The equation of state and structural stability of titanium obtained using the linear muffin-tin orbital band-structure method

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Abstract. Room-temperature isotherms of titanium in HCP and ω-phases are calculated by the first-principles linear muffin-tin orbital energy band method. Comparison with experimental data shows excellent agreement. Structural phase stability analysis by the Andersen force theorem shows that the ω-phase is the lowest-energy phase at 0 K and normal volume. The possibility that the s $\rightarrow$ d electronic transition is the cause of shock discontinuity at 17.5 GPa is also ruled out.

1. Introduction

The element titanium ($Z = 22$) has been extensively studied under high static and shock pressures (for a review see Sikka *et al* (1982)). Static experiments show that Ti, which crystallises in the hexagonal close-packed (HCP) structure α at ambient conditions, undergoes a phase transition to a three-atom simple hexagonal structure (ω) in the 2.9–7.5 GPa pressure range (Jamieson 1963, Jayaraman *et al* 1963). Recent diamond anvil cell experiments have shown that this ω-phase continues to exist at least up to 23 GPa (Gyanchandani *et al* 1988). Shock wave measurements carried out by McQueen *et al* (1970) showed a discontinuity in the shock velocity–particle velocity plot at 17.5 GPa, indicating a phase transition. They associated this with the $\alpha \rightarrow \beta$ change (β is the BCC high-temperature phase), as they observed some traces of the BCC phase in the shock-recovered samples. Carter (1973), however, speculated that this discontinuity is related to some electronic transition, but Kutsar and German (1976) found a considerable amount of ω-phase in the recovered samples which had been shock loaded in the vicinity of the above discontinuity. Moreover, time-resolved shock wave measurements display a two-wave structure. In one set of experiments it is at 11.9 GPa (Kutsar *et al* 1982) and in another at 6 GPa (Kiselev and Falkov 1982).

The theoretical work on Ti under pressure, especially on the ω-phase, has been very limited so far. Band-structure calculations using the augmented plane-wave method were carried out at normal volume by Vohra *et al* (1979), but these calculations were not self-consistent. Skriver (1985) analysed the phase stability of Ti by the linear muffin-tin orbital (LMTO) band-structure method and found that the α-structure has the lowest energy when compared with the β and FCC structures. He, however, did not include the ω-structure in his study.

In this paper, we present self-consistent band-structure calculations on the α- and ω-phases of Ti, using the LMTO method. The equation of state of these two phases are compared with each other and with experimental data. The stability of the ω-phase with respect to the other structures is also analysed. Also ruled out is the possibility that the s $\rightarrow$ d electronic transition is the cause of the observed shock discontinuity at 17.5 GPa.

2. Method of calculation

The first-principles band-structure calculations have been performed utilising the LMTO method (Andersen 1975) for the α, β, ω and FCC structures. A detailed description of the LMTO method has been given by Skriver (1984). We included all relativistic contributions except the spin–orbit contribution, employed the exchange–correlation potential of von Berth and Hedin and retained all angular momentum components up to $1 = 3$. The electronic configuration employed for Ti was $(Ar) (3d4s4p)^4$. The electronic states of the (Ar) core were kept 'frozen'. The pressure contribution due to the core overlap calculated using the procedure of Sikka and Godwal (1987) is negligibly small for the compressions considered in this paper. The electronic pressure of the $(3d4s4p)^4$ states at 0 K is evaluated using the following relation:

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

where $N_l(E)$ is the projected density of states of angular momentum l and $\varphi_l(E)$ is the amplitude at the sphere radius S of the normalised radial wavefunction at energy E. $D_l(E)$ is the logarithmic derivative and E_{xc} is the exchange–correlation energy density at the sphere radius S.

The energy differences between various structures have been calculated using the Andersen force theorem (Mackintosh and Andersen 1980). This has been demonstrated to work for many elements and ordered compounds (Skriver 1985, McMahan 1984, Christensen *et al* 1986). Firstly, self-consistent band-structure calculations were performed for the FCC structure and the ground-state electron density n_{FCC} and the potential parameters determined. Then the eigenvalues were determined for the other structures employing the same potential parameters. This way the energy difference between the two structures is given by the relation

$$\Delta E_{st-FCC} = \int_0^{E_F} EN_{st}(E) \, dE - \int_0^{E_F} EN_{FCC}(E) \, dE$$

as the double-counting terms and the exchange–correlation terms cancel. The muffin-tin correction which corrects the electrostatic energy for the non-sphericity of the Wigner–Seitz cell is estimated from the expression

$$\Delta E_M = (1.8 - \alpha_M)q_S^2/S$$

for each structure. Here α_M is the Ewald constant and q_S is the charge per atom corresponding to the electron density $n(S)$ at the sphere radius S.

The ω-phase, which has the AlB_2 simple hexagonal structure (space group, P6/mmm; $c/a = 0.61$) with three atoms per unit cell, was treated as a compound in the LMTO procedure. In this structure, there are two non-equivalent types of atom: A type at
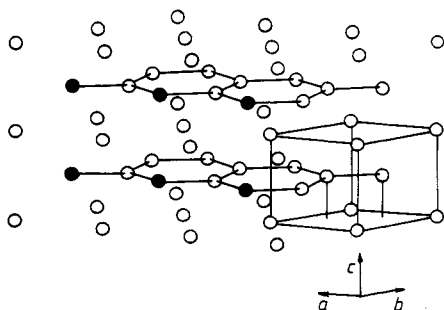
Figure 1. AlB$_2$ structure showing the graphite-like net of B atoms.

Table 1. Structural energy differences for Ti at R_{WS} = 3.052 au.

$\Delta E_{BCC \to FCC}$ = −0.0010 Ryd/atom
$\Delta E_{HCP \to FCC}$ = −0.0048 Ryd/atom
$\Delta E_{\omega \to FCC}$ = −0.0147 Ryd/atom

position (0 0 0) and B type at positions $(\frac{1}{3}\frac{2}{3}\frac{1}{2})$ and $(\frac{2}{3}\frac{1}{3}\frac{1}{2})$. As shown in figure 1, B-type atoms form a graphite-like net. This structure is a fairly close-packed one, as evidenced by its Ewald constant α_M = 1.788 837, to be accurately treated by the LMTO method (for a discussion of this point, see McMahan (1984)). The atomic sphere radii for the two types of atom were taken to be equal. Andersen *et al* (1986) noted that self-consistent band-structure calculations were relatively insensitive to the choice of sphere radii. Further, the same prescription has been used by Christensen *et al* (1986) for analysing the structural stability of compounds using Andersen force theorem.

The valence bands were sampled with 240, 285, 150 and 81 points per irreducible wedge of the Brillouin zone for the FCC, BCC HCP and ω structures, respectively. The c/a ratio for the HCP structures was kept fixed at 1.586, the experimental value (Kittel 1977). The uncertainties in the calculated energy differences were estimated to be about 0.5 mRyd/atom or less.

3. Results and discussion

The calculated structural energy differences for the α-, β- and ω-phases from the reference FCC structure at normal volume (V_0 = 119.02 au; S = 3.052 au) are presented in table 1. We find that the energy of the ω-phase is the lowest, followed by that of α and then that of the β-phase. These results are in agreement with those of Skriver (1985), who found that the α-phase is more stable than the β-phase, and also with those of Ho *et al* (1984) (for Zr) who determined that the ω-phase has a lower energy than the β-phase. Since the pressure at this volume is negative for the ω-structure, it will, however, have equilibrium volume at a lower value. (This is qualitatively in agreement with the 2% difference between the densities of the α- and the pressure-quenched ω-phase observed experimentally.) The linear extrapolation of the experimental $\alpha \to \omega$-phase line to lower temperatures indicates that the ω-phase would be more stable than the α-phase below 62 K.
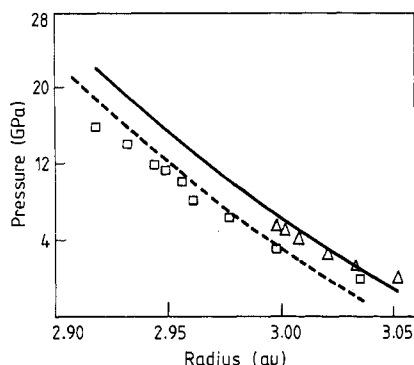
Figure 2. Room-temperature isotherms of Ti: ———, calculations, HCP phase; − − −, calculations, ω phase; $\square$, experimental, ω-phase; $\triangle$, experimental, α-phase.
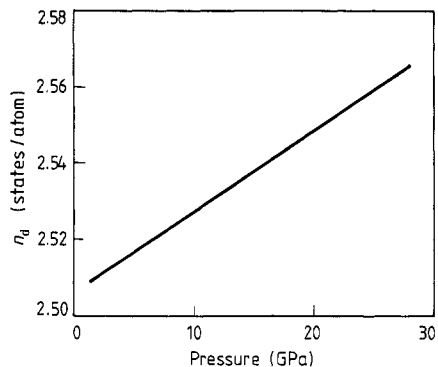

Figure 3. Calculated d-occupation number against pressure for the α-phase.

The crystal structures of the transition metals have been correlated with the number of d valence electrons (Pettifor 1977). From the fact that the ω-phase occurs in Ti on alloying with d-rich transition elements (V, Nb, Cr, W, etc), Vohra (1979) pointed out that the stability of the ω-phase under pressure is also related to this d-electron occupancy. We corroborate this qualitatively. It should be noted that the average d population of the two sites in the ω-structure is more than the α-phase by 0.015 electron/ atom. This makes a bonding contribution and hence lowers the energy of the ω-phase with respect to that of the α-phase.

In figure 2, we plot our calculated room-temperature isotherms for the α- and ω-phases up to 20 GPa. Also plotted are the experimental data of Vohra *et al* (1981) obtained using energy-dispersive x-ray diffraction with a diamond anvil cell. The thermal contribution to the pressure at a given volume is approximated by the well known Grüneisen equation

$$P_T = \gamma C_v T.$$

Here, C_v is the specific heat and γ is the Grüneisen parameter, which is estimated from the relation $\rho\gamma = \rho_0\gamma_0$. (The subscript zeros denote room-temperature values.) The value of C_v and γ_0 are taken from McQueen *et al* (1970). It should be noted that the uncertainty in γ_0 and the assumption $\rho\gamma = \rho_0\gamma_0$ would have a negligible effect on the calculated 293 K isotherm (Godwal *et al* 1983). The curve of the α-phase is in close agreement with the experimental data up to 7 GPa, the $\alpha \rightarrow \omega$ transition pressure. The computed isotherm for the ω-phase also agrees well with the loading data above 7 GPa and also the unloading data; the ω-phase, as is well known, is retained metastably.

The number of occupied states of d orbitals as a function of pressure up to 30 GPa for the α-phase are plotted in figure 3. The d-band population smoothly increases and does not display any anomalous behaviour. Also, McMahan (1986) has shown that for the complete s $\rightarrow$ d transition the pressure increased by a factor of 2 for each successive element to the right in a given period. Carrying out such computations from K (60 GPa), we obtain an estimate of 480 GPa for Ti. This is far too high compared with the pressure (17.5 GPa) corresponding to the discontinuity observed in shock measurements. Thus

the s→d transition does not appear to be the cause of shock discontinuity in this material.

Acknowledgments

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