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Bravais phases of Fe under pressure from first principles

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Abstract

The structure and stability of four Bravais phases of Fe under pressure are determined by a procedure which first looks for minima of the internal energy E at constant volume V and then tests the states at the minima for stability (or instability) by showing that the Gibbs free energy G at constant pressure p is a minimum (or not a minimum) with respect to all possible strains. The phases considered here are either body-centered tetragonal (bct), which includes body-centered cubic (bcc) and face-centered cubic (fcc), or rhombohedral (rh). The results include showing that bcc Fe becomes unstable at 1500 kbar, that fcc Fe is stable at $p = 0$, that a phase transition from bcc to fcc is thermodynamically favored at 290 kbar, that a bct phase at $c/a = 0.89$ is unstable up to 2700 kbar and that a rh phase with angle $\alpha = 60.5^\circ$ is stable at $p = 0$ with E slightly higher than that for fcc Fe.

1. Introduction

First-principles theory can now find metastable phases of elements with good accuracy. The number of such phases, i.e., of periodic atomic bonding arrangements with local stability, grows substantially under stress. A finite fraction of them can be specified by limiting attention to Bravais phases, i.e., one-atom per unit cell of a crystal, at pressures under a specified maximum value of hydrostatic pressure for a rigid lattice. In this work a systematic procedure for finding metastable phases is illustrated for four Bravais structures of Fe which possibly could be extended to all the Bravais structures.

The first part of the procedure finds equilibrium states of a given Bravais structure from calculating the internal energy E at constant volume V ; the second part uses the Gibbs free energy G around the equilibrium states to check if they are stable at constant pressure by showing G is a minimum for all small strains.

Some results disagree with other recent first-principles calculations, e.g., we verify the instability pressure for bcc Fe to be 1500 kbar as found in our 2002 papers [1, 2], which differs from the instability pressure given in several recent papers [3–7]. We note that in some cases the difference appears to be due to neglect of a ‘pressure correction’, which we derive here more simply than the classical abstract derivations in the literature [8].

We show that fcc FM Fe at zero pressure is stable, which disagrees with several other calculations [9–11], and we show

why we differ. We show that the bct phase found in our previous paper [2] is unstable at all pressures up to 2700 kbar. It is still an equilibrium state, i.e., contains no internal stresses other than an internal pressure matched by an equal applied pressure. However the phase does not pass the absolute stability test, i.e., that no small strain exists that decreases G .

We find an unexpected stable rhombohedral (rh) phase at zero pressure (and above) with E close to but greater than that of fcc FM Fe, which would complicate the structure of Fe films on various substrates.

Section 2 contains the thermodynamic theory and strain expansions.

Section 3 describes procedures and results.

Section 4 discusses the need to use both E and G to find stable phases, notes when a pressure correction to elastic constants is needed, and comments on the instability pressure of bcc FM Fe.

2. Thermodynamic theory and strain expansions

Our procedure for finding stable atomic bonding arrangements under pressure uses three basic theoretical tools.

(1) The capability of first-principles band structure programs to calculate the total energy E of an arbitrary periodic structure with relative accuracy $\cong 10^{-6}$ Ryd, (2) the thermodynamic theorem that relates E to equilibrium states, (3) the thermodynamic theorem that relates the Gibbs free

energy G to the stability of an equilibrium state at constant pressure.

The E theorem states that in the equilibrium state of a system constrained to constant volume, E is a minimum with respect to all strains satisfying the constraint [12]. However the equilibrium state is not necessarily stable, i.e., under certain strains that do not satisfy the constraint the strains generate stresses that increase the strain. To establish stability under pressure the G theorem is needed.

The G theorem states that in a system held at constant applied pressure p , the Gibbs free energy $G \equiv E + pV$ (for the rigid lattice) is a minimum with respect to all strains [12]. Hence a state found as a minimum of E at some volume can be tested for stability by checking whether G is a minimum too at the pressure corresponding to the volume of the phase.

For finding and characterizing the phases of a two-parameter structure like bct (structural parameters a and c) it is convenient to look for minima of E at constant V as a function of one parameter, e.g., c/a ; at each c/a no further minimization is needed since V and c/a fix the structure. Then p is found from the equilibrium E (of the minimum corresponding to a particular phase) at several adjacent V values and G calculated at that minimum is tested to see if G is also a minimum. The test involves the elastic constants, as will be shown later. If the structure has more than two parameters, the E values found at the minima of E as one parameter varies will have to be minimized with respect to additional parameters while continuing to constrain the volume. A quantitative description of the procedure for finding stable phases in bct, and later in rh structure, using E and G follows.

An arbitrary homogeneous deformation of the crystal around equilibrium can be specified by the six components of Eulerian strain ε_i , $i = 1-6$, with rigid rotation removed (the ε_i are symmetrized displacement gradients [13]), since E and V are assumed independent of rotations. Then for small deformations and the corresponding small ε_i the change in G from the equilibrium value G_0 can be expanded in powers of the ε_i (up to second order) in the form,

$$\frac{\delta G}{V_0} \equiv \frac{G - G_0}{V_0} = \frac{1}{2} \sum_{i,j=1}^6 c_{ij} \varepsilon_i \varepsilon_j. \quad (1)$$

Since G is a minimum at equilibrium, the expansion (1) has no linear terms and must start with second-order terms $\varepsilon_i \varepsilon_j$. The coefficients of the second-order terms c_{ij} can be evaluated by calculating G and δG for various values of the ε_i .

The c_{ij} will in general be functions of p and non-linear behavior of $c_{ij}(p)$ can occur. Usually the c_{ij} will increase with increasing p as compressed material becomes denser and harder. However in the case of bcc FM Fe, increase in p weakens the ferromagnetic binding energy (by the Pauli principle that discourages two electrons with the same spin from coming close to each other) and the elastic shear constant $C' \equiv (c_{11} - c_{12})/2$ decreases and goes to zero at a pressure p_s . The general indication of instability of an equilibrium state at some p is failure of the quadratic form in the ε_i in (1) to be positive definite for that equilibrium structure. Then the

quadratic form is negative for some set of ε_i at p , hence the crystal is unstable at that p . The occurrence of instability can be indicated by the vanishing of certain elastic constants at $p = p_s$, or, more generally, by a negative value of an eigenvalue of the 6×6 c_{ij} matrix. Thus the values of the $c_{ij}(p)$ determine the stability at p . The $c_{ij}(p)$ are in fact the elastic constants (also called elastic stiffness coefficients) and enter the stress-strain relations for a crystal at p and the equation of motion of disturbances of equilibrium in the crystal at p ; these properties of the c_{ij} are shown by Barron and Klein [8].

We relate (1) to the work of Barron and Klein by rearranging (1) as an equation for δE , the change in E for a homogeneous deformation ε_i , $i = 1-6$ at constant p ,

$$\begin{aligned} \frac{\delta E}{V_0} &\equiv \frac{E - E_0}{V_0} = \frac{\delta G}{V_0} - p \frac{\delta V}{V_0} \\ &= -\frac{p}{V_0} \sum_{i=1}^6 \left(\frac{\partial V}{\partial \varepsilon_i} \right)_0 \varepsilon_i \\ &\quad + \frac{1}{2} \sum_{i,j=1}^6 \left(c_{ij} - \frac{p}{V_0} \left(\frac{\partial^2 V}{\partial \varepsilon_i \partial \varepsilon_j} \right)_0 \right) \varepsilon_i \varepsilon_j. \end{aligned} \quad (2)$$

In (2) δV has been expanded in a power series in strains ε_i around equilibrium to second order.

The strain derivatives of V can be evaluated by expressing V as the determinant of the matrix of orthogonal components of the strained lattice vectors of the unit cell. The matrix of strained orthogonal components is given by the product of the strain matrix plus the identity matrix acting on the matrix of the equilibrium lattice vectors, as shown in (3) (to second order)

$$\begin{aligned} V(\{\varepsilon_i\}) &= \begin{vmatrix} 1 + \varepsilon_1 & \frac{\varepsilon_6}{2} & \frac{\varepsilon_5}{2} \\ \frac{\varepsilon_6}{2} & 1 + \varepsilon_2 & \frac{\varepsilon_4}{2} \\ \frac{\varepsilon_5}{2} & \frac{\varepsilon_4}{2} & 1 + \varepsilon_3 \end{vmatrix} \begin{vmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{vmatrix} \\ &= [1 + \varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \varepsilon_1 \varepsilon_2 + \varepsilon_2 \varepsilon_3 + \varepsilon_3 \varepsilon_1 \\ &\quad - \frac{1}{4}(\varepsilon_4^2 + \varepsilon_5^2 + \varepsilon_6^2)] V_0, \end{aligned} \quad (3)$$

where $\{\varepsilon_i\}$ means the six ε_i , the a_i , b_i and c_i are the unstrained orthogonal components of the lattice vectors which define the unit cell and the matrix product gives the strained components [13]. Differentiation of the polynomial in the ε_i shows that the only non-zero first and second strain derivatives are

$$\begin{aligned} \frac{\partial V}{\partial \varepsilon_i} &= V_0, & i = 1, 2, 3; \\ \frac{\partial^2 V}{\partial \varepsilon_i^2} &= -\frac{V_0}{2}, & i = 4, 5, 6; \\ \frac{\partial^2 V}{\partial \varepsilon_i \partial \varepsilon_j} &= V_0, & i, j = 1, 2, 3; i \neq j. \end{aligned} \quad (4)$$

Putting (4) into (2) gives for the expansion of δE around equilibrium, where coefficients \bar{c}_{ij} are defined,

$$\begin{aligned} \frac{\delta E}{V_0} &= -p(\varepsilon_1 + \varepsilon_2 + \varepsilon_3) + \frac{1}{2} \sum_{i,j=1}^6 \bar{c}_{ij} \varepsilon_i \varepsilon_j, \\ \bar{c}_{ii} &\equiv c_{ii} & i = 1, 2, 3, \\ \bar{c}_{ii} &\equiv c_{ii} + p/2 & i = 4, 5, 6, \\ \bar{c}_{ij} &\equiv c_{ij} - p & i, j = 1, 2, 3, i \neq j. \end{aligned} \quad (5)$$

The relations in (3)–(5) hold for arbitrary symmetry.

For cubic symmetry (5) gives

$$\begin{aligned} c_{11} &= \bar{c}_{11} \\ c_{12} &= \bar{c}_{12} + p \\ c_{44} &= \bar{c}_{44} - p/2 \\ C' &\equiv (c_{11} - c_{12})/2 = (\bar{c}_{11} - \bar{c}_{12})/2 - p/2 \equiv \bar{C}' - p/2. \end{aligned} \quad (6)$$

Note from (5) that E does not have a minimum at equilibrium for all strain tensors, but only for tensors which make $\varepsilon_1 + \varepsilon_2 + \varepsilon_3 = 0$, hence keep V constant to first order and make the linear terms in the ε_i vanish. However G does have a minimum at stable equilibrium for a given p for all variations of the ε_i . A particular variation used in [1, 2] is along the epitaxial Bain path (EBP), which is defined and discussed in [14].

The elastic constant C' of a phase can be evaluated directly from minima of the function $E(c/a)$ at constant V from the curvature of $E(c/a)$ at the minimum [15]. From (5) by changing variables from $\varepsilon_1 = \varepsilon_2 = \delta a/a$, $\varepsilon_3 = \delta c/c$ to $\delta(c/a)$ and δV where $V = ca^2/2$, the quadratic term in δE for $[\delta(c/a)]^2$ gives (at the minimum corresponding to a particular cubic phase)

$$\frac{1}{V_0} \left(\frac{\partial^2 E}{\partial (c/a)^2} \right)_V = \frac{4}{3} \bar{C}' = \frac{4}{3} C' + \frac{2}{3} p. \quad (7)$$

The coefficient \bar{C}' of the quadratic term $[\delta(c/a)]^2$ in δE requires the pressure correction $-p/2$ to give C' , which vanishes when bcc Fe becomes unstable. Note that the vanishing of the curvature of $E(c/a)$ does not occur at the instability pressure, but at a different pressure.

The formula corresponding to (7) for the more general case of a bct structure is

$$\frac{1}{V_0} \left(\frac{\partial^2 E}{\partial (c/a)^2} \right)_V = \frac{2}{9(c/a)^2} [\bar{c}_{11} + \bar{c}_{12} - 4\bar{c}_{13} + 2\bar{c}_{33}], \quad (8)$$

which reduces to (7) for bcc symmetry where $\bar{c}_{13} = \bar{c}_{12}$, $\bar{c}_{33} = \bar{c}_{11}$, $c/a = 1$.

3. Procedures and results

3.1. Calculation on bct structures

The total-energy calculations for each periodic structure were made with the well-tested WIEN2k band structure program [16] with the Perdew–Burke–Ernzerhof generalized-gradient-approximation. The computation parameters in all cases were: plane wave cutoff $R_{\text{MT}} K_{\text{max}} = 7$, $R_{\text{MT}} = 1.5$ au, $G_{\text{max}} = 14$, mixer = 0.05 and 1000 k -points in the irreducible Brillouin zone, convergence criterion on the energies 1×10^{-3} mRyd (10^{-6} Ryd). All calculations were spin polarized. All the four phases have pressure-dependent finite moments.

In the first stage (of three stages) a comprehensive set of functions $E(c/a)$ at $V = V_i$, $i = 1-36$ were calculated which cover a range of pressure from 0 to 2800 kbar. A selected set of $E(c/a)$ curves is shown in figure 1 to illustrate the presence of up to three minima corresponding to bct, bcc and fcc phases.

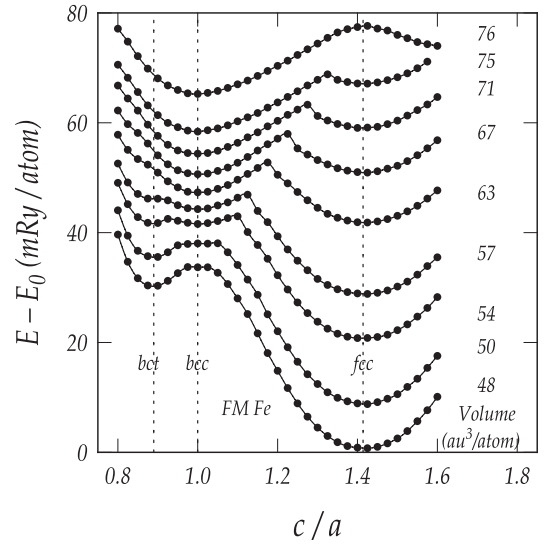


Figure 1. Total internal energy as a function of c/a (called $E_V(c/a)$ curves) of FM Fe at selected volumes; E_0 is the total energy of fcc Fe at $V = 48 \text{ au}^3/\text{atom}$. For clarity the $E_V(c/a)$ curves at volumes from 50 to 76 au^3 are shifted toward E_0 by 36.20, 89.90, 120.0, 158.5, 175.2, 186.9, 194.7, 201.9 mRyd/atom respectively. The vertical dashed lines indicate the bct, bcc and fcc phases at $c/a = 0.89, 1.00$ and 1.414 respectively. The solid lines interpolate between the calculated points.

Each of the minima corresponds to an equilibrium state of a phase at volume V_i , since E has been minimized at that V_i with respect to all structural parameters satisfying the constraints $V_i(a, c)$ constant—in the bct case only c/a since c/a and V fix the structure. However the existence of a minimum does not mean stability. In fact in figure 1 there is a gap between the V_i at which the curvature of $E(c/a)$ vanishes and the smaller V_i (and higher pressure) at which each phase stabilizes, as will be illustrated later. In the gap all minima are equilibrium states that are unstable.

In the second stage the separate minima, which determine the structure $(c/a)_m^{\text{ph}}$ and energy $E_m^{\text{ph}}(V)$ of the separate phases, are used to find the equation of state (EOS) of each phase from

$$p^{\text{ph}}(V) = -dE_m^{\text{ph}}(V)/dV, \quad (9)$$

where ph = bct, bcc, fcc with different $(c/a)_m$ values. Figure 2 plots the separate EOS.

The $p^{\text{ph}}(V)$ then determine the Gibbs free energies at each minimum from

$$G^{\text{ph}}(p) = E_m(V^{\text{ph}}(p)) + pV^{\text{ph}}(p). \quad (10)$$

Differences of $G^{\text{ph}}(p)$ from the bcc phase are plotted in figure 3 to find the thermodynamic transition pressure from bcc \rightarrow fcc at 290 kbar.

Finally the stability of each of the equilibrium states is determined by a calculation of the eigenvalues of the 6×6 c_{ij} , $i, j = 1-6$ matrix. A minimum path (MNP) program which converges on minima of G , finds the c_{ij} from trial sets of strains in (1) and calculates the eigenvalues [17]. A negative eigenvalue means the expansion in (1) is not positive definite

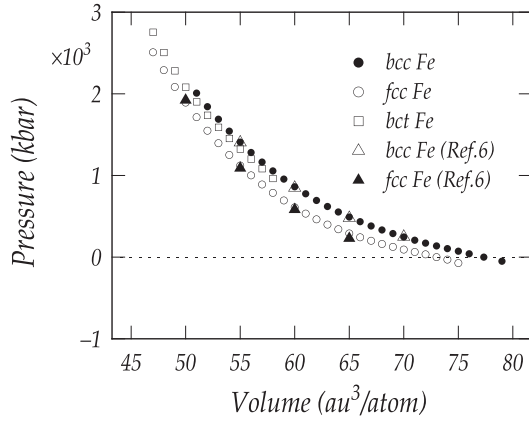


Figure 2. $p(V)$ curves for bcc phase (filled circles), bct phase (open squares) and fcc phase (open circles) of FM Fe. The crossing of the $p(V)$ curve and the dashed line ($p = 0$) gives the equilibrium volume: $V_0^{\text{fcc}} = 72.8 \text{ au}^3/\text{atom}$, $V_0^{\text{bcc}} = 77.3 \text{ au}^3/\text{atom}$. For comparison selected $p(V)$ data of bcc Fe (open triangles) and of fcc Fe (filled triangles) (deduced from figure 2 of [6]) are plotted.

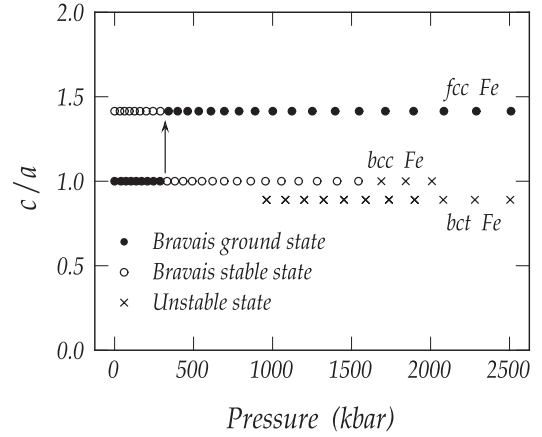


Figure 4. c/a versus pressure for bct, bcc and fcc phases of FM Fe. The meanings of the symbols are: filled circle—Bravais ground state, open circle—Bravais stable state, cross—unstable state. The phase transition from bcc to fcc at 290 kbar is indicated by an arrow.

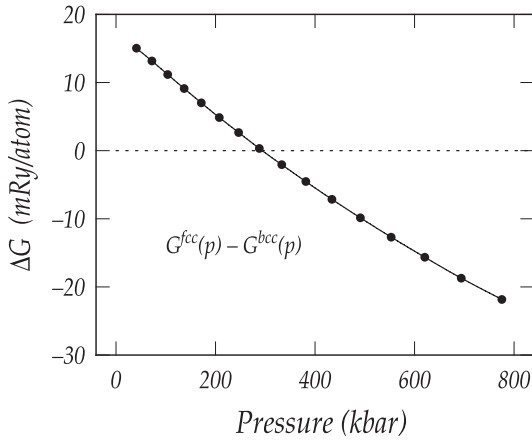


Figure 3. Free energy difference curve $G^{\text{fcc}}(p) - G^{\text{bcc}}(p)$ of FM Fe indicating the phase transition from bcc to fcc phase at 290 kbar. The solid line interpolates between the calculated points.

and indicates instability. In this way the X's used in figure 4 for instability were found including the instability of the bct phase at $c/a = 0.89$ found in [2], where the bct phase was incorrectly called stable above 1825 kbar.

The curvatures at the minima of $E(c/a)$ at V give values of the elastic constant $C' = (c_{11} - c_{12})/2$ for the cubic phases from (7). In figure 5 $C'(p)$ obtained from (7) is compared to $\bar{C}'(p)$ obtained from second derivatives of $G(p)$. Both show instability around 1500 kbar, and an anomaly in $C'(p)$ below 500 kbar. The instability pressure 1500 kbar found here in two different calculations is substantially lower than some values found in recent first-principles calculations [3–5], generally due to neglect of the pressure correction. Table 1 lists various published values of the instability pressure.

3.2. The ground state of γ -Fe at zero pressure

We refer to fcc Fe and phases near fcc structure as phases of γ -Fe. An important result of this detailed study of the

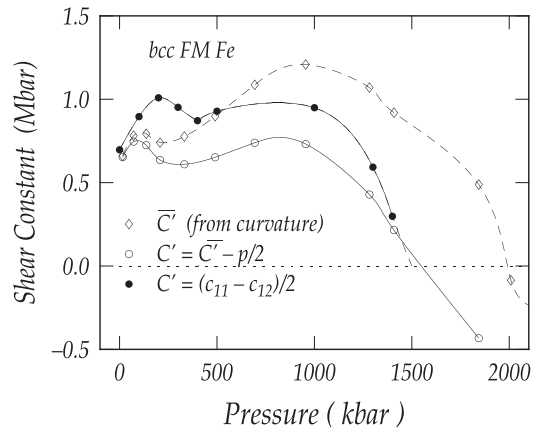


Figure 5. Shear elastic constants C' and \bar{C}' of bcc FM Fe as functions of pressure. The data of C' are calculated in two ways: the filled circles are obtained from $C' = (c_{11} - c_{12})/2$ (equation (6)) where c_{11} and c_{12} are obtained from second derivatives of $G(p)$; the open circles are obtained from $C' = \bar{C}' - p/2$, where the data of \bar{C}' are calculated from the curvature of the $E(c/a)$ curves using (7). Both filled and open circles show that C' vanishes at the instability pressure of bcc Fe $p_s \approx 1500$ kbar. In contrast, \bar{C}' , or the curvature at minima of $E(c/a)$ curves at constant V , does not vanish at p_s but at a higher pressure around 2000 kbar.

phases of Fe and their pressure dependences is the conclusion that the fcc magnetic phase of Fe under ambient conditions is stable. This conclusion disagrees with previous first-principles studies of Fe [9–11]. From the EOS of fcc Fe in figure 2 at $p^{\text{fcc}} = 0$, $V_0^{\text{fcc}} = 72.8 \text{ au}^3/\text{atom}$. A stability test with the MNP program [17] shows that the fcc phase is stable. Note that if we had wrongly used the bcc EOS which shows at $p^{\text{bcc}} = 0$ a value of $77.3 \text{ au}^3/\text{atom}$, then figure 1 would show a maximum at $c/a = 1.414$ and the fcc phase would be called unstable.

In [9] Peng and Jansen calculate $E(c/a)$ at $V = 79 \text{ au}^3/\text{atom}$ and find a maximum for fcc structure, hence conclude fcc Fe is unstable. But figure 2 shows that at $V = 79 \text{ au}^3/\text{atom}$ fcc is under negative pressure and the condition of instability found in [9] does not apply at $p = 0$.

Table 1. Instability pressure p_s of bcc FM Fe calculated from first principles in recent papers.

References	Instability pressure p_s (kbar) of bcc FM Fe
This work and [2]	1500
[3]	3200
[4]	2000
[5] ^a	1800
[6]	1000
[7]	1600

^a From a gap in the phonon dispersion curves of bcc Fe.

In [10] Spišák and Hafner state that fcc Fe is unstable in agreement with [9], but give no details. In [11] they look for a stable monoclinic phase of Fe by minimizing E with respect to two structural parameters c/a and δ (which determines angle γ) and find a minimum at $V = 78 \text{ au}^3/\text{atom}$. The state they find is unlikely to be an equilibrium state because a monoclinic crystal has four structural parameters (a, b, c, γ), hence one more minimization of E is needed. Even if the state is close to equilibrium, the pressure is unlikely to be zero, since the pressure has not been controlled, the value of V is large compared to fcc Fe at $p^{\text{fcc}} = 0$ and is in the range of instability for fcc Fe. To find a monoclinic stable phase at $p = 0$ the minimization of E at constant V must be made with respect to three structural parameters and must be repeated over a range of V to obtain pressures from (9) to be searched for a zero value of p . In a calculation with the MNP program starting from the state in [11] and assuming $p = 0$ the result indicates that the state found in [11] is not a phase at $p = 0$, i.e., is not a minimum of the Gibbs free energy G . The MNP program is able to find a monoclinic equilibrium state near the state in [11] if the state in [11] approximates a phase, since the MNP program homes in on minima of G ; however the MNP program starting from the monoclinic phase of [11] converges to the fcc phase at $V = 72.8 \text{ au}^3/\text{atom}$.

Our procedures are able to find phases of two-parameter structures like the bct calculations in section 3.1 and also for rh structures, parameters a and α . Figure 6(a), like figure 1, shows equilibrium states by the presence of minima of $E(\alpha)$ at constant V which includes the fcc structure. Several rh minima appear, and we focus on the one at $\alpha \cong 60.5^\circ$. A plot of $E_m^{\text{rh}60.5^\circ}(V)$ values in figure 6(b) shows the minimum and the equilibrium volume at $p^{\text{rh}} = 0$ to be $72.45 \text{ au}^3/\text{atom}$. The E value of rh FM Fe at the lowest data point ($V = 72.5 \text{ au}^3/\text{atom}$) in figure 6(b) is $-2545.539266 \text{ Ryd/atom}$ which is slightly higher than $-2545.539362 \text{ Ryd/atom}$ of fcc FM Fe at $p^{\text{fcc}} = 0$. A stability check with the MNP program shows the rh phase to be stable.

4. Discussion

The procedure used here to find and describe phases of Fe requires evaluation of both the internal energy E and the Gibbs free energy G . Equilibrium states at constant volume, which

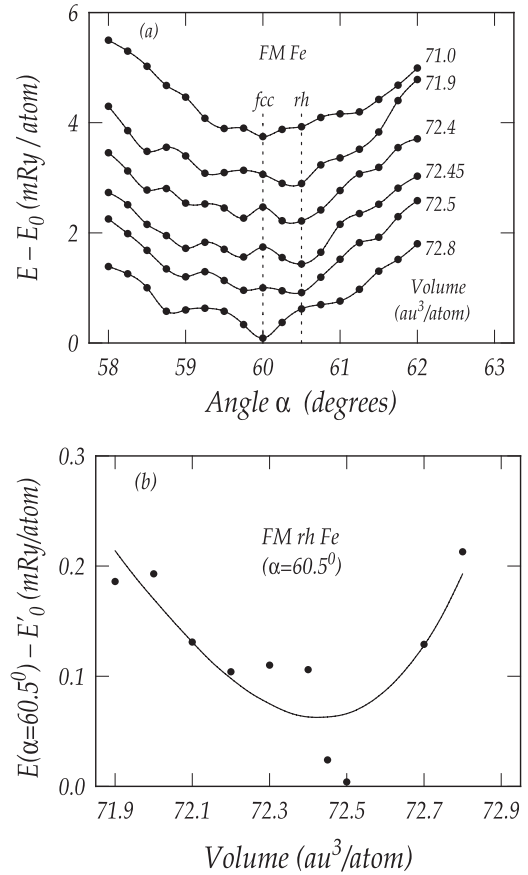


Figure 6. (a) Total internal energy as a function of angle α (called $E(\alpha)$ curves) of the 1-atom rh unit cell of FM Fe at selected volumes near $p^{\text{fcc}} = 0$; E_0 is the total energy of fcc FM Fe at $V = 72.8 \text{ au}^3/\text{atom}$. For clarity the $E(\alpha)$ curves at volumes from 72.5 to 71.0 au^3/atom are shifted away from E_0 by 0.75, 1.25, 2.04, 2.55 and 3.15 mRyd/atom respectively. The solid lines interpolate between the calculated points. The vertical dashed line at $\alpha = 60^\circ$ denotes the fcc phase, while the vertical dashed line at $\alpha = 60.5^\circ$ denotes the rh phase. (b) Total internal energy at $\alpha = 60.5^\circ$ on the $E(\alpha)$ curve as a function of volume; E'_0 is the total energy of rh FM Fe at $V = 72.5 \text{ au}^3/\text{atom}$. The solid curve is the result of fitting the data points with a third-order polynomial, which shows that the equilibrium state of the rh phase of FM Fe is at $V = 72.45 \text{ au}^3/\text{atom}$.

are possible phases, are located by searching for minima of E in a given structure as a function of one structure parameter at constant V . Advantages of this search are that the number of variables by which E needs to be minimized is reduced by one by the constraint to constant volume, and also that all phases with the given structure are treated together in the same way, which improves the accuracy of differences between phases. In the case of two-parameter systems like bct and rh, the value of a single parameter and the volume fix both the structure and E and no further minimization is required.

The equilibrium states found from E are not necessarily stable; establishing stability of a state under pressure requires evaluation of G and proving that G is a minimum with respect to all possible small deformations around the equilibrium state. Proving a minimum of G is equivalent to showing the positive definiteness of the quadratic form in the strains in

the expression of δG in (1), whose coefficients are the elastic constants c_{ij} , $i, j = 1-6$. All the c_{ij} are evaluated using the δG produced by different strains—in the general case 21 strains are needed. Positive values of all six eigenvalues of the 6×6 c_{ij} matrix then prove stability.

If the coefficients of the second-order strain terms in the expansion of δE in (2) are evaluated, the \bar{c}_{ij} are obtained and must be modified by the pressure corrections (5) to obtain the c_{ij} . Equations (7) and (8) show directly that second derivatives of E give \bar{c}_{ij} , and figure 5 shows the important effect of the pressure correction in determining the instability pressure of bcc Fe.

The fact that some equilibrium states corresponding to minima of E at constant V are not stable gives meaning to the theoretical description of some states as ‘unstable phases’. A critical pressure can be evaluated at which a minimum appears in $E(c/a)$ at constant V , which only becomes stable at a larger pressure. Each phase can be characterized by the pressures of appearance and disappearance, by the pressures of the onset of stability and instability and by the pressures at which transitions to and from other phases are thermodynamically permitted.

The geophysically interesting pressure at which bcc Fe becomes unstable has been found to be 1500 kbar in three separate calculations: (1) in our 2002 papers [1, 2] using the WIEN97 band structure program and evaluation of second strain derivatives of G , (2) by the WIEN2k program and evaluation of δG using various strains; the data are shown in figure 5 with filled circles, (3) by the evaluation of the second derivatives of $E(c/a)$ at constant V from the curvatures at minima of E , from which the shear elastic constant C' is calculated using (7) and plotted in figure 5 with open circles. A number of first-principles papers have found different values of the instability pressure, in some cases due to neglect of the pressure correction. The proposed values for the instability pressure of bcc ferromagnetic (FM) Fe are tabulated in table 1.

In summary in this paper the effectiveness of procedures for finding stable phases based on calculating E at constant V and δG at constant p is shown, e.g., the proof that bcc Fe is unstable at 1500 kbar, the proof that fcc Fe is stable at $p^{\text{fcc}} = 0$, the proof that bct Fe at $c/a = 0.89$ is unstable at all pressures up to 2700 kbar, the observation of a stable rh phase at $p^{\text{rh}} = 0$.

Essential elements of the procedure are the use of separate EOS for different phases, and the capability of testing an equilibrium state for stability.

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