Eur. Phys. J. B **45**, 39–46 (2005)
DOI: 10.1140/epjb/e2005-00162-y

The European Physical Journal B

Automatic procedure for stable tetragonal or hexagonal structures: application to tetragonal Y and Cd

P.M. Marcus and F. Jona[a]

Department of Materials Science and Engineering State University of New York, Stony Brook, NY 11794-2275, USA

Received 28 September 2004 / Received in final form 17 December 2004

Abstract. A simple effective procedure (MNP) for finding equilibrium tetragonal and hexagonal states under pressure is described and applied. The MNP procedure finds a path to minima of the Gibbs free energy G at $T = 0$ K ($G = E + pV$, E = energy per atom, p = pressure, V = volume per atom) for tetragonal and hexagonal structures by using the approximate expansion of G in linear and quadratic strains at an arbitrary initial structure to find a change in the strains which moves toward a minimum of G. Iteration automatically proceeds to a minimum within preset convergence criteria on the calculation of the minimum. Comparison is made with experimental results for the ground states of seven metallic elements in hexagonal close-packed (hcp), face- and body-centered cubic structures, and with a previous procedure for finding minima based on tracing G along the epitaxial Bain path (EBP) to a minimum; the MNP is more easily generalized than the EBP procedure to lower symmetry and more atoms in the unit cell. Comparison is also made with a molecular-dynamics program for crystal equilibrium structures under pressure and with CRYSTAL, a program for crystal equilibrium structures at zero pressure. Application of MNP to the elements Y and Cd, which have hcp ground states at zero pressure, finds minima of E at face-centered cubic (fcc) structure for both Y and Cd. Evaluation of all the elastic constants shows that fcc Y is stable, hence a metastable phase, but fcc Cd is unstable.

PACS. 64.60.My Metastable phases – 71.15.Nc Total energy and cohesive energy calculations – 62.20.Dc Elasticity, elastic constants

1 Introduction

Modern band-structure programs, such as the WIEN programs [1], can find the total energy of arbitrary crystals with a moderate number of atoms in the unit cell. Knowing the total energy as a function of structure provides a first-principles theoretical procedure for determining the stable structures (which include metastable structures) that a given set of atoms can form. The range of such determinations has been greatly expanded by introduction of finite pressures p, which can substantially change the material properties and can make different phases the ground state. The equilibrium structures of these phases at p can be found directly as functions of p by minimizing the Gibbs free energy $G = E + pV$ at $T = 0$ K with respect to structure (E = energy per atom, V = volume per atom). Reasons are given in [2] why the procedure based on minimizing G at constant p is more accurate than the usual procedure of minimizing the internal energy E at constant volume: a principal reason is that the equation of state $p(V)$ is not needed.

To find the equilibrium structures over the great range of pressures now available experimentally (to several megabars) it is desirable to have a fast, reliable procedure that automatically finds the structure at each p. The program MNP (for minimum path) is designed for that purpose. We show that it is accurate in finding lattice constants, efficient in requiring only a few structural trials and reliable in rarely failing to find the minima. The present version considers structures with two structural degrees of freedom, including the important cases of tetragonal, body-centered tetragonal, hexagonal, hexagonal close-packed, omega, diamond and trigonal structures. Based on current experience, expansion to lower symmetries and more atoms in the unit cell seems straightforward with good prospects of success.

The MNP procedure is presently tested against experimental structures for seven metallic elements with hcp, fcc (face-centered cubic) and bcc (body-centered cubic) ground states. It is also compared with the procedure used previously [3] based on the epitaxial Bain path (EBP) to show their similarities and differences. Both procedures can find structures stable against deformations that preserve tetragonal or hexagonal symmetry, but the structures may be unstable against deformations that break those symmetries. Hence each minimum is tested for stability against all deformations by evaluating the elastic

---

[a] e-mail: `franco.jona@sunysb.edu`

constants and applying the appropriate stability conditions. Application is made by both procedures to the elements Y and Cd (which have hcp ground states) in bct structure. We observe that the MNP procedure is completely automated and is more easily generalized to structures with less symmetry and more atoms in the primitive unit cell than the EBP procedure.

We also compare MNP with molecular dynamics (MD) techniques, which can also find equilibrium states of periodic lattices under pressure when modified to work at finite pressure and to allow changes in cell structure [4]; the MD techniques are not suitable at low temperatures because the atoms follow classical orbits, whereas MNP is all quantum-mechanical. The success of MNP in finding equilibrium states of two-parameter structures by a few curvature-controlled jumps suggests that the generalization to less symmetry and more atoms in the unit cell will also succeed.

We also compare MNP with the CRYSTAL program [5], which uses a similar mathematical procedure. However, MNP has much simpler operations, since it is designed for simpler systems.

The formulation and application of the automatic procedure MNP are in Section 2. Comparisons of the MNP procedure with the EBP, the MD and the CRYSTAL procedures are in Section 3. Discussion of the significance of the MNP procedure and of the structural and elastic results for Y and Cd are in Section 4.

2 Automatic path MNP to free energy minima

For a given set of atoms and a given structure, i.e., specification of the unit cell and positions of atoms in the cell, we mean by a *state* the self-consistent solution of the Kohn-Sham equations, supplemented by corrections to the electron-electron interactions beyond the local-density approximation [6]. A state is said to be in equilibrium at p if there are no stresses present in addition to p, corresponding to vanishing of the gradient of G as a function of structure. Minima of G in tetragonal or hexagonal structure have vanishing additional stress, but to prove static stability the states must be tested against deformations that break the symmetries of those structures. States stable against all small deformations, which includes metastable states, can be called phases. The calculations here will find tetragonal or hexagonal minima, but are for rigid lattices; they neglect zero-point and temperature vibrations and are not tested for dynamical instabilities.

Hence the computational problem of finding stable states in tetragonal or hexagonal structure reduces to finding first the minima of the Gibbs free energy G, which equals E at $p = 0$, as a function of structure and then evaluating elastic constants at the minima. For brevity, we will limit the description to the case of tetragonal Bravais lattices (usually bct). For such lattices G is a function of a, the side of the square cross section, and c, the height of the unit cell. We therefore seek the minima of a computable function $G(a, c)$. The MNP procedure for finding minima uses the first terms of the Taylor expansion of the free energy density G/V in any given state in powers of the strains in the form

$$\frac{\delta G(a,c)}{V} \cong \sum_{i=1}^{3} c_i\,\epsilon_i + \frac{1}{2}\sum_{i,j=1}^{3} c_{ij}\,\epsilon_i\,\epsilon_j. \tag{1}$$

In (1) the ϵ_i, $i = 1, 2, 3$ are the tetragonal strains, $\epsilon_1 = \epsilon_2 = \delta a/a$, $\epsilon_3 = \delta c/c$, the c_i are the components of the strain gradient of G and give the (usually) anisotropic additional stress added to p in the crystal in the given state, and the c_{ij}'s can be interpreted as elastic constants in a crystal under p plus the applied stress given by the c_i. The strains ϵ_4, ϵ_5, ϵ_6 break tetragonal symmetry, hence are omitted.

For tetragonal symmetry we always have

$$\epsilon_1 = \epsilon_2, \quad c_1 = c_2, \quad c_{11} = c_{22}, \quad c_{13} = c_{23} \tag{2}$$

and (1) takes the form

$$\begin{aligned}\frac{\delta G(a,c)}{V} &= 2\,c_1\,\epsilon_1 + c_3\,\epsilon_3 + (c_{11}+c_{12})\epsilon_1^2 \\ &\quad + \frac{c_{33}}{2}\,\epsilon_3^2 + 2\,c_{13}\,\epsilon_1\,\epsilon_3 \\ &\equiv 2\,c_1\,\epsilon_1 + c_3\,\epsilon_3 + f(\epsilon_1,\epsilon_3),\end{aligned} \tag{3}$$

where f is a quadratic form in the strains ϵ_1 and ϵ_3.

At an initial arbitrary tetragonal state, we evaluate the coefficients in (3). Five independent choices of ϵ_1 and ϵ_3 give five strained structures ($a + \delta a$, $c + \delta c$) for which five values of δG are calculated; then (3) gives five linear equations for c_1, c_3, $c_{11} + c_{12}$, c_{33} and c_{13}.

We now must consider two cases. In Case 1 the function $f(\epsilon_1, \epsilon_3)$ is a positive definite form [$f(\epsilon_1, \epsilon_3)/\epsilon_1^2$ has complex roots for ϵ_3/ϵ_1]. Then we can find the minimum of G in (3) by putting

$$\frac{1}{V}\frac{\partial \delta G}{\partial \epsilon_1} = 2\,c_1 + 2\,(c_{11}+c_{12})\,\epsilon_1 + 2\,c_{13}\,\epsilon_3 = 0, \tag{4a}$$

$$\frac{1}{V}\frac{\partial \delta G}{\partial \epsilon_3} = c_3 + 2\,c_{13}\,\epsilon_1 + c_{33}\,\epsilon_3 = 0. \tag{4b}$$

Solution of the linear equations (4) for ϵ_1 and ϵ_3 gives a state for which G would be a minimum if (3) were exact. Since the expansion of δG will usually have significant terms with higher powers of ϵ_1 and ϵ_3 than the second power, the strained state will usually not be the exact minimum, but should be nearer the exact or true minimum than the initial state. Hence usually the calculation needs to be iterated, which requires recalculating the c_i and c_{ij}. The procedure continues until the calculation is converged to a preset convergence criterion on the magnitudes of c_1 and c_3.

In Case 2 the quadratic form $f(\epsilon_1, \epsilon_3)$ in (3) is not positive definite, which occurs when

$$2\,c_{13}^2 > c_{33}(c_{11}+c_{12}) \tag{5}$$

Table 1. Comparison between MNP results and experiment. Lattice constants a and c (in bohr) of selected elements with different ground-state structures (hcp=hexagonal close-packed; fcc = face-centered cubic; bcc=body-centered cubic) as calculated with the MNP procedure and as determined experimentally [20]. The column "Error" lists the percentage difference (theory minus experiment). For fcc materials a and c are the parameters of the corresponding body-centered tetragonal unit cell ($c/a = \sqrt{2}$).

Element	Structure	a			c		
		MNP	expt.	Error	MNP	expt.	Error
Mg	hcp	6.014	6.065	−0.8%	9.810	9.846	−0.4%
Ti	hcp	5.530	5.577	−0.8%	8.861	8.852	+0.1%
Cu	fcc	4.840	4.830	+0.2%	6.823	6.831	−0.1%
Mo	bcc	5.983	5.947	+0.6%	—	—	—
Rh	fcc	5.141	5.083	+1.1%	7.254	7.189	+0.9%
Pd	fcc	5.283	5.199	+1.6%	7.402	7.352	+0.7%
Ag	fcc	5.530	5.459	+1.3%	7.783	7.722	+0.8%

and $f(\epsilon_1, \epsilon_3)/\epsilon_1^2$ has real roots for ϵ_3/ϵ_1. Then values of ϵ_3/ϵ_1 exist which make the quadratic form negative. The minimum of $f(\epsilon_1, \epsilon_3)/\epsilon_1^2$ as a function of ϵ_3/ϵ_1 will be negative and gives the direction of change of ϵ_1 and ϵ_3 that will most rapidly reduce E. At the minimum

$$\frac{\epsilon_3}{\epsilon_1} = -\frac{2\,c_{13}}{c_{33}}. \tag{6}$$

Then (6) gives the direction of change of ϵ_1 and ϵ_3 to reduce G and steps are taken in that direction until a minimum of G is reached. There *must* be a minimum since G cannot go below the ground state at p. The test for positive definiteness is then repeated with the c_{ij} at the new minimum, which will be closer to the true minimum in both a and c than the initial state. Case 2 is iterated until Case 1 occurs and then is iterated to convergence of c_1 and c_3 to small values.

The MNP procedure has been implemented in a computer program which finds the minima. We have tested the program on the ground states of several metallic elements at zero pressure. In each case the procedure consists in choosing an arbitrary initial state and testing how close the final state found by the program is to the known experimental data. In these tests the total-energy calculations were done with a rather small number of k-points in the Brillouin zone (mostly 2000) in order to limit the overall computer times. The results are shown in Table 1. The agreement between MNP results and experimental data is good, being within less than 1% with three exceptions, where agreement is within less than 2%.

A possible concern about accuracy is whether differences in the number of plane waves used in the expansion of the interstitial wave function produces significant changes in the equilibrium structures. Corrections for these differences, known as Pulay corrections, are important for pseudo-potential calculations, which are made entirely in a plane-wave basis. All-electron APW calculations are much less sensitive to those differences, and Pulay corrections have not been incorporated in the LAPW band-structure programs. A direct test of the sensitivity has been made here by repeating calculations of the equilibrium structure of Cu with different numbers of plane waves. The differences in equilibrium structure using $R_{\mathrm{mt}}K_{\mathrm{max}} = 7, 8, 9$, which changes the number of plane waves (proportional to the cube of $R_{\mathrm{mt}}K_{\mathrm{max}}$) by more than a factor of 2, are small (from 0 to 0.45%).

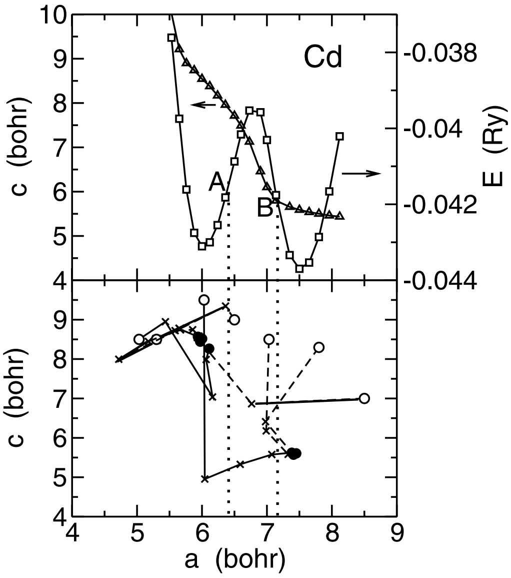

Fig. 1. Tetragonal states of cadmium. *Top panel*: Epitaxial Bain path $c(a)$ (left ordinate) and energy along the EBP $E(a)$ (right ordinate). The energy minima are (in bohr units) at $a = 6.03$, $c = 8.50$ for the fcc phase, and at $a = 7.52$, $c = 5.58$ for the bct structure. A and B mark the points at which the curvature in the energy curve changes sign from concave upward to convex upward. In the range of a between the two vertical dotted lines the structure is unstable (see text). *Bottom panel*: Paths to the minima of E starting from several initial states as found with the MNP procedure. The initial states are indicated by open circles, the final states by full circles. The solid (dashed) lines between X points are Case 1 (Case 2) stages (see text).

In general, different initial states can lead to different minima. In Figure 1 (bottom panel) the paths to the minima of E at $p = 0$ for bct Cd starting from several initial

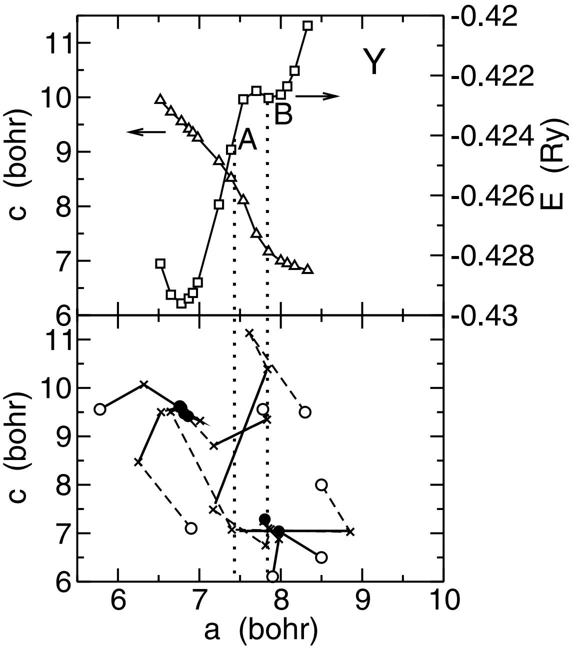

Fig. 2. Tetragonal states of yttrium. The description is the same as in the caption of Figure 1, except that for Y the energy minima are (in bohr units) at $a = 6.78$, $c = 9.56$ for the fcc phase, and at $a = 7.89$, $c = 7.11$ for the bct structure.

states (open circles) are shown. The solid lines between X points are Case 1 stages; at each X the c_i, c_{ij} are re-evaluated; the dashed lines are made up of Case 2 steps — terminating in an X at a new minimum in a particular direction. Two true minima of E (full circles) are found, and can then be refined by adding a stage with stronger convergence criteria on the E calculation. The same MNP procedure is applied to Y in Figure 2.

The outstanding feature of these results with the MNP is that the program succeeded in finding a minimum for all the assumed initial structures, which were chosen to cover several directions. Moreover, the greatest number of stages required was 7 and the average was 4 to 5. The termination values showed a scatter of 1 to 2%, but are functions of the convergence criteria (set at a precision of 10^{-4} Ry/atom for E and 10^{-4} Ry/bohr^3 for c_1 and c_3), which are easily made smaller. The maximum number of steps in Case 2 was 16, the average about 8 (step size was set at strains of 2%); about 1/4 of the stages were Case 2.

Apparently the topology of the energy function in a two-dimensional structure space (coordinates a and c) is favorable to a procedure which uses the local slope and curvature to move toward a minimum. Retention of this property of the topology seems plausible in higher-dimension structure spaces, since the same interaction between atoms will control the energy function. Hence we expect comparable success in dealing with generalizations to less symmetry and more atoms.

3 Comparison of the MNP with the EBP, MD and CRYSTAL procedures

Our previous procedure for finding minima of G as a function of structure was based on the EBP adapted to finite p [3]. First derivatives of E with respect to strain in the c direction are found as a function of c at one a (but not second strain derivatives) in order to satisfy the boundary condition $(2/a^2)(\partial E/\partial c)_a = -p$ (for tetragonal structures). At each a one point is thereby found on the EBP, which is followed continuously by steps δa until minima of G on the EBP are found. At the minima the derivative of G vanishes in two directions, hence vanishes in all directions in a simple two-dimensional minimum, which is a tetragonal equilibrium state at p in which all stresses equal $-p$.

In contrast to this point-by-point tracing of a path on the tetragonal structure plane to find the minima of G, the MNP starts at an arbitrary, but plausible, tetragonal structure, such as a body-centered cubic (bcc) or fcc structure using standard average atomic radii, and calculates the first and second strain derivatives of G for that initial structure. The positive definiteness of the quadratic form $f(\epsilon_1, \epsilon_3)$ in (3) tells us if the initial structure is in the "bowl" of rising G values with positive curvature around a minimum. If the structure is in such a bowl, a stage can be made consisting of a jump to the vicinity of the minimum by choosing strains that cancel the linear terms, i.e., by satisfying (4a) and (4b). The jump will come close to the minimum if the bowl is well-approximated by an expansion through quadratic terms in the strains. Iteration can then converge the structure within the convergence criteria in c_1 and c_3; more stringent convergence criteria in the calculation of G can be introduced in the final stages to get a more accurate minimum structure. At the minimum we have then found a, c, E, G, $c_{11} + c_{12}$, c_{13} and c_{33}.

If the initial structure is not in such a bowl, a direction of change of the strains can be found from $f(\epsilon_1, \epsilon_3)$ that decreases G (the minimum of $f(\epsilon_1, \epsilon_3)/\epsilon_1^2$ gives the ϵ_3/ϵ_1 that most rapidly decreases G); steps along that direction must lead to a minimum closer to a true two-dimensional minimum. The new minimum can then be tested for positive definiteness and Case 1 or Case 2 pursued. Thus each stage always has a successor; the sequence terminates when a minimum is found within the convergence criteria. The only failures we have found are when the preset number of allowed stages is too small to reach the minimum or the preset number of steps in a Case-2 stage is too small to reach the minimum in that direction. Options to go on in these cases can be provided.

The EBP procedure finds the minimum structure, but does not directly find any elastic constants. However we note that at the a_0, c_0 of the minimum the slope of the EBP and the curvature of G along the EBP are related to the c_{ij}. Thus if we put the condition $(1/V)\partial E/\partial \epsilon_3 = -p$ into (3) (a condition which defines the EBP), we get (4b). At the minimum of G, $c_3 = 0$ and (4b) gives, just as in (6),

$$\frac{\epsilon_3}{\epsilon_1} = \frac{a}{c}\left(\frac{d\,c}{d\,a}\right)_{EBP} = -\frac{2\,c_{13}}{c_{33}}. \qquad (7)$$

Table 2. Lattice parameters and elastic constants of tetragonal states of Y and Cd. a_0 and c_0 are the equilibrium parameters of the tetragonal unit cell in Å units; V_0 is the volume per atom in Å^3; E_0 is the energy per atom of each corresponding state in Ry; the c_{ij} and C' are elastic constants in Mb.

	Yttrium		Cadmium	
	fcc	bct	fcc	bct
a_0	3.586	4.177	3.192	3.981
c_0	5.061	3.761	4.497	2.953
c_0/a_0	1.411	0.900	1.409	0.742
V_0	32.53	32.81	22.91	23.40
E_0	−6771.429606	−6771.422773	−11192.043122	−11192.043712
c_{11}	0.562	−0.308	0.344	0.529
c_{12}	0.309	0.805	0.015	0.273
C'	0.126	−0.556	0.164	0.128
c_{44}	0.311		−0.019	0.283

If we substitute ϵ_3 in terms of ϵ_1 from (7) in (3) and differentiate twice with respect to a, we find [3]

$$\frac{1}{c_0}\left(\frac{d^2G}{da^2}\right)_{EBP} = c_{11} + c_{12} - 2\,\frac{c_{13}^2}{c_{33}}, \tag{8}$$

which is called Y' in [3], since it is an analogue of Young's modulus for epitaxial strain.

We note that there is a complementary path through the minima in the tetragonal structure plane based on condition (4a) (vanishing of stress in the a direction), called the uniaxial Bain path (UBP) in [7]. From (4a) the slope of the path at the minimum is

$$\frac{\epsilon_3}{\epsilon_1} = \frac{a}{c}\left(\frac{d\,c}{d\,a}\right)_{UBP} = -\frac{c_{11}+c_{12}}{c_{13}}. \tag{9}$$

Then (7), (8) and (9) determine $c_{11}+c_{12}$, c_{13} and c_{33} with the EBP and UBP procedures.

The EBP's of Y and Cd $c(a)$ are plotted above the stages of the MNP in Figures 1 and 2, as well as $E_{EBP}(a)$ [8]. We note that there are two points A and B in $E_{EBP}(a)$ at which the curvature changes sign from concave upward to convex upward. In the range of a between these points E_{EBP} is convex and the structure is unstable because the curvature

$$Y' \equiv c_{11} + c_{12} - 2\,\frac{c_{13}^2}{c_{33}} < 0, \tag{10}$$

which is the condition that makes $f(\epsilon_1,\epsilon_3)$ in (3) fail to be positive definite. With MNP an initial state chosen in this range produces a Case-2 situation.

The condition (10) is a failure of one of the four stability conditions [9] that determine stability of a tetragonal structure. It is the only one that tests static stability without breaking the tetragonal symmetry, i.e., it indicates tetragonal instability. The other three stability conditions are

$$C' = \frac{c_{11}-c_{12}}{2} > 0, \tag{11a}$$

$$c_{44} > 0, \tag{11b}$$

$$c_{66} > 0. \tag{11c}$$

The range of unstable states forms a multiply-connected region in the tetragonal structure plane which separates bowls of stability that surround the minima. The regions of instability could be traced out by plotting additional EBP's at finite pressures [3].

The evaluation of all the elastic constants at the minima of Y and Cd is in Table 2 [10]. For Y the fcc minimum is shown to be stable, but the bct minimum is unstable ($C' < 0$). For Cd the fcc minimum is unstable ($c_{44} < 0$). The stability of the bct state of Cd is uncertain because numerical instabilities in the energy calculation gave contradictory results for c_{66}.

It is interesting to compare the MNP with the MD technique extended to variable cell structure and finite pressures [4]. In this extension the MD can be and has been applied to the phases of elements, but has different strengths and weaknesses versus the MNP. The MD calculates electronic structure and forces on the atoms quantum mechanically, but the atoms then follow classical orbits. Hence the MD is not suitable for accurate descriptions of low-temperature equilibrium behavior. Quong and Liu [11], who made a good first-principles calculation of thermal expansion in some cubic materials, but rejected the MD, remark: "First-principles molecular dynamics methods such as the Car-Parrinello method can be used to determine thermal properties expressed as statistical averages. However since the ionic degrees of freedom are treated classically these simulations are not valid at temperatures comparable to or lower than the Debye temperature. A further drawback is that the entropy, and hence the free energy, cannot be expressed as an ensemble average." In contrast to MD, the MNP is completely first-principles quantum-mechanical and could readily add the generalized Debye evaluation of the zero-point vibrational energy that is an intrinsic part of the zero-temperature crystal, but is not present in the MD calculation. The MNP could also add the vibrational Helmholtz free energy at finite temperature in the quasi-harmonic Debye approximation to give accurate low-temperature equilibrium structures. The MNP technique evaluates properties of the infinite lattice with the high accuracy of the WIEN band-structure program, whereas MD finds statistical averages over a finite number of atoms, which are subject to fluctuations.

It is instructive to discuss the MD calculation of the phase transition between hcp and bcc Mg [12] compared to that phase transition found by the EBP (equivalent to the MNP) [13]. The MD using a small cell at elevated temperature starting from one phase generated the other phase at the appropriate pressure in about 500 time steps, and gave strongly fluctuating values of structural parameters. The structural parameters at equilibrium were somewhat distorted and the transition pressure was low by 30% compared to the experimental value. More atoms in the MD calculation would give more accuracy, at the expense of increased computation time. In contrast the EBP calculation gave precise lattice constants in each phase separately and a transition pressure close to experiment from the crossing of Gibbs free-energy curves as functions of pressure.

The MD calculation appears to be more computationally intensive than the MNP calculation, since it approaches equilibrium through many small damped time-steps. At each time-step the self-consistent wave function and atomic forces must be computed. The MNP makes a sequence of jumps in structure controlled by the local free energy curvature and slope as a function of strain. Rather few jumps are needed to find the minimum, and the final approach to such minima is second-order in the strains.

Finally we note that among the MD advantages are the ability to handle many atoms in a unit cell at finite temperatures and give plausible intermediate configurations between an initial and final structure. The MNP calculation will grow rapidly with addition of more atoms in the unit cell and the intermediate configurations apply just to a single cell, i.e., are homogeneous, and are not related to the path that an actual system would follow.

It is also of interest to compare MNP with the procedure in the program CRYSTAL [5], which was adapted from programs to find equilibrium structures of molecules [14]. Both MNP and CRYSTAL are based on the well-known mathematical procedure that uses second derivatives of a function at an initial set of values of the variables to find a new set of values at which the first derivatives are smaller. If the function has positive curvature at the initial variable, a change in the variable can be found which reduces the first derivative. Iteration should then lead to variable values at which the first derivatives fall below a preset small value.

The most striking difference between MNP and CRYSTAL is that MNP, which is designed to solve a simpler structural problem than CRYSTAL, is much simpler in its operations and has much fewer operations. There are also many differences in detail. We note the following:

- CRYSTAL at each stage n finds a new direction along which to vary the structure from the structure at n to search for a minimum; MNP at each stage n finds a new structure which would be the minimum if the quadratic expansion of G in the variables were exact.
- CRYSTAL uses structural variables about which there is physical knowledge — bond lengths, bond angles, dihedral angles — which it orthogonalizes and tests for linear dependence; MNP uses the natural variables of crystal elasticity theory, the strains, so that all deformations are free of rotations.
- CRYSTAL calculates accurate analytic first derivatives in a Hartree-Fock formulation [15], which are used to update the matrix of second derivatives (the Hessian matrix) at each stage with elaborate formulas, hence accurate value of the first derivatives are needed; MNP calculates the first and second derivatives numerically in a density-functional formulation with about 1% accuracy at each stage, hence does not need accurate values because the procedure is self-correcting.
- MNP has just two basic operations: (1) finding first and second derivatives numerically and applying the Hessian matrix to the vector of first derivatives to find a structure closer to the minimum energy; (2) if the Hessian matrix is not positive definite steps are taken in the steepest descent direction to a one-dimensional minimum and the process is repeated. CRYSTAL adds operations on the coordinates, operations to update the Hessian matrix from an initial estimate based on a physical knowledge, and search operations for one-dimensional minima. Some of these more elaborate operations may be needed when MNP is modified to include more atoms in the unit cell. But MNP has been proved adequate for the interesting and important question of the existence of stable and metastable phases of elements in several symmetrical common structures of metallic elements under pressure. In the simple case of low-dimensional structure spaces MNP and its generalizations should be able to locate all minima of G, i.e., all stable and metastable phases. The search can be started with initial structures covering in the two-dimensional case a circle around the physically reasonable region. Generalization to lower-symmetry Bravais lattices should work well with the same simple operations, and the addition of temperature-dependent terms in the quasi-harmonic Debye approximation to G is straightforward.

4 Discussion

Both the EBP and MNP procedures find the minima of $G(a, c)$, but may differ in the number of calculations of E required (the heaviest part of the calculation) and they differ in basic approach. The EBP usually requires somewhat fewer E values, but proceeds by a sequence of a values, each of which requires several E calculations to locate the value of E at that a and gives one point on the EBP. The EBP thus traces out a continuous path in the tetragonal structure plane which leads to a two-dimensional minimum of G. The process generates much information about the energy surface which is not relevant to the minima.

The MNP procedure, in contrast to the EBP, does not trace out a continuous path, but goes through a series of controlled stages in which jumps are made to structures closer and closer to the minima of G. At each stage determination of five coefficients requires five calculations of E. The two procedures are comparable in efficiency for locating tetragonal minima. One advantage of the MNP is that it is easily fully automated. Another important advantage of the MNP is that it is readily generalizable in more ways than the EBP.

Both procedures apply to both tetragonal and hexagonal structures, which have a two-dimensional structure space and apply to arbitrary hydrostatic pressure by searching for minima of the Gibbs free energy at zero temperature. However, the MNP is immediately generalizable to deal with structures of lower symmetry than tetragonal or hexagonal symmetry and with more atoms in the unit cell. The stages of the path to a minimum will take place in a three-dimensional structure space for orthorhombic Bravais lattices, in a four-dimensional structure space for Bravais monoclinic lattices (coordinates a, b, c, γ) and in a six-dimensional structure space for triclinic Bravais lattices. In the primitive unit cell each additional atom (which can be a different element) brings three additional degrees of freedom in general, but fewer if the atom has a symmetrical position.

The current MNP is thus the initial program in a sequence of generalizations. Now it can find stable states (i.e., phases) at any p if they are tetragonal or hexagonal. The generalizations should be able to find all the stable states in n-particle cells, where n will probably be limited to a small integer by computational capacity. We observe that for each n, each element *must* have at least one stable state at each p; the lowest of these is the ground state at that p and the others are metastable phases. This array of n-particle stable states of the elements is enriched by finite pressure and by anisotropic stress. A large increase in possible phases is produced by allowing the atoms for $n \geq 2$ to be different.

The elements Y and Cd were chosen to test the MNP in tetragonal structure at $p = 0$ for two reasons: (1) because they have hcp ground states, but with different elastic anisotropies [16], hence any stable tetragonal state would be a new metastable phase, since it will have a greater E than the hcp ground state; and (2) because MNP might behave differently in crystals with different elastic anisotropies. The close connection of hcp and fcc structures because both can be ideally close-packed has frequently found both the fcc and hcp structures stable for either an hcp or fcc ground state, respectively (so we expect a metastable phase for fcc Y and Cd). But if the fcc state is unstable there must exist a new metastable Bravais phase with one atom in the primitive unit cell with symmetry less than tetragonal and energy above the hcp ground state. Finding such metastable phases will be possible when the MNP is generalized to operate in structure spaces up to six dimensions.

Both Y and Cd satisfy the general rule that transition metals have one tetragonal equilibrium state with cubic symmetry and one which is noncubic [3]. But Y and Cd differ in that Y has a stable fcc phase (like Mg, Zr, Co), but Cd has an unstable fcc equilibrium state ($c_{44} < 0$, like Zn). The bcc and bct equilibrium states of Y are both unstable; see Table 2. The bcc equilibrium state of Cd is also unstable; the status of the bct equilibrium state of Cd is uncertain, since the sign of c_{66} was not clearly established. It seems significant that Cd and Zn are far from ideal close-packing in their hcp ground states [the close-packed (0001) planes are well-separated] and that the elastic constant c_{44} of their fcc equilibrium states opposes sliding on each other of close-packed (111) planes, which are not well-separated in the fcc structure. However, hcp Y is almost close-packed and shows almost isotropic elastic behavior [17], hence may be expected to differ from Cd.

For Y, there is a previous theoretical calculation by Min and Ho [17] of the energies of the bcc, fcc and hcp structures as functions of volume per atom. Min and Ho used a pseudopotential in the local-density approximation. They reported no numerical results, but from their Figure 3 we can estimate the zero-pressure difference in energy between bcc and fcc phases as 7.2 mRy, in good agreement with the value 7.1 mRy found on the Y-EBP in Figure 1. Since the elastic constants were not evaluated, Min and Ho did not know that the bcc structure is unstable, that an unstable bct equilibrium state exists, and that the fcc structure is stable. Since Y has an hcp ground state, the fcc phase is necessarily a metastable phase.

The metastability of fcc Y found here makes this phase a good candidate for experiments aimed at stabilization by pseudomorphic epitaxy, as we have done for other materials [18]. Since the a parameter of fcc Y is 3.59 Å, a rather large value, the choice of a suitable substrate (i.e., one with a small misfit to fcc Y) is somewhat limited. The refractory metals Ta and W have large lattice parameters, but their misfits of about 8 and 12% are probably too large (in fact, using W{001} as a substrate we have failed to achieve epitaxy), so that the only possible candidate seems to be Pb{001} ($a = 3.400$ Å, hence a misfit of 2.5%).

The EBP or the MNP procedure at finite pressure could be applied to find the transition pressure from hcp Y to fcc Y predicted by Min and Ho [17]. To be complete the calculations would have to be extended to cover the intermediate crystal phases found experimentally [20], the sequence being hcp→ Sm-type→ dhcp→ fcc, and zero-point energies should be included.

We gratefully acknowledge partial support of this work by the National Science Foundation with Grant DMR0089274. We are also grateful to Stefaan Cottenier for his kind and competent advice regarding WIEN calculations. P.M. Marcus thanks IBM for providing facilities at the Thomas J. Watson Research Center.

References

1. P. Blaha, K. Schwarz, J. Luitz, WIEN97, Vienna University of Technology 1997. [Improved and updated UNIX version of the original copyrighted WIEN-code which was published by P. Blaha, K. Schwarz, P. Sorantin, S.B. Trickey in Comput. Phys. Commun. **59**, 399 (1990)]
2. S.L. Qiu, F. Apostol, P.M. Marcus, J. Phys.: Condens. Matter **16**, 6405 (2004)
3. P.M. Marcus, F. Jona, S.L. Qiu, Phys. Rev. B **66**, 064111 (2002)
4. R.M. Wentzcovitch, J.L. Martins, G.D. Price, Phys. Rev. Lett. **70**, 3947 (1993)
5. B. Civalleri, Ph. D'Arco, R. Orlando, V.R. Saunders, R. Dovesi, Chem. Phys. Lett. **348**, 131 (2001)
6. W. Kohn, L.J. Sham, Phys. Rev. A **140**, 1133 (1965); J.P. Perdew, S. Burke, M. Enzerhof, Phys. Rev. Lett. **77**, 3865 (1996)
7. P. Alippi, P.M. Marcus, M. Scheffler, Phys. Rev. Lett. **77**, 3892 (1997)
8. For both Y and Cd in the EBP calculations calculations we used $RMT = 2.4$ bohr and a plane-wave cutoff of $RK_{max} = 9$ (resulting in 1000 to 1100 plane waves), $G_{MAX} = 16$ bohr^{-1}, 12000 k-points in the full Brillouin zone (828 k-points in the irreducible wedge of the Brillouin xone), convergence criterion for E of 1×10^{-6} Ry. In the MNP calculations we reduced the total number of k points to 4000 and the convergence criterion for E to 1×10^{-4} Ry
9. J.F. Nye *Physical Properties of Crystals*, Oxford Clarendon Press, London (1957), p. 142. Nye gives the stability conditions for hexagonal lattices. For tetragonal lattices the condition $c_{66} > 0$ must be added
10. WIEN97 normally calculates the Fermi energy with the tetrahedron procedure (called TETRA), which was used for the tetragonal calculations. However, calculations of the elastic constants c_{44} and c_{66} require breaking tetragonal symmetry and almost never converged. Those calculations were done with a Gaussian smearing method (called GAUSS) with a small width of 0.003
11. Andrew A. Quong, Amy Y. Liu, Phys. Rev. B **56**, 7767 (1997)
12. R.M. Wentzcovitch, Phys. Rev. B **50**, 10558 (1994)
13. F. Jona, P.M. Marcus, J. Phys.: Condens. Matter **15**, 7727 (2003)
14. H. Bernhard Schlegel, J. Comp. Chem. **3**, 214 (1982)
15. K. Doll, R. Dovesi, R. Orlando, Theor. Chem. Acc. **112**, 394 (2004)
16. H. Olijnyk, A.P. Jephcoat, Solid State Commun. **115**, 335 (2000) discuss anisotropy of hcp elements
17. B.J. Min, K.-M. Ho, Phys. Rev. B **40**, 7532 (1989)
18. S.K. Kim, F. Jona, P.M. Marcus, J. Phys.: Condens. Matter **8**, 25 (1996)[Ti]; Y. Tian, F. Jona, J. Phys.: Condens. Matter **13**, 1805 (2001) [Mn]; X.Z. Ji, Y. Tian, F. Jona, Phys. Rev. B **65**, 155404 (2002) [Pd]; X.Z. Ji, F. Jona, J. Phys.: Condens. Matter **14**, 12451 (2002) [Mg]
19. W.A. Grosshans, Y.K. Vohra, W.B Holzapfel, Phys. Rev. Lett. **49**, 1572 (1982); Y.K. Vohra, V. Vijayakumar, B.K. Godwal, S.K. Sikka, Phys. Rev. B **30**, 6205 (1984)
20. W.B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, Vol. 2 (Pergamon Press, Oxford, 1967)