Epitaxial Bain paths and metastable phases from first-principles total-energy calculations

P. M. Marcus

IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, New York 10598

F. Jona

Department of Materials Science and Enginering, State University of New York, Stony Brook, New York 11794-2275

S. L. Qiu

Department of Physics, Alloy Research Center, Florida Atlantic University, Boca Raton, Florida 33431-0991

A systematic two-stage procedure for finding metastable phases from first-principles total-energy calculations is derived and applied to tetragonal structures. In the first stage we calculate the system's epitaxial Bain path (EBP) in the tetragonal plane, whose coordinates are the tetragonal lattice constants; the EBP is defined so that it goes through all tetragonal energy minima. In the second stage we prove or disprove metastability by evaluating the elastic constants at the minima and checking the stability conditions. Application of the procedure to some metallic elements and compounds has led to a substantial number of metastable phases, many of them new, which exist in addition to the ground state. A generalization to finite hydrostatic pressure permits finding metastable phases under pressure, but a third stage must be added which converts the energy to a free energy whose minima now give the phases. Various properties of EBP's are described, including the existence of inherently unstable states along the EBP which cannot be stabilized by application of external stresses, and determination of the point on the EBP at which a thermodynamic phase transition between tetragonal phases occurs that is produced by epitaxial strain.

I. INTRODUCTION

Metastable phases of a material of given composition are essentially new materials, which may have properties very different from the ground-state phase, e.g., metastable diamond and graphite. Much effort has been made to find other phases of a material by applying pressure, changing temperature, and varying concentrations of components. These experimental procedures can change the ground-state phase to a different phase. This different phase may at ambient conditions be a metastable phase, which is locally stable against small perturbations, although higher in energy than the ground state at ambient conditions. Hence experiment can sometimes indicate possible metastable phases. Stabilization of these different phases can then be sought to confirm their metastability experimentally. This paper shows how modern electronic theory can find metastable phases systematically from first principles, and can both confirm and extend the experimental indications.

Modern first-principles electronic theory has given us a reliable theoretical procedure for finding total energies of crystalline materials, although there are computational limitations on the number of atoms allowed in the unit cell. Band-structure programs, such as WIEN97,[1] can calculate total energies for any configuration of atoms in the unit cell. Hence we can search for metastable phases by looking for energy minima that are locally stable, i.e., configurations for which the energy increases for *all* small displacements of the atoms in the unit cell.

When discussion is limited to crystals with just one basis atom in the unit cell (a Bravais lattice), the structure space to be searched has at most six dimensions (the three sides and three angles of the parallelopiped unit cell); a second basis atom adds three more degrees of freedom, so that the structure space then has at most nine dimensions. However symmetry reduces the number of structural degrees of freedom. This paper makes the computational burden practicable by considering just body-centered tetragonal lattices, either as Bravais lattices or as the related lattices with two basis atoms such as the CsCl and the Cu-Au lattice ($L1_0$) with the second basis atom at the body center. Symmetry then limits the structure space to just two dimensions.

It will be shown that calculation of energies along a unique path through tetragonal states, the epitaxial Bain path (EBP), locates all the states that can be tetragonal metastable phases of the given crystal. Calculation of the elastic constants of these states then determines whether the state is in fact metastable. In this way 13 metastable tetragonal phases in addition to the ground state have been found in 16 metallic crystals. A table of stabilities of tetragonal phases of these metallic crystals is given, which includes several magnetic phases for each magnetic element.

Other useful properties of the EBP are described: the EBP gives the states that are maintained stable by applied isotropic epitaxial (biaxial) stress; it shows the nonlinear elastic behavior as phases are strained; it finds states that are inherently unstable and cannot be stabilized by applied stresses; and it can be generalized to find metastable phases under hydrostatic pressure, and also generalized to apply to structures with symmetries other than tetragonal.

In Sec. II we define the EBP and describe its properties and applications. In Sec. III we list and classify the stabilities of the tetragonal metastable phases of some elements and binary compounds. In Sec. IV we discuss the value of the

EBP approach to tetragonal metastable phases and extensions of that approach; some comments are made on the language used for discussing phases and questions are raised for further study.

II. DEFINITION, PROPERTIES, AND APPLICATIONS OF THE EBP

A. Tetragonal phases and Bain paths

The structure space for the body-centered tetragonal (bct) crystals considered here (lattice constant a for the square base and c for the height of the two-atom cell) is the tetragonal plane, which has coordinates a and c or, equivalently, c/a and the volume per atom $V = ca^2/2$. At every point in the tetragonal plane there is a self-consistent solution of the Kohn-Sham equations,[2] which we will call a state of the system. The solution provides the total energy per atom $E(a,c)$ and the first derivatives of $E(a,c)$ provide the in-plane [(001) plane] stresses $\sigma_1 = \sigma_2$ and the out-of-plane ([001] direction) stress σ_3. We seek the states at the minima of $E(a,c)$ (referred to as tetragonal minima), which will be called equilibrium states because the stresses vanish for these states—saddle points of $E(a,c)$ are also equilibrium states, but are always unstable. The tetragonal minima are not necessarily stable or metastable because breaking the tetragonal symmetry might decrease the energy.

Almost always there are two minima in the tetragonal plane and a saddle point between them; the minima correspond either to dominant binding between (001) planes (small c/a) or to dominant binding in the (001) planes (large c/a). We show later by symmetry arguments that an element in bct structure *must* have at least two minima. However the two-atom crystal with the Cu-Au structure need not have two minima, although it usually does. Note that at small and large c/a, E will increase strongly, since atoms will begin to overlap.

A systematic procedure for finding tetragonal minima consists of calculating first a particular path in the tetragonal plane that *must* go through the tetragonal minima. That path is the EBP. The tetragonal minima are then at the minima on that path, as will now be shown. A Bain path meant originally a path through tetragonal states between equilibrium bcc and fcc structures.[3] This original definition implicitly assumed that at both cubic structures there were minima of $E(a,c)$. However, total-energy calculations have shown that the tetragonal minima are not necessarily both at cubic[4-6] structures. Hence a more appropriate definition of a Bain path is a path in the tetragonal plane that goes through both tetragonal minima, whether the corresponding structures are cubic or not. There are still many Bain paths, but note that a constant-volume path, which is frequently called a Bain path,[4,7] does not in general satisfy the definition, since the tetragonal minima usually have different volumes.

The EBP is the unique Bain path which is defined as the path along which the stress in the [001] or c direction vanishes. This condition is satisfied on epitaxial films with a vacuum interface and defines the EBP even when there is only one tetragonal minimum, as can be the case for the Cu-Au structure. The EBP is calculated by finding at each a the c at which[5,6]

$$\sigma_3 = \frac{2}{a^2}\left(\frac{\partial E(a,c)}{\partial c}\right)_a = 0. \tag{1}$$

Satisfaction of Eq. (1) gives directly c^{EBP} and E^{EBP} at a, hence also the in-plane stresses $\sigma_1 = \sigma_2$ from $\partial E(a,c)/\partial a$ at the point (a, c^{EBP}) and $V^{\text{EBP}} = c^{\text{EBP}}a^2/2$. For convenience of discussion we use a standard model of the EBP, which has two minima and a maximum of energy between them; we will mention explicitly if the standard model does not apply.

At a minimum of $E^{\text{EBP}}(a)$, coordinates (a_0, c_0), the first derivative of $E(a,c)$ vanishes in two directions in the tetragonal plane: along [001] by construction of the EBP and along the EBP, since the point (a_0, c_0) is at a minimum of $E^{\text{EBP}}(a)$. Hence the derivative of $E(a,c)$ at (a_0, c_0) must vanish in all directions so that at (a_0, c_0) the stresses $\sigma_1 = \sigma_2 = \sigma_3 = 0$ and

$$\left(\frac{\partial E(a,c)}{\partial a}\right)_{a_0, c_0} = \left(\frac{\partial E(a,c)}{\partial c}\right)_{a_0, c_0} = 0. \tag{2}$$

Thus (a_0, c_0) is an extremum of $E(a,c)$ and, as stated above, $E^{\text{EBP}}(a)$ must go through all minima of $E(a,c)$, and also through all maxima and saddle points, i.e., through all equilibrium points. The stability of the state at (a_0, c_0) must then be tested to determine if it is a metastable phase.

Figure 1 illustrates the EBP functions for vanadium. Figure 1(a) is a plot of $E^{\text{EBP}}[c^{\text{EBP}}(a)/a]$, which shows the standard model with two minima and a maximum between; vanadium has cubic symmetry at the first minimum (the bcc ground state) and also at the fcc maximum (which is a saddle point in the tetragonal plane), but has noncubic tetragonal symmetry at the second minimum. Figure 1(b) is a plot of $V^{\text{EBP}}[c^{\text{EBP}}(a)/a]$, which gives the equilibrium values of $V(a,c)$ at the two minima of E^{EBP} (points A and E); Fig. 1(c) is a plot of $c^{\text{EBP}}[c^{\text{EBP}}(a)/a]$; Fig. 1(d) shows the in-plane stress σ_1^{EBP} along the EBP as a function of $c^{\text{EBP}}(a)/a$. The figures were made by using the power-series expansions of total tetragonal energies by Sliwko, Mohn, Schwarz, and Blaha.[7]

B. Conditions for metastability

As noted above, the tetragonal energy minima are not necessarily metastable states, because a deformation that breaks tetragonal symmetry could lower the energy. The test of local stability against all small deformations is given by four stability conditions expressed in terms of the six elastic constants of a tetragonal structure.[8] The conditions are derived from the requirement that the strain energy be positive definite for all small strains of the state at the minimum. We write these conditions in the form
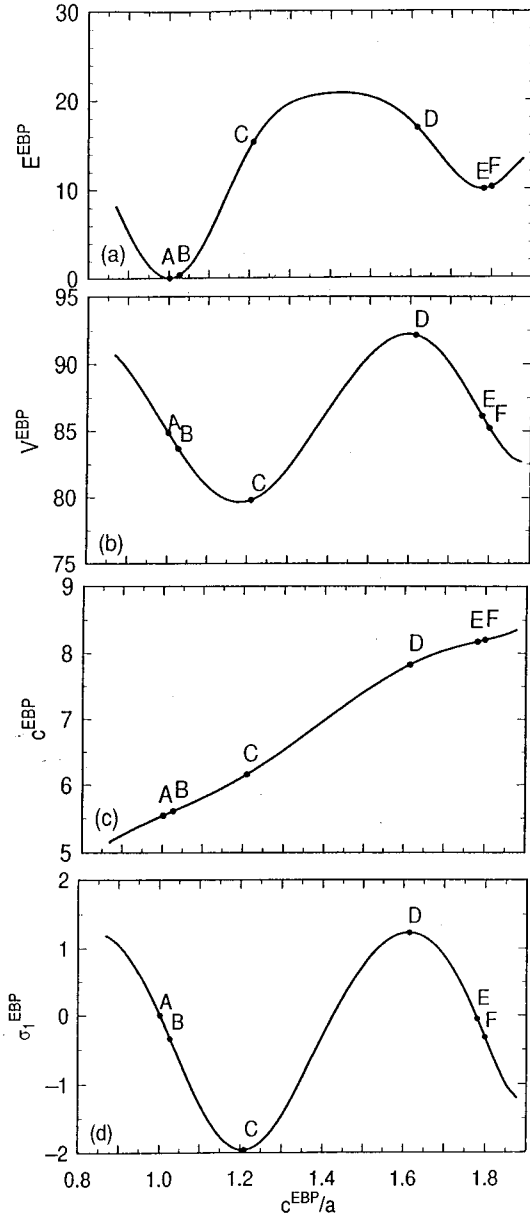
$$C' \equiv \frac{(c_{11} - c_{12})}{2} > 0, \tag{3a}$$

FIG. 1. Functions along the EBP defined in Sec. II A plotted against $c^{\mathrm{EBP}}(a)/a$ for vanadium. (a) $E^{\mathrm{EBP}}(c^{\mathrm{EBP}}/a)$ in mRy/atom: A marks the bcc phase, B marks the thermodynamic phase-transition point, C marks the stability limit of the bcc phase, D marks the stability limit of the bct phase, E marks the bct phase, and F marks the thermodynamic transition point coupled to B; (b) $V^{\mathrm{EBP}}(c^{\mathrm{EBP}}/a)$ in bohr^3; (c) $c^{\mathrm{EBP}}(c^{\mathrm{EBP}}/a)$ in bohr; (d) $\sigma_1^{\mathrm{EBP}}(c^{\mathrm{EBP}}/a)$ in mRy/bohr^3. The letters mark the same points for all the functions.

$$Y' \equiv c_{11} + c_{12} - \frac{2c_{13}^2}{c_{33}} > 0, \tag{3b}$$

$$c_{44} > 0, \tag{3c}$$

$$c_{66} > 0. \tag{3d}$$

Some assumptions have been made in writing Eq. (3) compared to the cases considered by Nye[8]—namely, we assume

that c_{12} and c_{33} are always greater than zero. These assumptions simplify the determination of stability and have never been violated in any of the tetragonal structures we have studied. Also for the tetragonal lattice we add Eq. (3d) to the hexagonal structure stability conditions given by Nye.

The instabilities that we find for minima of the EBP all come from violations of Eqs. (3a), (3c), or (3d); the condition (3b) is always satisfied at tetragonal minima because the curvature at the minima, which gives Y', is positive since

$$Y' = \frac{1}{c_0} \left(\frac{d^2 E^{\mathrm{EBP}}(a)}{da^2} \right)_{a_0}. \tag{4}$$

In addition to Y' the EBP also determines

$$\frac{c_{13}}{c_{33}} = -\frac{1}{2} \left(\frac{dc^{\mathrm{EBP}}(a)}{da} \right)_{a_0}. \tag{5}$$

Condition (3a) can be checked by calculating C' from

$$C' \equiv \frac{c_{11} - c_{12}}{2} = \frac{1}{2c_0} \left(\frac{\partial^2 E[a_1, a_2(a_1), c]}{\partial a_1^2} \right)_{a_0, a_0, c_0}, \tag{6a}$$

where a_1 and a_2 designate the in-plane tetragonal lattice constants separately and

$$a_2(a_1) = 2a_0 - a_1. \tag{6b}$$

In Eq. (6a) E is regarded as a function of the three sides of the tetragonal cell separately, but a_2 is coupled to a_1. The tetragonal symmetry is broken by the deformation to give an orthorhombic cell. Equations (6a) and (6b) are equivalent to the usual combination shear strain $\varepsilon_1 = -\varepsilon_2$.

The shear constants c_{44} and c_{66} are evaluated from strains which change the angle θ_{23} between the sides a_2 and $a_3 \equiv c$ and the angle θ_{12} between the sides a_1 and a_2, respectively; with θ in radians, we have[9]

$$c_{44} = \frac{2}{c_0 a_0^2} \left(\frac{\partial^2 E(a, c, \theta_{23})}{\partial \theta_{23}^2} \right)_{a_0, c_0, \pi/2}, \tag{7}$$

$$c_{66} = \frac{2}{c_0 a_0^2} \left(\frac{\partial^2 E(a, c, \theta_{12})}{\partial \theta_{12}^2} \right)_{a_0, c_0, \pi/2} \tag{8}$$

As for Eq. (6), the deformations in Eqs. (7) and (8) also break tetragonal symmetry; the deformation for c_{44} produces a monoclinic cell and for c_{66} an orthorhombic cell.

For cubic symmetry $c_{33} = c_{11}$ and $c_{13} = c_{12}$ and the stability conditions (3) reduce to[8]

$$C' > 0, \tag{9a}$$

$$c_{11} + 2c_{12} > 0, \tag{9b}$$

$$c_{44} > 0, \tag{9c}$$

since then Eq. (3b) becomes

$$Y' = \frac{(c_{11}+2c_{12})(c_{11}-c_{12})}{c_{11}} > 0. \qquad (10)$$

Then Eq. (9b) is satisfied if c_{11} and c_{12} are greater than zero, and Eq. (9a) then follows from Eq. (10). Hence only violations of Eq. (9c) can produce instability at a minimum with cubic symmetry.

C. Symmetry theorems and special properties of cubic structures

An element with the bct Bravais lattice has two structures with cubic symmetry: bcc at $c/a = 1$ and fcc at $c/a = \sqrt{2}$. Note that the Cu-Au structure has cubic symmetry only at $c/a = 1$. There are two useful symmetry theorems for tetragonal deformations of states of cubic symmetry.

The first theorem is that the EBP must have an extremum in energy at all structures with cubic symmetry. This result follows because $(\partial E/\partial c)_a = (\partial E/\partial \varepsilon_3)/c = 0$, where $\varepsilon_3 = \delta c/c$, at all points of the EBP by construction; then at a point on the EBP with cubic symmetry $\partial E/\partial \varepsilon_1 = \partial E/\partial \varepsilon_2 = \partial E/\partial \varepsilon_3$, where $\varepsilon_1 = \delta a_1/a$, $\varepsilon_2 = \delta a_2/a$, so that $(\partial E/\partial a_1)_{a,c} = (\partial E/\partial a_2)_{a,c}$ also vanish. Hence E must have a vanishing derivative at that point in the tetragonal plane in all directions, including the direction along the EBP.

The second theorem is that on paths in the tetragonal plane on which the volume $V = ca^2/2$ is constant, E as a function of a or c/a is an extremum at points of cubic symmetry. At such points, as noted above, $\partial E/\partial \varepsilon_1 = \partial E/\partial \varepsilon_2 = \partial E/\partial \varepsilon_3$; then at constant V we have $\delta E = (\partial E/\partial \varepsilon_1)\varepsilon_1 + (\partial E/\partial \varepsilon_2)\varepsilon_2 + (\partial E/\partial \varepsilon_3)\varepsilon_3 = (\partial E/\partial \varepsilon_1)(\varepsilon_1 + \varepsilon_2 + \varepsilon_3) = 0$, since $\delta V/V = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 = 0$.

The first theorem has the interesting consequence that for elements in bct structure, which always includes two structures with cubic symmetry, there must be at least two extrema on the EBP. But then there must be at least three—two minima and a maximum between, as in the standard model, because the EBP rises for both small and large c/a. Two of the extrema have cubic symmetry; the third then has noncubic tetragonal symmetry.

There are three possible configurations, since the noncubic extremum can be in three positions with respect to the cubic extrema. All three configurations occur in the elements discussed in Sec. III. However for the binary compound in Cu-Au structure, which always has just one cubic structure (CsCl), the cubic structure has three positions with respect to two noncubic extrema (if there are two minima). If there is only one minimum, i.e., an EBP curve different from the standard model, that minimum must be at $c/a = 1$. The type-1 antiferromagnetic bct structure of a magnetic element[10] also has just one cubic structure, hence the EBP also has three configurations of one cubic and two noncubic extrema.

The second symmetry theorem says that E for elements on all constant V paths in the tetragonal plane also must have at least two minima and a maximum. Again three configurations are possible, as was the case along the EBP. If $V_0 = c_0 a_0^2/2$ is the volume of a tetragonal minimum, then $E_{V_0}(a)$ will also have a minimum at a_0; if V is close to V_0,

$E_V(a)$ will have a minimum close to a_0. A useful extension of this property of $E_V(a)$ to tetragonal systems under pressure is given in Sec. II E.

D. Properties of the EBP away from the minima

Section II C considered properties of the EBP at the minima, including the elastic constants and stabilities of the phases at the minima. These phases might be called unconstrained phases to distinguish them from phases under epitaxial stress. We can regard the EBP as an analytic connection between two unconstrained phases. Going away from the minima along the EBP, the phases come under isotropic epitaxial stress. Then for the point (a,c) on the EBP

$$\sigma_1 = \sigma_2 = \frac{2}{ca}\left(\frac{\partial E(a_1,a_2,c)}{\partial a_1}\right)_{a,a,c}$$

$$= \frac{1}{ca}\left(\frac{\partial E(a,c)}{\partial a}\right)_{a,c}, \qquad (11a)$$

$$\sigma_3 = \frac{2}{a^2}\left(\frac{\partial E(a,c)}{\partial c}\right)_{a,c} = 0. \qquad (11b)$$

In Eq. (11a) the notation indicates that the in-plane stress can be calculated either by changing just one side of the square base or by changing both sides of the base by equal amounts.

As the state moves away from one minimum toward the other minimum along the EBP, the in-plane stresses $\sigma_1 = \sigma_2$ change in magnitude, initially increasing from zero. A state will be reached at which a thermodynamic transition to the other phase, also under stress, is favored. This transition state can be located by defining a free energy for the epitaxially strained states along the EBP. This free energy will also show that the system state can be driven beyond the thermodynamic transition state into a "superheating" region, which persists until a state is reached which is inherently unstable and hence can be expected to break up, i.e., a stability limit. The range of inherently unstable states extends to the stability limit of the other phase (see Figs. 2 and 3).

These various stages in a first-order transition between tetragonal phases can be derived and explained by the epitaxial free energy (at zero temperature) that we now define along the EBP,[11]

$$G^{\text{EBP}}(a) \equiv E^{\text{EBP}}(a) + \sigma_1^{\text{EBP}}(a)U(a) - TS, \qquad (12)$$

where T is absolute temperature, S is entropy, and

$$U(a) \equiv -\int_{a_0}^{a} ac^{\text{EBP}}(a)da. \qquad (13)$$

We drop the entropy term in G by considering behavior only at $T = 0$. The quantity $U(a)$ along the EBP defined in Eq. (13) is an extensive variable conjugate to σ_1 (U replaces the similar quantity S in Ref. 11 to avoid confusion with entropy, but has the opposite sign to simplify its relation to G). Then at a point (a,c) on the EBP,
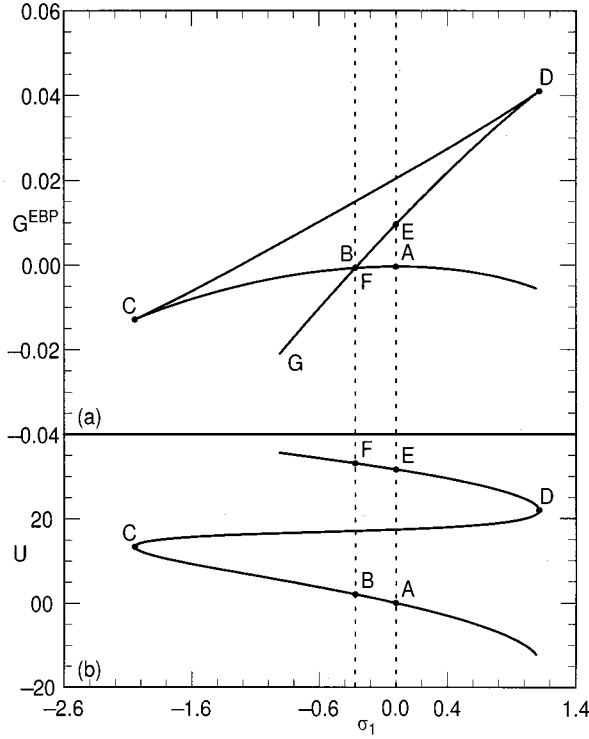
FIG. 2. (a) The free-energy function $G^{EBP}(\sigma_1)$ in mRy/atom, which is defined in Eq. (12) at points on the EBP of vanadium as a function of the in-plane isotropic stress at those points. (b) The function U defined in Eq. (13) as a function of in-plane stress along the EBP in bohr^3, where $U(\sigma_1) = dG^{EBP}/d\sigma_1$. The letters correspond to those in Fig. 1. The vertical dashed lines join the equilibrium states A and E where $\sigma_1 = 0$ and the thermodynamic transition states B and F where G^{EBP} has equal values.

$$dE^{EBP} = \left(\frac{\partial E(a,c)}{\partial a} + \frac{\partial E(a,c)}{\partial c} \frac{dc^{EBP}(a)}{da} \right) da$$
$$= \sigma_1^{EBP} c a \, da = -\sigma_1^{EBP} dU, \qquad (14)$$

since $\partial E/\partial c = 0$ on the EBP, $\partial E/\partial a = \sigma_1^{EBP} ca$ from Eq. (11a), and $dU = -c^{EBP}(a) a \, da$ from Eq. (13). In analogy to a system under hydrostatic pressure the stress σ_1^{EBP} is analogous to p and U is analogous to volume V. Then from Eqs. (12) and (14),

$$dG^{EBP} = dE^{EBP} + \sigma_1^{EBP} dU + U d\sigma_1^{EBP} = U d\sigma_1^{EBP}. \quad (15)$$

Thus G^{EBP} is constant in a transformation at constant σ_1^{EBP}.

A calculation of G^{EBP}, σ_1^{EBP}, and U as functions of σ_1^{EBP} along the EBP of vanadium appears in Fig. 2; Fig. 2(a) plots $G^{EBP}(\sigma_1^{EBP})$ and Fig. 2(b) plots $U(\sigma_1^{EBP})$, the derivative of $G^{EBP}(\sigma_1^{EBP})$. The figure shows the sequence of states between the unconstrained phases corresponding to the two minima of E (at points A and E). We note these features. The curves $G^{EBP}(\sigma_1^{EBP})$ have three branches. The first and third branches cross at a σ_1^{EBP} which corresponds to the thermodynamic transition (between points B and F). Note that making the phase transition and then continuing in the new phase
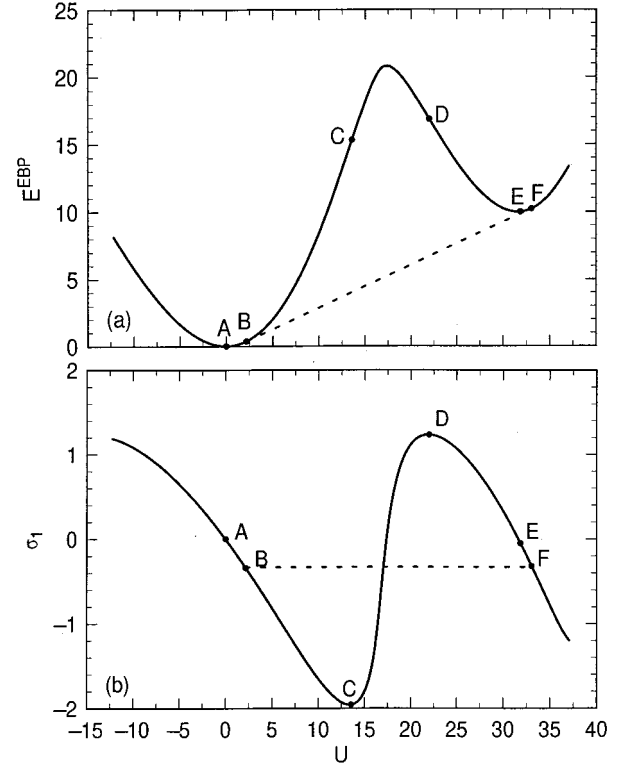

FIG. 3. (a) $E^{EBP}(U)$ for vanadium showing the thermodynamic transition between B and F by the common-tangent construction (dashed line); (b) $\sigma_1^{EBP}(U)$ showing the thermodynamic transition by the equal-area (Maxwell) construction (dashed line). $\sigma_1^{EBP}(U)$ for the epitaxially strained system is analogous to the equation of state $p(V)$ for the vapor-liquid system.

gives lower values of G compared to continuing in the original phase, e.g., for increasing c/a the sequence ABFG in Fig. 2(a) gives lower G values than the sequence ABC on the original branch. Similarly for decreasing c/a compare FBA to FED. The intersections of the first and third branches with the second branch show a characteristic cusp or point of discontinuous curvature when a phase goes inherently unstable; the second branch contains the inherently unstable states. The states at the cusps also correspond to the condition that the second-order differential of energy loses positive definiteness for small tetragonal strains around the cusp states.[11]

There is a complete analogy in the behavior of a tetragonal system under epitaxial stress to the first-order phase transition between liquid and vapor states of a van der Waals gas; the analogy is discussed in detail in Ref. 11. The function $\sigma_1^{EBP}(U)$ is analogous to the equation of state $p(V)$ along an isotherm. A common-tangent construction on the first and third branches of $E^{EBP}(U)$ gives the strained phases that are in equilibrium (Fig. 3a), as does the equal-area construction (Fig. 3b) on the function $\sigma_1^{EBP}(U)$, which is the negative of the derivative of $E^{EBP}(U)$; this construction corresponds to the Maxwell construction on $p(V)$ for liquid and vapor phases in equilibrium.

However, there is a significant conceptual difference be-

tween the phase transition described by the EBP and the one described by the van der Waals equation. The latter is an empirical equation of qualitative validity, whereas the EBP is based on first-principles calculations of good known reliability, although the phase transition is described within a mean-field approximation.

The $G^{EBP}(\sigma_1^{EBP})$ function shows clearly three kinds of instability in epitaxially strained tetragonal phases. For the initial tetragonal deformations from equilibrium, application of an external epitaxial stress maintains the state as a constrained phase. For deformations beyond the phase-transition point, hence in the "superheating range," the external stress may maintain the state, but an abrupt transition to a state of lower free energy is possible and could be nucleated. However when the deformation goes beyond the stability limit, the strained phase can be expected to break up, since a runaway situation exists analogous to the states on the $p(V)$ curve where increase of p *increases* V; here increase of epitaxial tension in the inherently unstable states decreases a, which further increases the tension.

E. EBP's under hydrostatic pressure

Generalization of the EBP for systems under hydrostatic pressure p requires two changes in the procedures used at $p=0$. The first change consists of substituting for the condition (1) (i.e., that $\sigma_3=0$) the new condition that $\sigma_3=-p$, so that at every a,

$$\left(\frac{\partial E(a,c)}{\partial c}\right)_a = -\frac{a^2}{2}p. \qquad (16)$$

The condition (16) produces the functions $E^{EBP}(a;p)$, $V^{EBP}(a;p)$, and $c^{EBP}(a;p)$, where the notation indicates that the functions contain p as a parameter.

The second change consists in introducing a Gibbs free energy per atom (at zero temperature so that the entropy term vanishes) defined throughout the tetragonal plane by

$$G(a,c;p) \equiv E(a,c) + pV(a,c). \qquad (17)$$

Then at any point (a,c) on the EBP for pressure p,

$$\left(\frac{\partial G(a,c;p)}{\partial c}\right)_a = \left(\frac{\partial E(a,c)}{\partial c}\right)_a + p\left(\frac{\partial V(a,c)}{\partial c}\right)_a$$

$$= -\frac{a^2}{2}p + \frac{a^2}{2}p = 0, \qquad (18)$$

where Eq. (16) and $V=ca^2/2$ have been used. Now from Eq. (17) the function G along the EBP at p is given by

$$G^{EBP}(a;p) = E^{EBP}(a;p) + pV^{EBP}(a;p). \qquad (19)$$

Let (a_0,c_0) be the tetragonal lattice parameters of a minimum of $G^{EBP}(a;p)$. Then at (a_0,c_0) the derivative of $G(a,c)$ vanishes both along the EBP and by Eq. (18) along c, hence just as for the case $p=0$, where the derivative of E vanishes in all directions [see Eq. (2)], the derivative of G at (a_0,c_0) vanishes in all directions in the tetragonal plane. The in-plane stresses at (a_0,c_0) are then given by

$$\sigma_1 = \sigma_2 = \frac{1}{a_0 c_0}\left(\frac{\partial E(a,c)}{\partial a}\right)_{a_0,c_0} = \frac{1}{a_0 c_0}\left(\frac{\partial G(a,c)}{\partial a}\right)_{a_0,c_0}$$

$$- \frac{1}{a_0 c_0}\left(\frac{\partial pV(a,c)}{\partial a}\right)_{a_0,c_0} = -p. \qquad (20)$$

In Eq. (20) $\partial G/\partial a=0$ at (a_0,c_0) and $V=ca^2/2$ have been used. Since $\sigma_3=-p$ by construction of the EBP at p, the state at (a_0,c_0) is under hydrostatic pressure p.

It is also possible to find an equilibrium state under hydrostatic pressure from the constant-volume energy function $E_V(a)$. At a minimum of $E_V(a)$ the pressure is shown to be hydrostatic by transforming the variables from (a,V) to variables (a,c) and evaluating the stresses. Then at any point (a,c),

$$\sigma_1 = \sigma_2 = \frac{1}{ca}\left(\frac{\partial E}{\partial a}\right)_c = \frac{1}{ca}\left(\frac{\partial E}{\partial a}\right)_V + \left(\frac{\partial E}{\partial V}\right)_a, \qquad (21a)$$

$$\sigma_3 = \frac{2}{a^2}\left(\frac{\partial E}{\partial c}\right)_a = \left(\frac{\partial E}{\partial V}\right)_a. \qquad (21b)$$

Since at the minimum of $E_V(a)$ $(\partial E/\partial a)_V=0$, Eqs. (21a) and (21b) give

$$\sigma_1 = \sigma_2 = \sigma_3 = \left(\frac{\partial E}{\partial V}\right)_a = -p \qquad (22)$$

and the tetragonal system is under hydrostatic pressure at the assumed volume V. However we do not know the value of p at the given V. If the V is $c_0 a_0^2/2$, then that p is the value used for determining $G^{EBP}(a;p)$.

Thus an equilibrium state with volume per atom V can be found from minima of $E_V(a)$. To determine the corresponding pressure requires the equation of state $p(V)$, which can be found from $E(V)$ evaluated at the minima of $E_V(a)$ as V varies. This property of $E_V(a)$ is a generalization of the second theorem of Sec. II C to systems under pressure, which now includes cases in which the minimum of $E_V(a)$ does not necessarily have a cubic structure.

For a closed system, such as a crystal in vacuum, $dE=0$ for small changes in structure around the equilibrium structure. This flatness of E around equilibrium corresponds to the system being at an extremum of E. However if the crystal is in an open system, such as a system at constant hydrostatic pressure, then $dE=-pdV$ for changes in structure and dE does not vanish, but now $dG=0$ for small changes in structure; equilibrium for the system now corresponds to an extremum of G. Of course for stability the extremum must be a minimum and the system under pressure will achieve equilibrium by minimizing G.

Metastable phases under pressure are found by a three-stage process: First calculate $E^{EBP}(a;p)$. Second find $G^{EBP}(a;p)$ and its minima. The minima are tetragonal phases under hydrostatic pressure and may be metastable. Third find the elastic constants from the second derivatives of G with respect to strain at the minima to check stability. Note that the minima of $E^{EBP}(a;p)$ cannot be phases under

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TABLE I. Stabilities at tetragonal minima. Column 1 identifies the crystalline structure; AF1 is antiferromagnetic of the first kind (Ref. 10), FM is ferromagnetic, and NM is nonmagnetic. Columns 2–4 classify the configuration of extrema from small c/a to large c/a in the order first minimum, maximum, and second minimum, where C is cubic and N is noncubic structures. Columns 5–7 give the signs of $C' \equiv (c_{11-12})/2$, c_{44}, and c_{66} for the first minimum; c_{66} is omitted for cubic structures. Columns 8–10 give the signs of the same quantities for the second minimum. The minimum of lower energy is indicated by (L).

Material	Extremum sequence	First minimum C' c_{44} c_{66}	Second minimum C' c_{44} c_{66}
Co(FM)	N C C	− + +	+ + ...(L)
Cu	N C C	− + +	+ + ...(L)
CuZn	C N N	+ + ...(L)	+ + +
Fe(AF1)	N C N	+ + +	+ + +(L)
Fe(FM)	C C N	+ + ...(L)	+ + −
Fe(NM)	N C C	− + +	+ + ...(L)
K	C N C	+ + ...	+ + ...(L)
Li	C N C	+ + ...	+ + ...(L)
Mg	N C C		+ + ...(L)
Mn(AF1)	N C N	− + +	+ + +(L)
Pd	N C C	− + +	+ + ...(L)
Rb	C N C	+ + ...	+ + ...(L)
Sr	C N C	+ + ...(L)	+ + ...
Ti	N C C	− + +	+ + ...(L)
V	C C N	+ + ...(L)	+ + −
Zn	N C C	− + +	+ − ...(L)

hydrostatic pressure, because the in-plane stress vanishes in the direction along the EBP. An application of EBP's under pressure has been made to ferromagnetic (FM) iron, which shows that the bcc phase becomes unstable at 1500 kbar of pressure and that a new bct phase comes into existence at 1300 kbar and becomes stable at 1825 kbar and above.[12]

III. EXAMPLES OF TETRAGONAL MINIMA ON THE EBP

The procedure described in Sec. II for locating possible metastable phases by use of the EBP and then testing their stabilities has been applied to 16 metallic crystals in body-centered tetragonal structure; the results are tabulated in Table I. There are enough energy minima to suggest regularities in the occurrence of stable and unstable phases. The total-energy calculations were made with WIEN97,[1] usually with both LSDA and GGA assumptions. In the table different magnetic phases of Fe are counted as different materials. The table gives only the *signs* of the shear constants which determine the stability [C', c_{44} and c_{66} for non-cubic (N) minima, C' and c_{44} for cubic (C) minima]—there is no entry for c_{66}, since it is equal to c_{44}. The local spin-density approximation and generalized gradient approximation results agree in sign, although they may differ in magnitude.

All the EBP's of these materials conformed to the standard model, including CuZn. However a slight increase in Zn concentration above 50% gives an EBP with just one

minimum.[13] In column 2 the table gives the cubic or noncubic character of the three extrema in the sequence: first minimum (at low c/a), maximum, and second minimum (at high c/a). Then the signs of the elastic constants at the first minimum are given, which are followed by the signs of the elastic constants at the second minimum. The minimum with the lower energy is marked by (L). All three configurations of two cubic extrema and one noncubic extremum occur (CNC, CCN, NCC). The compound CuZn and the antiferromagnetic (AF) phases AF1-Fe, AF1-Mn show two of the three possible configurations of one cubic and two noncubic extrema (CNN, NCN).

The 16 crystals have 31 EBP minima; the first minimum for Mg is too shallow for reliable computation of the elastic constants and is omitted. The 31 minima show 21 stable phases and 10 unstable phases. All minima are called phases, whether stable or unstable. The designation stable is used for both ground-state phases and metastable phases.

The 20 minima with cubic symmetry have 19 stable phases and one unstable phase. The unstable cubic phase (fcc, Zn) has $c_{44} < 0$ in agreement with the conclusion at the end of Sec. II B about Eq. (9c). The 11 noncubic phases have two stable phases and nine unstable phases. The instabilities of the phases at the first minimum are all due to $C' < 0$; the instabilities of the phases at the second minimum (both cubic and noncubic) are all due to $c_{66} < 0$; this includes fcc Zn, which has $c_{44} = c_{66} < 0$. Only one material has two unstable tetragonal minima (Zn).

The number of metastable phases is not completely definite, because the ground-state phase must be known and subtracted from the count if it is one of the tetragonal phases. There are 13 metastable phases if we assume that the ground-state phases of Co, Li, Mg, Mn, and Ti are not tetragonal as experiment indicates. Also we count all the stable minima of AF1-Fe and nonmagnetic (NM)-Fe as metastable, since the ground state is FM-bcc.

The stability of fcc Co, Mg, and Ti could be expected, because fcc and hcp are both close-packed phases, but the instability of fcc Zn is unexpected. A paper by Müller *et al.*[14] finds the instability of fcc Zn for rhombohedral (trigonal) deformation along [111] and uses the instability to explain the behavior of Al-Zn alloys. The stability of N_2 CuZn (N_2 means the noncubic second minimum) and of N_2 AF1-Mn are interesting because the α phase of CuZn alloys has been observed only up to 35 at. % Zn and not at 50% Zn, and tetragonal AF1-Mn has been made only with 10% or more impurities that increase the electron density.

IV. DISCUSSION

The procedure for finding metastable phases from the EBP described in Sec. II and applied in Sec. III has been highly productive, demonstrating the existence of about 13 metastable phases for the 16 materials studied. A valuable feature of these results is that they have been obtained with first-principles calculations, which have a known good reliability, unlike empirical potentials.

The results of the stability of the tetragonal phases indicate some regularities, such as the fact that cubic phases are

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almost always stable, whereas noncubic phases are usually unstable. The C' shear constant {[110] shear in the (001) plane} determines the stability of the first minimum of E (at or near bcc structure); the c_{66} shear constant ([100] shear in the (001) plane) determines the stability of the second minimum (at or near fcc structure). Almost all materials have at least one locally stable tetragonal phase when both ground-state phases and metastable phases are included.

The EBP procedure for finding metastable phases for bct crystal lattices clearly extends directly to hexagonal-close-packed (hcp) and trigonal crystal lattices, since they also have just two degrees of freedom. However they require a more elaborate calculation, since they have additional non-equivalent atoms in the unit cell. The extra atoms do not strain homogeneously and must be independently relaxed. Although the usual unit cell of the bct lattice also has an extra atom in the unit cell, it has enough symmetry so that it can be strained homogeneously; the bct lattice of an element is a Bravais lattice.

Pressure provides a large extension of the domain of existence of metastable phases, which can be explored by the EBP procedure, generalized as in Sec. II E. It seems very likely that the number of metastable phases is very large, since so many have been found just in tetragonal structures of elements at zero pressure. Under pressure with additional symmetries and additional basis atoms many more metastable phases should occur.

The language used here for describing phases arose from the procedure. All tetragonal structures have a solution of the Kohn-Sham equations, which we call a state. Each such calculation is really a constrained ground-state calculation and the state is in general under applied stress. The special states at tetragonal minima do not have applied stresses and are stable under all small *tetragonal* deformations. Hence it is natural to call the states at the minima tetragonal phases or tetragonal equilibrium phases. When the states at these minima prove unstable with respect to strains that break the

tetragonal symmetry, these minima are called unstable phases. This usage extends the meaning of the term phase, but calls attention to the special character of these states at tetragonal minima and retains the idea that they might be stabilized in some way.

The states produced by putting a tetragonal equilibrium phase under epitaxial stress are properly called constrained phases, which is the common usage, e.g., a phase under hydrostatic pressure. The term phase applies beyond the region of linear elastic behavior and applies also as the strained material changes its elastic constants. An interesting question that could be studied from first principles by the methods of this paper is whether the constrained phases starting from a stable phase could become unstable even before the region of inherently unstable states is reached. However when the region of inherently unstable states is reached, the characterization as a phase should be dropped. These states no longer have a special connection to the original equilibrium phase and lie between two tetragonal equilibrium phases.

The existence of regions of inherently unstable states in the tetragonal plane separating the regions of constrained phases suggests that structure space may be generally divided into regions of constrained phases separated by regions of inherently unstable states. Then each constrained phase has a unique "mother" phase from which it is generated by stress. Further study of metastable phases should clarify this description of structure space.

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