sigma_{ij} \delta \epsilon_{ij} \delta \epsilon_{ij}. \]  

(20)

The matrix of elastic coefficients is obtained by dividing by 2 the four last diagonal terms of matrix (18); then we have for a bct structure:

\[
\begin{align*}
\sigma_{11} - \sigma_{22} &= \frac{1}{2} (C_{11} - C_{12}) \frac{k}{\sqrt{2}} \eta_3 \\
\sigma_{23} &= \frac{C_{44}}{\sqrt{6}} \eta_3, \quad \sigma_{13} = \frac{C_{44}}{\sqrt{6}} \eta_3, \quad \sigma_{12} = C_{66} \eta_1.
\end{align*}
\]

(21)

Since for the bct structures \(\eta_3, \eta_{13}, \eta_{23}, \eta_{12}\) are zero it follows:

\[
\begin{align*}
\sigma_{11} - \sigma_{22} &= 0 \\
\sigma_{23} &= \sigma_{13} = \sigma_{12} = 0.
\end{align*}
\]

(22)

Furthermore, as indicated at paragraph 3, each point of the surface \(W(\gamma, \gamma')\) is the minimum energy with respect to the volume and in particular for the bct structures we have:

\[
\frac{dW}{d\eta_2} = 0 \iff \sigma_{11} + \sigma_{22} + \sigma_{33} = 0
\]

(23)

This means that, to obtain one of these bct structures, the applied stress system must satisfy conditions (22) and (23); such a stress tensor has the form:

\[
\begin{bmatrix}
-\sigma & 0 & 0 \\
0 & -\sigma & 0 \\
0 & 0 & 2\sigma
\end{bmatrix}
\]

(24)

Taking into account the expression of matrix (18), the energy variation becomes:

\[
dW = 6k \sigma \left( \frac{k}{\sqrt{6}} \delta \eta_1 \right) + \frac{1}{2} K_1 \left( \frac{k}{\sqrt{6}} \delta \eta_1 \right)^2 + K_2 \left( \frac{k}{\sqrt{6}} \delta \eta_1 \right) \left( \frac{1}{\sqrt{3}} \delta \eta_2 \right) + \frac{1}{2} K_3 \left( \frac{1}{\sqrt{3}} \delta \eta_2 \right)^2
\]

\[+ (C_{11} - C_{12}) \left( \frac{1}{\sqrt{2}} \delta \eta_3 \right)^2 + 2C_{44}(\delta \epsilon_{23} + \delta \epsilon_{13}) + 2C_{66} \delta \epsilon_{12} \]  

(25)

The condition for the path \((\eta_1, 0, 0, 0, 0, 0)\) or \(\gamma = \gamma'\), to be a minimum energy path is that the energy variation \(dW\) in a deformation which leaves \(\eta_1\) unchanged is positive. We can write for such a deformation:

\[
dW = W(\eta_1, \delta \eta_2, \delta \eta_3, \delta \epsilon_{23}, \delta \epsilon_{13}, \delta \epsilon_{12}) - W(\eta_1, 0, 0, 0, 0, 0) =
\]

\[= \frac{1}{2} B \delta \eta_1^2 + (C_{11} - C_{12}) \left( \frac{1}{\sqrt{2}} \delta \eta_3 \right)^2 + 2C_{44}(\delta \epsilon_{23} + \delta \epsilon_{13}) + 2C_{66} \delta \epsilon_{12}^2. \]

(26)
4.3 Elastic coefficients of the bct intermediate structures. — The condition $dW$ positive is equivalent to:

$$\left\{ \begin{array}{l}
B = \frac{1}{3} K_3 = \frac{1}{9} (2C_{11} + 2C_{12} + 4C_{13} + C_{33}) > 0, \\
\frac{1}{2}(C_{11} - C_{12}) > 0, \quad C_{44} > 0, \quad C_{66} > 0.
\end{array} \right. \quad (27)$$

for all bct structures intermediate between bcc and fcc. The condition $B > 0$ is always satisfied because at each point of the surface the energy $W(\gamma, \gamma')$ is minimized with respect to the volume:

$$\frac{dW}{dv} = 0 \quad \text{and} \quad \frac{d^2W}{dv^2} = \frac{d^2W}{3dn_2^2} = \frac{K_3}{9} > 0. \quad (28)$$

The condition $1/2(C_{11} - C_{12}) > 0$ has, in fact, already been checked in the analysis of the surface $W(\gamma, \gamma')$: since $\Gamma'$ represents a $\{110\} <110>$ shear the coefficient $C(\Gamma)$ of relation 7 is proportional to $1/2 (C_{11} - C_{12})$. On figure 5 are shown values, calculated with potential I, of the bulk modulus $B$ and of the shear constants $1/2 (C_{11} - C_{12})$, $C_{44}$, $C_{66}$ for all bct structures between bcc and fcc; all these quantities are positive. We have also calculated the same elastic coefficients with potentials II and III and found them to be positive.

In summary, the path defined by $0 \leq \eta_1 \leq 1$ and $\eta_2 = \eta_3 = \epsilon_{23} = \epsilon_{13} = \epsilon_{12} = 0$ which keeps the crystal in a bct structure is a minimum energy path to go from bcc to fcc by homogeneous deformations. The addition of any homogeneous deformation deviates from this path and increases the crystal energy; since there is no first order term in equation 26 and since $B, 1/2 (C_{11} - C_{12}), C_{44}$, $C_{66}$ are positive the equilibrium of the bct structure with respect to deformations which leave $\eta_1$ unchanged is stable. This is independent of the pair potential as long as it gives positive values for the four here above elastic coefficients. It is not a very restrictive requirement on the potential since, in any case, the potential must give positive elastic constants at both ends of the path to ensure the mechanical stability of both bcc and fcc structures. If a potential had a particular form which would cause elastic coefficients to vanish between bcc and fcc, the line considered here would no longer be a minimum energy path and there would be symmetric minimum energy paths.

4.4 Effect of large deformations. — We have made, by the summation of pair interactions, the numerical calculation of the crystal energy density for large values of $\eta_2$, $\eta_3$, $\epsilon_{23}$, $\epsilon_{13}$, $\epsilon_{12}$ to explore a wider region of the six dimension deformation space around $\eta_1$. Figure 6 shows the schematic form of the surfaces $W(\eta_1, \eta)$ where $\eta$ is one of the five above parameters; it must be stated that $W(\eta_1,\eta_2)$ is not symmetric with respect to the $\eta_1$ axis, contrary to the four other surfaces, and that $W(\eta_1,\epsilon_{23})$ and $W(\eta_1,\epsilon_{13})$ are identical. The range of variations of $\eta_1$ has been chosen so that it corresponds to a deformation up to around $10\%$ which is comparable to the amplitude of the Bain strain $1/6 \log 2 = 0.115$. On all five surfaces the energy keeps increasing when $|\eta_1|$ increases, so that no sign of any other minimum energy path appears. This shows only the behaviour of the six variables function $W(\eta_1, \eta_2, \eta_3, \epsilon_{23}, \epsilon_{13}, \epsilon_{12})$ on five particular planes ($\eta_1, \eta$) and is not sufficient to prove that no other minimum energy path exists. In any case, no other possible minimum energy path would exhibit the remarkable symmetry properties of the one discussed here.

5. Critical points on the bct path.

In paragraph 4, we have studied the stability of the bct structures with respect to deformations which leave the $c/a$ ratio unchanged. We shall consider here deformations along the minimum energy path and focus on stresses involved which allows unstability discussion. The energies $W(\eta_1)$ of the bct structures for which the atomic volume minimizes the crystal energy are represented on figure 7; this curve is derived from the cross section of the surface $W(\gamma, \gamma')$ calculated with potential I (Fig. 3) by the plane $\gamma = \gamma'$ when applying the correspondence between $1/2(\gamma + \gamma')$...
and \( \eta_1 \). We have shown that, to obtain one of these bct structures, the stress tensor must have the form (24).

Consider a crystal in the deformation state \( \eta_1 \) in equilibrium under the stress tensor (24). If \( \sigma \) varies by \( d\sigma \), the point \( \eta_1 \) goes to \( \eta_1 + d\eta_1 \) and consequently the atomic volume changes : \( \eta_2 \) goes from 0 to \( d\eta_2 \). The corresponding energy variation, deduced from relation (25), is:

\[
\frac{dW(\eta_1)}{d\sigma} = 6 \sigma \left( \frac{k}{\sqrt{6}} d\eta_1 \right) + \frac{1}{2} K_1 \left( \frac{k}{\sqrt{6}} d\eta_1 \right)^2 + K_2 \left( \frac{k}{\sqrt{6}} d\eta_1 \right) \left( \frac{1}{3} d\eta_2 \right) + K_3 \left( \frac{1}{3} d\eta_2 \right)^2.
\]

(29)

The quantities \( d\eta_1 \) and \( d\eta_2 \) are not independent ; the above stress system satisfies:

\[
d\sigma_{11} + d\sigma_{22} + d\sigma_{33} = 0
\]

and, by considering the second line of the matrix of elastic coefficients deduced from (18), this is equivalent to:

\[
K_2 \left( \frac{k}{\sqrt{6}} d\eta_1 \right) + K_3 \left( \frac{1}{3} d\eta_2 \right) = 0.
\]

(30)

The energy variation reduces to:

\[
\frac{dW(\eta_1)}{d\sigma} = 6 \sigma \left( \frac{k}{\sqrt{6}} d\eta_1 \right) + \frac{1}{2} K' \left( \frac{k}{\sqrt{6}} d\eta_1 \right)^2
\]

(31)

with

\[
K' = K_1 - \frac{K_2^2}{K_3}.
\]

(32)

Thus the slope of the curve \( W(\eta_1) \) is \( 6 \sigma k/\sqrt{6} \) and the second derivative \( K' k^2/6 \). When applying increasing \( \sigma \) on the bcc structure, the point \( \eta_1 \) is displaced towards the fcc structure until it reaches the inflexion point \( \eta_{1c} \) where the second derivative \( d^2W/d\eta_1^2 \), or the elastic coefficient \( K' \), becomes negative. At this point, \( \sigma \) reaches the maximum value the crystal can endure. This stress is the critical stress \( \sigma_c \) capable of triggering the bcc \( \rightarrow \) fcc transformation. Similarly, to transform a fcc into a bcc crystal, the application of a stress system (24), where \( \sigma \) is negative and increases in absolute value, keeps the crystal in a bct structure the \( c/a \) ratio of which decreases until \( \eta_1 \) reaches the inflexion point \( \eta_{1c} \); this defines critical strain and stress \( \sigma_c \) for fcc \( \rightarrow \) bcc transformation.

For the bcc \( \rightarrow \) fcc transformation, \( \eta_{1c} = 0.298 \) and the corresponding deformation tensor, which takes into account the volume change, is:

\[
\begin{bmatrix}
-0.040 & 0 & 0 \\
0 & -0.040 & 0 \\
0 & 0 & 0.0645
\end{bmatrix}.
\]

For the reverse transformation, \( \eta_{1c} = 0.653 \). If it is referred to the fcc structure \( (1 - \eta_{1c}) = 0.347 \) and the deformation tensor containing volume variation is:

\[
\begin{bmatrix}
0.0398 & 0 & 0 \\
0 & 0.0398 & 0 \\
0 & 0 & -0.0780
\end{bmatrix}.
\]

Clapp [14] has calculated the energy of a bcc crystal deformed towards fcc, using a third order energy expansion in deformations. In this way he could define critical points and those corresponding to the minimum energy increase are very close to the value obtained here for the bcc \( \rightarrow \) fcc transformation. Clapp [14] noted that the critical points for which the energy increase is minimum are very near the Bain path [1]; it has been shown here that they are exactly on this path.

Figure 8 shows the variations of the stress \( \sigma \) (tensor 24). At the critical points the absolute value of \( \sigma \) reaches maxima : for the bcc \( \rightarrow \) fcc transformation \( \sigma_c = 3.22 \text{ GPa} \) and for the reverse transformation \( \sigma_c = -1.63 \text{ GPa} \). These critical stresses are smaller than the theoretical shear strength \( \mu/2\pi \), larger than 10 GPa, that must be applied to make atomic planes glide on each other in the absence of dislocations. Milstein and Farber [15] calculated, with a potential

\[
\begin{bmatrix}
0.040 & 0 & 0 \\
0 & -0.040 & 0 \\
0 & 0 & 0.0645
\end{bmatrix}.
\]
for copper different from potential I, the effect of a simple tension along <001>, which is a stress tensor with a non-zero hydrostatic component, and computed a value of the critical axial stress of $-2.51$ GPa for the fcc $\rightarrow$ bcc transformation; this value is of the same order as the critical stress obtained here.

Although one could think of some similarities with the spinodal decomposition of solid solutions (Clapp [14], Suzuki and Wuttig [16]) two remarks can be made which underline the difference with the analysis presented here:

— first, in solid solutions the total number of solute atoms does not change, so that a region of higher concentration has to be compensated by a region of lower concentration: the average value of concentration is constant; in the problem studied here, there is no reason to impose the average deformation over the whole crystal to be constant;

— second, the part of the curve $W(\eta_1)$ situated between the two inflexion points $\eta_{1c}$ and $\eta_{1u}$, drawn in dashed line on figure 7, is characterized by $d^2W/d\eta_1^2 < 0$, these states are unstable: no stress system exists which could maintain the crystal in such deformation state: as soon as one of the critical points is reached there has to be an immediate structure change so that the crystal reaches a new equilibrium; on the contrary, spinodal decomposition which involves diffusional processes cannot immediately reach the equilibrium.

6. Critical lines in the ($\eta_1$, $\eta_3$) planes.

To be able to determine the stresses associated with any deformation, it would be necessary to know completely the six variables function $W(\eta_1, \eta_2, \eta_3, \varepsilon_{23}, \varepsilon_{13}, \varepsilon_{12})$. However, the crystal behaviour under some particular stress orientations can be deduced from the energy calculations already mentioned and, in particular, from the quantities $W(\eta_1, \eta_3)$ where $\eta_3$ is any of the five quantities $\eta_2, \eta_3, \varepsilon_{23}, \varepsilon_{13}, \varepsilon_{12}$.

6.1 CRITICAL LINES IN THE ($\eta_1$, $\eta_3$) PLANE. — We first consider the addition of a (110) [1T0] shear $\eta_3$ to a deformation along the minimum energy path. The state of the crystal is represented by $\eta_1, \eta_3$ and $\eta_2 = \varepsilon_{23} = \varepsilon_{13} = \varepsilon_{12} = 0$. The stress tensor maintaining the crystal in this state of deformation is known from the derivatives of the crystal energy with respect to deformations. Relation 8 gives, when using definition 12 of $d\eta_1$ and $d\eta_3$:

$$dW = W(\eta_1 + d\eta_1, \eta_3 + d\eta_3) - W(\eta_1, \eta_3) = (\sigma_{11} + \sigma_{22} - 2\sigma_{33}) \frac{k}{\sqrt{6}} d\eta_1 +$$

$$+ (\sigma_{11} - \sigma_{22}) \frac{1}{\sqrt{2}} d\eta_3 +$$

$$\frac{1}{2} (d\sigma_{11} + d\sigma_{22} - 2d\sigma_{33}) \frac{k}{\sqrt{6}} d\eta_1 +$$

$$+ \frac{1}{2} (d\sigma_{11} - d\sigma_{22}) \frac{1}{\sqrt{2}} d\eta_3. \quad (33)$$

For $\eta_3 = 0$ the hydrostatic $(\sigma_{11} + \sigma_{22} - 2\sigma_{33})$ and shear stresses $\sigma_{23}, \sigma_{13}, \sigma_{12}$ are zero as well as $(\sigma_{11} - \sigma_{22})$. At a point $(\eta_1, d\eta_3)$ close to the minimum energy path we have also:

$$\begin{cases} d\sigma_{11} + d\sigma_{22} + d\sigma_{33} = 0 \\ d\sigma_{11} + d\sigma_{22} - 2d\sigma_{33} = 0 \\ d\sigma_{23} = d\sigma_{13} = d\sigma_{12} = 0, \end{cases}$$

and, thus, the applied stress tensor has the form:

$$\begin{bmatrix} -\sigma + d\sigma' & 0 & 0 \\ 0 & -\sigma - d\sigma' & 0 \\ 0 & 0 & 2\sigma \end{bmatrix}. \quad (34)$$

It is the sum of a stress tensor of type (24) and of a $\{110\} <1T0>$ shear stress $d\sigma'$. The energy variation is:

$$dW = W(\eta_1, d\eta_3) - W(\eta_1, 0) = d\sigma' \left(\frac{1}{\sqrt{2}} d\eta_3\right). \quad (35)$$

From the expression of the matrix of elastic coefficients of a quadratic structure we know that this energy variation is also:

$$dW = (C_{11} - C_{12}) \left(\frac{1}{\sqrt{2}} d\eta_3\right)^2. \quad (36)$$

Thus:

$$d\sigma' = (C_{11} - C_{12}) \left(\frac{1}{\sqrt{2}} d\eta_3\right). \quad (37)$$

The behaviour of $W(\eta_1, \eta_3)$ is such that it is possible
to write with a good accuracy for finite deformations \( \eta_3 \):

\[
\sigma_{11} - \sigma_{22} = 2(C_{11} - C_{12}) \frac{\eta_3}{\sqrt{2}}.
\]

(38)

Numerical calculations show that the deviation from this relation decreases from less than 10 \(\%\) (for deformations \( \eta_3 \sqrt{2} \) up to 4 \(\%\)) in the vicinity of the bcc phase, to 0.03 \(\%\) (for \( \eta_3 \sqrt{2} \leq 6 \)) near the fcc phase.

The stability of the equilibrium of the crystal in the deformation state defined by \( \eta_1 \) and \( \eta_3 \) is determined by the sign of the two main second derivatives which are the eigenvalues of the \( 2 \times 2 \) matrix:

\[
\begin{bmatrix}
\frac{d^3W}{d\eta_1^2} & \frac{d^2W}{d\eta_1 d\eta_3} \\
\frac{d^2W}{d\eta_3 d\eta_1} & \frac{d^2W}{d\eta_3^2}
\end{bmatrix}
\]

(39)

If one of the two main second derivatives vanishes, equilibrium becomes unstable. We have made the numerical calculation of these main second derivatives and, thus, determined two critical lines in the plane \((\eta_1, \eta_3)\) where one of these vanishes. The critical lines are represented on figure 9 by curves 1 and 1'; the range of values of \( \eta_3 \) for which these lines have been calculated corresponds to a deformation \( \eta_3 \sqrt{2} \) as large as the Bain deformation \( k/6 = (\log 2)/6 = 0.115 \). The critical lines cross the \( \eta_1 \) axis at the points \( \eta_{1c} \) (bcc \( \rightarrow \) fcc) and \( \eta_{1c}' \) (fcc \( \rightarrow \) bcc) already discussed. On this axis the \( 2 \times 2 \) matrix (39) reduces to the diagonal form:

\[
\begin{bmatrix}
\frac{k}{\sqrt{6}} & 0 \\
0 & C_{11} - C_{12}
\end{bmatrix}
\]

(40)

Remember that \( K' \) and \( C_{11} - C_{12} \) are functions of \( \eta_1 \). At the critical points it is \( K' \) which vanishes; figure 6 shows that \( (C_{11} - C_{12}) \) is never equal to zero.

It is possible to show that the critical lines cross the \( \eta_1 \) axis perpendicularly. For this we look for the expression of the second derivatives matrix at a point \((\eta_1, d\eta_3)\) close to the axis \( \eta_1 \). Assuming that \( W(\eta_1, \eta_3) \) is three times derivable with respect to \( \eta_1 \) and \( \eta_3 \), this matrix writes:

\[
\begin{bmatrix}
\frac{d^2W}{d\eta_1^2} + \frac{d^2W}{d\eta_3^2} & \frac{d^2W}{d\eta_1 d\eta_3} \\
\frac{d^2W}{d\eta_3 d\eta_1} & \frac{d^2W}{d\eta_3^2} + \frac{d^3W}{d\eta_1 d\eta_3 d\eta_3}
\end{bmatrix}
\]

(41)

\( W(\eta_1, \eta_3) \) is symmetric with respect to the axis \( \eta_1 \):

\[
W(\eta_1, \eta_3) = W(\eta_1, -\eta_3)
\]

so that:

\[
\frac{dW}{d\eta_3} = 0, \quad \frac{d^3W}{d\eta_3^3} = 0, \quad \frac{d}{d\eta_3} \left( \frac{d^2W}{d\eta_1^2} \right) = 0
\]

at \( \eta_3 = 0 \).

The matrix of second derivatives is then, at first order in \( \eta_3 \):

\[
\begin{bmatrix}
\frac{d^2W}{d\eta_3^2} & \frac{d}{d\eta_3} \left( \frac{d^2W}{d\eta_1 d\eta_3} \right) \\
\frac{d}{d\eta_3} \left( \frac{d^2W}{d\eta_1 d\eta_3} \right) & \frac{d^2W}{d\eta_3^2}
\end{bmatrix}
\]

(43)

This is a matrix of the type:

\[
\begin{bmatrix}
A & dC \\
dC & B
\end{bmatrix}
\]

(44)

The eigenvalues \( \lambda \) are the solutions of the equation:

\[
(\lambda - A)(\lambda - B) - (dC)^2 = 0.
\]

(45)

Then:

\[
\lambda = \frac{1}{2} (A + B) \pm \frac{1}{2} [(A - B)^2 + 4(dC)^2]^{1/2}.
\]

(46)

We are interested in the shape of the critical lines, that is in the variations of the main second derivatives near the critical points \( \eta_{1c} \) and \( \eta_{1c}' \); at these points \( A = 0 \) and the corresponding eigenvalue at \( \eta_{1c} + d\eta_3 \) or \( \eta_{1c}' + d\eta_3 \) is:

\[
\lambda = \frac{B}{2} \left( 1 - \left[ 1 + 4\left( \frac{dC}{B} \right)^2 \right]^{1/2} \right) \approx \frac{(dC)^2}{B}.
\]

(47)

The eigenvalue which is zero at \( \eta_{1c} \) or \( \eta_{1c}' \) varies only by a second order term in \( d\eta_3 \); this means that the critical line crosses the \( \eta_1 \) axis perpendicularly. Figure 9 shows that, in fact, the critical lines remain perpendicular to the axis \( \eta_1 \) even for the large values of \( \eta_3 \). This is an important point of the present study: it shows that the addition of a \( \{110\} \{110\} \) shear stress \( \sigma' \) to the stress tensor (24) does not make the deformation state of the crystal come nearer or further from the critical line. The occurrence of the phase transformation is indifferent to \( \sigma' \) and to the \( \{110\} \{110\} \) shear it produces. What is important is \( \eta_1 \) (Bain path) and the associated stress tensor (24).

This can be applied to Bogers and Burgers [6] deformations to make an estimate of the critical shear of dense planes \{110\} in the bcc phase and \{111\} in the fcc phase. It can be assumed that \( \eta_{1c} \) and \( \eta_{1c}' \) are approximately halfway between a minimum (bcc or fcc) and the maximum of the energy curve, the maximum itself being close to \( \eta_3 = 0.5 \). In the plane \((\eta_1, \gamma')\) of figure 3 a displacement normal to the first diagonal is a \{110\} \(<110>\) shear of the bct cell. The
critical lines, if drawn on figure 3, would be perpendicular to the first diagonal and a B. & B. path, for instance (0, 0) → (0, 1) → (1, 1), would cross the first critical line at \( \gamma = 0 \) and \( \gamma' \) around 0.5. This critical deformation is thus half of that envisaged by B. & B. (point (0, 1)). The same would apply to symmetric and reverse paths. Such a critical deformation can be realized by partial dislocations regularly spaced between \{110\} planes with a Burgers vector \((a_{\text{bcc}} < 110>)/16\) instead of \((a_{\text{bcc}} < 110>)/8\). Similarly, in the fcc phase, the critical shear on \{111\} planes could be due to \((a_{\text{fcc}} < 112>)/30\) partial dislocations between every \{111\} plane; such dislocations would of course, require, much less energy than those proposed by B. & B.

6.2 CRITICAL LINES IN THE OTHER \((\eta_1, \eta_2)\) PLANES. — We have examined the crystal behaviour when a \(\eta_3\) deformation is added to a deformation along the minimum energy path. The same analysis could be made in the deformation planes \((\eta_1, \epsilon_{13})\) (or \((\eta_1, \epsilon_{23})\)) and \((\eta_1, \epsilon_{12})\). The corresponding critical lines are again normal to the \(\eta_1\) axis and cannot be distinguished on figure 9 from those drawn for \(\eta_3\). It follows that the shears \(\epsilon_{13}\) (or \(\epsilon_{23}\)) and \(\epsilon_{12}\) do not play any important part in the transformation initiation.

The situation is different for deformations which involve imposed volume changes. The particular role of hydrostatic stress and strain arises because of the existence of a non-zero off-diagonal term \(K_2\) between \(\eta_1\) and \(\eta_2\) in the matrix of elastic coefficients deduced from (18). The critical lines in the plane \((\eta_1, \eta_2)\) are not perpendicular to the \(\eta_1\) axis and, thus, hydrostatic stresses must have an influence on the occurrence of the phase change. With potential I the addition of a hydrostatic pressure on the fcc structure will displace the point representing the deformation towards the critical line and, thus, help the fcc → bcc transition. It must be noted, however, that pressures must be very high to have a significant effect. For instance, if only a hydrostatic pressure were applied on the fcc phase (\(\sigma\) in tensor (24) equal to zero) the volume decrease at the transition point would be of the order of 25 % and the pressure which could produce the transformation would be as large as 30 GPa. Of course these numbers must be regarded only as indicative and do not represent the precise behaviour of any particular metal or alloy.

The critical lines discussed above are the intersections of a critical hypersurface in the six dimension space \((\eta_1, ..., \eta_6)\) with the planes \((\eta_i, \eta_j)\) with \(i = 2, ..., 6\). Considering the very simple shape of these intersections, it is not expected that the critical hypersurface presents any remarkable anomalies which would not leave any trace on the five planar intersections. However, it would be of interest to know the critical surface on some particular paths, for instance on the \{112\} \(<110>\) shear of the bcc structure; this deformation is the usual twinning shear of bcc crystals and is very close to the « special phonon vibration mode » discussed by Nagasawa, Nakanishi and Enami [17].

7. Comparison with a martensitic nucleation model (Foos, Frantz and Gantois [18]).

We have studied the problem of a crystal submitted to homogeneous deformations, which allows derivation of associated stresses and thus stability discussion. In this framework, it is shown that what is important for the bcc – fcc transformation is the amount of tetragonal distortion defined by \(\eta_1 = (\log c/a)/\log \gamma/2\). The other deformation components have no, or little, effect. In real crystals deformations are not homogeneous, but this analysis can apply to deformations slowly varying with the atomic distance, either static around defects, or dynamic for long wave lattice vibrations.

Foos et al. [18] propose, for ordered Fe₃Pt alloys, a martensite nucleation model by tetragonal distortion of the high temperature fcc cell. Note that in the following the fcc cell is taken as reference and its tetragonal distortion transforms it into a face-centred-tetragonal structure with \(c/a\) ratio decreasing to \(1/2\) for bcc. This elastic deformation is completely equivalent to that used above. The elastic coefficients and lattice distortion notation refer now to the fcc structure. Their X-ray and electron microscopy observations show, as pre-martensitic phenomena, an increase of the amplitude of \{110\} \(<110>\) transverse vibrations when the temperature is decreased. They propose that the tetragonal distortion necessary to produce the transformation is obtained by adding two \{110\} \(<110>\) shears of same amplitude on two planes at 60°.

Consider the effect of the first \{110\} \(<110>\) shear on the fcc cell, a \((0\bar{1}\bar{1}) [011]\) shear for instance; it can be decomposed into two parts:

\[
\begin{bmatrix}
0 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{bmatrix}
= \frac{\epsilon_{13}}{2} \begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -2
\end{bmatrix} + \frac{\epsilon_{12}}{2} \begin{bmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 0
\end{bmatrix}
\]

and it is the sum of a tetragonal distortion and of a \((110) [1\bar{1}0]\) shear; when referring to the bcc cell this latter shear is \(\epsilon_{12}\). If the amplitude of the \((0\bar{1}\bar{1}) [011]\) shear is large enough the tetragonal distortion can reach the critical point \(\eta_{1c}\). We have seen that the additional \((110) [1\bar{1}0]\) shear is of no importance. As proposed by Foos et al. [18], it is energetically more favourable to combine a \((0\bar{1}\bar{1}) [011]\) and a \((10\bar{1}) [101]\) shear of the same amplitude : the \((110) [1\bar{1}0]\) components cancel and the result is a pure tetragonal distortion which is situated on the minimum energy path. Measurements of the tetragonality ratio \(q = a_{\text{cel}}/c_{\text{cel}}\)
have been made at different temperatures. At first
order, the relation between \( q \) and \( \eta_1 \) writes:

\[
\frac{q - \sqrt{2}}{1 - \sqrt{2}} = 1 - \eta_1.
\]

(49)

At \(-195^\circ\text{C}\) and \(-235^\circ\text{C}\) the mean values of \( q \) are
0.96 and 0.92 which correspond to \((1 - \eta_1)\) equal to
0.14 and 0.27 respectively. This is quite of the same
order of magnitude as the critical value \((1 - \eta_{1c})\)
which must be around 0.25 in general and that we
find equal to 0.35 with potential I. In these conditions
it is quite conceivable that the crystal deformation
crosses the critical hypersurface in a region where two
long wave \{110\} \(\langle 110 \rangle\) phonons add. It seems impor-
tant to remark that in this scheme \{110\} \(\langle 110 \rangle\) phonons are not soft modes, or that the elastic coefficient
\(1/2(C_{11} - C_{12})\) associated with a \(\{110\} \langle 110 \rangle\)
shear, is not zero. But what becomes soft is the addi-
tion of two such phonons; the elastic coefficient which
becomes zero is \(K' = (K_1 - K_2^2/K_3)\) (relation 32)
associated with the quadratic distortion; this coeffi-
cient vanishes at the critical point.

8. Conclusion.

In this paper we have calculated the energy variations
of a crystal submitted to various homogeneous deforma-
tions which can transform a bcc into a fcc structure
(or a fcc into a bcc). Particular attention must be
brought to the choice of the pair potential which must
ensure mechanical stability of both structures; in our
calculation we have used three potentials which satisfy
this condition.

We have first determined the energy in all deforma-
tion states obtained by varying the angles \(\theta\) and \(\theta'\)
of the elementary tetrahedron. For each couple \((\theta, \theta')\)
the volume is that for which the crystal energy is mini-
imum. The choice of variables \(\theta\) and \(\theta'\), or equivalently
\(\gamma\) and \(\gamma'\), is made by reference to the Rogers and Bur-
gers mechanism: the deformations considered by these
authors are two perpendicular straight lines in the
plane \((\gamma, \gamma')\). It can be remarked that the calculation
gives information on all double « shear » mechanisms
which, like B. & B. model, begin with a \(\{110\} \langle 110 \rangle\)
shear for the bcc \(\rightarrow\) fcc transformation, and with a
\(\{111\} \langle 112 \rangle\) twinning shear for the fcc \(\rightarrow\) bcc
transformation. When examining equal energy lines it
appears that the B. & B. paths are not associated with
any special feature of the energy surface as would be
expected from the hard-sphere model: in this frame-
work B. & B. paths give the minimum volume increase
and are, thus, naturally regarded as « easy » paths. The
only remarkable path on the surface \(W(\gamma, \gamma')\) is the
line \(\gamma = \gamma'\). It is situated in the symmetry plane of the
energy surface and along it the crystal is kept in a bct
structure. Since a displacement from any point of the
line, and perpendicular to it, increases the energy, it
has been called a « minimum energy path ». It follows
that this path gets through a saddle point between the
two local minima bcc and fcc. No other saddle
point is found over the large range of values of \(\gamma\)
and \(\gamma'\) explored. The saddle point energy is much lower
than that of the points considered by B. & B. as natural
intermediates.

To know whether the line \(\gamma = \gamma'\) remains a mini-
imum energy path when any kind of deformation is
considered, we have made a change of variables in the
deformation space to express the elastic energy of the
distorted tetragonal structure in its simplest form. To
second order the energy of a distorted bct structure
intermediate between bcc and fcc is obtained by adding
to the undistorted bct structure energy \(W(\eta_1)\) (where
\(\eta_1 = (\log c/a)/(\log \sqrt{2})\) only second order terms:
the first order volume term is zero because of the
minimization mentioned above and all other first
order terms vanish for symmetry reasons. The calcu-
lated elastic coefficients associated with deformations
leaving \(\eta_1\) unchanged have been found positive for all
three potentials; thus, for these potentials the line
\(\gamma = \gamma'\) remains a minimum energy path with respect
to any kind of deformation. In general it is not a very
restrictive requirement for a potential to give positive
elastic constants for all points \(\eta_1\) between 0 and 1,
since the potential must in any case satisfy this condi-
tion at both ends \(\eta_1 = 0\) and \(\eta_1 = 1\) in order to have
stable bcc and fcc phases. We have computed the five
cross sections \(W(\eta_1, \eta_2)\), where \(\eta_1\) are the five other
deformation variables beside \(\eta_1\); no sign of any other
minimum energy path appears on these intersections.
Another minimum energy path, if any, would not
have the symmetry properties of the one discussed in
this paper.

To follow the minimum energy path one must apply
a stress tensor of the form:

\[
\begin{bmatrix}
-\sigma & 0 & 0 \\
0 & -\sigma & 0 \\
0 & 0 & 2\sigma
\end{bmatrix}
\]

The crystal energy \(W(\eta_1)\) of the intermediate bct
structures presents two minima for \(\eta_1 = 0\) (bcc) and
\(\eta_1 = 1\) (fcc) separated by a maximum. The value of
\(\sigma\) is proportional to the slope of this curve and thus \(|\sigma|\)
is maximum at the inflexion points. The part of the
curve situated between the two inflexion points cor-
responds to deformation states in which the crystal
cannot be held. The inflexion points define critical
states for the triggering of the transformation. The
critical stresses are found to be lower than the crystal
theoretical shear strength.

The addition on the bct structures of one of the
shear deformations \(\{110\} \langle 110 \rangle\) \(\langle \eta_3, \epsilon_{23}, \epsilon_{13}, \epsilon_{12} \rangle\)
does not modify the position of the critical point:
the planes \((\eta_1, \eta_2)\) (for \(\eta_1 = \eta_3\), or \(\epsilon_{23}\), or \(\epsilon_{13}\),
or \(\epsilon_{12}\)) have been drawn the critical lines which are
the intersections with these planes of the critical hyper-
surface in the six dimension deformation space; it is
shown that these lines cross the $\eta_1$ axis perpendicularly; for the potential used, they remain perpendicular to this axis for deformations $\eta_i$ up to some per cent. This means that what is important for the triggering of the martensitic transformation is only the amount of tetragonal distortion and not the additional shears. This can be illustrated, for instance, in the case of the Bogers and Burgers model: the partial dislocations regularly spaced between dense planes could initiate the transformation with a Burgers vector half of that proposed by these authors.

Contrary to shears, volume changes $\eta_2$ due to hydrostatic stresses have an effect on the critical point: in the plane $(\eta_1, \eta_2)$ the critical lines are not perpendicular to the axis $\eta_1$ and with potential $I$, for instance, the fcc $\rightarrow$ bcc transformation should be facilitated by the application of a hydrostatic pressure.

Finally, the comparison with the Foos et al. work indicates that the analysis presented here could have some relevance with experimental facts: the mean values of tetragonal distortion measured by these authors, values which are of the order of the critical strain calculated here, are quite compatible with their martensite nucleation model for Fe$_3$Pt alloy.

References