Calculated Pressure Induced BCC-FCC Phase Transitions in Alkali Metals

Hamdi DAĞISTANLI, R. Haluk MUTLU

Ankara University, Faculty of Engineering, Department of Engineering Physics,
06100 Ankara-TURKEY
e-mail: Haluk.Mutlu@eng.ankara.edu.tr

Abstract

The partial occupation numbers and density of states (DOS), and the total DOS at the Fermi level are calculated as a function of reduced atomic volume for bcc and fcc alkali metals employing the linear-muffin-tin-orbital (LMTO) method. By means of the abrupt changes obtained in the partial and total DOS values at the Fermi level, good agreement with regard to experiment were found in predicting the bcc-fcc transition volumes of the alkali metals.

Key Words: Pressure, Phase Transformations, Alkali Metals, Electronic Structure Calculations, LMTO Method.

1. Introduction

All the alkali metals crystallize in bcc structure [1] at ordinary conditions and all of them transform to fcc structure under pressure [2–6]. In the theoretical determination of the pressure-induced structural phase transitions, conventionally total-energy calculations as a function of pressure or reduced atomic volume are performed employing first-principles techniques of the density-functional formalism [7]. However, total-energy calculations have some drawbacks for the alkali metals: (1) The total-energy differences are very small [3, 8], leading to controversial results with regard to experiment even at zero pressure. For instance, equilibrium space group of Li and Na was predicted as bcc [9–11, 3], whereas K and Cs were found to be crystallize in fcc structure [12]. (2) Since all the electronic structure calculations are performed at absolute zero, no bcc-fcc transition under pressure was predicted for Li and Na from total energy calculations [13–17] where the equilibrium stable structure was correctly predicted as hcp (or fcc). The phase stability of elemental solids under pressure is related to the characteristic shape of the density of states (DOS) and d-occupancy [11] near the Fermi level, and therefore total-energy calculations, barely, do not include any information about the triggering mechanism of the bcc-fcc transition for the alkali metals.

We, therefore, intended to calculate the partial occupation numbers (NOS), partial and total DOS at the Fermi level as a function of reduced atomic volume (V/V_0) to determine and to enlighten the mechanism for the pressure-induced bcc-fcc transitions in the alkali metals.

2. Results and Discussion

For this purpose electronic band structure calculations are carried out self-consistently by means of the linear-muffin-tin-orbital (LMTO) method [18] using the codes of Skriver [19]. The calculations are performed first within the Langreth-Perdew-Mehl (LPM) exchange-correlation formalism [20], which proved to yield substantial improvement especially for the heavy alkali metals [8, 21]. Since we have concentrated on the very sensitive calculation of NOS and DOS values at the Fermi level, we have used 1505 and 1785 k-points in the irreducible wedge of the Brillouin zone for fcc and bcc structures, respectively. All the related quantities are obtained as described in [22].

In Figure 1, we present the variation of the partial NOS at the Fermi level as a function of V/V_0 for bcc Li. According to Figure 1, application of pressure leads to s-p electron transfer whereas d- NOS values are unaffected, since d-states lie well above the Fermi level for Li. However, sp-hybridization plays an important role here as a bcc-fcc transition trigger, which shows itself by an abrupt change in the p-DOS values at a certain V/V_0 value (see Figure 2). In other words for Li, the p-states perform the same function as the d-states play in heavier alkali metals. This can be readily seen from the data obtained for bcc Na (see Figure 3 and Figure 4). That is for Na, sp-d hybridization constitutes a sufficient mechanism to induce bcc-fcc transition which shows itself as a substantial change in the d-DOS values at a certain reduced atomic volume (Figure 4).
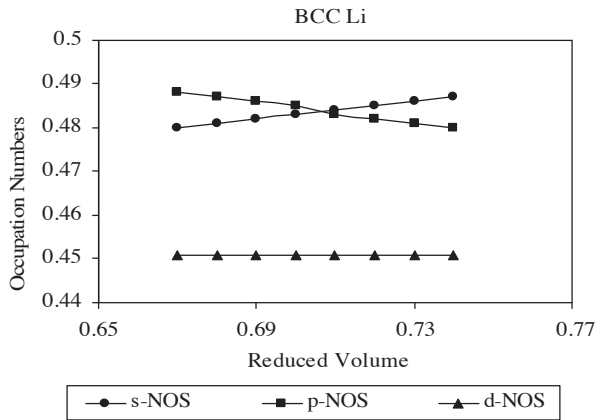

Figure 1. Calculated partial occupation numbers (NOS) at the Fermi level vs. reduced atomic volume for bcc Li, obtained within the LPM scheme.
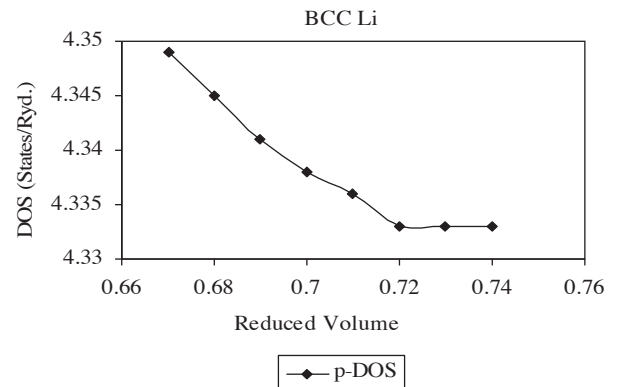

Figure 2. Calculated p-density of states (DOS) at the Fermi level vs. reduced atomic volume for bcc Li, obtained within the LPM scheme.
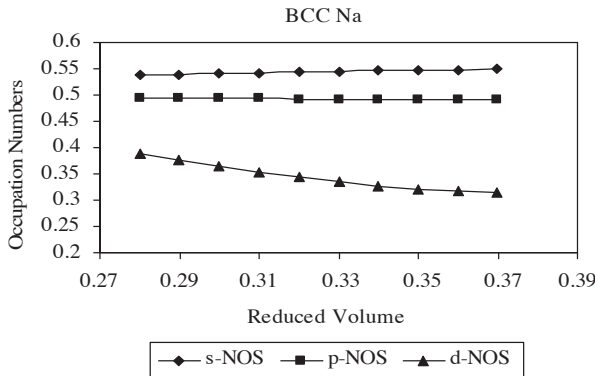

Figure 3. Calculated partial occupation numbers (NOS) at the Fermi level vs. reduced atomic volume for bcc Na, obtained within the LPM scheme.
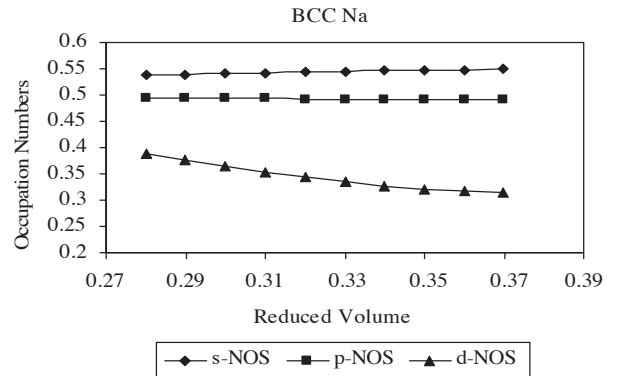

Figure 4. Calculated d-density of states (DOS) at the Fermi level vs. reduced atomic volume for bcc Na, obtained within the LPM scheme.

Starting from the fcc structure, we have repeated the NOS and DOS calculations for Li and Na, and we have found the similar behaviors; that is, substantial change in the features of p-DOS and d-DOS occurs for Li and Na at certain V/V_0 values under decompression, respectively (Figure 5a and Figure 5b). It should be emphasized that the Fermi level lies within the s-band, under the p-band edge, throughout the V/V_0 range considered for Li and Na. Therefore, due to the broadening of s-band under pressure, the total DOS at the Fermi level $g(E_F)$ decreases smoothly with pressure for bcc Li and Na (see Figure 6).
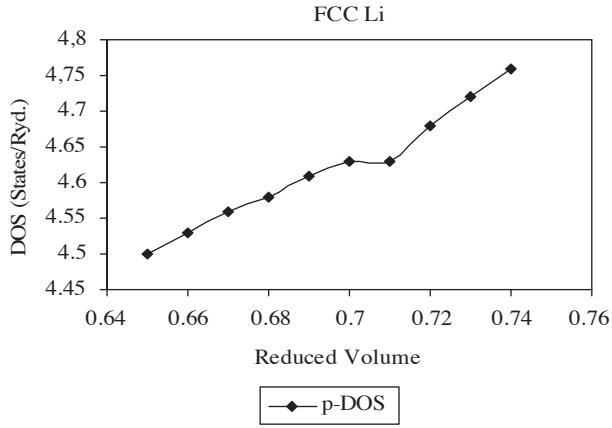

Figure 5a. Calculated p-density of states (DOS) at the Fermi level vs. reduced atomic volume for fcc Li, obtained within the LPM scheme.
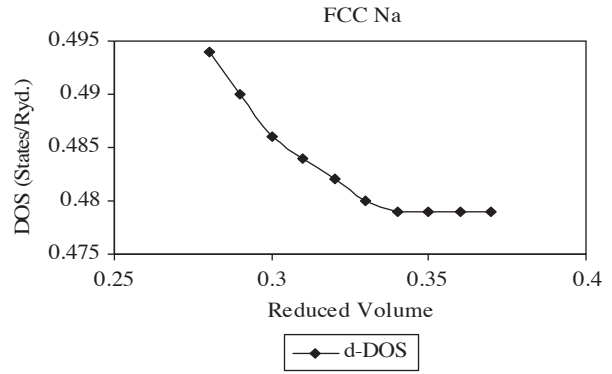
Figure 5b. Calculated d-density of states (DOS) at the Fermi level vs. reduced atomic volume for fcc Na, obtained within the LPM scheme.
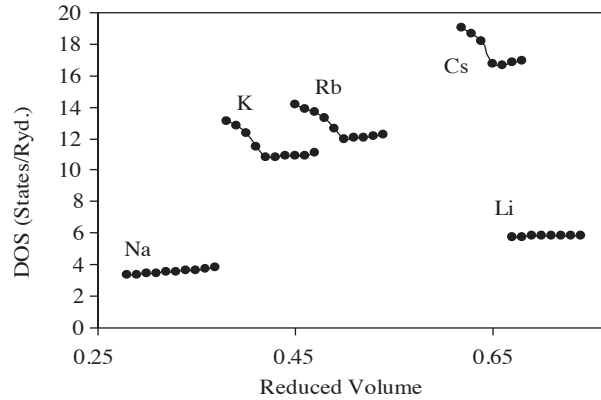

Figure 6. Calculated total density of states (DOS) at the Fermi level vs. reduced atomic volume for bcc alkali metals, obtained within the LPM scheme.

For the heavier alkali metals, on the other hand, the situation is different. The partial NOS and DOS data obtained for K, Rb and Cs did not exhibit any abrupt changes; however we have obtained, for the first time, substantial changes for $g(E_F)$ at certain V/V_0 values for the heavy alkali metals (see Figure 6). The reason of these abrupt changes shown in Figure 6 can be understood, as follows, in terms of the core repulsion. At low pressures E_F lies within the s-band below the p-band edge and $g(E_F)$ decreases with pressure due to the broadening of the bands with pressure. However, as the pressure increases, repulsion of the core electrons also increases leading to the shift of the band centers and the Fermi level to higher energies [23]. Hence, a substantial increase in the $g(E_F)$ occurs whenever the Fermi level lies within sp-band overlap.

Finally we have repeated all the calculations using five different exchange-correlation potentials [24–28] in addition to the LPM scheme, and we found similar results. In Table 1 we show V/V_0 values for the bcc-fcc

phase transitions obtained from the partial and total DOS data for the alkali metals. The excellent agreement is obtained with regard to experiment reveals that, the pressure induced structural phase transitions, at least for the alkali metals, can not be explained by the d-band filling alone; it can be attributed to substantial changes in the features of DOS at high pressure.

Table 1. Calculated reduced atomic volumes for the bcc-fcc transitions in the alkali metals obtained with different exchange-correlation potentials (ECP). Experimental values, [2–6] respectively, are also included for comparison.

ECP	Reference	Li	Na	K	Rb	Cs
LPM	20	0.72	0.32	0.42	0.49	0.66
BH	24	0.72	0.33	0.41	0.48	0.63
BHJ	25	0.72	0.32	0.41	0.48	0.63
VWN	26	0.72	0.33	0.41	0.48	0.63
WXC	27	0.71	0.33	0.41	0.48	0.63
CA	28	0.72	0.33	0.41	0.48	0.63
Expt.	2–6	0.71	0.31	0.45	0.48	0.62

References

[1] A. Taylor, B. J. Kagle, *Crystallographic data on metal and alloy structures*, (Dover, New York, 1963).

[2] B. Olinger, J. W. Shaner, *Science*, **219**, (1983), 1071.

[3] M. Hanfland, I. Loa, K. Syassen, *Phys. Rev. B*, **65**, (2002), 184109.

[4] H. Olijnyk, W. B. Holzapfel, *Phys. Lett. A*, **99**, (1983), 381.

[5] K. Takemura, K. Syassen, *Solid State Commun.*, **44**, (1982), 1161.

[6] H. T. Hall, L. Merril, J. D. Barnett, *Science*, **146**, (1964), 1297.

[7] P. Hohenberg, W. Kohn, *Phys. Rev.*, **136**, (1964), B864; W. Kohn, L. J. Sham, *Phys. Rev.*, **140**, (1965), A1133.

[8] R. H. Mutlu, *Phys. Rev. B*, **52**, (1995), 1441.

[9] H. Bross, R. Stryczek, *Phys. Status Solidi B*, **144**, (1987), 675.

[10] S. G. Louie, S. Froyen, M. L. Cohen, *Phys. Rev. B*, **26**, (1982), 1738.

[11] H. L. Skriver, *Phys. Rev. B*, **31**, (1985), 1909.

[12] M. Sigalas, N. C. Bacalis, D. A. Papaconstantopoulos, M. J. Mehl, A. C. Switendick, *Phys. Rev. B*, **42**, (1990), 11637.

[13] A. K. McMahan, J. A. Moriarty, *Phys. Rev. B*, **27**, (1983), 3235.

[14] J. C. Boettger, S. B. Trickey, *Phys. Rev. B*, **32**, (1985), 3391.

[15] J. C. Boettger, R. C. Albers, *Phys. Rev. B*, **39**, (1989), 3010.

[16] J. H. Cho, S. H. Ihm, M. H. Kang, *Phys. Rev. B*, **47**, (1983), 14020.

[17] M. I. Katsnelson, G. V. Sinko, N. A. Smirnov, A. V. Trefilov, K. Y. Khromov, *Phys. Rev. B*, **61**, (2000), 14420.

[18] O. K. Andersen, *Phys. Rev. B*, **12**, (1975), 3060.

[19] H. L. Skriver, *The LMTO method*, (Springer, New York, 1984).

[20] D. C. Langreth, J. P. Perdew, *Phys. Rev. B*, **15**, (1977), 2884; D. C. Langreth, M. J. Mehl, *Phys. Rev. B*, **28**, (1983), 1809.

[21] M. Peder, R. H. Mutlu, N. Tugluoglu, *Phys. Rev. B*, **55**, (1997), 9200.

[22] R. H. Mutlu, *J. Phys. Condens. Matter*, **7**, (1995), 1283.

[23] H. G. Drickamer, C. W. Frank, *Electronic transitions and the high pressure chemistry and physics*, (Chapman-Hall, London, 1973).

[24] U. von Barth, L. Hedin, *J. Phys. C*, **5**, (1972), 1629.

[25] J. F. Janak, V. L. Moruzzi, A. R. Williams, *Phys. Rev. B*, **12**, (1975), 1257.

[26] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.*, **58**, (1980), 1200.

[27] E. Wigner, *Phys. Rev.*, **46**, (1934), 1002.

[28] D. M. Ceperley, B. J. Alder, *Phys. Rev. Lett.*, **45**, (1980), 556.