

On the stability of rhenium up to 1 TPa pressure against transition to the *bcc* structure

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Abstract. We have carried out electronic structure total energy calculations on rhenium in the hexagonal close packed (*hcp*) and body centred cubic (*bcc*) phases, by the full potential linear muffin–tin orbital method, in order to verify the stability of the ambient pressure *hcp* phase against transition to the *bcc* structure at high pressures. As per our results, no *hcp* to *bcc* structural transition can occur up to 1 TPa pressures. Moreover, our Bain path calculations show that face centred cubic and body centred tetragonal structures are also not energetically preferred over *hcp* in this pressure range. The axial ratio (*c/a*) of Re changes by less than 0.33% in the pressure range studied.

Keywords. High pressure; rhenium; structural transition; electronic structure; Bain path.

1. Introduction

First principles electronic structure calculations form an important component of the theoretical methods for predicting phase transitions in solids, and are particularly well suited for high pressure studies. The accuracy of the computed total energies, based on the density functional theory depends upon the method employed for the calculations, and the approximations made for the effective potential in the Schrödinger equation. With state-of-the-art full potential methods, the only uncertainty in these calculations arises from the approximations made for the exchange–correlation terms in the total energy and potentials. Thus their predictive capability under conditions which may be currently difficult to achieve in the laboratory (like ultrahigh pressure), enables the proper planning of difficult experiments. Also, the dependable accuracy of these first principle calculations can verify the predictions of other theoretical models in which certain approximations may be inherent.

Rhenium is one of the strongest materials known, with its bulk and shear moduli being among the highest known for metals (Jeanloz *et al* 1991), and this property leads to many useful applications, like its use as a gasket material in diamond anvil cells. Though some high pressure studies on Re exist in the literature (Liu *et al* 1970; Manghnani *et al* 1974; Vohra *et al* 1987; Sikka and Vijayakumar 1988; Jeanloz *et al* 1991; Steinle-Neumann *et al* 1999), very little is known about its phase diagram (Young 1991). Initially it was speculated that the hexagonal close packed (*hcp*) Re might transform to the body centred

cubic (*bcc*) structure under compression (Kaufman 1967). Kaufman predicted this structural transition based on the extrapolation of Gibbs free energy estimates and the densities in the two phases, and gave a broad range from 4.5 to 110 GPa for the transition pressure at room temperature. However, high-pressure X-ray diffraction (XRD) studies following this prediction, did not reveal any structural change up to 35 GPa (Liu *et al* 1970). Later it was proposed that, unless electronic transitions are involved, the *hcp* to *bcc* transition is unlikely to occur at high pressures (Liu 1983), and was supported by the subsequent experiments of Vohra *et al* (1987), which showed that Re retains the *hcp* structure up to 216 GPa. First principles calculations can evaluate accurate total energies for quantitative comparison between *bcc* and *hcp* structures, and can thus verify Kaufman's predictions and suggest whether this transition could occur at a different pressure than predicted by him.

Among some of the other experimental investigations on Re related to its electronic structure, Manghnani *et al* (1974) measured the elastic constants and their pressure derivatives at moderately high pressures (up to 0.42 GPa) and suggested the occurrence of electronic topological transitions under pressure. Chu *et al* (1970) measured the superconducting transition temperatures of Re and its dilute solid solutions with Mo, W, and Os, up to 1.8 GPa pressure, and again interpreted the results in terms of electronic topological transitions.

On the theoretical side, Mattheiss (1966) carried out detailed relativistic band structure of Re and found that spin–orbit coupling plays an essential role in determining the Fermi surface topology, and predicted the effects of dilute alloying with W and Os. His calculations showed a few band extrema near the Fermi level, some of which

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having significant relativistic splitting, and could lead to electronic topological transitions under compression, even at moderate pressures. Some first principle calculations of pressure estimates (Sikka and Vijayakumar 1988), and elastic constant calculations at ambient and high pressures (Fast *et al* 1995; Steinle-Neumann *et al* 1999) have also been reported. But no detailed comparison has been made of different structures to understand the stability of its ambient pressure *hcp* phase at multi-gigabar pressures.

We have explored the stability of the *hcp* phase of Re, as compared to *bcc*, by evaluating the total energies in these two structures for comparison. With the full potential linear muffin-tin orbital (FPLMTO) method, we get state-of-the-art accuracy to verify the theoretical prediction of Kaufman (1967) and comment upon Liu's (1983) observation, in view of the fact that the *bcc* phase has not been experimentally observed so far. We report here the results of total energy calculations up to 1 TPa pressure. We find that the *bcc* phase corresponds to higher energy than that of *hcp* phase, and the magnitude of the energy difference between the two structures increases with pressure. Thus there is no possibility of the *hcp* to *bcc* structural transition up to 1 TPa (well beyond the range predicted by Kaufman), and indications are that it is unlikely to occur beyond 1 TPa also. We have also studied the constant volume distortion of the *bcc* lattice along the Bain path, i.e. via body centred tetragonal (*bct*) to the face centred cubic (*fcc*) structure. We have found that the *bcc* structure corresponds to a maximum internal energy in this *bcc*–*bct*–*fcc* distortion in the entire range up to 1 TPa pressure. Although the *fcc* structure gives a minimum in the Bain path, its energy is higher than that of *hcp* phase and, like in the *bcc* case, the energy difference from the *hcp* phase increases with pressure. Thus up to 1 TPa pressure, there is no transition from the ambient *hcp* phase to other commonly occurring phases like *fcc*, *bcc*, and *bct*. Even though we have not computed the temperature effects in the present work, our results show that the *hcp* to *bcc* transition is unlikely to occur even with electronic excitations, especially as the *fcc* structure corresponds to much lower energy than *bcc*. Our calculations of the optimum axial ratio (*c/a*) at each volume compression show that it has little variation in the studied pressure range.

We give a brief outline of the techniques involved in our calculations in §2 below, present our results in §3, and summarize the conclusions in §4.

2. Details of the calculations

The full-potential LMTO (Wills and Cooper 1987; Price and Cooper 1989; Wills *et al* 2000) calculations presented in this paper are all electron with no shape approximation to the charge density or potential. The base

geometry in this computational method consists of a muffin-tin part and an interstitial part. The ratio of the interstitial volume to the muffin-tin volume is 0.72 in the present calculation. The basis set is comprised of augmented linear muffin-tin orbitals (Andersen 1975). Inside the muffin-tin spheres the basis functions, charge density and potential are expanded in symmetry adapted spherical harmonic functions together with a radial function, and a Fourier series in the interstitial. In the present calculations the spherical harmonic expansion of the charge density, potential and basis functions are carried out up to $l_{\max} = 8$. The tails of the basis functions outside their parent spheres are linear combinations of Hankel or Neumann functions depending on the sign of the kinetic energy of the basis function in the interstitial region. For the core charge density, the Dirac equation is solved self-consistently, i.e. no frozen core approximation is used. The \mathbf{k} -space integration is performed using the special point method with about 1000 \mathbf{k} -points in the first BZ of the *hcp* lattice and the same density of \mathbf{k} -points is used for the other structures considered. As Re is a heavy element, relativistic effects may be important to describe the structural stability correctly. Therefore, the spin-orbit (*s*–*o*) term is included directly in the Hamiltonian matrix elements for the part inside the muffin-tin spheres. The calculations are based on the generalized gradient corrected density functional theory, with the exchange–correlation potential parametrized according to Perdew *et al* (1992). Due to core ionization at extreme pressures the pseudo-core electrons usually contribute to the structural stability (Ahuja *et al* 1994). Hence, apart from the valence 6*s*, 6*p* and 5*d* states, the pseudo-core 5*s* and 5*p* states are also included in our calculations. Moreover, the present calculations make use of a so-called multi-basis to ensure a well converged wave function. This means that we use different Hankel or Neumann functions each attaching to its own radial function. This is important to obtain a reliable description of the low lying pseudo-core states. In the method used here, bases corresponding to multiple principal quantum numbers are contained within a single, fully hybridizing basis set. The total energy convergence criterion for the self-consistent cycles is set to 0.1 mRy.

The optimum value of the axial ratio (*c/a*), for each volume compression, V/V_0 (V_0 being the ambient pressure volume), is obtained by total energy minimization with respect to (*c/a*). The computed total energies (at optimum axial ratios) have been fitted to polynomials in different regions of volume compression, to obtain the derivative and hence the pressure (*P*). This type of piecewise fitting retains any local structure in the (total energy vs volume) curve, which might otherwise be wiped out in an overall fitting in the entire range of volume.

To compare with the experimental data, the thermal contribution to the pressure at room temperature has been estimated by using Debye–Grüneisen model (Godwal and

Jeanloz 1989), as the static pressure measurements for some of these data were carried out at room temperature.

3. Results and discussion

Our total energy vs volume curve in the *hcp* structure (figure 1) shows a minimum at $102.25 (b.u.)^3$, which is our theoretical estimate of the value of V_0 . It agrees well with the estimates of other generalized gradient approximation (GGA) based calculations (see Steinle-Neumann *et al* 1999), as compared to the ambient pressure experimental value of $99.28 (b.u.)^3$ (Vohra *et al* 1987). Note that disagreements on this scale (within 6% in the volume) are common in first principles calculations based on the density functional theory, and are often sensitive to the exchange–correlation terms employed. But the merit of the first principle calculations is in estimating its variation under pressure, which is orders of magnitude more accurate, apparently due to (cancellation of) common or comparable errors in the estimated total energy at different compressions.

The evaluated pressure from the derivatives of the curve of figure 1, as described in §2, varies with volume as shown in figure 2. Some of the experimental data of Vohra *et al* (1987), and of McQueen *et al* (1970), have also been shown in this figure for comparison with the computed equation of state. Note that the single experimental point (symbol ■) of Vohra *et al* (1987) shows excellent agreement with our results. The room temperature thermal contribution to the pressure is estimated by us as 0.35 GPa at this compression, and gives negligible

shift in the scale shown in figure 2, and as Re is not a light element (mass number: 186.2), the zero-point energy contribution to pressure is expected to be negligible. It may be noted that Sikka and Vijayakumar (1988) had predicted, based on the LMTO calculations with atomic sphere approximation (ASA), that the pressures obtained in the experiments of Vohra *et al* should be more than reported by them, in contrast to the excellent agreement seen in figure 2 with our calculations. We are of the opinion that the disagreement obtained by Sikka and Vijayakumar should mainly be due to the limitations of the ASA (which was being used extensively during that time) employed in their calculations. More accurate calculations are currently possible, by employing the full potential techniques, like the one adopted for the present work.

Other experimental data shown in figure 2 (symbol Δ) are from the shock data reduced to 0 K isotherm (McQueen *et al* 1970), and show good agreement for moderate compressions, but deviate systematically at higher compressions. The discrepancy at higher compressions may be due to uncertainty in the reduction procedure of the shock data to 0 K by the Mie–Grüneisen equation (McQueen *et al* 1970). Also, electronic excitations are neglected in their reduction process. More accurate thermal contributions due to phonon and electronic excitations are being evaluated by us with modern techniques, and will be reported elsewhere. The DAC data (symbol ●, Liu *et al* 1970) correspond to much lower compressions.

Our estimated bulk modulus of 345 GPa, deduced from the equation of state curve of figure 2, shows reasonably

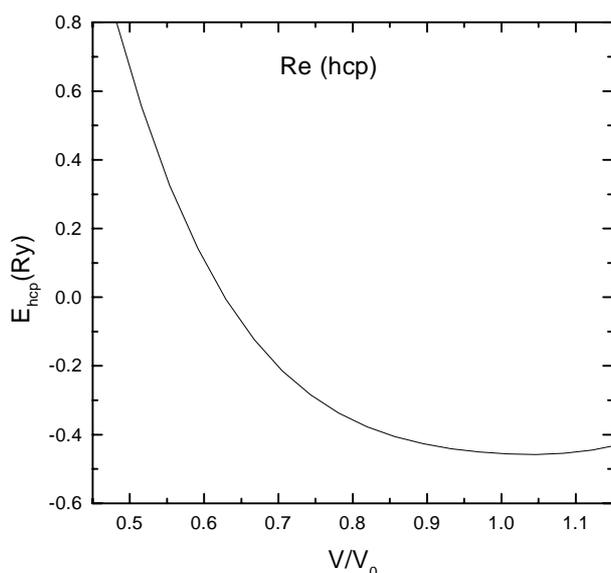


Figure 1. Variation of the total energy per atom of Re in the *hcp* phase [at optimum (*c/a*) ratio] with volume compression, $V/V_0 = 1.0$. The total energy scale is shifted by 33439 Ry.

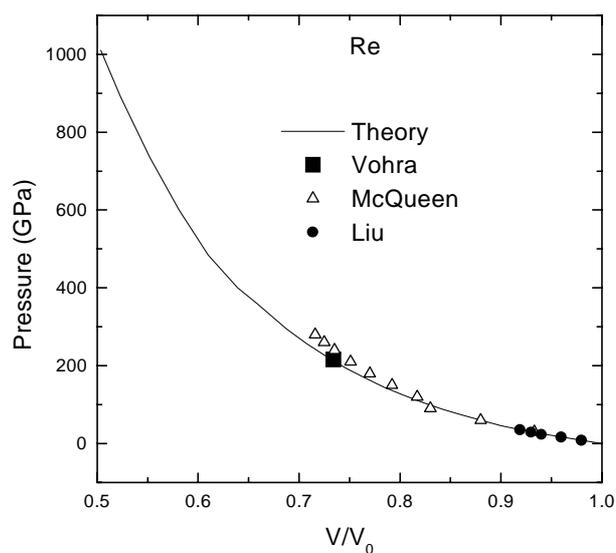


Figure 2. Equation of state for Re. High pressure experimental data, ■ from Vohra *et al* (1987), ● from Liu *et al* (1970) and Δ from McQueen *et al* (1970) are shown for comparison.

good agreement with the experimental value of 372 GPa (Manghnani *et al* 1974; Vohra *et al* 1987).

Figure 3 shows the variation of the axial ratio c/a in the ambient phase *hcp* structure of Re. The variation below 1 TPa is less than 0.33%, corresponding to the total range of variation in the value of c/a by less than 0.006. As these variations are small, their signatures are not expected to be seen distinctly in the total energy curve under compression (figure 1). Our estimate of 1.620 for the axial ratio at ambient condition is in good agreement with the experimental value of 1.615 (Manghnani *et al* 1974; Vohra *et al* 1987). As the deviation of the (c/a) ratio from the ideal close-packing value of 1.633 is a measure of anisotropy in *hcp* systems, the insignificant change in the axial ratio, depicted in figure 3, establishes that volume compression of Re under pressure occurs with little change of its anisotropic properties. These deductions are consistent with the observation that linear compressibilities in the axial direction and in the direction normal to it differ by only about 1% in Re (Manghnani *et al* 1974).

In view of the good agreement, seen above, between our first principle estimates for Re in the ambient *hcp* phase and the various experimental data, we can confidently compare the total energies between the *hcp* and *bcc* structures to estimate their relative structural stability. Figure 4 shows that the total energy per atom of Re in the *bcc* structure is higher than that of *hcp* phase by 40 to 80 mRy in the range of the relative volume, V/V_0 from 1.0 to 0.5. More importantly, the mismatch in energy between the two structures increases with increase in pre-

ssure. Thus it is clear that a high pressure transition from the *hcp* structure to the *bcc* phase is not feasible for Re.

For comparison with other close packed structures, we have studied the Bain path for Re, shown in figure 5 for $V/V_0 = 0.6$. It is clear that in the Bain path for the given volume, the *bcc* structure is of the highest energy. There is only one minimum in the Bain path for all the studied compressions and it corresponds to the *fcc* structure ($c/a = \sqrt{2}$). Even *fcc* structure has higher energy than that of *hcp* by 4 to 12 mRy per atom in the studied range of pressure (see figure 4).

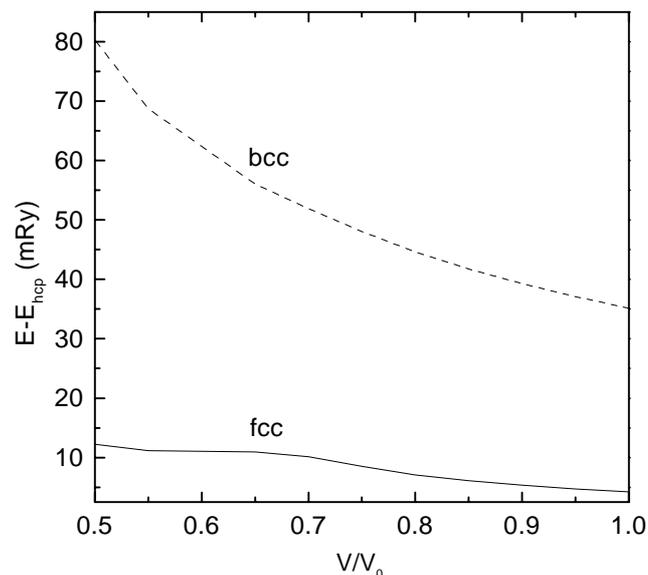


Figure 4. Total energy (per atom) variation under compression of *bcc*, and *fcc* structures of Re with respect to that of *hcp* at the same volume compression.

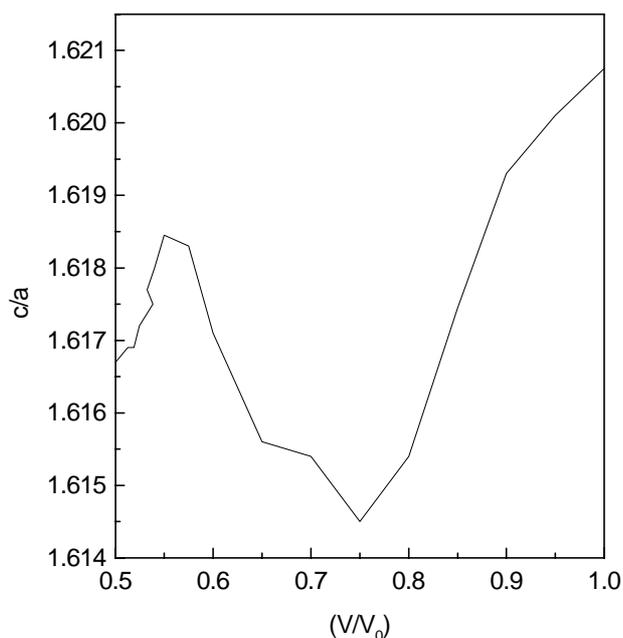


Figure 3. Variation of the axial ratio (c/a) in the *hcp* structure of Re.

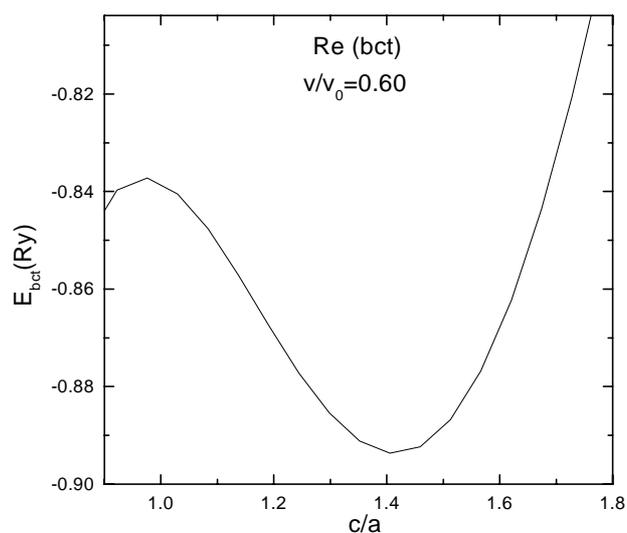


Figure 5. Total energy per atom as a function of c/a ratio in the *bct* structure for Re for $V/V_0 = 0.6$. The total energy scale is shifted by 33438 Ry.

In the Bain path, the total energy increases monotonically from the *fcc* to *bcc* phase, as the *c/a* value decreases from $\sqrt{2}$ to 1 in the *bct* lattice (see figure 5). We have carried out the calculations for 20 values of *c/a* for each compression. All the curves obtained with the *bct* cell correspond to higher energy than that of *hcp* phase at the same volume compression. Thus the *hcp* phase is stable against cubic (and tetragonal) distortion at least up to $V/V_0 = 0.5$, which corresponds to 1 TPa pressure (see figure 3). These findings are in contrast to the expectations of Kaufman referred above, where transition from *hcp* to *bcc* was speculated below 110 GPa. The increasing trend of the curves depicted in figure 4 for the *bcc* and *fcc* structures suggests that, even at pressures higher than 1 TPa, transition of Re to any of these two cubic structures is unlikely. Even if electronic excitations were to play any role (Liu 1983), the *fcc* structure should be preferred over *bcc* for a transition from the *hcp* phase.

Comparison of the calculated total energies in the *fcc* and *bct* (with *c/a* = 1.414) lattices, and also in *bcc* and *bct* (with *c/a* = 1.0) structures, show that the accuracy limit of our total energy calculations is 1 mRy or less. As Re is a hard material, total energy changes among the different structures range from 10 to 100 mRy (see figure 1), and thus better accuracy limitation is not warranted for the evaluation of structural stability in the present work.

Our detailed relativistically split electronic band structure studies reveal that a few electronic topological transitions are likely to occur under pressure which could be related to the variation in superconducting transition temperature (Chu *et al* 1970) and changes in elastic constants (Manghnani *et al* 1974) under compression, referred in §1. Detailed work on these properties demand calculations at close intervals of pressure near the compression at which the electronic transitions occur, and will be reported elsewhere separately.

4. Conclusions

In summary, our calculations show that the ambient pressure *hcp* phase of Re is stable up to pressures over 1 TPa,

among the commonly occurring close-packed structures. Especially, there is no transition to the *bcc* structure up to 1 TPa. The equation of state gives a bulk modulus of 345 GPa. Its axial ratio shows less than 0.33% variation (i.e. less than 0.006 change in its value) in this pressure range, thus indicating little change in the anisotropic properties of Re under compression.

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