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Structural properties of copper

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First-principles total-energy calculations on the tetragonal states of bulk elemental copper have been made with a full-potential electronic structure program with both the local-density approximation (LDA) and the generalized gradient approximation (GGA). The unique path through tetragonal states produced by epitaxial strain on equilibrium states has been found. This path, called the epitaxial Bain path, shows that body-centered cubic Cu (at axial ratio $c/a=1$) is unstable, but a shallow energy minimum exists for a body-centered tetragonal (bct) state with axial ratio $c/a=0.93$. Structure parameters and elastic constants of both the face-centered cubic (fcc) ground state and the bct state are determined and the fcc values are compared to experiment: the GGA results are better than the LDA results. The procedures for evaluating the three fcc elastic constants and the six tetragonal elastic constants are described in detail. Tests of the stability of the bct phase at $c/a=0.93$ show that this phase, although stable with respect to tetragonal deformations, is unstable with respect to [110] shear in the (001) plane. A lower-energy body-centered orthorhombic phase is found that may be metastable.

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I. INTRODUCTION

The electronic and structural properties of elemental Cu have been studied extensively, both theoretically and experimentally, in the past fifteen to twenty years. Fueling some of those studies was the controversy that was started by a claim of Kang *et al.*[1] about double minima in the energy-volume curve of a body-centered cubic (bcc) structure of copper. That claim was later disproven, but it generated several interesting reports of calculations of lattice parameters and elastic constants of both the stable face-centered-cubic (fcc) and a hypothetical metastable bcc phase of Cu.[2–10]

The calculations were made with different theoretical methods: mostly the full potential linearized augmented plane wave (FLAPW), both semirelativistic and nonrelativistic, in the local-density approximation (LDA) and in the generalized gradient approximation (GGA), but also with plane waves and pseudopotentials, Gaussian orbitals, etc. The calculations found either the total energy versus volume or the total energy at constant volume versus the axial ratio c/a of the body-centered-tetragonal (bct) unit cell that characterizes both the fcc structure ($c/a=\sqrt{2}$) and the bcc structure ($c/a=1$). Almost all the older reports quote values for the lattice constant of bcc Cu that range between 2.80 and 2.87 Å, although some of them state that bcc Cu is unstable,[5,6,10] and two of them find shallow minima at $c/a<1$, i.e., $c/a=0.95$[8] and $c/a=0.92$,[10] in the curve of energy versus c/a at constant experimental volume.

These theoretical results stimulated a number of experimental attempts at stabilizing bcc Cu at room temperature by pseudomorphic epitaxy. Ultrathin films of Cu were grown on different substrates, and the structure of the films was studied by quantitative low-energy electron diffraction (QLEED)[11–14] or by STM.[15] The substrates were chosen in such a way as to minimize the mismatch between the lattice constant of the substrate surface and the lattice constant of bcc Cu as predicted by the theoretical calculation mentioned above. Copper films grown on Pd{001} and Pt{001} were found to have a bct structure derived from strained fcc,[12,13] while Cu films grown on Fe and Ag{001}[11,14] were judged to have some small regions of a highly strained bcc structure, although the lattice parameters were tagged with an unusually large experimental error. That *unstable* bcc Cu could possibly grow epitaxially on Ag{001} was explained[5] by the fact that while the shear constant $C'\equiv(c_{11}-c_{12})/2$, which would oppose sliding of {110} planes, was found to be negative, the shear constant c_{44}, which opposes sliding of {001} planes, is finite. Then it was suggested that the epitaxial constraint of the films by the substrate would prevent {110} planes from sliding on each other.

The STM experiment involved ultrathin films of Cu on Pd {001}[15] and was interpreted as revealing the presence of a high-coverage metastable bct phase and a low-coverage strained fcc phase. However, both these claims were found to be incorrect by Jeong,[8] who stated that the high-coverage phase should be assigned to strained fcc, while the interpretation of the low-coverage phase as strained fcc implies a vanishing Poisson ratio and is therefore unacceptable.

Recently new experiments have been reported in the literature in which regions of ''bcc Cu'' were identified.[16–18] In contrast to the experiments mentioned above, these experiments were not done for the specific purpose of stabilizing the metastable phase of Cu—but rather involved the growth of multilayers of Cu with Nb. Such multilayers are notable in that they exhibit high mechanical strengths which increase with decreasing thickness of the individual layers. The multilayers were polycrystalline, but electron microscopy and electron diffraction detected the presence in the thinner Cu layers of a crystalline phase that was labeled strained bcc Cu.

The present work verifies that bcc Cu is tetragonally unstable and finds a bct state at $c/a<1$ that is tetragonally stable by calculation of the epitaxial Bain path (EBP) of Cu with the WIEN97 computer program.[19] The EBP[20,21] is a path through tetragonal states which passes through all tetragonal equilibrium states, where the energy is a minimum, and through tetragonal states produced by epitaxial (biaxial) strain of the equilibrium states. The EBP has been used previously to locate equilibrium states of bct Co,[21,22] V,[23] and fcc Ti.[24]

In addition to locating the two equilibrium states of Cu at the two minima of energy on the EBP, we calculate the three elastic constants of fcc Cu, which we compare with experiment, and the six elastic constants of the bct state. The six elastic constants are then used to check the four stability conditions of a tetragonal structure. The interesting result is that the bct state fails one stability condition, hence is not truly metastable. A step toward locating a truly metastable phase is taken by following a path through orthorhombic states leading to an energy minimum, whose metastability is not yet established.

We describe in Sec. II the procedure followed for the calculations, the results and their comparison with those published in the literature; in Sec. III, a discussion of the conclusions; and in an Appendix the details of the procedures followed for the determination of elastic constants.

II. CALCULATIONS AND RESULTS

The WIEN97 program[19] uses the FLAPW method and can calculate total energies for a variety of crystal structures and space groups with a choice of nonrelativistic (NREL) or relativistic (REL) calculations in either the LDA or the GGA approximation. The program was implemented and executed on a LINUX-based desktop PC. All calculations discussed in this paper were done twice, once with the NREL-LDA and once with the REL-GGA formulation.

The structures considered for the construction of the EBP all had a bct cell with parameters a (the edge of the primitive square base) and c (the height of the cell). The procedure was as follows: a value of a was chosen and several calculations of the total energy were done for a series of values of c. (Energy will throughout mean the energy per atom.) Usually, five values of c would be chosen in such a way that the corresponding energies would straddle a minimum. A least-squares fit of a cubic polynomial to the five calculated values then gave the minimum energy and the value of c that corresponds to the minimum energy.

This procedure produces values of a and c on the EBP which can be plotted as c vs. a, or c vs. c/a. The procedure is then repeated for values of a usually spaced about 2% apart. About 22 to 25 values of a would be chosen to cover the range of c/a values from 0.8 to 1.6. The resulting plot of c vs. c/a is depicted in the top panel of Fig. 1 for both LDA and GGA.

For each (a,c) pair we also plot the energy versus c/a, relative to the ground state, as shown in the middle panel of Fig. 1. This plot gives three important pieces of information: (1) the curves (for LDA and GGA) have a deep minimum at $c/a = 1.417$, very close to the value $c/a = \sqrt{2}$, corresponding to the fcc ground state of Cu. The energy minima are $-3310.060\,442$ Ry for the GGA and $-3275.878\,584$ Ry for the LDA formulation. (2) There is a maximum at $c/a = 1$, confirming the fact that the bcc phase is tetragonally unstable. (3) A shallow, higher minimum is found at $c/a = 0.936$ for LDA and at $c/a = 0.927$ for GGA. This minimum is about 3 mRy/atom higher than that of the stable phase, and *may* be a metastable phase of Cu.

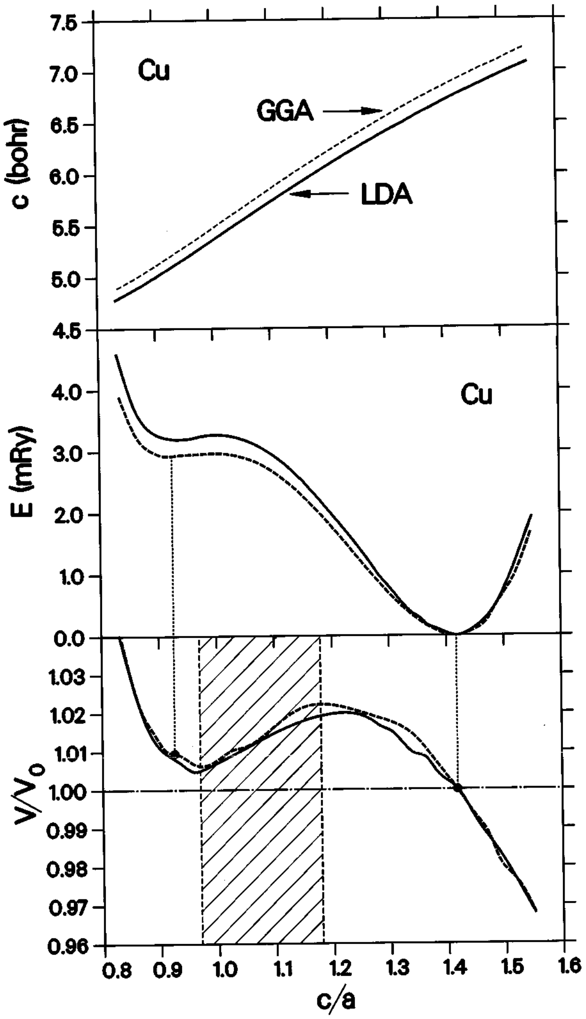

FIG. 1. Epitaxial Bain Path of Cu: solid curves were calculated with the LDA approximation, dashed curves, with the GGA approximation. Top panel: tetragonal parameter c vs. c/a. Middle panel: Energy per atom vs. c/a referred to zero at the equilibrium fcc phase ($c/a = \sqrt{2}$). Lower panel: Normalized volume (V/V_0) vs. c/a, where the reference volume V_0 is the theoretical volume per atom of the equilibrium fcc phase of Cu.

It may be worth emphasizing that this curve is *not* a plot of the energy vs. c/a at constant volume, as commonly displayed in many other publications, since here the volume changes along the curve, and at each a has the value of the volume per atom ($V = a^2c/2$) that corresponds to the minimum energy. Constant-volume curves find approximate values of the equilibrium c/a values, but the EBP is needed to find the correct c/a and the equilibrium volume.

A useful aspect of the EBP is produced by plotting the magnitude of V/V_0 as a function of c/a, as done in the bottom panel of Fig. 1: V_0 is the *theoretical* value of the volume of the unstrained stable phase (at $c/a = \sqrt{2}$). The points corresponding to the unstrained stable phase and the bct phase at $c/a = 0.93$ are marked with solid circles (only for the GGA calculation, to avoid complicating the plot). The

TABLE I. Lattice parameters and elastic constants of fcc Cu and bct Cu: a_0' and c_0' are the parameters of the bct unit cell, in Å units; V is the volume per atom, in Å^3; the c_{ij} are elastic constants, in Mb; $B=(c_{11}+2c_{12})/3$ is the bulk modulus, in Mb; $C'=(c_{11}-c_{12})/2$ is the shear modulus, in Mb. The values of B and C' given in the first two columns and in the Expt. column were calculated from the corresponding values of c_{11} and c_{12} in order to allow direct comparison with the data reported by others in the literature. For both fcc and bct Cu the present calculations were done with the WIEN97 (FLAPW) program (Ref. 19) both in the nonrelativistic local-density approximation (LDA) and in the relativistic generalized-gradient approximation (GGA). The column headings of the literature data are the initials of the authors of the references cited in the footnotes. The experimental data stem from Pearson (Ref. 29) for the lattice constants (room-temperature values), and from Simmons and Wang (Ref. 30) for the elastic constants (0 K values).

	fcc Cu									bct Cu Theory This work	
	Theory										
	This work		Literature data								
	LDA	GGA	CC	LWZ	KMMS	J	MP	WS	Expt.	LDA	GGA
a_0'	2.514	2.568							2.556	2.892	2.968
$c_0'=c_0$	3.563	3.639	3.62^a	3.61^b 3.56^c	3.58^d	3.61^e	3.52^f	3.52^g 3.61^h	3.615	2.708	2.750
c_0'/a_0'	1.417	1.417							1.414	0.936	0.927
V	11.26	12.00							11.81	11.33	12.11
c_{11}	2.256	1.897					1.56^f		1.762		
c_{12}	1.537	1.282					1.06^f		1.249		
c_{44}	1.156	0.944			0.86^d		0.80^f	0.82^g	0.818		
B	1.777	1.487	1.88^a	1.62^b 1.83^c	1.53^d	1.66^e		1.90^g	1.420		
C'	0.360	0.308			0.272^d			0.271^g	0.257		
c_{11}										1.609	1.245
c_{12}										1.752	1.631
c_{13}										1.681	1.394
c_{33}										1.937	1.580
c_{44}										1.212	0.975
c_{66}										1.365	1.314

[a] Reference 3, pseudopotential Gaussian orbitals, Hedin-Lundqvist parameterization.

[b] Reference 4, nonrelativistic FLAPW, LDA, Wigner exchange-correlation (*xc*).

[c] Reference 4, semirelativistic FLAPW, LDA, Wigner *xc*.

[d] Reference 5, NR full-potential linear muffin-tin orbital, Ceperley-Alder *xc*, and Vosko-Wilk-Nusair parametrization.

[e] Reference 8, plane wave, Ceperly-Alder *xc* and Perdew-Zunger parametrization.

[f] Reference 9, LAPW, Hedin-Lundqvist, *xc*.

[g] Reference 10, FLAPW, WIEN95, LDA, Perdew-Wang *xc*.

[h] Reference 10, FLAPW, WIEN95, GGA, Perdew-Wang *xc*.

shaded area, covering the range of positive slope of the EBP, indicates a region in which the strain energy is not positive definite, i.e., a region of states that are intrinsically unstable with respect to tetragonal deformations.[20] The portion of the EBP on the right of the unstable region defines the strained states that can be obtained by pseudomorphic epitaxy of the stable phase on substrates that preserve the tetragonal structure. The portion on the left of the unstable region serves the same purpose for strained states of the bct phase at $c/a=0.93$.

The numerical results are summarized in Table I, where a_0' denotes the specific values of a of the bct cell for the two equilibrium states, and c_0' denotes the corresponding values of the c parameter. Related values taken from the literature are also listed for comparison.

Table I also shows the values of elastic constants, both for the stable fcc phase (which can be compared with the available experimental data) and for the possibly metastable bct phase. Determination of the elastic constants requires knowledge of the curvature of the energy curve as a function of strain for selected deformations of the unit cell. Some of these deformations change the volume of the unit cell, but maintain the tetragonal symmetry, whereas others break the tetragonality. The formulas and procedures for the calculations of elastic constants are given and discussed in the Appendix.

III. DISCUSSION

For fcc Cu both the NREL-LDA and the REL-GGA produce lattice parameters a_0', c_0', and atomic volume V in good agreement with the experimental values: 1.6, 1.4, and 4.7% low, respectively, for the LDA, and 0.5, 0.7, and 1.6% high, respectively, for the GGA. The theoretical values found in the literature for c_0' are also in good agreement with the experimental counterpart (0 to about 3% low).

For the elastic constants the agreement with the experimental values is less good: 20 to 40% high for the LDA and 3 to 15% high for the GGA. Thus the agreement with experiment for the GGA is better in the present case than for the LDA. This conclusion, however, does not have general validity, e.g., in the case of Pd we find that the LDA is better, overall, than the GGA.

Comparison of elastic constants with the theoretical literature values is fairly limited, as most of the published data do not include individual c_{ij} values. A more extensive comparison can be made for the bulk modulus B, which is often reported in the literature and which we can calculate from our values of c_{11} and c_{12}: with respect to the experimental value our numbers for B are 25% (LDA) and 5% (GGA) high, while the theoretical values in the literature range from 8% to 34% high.

The overall reasonable agreement for fcc Cu of both the structural and the elastic calculated data with their experimental counterparts gives some confidence in the program and the procedures followed for the calculations. Thus, the present work confirms the fact that bcc Cu is tetragonally unstable.

Nevertheless, the bcc phase may possibly be stabilized, as mentioned in Sec. I, by pseudomorphic epitaxy. Thus, the QLEED and photoemission experiments of Li *et al.*[14] on ultrathin films of Cu on Ag{001} may have produced small regions of strained bcc Cu. Also, Heinrich *et al.*[25] claimed to have grown Cu{001} films as thick as ten layers on Fe{001}/Ag{001} in a ‘‘nearly perfect bcc structure.’’ These films were grown by molecular-beam epitaxy (MBE) and were found to have an in-plane lattice constant 1.2% larger than that of the Fe{001} layers (hence the Cu films were epitaxial, but not pseudomorphic). The bulk interlayer spacing was found to be close to that of Fe{001} or Ag{001}, but no quantitative measurements were made, hence the values of the axial ratio c/a and of the volume/atom cannot be determined and plotted on the EBP. Similarly, the experiments involving MBE-grown nanolayer composites of Cu and Nb[16–18] with Cu films thinner than 12 Å were claimed to have a ‘‘slightly distorted bcc structure.’’[16] But, again, no quantitative data for the lattice parameters were reported.

Another possible candidate for the stabilized phase in the above experiments is of course the bct phase found in this work at $c/a = 0.93$. A question that needs to be considered is whether this phase is truly metastable.

The stability of a crystalline phase requires that the strain energy be positive definite with respect to all strains, which, in turn, imposes restrictions on the elastic constants. For a tetragonal crystal these restrictions include the three listed by Nye[26] for hexagonal crystals (labeled Sc1,Sc2,Sc3 below) to which a fourth (Sc4) is added:

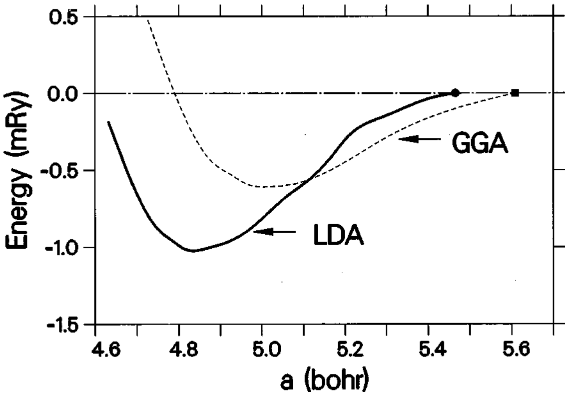

FIG. 2. Energy referred to the minimum of the bct phase of Cu at $c/a = 0.93$ vs. the a parameter of body-centered orthorhombic Cu as described in the text. The full circle and square mark the bct minima for LDA and GGA, respectively.

$$\left.\begin{array}{ll} c_{11} > |c_{12}| & (\mathrm{Sc1}) \\ (c_{11}+c_{12})c_{33} > 2c_{13}^2 & (\mathrm{Sc2}) \\ c_{44} > 0 & (\mathrm{Sc3}) \\ c_{66} > 0 & (\mathrm{Sc_4}) \end{array}\right\} \tag{1}$$

The elastic constants listed in Table I for the bct phase at $c/a = 0.93$ fulfill stability conditions (Sc2), (Sc3), and (Sc4), but not (Sc1), which fails by 9% (LDA) and 30% (GGA). This result states that there are deformations of the bct cell that would decrease the energy, indicating that the corresponding bct phase is unstable.

We can test whether in fact the energy of the bct phase can be decreased by appropriate deformations. The stability condition (Sc1) stems from the requirement for positive definiteness of the part of the strain energy expression that remains when only ϵ_1 and ϵ_2 vary

$$\frac{E}{V} = \frac{1}{2} c_{11}(\epsilon_1^2 + \epsilon_2^2) + c_{12}\epsilon_1\epsilon_2 . \tag{2}$$

This formula can be obtained from the general expression for the strain energy of a tetragonal crystal, given in Eq. (A17) in the Appendix, by choosing strains $\epsilon_1 \neq 0$ and $\epsilon_2 \neq 0$, and all other $\epsilon_i = 0$. Equation (2) has a minimum for

$$\frac{\epsilon_1}{\epsilon_2} = -\frac{c_{12}}{c_{11}}, \tag{3}$$

whence the strain ratio that decreases E most rapidly can be calculated from the data in Table I. We find, for the LDA results: $\epsilon_1/\epsilon_2 = -1.089$, and for the GGA results: $\epsilon_1/\epsilon_2 = -1.310$. Since $\epsilon_1 = \delta a/a$ and $\epsilon_2 = \delta b/b$, these strain ratios require for LDA: $\delta a = -1.089\delta b$, and for GGA: $\delta a = -1.310\delta b$.

We calculated the strain energy for a series of deformations fulfilling the above conditions, and found that in fact the energy decreases below the value of the bct minimum found in Fig. 1. Figure 2 shows that new minima are found about 1 and 0.6 mRy below the corresponding bct minima for LDA and GGA, respectively. The unit cells at the new minima are body-centered orthorhombic (bco) with parameters (in Å): $a=2.563$, $b=3.195$, $c=2.708$ for LDA, and $a=2.658$, $b=3.204$, $c=2.750$ for GGA. Thus, the edges of the bct cells are changed by about 10% and the volumes are decreased in order to reach the new minima.

Whether this bco state is metastable is not yet known. An analysis similar to that given above for the bct state, but more complicated by the lower symmetry, is required, which might find structural paths that further decrease the energy. However, eventually this downward sequence must end either in at least one metastable structure in which the energy is a minimum with respect to all small deformations or in the fcc ground state.

ACKNOWLEDGMENT

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APPENDIX

1. Elastic constants of the fcc phase

Along the EBP we consider bct states. Hence the procedure to find elastic constants at the equilibrium states is naturally formulated in the tetragonal axes. However, to determine elastic constants of the fcc phase we must keep in mind that the elastic constants are defined with respect to the *cubic* axes, while the deformations that we impose in order to calculate the elastic constants are described in the tetragonal axes. Hence, we need the relations between the elastic constants in the bct (or tetragonal) axes and those in the fcc (or cubic) axes.

The fcc unit cell has sides $a_0=b_0=c_0$ and elastic constants c_{ij}. The bct unit cell has sides $a_0'=a_0/\sqrt{2}$; $b_0'=a_0'$; $c_0'=c_0$; and elastic constants c_{ij}'. Figure 3 shows the relation between the fcc axes and the bct axes in the basal plane: the axes x_1 and x_2 of the fcc surface mesh are the cubic axes, the axes x_1' and x_2' are the tetragonal axes; x_3 and x_3' are the same.

In the cubic system there are three elastic constants: c_{11}, c_{12}, and c_{44}. The strain energy in the cubic axes around the equilibrium state is

$$\frac{E}{V}=\frac{1}{2}c_{11}(\epsilon_1^2+\epsilon_2^2+\epsilon_3^2)+c_{12}(\epsilon_2\epsilon_3+\epsilon_3\epsilon_1+\epsilon_1\epsilon_2)+\frac{1}{2}c_{44}(\epsilon_4^2+\epsilon_5^2+\epsilon_6^2), \tag{A1}$$

where V is the volume per atom and the c_{ij}'s and ϵ_i's are the elastic constants and strains in matrix notation [Ref. 26, pp. 133,134].

In the tetragonal system there are six elastic constants: c_{11}', c_{12}', c_{13}', c_{33}', c_{44}', and c_{66}', and the strain energy in the bct axes is

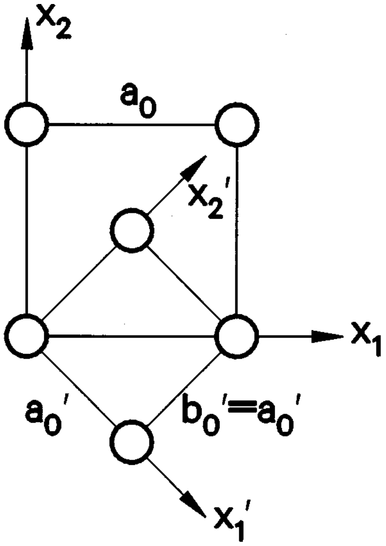

FIG. 3. Relation between the centered unit mesh (sides a_0) in the cubic axes x_1,x_2, and the primitive unit mesh (sides $a_0',b_0'=a_0'$) in the bct axes x_1',x_2'.

$$\frac{E}{V}=\frac{1}{2}c_{11}'(\epsilon_1'^2+\epsilon_2'^2)+c_{12}'\epsilon_1'\epsilon_2'+c_{13}'(\epsilon_1'\epsilon_3'+\epsilon_2'\epsilon_3')+\frac{1}{2}c_{33}'\epsilon_3'^2+\frac{1}{2}c_{44}'(\epsilon_4'^2+\epsilon_5'^2)+\frac{1}{2}c_{66}'\epsilon_6'^2. \tag{A2}$$

The relations between the strains ϵ_i' and the elastic constants c_{ij}' in the tetragonal axes to the strains ϵ_i and elastic constants c_{ij} in the cubic axes are given by the tensor transformation rules. These rules must be applied to the second-rank-tensor components of strain and fourth-rank-tensor elastic constants, i.e.,

$$\epsilon_{ij}'=\sum_{k,l=1}^{3}\chi_{ik}'\chi_{jl}'\epsilon_{kl}, \tag{A3}$$

$$c_{ijkl}'=\sum_{l,m,n,o=1}^{3}\chi_{il}'\chi_{jm}'\chi_{kn}'\chi_{lo}c_{lmno}, \tag{A4}$$

where χ_{ik}' is the cosine of the angle between axes $\mathbf{x}_i'$ and $\mathbf{x}_k$, i.e., the tensor transformation matrix is

$$\mathbf{x}'=\begin{pmatrix}\frac{\sqrt{2}}{2} & -\frac{\sqrt{2}}{2} & 0\\ \frac{\sqrt{2}}{2} & \frac{\sqrt{2}}{2} & 0\\ 0 & 0 & 1\end{pmatrix}. \tag{A5}$$

Summing the 9 terms in Eq. (A3) and the 81 terms in (A4), and converting back to matrix notation we find the relations

$$\left.\begin{array}{ll} \epsilon_1'=\frac{1}{2}(\epsilon_1+\epsilon_2+\epsilon_6); & \epsilon_2'=\frac{1}{2}(\epsilon_1+\epsilon_2-\epsilon_6);\\[2ex] \epsilon_3'=\epsilon_3; & \epsilon_4'=(\epsilon_4-\epsilon_5)\frac{\sqrt{2}}{2};\\[2ex] \epsilon_5'=(\epsilon_4+\epsilon_5)\frac{\sqrt{2}}{2}; & \epsilon_6'=-\epsilon_1+\epsilon_2, \end{array}\right\} \tag{A6}$$

and

$$\left.\begin{array}{ll} c_{11}'=\frac{1}{2}(c_{11}+c_{12})+c_{44}; & c_{12}'=\frac{1}{2}(c_{11}+c_{12})-c_{44};\\[1ex] c_{13}'=c_{12}; & c_{33}'=c_{11};\\[1ex] c_{44}'=c_{44}; & c_{66}'=\frac{1}{2}(c_{11}-c_{12}). \end{array}\right\}. \tag{A7}$$

From Eq. (A7) we select the repeated-index constants c_{11}', c_{33}', c_{66}', which are easier to evaluate than the mixed-index constants c_{12}', c_{13}'. Then the c_{ij} are found from

$$\left.\begin{array}{r} c_{11}=c_{33}',\\ c_{12}=c_{33}'-2c_{66}',\\ c_{44}=c_{11}'-c_{33}'+c_{66}'. \end{array}\right\}. \tag{A8}$$

We must therefore determine the three constants c_{11}', c_{33}', and c_{66}'. We consider the three determinations separately.

a. Determination of c_{11}'

Take $\epsilon_1'=(a'-a_0')/a_0'$ finite, but $\epsilon_i'=0$, $i=2$ to 6 in the energy in Eq. (A2) by changing a', but keeping b_0' and c_0' fixed. Then only the term in ϵ'^2 survives and

$$\begin{aligned} c_{11}' &= \frac{1}{V}\left(\frac{\partial^2 E}{\partial \epsilon_1'^2}\right)_{\epsilon_1'=0,\ i=2\ \text{to}\ 6}\\ &= \frac{a_0'^2}{V}\left(\frac{\partial^2 E}{\partial a'^2}\right)_{b_0',c_0'}\\ &= \frac{2}{c_0'}\left(\frac{\partial^2 E}{\partial a'^2}\right)_{b_0',c_0'}, \end{aligned} \tag{A9}$$

since $V=(a_0'^2c_0')/2$. Then Eq. (A9) applies to a general bct equilibrium state, stable or metastable. In the special case of the fcc structure, $c_0'=a_0'\sqrt{2}$ and Eq. (A9) becomes

$$c_{11}'=\frac{\sqrt{2}}{a_0'}\left(\frac{\partial^2 E}{\partial a'^2}\right)_{b_0',c_0'},\quad (\text{fcc structure}). \tag{A10}$$

Note that after this deformation the unit cell is no longer tetragonal, as the original square base is now rectangular. The strained cell can be considered either as body-centered orthorhombic (sides a', b_0', c_0') or as primitive triclinic (sides a', b_0', and the line joining the origin to the body-center atom).

Five energies at five values of a' around a_0' (the theoretical value of the unit-mesh edge at the energy minimum in the EBP) fitted to a cubic polynomial in a' yield the second derivative needed in Eq. (A10).

b. Determination of c_{33}'

Take $\epsilon_3'=(c'-c_0')/c_0'$ finite and $\epsilon_i'=0$, $i=1,2,4,5,6$, in the energy in Eq. (A2), so that only the term in $\epsilon_3'^2$ survives. Then as in Eq. (A9)

$$\begin{aligned} c_{33}' &= \frac{1}{V}\left(\frac{\partial^2 E}{\partial \epsilon_3'^2}\right)_{\text{other}\ \epsilon_i'=0}\\ &= \frac{c_0'^2}{V}\left(\frac{\partial^2 E}{\partial c'^2}\right)_{a_0',b_0'}\\ &= \frac{2c_0'}{a_0'^2}\left(\frac{\partial^2 E}{\partial c'^2}\right)_{a_0',b_0'}, \end{aligned} \tag{A11}$$

which, like Eq. (A10), applies to all tetragonal equilibrium states. For the fcc structure equation (A11) becomes

$$c_{33}'=\frac{2\sqrt{2}}{a_0'}\left(\frac{\partial^2 E}{\partial c'^2}\right)_{a_0',b_0'},\quad (\text{fcc structure}). \tag{A12}$$

Again the derivative in Eq. (A12) is evaluated by fitting a cubic to five values of E at values of c' around c_0'.

c. Determination of c_{66}'

Putting all $\epsilon_i'=0$ except ϵ_6' we find

$$c_{66}'=\frac{1}{V}\left(\frac{\partial^2 E}{\partial \epsilon_6'^2}\right)_{\epsilon_i'=0,\ i=1\ \text{to}\ 5}. \tag{A13}$$

To evaluate c_{66}' from Eq. (A13), observe that ϵ_6', a shear strain in the [110] direction, is given by the change in θ_{ab}, the angle between sides *a* and *b*,[27] with *a*,*b*,*c* held constant,

$$\epsilon_6'=\phi\equiv\frac{\pi}{2}-\theta_{ab}, \tag{A14}$$

and to first-order in ϕ all other strains vanish. Then from Eq. (A13)

$$\begin{aligned} c_{66}' &= \frac{1}{V}\left(\frac{\partial^2 E}{\partial \phi^2}\right)_{a_0',b_0',c_0',\theta_0'}\\ &= \frac{1}{V}\left(\frac{\partial^2 E}{\partial \theta'^2}\right)_{a_0',b_0',c_0',\theta_0'}\\ &= \frac{2}{c_0'a_0'^2}\left(\frac{\partial^2 E}{\partial \theta'^2}\right)_{a_0',b_0',c_0',\theta_0'} \end{aligned} \tag{A15}$$

and for the fcc structure

$$c'_{66}=\frac{\sqrt{2}}{a_0'^{3}}\left(\frac{\partial^2 E}{\partial \theta'^2}\right)_{a_0',b_0',c_0',\theta_0'},\quad (\text{fcc structure}). \tag{A16}$$

Thus, the original bct cell is strained to become body-centered monoclinic (not a Bravais lattice), which is best described as primitive triclinic with sides a_0',b_0' (angle θ'), and $c'=$distance between the origin and the body-center atom.

For the determination of c'_{66} we choose five values of θ' (around θ_0'); for each such value we find the parameters of the corresponding triclinic cell, and with these parameters we calculate the energy/atom. Fitting the five values of the energy to a cubic polynomial in θ' we determine the second derivative needed in Eq. (A15).

Finally, having found c'_{11}, c'_{33}, and c'_{66} we can calculate c_{11}, c_{12}, and c_{44} with Eq. (A8).

2. Elastic constants of the bct phase

The strain energy of a tetragonal crystal was written in Eq. (A2) with primed quantities because they were referred to tetragonal axes obtained by in-plane rotation of the cubic axes. We rewrite it here for convenience with unprimed quantities referred to the bct axes:

$$\frac{E}{V}=\frac{1}{2}c_{11}(\epsilon_1^2+\epsilon_2^2)+c_{12}\epsilon_1\epsilon_2+c_{13}(\epsilon_1\epsilon_3+\epsilon_2\epsilon_3)+\frac{1}{2}c_{33}\epsilon_3^2+\frac{1}{2}c_{44}(\epsilon_4^2+\epsilon_5^2)+\frac{1}{2}c_{66}\epsilon_6^2. \tag{A17}$$

Start from a bct unit cell in equilibrium with edges a_t and $b_t=a_t$ along the axes x_1 and x_2, and c_t along x_3. Apply equal strains along x_1 and x_2, so that $\epsilon_1=\epsilon_2=(a-a_t)/a_t$, all other strains being kept at zero. Then, as in Eq. (A9),

$$\begin{aligned} c_{11}+c_{12}&=\frac{1}{2V}\left(\frac{\partial^2 E}{\partial \epsilon_1^2}\right)_{\epsilon_i=0,\ i=3\ \text{to}\ 6}\\ &=\frac{a_t^2}{2V}\left(\frac{\partial^2 E}{\partial a^2}\right)_{c=c_t}\\ &=\frac{1}{c_t}\left(\frac{\partial^2 E}{\partial a^2}\right)_{c=c_t}, \end{aligned} \tag{A18}$$

since $V=(a_t^2c_t)/2$.

If only $\epsilon_1\neq 0$, as in Eq. (A9)

$$c_{11}=\frac{1}{V}\left(\frac{\partial^2 E}{\partial \epsilon_1^2}\right)_{\epsilon_i=0,\ i=2\ \text{to}\ 6}=\frac{2}{c_t}\left(\frac{\partial^2 E}{\partial a^2}\right)_{b_t,c_t}. \tag{A19}$$

Then Eqs. (A18) and (A19) together determine c_{12}.

If only $\epsilon_3=(c-c_t)/c_t\neq 0$, $\epsilon_i=0$, $i=1,2,4,5,6$, then, as in Eq. (A11)

$$c_{33}=\frac{1}{V}\left(\frac{\partial^2 E}{\partial \epsilon_3^2}\right)_{\epsilon_i=0,\ i=1,2,4,5,6}=\frac{2c_t}{a_t^2}\left(\frac{\partial^2 E}{\partial c^2}\right)_{a_t,b_t}. \tag{A20}$$

Having so far determined c_{11},c_{12},c_{33} we now proceed to determine c_{13}. We can do this in three ways, two ways requiring and one way not requiring the EBP.

(1) From the epitaxial condition, which holds along the EBP, we have

$$\sigma_3=c_{13}\epsilon_1+c_{13}\epsilon_2+c_{33}\epsilon_3=0, \tag{A21}$$

where $\epsilon_1=\epsilon_2$, hencel

$$\frac{\epsilon_3}{\epsilon_1}=\frac{a}{c}\frac{dc}{da}=-2\frac{c_{13}}{c_{33}}. \tag{A22}$$

But $\epsilon_3=dc/c_t$ and $\epsilon_1=da/a_t$ are related as follows

$$\epsilon_3=\frac{dc}{c_t}=\frac{a_t}{c_t}\left(\frac{dc}{da}\right)\epsilon_1 \tag{A23}$$

so that

$$c_{13}=-\frac{c_{33}}{2}\frac{a_t}{c_t}\left(\frac{dc}{da}\right)_{a=a_t}. \tag{A24}$$

(2) Another expression for c_{13} can be found as follows. Utilizing again the fact that for an epitaxial strain the out-of-plane stress vanishes (the condition along the EBP), we can rewrite the energy expression as follows[28]

$$\left.\begin{aligned} &E^{\text{EBP}}=VY'\epsilon_1^2\\ &Y'\quad\equiv c_{11}+c_{12}-2\frac{c_{13}^2}{c_{33}}, \end{aligned}\right\}. \tag{A25}$$

Now from Eq. (A25) we can calculate a value for Y' from the second derivative of the energy along the EBP at the equilibrium state

$$Y'=\frac{1}{c_t}\left(\frac{d^2E^{\text{EBP}}}{da^2}\right)_{a_t} \tag{A26}$$

and so from the second part of Eq. (A25)

$$c_{13}=\sqrt{(c_{11}+c_{12}-Y')\frac{c_{33}}{2}}. \tag{A27}$$

(3) A third way of determining c_{13}, which does not require knowledge of the EBP, is through an equation similar to Eq. (A18), viz.,

$$\begin{aligned} \frac{c_{11}+c_{33}}{2}+c_{13}&=\frac{1}{2V}\left(\frac{\partial^2 E}{\partial \epsilon_1^2}\right)_{\epsilon_1=\epsilon_3,\ \epsilon_2=\epsilon_4=\epsilon_5=\epsilon_6=0}\\ &=\frac{1}{c_t}\left(\frac{\partial^2 E}{\partial a^2}\right)_{\epsilon_1=\epsilon_3,\ \epsilon_2=\epsilon_4=\epsilon_5=\epsilon_6=0}, \end{aligned} \tag{A28}$$

where $\epsilon_1=\delta a/a_t=\epsilon_3=\delta c/c_t$ and all other ϵ_i's$=0$, i.e., a and c change by different amounts, and $b=a_t$.

Finally, c_{66} is found as in Eq. (A15) by varying θ_{ab}, the angle between sides a and b. Similarly, $c_{44}=c_{55}$ is found by varying θ_{bc}, the angle between sides b and c, by

$$\epsilon_4=2\epsilon_{23}, \tag{A29}$$

$$c_{44}=\frac{1}{V}\left(\frac{\partial^2 E}{\partial \epsilon_4^2}\right)_{\epsilon_i=0,\ i=1,2,3,5,6}=\frac{1}{V}\left(\frac{\partial^2 E}{\partial \theta_{bc}^2}\right)=\frac{2}{c_0' a_0'^2}\left(\frac{\partial^2 E}{\partial \theta_{bc}^2}\right). \tag{A30}$$

The structure is again treated as triclinic with $b=b_t$, $c=c_t$, angle θ_{bc} varying around 90°, and the distance to the center atom as the third side.

Special case of bcc phases

For a bcc phase, Eq. (A18) determines $C=c_{11}+c_{12}$, and Eq. (A20) determines $c_{33}=c_{11}$. Hence, we can calculate $c_{12}=C-c_{11}$. Since $c_{13}=c_{12}$, Eqs. (A24), (A27), and (A28) are three other ways to determine c_{12}. Thus, for a bcc phase we can calculate c_{12} in four different ways.

For c_{44} we note that $c_{44}=c_{66}$, hence we can follow the same procedure based on Eq. (A15) for the determination of c_{66}'.

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