Gradient-corrected density functional calculation of structural and magnetic properties of BCC, FCC and HCP Cr

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Abstract

To understand the stability of artificial ultrathin FCC and HCP Cr films, we have performed total energy calculations based on spin-density functional theory with generalized gradient corrections for Cr in BCC, FCC and HCP structures. The calculated lattice and elastic constants of BCC Cr are in reasonable agreement with experiments. The calculated lattice constants of FCC and HCP Cr are close to the reported FCC and HCP thin film lattice constants, respectively. The calculated elastic constants suggest that both FCC and HCP Cr are elastically unstable. No ferromagnetic state is found for all the three structures. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Density functional calculation; Elastic constants

The recent advent of advanced thin film growth techniques has stimulated enormous interest in making artificial crystalline structures that do not exist in nature [1–3]. These artificial systems would allow one to better understand the growth mechanism and structural phase transition and to explore novel physical properties distinct from that of the natural crystals. Well-known artificial structures include FCC Fe on Cu [1], BCC Co on GaAs [2] and BCC Ni on Fe [3]. Under ambient conditions, Cr crystalizes in a BCC structure. Recently, experimental evidence for the formation of ultrathin HCP Cr films in epitaxial Co/Cr multilayers has been reported [4,5]. Stimulated by this interesting finding, we have performed first-principles density functional total energy calculations for Cr in BCC, FCC and HCP structures in both ferromagnetic and nonmagnetic states. Furthermore, it was suggested in early 1970s [6] that thin Cr films grown on Au (1 1 1) by vapor deposition have a FCC structure. The purpose of this work is primarily to determine theoretically the lattice constants of FCC and HCP Cr and also to study the stability of these structures.

We have used the highly accurate all-electron full-potential linear augmented plane wave (FLAPW) method [7]. The standard local density approximation to the electron exchange-correlation potential was used together with the latest generalized gradient corrections of Perdew–Burke–Ernzerhof [8]. The muffin-tin radius used is 2.2 a.u. The number of the augmented plane waves (PW) included is about 70/atom. More details about the computational method have been given in Ref. [7]. The calculated total energy as a function of atomic volume for BCC, FCC and HCP structures is displayed in Fig. 1. For the total energies of the HCP structure in Fig. 1, the theoretical c/a ratio of 1.78 has been used. The c/a ratio was determined as follows. It was initially fixed at the ideal value of 1.63 while the total energy was calculated for different volumes. The volume was then fixed at the minimal energy one while the total energy was calculated for different c/a ratios. This procedure was repeated till we found a converged c/a (within 1%).

Fig. 1 shows that BCC Cr has the lowest total energy, as expected, while HCP Cr has the highest one. The calculated lattice constant (a), bulk modulus (B), tetragonal and trigonal shear constants ($C' = (C_{11} - C_{12})/2$ and C_{44}) of BCC Cr are respectively, 2.85 Å, 2.83, 1.69 and 1.27 Mbar, in reasonable agreement with their corresponding experimental values (2.88 Å, 1.91, 1.51 and 1.03 Mbar) at 77 K [9]. In particular, the theoretical a is smaller than the experimental value by about 1%. The discrepancy between theoretical and experimental bulk moduli may be attributed to the fact that the

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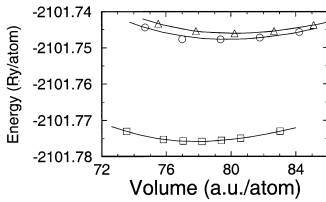
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Fig. 1. Total energy of Cr as a function of atomic volume for BCC (squares), FCC (circles) and HCP (triangles). The curves are a polynomial fit to the total energies.
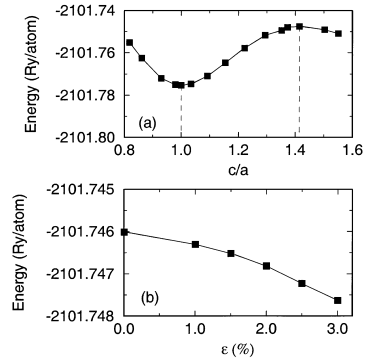

Fig. 2. (a) Total energy of deformed FCC Cr as a function of c/a. The volume is fixed at the fcc minimal energy volume. (b) Total energy of deformed HCP Cr as a function of the monoclinic strain (ε) (see text).

measurements were made on the antiferromagnetic BCC Cr [9]. The lattice constant (a) of FCC and HCP Cr determined from the total energy–volume curves in Fig. 1 is 3.62 and 2.49 Å, respectively. Note that the theoretical lattice constant of FCC Cr is close to that of thin Cr films on Au (1 1 1) grown by vapor deposition [6]. The Cr films on Au (1 1 1) were suggested to have a FCC structure [6]. We further calculated the elastic constants of FCC Cr and found that C' and C_{44} are negative (-1.41 and -0.76 Mbar). Thus, FCC Cr is elastically unstable. The total energy of body-centered tetragonal Cr as a function of c/a is displayed in Fig. 2a. Clearly, BCC structure ($c/a = 1$) is located at the energy minimum while FCC structure ($c/a = \sqrt{2}$) sits on the energy maximum. This perhaps explains why there has been no report on epitaxial FCC Cr thin films. We believe that in Ref. [6], Cr atoms diffused into Au substrate, forming thin FCC Cr–Au alloy films on Au (1 1 1), and the FCC LEED patterns were due to the formation of the FCC Cr–Au alloys. Further experiments are necessary to clarify this issue.

Interestingly, the calculated HCP Cr lattice constant differs from that of HCP Co (2.51 Å) [4] only by 1%. This appears to be one of the reasons why an ultrathin HCP Cr film was grown in epitaxial Cr/Co multilayers. We also calculated the elastic constants of this structure. The theoretical bulk modulus B, elastic constants C_{33}, $(C_{11} + C_{12})$ and $(C_{11} - C_{12})$ are, respectively, 1.28, 4.33, 6.72 and -2.33 Mbar. Note that $C_{11} - C_{12}$ is negative, indicating HCP Cr is elastically unstable. The shear constant $(C_{11} - C_{12})$ was calculated by introducing a monoclinic distortion with the strain matrix

$$\begin{pmatrix} 1 + \varepsilon & 0 & 0 \\ 0 & 1 - \varepsilon & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{1}$$

This distortion increases the x-axis and decreases the y-axis. Fig. 2b shows the calculated total energy as a function of strain ε. Since the total energy is symmetric with respect to ε, the negative ε values are not shown. Clearly, $\varepsilon = 0$ corresponds to the total energy maximum. The total energy decreases monotonically as

ε increases. Therefore, HCP Cr is unstable against this shear deformation. The reported ultrathin (up to 3 monolayers) HCP Cr films in epitaxial Cr/Co multilayers could be stabilized by Cr/Co interface energy. However, because of the large energy difference (0.4 eV/atom) between HCP and BCC Cr structures (see Fig. 1), a thin FCC Cr film would transform into the stable BCC structure as film thickness increases beyond, say, three monolayers. We plan to calculate HCP Cr/Co interface energy in the near future in order to quantify this plausible explanation.

Finally, we have performed spin-polarized self-consistent calculations of all the three structures of Cr. However, no ferromagnetic state was found, thereby predicting that the artificial FCC and HCP Cr would not be a ferromagnet.

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