Role of s and d-electrons in Density of State of Titanium in high pressure

Mahmoud Jafari; Kamran Bayati; Atefeh Jahandoost; Niloofer Zarifi; Maryam Nobakhti and Hassan Jamnezhad

Physics Department, K.N.Toosi University of Technology, P.O.Box:16315-1618, Tehran, Iran

E-mail:jafari@kntu.ac.ir

Abstract. In this work first-principle calculations on hcp and bcc Ti were performed using the wien2k package which is an implementation of the full-potential augmented-plane-wave method. It has been shown in our calculations that the electronic density of states at the Fermi level increases in the phase sequence $\alpha$ (hcp) $\rightarrow$ $\beta$ (bcc) and this behavior is unambiguously reflected in all the theoretical data as well. Furthermore, the electronic density of state $N(E_F)$, the energy of electrons for d and s-band and also the Fermi energy for both phases $\alpha$ and $\beta$ were calculated. It was found that with an increase in pressure, the electrons of s-band will be transferred to d-band and the orbital of $\alpha$- phase will be more localized than $\beta$- phase.

1. Introduction

As we know, Ti in its hardness is in the range of steel and harder twice than Al, but 45 percents lighter than steel and 60 percents heavier than Al ( density of Ti is 4.5 gr/cm$^3$ ), its melting temperature is 1670 $^\circ$C which in comparison to the Fe, Ni and Al is higher. The technological interest of this metal lies on its high strength, lightness,….which makes it to be used in aeronautical industry, army equipment and so on.

Ti appears in 5 phases of P-T diagram as: $\alpha$ (hcp structure), $\gamma$ (distorted hcp), $\omega$ (hexagonal), $\delta$ (distorted bcc) and $\beta$ (bcc) [1,2,3]. Among these, we have studied the most stable phases, namely the alpha and beta phases.

It should be mentioned that $\alpha$ (hexagonal closed –packed structure) is stable at room temperature and atmospheric pressure, having 24 symmetry and 12 first neighborhood, on the other hand $\beta$ (body-centered cubic structure) is stable at high pressure having 48 symmetry and 8 first neighborhood.

In this paper we will present density functional theory (DFT) calculations of the density of states (DOS) of the alpha and beta phases of Ti, and discuss their consequences on the electrical properties.

2. Calculation

All the calculations were performed with the wien2k package, which employs a self-consistent Full-Potential Linearized Augmented Plane Wave (FLAPW)+ local orbital (lo) method, under the generalized gradient approximation (GGA) [4] with the Perdew –Burke-Emzerh of 96 exchange correlation functional.

The values of planewave cutoff $R_{k_{\text{max}}}$ obtained for $\alpha$ and $\beta$ respectively were 8 and 8.5. The largest value of the charge density in Fourier expansion is $G_{\text{max}}=12\ bhor^{-1}$ and the charge tolerance (convergence) for both phases is $1\times10^{-4}$e.

We employed a mesh of 764 and 512 k-points in the first Brillouin zone (1BZ) for the alpha and beta phases, respectively, amounting to 64 and 26 k-points in the irreducible 1BZ, respectively. The muffintin radius used for both phases was $R_{\text{MT}}=2.6$ a.u.

For our calculations we were used the space group 194-P63/mmc for $\alpha$ and 229-Im3m for $\beta$ phases which corresponds to the position of the unit cell (1/3 , 2/3 , 1/4 ), (2/3 , 1/3 , 3/4) for $\alpha$ and (0,0,0) for $\beta$ ones[5].
The lattice constants used from experimental data are \( a=3.31 \, \text{Å} \) for \( \beta \) [6], \( a=2.957 \) and \( c=4.685 \, \text{Å} \) for \( \alpha \) [7]. The cut-off energy is equal to -6.0 Ryd and mixing of charge density is 0.2.

As Ti is paramagnetic in the bulk, spin-polarization has been neglected. Therefore the effect of spin-orbit coupling was not taken into account. For this reason Ti has not been considered as a correlated system. Therefore the effect of spin-orbit is not calculated.

3. Results and Discussion

The total DOS of the alpha and beta phases are shown in Figs. 1a and 1b.

The Figures shown that Fermi energy for \( \alpha \) and \( \beta \) are 0.51304 and 0.48751 Ryd. Electronic density of state at the Fermi level from the present total DOS calculation indicate that \( N(\beta_{\text{Fermi}}) > N(\alpha_{\text{Fermi}}) \). The above results are in good agreement with previous work of Blaha [8] and Bakonyi [9].

Knowing that the conductivity is proportional to \( N(E_{\text{Fermi}}) \), so it was respected that \( N(\beta_{\text{Fermi}}) \) to be great than \( N(\alpha_{\text{Fermi}}) \). All of the results are summarized in Tab.1.

We expected that by increasing pressure or reducing volume on Ti the electrons of s-band transfer to the d-band, which express that the number of electrons of s-band for \( \alpha \) phase are more than \( \beta \) and electrons of d-band for \( \beta \) phase are more than \( \alpha \). This expectation has been confirmed in Figs. 2 and 3 on comparing s and d-band of \( \alpha \) and \( \beta \) phases. The calculation of s and d-band for these phases up to Fermi energy confirm this statement too.

On analyzing the height of the peaks in Fig. 3, the localization of the s- and d-bands of the alpha and beta phases is confirmed too (s-band at \( \alpha \) and \( \beta \) are respectively 0.314 Ryd (-0.189051 ev) and 0.326 Ryd (-0.1255 ev)). So we can state that if the peak of DOS is located on smaller energy, the orbitals will be more localized.

| phase | \( E_{\text{Tot}} \) (Ryd) | \( N(E_{\text{Fermi}}) \) \( (\text{s-band/\text{Ryd}}) \) | \( N_{\text{s}}(E_{\text{Fermi}}) \) \( (\text{s-band/\text{Ryd}}) \) | \( N_{\text{p}}(E_{\text{Fermi}}) \) \( (\text{s-band/\text{Ryd}}) \) | \( N_{\text{d}}(E_{\text{Fermi}}) \) \( (\text{s-band/\text{Ryd}}) \) | \( N_{\text{d}} \) | \( N_{\text{s}} \) |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|--------|--------|
| \( \alpha \) | -1707.635773 | 26.35 | 0.09 | 1.14 | 9.19 | 2.06844 | 0.3798 |
| \( \beta \) | -1707.502302 | 29.51 | 0.13 | 2.92 | 19.83 | 2.1266 | 0.37085 |

Our calculations are based on the density functional theory (DFT), the density of state(DOS) and band dispersion of hcp and bcc Ti were performed using the wien2k package[10].

![Fig1.a:Total DOS of α phase](image1)

![Fig1.b:Total DOS of β phase](image2)
Fig2.a: DOS of d-band of $\alpha$ phase
Fig2.b: DOS of d-band of $\beta$ phase

Fig3.a: DOS of s-band of $\alpha$ phase
Fig3.b: DOS of s-band of $\beta$ phase

References

[1] Yuichi Akahama,1 Haruki Kawamura,1 and Tristan Le Bihan :Phys.Re.L. V87.No.27(2001).
[2] A Yogesh K. Vohra and Philemon T. Spencer : Phys.Re.L. V86.No.14 (2001).
[3] J.Zhang , Y.Zhao , R.s.hilson , G.T.Gray , J. Phys.Chem. Solids 69 (2008)2559.
[4] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[5] International table for crystallography : Volume A: Space-Group Symmetry Editor Theo Hahn
First Edition 1983, Fifth Edition 2002.
[6] O.N. Senkova, B.C. Chakoumakosb, J.J. Jonasc, F.H. Froesd Materials Research Bulletin 36
(2001) v1431–1440.
[7] D. Errandonea , Y.Hang , M.Somayazulu , and D.Hauserman , Cond-mat:0401544 (2004).
[8] P. Blaha , K.Schwarz . P.H.dederichs , Phys.Rev.B 38 , 9368 (1988).
[9] I. Bakonyi, H. Ebert, A.I. Liechtenstein, Phys.Rev.B 48. 7841 (1993).
[10] P. Blaha, K.Schwarz, Wien2k, Viena University of Technology Austria (2008).