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Hexagonal and tetragonal states of magnesium by first principles

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First-principles total-energy calculations on hexagonal-close-packed (hcp) and body-centered-tetragonal (bct) states of bulk elemental magnesium have been made with a full-potential electronic structure program with both the local-density approximation and the generalized gradient approximation. The unique paths [called epitaxial Bain paths (EBP's)] through hexagonal or tetragonal states produced by epitaxial strain on equilibrium states have been found. The hexagonal EBP reveals the existence of an hcp phase with axial ratio $c/a \sim 0.72$ and about 20 mRy/atom higher energy than the hcp ground state. Structure parameters and elastic constants of both the ground state and the higher-energy state are determined, and the ground-state values are compared to experiment. Tests of the stability of the hcp phase at $c/a \sim 0.72$ show that this phase is unstable. The tests for stability require calculations of the elastic constants, which in the case of hcp crystals are composed of a homogeneous and an inhomogeneous contribution. We describe a considerably simplified calculation of the inhomogeneous contribution obtained by using a symmetrical orientation of the unit cell and finding all the elastic constants with symmetrical strains. The tetragonal EBP shows the existence of a face-centered-cubic phase of Mg with about 1 mRy/atom higher energy than the hcp ground state. The elastic constants of this phase satisfy the stability conditions: hence, this phase is metastable.

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I. INTRODUCTION

In our ongoing search for metastable phases of metallic elements we have undertaken a study of hexagonal-close-packed (hcp) structures and of body-centered-tetragonal (bct) structures [which include both body-centered-cubic (bcc) and face-centered-cubic (fcc) structures] of magnesium, and we report here the results of that study. Our goals are (1) to find new crystalline phases, which correspond to minima of the total energy for particular values of the lattice parameters, and (2) to determine whether such phases are stable, metastable, or unstable.

The first goal is achieved by calculating the so-called epitaxial Bain path[1,2] (EBP) for both hcp and bct Mg. The EBP is a path through hexagonal (tetragonal) states which passes through all hexagonal (tetragonal) equilibrium states, where the energy is a local minimum, and through hexagonal (tetragonal) states produced by epitaxial or biaxial strain of the equilibrium states. The lowest-energy minimum is usually the ground state; higher-energy minima define possible metastable states. The procedure for the calculation of the tetragonal EBP has been described before;[3–5] that for the calculation of the hexagonal EBP is similar and will be described below. We show that the hexagonal EBP reveals the existence of an hcp phase of Mg with energy about 20 mRy/atom higher than the ground state, while the tetragonal EBP shows the presence of an fcc phase of Mg with energy only about 1 mRy/atom higher than the hcp ground state.

The second goal is achieved by calculating the elastic constants of each phase and then testing whether the stability conditions for its structure are fulfilled. The stability conditions arise from the requirement that the quadratic form of the strain energy for small strains be positive definite, i.e., greater than zero for all real nonzero values of the strains (Ref. 6, p. 142). A complication for hcp crystals, common to all noncentrosymmetric structures, is that the elastic constants comprise two contributions, a homogeneous and an inhomogeneous one. The inhomogeneous contribution arises from an internal relaxation, due to the fact that the unit cell contains an extra atom, which has a different environment from the atom at the origin, and can move independently when strains are applied. Thus the calculations of hcp elastic constants are done in two steps: first, by determining the response of the crystal when a uniform (homogeneous) strain is applied and, second, by allowing the extra atom to change position in order to lower the energy (called an internal relaxation). Internal relaxation can reduce the values of some elastic constants substantially. The calculation procedure is described in detail below.

The ground state of hcp Mg has been the object of a number of theoretical studies published in the literature;[7–13] some of them include calculations of elastic constants, but only a few take internal relaxation into account.[8,9,13] Our results compare well with both experimental values and theoretical literature data.

For the hcp phase with 20 mRy/atom higher energy than the ground state the elastic constants show that phase to be unstable. For the fcc phase, the elastic constants satisfy the stability conditions: hence, that phase is metastable.

We describe the procedures followed for the calculations in Sec. II, with Sec. II A devoted to determination of the EBP's and Secs. II B and II C concerned with the calculations of elastic constants of hcp and bct phases, respectively. The results are reported in Sec. III A for the hcp phase and in Sec. III B for the tetragonal phases. A brief discussion of the results is then presented in Sec. IV.

II. CALCULATIONS

The total-energy calculations were done with the WIEN97 program developed by Blaha and co-workers.[14] This program uses the full-potential linearized augmented planewave (FLAPW) method and can calculate total energies for a variety of crystal structures and space groups with a choice of nonrelativistic (NREL) or relativistic (RELA) calculations in either the local-density approximation (LDA) or the generalized gradient approximation (GGA). The program was implemented and executed on a LINUX-based desktop PC. All calculations discussed in this paper were done twice, once with the NREL-LDA and once with the RELA-GGA formulation.

A. Epitaxial Bain path

The structures considered in the present calculations are either hcp, for the construction of the hexagonal EBP, or bct, for the construction of the tetragonal EBP. In either case the parameters of the unit cell are a (the edge of the primitive rhombus with angle $\gamma = 120°$ for hcp cells or the edge of the primitive square base for bct cells) and c (the height of the cell). A value of a is chosen and several calculations of the total energy per atom are done for a series of values of c. A least-squares fit of a cubic polynomial to the calculated energy values then gives the minimum energy and the value of $c = c_{\mathrm{min}}$ that corresponds to the minimum energy. Thus a pair of values (a and c) are found which define an hcp or bct state on the EBP. The procedure is then repeated for a different choice of a to produce a new pair of a and c parameters. About 20–25 such pairs are determined to cover the range of c/a values from 0.5 to 2.1 for hcp Mg and from 0.8 to 1.6 for bct Mg. These pairs of values trace out the EBP.

The EBP is generally presented in three ways: (1) a plot of c versus c/a, (2) a plot of total energy per atom versus c/a, and (3) a plot of normalized volume per atom versus c/a. The energy plot reveals minima at certain values of c/a, corresponding to as many crystalline phases, the lowest of which can be the ground state. The other energy minima identify phases which may be metastable or unstable, depending on whether the stability conditions are satisfied or not. Testing the stability conditions requires determination of the elastic constants of the phase under scrutiny. We describe next how such a determination is made for both hexagonal and tetragonal phases.

B. Elastic constants of hexagonal phases

Hexagonal crystals have five independent elastic constants (Ref. 6, p. 141) c_{11}, c_{12}, c_{13}, c_{33}, and $c_{44} = c_{55}$. A sixth nonindependent constant is $c_{66} = (c_{11} - c_{12})/2$. With the simplifying assumption that both c_{12} and c_{33} are positive, the stability conditions are (Ref. 6, p. 142)

$$c_{66} = \frac{c_{11} - c_{12}}{2} > 0, \tag{1a}$$

$$c_{11} + c_{12} - \frac{2c_{13}^2}{c_{33}} > 0, \tag{1b}$$

$$c_{44} > 0. \tag{1c}$$

The general procedure for the determination of elastic constants is to apply suitable small strains to the unit cell, calculate the total energy per atom, and then find the second derivative of the energy with respect to the strain. This procedure produces a homogeneous strain of the lattice, which is sufficient for crystals with Bravais lattices. Hexagonal-close-packed crystals, however, have a nonprimitive unit cell: there is an additional nonequivalent atom in the cell which is free to move away from the position imposed by the homogeneous strain. Therefore the extra atom must be independently relaxed, a behavior called internal relaxation, which makes the strain inhomogeneous. Hence for hcp crystals it is important to distinguish between the elastic constants determined with homogenous strains, which we refer to as *unrelaxed*, and those determined with inhomogeneous strains, which we call *relaxed*.

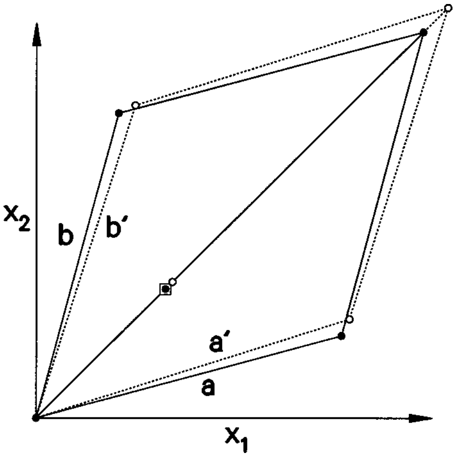

FIG. 1. The basal plane of the undistorted unit cell of hcp Mg, axes **a** and **b** at 60° to one another, is drawn with solid lines (atoms as solid circles). The rhombus has been rotated by 15° around the c axis (perpendicular to the page) in order to be symmetric with respect to the Cartesian axes x_1 and x_2. A 10% homogeneous shear deforms the 60° rhombus into the dotted 55.2° rhombus, axes $\mathbf{a}'$, $\mathbf{b}'$, atoms as open circles. Internal relaxation moves the extra atom back to almost the original position (open square).

1. Determination of unrelaxed elastic constants

The conventional unit cell of hcp crystals has the angle γ between the a and the $b = a$ axes equal to 120° (with $\alpha = \beta = 90°$) and the extra atom in position $(a/3, 2a/3, c/2)$. This notation says that the components of the position vector of the extra atom along the lattice vectors have lengths $a/3$, $2a/3$, and $c/2$. But for the study of internal relaxation it is more convenient to consider the unconventional unit cell with $\gamma = 60°$ and to rotate the unit cell by 15° around the c axis, so as to have the basal rhombus symmetrically oriented with respect to the Cartesian axes x_1 and x_2, as indicated in Fig. 1 (solid lines). In this unit cell the extra atom has components $(a/3, a/3, c/2)$. The advantage of this choice is that when symmetrical strains are applied the extra atom is expected to move only *within* the bisecting plane of γ, which is at 45° to the x_1 and x_2 axes.

Since the hexagonal EBP was calculated for the conventional cell ($\gamma = 120°$), we tested that the use of the unconventional cell ($\gamma = 60°$) would produce the same energy values. We found this to be the case to within less than 0.1 mRy/atom, thus in acceptable agreement.

Strains are defined in terms of Cartesian coordinates: so when a strain is applied to a hexagonal cell, it is necessary to consider the Cartesian components of the lattice vectors. A strain changes the lengths of the lattice vectors and the angles between them, which are the quantities needed as inputs to the WIEN97 program. To find these quantities we adopt and modify the matrix procedure outlined by Fast *et al.*[10] We define a lattice matrix

$$R=\begin{pmatrix} a_x & b_x & c_x & d_x \\ a_y & b_y & c_y & d_y \\ a_z & b_z & c_z & d_z \end{pmatrix}, \tag{2}$$

whose elements are the Cartesian components a_x, b_x, c_x, a_y, b_y,..., c_z of the hexagonal lattice vectors **a**, **b**, and **c**, respectively, to which we have added the components d_x, d_y, d_z of the vector **d** from the origin to the extra atom in the unit cell. To find the strained lattice vectors we multiply the matrix R with the strain matrix

$$E=\begin{pmatrix} 1+\epsilon_{11} & \epsilon_{12} & \epsilon_{13} \\ \epsilon_{12} & 1+\epsilon_{22} & \epsilon_{23} \\ \epsilon_{13} & \epsilon_{23} & 1+\epsilon_{33} \end{pmatrix}, \tag{3}$$

where the ϵ_{ij}'s are the strains as defined, e.g., in Ref. 6 (p. 99).

The result of this product is a matrix R' whose elements are the Cartesian components a'_x, b'_x,..., d'_z of the strained hexagonal lattice vectors $\mathbf{a}'$, $\mathbf{b}'$, $\mathbf{c}'$, and $\mathbf{d}'$. We need to find the components $d'_{a'}$, $d'_{b'}$, $d'_{c'}$ of the $\mathbf{d}'$ vector along the $\mathbf{a}'$, $\mathbf{b}'$, and $\mathbf{c}'$ axes. If we rewrite the vector equation

$$\mathbf{d}'=d'_{a'}\frac{\mathbf{a}'}{a'}+d'_{b'}\frac{\mathbf{b}'}{b'}+d'_{c}\frac{\mathbf{c}'}{c'}, \tag{4}$$

in terms of the *x,y,z* components of each vector (components which are known from the R' matrix), we get three simultaneous equations for the components $d'_{a'}$, $d'_{b'}$, $d'_{c'}$ along the hexagonal axes.

The procedure just described produces the input quantities to the WIEN97 program. In order to determine the five elastic constants of the hexagonal phases we need to apply five different strains. To find which strain to apply it is convenient to start with the expression for the strain energy density for hexagonal structures written in terms of one-index strains:

$$\frac{E}{V}=\frac{1}{2}c_{11}(\epsilon_1^2+\epsilon_2^2)+c_{12}\epsilon_1\epsilon_2+c_{13}(\epsilon_1\epsilon_3+\epsilon_2\epsilon_3)+\frac{1}{2}c_{33}\epsilon_3^2 + \frac{1}{2}c_{44}(\epsilon_4^2+\epsilon_5^2)+\frac{1}{2}c_{66}\epsilon_6^2, \tag{5}$$

where (Ref. 6, p. 134) $\epsilon_1=\epsilon_{11}$, $\epsilon_2=\epsilon_{22}$, $\epsilon_3=\epsilon_{33}$, $\epsilon_4=2\epsilon_{23}$, $\epsilon_5=2\epsilon_{13}$, $\epsilon_6=2\epsilon_{12}$.

The five strains needed (all of which preserve the reflection symmetry of the bisecting plane) are as follows.

(i) Choosing $\epsilon_1=\epsilon_2=\epsilon\neq 0$, all other $\epsilon_i=0$, we get

$$c_{11}+c_{12}=\frac{1}{2V}\left(\frac{\partial^2 E}{\partial\epsilon^2}\right)_{\epsilon_i=0,\ i=3-6} \tag{6}$$

(ii) Choosing $\epsilon_3=\epsilon\neq 0$, all other $\epsilon_i=0$, we get

$$c_{33}=\frac{1}{V}\left(\frac{\partial^2 E}{\partial\epsilon^2}\right)_{\epsilon_i=0,\ i=1,2,4,5,6} \tag{7}$$

(iii) Choosing $\epsilon_1=\epsilon_2=\epsilon_3=\epsilon\neq 0$, all other $\epsilon_i=0$, we get

$$c_{11}+c_{12}+2c_{13}+\frac{1}{2}c_{33}=\frac{1}{2V}\left(\frac{\partial^2 E}{\partial\epsilon^2}\right)_{\epsilon_i=0,\ i=4-6} \tag{8}$$

(iv) Choosing $\epsilon_4=\epsilon_5=\epsilon\neq 0$, all other $\epsilon_i=0$, we get

$$c_{44}=\frac{1}{2V}\left(\frac{\partial^2 E}{\partial\epsilon^2}\right)_{\epsilon_i=0,\ i=1,2,3,6} \tag{9}$$

(v) Choosing $\epsilon_6=\epsilon\neq 0$, all other $\epsilon_i=0$, we get

$$c_{66}=\frac{1}{V}\left(\frac{\partial^2 E}{\partial\epsilon^2}\right)_{\epsilon_i=0,\ i=1,2,3,4,5} \tag{10}$$

From Eqs. (6) and (10) (since $2c_{66}=c_{11}-c_{12}$) we calculate c_{11} and c_{12}; then from Eqs. (7) and (8) we calculate c_{13}. (Note that $c_{11}-c_{12}$ could also be calculated by choosing $\epsilon_1=-\epsilon_2=\epsilon\neq 0$, all other ϵ_i's equal to 0, but such a strain would not be symmetric with respect to the bisecting plane, and the extra atom could move out of the bisecting plane. Similarly, using ϵ_4 alone to determine c_{44} would lose the symmetry of the bisecting plane.)

2. Determination of relaxed elastic constants

The strains listed above in Eqs. (6), (7), and (8) change the lengths of the hexagonal lattice vectors, but maintain hexagonal symmetry: hence, the extra atom is expected to remain in the position ($a'/3$,$b'/3$,$c'/2$)—no internal relaxation occurs. By contrast, the strains listed in Eqs. (9) and (10) ($\epsilon_4=\epsilon_5$ and ϵ_6, respectively) change the angles $\alpha=\beta$ and γ, respectively, and thereby change the symmetry to triclinic and orthorhombic, respectively. As a consequence, the extra atom might be expected to move away from the homogeneous position, but the fact that the strains are symmetric will keep the atom in the bisecting plane.

However, in Eq. (9), for strains $\epsilon_4=\epsilon_5$, the rhombus in the $(00\frac{1}{2})$ plane is the same as in the basal plane, only shifted, so that the extra atom is expected to stay at or close to the homogeneous position. By contrast, in Eq. (10), for strain ϵ_6, the 60° rhombus is distorted to a rhombus with the angle $\gamma\neq 60°$: hence, the extra atom is likely to move, although the mirror plane at $(00\frac{1}{2})$ will keep it at $c/2$.

We describe now the procedure followed for the quantitative determination of the unrelaxed and relaxed elastic constant c_{66} (the procedure is the same for c_{44}). We apply three strains $\epsilon_6 = +0.1$, $\epsilon_6 = +0.002$, and $\epsilon_6 = -0.1$ (we avoid $\epsilon_6 = 0$ in order to keep the same crystallographic symmetry, i.e., orthorhombic, for all three strains; also, we choose rather large strains in order to avoid inherent inaccuracies of the relative energies from the computer program at the hundreths of a mRy level). For each strain we calculate the total energy with the procedure outlined in the preceding section with the extra atom in the unrelaxed position $(a'/3, a'/3, c'/2)$. The curvature at the minimum of the curve through the three energy values allows the calculation of unrelaxed c_{66} as per Eq. (10).

Then for each one of the three strains we do two more energy calculations with the extra atom away from the homogeneous position, say, at positions $(0.293333a', 0.293333a', 0.5c')$ and $(0.373333a', 0.373333a', 0.5c')$. The two energy values thus calculated, together with the energy for the homogeneous position, define a curve that determines at its minimum the relaxed position of the extra atom and the relaxed energy for each strain. Thus each one of the three strains is associated with a minimum energy value: the second derivative of the curve through the three minimum energy values allows then the calculation of the relaxed c_{66} with Eq. (10). An example of this procedure will be given explicitly below and discussed in Fig. 3, below.

C. Elastic constants of tetragonal phases

The procedure for the calculations of elastic constants of fcc and bct phases was described in Ref. 4, with some modifications added in Ref. 15, and will not be recounted here. We note only, in contrast to the hcp phase, that while a bct phase also has an extra atom in the tetragonal unit cell, the bct phase is a Bravais lattice: hence, the extra atom behaves as the atom at the origin: there is only homogeneous strain: no internal reaxation occurs.

III. RESULTS

A. Hexagonal Mg

The results are presented graphically in Fig. 2. The top panel of this figure is a plot of c versus c/a for both the LDA and GGA. The middle panel is a plot of the energy per atom versus c/a, relative to the ground state. This plot gives two pieces of information: (1) the curves have a deep minimum at $c/a = 1.629$ for the LDA and $c/a = 1.626$ for the GGA, close to the experimental value $c/a = 1.624$, which corresponds to the hcp ground state of Mg. The energy minima are -398.401240 Ry for the LDA and -400.669749 Ry for the GGA formulation. (2) There is a shallow minimum at $c/a = 0.725$ for LDA and at $c/a = 0.715$ for GGA. This minimum is about 20 mRy/atom higher than that of the ground state and defines a new phase of Mg with hcp structure.

The bottom panel of Fig. 2 is a plot of the relative volume V/V_0 as a function of c/a: V_0 is the *theoretical* value of the volume of the ground state (at $c/a = 1.629$ for the LDA and 1.626 for the GGA). The point corresponding to the ground state is marked with a solid circle. The shaded area, covering the range of positive slope of the V/V_0 curve, indicates a region in which the strain energy is not positive definite, i.e., a region of states that are intrinsically unstable, here with respect to deformations that preserve hexagonal symmetry.[1,2] The portion of the EBP on the right of the unstable region defines the strained states that can be obtained by pseudomorphic epitaxy of the stable phase on substrates that preserve the hcp structure. The portion on the left of the unstable region serves the same purpose for strained states of the phase at $c/a \sim 0.72$.

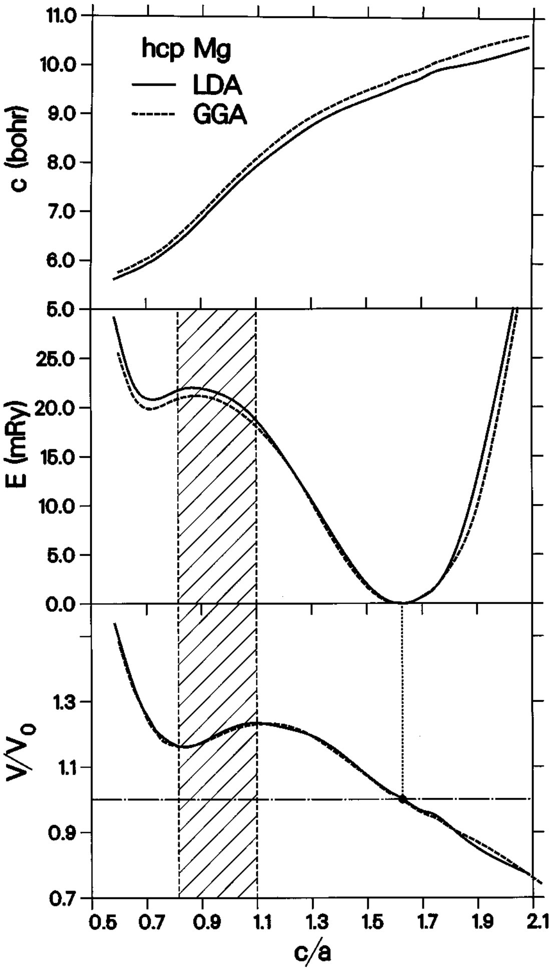

FIG. 2. Epitaxial Bain path of hcp Mg: solid curves calculated with the local-density approximation (LDA), dashed curves calculated with the generalized-gradient approximation (GGA). *Top panel:* c vs axial ratio c/a. *Middle panel:* total energy per atom, referred to the ground state, vs axial ratio c/a. *Bottom panel:* relative volume per atom V/V_0 vs axial ratio c/a (V_0 is the theoretical atomic volume of the ground state). The solid circle marks the relative volume of the ground state. The shaded area covers a region of intrinsically unstable states.

The results are summarized in Table I which lists the lattice parameters of the ground state of hcp Mg as calculated in this work and the corresponding experimental data. The agreement between theory and experiment is satisfactory, being about 2.5% for the LDA and 0.4% for the GGA. The crystallographic data for the phase at $c/a \sim 0.74$ do not, of course, have experimental counterparts.

The table lists also the values of the elastic constants. Some literature data are also listed for comparison. The un-

TABLE I. Lattice parameters and elastic constants of hexagonal states of Mg. a_0 and c_0 are the parameters of the hexagonal unit cell, in Å units; V_0 is the volume per atom, in Å^3; the c_{ij} are elastic constants, in Mb. The superscript u in c_{44}^u and c_{66}^u denotes *unrelaxed* elastic constants (calculated with homogeneous strain), while the superscript r refers to *relaxed* elastic constants (inhomogeneous-strain considered). The calculations were done with the WIEN97 (FLAPW) program (Ref. 14) both in the nonrelativistic local-density approximation (LDA) and in the relativistic generalized-gradient approximation (GGA). The column headings of the literature data are the initials of the authors of the references cited in the footnotes. the "higher-E state" heading of the two right-hand-side columns refers to the shallow energy minima at $c/a \sim 0.72$. The experimental data stem from Person (Ref. 17) for the lattice constants (room-temperature values), and from Simmons and Wang (Ref. 18) for the elastic constants (0 K values).

	hcp Mg (ground state)						Higher-E state	
	Theory						Theory	
	This work		Literature data				This work	
	LDA	GGA	vMS	MRBP	LAEM	Expt.	LDA	GGA
a_0	3.129	3.196			3.206[e]	3.2094	4.384	4.499
c_0	5.096	5.196			5.187[e]	5.2105	3.177	3.217
c_0/a_0	1.629	1.626			1.623[e]	1.6235	0.725	0.715
V_0	21.60	22.98				23.240	26.44	28.20
c_{11}	0.7473	0.6077	0.607[a] 0.627[b]	0.7145[c] 0.6738[d]	0.618[e]	0.6348		
c_{12}	0.3575	0.3136	0.295[a] 0.265[b]	0.2824[c] 0.2336[d]	0.259[e]	0.2594		
c_{13}	0.1825	0.2097			0.219[e]	0.2170		
c_{33}	0.7181	0.6535			0.675[e]	0.6645		
c_{44}^u	0.2077	0.1605					0.371	0.352
c_{44}^r	0.2051	0.1532			0.182[e]	0.1842	0.371	0.355
c_{66}^u	0.2371	0.1870		0.1695[c] 0.2383[d]			0.065	0.058
c_{66}^r	0.1949	0.1737	0.156[a] 0.181[c]		0.180[e]	0.1877	−0.115	−0.097

[a] Reference 8, inhomogeneous contribution calculated from the potential defined in Ref. 19.
[b] Reference 8, inhomogeneous contribution calculated from the potential defined in Ref. 7.
[c] Reference 12, calculated with pseudopotential defined in Ref. 20.
[d] Reference 12, calculated with pseudopotential defined in Ref. 21.
[e] Reference 22, calculated with an empirical EAM potential created by fitting *ab initio* forces and 37 experimental data, among others, the elastic constants.

relaxed elastic constants are labeled with the superscript u, the relaxed ones with the supercript r. The agreement with experiment is, as usual, not as good as for the lattice parameters, but is in the range normally found in this kind of comparison, averaging 15%–20%.

Some comments on the effect of internal relaxation may be appropriate. The effect is small for c_{44}, as expected, but is large for c_{66}, its value being reduced by about 17% for the LDA and 7% for the GGA. The shift of the extra atom produced by the internal relaxation is presented graphically in Fig. 3. The top panel is a plot of the total energy versus the relative position of the extra atom along the strained lattice vectors for two applied strains ϵ_6. The unrelaxed (homogeneous) position is at $(a'/3, a'/3, c'/2)$, marked in the figure with the vertical dash-dotted line. With a positive 10% strain (which reduces γ) the extra atom moves toward the origin to about $(0.317a', 0.317a', c'/2)$, while with a negative 10% strain it moves away from the origin to about $(0.364a', 0.364a', c'/2)$. A graphical description of the effect of internal relaxation is given in Fig. 1 for the case $\epsilon_6 = +0.1$. The figure shows that the unstrained (solid) 60° rhombus with axes $\mathbf{a}$, $\mathbf{b}$ is distorted by ϵ_6 to the (dotted) rhombus with axes $\mathbf{a}'$, $\mathbf{b}'$. The extra atom, originally at the position marked with a solid circle on the bisectrix, is shifted to the position marked with an open circle by the homogeneous strain, but is moved back almost to the original position by the inhomogeneous strain (open square). The net effect of the ϵ_6 strain (homogeneous and inhomogeneous) is therefore to change the shape of the base of the hexagonal cell, with very little effect on the position of the extra atom, which practically stays at its original location.

The bottom panel of Fig. 3 shows a plot of the energy versus the ϵ_6 strain, showing that, indeed, the energy is lowered by the internal relaxation. The curvature of the relaxed energy curve is smaller than that of the unrelaxed curve, which by Eq. (10) reduces the magnitude of the c_{66} elastic constant.

Table I lists also the results of calculations of the c_{44} and c_{66} constants for the hcp phase at $c/a \sim 0.72$. Our purpose was to test whether this phase is stable or unstable: hence, we

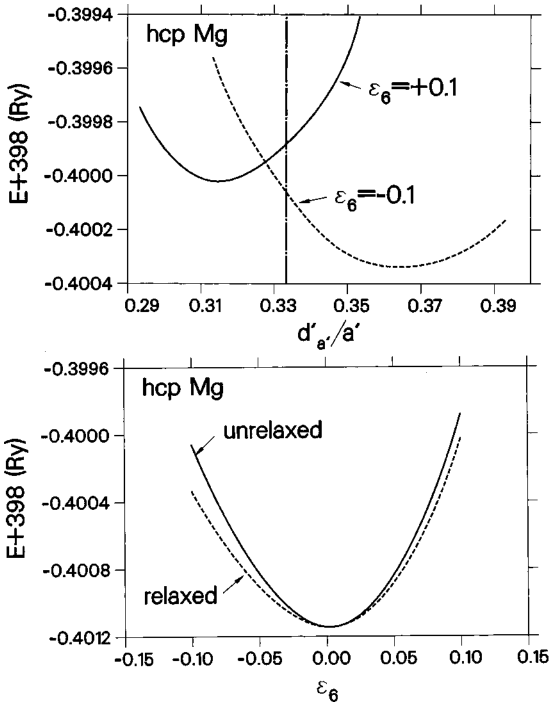

FIG. 3. *Top*: total energy (LDA) vs the in-plane components relative to the strain lattice vectors of the vector d' from the origin to the extra atom after application of ±10% shears. The dash-dotted vertical line marks the corresponding relative component for homogeneous strain. *Bottom:* total energy (LDA) as a function of shear ε_6 for homogeneous (unrelaxed) and inhomogeneous (relaxed) strain.

limited our study to the two shear constants, because our previous experience has shown[16] that instabilities of tetragonal phases always come from violation of stability conditions (1a) or (1c). In the present case the interesting result is that the phase would appear to be stable if only homogeneous strain were considered (both c_{44}^u and c_{66}^u are positive), but turns out to be clearly unstable when internal relaxation is taken into account ($c_{66}^r<0$).

B. Tetragonal Mg

The tetragonal EBP of Mg is depicted in Fig. 4. The energy-versus-c/a plot (middle panel) reveals a deep minimum at $c/a\sim\sqrt{2}$, for both the LDA and GGA and a very shallow minimum at $c/a\sim0.92$. The deep minimum is indicative of an fcc phase of Mg that does not seem to have been reported before. The energy minima for the LDA and GGA are -398.400173 and -400.668752 Ry, respectively, hence about 1 mRy/atom higher than those of the hcp ground state. The crystallographic data for the fcc phase are listed in Table II.

In order to find out whether this phase is stable (actually, *meta*stable, since its energy is higher than that of the ground state) we have calculated its elastic constants. We recall that fcc crystals have three independent elastic constants: c_{11}, c_{12}, and c_{44},[6] and the stability conditions are, again assuming that $c_{12}>0$,

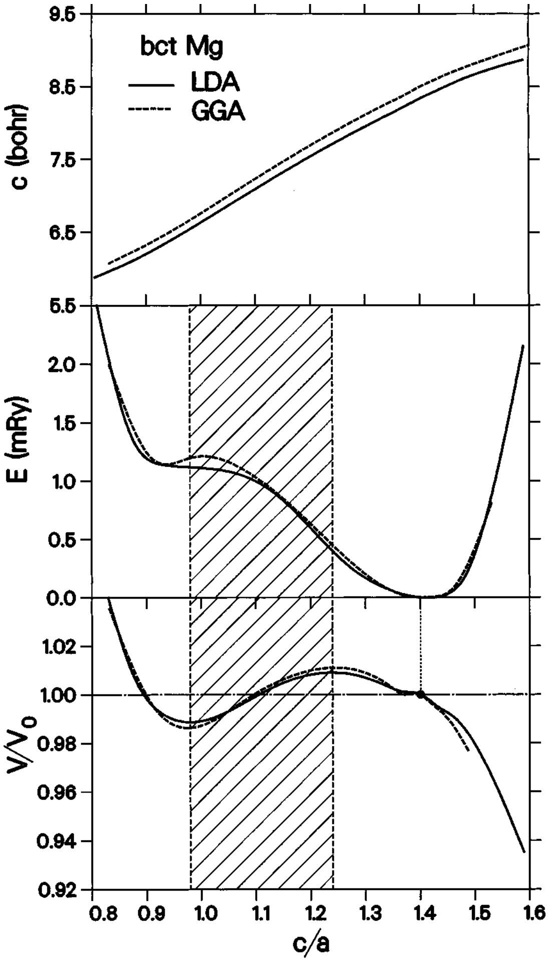

FIG. 4. Epitaxial Bain path of bct Mg: solid curves calculated with the local-density approximation (LDA), dashed curves calculated with the generalized-gradient approximation (GGA). *Top panel:* c vs axial ratio c/a. *Middle panel:* total energy per atom, referred to the lowest-energy (fcc) state at $c/a\sim\sqrt{2}$, vs axial ratio c/a. *Bottom panel:* relative volume per atom V/V_0 vs axial ratio c/a (V_0 is the theoretical atomic volume of the fcc state). The solid circle marks the relative volume of the fcc state. The shaded area covers a region of intrinsically unstable states.

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

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

We also recall that for fcc crystals one calculates first the c'_{ij} elastic constants, the prime indicating that these are the elastic constants of the bct cell of the fcc lattice, i.e., elastic constants in tetragonal axes,[4,15] and then one converts these constants to those referred to the conventional fcc axes (unprimed symbols). This procedure may create some small ambiguity for the c_{44} constant, because this constant can be calculated from the c'_{ij} in two ways:[15] an *indirect* way, giving $c_{44}^{\mathrm{ind}}=c'_{11}-c'_{33}+c'_{66}$, and a *direct* way, yielding $c_{44}^{\mathrm{dir}}=c'_{44}$. The two are not always identical, presumably owing to numerical inaccuracies of the computer program.

TABLE II. Lattice parameters and elastic constants of fcc Mg. a_0 and c_0 are the parameters of the bct unit cell, in Å units; V_0 is the volume per atom, in Å^3; the c_{ij} are elastic constants, in Mb. Two values are given for c_{44}, designated $c_{44}^{\mathrm{ind}} = c'_{11} - c'_{33} + c'_{66}$, and $c_{44}^{\mathrm{dir}} = c'_{44}$ (the c'_{ij} are elastic constants of the bct cell of the fcc lattice, i.e., elastic constants in tetragonal axes). $C' \equiv (c_{11} - c_{12})/2$ is also listed for convenience. The calculations were done with the WIEN97 (FLAPW) program (Ref. 14) both in the nonrelativistic local-density approximation (LDA) and in the relativistic generalized-gradient approximation (GGA).

	a_0	c_0	c_0/a_0	V_0	c_{11}	c_{12}	c_{44}^{ind}	c_{44}^{dir}	C'
LDA	3.137	4.435	1.414	21.83	0.481	0.353	0.248	0.267	0.064
GGA	3.204	4.508	1.407	23.14	0.436	0.310	0.242	0.241	0.063

The calculated elastic constants of fcc Mg are also listed in Table II. Although C' is small, it is still positive: hence, the stability conditions are satisfied: fcc Mg is metastable.

We have made no effort to test the stability of the higher energy minimum (at $c/a \sim 0.92$), because it is in fact very shallow for the GGA and almost just an inflexion point for the LDA.

IV. DISCUSSION

For the hcp ground state of Mg satisfactory agreement was found between calculated and experimental values of the lattice parameters and the elastic constants. We wish to emphasize, in agreement with the explicit statement of van Midden and Sasse[8] and the implicit one of Johnson,[9] that while the contribution of internal relaxation to the elastic constants of hexagonal crystals is frequently *not* taken into account, it is in fact important and should not be neglected. The contribution can be as large as 20% and more;[8] also it can reveal the actual instability of a phase that would otherwise be labeled stable, as is the case in this work for the hcp phase of Mg at $c/a \sim 0.72$.

It is worth pointing out that the unconventional choice of a 60° angle between the **a** and **b** axes in the basal plane of the hexagonal cell is computationally much more convenient for internal relaxations than the conventional 120°, since with the 60° angle the extra atom remains within the (110) bisecting plane, as long as the applied strains are symmetrical. The latter requirement is particularly important for the $c_{44} = c_{55}$ constant, for which an ϵ_{13} strain or an ϵ_{23} strain alone would not produce a symmetrical deformation of the unit cell, whereas application of *both* strains does. The calculation of inner relaxation is also simplified by the use of just the dimensionless fractional components of $\mathbf{d}'$ along the lattice vectors $\mathbf{a}'$ and $\mathbf{b}'$, i.e., vary $d'_{a'}/a' = d'_{b'}/b'$ around 1/3 to find the minimum energy; the actual change of d' is not needed, only the energy change from the homogeneous-strain energy.

For both c_{44} and c_{66}, relaxed and unrelaxed, the agreement between our results and the theoretical values published in the literature is fair, fluctuating between about 15% and 40%. Greef and Moriarty[13] present their results graphically, so that numerical comparisons are not precise, but do quote numbers for the quantity $(c_{11} - c_{12})/2$—namely, 0.225 Mb for the unrelaxed and 0.1863 Mb for the relaxed value, in good agreement with our unrelaxed 0.2371 and relaxed 0.1949 LDA values and in fair agreement with unrelaxed 0.1870 and 0.1737 GGA values. Thus the decrease of c_{66} of 17% due to inner relaxation found here from first principles agrees well with the only other calculation that does not use an empirical potential,[13] which found a decrease of 21%. Also the relaxed value of c_{66} found here with the LDA is just 3.7% higher than experiment, and the value from Ref. 13 is less than 1% low.

The states at the minima of the EBP for both bct and hcp structures have been called phases even when they are unstable with respect to shear strains that break the tetragonal or hexagonal symmetry. Since these special equilibrium states may have only partial stability, i.e., just with respect to strains that preserve the symmetry, they can be forced to change by very small shear stresses. Conversely, they can be stabilized by very small barriers or constraints against these shear strains, such as could be provided by small impurity concentrations, or by pseudomorphic epitaxy of thin films, or by pressure. The designation of phase for these states is analogous to calling, say, a bcc structure under pressure a phase under pressure, even though stability is only maintained by the pressure. In fact, in a study of ferromagnetic iron under pressure,[23] it has been shown that just such an unstable bct phase comes into existence at 1300 kbar of pressure and becomes a stable phase at 1825 kbar when the C' elastic constant becomes positive.

The study of tetragonal states of Mg has produced the interesting result that fcc Mg is metastable. It would therefore perhaps be possible to stabilize this structure in ultrathin-film form by pseudomorphic epitaxy on a suitable substrate. Experiments aimed at this stabilization are presently in progress.

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