The Electronic and Thermal Properties of ZrV_2 Compound: An *ab initio* Study

V. S. Sathyakumari, S. Sankar*, K. Mahalakshmi, G. Subhashree and R. Krithiga
Condensed Matter Laboratory, Department of Physics,
Madras Institute of Technology Campus, Anna University,
Chennai – 600044, Tamilnadu, India.
*e-mail: drshree@gmail.com

Abstract – A systematic study of thermal properties such as the Debye temperature and electronic specific heat co-efficient have been carried out using the results of ab initio studies of the electronic band structure and related characteristics, for the ZrV_2compound in cubic phase, using tight-binding linear muffin-tin orbital method (TB-LMTO) within local density approximation (LDA). Apart from the electronic band structure, the density of states (DOS) and Fermi energies (E_F) are also calculated. The calculated results are found to be in good agreement with the available results in literature.

Keywords-TB-LMTO; Debye temperature; specific heat coefficient; DOS; Fermi energy.

I. INTRODUCTION

Most of the Laves phase alloys have either an $MgZn_2$-type (C14) or $MgCu_2$-type (C15) structure. Laves phases with zirconium forms a number of inter metallic binary alloys of general formula ZrX_2 [1]. Subsequently, it was established that ZrV_2 has a cubic lattice of $MgCu_2$ type (C15). At high temperature number of physical properties exhibit anomalous behavior, such as resistivity [2], heat capacity [3], susceptibility and internal friction [4]. The low-temperature lattice properties have also been found interesting [5]. A lot of experimental work is available for ZrV_2, regarding the high-pressure structural phase transition [6]. To have such a comprehensive understanding of the basic electronic properties of the material, we have carried out the electronic band structure studies using the well-known and versatile TB-LMTO method and hence the results of electronic, ground state and thermal properties of ZrV_2 compound are presented here. The results have been analyzed and compared with the literature data.

II. COMPUTATIONAL DETAILS

The space group of ZrV_2 is *Fd-3m* (227) in cubic MgCu2-type (C15) structure. The atomic position in ZrV_2 is, V: 0, 0, 0 and Zr: 0.375, 0.375, and 0.375. The band structure calculations for this inter metallic compound has been carried out by using the first principle tight-binding-linear–muffin-tin-orbital method within the atomic sphere approximation [7]. The density of states (DOS) is calculated by the method of tetrahedron [8]. All the muffin-tin radii and number of *k*-points were varied to ensure total energy convergence. The ground-state properties were calculated for the lattice parameter that corresponds to the minimum of the total energy. The basis set included *s*-, *p*-, *d*- and *f*-orbitals. The structure is shown in Fig.1. The following basis set was used for the calculations: Zr: *[Kr]* $5s^2\ 4d^2$, V: *[Ar]* $3d^3\ 4s^2$

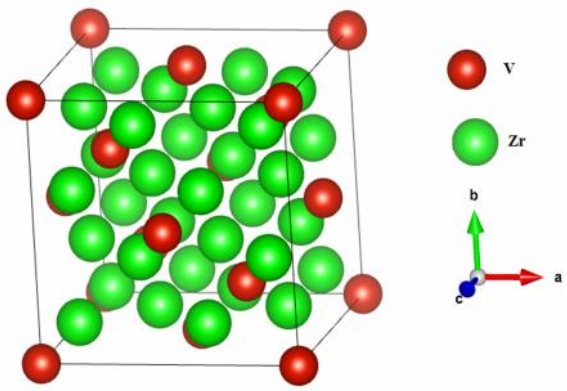

Figure 1. Hexagonal structure for ZrV_2

III. RESULT AND DISCUSSION

All the electronic properties such as the density of states and energy bands of the cubic phase of ZrV_2 were computed for the equilibrium lattice parameter. The plot of total energy as a function of cell volume of ZrV_2 is shown in Fig. 2. The present calculated lattice parameter is 7.33(Å). It is good agreement with the experimental value 7.43(Å) [1].

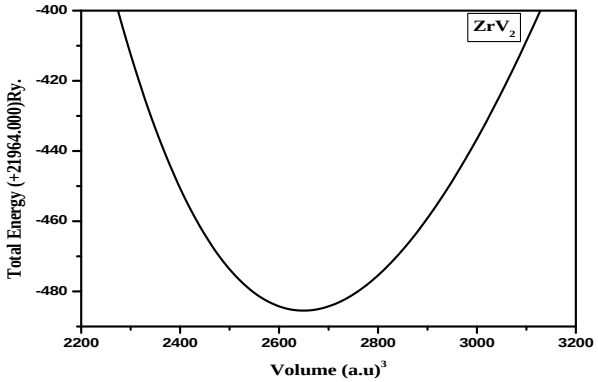

Figure 2. Total energy *vs* Volume for ZrV_2

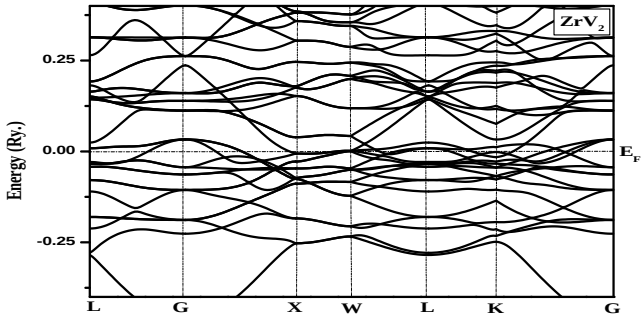

Figure 3. Band structure of ZrV_2 along symmetry directions

Transition metals have large *d*-electron shells and are characterized by high binding energy [9]. The electronic bandstructure of ZrV_2 along with the high symmetry directions of the Brillouin zone is shown in Fig.3. It is clearly evident in the material that these *d*-bands dominate in their conduction. The Fermi energy of ZrV_2 is 0.6872. The partial DOS of the cubic phase of ZrV_2 is presented in Fig.4. The high DOS around E_F is evidently due to the strong pile up of the *p*- and *d*-states in cubic (C15) phase of ZrV_2. The DOS at E_F for ZrV_2 are presented in Table 1. The calculated and experimental [10] values of DOS are presented in Table 3.

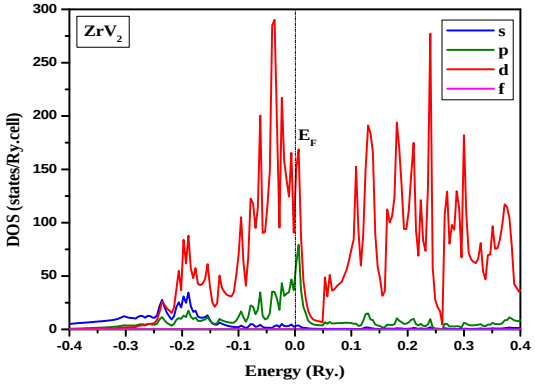

Figure 4. Partial density of states at the Fermi level for ZrV_2

TABLE 1. ELECTRONIC DENSITY OF STATES AT THE FERMI ENERGY FOR ZRV_2 FOR FOR *s*-, *p*-, AND *d*-STATES OF VARIOUS ATOMIC ELEMENTS

Bands	**Dos at E_F ((states/Ry)/atom)**		
	ZrV_2		
	V	*Zr*	*Total*
s	2.729	0.686	3.415
p	31.045	29.896	60.941
d	120.608	29.082	149.69

The Debye temperature (Θ_D) and electronic specific heat coefficient (γ) are important parameters that are closely related to the thermal properties of materials. To calculate the thermal properties of a vibrating Debye lattice we have used the Debye - Gruneisen model [11-13]. In the present work, the Debye temperature is calculated using expression (1).

$$\Theta_D = 67.48\sqrt{\frac{r_0 B_0}{M}} \quad (1)$$

where r is the Wigner-seitz radius in a.u., $r = r_o$ (at equilibrium) B_0 is the bulk modulus in kbar and M is the average atomic weight. The electronic specific heat coefficient (γ) is related to the density of states $N(E_F)$ using the expression (2) [14].

$$¥ = \frac{1}{3}®^2 k_B^2 N(E_F) \quad (2)$$

where k_B is the Boltzmann constant. The calculated and experimental values [10, 15] of Θ_D and γ are presented in Table 3. The Debye temperature (Θ_D) and the electronic specific heat coefficient (γ) are important parameters of materials. The Θ_D and γ values estimated by the present work for ZrV_2 are agreed well with the experimental values reported earlier [10, 15].

TABLE 3 EQUILIBRIUM WIGNER-SEITZ RADII (R_0), BULK MODULII (B_0), DOS (STATES /RY. CELL), DEBYE TEMPERATURE (Θ_D) AND ELECTRONIC SPECIFIC HEAT COEFFICIENT (Γ) FOR ZRV_2

ZrV_2	**r_0 (a.u)**	**B_0 (GPa)**	**DOS (states /Ry. Cell)**		**Θ_D (K)**		**¥ ($mJmol^{-1}K^{-2}$)**	
			Present	*Expt.*	*Present*	*Expt.*	*Present*	*Expt.*
Cubic	2.97867	37.58	214.04	220.32 [10]	163	190 [10] 189 [10] 203 [15]	11	7.7(3) [10] 18.9[10] 16.2 [15]

IV. CONCLUSIONS

The electronic bandstructure studies of ZrV_2 compound is carried out using the self-consistent tight binding linear muffin-tin orbital method. The electronic band structures show a strong hybridization between *p*- and *d*-bands and are also narrowly piled up around the Fermi energy for the material and it is also evident in the density of states results. Furthermore, it is found that the band structure and related properties at the Fermi energy are dominated by the *d*-bands in general. The density of states at the Fermi energy is found to be strongly influenced by the *d*-states of vanadium, and, it is also evident in the band structure results. The calculated results are observed to be in good agreement with the available results existing in the literature.

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