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LETTER TO THE EDITOR

First-principles derivation of structural anomalies in hcp Zn and hcp Fe under pressure

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Abstract

A procedure for finding the equilibrium states of a hcp structure under pressure from minima of the Gibbs free energy using first-principles electronic theory has confirmed the existence of structural anomalies in hcp Zn and hcp Fe. Calculations of elastic constants as functions of pressure then show that the anomalies are large effects which cover a substantial range of pressure. These calculations permit reinterpretation of the experimental data to show that the structural anomaly, although small, can be seen in the data. These calculations contradict a recent first-principles calculation that found that the structural anomaly in hcp Zn disappeared when a large number of k-points were used in the Brillouin zone integrations.

Experimental measurements of a variety of properties of hcp Zn have indicated anomalous behaviour around 100 kbar, including the Lamb–Mössbauer factor [1], the phonon linewidth of optical phonons [2] etc. However, structural anomalies, i.e., abrupt changes in lattice vectors with pressure, have been described as too small to be certain in the best measurements [3, 4]. These measurements made at 40 K with He as the pressure-transmitting medium used to maintain hydrostatic conditions gave much smaller anomalies than previous measurements [5] and occurred at different values of pressure. The present calculations enable one to see that the small anomalies occur in the data with the same magnitude as indicated by the theory and at the same pressure.

A recent first-principles calculation on hcp Zn [6] found that the anomaly disappeared when the number of k-points in the irreducible Brillouin zone (IBZ) was increased to 5208 points, although the anomaly was present at smaller numbers of k-points. The present work repeats these massive calculations at 5300 k-points in the IBZ, but with a different procedure which finds the equilibrium structure directly as a function of pressure from minima of the Gibbs free energy. The results show that the anomaly is small but definitely present and not very different as compared to that for 550 k-points in the IBZ. (A longer work will show

this comparison.) Thus theory and experiment now agree on the existence of the structural anomaly.

Similar calculations for hcp Fe show anomalous structure below 500 kbar, which agrees with experimental measurements [7] on hcp Fe. Theory did not find the anomaly [8] before the present calculations [9]. The elastic constant behaviour shows that the anomaly is a substantial effect in both Zn and Fe.

The equilibrium state is found here from the thermodynamic result that at a given pressure p the Gibbs free energy (at zero temperature) $G \equiv E(a, c) + pV(a, c)$ is a minimum with respect to the hcp structure parameters a and c where E is the energy per atom and V the volume per atom. The minimum is conveniently found from a minimum of G along the epitaxial Bain path (EBP) [9–11]. The elastic constants are then found as second strain derivatives of G at equilibrium, while p remains constant. Justification of our procedure for calculating elastic constants appears in [9] and earlier references. Our elastic coefficients are in fact identical with the stress–strain coefficients defined by Barron and Klein [12]. The specially simplified procedure for determination of the relaxation correction to c_{66} also appears in [9].

First-principles total-energy calculations for hcp Zn and hcp nonmagnetic (NM) Fe under hydrostatic pressure were carried out using the WIEN2k implementation of the full-potential augmented-plane-wave plus local orbital (APW + lo) method with the Perdew–Burke–Ernzerhof exchange–correlation potential in a generalized-gradient approximation with relativistic corrections (GGA) [13]. A plane-wave cut-off $R_{\mathrm{MT}}K_{\max} = 7$, $G_{\max} = 14$ and mixer $= 0.05$ were used in all the calculations. Previous work [6] on hcp Zn found that the anomaly was not present for 5208 k-points in the irreducible wedge of the Brillouin zone (IBZ). Hence to check [6] we used 5300 k-points in the IBZ in both the EBP and the elastic constant calculations for Zn in all phases. In fact the difference in structural parameter values between the cases with 550 k-points and 5300 k-points is very small. For hcp NM Fe, 420 k-points in the IBZ were used in the EBP calculations, while 960 k-points in the IBZ were used in the elastic constant calculations. The k-space integration was done by the modified tetrahedron method [13]. Tests with larger basis sets and different Brillouin zone samplings yielded only very small changes in the results. The convergence criterion for the energies is set at 1×10^{-3} mRyd/atom.

Figures 1(a)–(c) show respectively the lattice constants a, c and the ratio c/a of hcp Zn as functions of pressure p in the range from 70 to 140 kbar. The open circles are the experimental data from [3] while the solid circles are the theoretical results of this work. The solid curves interpolate between the data points. Figure 1 shows the existence of the anomaly in hcp Zn and shows the agreement of the theory with the experimental results. Theory and the later experimental results [3, 4] show the anomaly to occur at the same pressure (at about 100 kbar) and to have about the same magnitude. The earlier measurements [5] do not fit as well, and show the anomaly to occur at 120 kbar and to be larger. Figure 1 also shows that the anomaly is a small effect on the lattice constants which is easily lost if the calculated equilibrium points scatter. However, the ratio of linear compressibilities [14] $k_c/k_a = (c_{11} + c_{12} - 2c_{13})/(c_{33} - c_{13})$ and the elastic constant c_{66} show that the anomaly is a large effect (figures 2(a) and (b) respectively). Figure 2(c) shows the free energy of Zn as a function of pressure in the hcp, fcc, bct, bcc and hexagonal omega phases, where G_0 is the free energy of hcp Zn at 70 kbar.

Figures 3(a)–(c) show respectively the lattice constants a, c and the ratio c/a of hcp NM Fe as functions of pressure p in the range from 0 to 1000 kbar. With the theory as a guide (solid circles connected by a solid curve), the anomaly is clearly seen in the experimental $a(p)$ data [7] (open circles connected by a dashed curve in figure 3(a)). A maximum in the ratio c/a from both experimental [7] and theoretical data is shown in figure 3 (c). As in the hcp Zn case the elastic constant ratio [14] k_c/k_a and the elastic constant c_{66} of hcp NM Fe (figures 4(a)

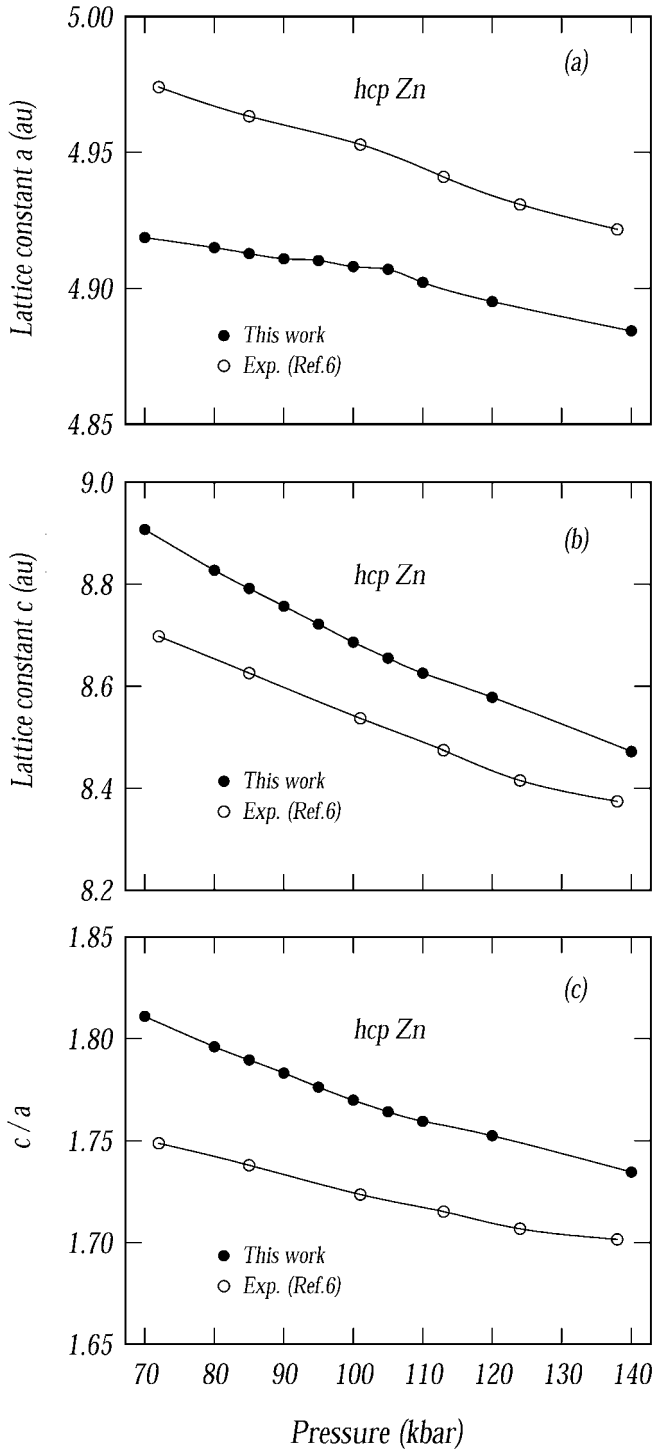

Figure 1. (a) The lattice constant a, (b) the lattice constant c and (c) the ratio c/a of hcp Zn as functions of pressure p. The open circles are the experimental data from [3]; the solid circles are the theoretical results of this work. The solid curves interpolate between the data points.

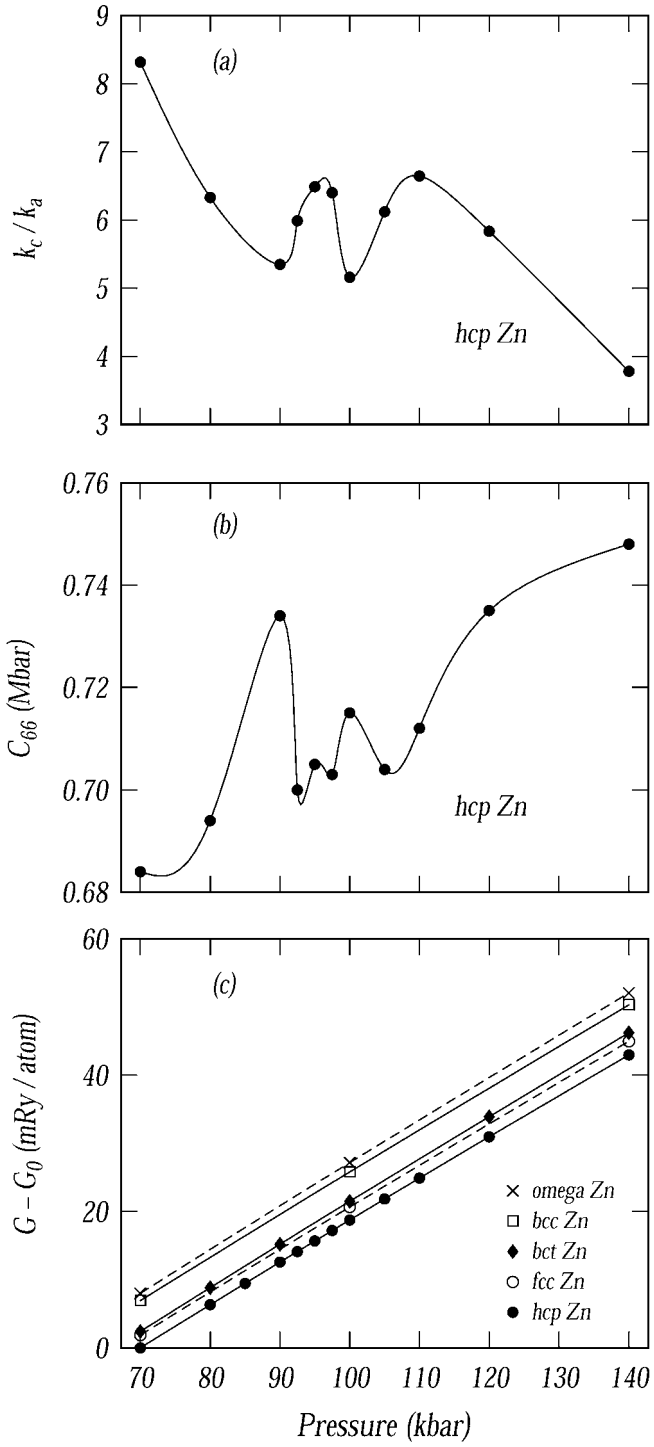

Figure 2. (a) The linear compressibility ratio k_c/k_a and (b) the elastic constant c_{66} of hcp Zn as functions of pressure p. (c) The free energy difference $G - G_0$ of Zn as a function of pressure in the hcp, fcc, bct, bcc and hexagonal omega phases, where G_0 is the free energy of hcp Zn at 70 kbar. The solid and dashed lines interpolate between the data points.

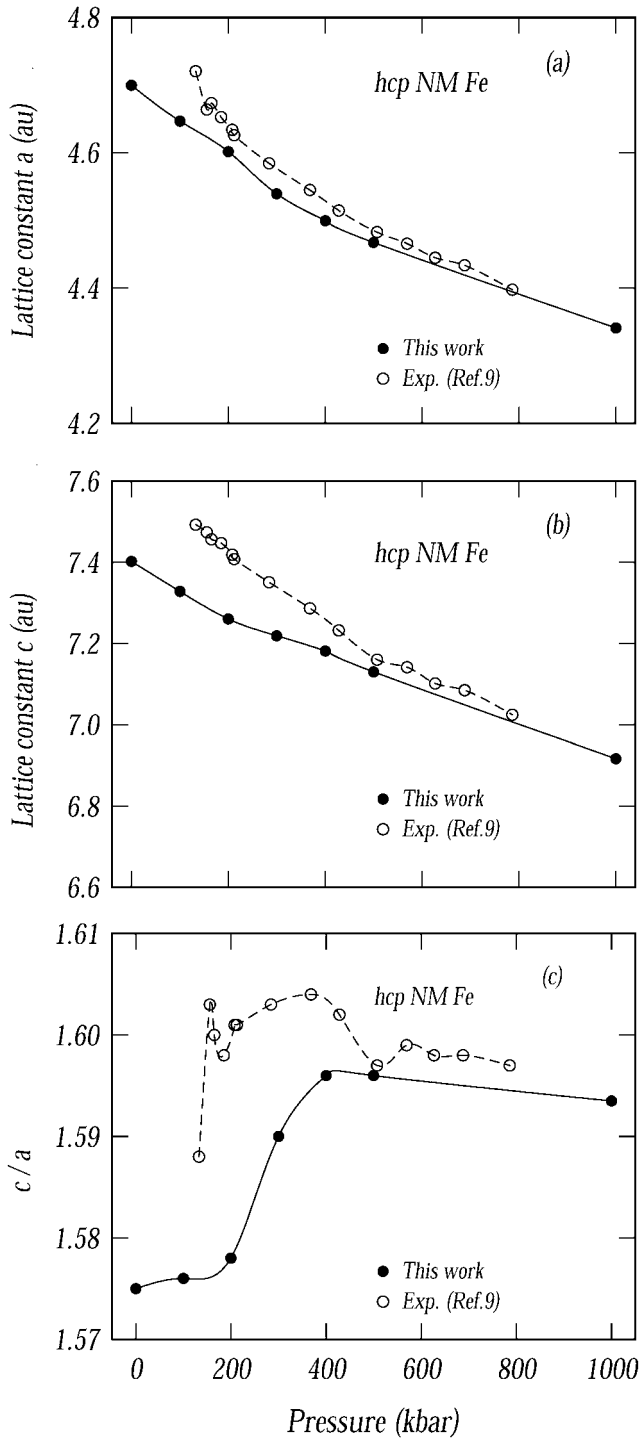

Figure 3. (a) The lattice constant a, (b) the lattice constant c and (c) the ratio c/a of hcp NM Fe as functions of pressure p. The open circles are the experimental data from [7]; the solid circles are the theoretical results of this work. The solid and dashed curves interpolate between the data points.

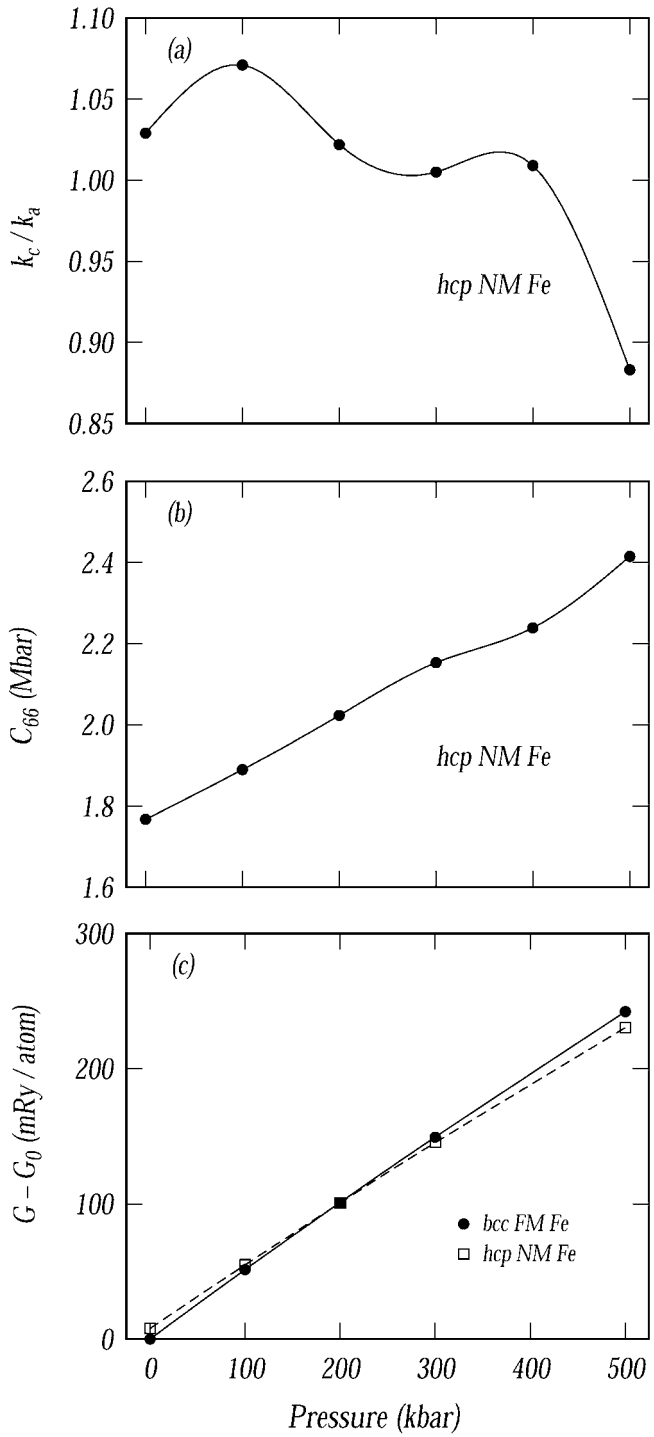

Figure 4. (a) The linear compressibility ratio k_c/k_a and (b) the elastic constant c_{66} of hcp NM Fe as functions of pressure p. (c) The free energy difference $G - G_0$ of Fe as a function of pressure in the hcp and bcc phases, where G_0 is the free energy of hcp NM Fe at $p = 0$. The solid and dashed lines interpolate between the data points.

and (b) respectively) show the anomaly as a large effect. Figure 4(c) shows that the anomaly in hcp NM Fe is accompanied by a phase transition (at about 200 kbar), but extends over a considerable range of p.

First-principles calculations of the structure in transition metals have generally proved very reliable. So the agreement with experiment of the small but definite anomalies of the structure is strong evidence for the existence of the anomalies. A distinct advantage of our procedure over previous theory is that $a, c, c/a$ are found directly as functions of pressure to compare with experiment. We do not use or need the equation of state $V(p)$ in making this comparison. The existence of the structure anomaly is well confirmed by the pressure dependence of the linear compressibility ratio k_c/k_a and the elastic constant c_{66}, which show strong oscillatory effects over a pressure range which includes the structural anomalies. Finally the demonstration that the structural anomaly is little changed by going to 5300 k-points in the IBZ from 550 k-points restores confidence in the many structural calculations that have been made with just a few hundred k-points in the IBZ.

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