

Reply to Comment on 'On the importance of the free energy for elasticity under pressure'

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REPLY**Reply to Comment on ‘On the importance of the free energy for elasticity under pressure’****P M Marcus¹ and S L Qiu²**¹ IBM Research Division, T J Watson Research Center, Yorktown Heights, NY 10598, USA² Department of Physics, Alloy Research Center, Florida Atlantic University, Boca Raton, FL 33431-0991, USA

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Abstract

All criticisms by Steinle-Neumann and Cohen of the correctness of our calculations of equilibrium structure and elastic constants under pressure from the Gibbs free energy are answered and the criticisms are rejected. The difference between the free energy and the internal energy as functions of structure is described to clarify the use of the free energy. The meaning of elastic constants in a system under pressure is discussed in order to derive the basic quadratic expansion of the free energy in the strains. The coefficients in the expansion are the elastic constants under pressure and are in agreement with well-known work. We give reasons why calculations based on the Gibbs free energy are simpler and more accurate than the usual calculations based on minima of the energy at constant volume.

Our reply to the comment by Steinle-Neumann and Cohen (SC) on our letter [1] permits us to clarify the use of the Gibbs free energy G for elasticity under pressure and to correct some features of our letter. However, we reject all the criticisms made in the comment, including the remarks in the abstract that we are incorrect in our statements about equilibrium and the minima of G and E (the internal energy) and about the calculation of elastic constants.

SC are wrong in the first paragraph (paragraph 1) of the comment when they criticize [1] as saying that G must be used to find equilibrium structure under pressure p . We just wish to say that it is simpler than procedures based on E at constant volume V . Also, we now believe use of G at constant p is probably a more accurate procedure; one reason is that the equation of state $p(V)$ is not needed to find the equilibrium value of p , since p is a given quantity that remains constant while the equilibrium structure is determined.

In paragraph 1 line 8 (l. 8) SC say that our plot in figure 1 in [1] of E for bcc Fe along the epitaxial Bain path (EBP) in the tetragonal structure plane (coordinates a and c or c/a and V) is ‘a result of misusing elementary thermodynamics’. On the contrary, SC have misunderstood

the purpose of figure 1. The purpose is to show that E does not have a minimum at equilibrium along the EBP in the tetragonal structure plane, thereby illustrating our statement that E is not a minimum at equilibrium as a function of structure at a given p , whereas G is such a minimum.

The statement that E is not a minimum at equilibrium at any p should have been discussed at greater length in [1], since the behaviour of E is complicated and there is an important difference between E and G to make clear. At equilibrium the slope of E in the c direction is proportional to p , which is large at high p , and the slope of E in the a direction is also proportional to p . But on the path between the c and a directions along which $V \propto ca^2$ is constant, E does have a minimum at equilibrium and the slope vanishes. This minimum at equilibrium is a consequence of the minimum theorem for E at constant V and S quoted by SC. The rapidly changing slope of E with direction in the structure plane is the reason for our statement that E does not have a minimum at equilibrium, whereas the slope of G at equilibrium vanishes in all directions in the structure plane and G has a simple two-dimensional minimum.

Previous papers have mainly found equilibrium from the minimum of E along the special path of constant V . However, the use of a minimum of $E(c/a)$ at constant V has encountered difficulties in some cases, such as in the study of anomalous structure in hcp Zn and Cd under pressure [2]. The $E(c/a)$ curves at constant V have flat bottoms or double minima in the pressure range of the anomalies (figure 10 of [2]), which make the equilibrium structure uncertain. Hence an advantage in using G to find equilibrium is that the minima are well defined.

It is inconsistent of SC to say we are incorrect in our statement that G has a minimum at equilibrium at a given pressure and E does not (abstract), when they say explicitly in paragraph 1 that ‘there is a minimum principle . . . for the Gibbs free energy $G = E - TS + PV$ at constant P and T ’ (which is in fact the basis of our formulation), but that ‘there is no minimum principle for E . . . at constant P ’, which agrees with our statement about E .

In paragraph 2 of the comment SC make the more serious criticism that all our elastic constants calculated from second strain derivatives of G are incorrect. Regardless of the derivation, this assertion is completely refuted by the fact, shown explicitly for the six tetragonal elastic constants in [1] and derived in [3], that our elastic constants c_{ij} for tetragonal structure are identical with those in the classic paper of Barron and Klein (BK) [4].

BK define the c_{ij} in a material under general initial stress as the multipliers of any introduced strain that give the additional stress produced by that strain. These c_{ij} then enter the equation of motion in the stressed material, since the gradients of the additional stress drive the system back toward equilibrium at the given general stress. By applying invariance of the stress–strain relation under rotation BK prove that the c_{ij} for uniform stress (hydrostatic pressure) is the sum of second strain derivatives of E plus a pressure correction proportional to p ([4], equation (5.5)). Our second strain derivatives of G are from its definition second strain derivatives of E plus second strain derivatives of pV at constant p , which we show give the same pressure corrections as BK for tetragonal and hexagonal structures, i.e., our c_{ij} are the same as BK’s.

If SC accept the formulae of BK for the c_{ij} (SC use a formula from BK in their equation (1)), they must accept our formulae. The agreement of our c_{ij} with those of BK checks the validity of our c_{ij} as second strain derivatives of G , which we derive more simply than BK from application of basic thermodynamic theory. From our derivation follows the important expansion for G around equilibrium

$$\frac{\delta G}{V} = \frac{1}{2} \sum_{ij} c_{ij} \varepsilon_i \varepsilon_j. \quad (1)$$

The positive definiteness of this quadratic form in the strains is the criterion for stability (or metastability) of a particular equilibrium structure.

In paragraph 2 (l. 8) SC give as a reason for calling our c_{ij} incorrect that we have ‘ignored the fact that the pressure and shear stresses vary as a function of strain’. This statement is a misunderstanding of the meaning of elastic constants in a material under pressure. When strains are introduced into the equilibrium structure, such as an acoustic wave, the pressure, which is maintained by an external source, *does not change*, in agreement with the principle that at equilibrium G is a minimum at constant p . However, there is an additional stress produced by the strains, which BK relate to the strains by the c_{ij} , as described above.

In paragraph 2 (l. 4) SC say about our work in [3] on bcc Fe ‘they find a shear instability at 150 GPa using $G(c')$ but not for $E(\bar{c}')$, implying that previous computational estimates of elastic constants at pressure are incorrect’. We are not aware of any previous calculation of c' for bcc Fe that found the p at which c' goes negative. Our plot of $c'(p)$ and $\bar{c}'(p)$ in [1] shows the great importance of the pressure correction at high p in decreasing the stability of the bcc phase of Fe. The calculation in [5] cited by SC (paragraph 1 (l. 13)) as ‘the correct analysis’ does not evaluate c' , and although [5] shows an instability occurs, it does not find the p at which the instability occurs.

We do not understand the criticism in paragraph 2 (l. 8) that ‘they did not obtain any thermodynamically valid second derivatives by their finite difference procedure. . . they did not even obtain the derivatives $(1/V)\partial^2 G(P)/\partial \varepsilon_i \partial \varepsilon_j$ ’. This criticism seems to question our numerical procedure for obtaining the second strain derivatives of G at equilibrium, which are the c_{ij} in equation (1). But the procedure is simple mathematics, which we can summarize briefly as follows: for tetragonal or hexagonal c_{ij} choose numerical values for six independent strains; calculate the strained atomic coordinates (by multiplying the matrix of orthogonal coordinates of the atoms in the unit cell by the first-order strain matrix [6], p. 99); then calculate the δG for these strains from δE and δV . The six choices of strains give six linear equations for the six c_{ij} . The simplest choices take the strains one and two at a time. By giving the same strains several values the part of δG quadratic in the strains can be separated from the higher powers of the strains.

In addition to the pressure correction that the use of G automatically includes, hcp structures, which have two atoms in the primitive unit cell, require an inner relaxation of the second atom, which must be considered for all strains that break the hexagonal symmetry; our procedure for calculating the effects of relaxation on the c_{ij} is given in [7]. The relaxation will always reduce δG and is required even for $p = 0$, but is frequently neglected, as it is in [8–11].

The remarks after paragraph 2 of the comment are mainly not relevant to criticisms of our work. However, SC show that we should make a change in the references in [1] that need a pressure correction. We comment briefly on the further points raised by SC.

In paragraph 3 SC mention confusion in the definition of elastic constants. However, there is no confusion about our elastic constants under pressure; they are the proportionality constants in the relation between introduced strain and the consequent additional stresses that give deviations from the pressure and they enter the equations of motion of the material under pressure.

In paragraph 4 SC note that a Gibbs free energy is not definable under non-hydrostatic stress. This difficulty is not one that we have considered in our papers so far. However, there is some evidence that a function can be defined with the same minimum property at equilibrium for anisotropic stress that the Gibbs free energy has for isotropic stress.

A re-examination of the calculation of the elastic constants in [10–12], which we said in [1] needed pressure corrections, should not have included [10], whose authors include SC. We did

not realize at that time that the second-order term added to the first-order strain matrix to keep V constant would make the pressure correction unnecessary, as SC show in their comment, paragraphs 5–7, using a formula from BK. In a later paper on hcp Fe [7] we accepted the volume-conserving procedure in [10] and only criticized [10] for omission of inner relaxations in hcp structure. However, [11] and [12] compute elastic constants under pressure from E with first-order strains and do not mention pressure corrections, hence require them. We note that SC in their equation (3) agree with our statement that [11] requires a pressure correction.

In paragraph 8 SC mention that computations based on E of the frequencies of long wavelength Raman-active optical modes of hcp lattices agree well with experiment, which supports the use of E for calculation of elastic quantities without making pressure corrections. However, in optical mode vibrations there is no change in V , hence E and G are equivalent for calculating these mode frequencies.

In conclusion, although calculations of E at constant V can be used to find equilibrium structure and elastic constants for a crystal under pressure, we believe that it is simpler and more accurate to use G at constant p for those properties and that there is no doubt about the validity of the procedure.

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