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Elastic constants of Cu and the instability of its bcc structure

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First-principles full-potential nonrelativistic calculations of the total energy of fcc Cu for various deformations of the cubic unit cell give values of the three elastic constants of fcc Cu in good agreement with experiment. Use is made of simple formulas for the strain energy of tetragonal and trigonal deformations in terms of the elastic constants. The total energy of Cu as a function of the shape of a body-centered-tetragonal cell at constant volume does not have a minimum at the bcc structure, and it is concluded that bcc Cu is unstable with respect to [110] shears. However, this instability does not prevent epitaxial growth on (001) surfaces.

I. INTRODUCTION

The metastable crystalline phases of a given material are interesting because they correspond to new bonding arrangements and new properties of the same atoms, but have an analytic connection to the stable phase. Thus from a first-principles point of view, i.e., finding solutions of the Kohn-Sham equations with no adjustable parameters, such phases correspond to additional solutions of the same problem which are local minima of the total energy. Hence when a theoretical first-principles calculation in 1987,[1] extended in 1989,[2] found not just one, but two metastable phases of copper, considerable interest was aroused. The stable phase, face-centered-cubic (fcc) copper, is a well-studied metal experimentally and theoretically because it has the simplicity of cubic symmetry, does not have the complications of partially filled d shells and magnetic effects, and its calculated properties from first principles agree well with experiment, as they did in Refs. 1 and 2. So the extensions of the theory to these new metastable phases seemed to be reliable.

The new metastable phases of copper found in Refs. 1 and 2 were a body-centered-cubic (bcc) phase ($c/a = 1$) and a body-centered-tetragonal (bct) phase with $c/a = 1.12$, where c is the dimension of a tetragonal cell along the tetragonal axis, and a is the side of the square cross section (see Fig. 1).[3] The metastable phases were found to have energies per atom a few mRy higher than the fcc phase ($c/a = 1.41$).

The occurrence of the metastable bct phase near the bcc phase in the work of Ref. 2 produced a nonparabolic curve with a near double minimum in the total energy per atom E as a function of the volume per atom V for the bcc phase. This distortion led a number of workers to doubt the correctness of the result.[4–6] These workers showed by several independent methods that the $E(V)$ curve for bcc Cu was smooth without any indication of the distorted shape found in Ref. 2. Hence it was concluded that the bct phase was doubtful and probably an artifact of the computation in Refs. 1 and 2.

However, the work on bcc Cu, which established from several sources a consistent $E(V)$ curve with a single minimum and disposed of the bct metastable phase, left the impression that bcc Cu was itself a well-behaved metastable phase. The purpose of this paper is to show by first-principles calculations, which find the total energy for noncubic configurations, that bcc Cu is in fact unstable. The new calculations show that Cu at constant volume does not have a local minimum of E at the bcc structure, but is unstable with respect to shears of the (110) planes. This instability is apparent from the absence of a minimum in E as a function of c/a for a bct cell at constant V at the bcc structure; hence a transformation of the bcc structure exists along which E continuously decreases.

The new calculations were aided by work by Jansen,[7] who calculated E as a function of c and a for tetragonal Cu with the full-potential augmented-plane-wave (FLAPW) method. Jansen also found that E had no local minimum at the bcc structure.

The accuracy of the calculations of E for noncubic configurations are checked by finding the two shear moduli of fcc Cu as well as the bulk modulus and showing that the values compare well with experiment. The changes in E for distortions around cubic structures are given by simple expressions, which will be derived in the next section, that lead directly to the shear constants. It will be shown that changes in c/a and V provide orthogonal strain parameters in terms of which the strain energy δE is quadratic in the two strain parameters without a cross term between them.

The apparent existence of a metastable bcc phase in all the previous calculations with lattice constant 2.88 Å and a metastable bct phase with $a = 2.76$ Å in Ref. 2

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induced experiments which tried to grow these phases in coherent epitaxy[8] on Pd(001), which has a square surface mesh of side 2.75 Å. The structure of the film could then be determined by low-energy electron-diffraction (LEED) analysis. A coherent tetragonal epitaxial film did grow, whose structure was found, but strain analysis (based on linear elastic theory) suggested that the film should be described as a highly strained fcc phase, and not a strained bcc or bct phase.[9] This reluctance of Cu to grow in the bcc structure suggested the conclusion that bcc Cu was unstable, but the more careful study of this paper shows that such a conclusion is unwarranted. In fact, later epitaxial experiments[10] under the still more favorable conditions for growth of bcc Cu on Ag(001) (the side of the substrate square unit cell is 2.89 Å) appear to have grown bcc Cu, but in a rather disordered condition. The discussion section will explain why an unstable structure such as bcc Cu can still be grown epitaxially on (001) surfaces.

II. CRYSTAL STRAIN AND ELASTIC MODULI

The previous calculations on bcc and fcc Cu referred to above[4–6] all found E as a function of V, which gave in addition to the equilibrium lattice constant the bulk modulus

$$B = \left(V \frac{\partial^2 E}{\partial V^2} \right)_{V=V_0} , \tag{1}$$

where V_0 is the equilibrium volume per atom. To uncover the instability of bcc Cu requires calculating shear moduli, which are obtained from strain energy values δE for more general strains than volume strains. Simple formulas for δE for two strain configurations will permit evaluation of the two shear constants of a cubic structure directly from the curvature of a calculated function of one variable.

Consider two types of strain:

(1) Tetragonal strain around a cubic structure which changes the dimension along the [001] direction, i.e., the cell dimension c, and isotropically changes the dimension in the (001) plane, i.e., the side a of the square cross section. Figures 1(a) and 1(c) show both the top and the side views of the tetragonal unit cells for the bcc and the fcc structures, respectively.

(2) Trigonal strain which changes the cell dimension c along [111] and changes isotropically the cell dimension in the (111) plane, i.e., changes the side a of the rhombic cross section. Figures 1(b) and 1(d) show the unit cells used for trigonal strain.

In general, the strain energy density *around* a cubic structure of volume V_0 per atom and side a_0 can be written[11]

$$\frac{\delta E}{V_0} = \frac{c_{11}}{2}({\varepsilon_1}^2 + {\varepsilon_2}^2 + {\varepsilon_3}^2) + c_{12}(\varepsilon_2\varepsilon_3 + \varepsilon_3\varepsilon_1 + \varepsilon_1\varepsilon_2) + \frac{c_{44}}{2}({\varepsilon_4}^2 + {\varepsilon_5}^2 + {\varepsilon_6}^2), \tag{2}$$

where the ε_i, i=1–6, are the components of the strain tensor in the crystal axes (unit vectors in the [100], [010], [001] directions) in which the elastic stiffness tensor components c_{ij} have cubic symmetry and hence consist of just three independent constants c_{11}, c_{12}, c_{44}.[11]

For the tetragonal strain the strain components are already in the crystal axis system and there are no shear strains,

$$\varepsilon_1 = \varepsilon_2 = \delta a/a \, , \; \varepsilon_3 = \delta c/c \, , \; \varepsilon_4 = \varepsilon_5 = \varepsilon_6 = 0 \; , \tag{3}$$

and we have, on putting Eq. (3) into Eq. (2),

$$\frac{\delta E}{V_0} = (c_{11} + c_{12})\varepsilon_1^2 + 2c_{12}\varepsilon_1\varepsilon_3 + \frac{c_{11}}{2}\varepsilon_3^2 \, . \tag{4}$$

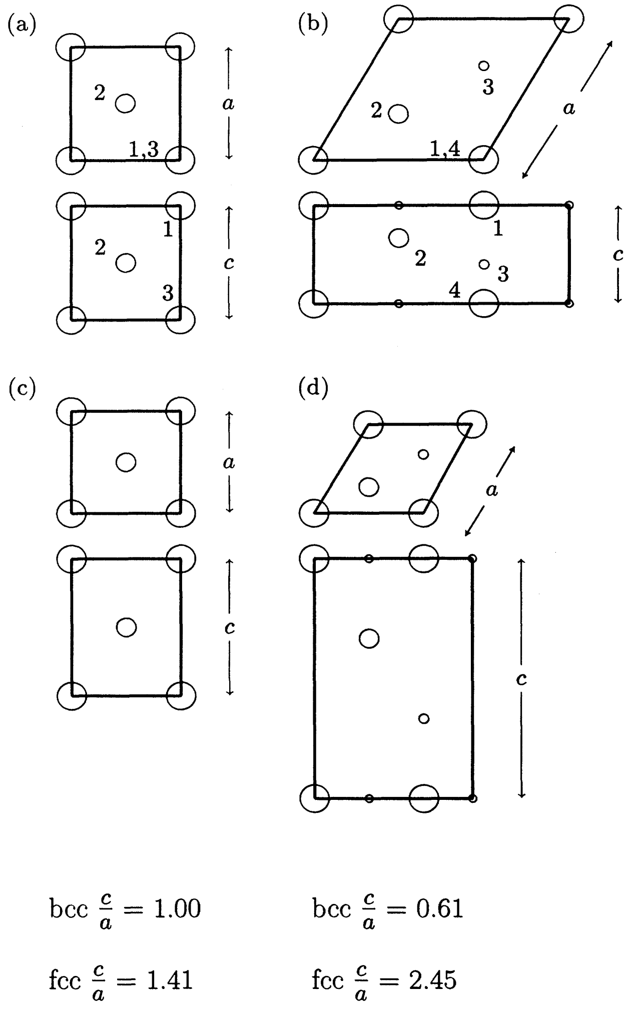

FIG. 1. Top and side views drawn to scale, all at the same volume per atom, of cells used for total-energy calculations: (a) tetragonal unit cell for bcc lattice, (b) trigonal unit cell for bcc lattice, (c) tetragonal unit cell for fcc lattice, and (d) trigonal unit cell for fcc lattice. Smaller circles represent atoms further from the plane of the plot (four sizes). For tetragonal strain, the c axis is parallel to the [001] direction. For trigonal strain, the a axis lies in the (111) plane and the c axis points into the [111] direction.

In terms of strain components $\delta a/a$ and $\delta c/c$, the quadratic form for δE in Eq. (4) has a cross term. But in terms of strain components

$$\frac{\delta V}{V} = 2\frac{\delta a}{a} + \frac{\delta c}{c}\ , \quad \frac{\delta(c/a)}{(c/a)} = \frac{\delta c}{c} - \frac{\delta a}{a}, \tag{5}$$

Eq. (4) becomes

$$\frac{\delta E}{V_0} = \frac{B}{2}\left(\frac{\delta V}{V}\right)^2 + \frac{2G}{3}\left(\frac{\delta(c/a)}{c/a}\right)^2 , \tag{6}$$

where $B = (c_{11} + 2c_{12})/3$ and $G = (c_{11} - c_{12})/2$ is the shear modulus for [110] shears, i.e., the modulus that resists sliding of (110) planes on each other.[11] Thus $\delta V/V$ and $\delta(c/a)/(c/a)$ are orthogonal strains for the strain energy of tetragonal distortions around a cubic structure.

The trigonal strain requires a more elaborate treatment, since the axes for c and a are not crystal axes. It is necessary to transform the strains in c and a to the crystal axes, where the elastic tensor has the symmetry of the crystal and is known. The tensor transformation rule is used to find the strain components in the crystal axes ε_i, i=1–6, in terms of the strain components in the surface axes (indicated by primes) ε'_i. The trigonal strain components in the surface axes are given by $\varepsilon'_1 = \varepsilon'_2 = \delta a/a$, $\varepsilon'_3 = \delta c/c$, $\varepsilon'_4 = \varepsilon'_5 = \varepsilon'_6 = 0$. The expressions for the ε_i in terms of the ε'_i are put into Eq. (2) to give δE (after some tedious algebra) in the form

$$\begin{aligned}\frac{\delta E}{V_0} = {}& \varepsilon_1'^2\left(\frac{2}{3}c_{11} + \frac{4}{3}c_{12} + \frac{2}{3}c_{44}\right)\\ &+ \varepsilon'_1\varepsilon'_3\left(\frac{2c_{11}}{3} + \frac{4c_{12}}{3} - \frac{4c_{44}}{3}\right)\\ &+ \varepsilon_3'^2\left(\frac{c_{11}}{6} + \frac{c_{12}}{3} + \frac{2c_{44}}{3}\right).\end{aligned} \tag{7}$$

If δE is now expressed in terms of strain parameters $\delta V/V$ and $\delta(c/a)/(c/a)$ using Eq. (5), δE simplifies to

$$\frac{\delta E}{V_0} = \frac{B}{2}\left(\frac{\delta V}{V}\right)^2 + \frac{2c_{44}}{3}\left(\frac{\delta(c/a)}{c/a}\right)^2 . \tag{8}$$

Equations (6) and (8) now give the shear moduli G and c_{44} directly from the curvature of calculated values of δE as a function of c/a at constant V around the values for the bcc and fcc structures.

III. CALCULATION PROCEDURE AND RESULTS

The total energies were calculated with the full-potential linear muffin-tin orbital method (FP-LMTO) (Ref. 12) using the Ceperley-Alder form of exchange-correlation potential[13] in the Vosko-Wilk-Nusair parametrization.[14] The **k**-space sampling was done on a uniform mesh of 288 **k** points in the irreducible part of the Brillouin zone (1/16th for the tetragonal cell, 1/12th for the trigonal cell). This mesh scales with the *distorted* lattice to take the variation in lattice axes into account. The **k** convergence was treated carefully. It turned out that approximately 160 **k** points are sufficient to have total energies converged to less than 0.1 mRy/atom. The results were obtained without relativistic corrections, since the relativistic corrections are known to introduce large errors in the bulk modulus (noted in Ref. 6, for example).

TABLE I. Lattice constants and elastic constants of fcc Cu.

	a	b	c
a (Å)	3.58	3.61	3.615
B (Mbar)	1.53	1.62	1.42
G (Mbar)	0.272		0.256
c_{44} (Mbar)	0.86		0.75

[a] This work.

[b] Ref. 5, nonrelativistic results.

[c] Experiment.

Comparing the calculated values of the three elastic constants for fcc Cu with experiment (see Table I) we get a useful test of the accuracy of the method and the precision of our calculation. The bulk modulus B and the shear modulus G are about 10% higher than experiment, and the other shear modulus c_{44} is about 15% high. These differences are reasonable for good calculations within the local-density approximation.[15]

Plots of $E(c/a)$ for bct structures over a range that includes the bcc value ($c/a = 1$) and the fcc value ($c/a = \sqrt{2}$) are shown in Fig. 2 at the bcc theoretical equilibrium value and at the fcc theoretical equilibrium value of V. Note the following features of these plots:

(1) There is no minimum of E at the bcc structure.

(2) The slope $\partial E/\partial(c/a) = 0$ at the c/a values of the cubic structures bcc and fcc, as it must be by symmetry.[16]

(3) The bcc equilibrium E is about 0.5 mRy/atom higher than the fcc equilibrium E and occurs at a V 4.3% smaller. This value of ΔE may be compared with 0.3 mRy in Ref. 4 (nonrelativistic, exchange-correlation potential $v_{\rm xc}$ in the Hedin-Lundqvist form) and with 1.7 mRy in Ref. 6 (nonrelativistic; with relativistic corrections Ref. 6 finds $\Delta E = 3.6$ mRy; $v_{\rm xc}$ in the Wigner form).

The function $E(c/a)$ for the trigonal cell at two values of V in Fig. 3 shows that the c_{44} constant of bcc Cu is

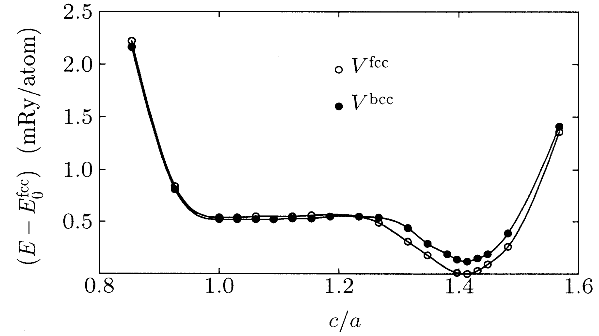

FIG. 2. Total energy per atom E in mRy of body-centered-tetragonal cells as a function of c/a at constant volume referred to zero at the fcc minimum energy. Open circles at the volume of the fcc minimum energy, solid circles at the volume of the bcc minimum energy.

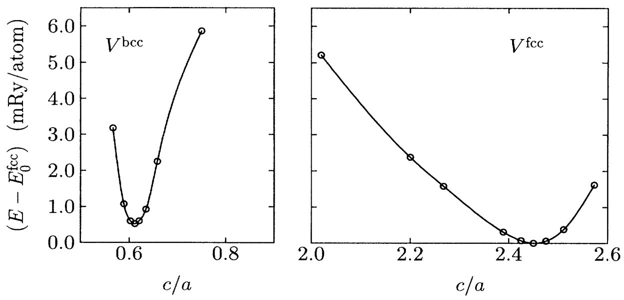

FIG. 3. Total energy per atom for trigonal cells as a function of c/a at the volume of the bcc energy minimum (left) and at the volume of the fcc minimum (right), referred to zero at the fcc minimum energy. The energy barrier between the two structures is ∼ 9 mRy and not completely drawn.

finite (0.69 Mbar) and 20% smaller than the value for fcc Cu (0.86 Mbar; see Table I).

IV. DISCUSSION

The bct calculations show that bcc Cu is unstable because there is no energy barrier for the shear deformation that increases c/a. Thus bcc Cu has a weak shear modulus G, which vanishes to the accuracy of this calculation. This weakness of the shear modulus is understandable if the binding of the bcc Cu lattice is reasonably described by near-neighbor central forces. Then the bonds will be perpendicular to (110) shears and hence will offer no resistance to such shears, which to first order do not stretch the bonds. However, this model would still show resistance to (100) shears, since such shears will stretch the bonds. We would like to point out that this vanishing resistance can be well understood in terms of band filling. For Cu, the d shell is completely filled; thus, their contribution to bonding effects is expected to be small. Obviously, this is not the case for other transition metals which need further specific investigation.

We can now explain why unstable bcc Cu is not obviously prevented from growing epitaxially on (001) surfaces, such as the Ag(001) substrate surface of Ref. 10. The reason is that only one shear constant G vanishes, but the shear constant that opposes sliding of (001) planes is the other shear constant c_{44}, which is finite. The epitaxial constraint of the film by the substrate prevents (110) planes from sliding on each other.

This lack of stability of bcc Cu with respect to shear is an obvious warning, often forgotten, that evaluation of total energies as a function of volume alone is not enough to establish the metastability of a phase. Proof of metastability requires a more extensive analysis; in principle, such proof requires showing that the energy increases for all possible infinitesimal deformations. Imposed constraints, however, can create stability or metastability.

V. SUMMARY

Full-potential nonrelativistic calculations of the total energy of Cu as a function of the c/a ratio of tetragonal and trigonal cells give values of the two shear constants and the bulk modulus of fcc Cu which agree well with experiment (10–15 % high). The calculations use a particularly simple form for the strain energy of tetragonal and trigonal deformations of a cubic structure. To obtain this simple form the strains in c/a and V are shown to be orthogonal, and so the elastic constants can be evaluated from the curvature of the energy as a function of just one variable. For bcc Cu the calculations show an instability with respect to [110] shears and a vanishing of the G modulus, but B and c_{44} are finite. Hence it is understandable that bcc Cu is not prevented from growing in coherent epitaxy on closely matched (001) surfaces.

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