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LETTER TO THE EDITOR

On the importance of the free energy for elasticity under pressure

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Abstract

It is shown that the theory of elasticity under hydrostatic pressure p at zero temperature is unified and simplified by the use of the Gibbs free energy G , rather than the energy E . The minima of G , but not of E , give the equilibrium structure; the second derivatives of G , but not of E , with respect to strains at the equilibrium structure give the zero-temperature elastic constants; the stability of a phase at p is then determined by the same Born stability conditions used at $p = 0$ when applied to the elastic constants from G . Examples are noted of mistakes due to use of E rather than G .

Modern first-principles total-energy calculations based on the Kohn–Sham equations with corrections have made possible reliable and reasonably accurate determination of crystalline equilibrium structures and elastic constants. See, for example, [1] for tetragonal structures and [2] for hexagonal structures, which are the structures used in the discussion here. However the extension of such calculations to crystals under hydrostatic pressure p introduces a number of complications that have not always been considered in recent work. In this paper we point out these complications, note some examples where they have been overlooked and show how they are readily dealt with by use of the Gibbs free energy $G \equiv E + pV - TS$, where V is the volume, T the absolute temperature and S the entropy, in the study of elasticity at p .

The existence of a Gibbs free energy for systems under hydrostatic pressure has been pointed out by Wang *et al* [3], although they find that under anisotropic stress a true thermodynamic potential does not exist. Hence we can assume such a free energy for analysis of elasticity under pressure. However at finite T the entropy term in G is less reliably known than the energy calculated by first-principles band-structure programs, hence the entropy term and the temperature variable will be dropped in the discussion below, which will then apply at $T = 0$. Addition of the TS term and the temperature dependence of E , when these quantities can be reliably calculated, would generalize the discussion to apply to isothermal elastic constants at any T . The discussion and illustrations given here will be for body-centred

tetragonal (bct) and hexagonal close-packed (hcp) structures, but many remarks will apply to other structures.

The first complication in discussing systems under pressure is that it is necessary to find the equilibrium structure at each p . The equilibrium structure at p is *not* at a minimum of E , but is at a structure at which the stress at each surface is $-p$; e.g., the stresses on the faces of a tetragonal structure should be $\sigma_1 = \sigma_2 = \sigma_3 = -p$. Thus an advantage of using G rather than E in discussing systems at p is that G is an extremum at equilibrium with respect to all small changes of structure in a system held at constant p and T , and if the extremum is a minimum the phase is stable.

Hence, to find a stable equilibrium bct or hcp structure at p requires finding the values of the lattice constants a and c at which $G(a, c; p) \equiv E(a, c) + pV(a, c)$ has a minimum. This two-variable minimization problem is readily solved for bct and hcp structures by use of the epitaxial Bain path (EBP), which is discussed in [1] for $p = 0$, but is generalized here for finite p . The generalized EBP is defined at each a by finding the value of c for which the stress in the c direction is $-p$, hence $\sigma_3 = (1/V)(\partial E/\partial \varepsilon_3) = (c/V)(\partial E/\partial c) = -p$. The calculation at each a gives one value of the functions $c^{\text{EBP}}(a; p)$, $E^{\text{EBP}}(a; p)$ and $G^{\text{EBP}}(a; p) \equiv E^{\text{EBP}}(a; p) + pV^{\text{EBP}}(a; p)$. The minimum of $G^{\text{EBP}}(a; p)$ at $(a_0, c_0 \equiv c^{\text{EBP}}(a_0))$ is then a minimum of $G(a, c; p)$, because the derivative of $G(a, c; p)$ vanishes in the tetragonal plane (coordinates a and c) in two directions, i.e. along the EBP direction because G is at a minimum on the EBP and along the c direction because $(c/V)(\partial G/\partial c)_a$ is given by $(c/V)(\partial E/\partial c)_a + (pc/V)(\partial V/\partial c)_a = -p + p = 0$, since V is linear in c . Hence the derivative of $G(a, c; p)$ vanishes in the tetragonal plane in all directions and (a_0, c_0) is an extremum of $G(a, c; p)$.

Figure 1 illustrates the functions E^{EBP} and G^{EBP} for ferromagnetic (FM) Fe at $p = 1000$ kbar plotted against the tetragonal shape parameter c/a . All total-energy calculations were made with Wien97 [4], which is a well tested reliable full-potential band structure program applicable to general structures. The energies are converged to a few hundredths of a mRyd/atom; lattice constants of metals usually agree with experiment to within 1–2% and elastic constants to within 10–15%. Note that $G(a, c; p)$ has a minimum at $c_0/a_0 = 1$, the bcc structure, but that E clearly does not have a minimum at (a_0, c_0) , since E has a finite slope along the EBP at (a_0, c_0) .

A second complication for systems under pressure is that the elastic constants are *not* given by second derivatives of E with respect to strains. Rather they are given by second derivatives of G with respect to strains at (a_0, c_0) , the minimum of G at p . Define $c_{ij} \equiv (1/V)\partial^2 G(a, c; p)/(\partial \varepsilon_i \partial \varepsilon_j)$ and $\bar{c}_{ij} \equiv (1/V)\partial^2 E(a, c)/(\partial \varepsilon_i \partial \varepsilon_j)$, where both derivatives are at (a_0, c_0) and the ε_j are Eulerian strains. Then the correct elastic constants c_{ij} are related to the \bar{c}_{ij} by $c_{ij} = \bar{c}_{ij} + (p/V)\partial^2 V(a, c)/(\partial \varepsilon_i \partial \varepsilon_j)$.

Since V is a known algebraic function (a cubic) in the components of the three lattice vectors defining the unit cell, derivatives of V with respect to the strains ε_i , which are small relative changes in those components, can be found analytically. Let $c_{ij} = \bar{c}_{ij} + \delta \bar{c}_{ij}$. Then, for example, using $V = a_1 a_2 c/2$,

$$\delta \bar{c}_{12} = (p/V)(\partial^2 V/(\partial \varepsilon_1 \partial \varepsilon_2)) = (pa_1 a_2/V)(\partial^2 V/(\partial a_1 \partial a_2)) = p,$$

and

$$\delta \bar{c}_{11} = (p/V)(\partial^2 V/(\partial \varepsilon_1^2)) = (pa_1^2/V)(\partial^2 V/\partial a_1^2) = 0.$$

References [1] and [2] give the six appropriate strains for each c_{ij} for tetragonal and hexagonal structures. Differentiation of V by these strains then gives the following simple pressure contributions to the c_{ij} from the pV term in G :

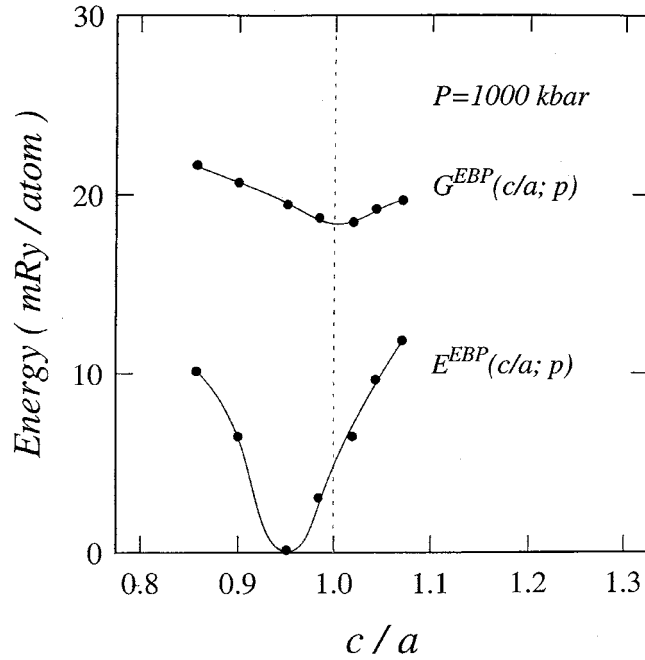


Figure 1. The energy E and the Gibbs free energy G along the EBP of bct FM Fe at a hydrostatic pressure of 1000 kbar. The bcc phase is at the minimum of G^{EBP} at $c/a = 1$. For clarity the minimum of the E^{EBP} curve is set to zero and the minimum of the G^{EBP} curve is shifted down by 392 mRyd/atom. The minimum of E^{EBP} is 46 mRyd/atom above the bcc ground state at $p = 0$.

$$\begin{aligned} c_{11} &= \bar{c}_{11}, & c_{12} &= \bar{c}_{12} + p, & c_{13} &= \bar{c}_{13} + p, \\ c_{44} &= c_{55} = \bar{c}_{44} - p/2 = \bar{c}_{55} - p/2, & c_{66} &= \bar{c}_{66} - p/2. \end{aligned}$$

These pressure corrections to the \bar{c}_{ij} were derived by Barron and Klein [5] by studying stress-strain relations under stress. In [6–8] the elastic constants are incorrectly calculated from second derivatives of E rather than G . However, the correct elastic constants are used by Karki *et al* [9] to determine stability under pressure. In figure 2 the shear constants of FM bcc Fe are plotted as functions of pressure to illustrate the difference between c_{ij} and \bar{c}_{ij} . Note that the instability of FM bcc Fe is shown by the vanishing of $C' \equiv (c_{11} - c_{12})/2$ at $p = 1500$ kbar, whereas $\bar{C}' \equiv (\bar{c}_{11} - \bar{c}_{12})/2$ requires a much higher pressure to vanish. The use of E in [8] rather than G to determine stability is the reason that the instability of FM bcc Fe was wrongly stated in [8] to occur above 2000 kbar.

Note that the bulk modulus B , unlike the c_{ij} , is a second derivative of E , rather than of G . Now B measures the change in equilibrium V produced by a change in p , i.e. $B = -V(dp/dV)$, which uses an ordinary derivative since at each p there is a unique equilibrium V and a unique equilibrium E . Then the dE produced by dV is given by the external work done by the system, $dE = -p dV$, hence $p = -dE/dV$ and $B = V(d^2E/dV^2)$. Since a cubic system remains cubic under pressure, the equilibrium $E(V)$ can be directly calculated as V changes, hence $p(V)$ and $B(V)$ from the derivatives of $E(V)$. Thus the equation of state $p(V)$ is correctly calculated for FM bcc Fe by Stixrude *et al* [10] and shown to agree well with experiment.

The definitions of the elastic constants in terms of G mean that the usual Born stability conditions [11] on the c_{ij} derived at $p = 0$, where they check that E is a minimum for all

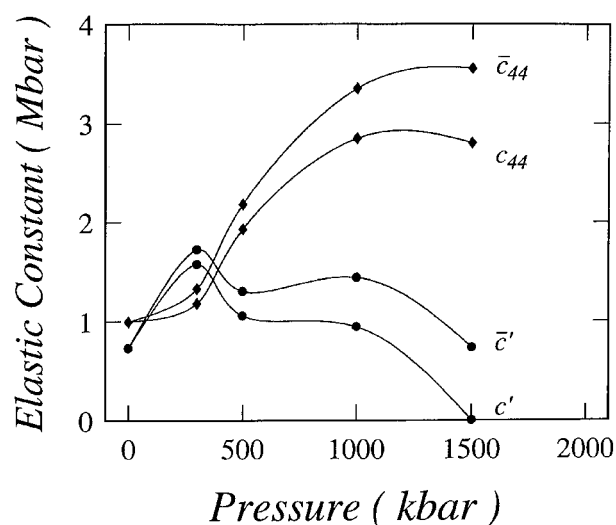


Figure 2. The shear elastic constants $C' \equiv (c_{11} - c_{12})/2$ and c_{44} of FM bcc Fe as functions of hydrostatic pressure p . The quantities C' and c_{44} are the correct elastic constants derived from derivatives of G at equilibrium at each p . Comparison is made with \bar{C}' and \bar{c}_{44} derived from derivatives of E at the same equilibrium at p . The vanishing of C' , but not of \bar{C}' , shows that bcc FM Fe becomes unstable at 1500 kbar.

strains, can be used at finite p to check that G is a minimum for all strains, hence that the system is stable.

In summary, G serves at finite p the same function as E at $p = 0$: its minima give the equilibrium states, its derivatives with respect to strain give the elastic constants and the occurrence of instability corresponds to the disappearance of one of its minima.

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