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Abstract. We report a theoretical calculation of the band structure and superconductivity of zirconium in the BCC phase under pressure. The effect of pressure on the band structure is obtained by means of the self-consistent linear muffin-tin orbital method. The superconducting transition temperature T_c is calculated using McMillan's formula. The parameters necessary to calculate T_c are taken from the band-structure results. The calculated value of T_c at 35.2 GPa is 12.07 K. The theoretically calculated value of T_c is in excellent agreement with the recent experimental observation.

1. Introduction

The group IV transition metal zirconium ($Z = 40$) crystallizes in a HCP structure (α-phase) under ambient conditions. It is known to transform to a BCC structure (β-phase) above 1135 K at atmospheric pressure. This metal was first studied by Bridgman (1952) who found a resistance discontinuity at 5.9 GPa indicative of a first-order phase transition. From an x-ray diffraction study, Jamieson (1963) indicated this transformation to be from HCP to a hexagonal structure (ω-phase; three atoms per unit cell). Jayaraman *et al* (1963) measured the slope of various phase boundaries at high temperatures and high pressures and located the triple point in the phase diagram of Zr. From shock measurements, McQueen *et al* (1970) observed a discontinuity in the slope of shock velocity–particle velocity plot at 26 GPa ($T = 540$ K). This is taken as an indication of phase transition. Since this discontinuity occurs at a higher pressure than the α-to-ω transition pressure observed under static pressures, it was suggested that the shock transition may be the $\omega \rightarrow \beta$ transition. Recently Hui Xia *et al* (1990) adopting an energy-dispersive x-ray diffraction technique observed a first-order phase transition between ω-phase and BCC phase in the pressure range of 30 ± 2 GPa. More recently, the superconducting transition temperature T_c of Zr has been studied as a function of pressure up to 50 GPa by Akahama *et al* (1990). Corresponding to a phase transition from hexagonal to BCC structure, they observed a discontinuous increase in T_c at 30 GPa.

On the theoretical side, Chen *et al* (1985) applied the first-principles frozen-phonon method to study the vibrational modes in BCC Zr. Recently, Gyanchandani *et al* (1990) presented results on the structural stability of Zr as a function of compression at 0 K, obtained by using the self-consistent linear muffin-tin orbital (LMTO) band-structure

Table 1. Fermi energies E_F, the total and partial densities of states at E_F and the numbers of electrons.

Pressure (GPa)	E_F (Ryd)	$N(E_F)$ (Ryd per atom spin)	Density of states (Ryd/atom spin)			Number of electrons (electrons/atom)		
			s	p	d	s	p	d
35.20	0.0343	8.0933	0.2253	1.833	6.035	0.6806	0.5606	2.7588
39.40	0.0461	7.7437	0.2257	1.697	5.821	0.6739	0.5496	2.7765
43.99	0.0644	6.9544	0.2244	1.544	5.186	0.6668	0.5387	2.7945
51.38	0.0883	6.3919	0.2299	1.370	4.792	0.6557	0.5227	2.8216
56.38	0.1047	6.0447	0.2307	1.243	4.571	0.6479	0.5121	2.8400

method of Andersen. This theoretically calculated pressure is lower than the experimental value of Hui Xia *et al* (1990).

In this paper we present our results on the pressure dependence of superconducting transition temperature of Zr in the BCC phase. The necessary inputs to calculate T_c are derived from the self-consistent LMTO method. The organization of the paper is as follows. The methodology of band structure calculations is given in section 2. Section 3 deals with the calculation of the superconducting transition temperature. The final section is devoted to results and discussion.

2. Method of calculation

The energy bands of Zr in the BCC phase have been obtained by means of the LMTO method (Andersen 1975) within the atomic sphere approximation (ASA). All relativistic contributions except spin–orbit coupling are included. The exchange correlation scheme of Von Barth and Hedin is employed. The basis set is corrected by including the correction terms for overlapping-sphere geometry. The total and *l* partial state densities are calculated by means of tetrahedron method (Jepsen and Andersen 1971) for 240 *k*-points in the irreducible part of the Brillouin zone. The Fermi energy, and the total and projected partial densities of state evaluated at the Fermi energy are given in table 1 along with the number of electrons for different pressures. The total and partial density of states at E_F are used later in the calculation of T_c.

The band structure of BCC Zr along the high-symmetry directions is given in figure 1. The band-structure profile of Zr exhibits characteristic features similar to other BCC transition elements, such as a single low-lying band of 5s character. Specific to Zr is a nearly half-filled 4d band which originates just above E_F.

3. Calculation of T_c

The superconducting transition temperature is calculated using McMillan's (1968) formula which is

$$T_c = (\Theta_D/1.45) \exp\{-1.04(1 + \lambda)/[\lambda - \mu^*(1 + 0.62\lambda)]\} \tag{1}$$

where λ is the electron–phonon coupling constant, μ^* the electron–electron interaction constant and Θ_D the Debye temperature. λ can be written as

$$\lambda = N(E_F)\langle I^2 \rangle / M\langle \omega^2 \rangle \tag{2}$$

where M is the atomic mass, $\langle \omega^2 \rangle$ an average of the phonon frequency square and $\langle I^2 \rangle$
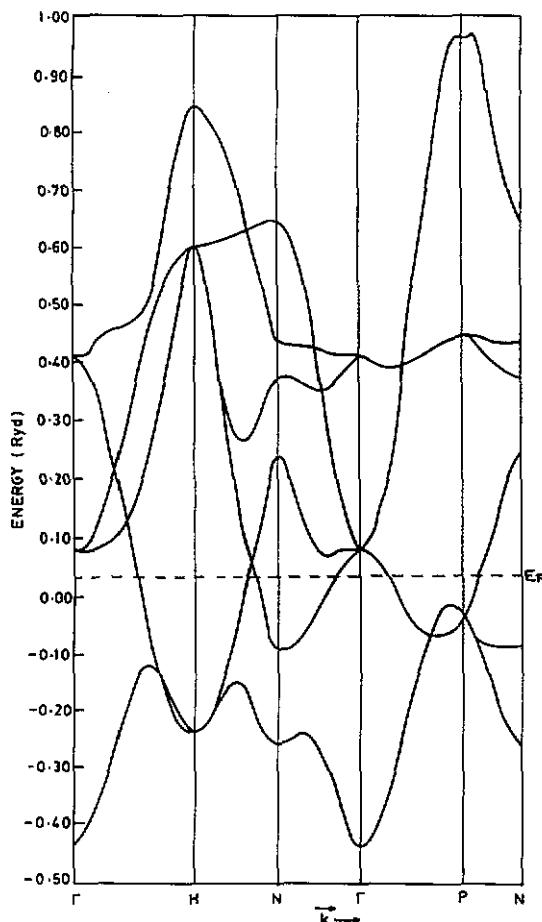
Figure 1. LMTO band structure for BCC Zr at 35.2 GPa.

the square of the electron–phonon matrix element averaged over the Fermi surface. $\langle I^2 \rangle$ (in Rydbergs) can be written as (Skriver and Mertig 1985)

$$\langle I^2 \rangle = 2 \sum_l \frac{(l+1)}{(2l+1)(2l+3)} M_{l,l+1}^2 \frac{N_l(E_F)N_{l+1}(E_F)}{N(E_F)N(E_F)} \tag{3}$$

where $M_{l,l+1}$ is the electron–phonon matrix element. The necessary parameters to calculate $M_{l,l+1}$ are taken from the band-structure results. The matrix elements $\langle I_{sp}^2 \rangle$ and $\langle I_{pd}^2 \rangle$ are calculated in a manner similar to our earlier work on P (Rajagopalan *et al* 1989) and Si (Azhagu Parvathi *et al* 1991). $\langle \omega^2 \rangle$ which appears in equation (2) is set equal to $0.5\Theta_D^2$ (Papaconstantopoulos *et al* 1977). Owing to the non-availability of the Θ_D value in the BCC phase, we are taking the value of Θ_D as 250 K, corresponding to the HCP phase. This can be justified as follows. If one looks at the experimental work of Akahama *et al* (1990), one can find that the resistance values of the HCP and BCC phases are almost the same. Since the resistances are so similar in the two cases, the Θ_D-values are assumed to be the same in the two phases.

To study the variation in Θ_D with pressure, one has to consider the Grüneisen parameter or the specific heat capacity data. These are not available for a number of

Table 2. Variations in λ, Θ_D and T_c with pressure.

Pressure (GPa)	λ	Θ_D (K)	T_c (K)
35.20	0.9931	247	12.07
39.40	0.9788	251	11.96
43.99	0.9424	256	11.20
51.38	0.8990	264	10.69
56.38	0.8779	267	10.30

materials under pressure. In order to overcome this difficulty, we have adopted a simple but straightforward procedure to compute the pressure dependence of Θ_D.

The ratio of the Debye temperature to the Fermi temperature can be written as (Ashcroft and Mermin 1981).

$$\Theta_D/T_F = 2(k_D/k_F)(c/v_F) \tag{4}$$

where k_D is the Debye wavevector, k_F is the Fermi wavevector, v_F is the Fermi velocity and c is the velocity of sound. Under the harmonic approximation, one can obtain the Debye temperature which is proportional to the square root of the Fermi energy divided by the cell parameter.

The variation in Θ_D with pressure can be computed in the case of the BCC structure using the expression

$$\Theta_D(P) = \Theta_D^0(a^0/a)\sqrt{E_F/E_F^0} \tag{5}$$

where the superscript zero refers to the corresponding quantities under normal conditions. The variation in Θ_D with pressure is calculated using the above equation from the Fermi energies obtained from the self-consistent calculation and the T_c-values are calculated. They are given in table 2 along with the other parameters involved in the calculation of T_c.

Recently Akahama *et al* (1990) measured the superconducting transition temperature of Zr as a function of pressure up to 50 GPa. From their studies, they found that the value of T_c increases up to 30 GPa. The pressure coefficient of T_c for hexagonal Zr has a positive value of about $0.12\,\text{K GPa}^{-1}$. A discontinuous increase in T_c is observed at 30 GPa corresponding to a phase transition from the HCP to the BCC structure. For the BCC phase, they observed a high T_c of 11 K. A further increase in pressure decreases the T_c-values with a pressure coefficient of $-0.14\,\text{K GPa}^{-1}$. The theoretically calculated value of T_c at 35.2 GPa is 12.07 K. A further increase in pressure decreases the value of T_c. Even though the magnitude of the theoretically calculated value at transition pressure (about 35 GPa) is a little high, the present result is in excellent agreement with the experimental observation for both magnitude and trend.

4. Results and discussion

To summarize, we have obtained the band structure of Zr in the BCC phase as a function of pressure using the self-consistent LMTO method. The band profile of Zr exhibits characteristic features similar to other BCC transition elements, such as a single low-lying
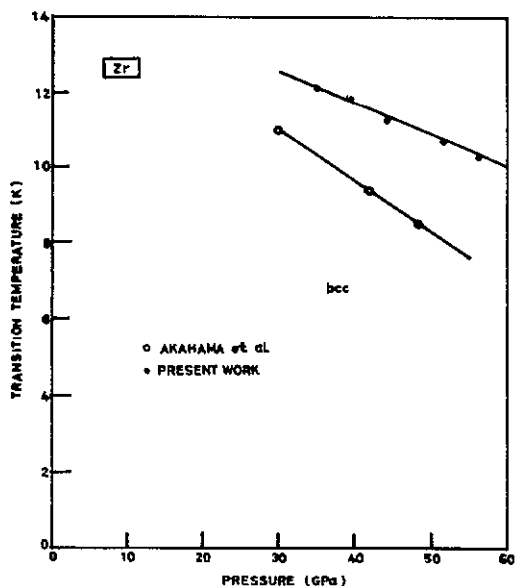
Figure 2. Pressure against T_c for BCC (β-phase) Zr along with the experimental result of Akahama *et al*.

band of 5s character. A nearly half-filled 4d band originates just above E_F. The band-structure outputs are used to calculate the value of T_c in conjunction with McMillan's formula. The theoretically calculated value of T_c as a function of pressure is given in figure 2 along with the experimental values of Akahama *et al*. From the figure it is seen that the value of T_c decreases with increase in pressure with a pressure coefficient of -0.09 K GPa^{-1} in the BCC phase whereas the experimental results show a pressure coefficient of -0.14 K GPa^{-1}.

The s $\rightarrow$ d electron transfer is qualitatively a common feature of many band-structure calculations. Under pressure the s electrons become trapped between the cores from which they are excluded by orthogonality requirements due to decreasing volume. They respond on increasing their kinetic energy whereby the s band rises relative to the d band, and s electrons are transferred into the d band. From our band-structure calculations we find that the 'd' electron number increases from 2.758 to 2.840 in the pressure range from 35.2 GPa to 56.38 GPa. The high T_c of BCC Zr is believed to be the result of the increase in the d-electron numbers. Our results show that the BCC structure of Zr is induced by pressure with the number of d electrons comparable with that of group VA element Nb. Moreover the calculated value of electron–phonon coupling constant is almost equal to that of Nb at ambient pressure. In the case of Nb the value of T_c decreases with increasing pressure up to 4 GPa and then begins to increase, but BCC Zr on the contrary shows a negative pressure coefficient of T_c. This behaviour is similar to a number of elemental transition metals under pressure. The decrease in the value of T_c may be due to stiffening of the lattice. This view is supported by the experimental work of Akahama *et al*.

Acknowledgments

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