Bitlis Eren Univ J Sci & Technol
4 (1), 9-11, 2014

ISSN 2146-7706

Research Note

Calculated pressure induced electronic and structural transitions in transition metals

Hamdi Dagıstanlı

Dean Office, NCO College Command, Air Technical School Command, Izmir, Turkey
** Corresponding author: hamdi.dagistanli@gmail.com*

Abstract

The partial occupation numbers and the density of states (DOS) at the Fermi level were calculated as a function of reduced atomic volume for transition metals by employing the linear-muffin-tin-orbital (LMTO) method. The pressure induced electronic transitions from sp states to d states are confirmed for early metals; and for the heavier elements, on the otherhand, pressure induced d→p electronic transitions were found. By means of the abrupt changes obtained in the p-DOS values, good agreement with regard to experiment were found in predicting the structural phase transition volumes and it is concluded that the phase stability of transition metals under pressure is related to the characteristic shape of DOS near the Fermi level.

Keywords: Pressure, occupation numbers, structural phase transitions, transition metals

1. Introduction

The transition metals are characterized by narrow d bands overlapping with broad s-p bands and it is accepted that the electronic sp→d transfer under pressure is the driving force behind the structural phase transitions in these materials (Vohra & Spencer 2001; Verma et al. 2007). It is reasonable to expect that an increase in the effective number of d electrons with pressure should cause a given element to become more like its neighbour on the right. However, pressure induced structural transitions occur only for certain elements although the electronic transitions exist for most of the transition metals (Skriver 1985). It has already been suggested that pressure induced structural phase transitions in metals can be understood, as McMahan & Moriarty (1983); Ahuja et al. (1994), in terms of detailed features of density of states (DOS) near the Fermi level, which has not been systematically investigated, and which constitutes the main objective of the present work.

2. Material and Method

For this purpose electronic structure calculations for the transition metals, except for Mn which has a very complex structure, as Hafner & Hobbs (2003), are carried out self-consistently by means of the linear-muffin-tin-orbital (LMTO) method, like Andersen (1975), using the codes of Skriver (Skriver 1984). The calculations were performed within the Vosko-Wilk-Nusair exchange-correlation formalism, like Vosko et al. (1980), and the number of k-points used in the irreducible wedge of the Brillouin zone for hcp, fcc, and bcc structures were chosen as 1500, 1505, and 1785, respectively. Starting from the theoretical equilibrium volume V_o, I have calculated the partial occupation numbers and the partial DOS at the Fermi level as a function of the reduced atomic volume V/V_o in this work. All the quantities at the Fermi level are obtained as described in (Mutlu 1995).

3. Results and Discussion

In Figure 1, I present the variation of the number of s and p electrons with V/V_o for 3d-metals. Figure 1 confirms the sp→d electronic transitions for early 3d-metals. The Fe electronic configuration is almost independent of pressure; for Co and Ni, on the otherhand, d→p electronic transitions occur. According to Figure 1, occupation numbers are smooth functions of pressure and it is impossible to determine the V/V_o value where a structural phase transition occurs.

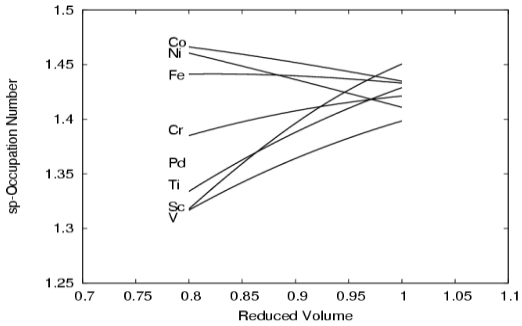

Figure 1. Occupation numbers vs reduced atomic volume V/V_o for 3d-metals.

I have found a similar behaviour in electron transfer under pressure for 4d- and 5d-metals that are presented in Figure 2 and Figure 3, respectively. Figure 2 confirms the d→p electronic transitions for the heavy 4d-metals (Ru, Rh, Pd) in contrast to the results of Cazorla et al. (2008), where almost no electron transfer was found. According to Figure 3, the electronic configuration is almost independent of pressure for Os which has the similar atomic configuration of d^6s^2 of Fe, as shown in Figure 1. It should be emphasized that pressure induced structural phase transitions in transition metals cannot be explained by the d-band filling alone as can be clearly seen from the variation of the occupation numbers of Sc, Ti, Fe, Y, Zr, and Hf with pressure, as shown in Figure 1-3.

Received 09 July 2013
Available online June 2014

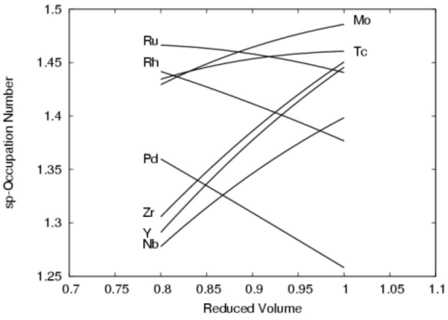

Figure 2. Occupation numbers vs reduced atomic volume V/V_o for 4d-metals.

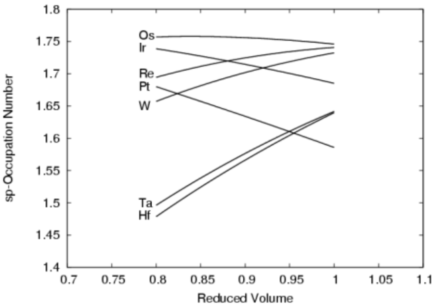

Figure 3. Occupation numbers vs reduced atomic volume V/V_o for 5d metals.

I, therefore, investigated the phase stability of the above metals under pressure by calculating the partial DOS as a function of V/V_o. In general the DOS values decrease with pressure due to the broadening of the energy bands with increasing pressure. However, the repulsion effect of the core electrons also increases with pressure, leading to the shift of the band centriods to higher energies. Therefore, the increase of pressure causes the position of the Fermi level to rise in energy with respect to the band edges and this effect determines the DOS value at the Fermi level.

I present in Figure 4 the variation of p-DOS with V/V_o for Sc and Y. The DOS values decrease from the zero pressure ($V/V_o = 1$) values with the increasing pressure, as expected. However, I have found abrupt increases at certain reduced atomic volumes for Sc and Y, as show in Figure 4.

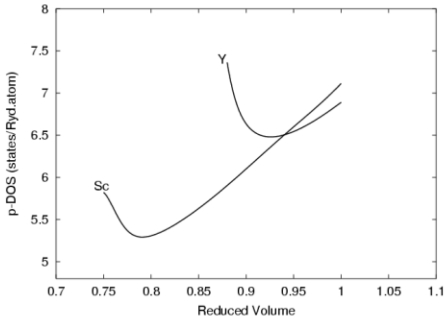

Figure 4. The p-DOS vs reduced atomic volume V/V_o for Sc and Y.

I have found similar abrupt changes in p-DOS for Zr, Hf, and Ti, as shown in Figure 5. However, no abrupt changes in the partial DOS values were found for Fe in the bcc structure; this is reasonable since the Local Density Approximation (LDA) fails in predicting the equilibrium structure of Fe as bcc (Perdew et al. 1992).

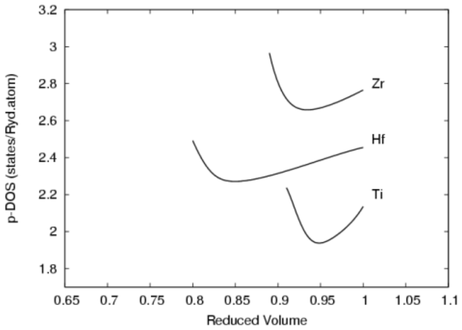

Figure 5. The p-DOS vs reduced atomic volume V/V_o for Zr, Hf and Ti.

The calculated V/V_o values, where an abrupt increase in the p-DOS value that occurred for the transition metals, are presented in Table 1. According to Table 1 the determined reduced atomic volumes are all in good agreement with the experimentally verified V/V_o values (Zhao et al. 1996; Xia et al. 1990; Melsen et al. 1993).

Table 1. Calculated V/V_o values for structural phase transitions. Experimental values are also given for comparison.

Element	V/V_o	Expt.
Sc	0.78	0.75[a]
Ti	0.94	0.98[b]
Y	0.91	0.93[c]
Zr	0.92	0.97[b]
Hf	0.84	0.78[b]

[a] (Perdew et al. 1993), [b] (Xia et al. 1990) , [c] (Melsen et al. 1993)

In summary, the results obtained in this work indicate that pressure induced structural phase transitions in transition metals cannot be explained by the d-band filling alone. Instead, the phase stability of transition metals under pressure can be attributed to substantial changes in the features of DOS near the Fermi level.

References

Ahuja R, Söderlind P, Wills JM, Johansson B, Eriksson O (1994). Electronic structure of plantinum at ultra high pressure. High Pres Res 12,161-170.

Andersen OK (1975). Linear methods in Band Theory. Phys Rev B 12, 3060-3083.

Cazorla C, Alfe D, Gillan M (2008). Zero temperature generalized phase diagram of the 4d transitions metals under pressure. Phys Rev B 77, 224103 1-11.

Hafner J, Hobbs D (2003). Understanding the complex metallic element MN I. Crystalline and noncollinear structure of α-Mn. Phys Rev B 68, 014407-014408.

McMahan AK, Moriarty JA (1983). Structural phase stability in third-period simple metals. Phys Rev B 27, 3235-3251.

Melsen J, Wills J M, Johansson B, Eriksson O (1993). Prediction of a bcc structure in compressed yttrium. Phys Rev B 48, 15574-15577.

Mutlu RH (1995). Structural phase transitions and specific heat coefficients of alkaline earth metals. J Phys Cond Mat 7, 1283-1286.

Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pederson MR, Singh DJ, Fiolhais C (1992). Atoms, molecules, solids and surfaces: Applications of the generalized gradient approximation for exchange and correlation. Phys Rev B 46, 6671-6678.

Skriver HL (1984). The LMTO Method, Springer, New York, 281 pp, ISBN: 0387115196.

Skriver HL (1985). Crystal structure from one-electron theory. Phys Rev B 31, 1909-1923.

Verma AK, Modak P, Rao RS, Godwal BK, Jeanloz R (2007). High pressure phases of titanium: First principles calculations. Phys Rev B 75, 014109 1-5.

Vohra YK, Spencer PT (2001). Novel γ-phase of Titanium metal at Megabar pressures. Phys Rev Lett 86, 3068-3071.

Vosko SH, Wilk L, Nusair M (1980). Accurate spin dependent electron of liquid correlation energies for local spin density calculations. Can J Phys 58, 1200-1211.

Xia H, Parthasarathy G, Luo H, Vohra YK, Ruoff AL (1990). Crystal structures of group IVa metals at ultra high pressures. Phys Rev B 42, 6736-6738.

Zhao YC, Porsch F, Holzapfel WB (1996). Evidence fort he occurence of a prototype structure in Sc under pressure. Phys Rev B 54, 9715-9720.