

Structural stability of hafnium under pressure

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1990 J. Phys.: Condens. Matter 2 6457

(<http://iopscience.iop.org/0953-8984/2/30/011>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 10/05/2010 at 22:24

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Structural stability of hafnium under pressure

Jyoti S Gyanchandani, Satish C Gupta, S K Sikka and R Chidambaram
Neutron Physics Division, Bhabha Atomic Research Centre, Bombay 400085, India

Received 25 April 1990

Abstract. A theoretical analysis on the structural stability of Hf under pressure, using the linear muffin-tin orbital method in conjunction with the Andersen force theorem, predicts a new phase transition to a BCC phase at high pressures, in agreement with recent diamond cell experiments.

The present work is a part of our study to understand the causes of the discontinuities observed in the plots of the experimental shock velocity (U_s) and particle velocity (U_p) data on group IV transition elements Ti, Zr and Hf using first-principles electronic structure calculations. McQueen *et al* (1970) found discontinuities in these materials at shock pressures of 17, 26 and 40 GPa, respectively and there have been many speculations regarding them. McQueen *et al* (1970) assumed they were due to an α (HCP) to β (BCC) transition based on the observation of β phase in the shock recovered samples of Ti. Kutsar and German (1976) associated these discontinuities with the $\alpha \rightarrow \omega$ (three atom simple hexagonal) phase change as they found ω phase in the shock recovered samples of Ti and Zr loaded to the pressure in the vicinity of the shock discontinuities. Also, Carter (1973) speculated that these could be due to some electronic transitions. (For more details see Sikka *et al* 1982.)

Our analysis on Ti and Zr has already been reported elsewhere (Gyanchandani *et al* 1989a, 1989b, 1990). By theoretically determining the one-electron structural energy differences between the α , β , and ω structures with reference to the FCC structure, we predicted a new $\omega \rightarrow \beta$ structural transition in Zr and suggested that this transition is the cause of shock discontinuities in it. Subsequently, this transition has been verified by Xia *et al* (1990a) using energy dispersive x-ray diffraction with a diamond anvil cell. A similar analysis on Ti suggested that no $\omega \rightarrow \beta$ structural transition occurred up to 26 GPa. This result was confirmed by our diamond cell experiments which showed that after the well known initial $\alpha \rightarrow \omega$ transformation at 6 GPa, the ω phase continued to exist up to 23 GPa, the upper limit of pressure in our experiments (Gyanchandani *et al* 1988). This led us to agree with Al'tshuler *et al* (1981) that the initial segment of the U_s - U_p plot of this material is not well established. This has since then been confirmed experimentally (Shaner 1989). Furthermore, the detection of β phase in the shock recovered samples of Ti was ascribed by us to heterogeneous heating of Ti subjected to a high strain rate. The locally heated shear bands could take the material to the high temperature β phase. The presence of shear bands in Ti has also now been verified (Holt *et al* 1989). Heartened by these successes of the one-electron theory, we have now applied the same calculational technique to Hf, for which very recent static pressure

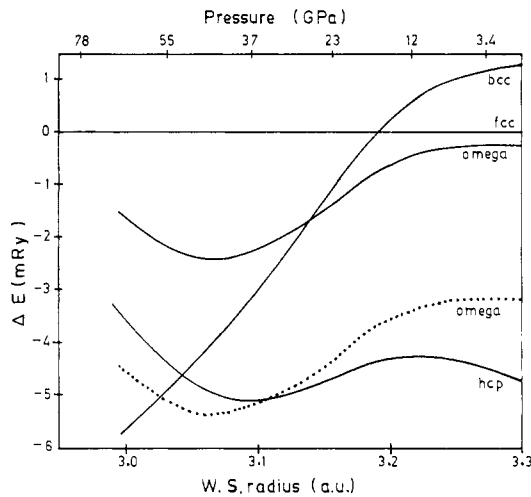


Figure 1. Structural energy differences for Hf. The dotted curve is shifted with respect to the calculated curve for the ω phase.

measurements up to 252 GPa show an $\alpha \rightarrow \omega$ transition at 38 ± 8 GPa and an $\omega \rightarrow \beta$ transition at 71 ± 1 GPa (Xia *et al* 1990a).

First, we give a brief summary of the computational technique. We have employed the Andersen force theorem to obtain the changes in total energy (Pettifor 1976, 1978, Pettifor and Varma 1979, Mackintosh and Andersen 1980). This theorem states that the difference in total energy, at a constant volume, between two structures (say I and II) is given by the differences in the sum of the one-electron eigenvalues, provided we use for structure II a frozen potential, obtained from a self-consistent calculation for structure I. A muffin-tin contribution is also added. This corrects the electrostatic energy for the non-sphericity of the Wigner-Seitz cell and is important for the relatively less close-packed ω structure. The required self-consistent band structures and eigenvalues were evaluated in our case by the linear muffin-tin orbital method (Andersen 1975, Skriver 1984). We included all relativistic contributions except spin-orbit, employed the exchange correlation potential of Von Barth and Hedin, and retained all angular momentum components up to $l = 2$. The electronic configuration employed for Hf was (Xe) $4f^{14} (5d6s6p)^4$ and the electronic states of (Xe) $4f^{14}$ were kept 'frozen'. The self-consistency was carried out such that the change in electronic pressure from the last iteration to the previous one was less than 0.1 GPa. As in the case of Ti and Zr, equal atomic radii were assumed for the two non-equivalent atoms in the ω phase, which has the AlB_2 simple hexagonal structure (Gyanchandani 1989a, 1989b, 1990). The c/a ratios for α (1.582) and ω (0.614) structures were kept fixed for all compressions (see also Xia *et al* 1990a, b). The valence bands were sampled at 240, 285, 392 and 275 points per irreducible wedge of the Brillouin zone for FCC, BCC, HCP and ω structures, respectively. The energy differences are accurate to within 0.5 mRyd.

Computed structural energy differences at 0 K for the α , β , and ω phases with reference to the FCC phase are displayed in figure 1. It shows that the α phase remains the lowest energy structure from the normal volume to the compression of $v/v_0 = 0.78$ and 51 GPa pressure. Beyond this compression, the β structure becomes the most stable. This predicted structural sequence (HCP-BCC) is in contrast to HCP- ω -BCC observed in experiments. This disagreement may be attributed to: (i) the approximation of equal

atomic spheres for the two non-equivalent atoms in the structure, and (ii) to the inadequacy of the atomic sphere approximation for the less close-packed ω structure. Consequently the Madelung correction will be less accurate. However, if we move the ω curve by 3 mRyd (see figure 1) which is 6% of the Madelung correction, we get agreement with the experiment so that the crystal structural sequence in Hf is also α - ω - β . A similar procedure in Cs IV (McMahan 1984) and α -U (Skriver 1985) had to be followed to produce agreement with experiment. To this extent the current one-electron methods are deficient for phase stability analysis.

The transition to β phase in Hf at higher pressures as in the case of Zr is in line with the correlation between crystal structures and the d electron population in the transition metal series (Pettifor 1977). It may be noted that the d occupancy increases with pressure in these group IV elements and the next element in each of the series is in the BCC phase. The occurrence of the ω and β phases in Hf at higher pressures than in Zr may also be understood as the d electron number in Hf is 2.33 as compared to 2.54 in Zr at normal volume. Again, the transition pressure of the $\alpha \rightarrow \omega$ phase change is close to the pressure of the shock discontinuity in this material. This suggests that the shock anomaly in this material near 40 GPa (44.5 GPa, according to Al'tshuler *et al* 1981) occurs due to this $\alpha \rightarrow \omega$ phase transition.

References

- Al'tshuler L V, Bakanova A A, Dudoladov I P, Dynin E A, Trunin R F and Chekin B S 1981 *Zh. Prikl. Mekh. Tekh. Fiz.* **2** 3–34
- Andersen O K 1975 *Phys. Rev. B* **12** 3060
- Carter W J 1973 *Metallurgical Effects of High Strain Rate* ed R W Rohde, R M Butcher, J R Holland and C H Carnes (New York: Plenum) p 171
- Gyanchandani J S, Gupta S C, Sikka S K and Chidambaram R 1989a *Proc. Int. Conf. on High Pressure Science and Technology (Paderborn, West Germany, July 1989)* at press
- 1989b *Proc. APS Topical Conf. on Shock Waves in Condensed Matter (New Mexico, USA, 1989)* at press
- 1990 *J. Phys.: Condens. Matter* **2** 301–5
- Gyanchandani J S, Vijaykumar V, Gupta S C, Sikka S K and Chidambaram R 1988 *Proc. Solid State Phys. Symp. 31C (Bombay, 1988)* p 279
- Holt W H, Mock W, Soper W G and Coffey C S 1989 *Proc. APS Topical Conf. on Shock Waves in Condensed Matter (New Mexico, USA, 1989)* at press
- Kutsar A R and German V N 1976 *Proc. 3rd Int. Conf. Titanium (Moscow, 1976)*
- Mackintosh A R and Andersen O K 1980 *Electron at the Fermi Surface* ed M Springford (Cambridge: Cambridge University Press) p 149
- McMahan A K 1984 *Phys. Rev. B* **29** 5982
- McQueen R G, Marsh S P, Taylor J W, Fritz J N and Carter W J 1970 *High Velocity Impact Phenomena* ed R Kinslow (New York: Academic) p 293
- Ming Li-Chang, Manghnani M H and Katahara K W 1981 *J. Appl. Phys.* **52** 1332
- Pettifor D G 1976 *Commun. Phys.* **1** 141
- 1977 *J. Phys. F: Met. Phys.* **4** 613
- 1978 *J. Chem. Phys.* **69** 2930
- Pettifor D G and Varma C M 1979 *J. Phys. C: Solid State Phys.* **12** L253
- Shaner J W 1989 Los Alamos National Laboratory private communication
- Sikka S K, Vohra Y K and Chidambaram R 1982 *Prog. Mater. Sci.* **27** 245–310
- Skriver H L 1984 *LMTO Method* (Berlin: Springer)
- 1985 *Phys. Rev. B* **31** 1909
- Xia H, Ducloux S J, Ruoff A L and Vohra Y K 1990a *Phys. Rev. Lett.* **64** 204
- Xia H, Huan L, Ruoff A L and Vohra Y K 1990b unpublished