Absence of Metastable States in Strained Monatomic Cubic Crystals

Michael J. Mehl, Aarón Aguayo, and Larry L. Boyer

Center for Computational Materials Science, Naval Research Laboratory, Washington, D.C. 20375-5345

Romeo de Cos

Departamento de Física Aplicada, Centro de Investigación y de Estudios Avanzados, A.P. 73 Cordemex 97310 Mérida, Yucatán, México

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A tetragonal (Bain path) distortion of a metal with an fcc (bcc) ground state will initially cause an increase in energy, but at some point along the Bain path the energy will again decrease until a local minimum is reached. Using a combination of parametrized tight-binding and first-principles LAPW calculations we show that this local minimum is unstable with respect to an elastic distortion, except in the rare case that the minimum is at the bcc (fcc) point on the Bain path. This shows that body-centered tetragonal phases of these materials, which have been seen in epitaxially grown thin films, must be stabilized by the substrate and cannot be free-standing films.

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I. INTRODUCTION

The concept of the tetragonal distortion of a face-centered cubic lattice into a body-centered cubic lattice, as well as the reverse transformation, was introduced by Bain in 1924 as a model for the formation of Martensite in steels. Although this model is not exactly correct, the concept of the “Bain path” has been useful in investigating the behavior of element and compound metallic systems. This usefulness has increased with the development of total energy electronic structure methods, which can investigate regions of the Bain path not accessible by experimental methods. By following the Bain path from fcc to bcc, Mehl and Boyer 3 (in the following referred to as MB) showed that the fcc elements aluminum and iridium are elastically unstable in the bcc phase, i.e., the Bain path reaches a local maximum at the position of the bcc lattice. Wills, et al. 4 did first-principles calculations of the Bain path of gold and platinum which showed that these elements were also unstable in the bcc phase. In addition they used the reverse Bain path, from bcc to fcc, to show that tantalum and tungsten were elastically unstable in the fcc phase. Craievich, et al. 5, 6 looked at the fcc elements nickel and rhodium, which were unstable in the bcc state, and the bcc elements cobalt, chromium, molybdenum, niobium, tantalum, and vanadium, which were elastically unstable in the fcc state. Jona and Marcus showed that both bcc copper 7 and palladium 8 are also elastically unstable along the Bain path. Even metals which are only metastable in the fcc phase, e.g., cobalt, manganese, osmium, rhenium, ruthenium, titanium, and hafnium 5, 9, 10, are elastically unstable to Bain path distortions in the bcc phase.

The above lists demonstrate that for elements to the right of the alkaline earths on the periodic table, a stable or metastable fcc (bcc) phase implies an elastically unstable bcc (fcc) phase. This, however, does not end the search for metastable phases along the Bain path. As noted by Craievich, et al. 3 the existence of a minimum and a local maximum in the Bain path implies the existence of another local minimum. This minimum must be outside the classical Bain path from fcc to bcc, though this does not preclude the existence of yet another minimum between fcc and bcc. MB 3 found a local minimum in the extended Bain path of aluminum by compressing along the [001] direction until c/a = 0.567, where c/a = 1 is the fcc phase and c/a = 1/√3 the bcc phase. Iridium was found to have a minimum at c/a = 0.566. These minima are very close to the special value c/a = 1/√3 ≈ 0.577, where the body-centered tetragonal lattice is 10-fold coordinated (bct10). Similar minima are found for copper 7, 11 gold 12 palladium 8 and fcc titanium 5, 13. This crystal structure has been observed in the α phase of protactinium and in the β phase of mercury 14 and was given the Strukturbericht designation A6 15.

For bcc crystals, the local minimum is at c/a > √2, where c/a = 1 is the bcc lattice and c/a = √2 is the fcc lattice. Sliwko, et al. 16, 17 found a local minimum in vanadium at c/a ≈ 1.8. There is no increased coordination at this site. Experimentally this structure is observed in indium 14 and has the Strukturbericht designation A6 15.

Given the increased coordination near the secondary minimum in the Bain path for fcc crystals, one is tempted to conclude that this state is metastable. This turns out not to be the case. As found by Boyer 18 there is an orthorhombic “magic strain” (properly, Physically Allowed Lattice-Invariant (PALI) strain) which transforms one fcc lattice into another fcc lattice. A similar orthorhombic magic strain transforms one bcc lattice into another. MB showed that the magic strain path for fcc aluminum passes through the secondary minimum of the aluminum Bain path, and that, when viewed in the space of the orthorhombic strains, this point is actually a saddle point and hence unstable. In terms of the elastic constants, C11 − C12 for the secondary minimum is negative. Jona and Marcus demonstrated this instability by direct calculation of the elastic constants of copper 7 and palladium 8.
at the secondary Bain path minimum.

The concept of magic strains was generalized by Van de Waal and applied to the study of metastable structures in various systems, including silicon and model two-dimensional lattices. In this paper we use the formalism to show that the secondary minimum along the Bain path of an elemental fcc or bcc solid is unstable with respect to an orthorhombic shear. We note that this need not be the case for more complicated unit cells – the metastable BCT5 state of silicon was found using the concept of magic strains. The magic strain formalism is a useful tool for searching for metastable structures. Indeed, this paper can be considered to be a search for metastable states due to orthorhombic distortions of stable fcc and bcc crystals. In this case, however, we will show that there are no such states.

In Section II we show an extension of the Bain path for both fcc and bcc metals. In Section III we show the construction of the orthorhombic strains required for fcc → fcc and bcc → bcc magic strains and explore large regions of strain space using parametrized fits to first-principles results via the NRL Tight-Binding method. These results show that, within the tight-binding model of fcc and bcc metals the Bain path minima discussed above are elastically unstable. In Section IV we employ first-principles density functional theory methods to directly compute the elastic constants for structures at the secondary Bain path minimum. These more accurate results show that such structures are indeed elastically unstable. We conclude in Section V with a brief summary and discussion of our results.

II. EXTENDING THE BAIN PATH

We can represent the Bain path of an elemental compound by the standard body-centered tetragonal unit cell,

\[
\begin{pmatrix}
    a_1 \\
    a_2 \\
    a_3
\end{pmatrix} = \begin{pmatrix}
    -\frac{1}{2} a & \frac{1}{2} a & \frac{1}{2} c \\
    \frac{1}{2} a & -\frac{1}{2} a & \frac{1}{2} c \\
    \frac{1}{2} a & \frac{1}{2} a & -\frac{1}{2} c
\end{pmatrix} \cdot \begin{pmatrix}
    \hat{x} \\
    \hat{y} \\
    \hat{z}
\end{pmatrix}.
\]  

(1)

If \(c = a\) in (1) we have a bcc lattice, while if \(c = \sqrt{2} a\) we have an fcc lattice. Alternatively, we can represent the Bain path using a face-centered cubic unit cell,

\[
\begin{pmatrix}
    a_1 \\
    a_2 \\
    a_3
\end{pmatrix} = \begin{pmatrix}
    0 & \frac{1}{2} a' & \frac{1}{2} c \\
    \frac{1}{2} a' & 0 & \frac{1}{2} c \\
    \frac{1}{2} a' & \frac{1}{2} a' & 0
\end{pmatrix} \cdot \begin{pmatrix}
    \hat{x} \\
    \hat{y} \\
    \hat{z}
\end{pmatrix},
\]  

(2)

where

\[a' = \sqrt{2} a.\]

(3)

Thus when \(c = a'\) we have an fcc lattice, while when \(c = a'/\sqrt{2}\) we have a bcc lattice. We stress that (1) and (2) are different representations of the same lattice. In this case, the unit cell represented by (2) is related to the one represented by (1) by a rotation of 45° about the z axis.

To illustrate our techniques we begin with platinum, which has an equilibrium fcc structure. Fig. I shows the energy along the platinum Bain path as a function of \(c/a\). The total energy of the system was evaluated using the NRL tight-binding parameters for platinum, with a Fermi broadening temperature of 5 mRy. By comparing with smaller k-point meshes, we estimate that the numerical error in the calculation of the total energy was less than 0.1 mRy for \(c/a < 1.5\), and less than 0.2 mRy over the entire range of Fig. I

As expected, the global minimum in Fig. I is at the fcc position, \(c/a = \sqrt{2}\). (Obtaining this result was considered a necessary condition to show k-point convergence.) As for other fcc elements there is a local minimum near the bct10 structure, which is at \(c/a = \sqrt{2/3} \approx 0.816\) using representation (1). Both protactinium and the β phase of mercury exist in stable or metastable configurations near this bct10 structure.

In a similar way we can study the extension of the Bain path for an element with a bcc ground state. This is most easily done starting with the face-centered primitive
FIG. 2: Bain path for tungsten using the tight-binding parameters and $k$-points described in the text. The notation is the same as in Fig. 1.

vectors [2], constructing a regular $k$-point mesh at $c = a'$, (the fcc lattice), again using space group $I4/mmm - D_{17}^{4h}$. We use a mesh with 4069 points in the irreducible part of the Brillouin zone. Figure 2 shows our results for tungsten, using our tight-binding parameters. We note that there is a local minimum near $c/a' = 1.15$. This minimum is required by the continuity of $E(c/a)$, since we know that the fcc structure of tungsten is elastically unstable and so a local maximum. Unlike the case of the strained fcc elements, there is no high-coordination structure near this point. Interestingly, we do see a small shoulder in the energy-strain curve at the location of the bct$_{10}$ structure. Experimentally, Indium exists in this structure, with $c/a' = 1.08$.14

III. ORTHORHOMBIC STRAINS

In the previous section we saw that the extension of the Bain path has a secondary minimum for elements with either fcc or bcc ground states. It is natural to ask whether or not this secondary minimum is in fact metastable. Here we show a procedure, based on MB, which answers this question, and, in the process shows that there is no evidence such a metastable state exists for any element at zero temperature.

A. Elements with an fcc ground state

The first check in determining the metastability of the bct structure in Fig. 1 would be to look at long-wavelength distortions of the unit cell, i.e., the elastic constants. We will, in fact, use the technique outlined in MB which will allow us to look at general strains about the bct position.

We begin by writing the primitive vectors for an arbitrary body-centered orthorhombic unit cell in a form reminiscent of [11]:

$$
\begin{pmatrix}
  a_1 \\
  a_2 \\
  a_3
\end{pmatrix} = \left( \frac{V}{4} \right)^{\frac{1}{2}} \begin{pmatrix}
  -x & y & z \\
  x & -y & z \\
  x & y & -z
\end{pmatrix} \begin{pmatrix}
  \hat{x} \\
  \hat{y} \\
  \hat{z}
\end{pmatrix},
$$

where $V$ is the volume of the unit cell, and

$$
x = \exp[r \cos(\theta + 2\pi/3)]
$$

$$
y = \exp[r \cos(\theta - 2\pi/3)], \text{ and}
$$

$$
z = \exp[r \cos(\theta)],
$$

so that $xyz = 1$ for all values of $(r, \theta)$. We immediately see that the energy of this unit cell, $E(V, r, \theta)$, is periodic in $\theta$ with period $2\pi/3$, and that $r = 0$ represents the bcc lattice for all values of $\theta$. Furthermore, in the special cases $\theta = (0, 2\pi/3, -2\pi/3)$ the orthorhombic lattice becomes tetragonal, with the tetragonal axis in the $z$, $x$, or $y$ direction, respectively. These lines are just the extended Bain path of the system, stretched along the [001], [100], or [010] direction. We find the face-centered cubic lattice when $r = (\ln 2)/3$ along any of these paths.
We used our platinum tight-binding parameters to map the energy surface $E(V, r, \theta)$ of (1), minimizing the total energy with respect to volume at each point $(r, \theta)$. The space group is now $Immm-D_{2h}^{23}(\#71)$, and we used a mesh of 3925 $k$-points in the irreducible Brillouin zone. The results are shown in Fig. 3. In particular, we note that along each Bain path, there is a saddle point about 5 mRy above the fcc ground state. These points represent the same lattice as the local minimum structure in Fig. 2. We see that this point is unstable with respect to an orthogonal distortion, which means that a least one linear combination of the lattice constants of the tetragonal structure must be negative. To see which one, let $a_0$ and $c_0$ be the lattice constants representing the secondary minimum in the Bain path using the primitive vectors (1). For a crystal with an fcc ground state and a maximum at the bcc position, we will have $c_0/a_0 < 1$, though this is not necessary for the following analysis. If we use (4) and (5) to represent this structure we have

\[ V = V_0 = 1/2 a_0^2 c_0 , \]
\[ r = r_0 = 2/3 \ln c_0/a_0 , \]
\[ \theta = \theta_0 = 0 . \]

Let us fix the volume and expand $r = r_0 + 2\alpha$ and $\theta$ about the equilibrium point. Then to first order in $\alpha$ and $\theta$, (1) becomes

\[
\begin{pmatrix}
  a_1 \\
  a_2 \\
  a_3 \\
\end{pmatrix} = \begin{pmatrix}
  -\frac{1}{2} a_0 (1 - \alpha + \beta) \\
  \frac{1}{2} a_0 (1 - \alpha + \beta) \\
  \frac{1}{2} a_0 (1 - \alpha + \beta) \\
\end{pmatrix} \begin{pmatrix}
  \frac{1}{2} a_0 (1 - \alpha - \beta) \\
  \frac{1}{2} a_0 (1 - \alpha - \beta) \\
  \frac{1}{2} a_0 (1 - \alpha - \beta) \\
\end{pmatrix} \begin{pmatrix}
  \hat{x} \\
  \hat{y} \\
  \hat{z} \\
\end{pmatrix},
\]

where

\[ \beta = \sqrt{3} r_0 \theta / 2 . \]

In terms of the standard elastic strain parameters for the body-centered tetragonal lattice we have

\[ e_1 = -\alpha + \beta , \quad e_2 = -\alpha - \beta , \quad e_3 = 2\alpha , \]
\[ e_4 = e_5 = e_6 = 0 . \]

The lowest order contribution to the elastic energy associated with this strain is

\[ \Delta E = V [(C_{11} + C_{12} - 4C_{13} + 2C_{33})\alpha^2 + (C_{11} - C_{12})\beta^2] . \]

If this structure was stable, the coefficients of the $\alpha^2$ and $\beta^2$ terms should be positive, in agreement with Born and Huang’s derivation of the elastic stability criteria. We note that keeping $\theta = 0$ and varying $\alpha$ moves the lattice along the Bain path. Since the point $\alpha = 0$ is a minimum along that path, the first linear combination of elastic constants must be positive. However, as seen in Fig. 3, fixing $\alpha = 0$ and varying $\theta$ (and therefore $\beta$) lowers the energy, implying that $C_{11} - C_{12} < 0$.

\[ \beta = \sqrt{3} r_0 \theta / 2 . \]

In analogy with (1), there are three Bain paths along the directions $\theta = (0, \pm 2\pi/3)$, but now $r = 0$ is an fcc lattice, and at the special value $r = (\ln 2)/3$ along any one of the Bain paths we find a bcc lattice.

Using the tungsten tight-binding parameters, we choose to describe the space group for $I\bar{4}m\bar{m}-D_{2h}^{23}(\#69)$. We use a mesh of 7813 $k$-points in the irreducible part of the Brillouin zone. The results of the calculation are shown in Fig. 3. The saddle points located along the extended Bain path, approximately 30 mRy above the ground state, represent the same structure as the local minimum found in Fig. 2. We can determine the nature of the elastic instability here in a manner similar to Sec. III A. Let $a_0'$ and $c_0'$ specify the local minimum on the Bain path in Figs. 2 and 4 using the primitive vectors (2). In terms of (4), this occurs at

\[ V = V_0 = 1/4 a_0^2 c_0 , \]
\[ r = r_0 = -2/3 \ln c_0/a_0 , \]
\[ \theta = \theta_0 = 0 . \]

Taking $r = r_0 + 2\alpha$ and expanding the lattice parameters in powers of $\alpha$ and $\theta$, we find that (1) can be written as

\[
\begin{pmatrix}
  a_1 \\
  a_2 \\
  a_3 \\
\end{pmatrix} = \begin{pmatrix}
  V / 2 \\
  0 \\
  0 \\
\end{pmatrix} + \begin{pmatrix}
  x \\
  y \\
  z \\
\end{pmatrix} ,
\]

where $V$ is the volume of the unit cell and

\[ x = \exp[-r \cos(\theta + 2\pi/3)] , \]
\[ y = \exp[-r \cos(\theta - 2\pi/3)] , \]
\[ z = \exp[-r \cos \theta] . \]
FIG. 4: Map of the total energy of the lattice (11) for tungsten, using the NRL tight-binding parameters, choosing the minimum energy volume at each point. The origin of the graph is the fcc lattice, the heavy straight lines radiating from the lattice are the Bain paths, and the lighter straight lines are the extensions of the Bain path. The labels indicate the orientation of the tetragonal axis along each Bain path. The contour interval is 2 mRy, and the energy of the fcc structure is 35.8 mRy above the energy of the bcc structure. The coordinates \((r, \theta)\) are described in (12).

To lowest order, the elastic strain parameters are

\[
e_1 = \alpha + \beta, \quad e_2 = \alpha - \beta, \quad e_3 = -2\alpha, \quad e_4 = e_5 = e_6 = 0,
\]

where \(\beta\) is defined in (3). Thus the elastic energy associated with this strain is identical to (10), and, once again, we see that at the Bain path minimum \(C_{11} - C_{12} < 0\).

IV. ELASTIC CONSTANTS OF THE STRUCTURES AT THE BAIN LOCAL MINIMA

In the previous section we showed that for typical fcc and bcc structured elements the secondary minima in the Bain path, as shown in Figs. 1 and 2, are actually saddle points in the space defined by the orthorhombic unit cells (4) and (11). From Figs. 3 and 4 we see that the only elastically stable structures along the Bain path are the fcc and bcc lattices. In rare cases both of these structures may be minima on the Bain path. In this section we will check this conjecture via first principles density functional theory calculations using the Linearized Augmented Plane Wave (LAPW) method as implemented...
TABLE I: Position of the secondary minimum along the extended Bain path, c/a, for the elemental metals which have fcc or bcc ground states. We also show the energy difference between the phases. All calculations were done by minimizing the total energy as a function of volume for fixed c/a, using the primitive vectors in (1). Energy differences are in mRy. Note that for strontium the secondary minimum coincides with the bcc lattice, and for barium the minimum coincides with the fcc lattice.

| Metal | Equil. | c/a | |E_{bcc} - E_{fccc}| |E_{bcc} - E_{bct}| |E_{fccc} - E_{bct}| |
|-------|--------|-----|----------------|----------------|----------------|
| Al    | fcc    | 0.814 | 7.287 | 1.544 | 5.743 |
| Ag    | fcc    | 0.894 | 2.404 | 0.164 | 2.240 |
| Au    | fcc    | 0.852 | 1.785 | 0.307 | 1.478 |
| Ba    | bcc    | 1.414 | 1.060 | 1.060 | 0.000 |
| Ca    | fcc    | 0.911 | 1.648 | 0.175 | 1.473 |
| Cu    | fcc    | 0.935 | 2.706 | 0.033 | 2.673 |
| Ir    | fcc    | 0.801 | 48.997 | 23.684 | 25.313 |
| Mo    | bcc    | 1.765 | 30.301 | 23.450 | 6.851 |
| Nb    | bcc    | 1.787 | 24.186 | 10.245 | 13.941 |
| Pd    | fcc    | 0.876 | 3.752 | 0.405 | 3.347 |
| Rh    | fcc    | 0.814 | 26.468 | 10.644 | 15.824 |
| Sr    | fcc    | 0.707 | 0.730 | 0.000 | 0.730 |
| V     | bcc    | 1.799 | 18.330 | 7.332 | 10.998 |
| W     | bcc    | 1.687 | 36.471 | 29.195 | 7.276 |

TABLE II: Elastic constants of at the secondary minimum in the Bain path for the elements described in Table I with \( C' = (C_{11} - C_{12})/2 \). All elastic constants are computed using the orientation and unit cell described by (1), and are expressed in GPa.

| Metal | Equil. | \( C' \) | \( C_{66} \) |
|-------|--------|----------|----------|
| Al    | fcc    | -18      | 127      |
| Ag    | fcc    | -56      | 133      |
| Au    | fcc    | -40      | 177      |
| Cu    | fcc    | -11      | 227      |
| Ir    | fcc    | -69      | 689      |
| Mo    | bcc    | 94       | -112     |
| Nb    | bcc    | 82       | -65      |
| Pd    | fcc    | -6       | 241      |
| Rh    | fcc    | -36      | 498      |
| V     | bcc    | 53       | -39      |
| W     | bcc    | 75       | -140     |

in the Wien code\(^{30}\) with the generalized gradient approximation (GGA) exchange correlation functional of Perdew, Burke, and Ernzerhof.\(^{31}\)

We begin by determining the position of the secondary minimum in the Bain path for cubic elemental metals. In Fig. 6 we show the results for several of the elemental bcc metals. In all cases there are two minima in the calculation, one at the bcc site and one at or beyond the fcc position on the Bain path. The results are shown in Table II where the ratio c/a is determined using the representation of the body-centered tetragonal lattice in (1). With the exceptions of barium and strontium, all of the metals shown here have a secondary minimum of the type described in Sec. III if the ground state is fcc, the minimum is at c/a < 1, while if the ground state is bcc, the minimum is at c/a > \( \sqrt{2} \). Barium and strontium are unique in that the secondary minimum is at the fcc point on the Bain path for barium, as shown in Fig. 5, and the at the bcc point for strontium. We will not consider these elements further in this paper.

For the remaining elements we compute the elastic constants of the tetragonal system using standard techniques\(^{7,28}\) using the primitive vectors (1) to describe the lattice. We present the results of our calculations in Table II. As predicted, all of the fcc ground state elements have \( C' = (C_{11} - C_{12})/2 < 0 \) at the secondary minimum, and all bcc ground state elements have \( C_{66} < 0 \), in agreement with the predictions of Sec. III.

V. SUMMARY

As noted in the introduction, it has previously been shown that the secondary minimum is elastically unstable in aluminum\(^{8}\) copper\(^{9}\), iridium\(^{7}\) and palladium.\(^{32}\) To our best knowledge the stability or instability of the secondary minimum of a bcc element has never before been determined. The calculations done here show that if the energy along the Bain path for a metal is at a minimum at the fcc (bcc) structure and a maximum at the bcc (fcc) structure, then there is a secondary minimum with a bct structure with is elastically unstable.

The implication of this work is that there can be no free standing body-centered tetragonal structures for these metals. Any bct structures observed, such as in thin films\(^{13}\) must be stabilized by an external force. In the case of epitaxially grown thin films, this force is presumably supplied by the substrate. For sufficiently thick films this supporting force will be insufficient to stabilize the bct structure, and the film will revert to its ground state, as Bencok et al.\(^{33}\) observed for thin vanadium films grown on Fe(100).

While we have not discussed the case of hcp metals such as titanium, where epitaxial bct structures are observed,\(^{33}\) we note that the minimum energy bcc structure of Ti is known to be elastically unstable.\(^{34}\) The conclusions of this paper thus apply to Ti as well.

Acknowledgments

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