Calculated elastic constants and electronic and magnetic properties of bcc, fcc, and hcp Cr crystals and thin films

G. Y. Guo^{1,2,*} and H. H. Wang¹

¹*Department of Physics, National Taiwan University, Taipei 106, Taiwan*

²*Synchrotron Radiation Research Center, Science-based Industrial Park, Hsinchu 300, Taiwan*

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In order to understand the phase stability and physical properties of artificial close-packed Cr films, we have performed electronic structure and total-energy calculations for Cr in bcc, fcc, and hcp structures based density functional theory with local-density approximation plus generalized gradient corrections. The calculated lattice and elastic constants of the antiferromagnetic bcc Cr are in good agreement with experiments. The lattice constants of fcc and hcp Cr determined from the total-energy-volume curves are close to that of the reported close-packed Cr thin films. However, the calculated elastic constants show that fcc Cr is unstable against any shear deformation while hcp Cr would be unstable against only symmetry-breaking lattice distortions. Based on these findings, it is argued that the recently observed ultrathin close-packed Cr films on hcp Co form a hcp structure, and that the thin Cr films deposited on Au (Ir) (111) reported in the early 1970's are unlikely to have a fcc structure. Comparison of the calculated and experimental x-ray absorption spectra also indicates the formation of a hcp Cr phase for close-packed Cr thin films on hcp Co. Though the density-of-states at the Fermi level of fcc and hcp Cr is large, no ferromagnetic state is found for these structures. No simple commensurate antiferromagnetic state is found for the fcc and hcp Cr either. The results of the same calculations performed for the (111) fcc Cr₃/hcp Co₆, hcp Cr₃/hcp Co₇, fcc (hcp) Cr₃/fcc Cu₆ (111) multilayers are also reported in order to see the effects of the interfaces.

I. INTRODUCTION

The advent of modern thin-film growth techniques has stimulated enormous interest in fabricating artificial crystal-line structures that do not exist in nature in recent years (see, e.g., Refs. 1–3 and references therein). These artificial systems would allow one to better understand the growth mechanisms and structural phase stabilities and also to explore 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

Cr crystalizes in a bcc structure under ambient conditions. Recently, experimental evidence for the formation of ultrathin close-packed fcc or hcp Cr films in epitaxial Co/Cr multilayers has been reported.^{4,5} In fact, it was already suggested in early 1970's (Ref. 6) that thin Cr films grown on Au and Ir (111) by vapor deposition have a fcc structure. Furthermore, these thin Cr films were reported to be a superconductor.⁷

These interesting observations or claims have already motivated several theoretical studies of the various phases of Cr. The band structure of fcc Cr was calculated by Xu *et al.*⁸ The density-functional total energy of Cr was calculated by Paxton, *et al.*,⁹ for several structures including bcc, fcc, and hcp phases. There is a minimum in the total energy vs volume curve for all the structures considered.⁹ However, this does not necessarily mean that fcc or hcp Cr is a metastable structure because they could be elastically unstable. Therefore, to gain insight into the phase stability of the artificial close-packed Cr thin films, one needs to know the elastic constants of these structures.

In this paper, we have performed systematic first-

principles density-functional calculations of total energies, elastic constants, and electronic structures for bcc, fcc and hcp Cr in both ferromagnetic and antiferromagnetic as well as nonmagnetic states. One of the principal purposes of the present paper is to investigate the stability of the suggested fcc and hcp structures of Cr. Another purpose of this paper is to find the possible electronic origins of the reported properties such as the superconductivity and magnetism as well as the relative phase stability of various Cr structures. It is well known that density-functional theory (DFT) with the standard local density approximation (LDA) does not accurately describe the properties of 3d transition metals.^{10–12} In particular, DFT-LDA gives a wrong ground state for Fe.^{10,12} Nevertheless, these errors can largely be removed by including so-called generalized gradient corrections (GGA)(see, e.g., Refs. 13–15 and references therein). Therefore, unlike in previous calculations, we have included GGA (Ref. 15) in all the present calculations. Indeed, as will be shown below, our calculated lattice and elastic constants of the antiferromagnetic bcc Cr are in good agreement with experiments, a marked improvement over the previous DFT-LDA calculations.¹¹

The organization of the rest of this paper is as follows. In the next section, we describe briefly the relevant elastic theory and the determination of the elastic constants of cubic and hexagonal systems via first-principles total-energy calculations. Also the computational details will be given. In Sec. III, we present the calculated total energy vs volume and the elastic constants for various Cr structures. In Sec. IV, we report the calculated band structure and the corresponding density-of-states for various Cr structures. In Sec. V, we will discuss the phase stability of fcc and hcp Cr films using the calculated elastic constants, and superconductivity and mag-

netism in terms of the calculated electronic structures. In Sec. VI, we present the calculated total energies and magnetic moments in the (111) fcc Cr₃/hcp Co₆, hcp Cr₃/hcp Co₇, and fcc (hcp) Cr₃/fcc Cu₆ (111) multilayers and discuss the effects of the Cr-Co and Cr-Cu interfaces. Finally, a short summary will be given in Sec. VII.

II. THEORY AND COMPUTATIONAL DETAILS

For small strains (ϵ) on a solid, the Hook's law is applicable and the elastic energy E_e is a quadratic function of the strains

$$E_e(V, \epsilon) = V \sum_{i,j=1}^6 \frac{1}{2} C_{ij} e_i e_j, \quad (1)$$

where C_{ij} are the elastic constants, V is the total volume, and e_i are the strain components

$$\epsilon = \begin{pmatrix} e_1 & e_6 & e_5 \\ e_6 & e_2 & e_4 \\ e_5 & e_4 & e_3 \end{pmatrix} \quad (2)$$

in conventional elastic theory notation.¹⁶ Under these strains, the original lattice vectors $\mathbf{a}$ would be transformed into the strained ones $\mathbf{a}'$ as $\mathbf{a}' = (I + \epsilon)\mathbf{a}$ where I is the identity matrix.

For a cubic crystal, there are only three independent elastic constants, namely, C_{11} , C_{12} and C_{44} . Furthermore, the bulk modulus B and tetragonal shear constant C' are related to C_{11} and C_{12} , i.e., $B = \frac{1}{3}(C_{11} + 2C_{12})$, and $C' = \frac{1}{2}(C_{11} - C_{12})$. C_{44} is the trigonal shear constant. $B = Vd^2E/dV^2$ is determined by a polynomial fitting of the calculated total energy E as a function of volume V . C' (C_{44}) is determined by a polynomial fitting of the calculated total energy E as a function of the tetragonal (trigonal) strain

$$\epsilon = \begin{pmatrix} \epsilon & 0 & 0 \\ 0 & \epsilon & 0 \\ 0 & 0 & -\epsilon(2 + \epsilon)/(1 + \epsilon)^2 \end{pmatrix} \times \left(\begin{pmatrix} 0 & \epsilon & 0 \\ \epsilon & 0 & 0 \\ 0 & 0 & \epsilon^2/1 + \epsilon^2 \end{pmatrix} \right). \quad (3)$$

For a hexagonal solid, there are five independent elastic constants, namely, C_{11} , C_{12} , C_{13} , C_{33} , and C_{55} . Total-energy calculation of the elastic constants of a hcp solid is rather involved. Indeed, the elastic constants of only a few elemental hcp metals have been calculated.¹⁷ The five elastic constants of a hcp solid are related to the bulk modulus (B) and four shear constants ($C_{11} + C_{12}$, $C_{11} - C_{12}$, $\frac{1}{2}C_{33}$, and $2C_{55}$).¹⁷ Here, we determine these shear constants (hence the elastic constants) by a polynomial fitting of the calculated total energy as a function of the shear strains, as described in Ref. 17.

We have used the highly accurate all-electron full-potential linearized augmented plane wave method¹⁸ to calculate the total energies and electronic structures of various Cr structures. The calculations are based on the first-

principles density-functional theory with the standard LDA to the exchange-correlation potential.¹⁹ The latest GGA of Perdew-Burke-Ernzerhof¹⁴ have been included in all the calculations. The muffin-tin radius used is 2.2 a.u. Cr $1s$, $2s$, and $2p$ are treated as core states, $3d$, $4s$, and $4p$ as band states, and the semicore states ($3s$ and $3p$) are also treated as band states by using the so-called local orbitals.¹⁸ Inside the muffin-tin spheres, the wave functions, charge densities, and potential are expanded in terms of the spherical harmonics. The cut-off angular momentum (L_{max}) is 10 for the wave functions and 6 for charge densities (potentials). The Brillouin-zone integration is carried out by using the improved tetrahedron method.²⁰ The number of the augmented plane waves included is about 70 per atom, i.e., $R_{mt}K_{max} = 8$.¹⁸ The numbers of the k points in the irreducible Brillouin-zone wedge (IBZW) for nonmagnetic and ferromagnetic bcc, fcc and hcp are, respectively, 104, 72, and 120. The numbers of the k points in the IBZW for antiferromagnetic bcc, fcc, and hcp are, respectively, 120, 280, and 320. The self-consistent cycles are terminated when the total energy converges to within 0.00001 Ry/atom. In the shear constant calculations, the crystal is elastic deformed and may have a lower symmetry. Furthermore, the total-energy change due to a shear strain is often very small (see Fig. 3 below). Thus more k points in the IBZW are used and the self-consistent cycles are terminated when the total energy converges to within 0.002 mRy/atom. For example, when calculating hcp C_{55} , we used about 900 k points. More details about the computational method have been given in Ref. 18.

To see the effects of the interfaces, we also performed the spin-polarized total-energy calculations for the fcc Cr₃/hcp Co₆, hcp Cr₃/hcp Co₇, and fcc Cr₃ (hcp Cr₃)/fcc Cu (111) superlattices. A larger number of the augmented plane waves (over 90 per atom) (i.e., $R_{mt}K_{max} = 9$) were used. The numbers of the k points in the IBZW are 74, 80, and 66, respectively. To estimate the interface formation energy, we also carried out the same calculations for bulk hcp Co, fcc, Cu, fcc and hcp Cr with the same parameters. The in-plane lattice constants were set to the theoretical lattice constant of hcp Co and fcc Cu, respectively. For the fcc Cr₃/hcp Co₆ and hcp Cr₃/hcp Co₇ superlattices, the total-energy calculations were performed for several Cr layer separations with the structural parameters for the Co slabs being fixed.

III. TOTAL ENERGY AND ELASTIC CONSTANTS

The calculated total energy as a function of volume per atom for bcc, fcc, and hcp Cr 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 the change in the c/a ratio to be within 1%. Fig. 1 shows that for the nonmagnetic phases, bcc Cr has the lowest total energy, as expected, while hcp Cr has the highest one, and the energy difference between the two is rather large, being 0.405 eV/atom. The minimal total energy of fcc Cr is slightly lower than that of

FIG. 2. Total energy (relative to that of fcc Cr) of deformed fcc Cr as a function of c/a . The volume is fixed at the fcc minimal energy volume.

spin moments of other 3d magnets, namely, Fe, Co, and Ni.¹⁵ Figure 1(b) shows that the moment depends significantly on the volume (lattice constant). A reduction of the lattice constant by 2.6% would bring the theoretical value in good agreement with the experiments.

The lattice constant (a) of fcc Cr determined from the total-energy-volume curves (Fig. 1) is 3.62 Å. Cr was reported to occur as a fcc phase at high temperatures above 2110 K and below its melting temperature of 2180 K.²³ The lattice constant of the high temperature is 3.68 Å, being 1.7% larger than the calculated low-temperature lattice constant. We further calculated the elastic constants of fcc Cr (Table I) and found that C' and C_{44} are negative (-1.41 and -0.76 Mbar, respectively). Thus, fcc Cr is predicted to be elastically unstable. The total energy of the body-centered tetragonal Cr as a function of c/a is displayed in Fig. 2. Clearly, the bcc structure ($c/a = 1$) is located at the energy minimum while the fcc structure ($c/a = \sqrt{2}$) sits on the energy maximum. However, the high-temperature elastic constants should be determined by the free energy rather than by the total energy. Free-energy calculation of high temperature elastic constants is beyond the scope of this paper. Nevertheless, the reported existence of the fcc Cr structure suggests that the shear constants C' and C_{44} would change sign at certain high temperatures and as a result, the fcc phase would become a metastable phase above these temperatures.

The lattice constant (a) of hcp Cr determined from the total-energy-volume curves (Fig. 1) is 2.49 Å. We also calculated the five elastic constants of hcp Cr (Table I). In Fig. 3, we plotted the calculated total-energy change as a function of various shear strains. We determined the corresponding shear constants by polynomial fitting of these curves. The theoretical shear constants $(C_{11} + C_{12})$, $(C_{11} - C_{12})$, $\frac{1}{2}C_{33}$, and $2C_{55}$ are, respectively, 6.72, -2.33 , 4.33, and -0.92 Mbar. Note that $(C_{11} - C_{12})$ and C_{55} are negative, indicating that hcp Cr is also elastically unstable. From these shear constants together with the bulk modulus $B = \frac{2}{9}(C_{11} + C_{12} + 2C_{13} + C_{33}/2)$, we have determined all the five elastic constants of hcp Cr (Table I).

IV. BAND STRUCTURE AND DENSITY-OF-STATES

The calculated energy bands along the usual high-symmetry lines in the Brillouin zone of nonmagnetic bcc, fcc, and hcp Cr are shown in Fig. 4. The band structure of the bcc structure [Fig. 4(a)] is almost identical to that obtained in a previous calculation.²⁴ The band structure of the

FIG. 3. Total-energy change of deformed hcp Cr as a function of the various strain size (ϵ) (see text). The lines are a guide to the eye only.

fcc structure is almost the same as that reported by Xu *et al.*,⁸ except that the Fermi level (E_F) in Fig. 4 is slightly higher relative to the t_{2g} bands at the Γ point. No band structure of hcp Cr has been reported before. Nonetheless, the calculated hcp band structure is similar to that of hcp Ti (Ref. 24) except that, of course, the E_F is higher because of the larger number of valence electrons in Cr.

The calculated density-of-states (DOS) of bcc, fcc, and

FIG. 4. Band structures of bcc, fcc, and hcp Cr. The energies are relative to the Fermi level.

FIG. 5. Density-of-states (DOS) of bcc, fcc, and hcp Cr. The energies are relative to the Fermi level.

hcp Cr as a function of energy is plotted in Fig. 5. The DOS at the E_F for bcc, fcc, and hcp Cr are, respectively, 0.59, 2.03, and 2.38 states eV atom. The DOS(E_F) for the antiferromagnetic bcc Cr is 0.57 states eV atom. Thus, the DOS at E_F of both the close-packed structures are much larger than that of the bcc structure. Clearly, the DOS spectra of the two close-packed structures (fcc, hcp) are similar while they differ significantly from that of the bcc structure. There is a pronounced pseudogap between the d - d bonding-antibonding bands [Fig. 5(a)] in the bcc structure, which is absent in the fcc and hcp structures. The E_F is located near the bottom of the pseudogap and thus, the DOS at the E_F is low. As a result, the bcc Cr is rather stable. In contrast, there is no clear pseudogap in the DOS spectra for the fcc and hcp structures [see Figs. 5(b) and 5(c)]. The DOS at the E_F for the both structures are very high. This explains why the fcc and hcp Cr structures are unstable.

V. DISCUSSION

In early reports,⁶ thin Cr films grown on Au (Ir) (111) were suggested to have a fcc structure with a lattice constant of 3.70 Å at room temperature. This suggestion was motivated by the earlier report on the existence of the fcc Cr phase above 2110 K. Interestingly, these lattice constants are close to the theoretical lattice constant of fcc Cr determined from the total-energy-volume curves in Fig. 1 (3.62 Å, Table I). However, we further calculated and found the shear elastic constants C' and C_{44} of fcc Cr are negative (−2.82 and −0.76 Mbar). Thus, fcc Cr would be elastically unstable. In particular, fcc Cr would be rather unstable against a tetragonal (001) shear deformation since the value of C' is large. The fcc Cr would also be unstable against orthorhombic (110) and trigonal (111) shear deformations since its C_{44} is negative. In short, fcc Cr would be unstable against any shear deformation. Consider that Cr grew coherently on Au (Ir) (111). Because the lattice constant of fcc Au (Ir) is 4.08 (3.84) Å, there would be an in-plane strain of about 9 (6)%.

However, fcc Cr films would be unstable against this trigonal lattice distortion. This could explain why there has been no further report on epitaxial fcc Cr thin films on Au (Ir) (111). It is believed that in Ref. 6, Cr atoms could diffuse into Au substrate, forming thin fcc Cr-Au alloy films on Au (111). Alternatively, the suggested fcc Cr thin films were in fact a hcp Cr phase, as will be argued below. The hexagonal low-energy electron diffraction (LEED) patterns observed were then due to either the formation of these fcc CrAu(Ir) alloys or the existence of the hcp Cr phase. Further experiments on Cr thin films on Au (Ir) (111) using modern techniques are necessary to clarify this interesting issue. It could also be worthwhile to try to grow close-packed Cr films on Cu (111) because fcc Cu has a lattice constant of 3.61 Å (Ref. 16) (but see Sec. VI).

Recently, thin close-packed Cr films have been grown on hcp Co.^{4,5} Furthermore, the latest x-ray absorption experiments suggested the formation of a hcp structure.⁵ Interestingly, the calculated hcp Cr lattice constant (2.49 Å) differs from that of hcp Co (2.51 Å) (Ref. 4) only by 1%. The calculated lattice constant of (111) layers of fcc Cr is 2.56 Å, being also close to that of hcp Co. As mentioned earlier, however, fcc Cr is unstable against any shear deformation including (111) in-plane and interlayer strains. On the other hand, not all the calculated shear constants of hcp Cr are negative though hcp Cr is also elastically unstable. Two shear constants [$(C_{11}-C_{12})$, C_{55}] out of four of hcp Cr are negative [−2.33, −0.92 Mbar] (see Fig. 3 and Table I). Importantly, however, the shear constants $(C_{11}+C_{12})$ and C_{33} are positive, and they correspond to the uniform in-plane strain and interlayer strain with the strain matrix

$$\begin{pmatrix} \varepsilon & 0 & 0 \\ 0 & \varepsilon & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (4)$$

and

$$\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \varepsilon \end{pmatrix}, \quad (5)$$

respectively. Therefore, hcp Cr is elastically stable against symmetry-maintaining strains. This would suggest the possibility of growing epitaxial hcp Cr thin films on hcp Co. The shear constant $(C_{11}-C_{12})$ was calculated by introducing a monoclinic distortion with the strain matrix

$$\begin{pmatrix} +\varepsilon & 0 & 0 \\ 0 & -\varepsilon & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (6)$$

This distortion increases the x axis and decreases the y axis. The shear constant C_{55} was calculated by introducing a triclinic distortion with the strain matrix

$$\begin{pmatrix} 0 & 0 & \varepsilon \\ 0 & 0 & 0 \\ \varepsilon & 0 & 0 \end{pmatrix}. \quad (7)$$

FIG. 6. Cr K-edge x-ray absorption spectrum of Cr in bcc (solid line), fcc (dotted line), and hcp (dashed line) structure. The spectra have been broadened with a Lorentzian of 2 eV to take the core hole lifetime into account.

These monoclinic and triclinic distortions would lower the symmetry of the hcp solid. It is thus speculated that for ultrathin hcp Cr films of a few atomic layers, the substantial Cr-Co interfacial bonding could provide sufficient force against symmetry-breaking strains corresponding to the negative shear constants ($C_{11}-C_{12}$) and C_{55} . However, because of the large energy difference (0.405 eV/atom) between hcp and bcc Cr structures (see Fig. 1), the hcp Cr film would transform into the stable bcc structure as the film thickness increases beyond a few monolayers, because the interfacial Cr-Co interaction should become insufficient to maintain the coherency, leading to a collapse of the hcp structure.

There are some discernable differences in the DOS spectrum between the fcc and hcp structures, as shown in Fig. 5. These differences could show up in x-ray experiments such as x-ray photoemission or core level x-ray absorption. Thus, one might be able to distinguish the hcp phase from the fcc phase by using these experiments. We display the calculated Cr K-edge x-ray absorption spectra (XAS) for the bcc, fcc and hcp structures in Fig. 6. These spectra were calculated by using a fine mesh in the k space with the number of k points in the IBZW of 560, 560, and 1026 for bcc, fcc, and hcp phases, respectively. The theoretical spectra have been broadened with a Lorentzian of 2.0 eV to take the core hole lifetime into account. Figure 6 shows that the calculated bcc Cr K-edge XAS agrees well with the experimental one⁵ in terms of both the line shape and the energy position of the features. The pronounced difference in the XAS between the bcc and the close-packed structures is that the peak near the energy of 20 eV in the bcc phase is split into two peaks at above and below 20 eV in the close-packed phases (see Fig. 6). However, the positions of these two peaks differ in the fcc and hcp structures. Having this in mind, an inspection of the experimental XAS for three monolayers Cr films⁵ suggests that the film would have a hcp structure.

As mentioned before, the calculated DOS at the E_F for both the close-packed (fcc, hcp) structures is large, suggesting that the systems might be on the verge of ferromagnetic instability. The Stoner condition for ferromagnetism is that $ID(E_F) \geq 1$ where I is the Stoner exchange parameter and $D(E_F)$ the DOS at the E_F . Using the calculated $D(E_F)$ and I (0.38 eV/atom) calculated for Cr by Janak,²⁵ we obtained for bcc, fcc, and hcp Cr an $ID(E_F)$ value of 0.22, 0.77, and 0.90, respectively. The $ID(E_F)$ value for the fcc and hcp phases is large but short of meeting the Stoner condition.

FIG. 7. Total energy (relative to the sum of the constituent atomic energies) of the fcc Cr_3 /hcp Co_6 (circles) and hcp Cr_3 /hcp Co_7 (squares) superlattices as a function of the Cr-layer separation. The structural parameters of the Co slabs as well as the in-plane lattice constant were fixed. The dotted lines are a guide to the eye only.

Nevertheless, we have performed spin-polarized self-consistent calculations of all the three structures of Cr. No ferromagnetic state was found for all the lattice constants considered, consistent with the Stoner theory. Thus, the artificial fcc and hcp Cr would not be a ferromagnet. We also performed simple antiferromagnetic calculations for fcc [wave vector $2\pi/a(1,0,0)$] and hcp [wave vector $2\pi/c(0,0,1)$] but found no stable or metastable antiferromagnetic state.

A nonmagnetic solid with a large $\text{DOS}(E_F)$ would be susceptible to other phase transitions such as superconductivity. Indeed, the superconductivity was claimed to occur at temperatures below 2.5 K in the thin Cr films sandwiched in Au (111).⁷ This work prompted Xu, *et al.* to calculate the superconducting transition temperature (T_c) by using their calculated fcc Cr band structure. Using the experimental Debye temperature Θ_D of bcc Cr, Xu, *et al.* found a very low T_c of 0.1 K. However, assuming a lower Θ_D of 450 K for fcc Ni, a right order of magnitude of T_c of 2.5 K was obtained. The calculated fcc band structure and $\text{DOS}(E_F)$ in the present paper are in good agreement with that reported in Ref. 9. However, we have also calculated the bulk modulus (B) for bcc, fcc, and hcp Cr (see Table I). Moruzzi, *et al.*,²⁶ argued that Θ_D may be estimated from the calculated B through $\Theta_D = C[rB/M]^{1/2}$ where r is the atomic radius, M the atomic weight, and C a constant between 41 and 67. We used a C of 52 so that the calculated Θ_D for bcc Cr is about 630 K. This allow us to obtain a Θ_D of 626 and 438 K for fcc and hcp Cr, respectively. Given that the $\text{DOS}(E_F)$ and electronic contribution to the electron-phonon interaction parameter (λ) are nearly the same in fcc and hcp Cr, we obtained a T_c of about 0.1 and 2.5 K for fcc and hcp Cr, respectively. This again points to the formation of the hcp rather than fcc Cr structure in the thin Cr films in Au (111) if these films existed in a close-packed structure.

VI. EFFECTS OF THE CR-CO AND CR-CU INTERFACES

We have also carried out self-consistent calculations for the fcc Cr_3 /hcp Co_6 , hcp Cr_3 /hcp Co_7 , and fcc Cr_3 (hcp Co_3)/fcc Cu_6 superlattices in order to see the influences of the interfaces. The calculated total energy E_{super} as a function of the Cr-layer separation in fcc Cr_3 /hcp Co_6 and hcp Cr_3 /hcp Co_7 is plotted in Fig. 7. The interface energy ΔE is

defined as

$$\Delta E = (3E_{bulk}^{Cr} + n_{Co}E_{hcp}^{Co}) - E_{super}, \quad (8)$$

where n_{Co} is the number of Co layers in the superlattice. Figure 7 shows that the minimal total energy is located at 2.20 Å Cr layer separation for both fcc and hcp Cr films. The energy gain (interface energy) at this interlayer distance is 0.10 eV/cell for hcp Cr₃/hcp Co₇ and 0.04 eV/cell for fcc Cr₃/hcp Co₆. This energy gain is smaller than the energy difference between bcc Cr and fcc (hcp) Cr (Fig. 1). Though further structural optimization of the superlattices might increase the interface energy, this small energy gain would indicate that the metastable hcp (fcc) Cr films be unlikely to exceed a few monolayers. Interestingly, this separation corresponds to the interlayer distance in the fcc and hcp Cr films elastically strained to match the in-plane lattice constant with that of hcp Co. The theoretical lattice constant and c/a of hcp Co are, respectively, 2.50 Å and 1.62 Å, being in very good agreement with experiments.¹⁶ For example, for bulk fcc Cr along the [111] direction, the minimal energy in-plane lattice constant is 2.56 Å and interlayer distance is 2.09 Å (see Table I). In the fcc Cr/hcp Co superlattice, the minimal interlayer distance is 2.20 Å with the volume per Cr atom of 11.9 Å³ being close to that of bulk fcc Cr (Table I). In contrast, the minimal Cr interlayer distance in bulk hcp Cr is nearly the same as that in the hcp Cr/hcp Co superlattice.

The averaged Cr spin magnetic moment is 0.15 μ_B for hcp Cr₃/hcp Co₇ and only 0.07 μ_B for fcc Cr₃/hcp Co₆. In both cases, the Cr spin moment is antiparallel to that of Co atoms. This Cr spin moment is small compared with that of the antiferromagnetic bcc Cr and also small compared with that of the bcc Cr/Fe(Co) multilayers (see, e.g., Ref. 27). This is somewhat surprising given that the calculated density-of-states at the Fermi level in bulk fcc and hcp Cr is rather high, as pointed out in previous sections. Furthermore, the Co atoms on the interface layers have their spin moments reduced by 20–30%.

As mentioned in Sec. V, the calculated lattice constant of fcc Cr is nearly identical to that of fcc Cu (Ref. 16) and thus one might try to grow close-packed Cr films on Cu (111). Here, to investigate the stability and magnetism in the possible Cr/Cu thin films, we have also calculated the total energy and magnetic moments in the fcc Cr₃ (hcp Cr₃)/fcc Cu₆ superlattices. The ideal superlattice structure with the theoretical lattice constant of fcc Cu is assumed for both the superlattices. The calculated lattice constant of fcc Cu is 3.63 Å, being in good agreement with experiments.¹⁶ Since the lattice mismatch is small, the strain would be small too and thus only the ideal superlattice is considered. No magnetic state could be stabilized in both the systems though the initial magnetic moments of around 4 μ_B decreased very slowly and eventually disappeared after more than 100 self-consistent iterations. The calculated interface energy as defined above is −0.44 eV/cell for the fcc Cr₃/fcc Cu₆ and

−0.39 eV/cell for the hcp Cr₃/fcc Cu₆. This means that there would be no energy gain in the formation of the fcc (hcp) Cr films on Cu (111). Therefore, it would not be possible to grow close-packed Cr films on Cu (111).

VII. CONCLUSIONS

Summarizing, we have performed systematic first-principles density-functional studies of structural, electronic, and magnetic properties of bcc, fcc, and hcp Cr. Density-functional theory with the local-density approximation including the generalized-gradient corrections describe well the lattice and elastic constants of bcc Cr. The lattice constants of fcc and hcp Cr determined from the total-energy-volume curves are close to that of the reported close-packed thin films. However, the calculated elastic constants show that fcc Cr would be unstable against any shear deformation while hcp Cr would be unstable against only symmetry-breaking deformations. This lends support to the notion that ultrathin close-packed Cr films grown on hcp Co form a hcp structure.⁵ This also lead one to conclude that the thin Cr films deposited on Au (Ir) (111) reported in 1970's (Ref. 6) are unlikely to have a fcc structure. The observed hexagonal LEED patterns were due to either the formation of fcc CrAu(Ir) alloys or the existence of a hcp Cr structure. A comparison of the calculated and experimental x-ray absorption spectra also suggest that the reported ultrathin close-packed Cr films grown on hcp Co (Ref. 5) form a hcp structure. Though the density-of-states at the Fermi level of fcc and hcp Cr is rather large, no ferromagnetic state is found for these structures. No simple commensurate antiferromagnetic state is found for the fcc and hcp Cr either. The total-energy and magnetic-moment calculations have also been carried out for the fcc Cr₃/hcp Co₆, hcp Cr₃/hcp Co₇, and fcc (hcp) Cr₃/hcp Co₆ superlattices in order to see the effects of the interfaces. There would be some energy gain in the formation of the fcc (hcp) Cr/hcp Co multilayers. This energy gain is however not large compared with the energy difference between fcc (hcp) Cr and bcc Cr, and thus the closed-packed Cr films would be a few monolayers thick at most. The induced Cr spin moments would be rather small (within 0.2 μ_B) and antiparallel to that of the Co atoms. There would be no energy gain in the formation of the fcc (hcp) Cr/fcc Cu (111) multilayers. Thus, one perhaps would not be able to grow closed-packed Cr films on Cu (111) even though the lattice constants of fcc Cr and fcc Cu are almost identical. No ferromagnetic state is found in the fcc Cr₃/Cu₆ (111) and hcp Cr₃/fcc Cu₆ (111).

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*Email: gygou@phys.ntu.edu.tw

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