Theoretical analysis of the isostructural transition in Zr at 53 GPa

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Abstract. Recent diamond anvil x-ray diffraction measurements in Zr show a first-order isostructural transition at 53 GPa ($V/V_0 = 0.68$), beyond the known HCP to ω and ω to BCC transitions at 6.7 GPa and 33 GPa respectively. This transition has been attributed to the completion of s $\rightarrow$ d electron transfer in Zr. Here, we report our *ab initio* band structure analysis of this transition. Our two-panel LMTO calculations (that also includes the 4p core states) rule out the completion of s $\rightarrow$ d electron transfer up to $V/V_0 = 0.55$. Also our calculated room-temperature isotherm does not display van der Waals loop.

1. Introduction

Over the past few years, there have been simultaneous theoretical as well as experimental high-pressure investigations on the group IV B elements Ti, Zr and Hf. Our initial primary interest in performing the *ab initio* electronic structure calculations on these elements (Gyanchandani *et al* 1990a, b, c, Gyanchandani *et al* 1992) was to explain the causes of discontinuities observed at 17.5, 26 and 40 GPa respectively in their shock velocity–particle velocity plots from shock wave experiments performed by Mcqueen *et al* (1970). Analysis of stability of the various phases (α = HCP, ω = a three atom hexagonal and β = BCC) in the pressure range of experimental measurements in Zr led us to predict a new $\omega \rightarrow \beta$ transition after the already known $\alpha \rightarrow \omega$ transition, and to link the 26 GPa shock discontinuity to this $\omega \rightarrow \beta$ transition (Gyanchandani *et al* 1990b). This transition was subsequently detected by Xia *et al* (1990) in energy dispersive x-ray diffraction (EDXRD) experiments with a diamond anvil cell. This demonstrated the predictive capability of the current *ab initio* methods based on the density functional approach (Gupta *et al* 1993).

Recent high-pressure measurements on Zr by Akahama *et al* (1991, 1992a, b) using a diamond anvil cell in conjunction with angle dispersive x-ray diffraction employing imaging plate shows a small volume discontinuity of 1% at 53 GPa and $V/V_0 = 0.68$ beyond the first two phase transitions. No change in the structure was observed across the discontinuity. Akahama *et al* (1991, 1992a, b) related this BCC $\rightarrow$ BCC isostructural transition to the completion of the s $\rightarrow$ d electron transfer. The concept of electron transfer between s to d bands under pressure is well known (Pettifor 1977). Under compression, the s band rises faster than the d band on account of greater increase in kinetic energy of the s band electrons as compared to the d band electrons, since they are more repelled by the orthogonality effects. The relative movement of the bands leads to an increase in d electron population. Ultimately, the bottom of the s band rises above the Fermi level depleting all the s electron population and the material becomes a pure d electron metal. The material at this point usually undergoes a phase transition.

Isostructural transitions under high pressure also occur in other materials, e.g, Ce and Cs, but these are accompanied by large volume changes. Ce displays a γ(FCC) to α(FCC) transition at 0.7 GPa with a 17% volume decrease (Kosenmaki *et al* 1978). The transition has not been very well understood and has been interpreted in terms of the 4f delocalization model (Mott transition) and various other models, namely the Kondo effect, Jahn–Teller effect, mixed valence, etc (Young 1991). On the other hand, the FCC–FCC isostructural transition at 4.2 GPa in Cs with 9.4% volume decrease is well analysed theoretically by Glotzel and McMahan (1979). They showed that the primary cause of this transition is s $\rightarrow$ d electronic transfer under pressure, which results in softening of the zero-degree isotherm and causes a negative curvature in it. This leads to a negative Gruneisen parameter and a corresponding negative contribution to the thermal pressure, creating a van der Waals loop in the room temperature isotherm and consequently culminating into the first-order isostructural transition.

The isostructural transition in Zr being accompanied by a small volume change would be interesting to investigate. In the present work, we have performed first principles band structure calculations to analyse this transition. We neither find the completion of the s $\rightarrow$ d electron transfer nor the formation of a van der Waals loop in the isotherm near the volume of this reported transition.

2. Method of calculations

The linear-muffin-tin-orbital (LMTO) method (Andersen 1985) based on the local density formalism and the atomic-sphere approximation (ASA) was employed for the electronic structure calculations. Although more sophisticated, full potential LMTO technique is available, the use of the LMTO-ASA method is adequate for Zr as the results of recent full potential calculations on this element (Ahuja *et al* 1993) showed no significant improvement with the experimental measurements as compared to our earlier LMTO-ASA results (see table 1). The present calculations include all relativistic contributions except spin–orbit and employ von Berth and Hedin exchange correlation potential. We retained all angular momentum components up to $l = 3$. The electronic configuration employed was [Zn] $4p^6(4d5s5p)^4$. Electron states of the Zn core were kept 'frozen'. Two-panel calculations (one panel for 4p levels and the other for rest of the conduction electrons) were performed to see whether the broadening of 4p core levels was the cause of observed discontinuity. The irreducible Brillouin zone sampling was done with 385 k points. The electronic pressure of the $4p^6$ and $(4d5s5p)^4$ states at 0 K was evaluated using the following expression

$$3PV = \sum_l \int_0^{E_F} dE \, N_l(E) S \phi_l^2(E, S)[(D_l(E) - 1)(D_l(E) + l + 1) + (E - E_{XC})S^2]$$

where $N_l(E)$ is the projected density of states of angular momentum l and $\phi_l(E, S)$ is the amplitude at the sphere radius S of the normalized radial wave function at energy E. $D_l(E)$ is the logarithmic derivative and E_{XC} is the exchange correlation energy density at the atomic sphere radius S. The pressure contribution due to Madelung correction over ASA has also been included. This is estimated from the volume derivative of the expression

$$\Delta E = (1.8 - \alpha)q^2/S.$$

Here α is the Ewald constant and q is the charge per atom corresponding to the electron density $n(S)$ at the sphere radius S. Pressure calculations were performed for a large number

of closely spaced volume intervals near the experimental volume of transition. To evaluate the 298 K isotherm from 0 K data, the following expression for pressure was used;

$$P(V, T) = P(V) + 3NkT\gamma(V)/V$$

wherein electronic excitation and electron–phonon coupling have been neglected at this temperature as these give negligible contributions. Here $P(V)$ is the $T = 0$ K static lattice pressure evaluated as described above. The second term is the contribution from quasiharmonic phonons evaluated in the high temperature limit. Here $\gamma(V)$, the Gruneisen parameter, is computed from the 0 K isotherm by Slater's relation (Slater 1939).

Table 1. Comparison of the theoretical calculations with experimental measurements on phase transition in Zr.

	LMTO-ASA calculations[†] (Gyanchandani et al 1990b)	Full potential calculations (Ahuja et al 1993)	Experimental data
$P_{\alpha-\omega}$ (GPa)	5	0	2–6[a]
$V/V_0\|_{(\alpha-\omega)}$	0.95	1.0	0.97[a]
$P_{\omega-\beta}$ (GPa)	11	48.3	30–33[b]
$V/V_0\|_{(\omega-\beta)}$	0.91	0.69	0.76[b]

[†] *These calculations were performed before the experimental observation of ω–β transition in Zr by Xia et al* (1990).

[a] Sikka et al (1982).

[b] Xia et al (1990), Akahama et al (1991).

3. Discussion and results

In figures 1 and 2, we plot the angular momentum decomposition of the density of states and the number of states at the Fermi level as a function of volume. On compression, all the projected density of states decrease smoothly without any abrupt change of slope or any discontinuity such as a Van Hove discontinuity. Figure 2 shows that, under pressure, the number of 4d electrons increases gradually at the expense of s and p electrons. The total number of d electrons has increased from 2.63 at $V/V_0 = 1.0$ to 2.97 at $V/V_0 = 0.68$ and it is 3.18 at even higher compression of $V/V_0 = 0.55$. Also, sufficient amount of 5s and 5p charge remains within the atomic sphere ($n_s + n_p = 0.797$ up to $V/V_0 = 0.55$). This suggests that up to the highest pressure of 126 GPa ($V/V_0 = 0.55$) the s to d electron transfer is not complete. This is clearly evident from figure 3, where we depict the energy of various l band edges against compression. The Fermi-energy E_F is also plotted. All levels move up under compression due to increasing kinetic energy, however, the same is relatively slow for the bottom of the 4d band. The Fermi energy moves almost parallel to this 4d band edge. It clearly rules out the completion of s → d electron transfer up to $V/V_0 = 0.55$ as the bottom of the 5s band is still below the Fermi level. According to our earlier estimates following McMahan's analysis (McMahan 1986) the complete s → d electron transfer in Zr should occur at 424 GPa (Gyanchandani et al 1990). This is far too high as compared to the pressure of the observed discontinuity.

In figure 4, we plot the pressure contribution to 0 K isotherm for various angular momentum components. The dominant bonding contribution at equilibrium is coming from the 4d orbitals; the 5s and 5p electrons become increasingly repulsive under compression.
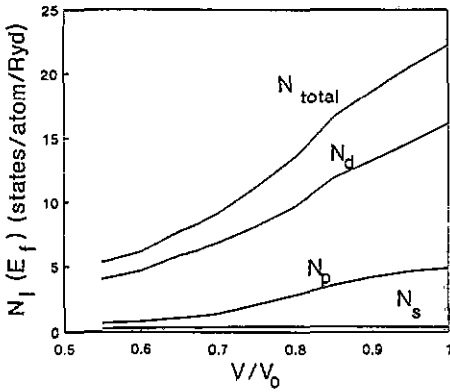
Figure 1. Total and projected density of states at E_F for 5s, 5p and 4d electrons as a function of volume.
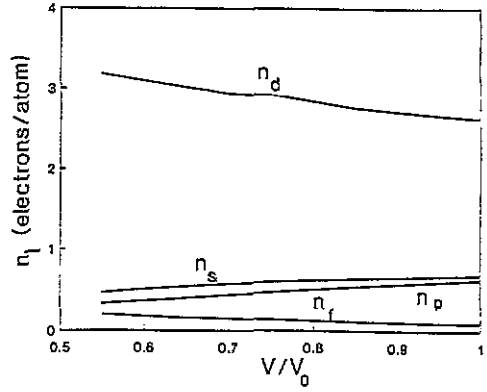

Figure 2. Number of valence electrons at E_F resolved into angular momentum components for 5s, 5p, 4d and 4f states as a function of volume.
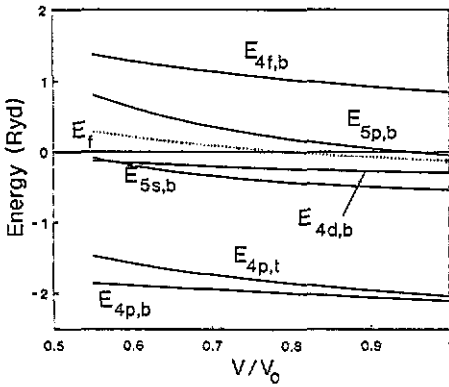

Figure 3. l band edges versus compression. $E_{nl,b}$ and $E_{nl,t}$ denote the bottom and top respectively of the nth l band.
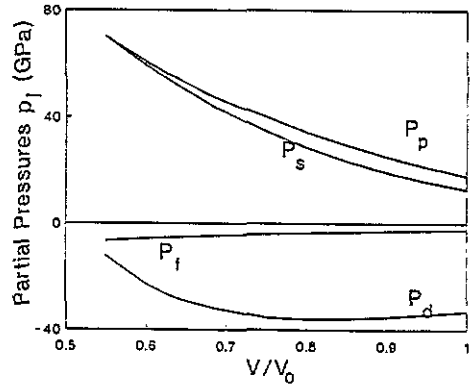

Figure 4. Electronic pressure of BCC Zr decomposed with respect to angular momentum as a function of compression.

In figure 5, we give the 298 K isotherm for the BCC Zr along with the experimental data of Xia *et al* (1990) and Akahama *et al* (1991, 1992a, b). The agreement between the computed isotherm and both the sets of experimental data is excellent below 53 GPa and is fairly good above this pressure. The calculated total pressure increases monotonically without exhibiting any van der Waals loop. Moreover, as can be noted from figure 3, even though the 4p core levels broaden to about 315 mRyd up to $V/V_0 = 0.55$, they contribute very little to the total pressure. (e.g. At 126 GPa the pressure contribution due to 4p core electrons is 1.16 GPa only.)

For further analysis we have plotted in figure 6, our computed 298 K isotherm in the form of universal equation of state (Rose *et al* 1984) i.e. $\ln H$ versus $(1 - x)$ where

$$\ln H = \ln K_0 + \eta(1 - x) \qquad \text{with } H = [px^2/3(1-x)], \quad x = (V/V_0)^{1/3}, \quad \eta = 3/2(K_0' - 1)$$

K_0 is the isothermal bulk modulus and K_0' is its pressure derivative. In most materials the plot of the isotherm in this form is linear. As shown by Sikka (1988), this linearity breaks
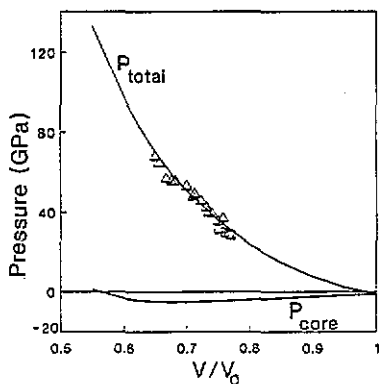
Figure 5. Pressure versus relative volume for BCC Zr (——, calculated); experimental data: □, Xia *et al* (1990); △, Akahama *et al* (1991, 1992a, b).
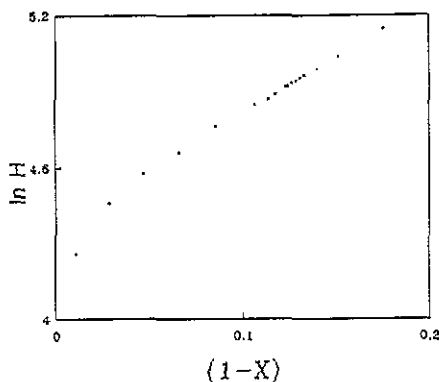
Figure 6. Computed 298 K isotherm of BCC Zr plotted in the form of universal equation of state, i.e., ln *H* versus $(1 - x)$.

down in presence of any electronic transfer, and also any structural or electronic transition may be easily discerned in such a plot as a discontinuity or an abrupt change of slope. As can be noted from this figure, although the plot is non-linear indicating an interband electronic transfer (s → d) no discontinuity in it or its slope occurs near the experimental volume of transition.

In summary, our analysis does not indicate existence of an isostructural transition around 53 GPa suggesting that its occurrence needs to be rechecked experimentally.

Acknowledgment

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