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Research Article

Calculated pressure induced fcc-hcp phase transition in aluminum

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Abstract

The linear-muffin-tin-orbital method within the local density approximation is used to calculate the total-energies, partial occupation numbers and density of states for aluminum as a function of reduced atomic volume. It is concluded that p→d electron transfer constitutes the driving force for the fcc→hcp transition in Al.

Keywords: Aluminum, electronic structure, fcc-hcp transition, pressure

1. Introduction

The simple metal Al crystallizes in fcc structure at ordinary conditions and it transforms to hcp structure at the reduced volume of $V/V_o = 0.51$ corresponding to the pressure of 217±10 GPa (Akahama et al. 2006). In the theoretical determination of the pressure induced fcc→hcp transition in Al, conventionally total-energy calculations as a function of pressure or reduced volume are performed (Moriarty & McMahan 1982; Lam & Cohen 1983; Boettger & Trickey 1995; Sin'ko & Smirnov 2002; Fanourgakis et al. 2003; Jona & Marcus 2006; Tambe et al. 2008). However, different electronic structure calculation techniques and exchange-correlation formalisms predict considerably different relative volumes and pressures for the fcc→hcp transition in aluminum (Table 1).

Table 1. Calculated relative volumes (V/V_o) and pressures (P) for the fcc→hcp transition in Al

V/V_o	P(Gpa)	Ref.
0.58	130	Moriarty & McMahan (1982)
0.54	240	Lam & Cohen (1983)
0.52	205	Boettger & Trickey (1995)
170		Sin'ko & Smirnov (2002)
0.55	167	Fanourgakis et al. (2003)
192		Jona & Marcus (2006)
175		Tambe et al. (2008)

Furthermore, total-energy calculations barely do not include sufficient information about the triggering mechanism of the pressure induced structural phase transitions in Al, as Moriarty & McMahan (1982), Lam & Cohen (1983), Boettger & Trickey (1995), Sin'ko & Smirnov (2002), Fanourgakis et al. (2003), Jona & Marcus (2006), Tambe et al. (2008), which constitutes the main objective of the present work.

2. Material and Methods

For this purpose, electronic structure calculations for Al are carried out selfconsistently by means of the linear-muffin-tin-orbital (LMTO) method, as Skriver (1984), within the Vosko-Wilk-Nusair exchange-correlation formalism (Vosko et al. 1980). The self-consistency is achieved in such a way that the total-energy values between the consecutive iterations were about ± 0.01 mRy.

We first calculated the total-energies corresponding to the fcc and hcp structures as a function of reduced volume V/V_o, where V_o is the theoretical equilibrium volume for fcc Al. As an emphasized, as Tambe et al. (2008); Tugluoglu & Mutlu (1996), earlier Brillouin zone scan sensitivity is important in the total-energy calculations. Therefore, total-energies corresponding to various number of k points in the irreducible Brillouin zone (IBZ) were calculated and the total-energies for fcc and hcp structures corresponding to infinite number of k points in the IBZ were obtained as described in (Tugluoglu et al. 1999). It should be emphasized that c/a ratio is kept fixed at the experimental value of 1.618 throughout the calculations for the hcp structure since it is independent of pressure (Akahama et al. 2006). The fcc – hcp total-energy differences as a function of V/V_o are presented in Table 2. According to Table 2, the fcc – hcp total-energy difference decreases with pressure and becomes almost zero at $V/V_o = 0.58$; fcc→hcp transition occurs at $V/V_o = 0.57$ which is relatively 12% larger than the experimental value of 0.51. It should be emphasized that the total-energy calculations do not provide any information about the presence of a possible hysteresis for the structural phase transition in Al.

Table 2. Calculated fcc – hcp total-energy differences ΔE as a function of reduced volume V/V_o for Al

V/V_o	ΔE(mRy.)
0.60	– 0.37
0.59	– 0.17
0.58	– 0.01
0.57	0.30
0.56	0.56
0.55	0.85

We, therefore, calculated the partial occupation numbers and the partial density of states (DOS) at the Fermi level as a function of relative volume for fcc and hcp Al. For these calculations, the number of k points used in the IBZ were chosen as 1505 and 1400 for fcc and hcp structure, respectively. The above quantities were obtained as described in (Mutlu 1995).

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The variation of the 3s and 3d occupation numbers with reduced volume for fcc Al is presented in Figure 1 which confirms the s→d electronic transition under pressure.

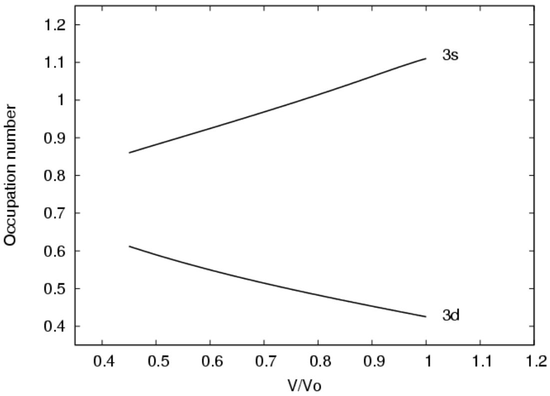

Figure 1. Calculated 3s and 3d occupation numbers vs reduced volume for fcc Al.

However, we note that 3s occupation number decreases almost linearly with V/V_o whereas 3d occupation number nonlinearly increases, indicating that s→d electronic transition is accompanied by the s→p electron transfer under pressure. Figure 2 confirms the s→p electronic transition under pressure. However, starting from zero pressure ($V/V_o = 1.0$), the number of electrons transferred from s-states to p-states with pressure decreases up to $V/V_o = 0.53$ (Figure 2).

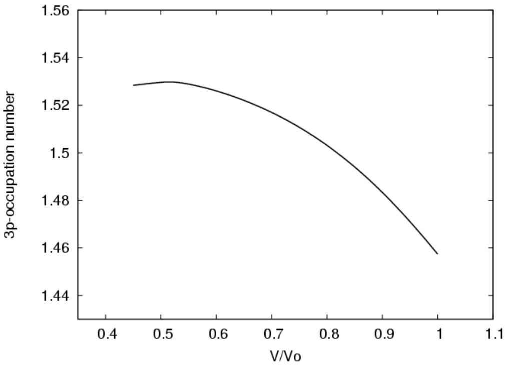

Figure 2. Calculated 3p occupation number vs reduced volume for fcc Al.

The 3p occupation number of fcc Al remains almost constant in the range of $V/V_o = 0.53$-0.51 and starting from the relative volume of 0.51, it decreases. According to Figure 2 and as Moriarty & McMahan (1982) emphasized earlier, the downward movement of the bottom of the 3d band begins at $V/V_o = 0.51$, initializing the p→d electron transfer which triggers the fcc→hcp phase transition in excellent agreement with experiment (Akahama et al. 2006). In other words, p→d electron transfer appears to be responsible for the pressure induced fcc→hcp transition in Al. In order to verify this mechanism, 3p occupation number of hcp Al is calculated under decompression and the result is presented in Figure 3. According to Figure 3, the 3p occupation number increases in the range of $V/V_o = 0.45$-0.51, it remains almost constant up $V/V_o = 0.55$ and then it decreases under decompression. These results (Figure 2 and Figure 3) suggest that the fcc→hcp transition in Al starts at $V/V_o = 0.51$ under compression and hcp→fcc transition starts at $V/V_o = 0.55$ under decompression, indicating the presence of a kind of hysteresis for the structural phase transition in Al that cannot be predicted by the total-energy calculations. It should be noted that the Fermi level lies within the p-band over the s-band upper edge throughout the calculations and therefore, due to the broadening of the p-band under pressure, all the partial DOS values decrease smoothly with pressure for fcc Al.

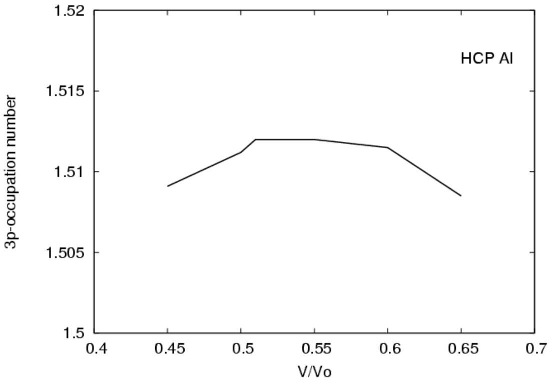

Figure 3. Calculated 3p occupation number vs reduced volume for hcp Al.

Finally, we have repeated all the calculations removing completely the 3d band for Al. In the absence of d-states, only s→p electronic transition occurs and therefore it is impossible to obtain the 3p electronic behaviour as in Figure 2 or Figure 3. The total-energy calculations also confirms that without d electrons Al would remain in the fcc structure under pressure, as Moriarty & McMahan (1982), emphasizing the phase stability of Al under pressure is related to the d-occupancy at the Fermi level. However, it has been suggested that the structural stability at high pressures cannot be explained by the d-band filling alone; instead it can be attributed to a substantial change in the features of DOS at high pressure (Ahuja et. al. 1982).

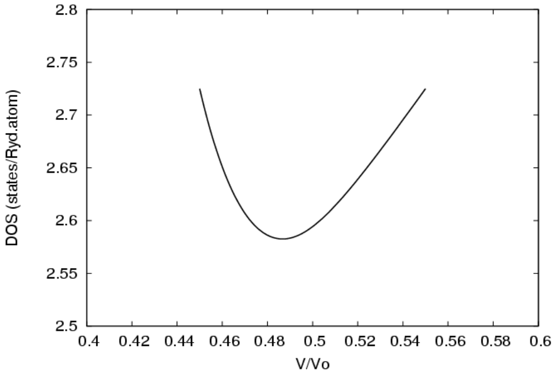

Figure 4. Calculated total density of states (DOS) in the absence of d-states vs reduced volume for fcc Al.

We have found such an abrupt change for the total DOS at $V/V_o = 0.47$ for fcc Al (Figure 4) in the absence of d-states, that can be attributed to the presence of the hcp phase or a different crystal structure and should be investigated which is beyond the scope of the present work.

3. Results

In summary, the pressure induced structural phase transition in Al is investigated employing the LMTO method. It is concluded that p→d electron transfers rather than the s→d electronic transition constitutes the driving force for the fcc→hcp transition in aluminum under pressure.

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