Calculated electronic structure of metastable phases of Cu

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The electronic energy band and ground-state properties for the existing body-centered-cubic (bcc) and body-centered-tetragonal (bct) crystals, and the predicted hexagonal-close-packed (hcp) structure of elemental copper have been calculated by using first-principles density-functional linear muffin-tin orbital methods in a unified scheme. Results are presented in the form of the energy-band structure in k space and the total energy as a function of the lattice constant. A recent proposed generalized gradient approximation scheme gives more accurate values than the standard local-density approximation. The calculated band structure of bct-Cu is in good agreement with that measured in photoemission experiments, on Cu films grown epitaxialy on Pd{001} and on Pt{001}. The equilibrium lattice constants given by us are in good agreement with those obtained from experiments on bct-Cu and bcc-Cu films. The possibility of the existence of an artificial structure of hcp-Cu has been discussed.

I. INTRODUCTION

The presumed metastable body-centered-cubic (bcc) and body-centered-tetragonal (bct) phases of elemental copper (Cu) in the form of epitaxial film have been made successfully in the recent literature, viz., bcc-Cu on Fe{001},[1] bcc-Cu on Ag{001},[2] bct-Cu on Pd{001},[3] and bct-Cu on Pt{001}.[4] These crystalline phases have never been found in the nature and have attracted a great deal of attention. This presents a challenging task to both theoretical understanding and experimental skill in preparing and stabilizing them. There is special interest in studying the electronic structure and ground-state properties of Cu, because one can obtain an accurate description of Cu by first-principles calculation in many methods; e.g., the face-centered-cubic (fcc) lattice constant is predicted correctly to within 0.3% by minimization of the total energy, and the theory accounts well for photoemission spectrum.

Up to now, the calculated results on these artificial epitaxial structures of Cu are positive compared with experiments. Calculations made by pseudopotential-local-orbital (PPLO)[5] and linear augmented-plane-wave (LAPW)[6] methods predict a metastable bcc-Cu phase with lattice constants $a=2.87$ and 2.84 Å, respectively. Another *ab initio* pseudopotential (AIPP) calculation of bcc-Cu shows $a=2.82$ Å with an additional unexpected minimum in the total energy curve.[7] They predicted a bct-Cu with $a=2.76$ Å and $c=3.09$ Å which had been confirmed experimentally by Li *et al.*[4] In addition, Li *et al.* reported for the first time the experimental band structure of bct-Cu by using photoemission spectrum.

In this paper, by using the LMTO-ASA method with standard LDA and the recent proposed generalized gradient approximation (GGA) approach, we have clarified the intriguing double minimum of total energy via volume curve of bcc-Cu in the pseudopotential calculation,[7] and have given the calculated band structure of bct-Cu in k space to interpret the photoemission spectrum in Ref. 4. We also predict another presumed metastable hcp-Cu. These new results for a series of artificial epitaxial structure of elemental Cu enable us to have a better understanding of the relation between the electronic properties and crystal structure of a typical metal.

II. METHOD

Density-functional theory (DFT) in the local-density approximation (LDA)[8] is the most widely used method for studying the electronic structure of various systems. It is very successful in predicting ground-state properties of many materials ranging from bulk crystals to surfaces and interfaces. Such predictive power, somewhat unexpected, is understood in terms of the sum rules that the LDA satisfies.[9] However, efforts to improve on the LDA have been made from the inception of the DFT[8] and have been pursued actively up to the present.[10] A recent attempt is that of Perdew and Wang (PW91).[11] The PW91 functional is an approximation within the so-called generalized gradient corrected (GGC) density-functional scheme.

The nonhomogeneity of the electron gas is taken into account through gradients of its density. This leads to a nonlocal density-functional form. The PW91 functional has presented a unified real-space-cutoff construction for exchange and correlation potential. Taking account for the nonlocality, the GGA approach has demonstrated useful improvement over LDA in applications to many systems.[12] For example, GGA correctly predicts the bcc-ferromagnetic structure as the ground state of Fe, while LDA gives the incorrect result.[13] So it is worth employing the GGA scheme in the controversial electronic structure calculation of metastable phases Cu.

In this paper, two types of the exchange-correlation potential, i.e., the Hedin-Lundqvist potential in LDA[14] and the PW91 potential in GGA[11] have been employed in first-principles calculation of the energy band of the metastable phase of Cu in the linear muffin-tin orbital (LMTO) within an atomic-sphere approximation (ASA).

The details of the PW91 functional can be found in the original references.

Our calculations for fcc-, bcc-, and bct-Cu are performed within the bct crystalline system with a different ratio of c/a as was done in Ref. 7. Inside the irreducible Brillouin zone (IBZ) we take 196 k points for the bct system and 12 special k points for hcp-Cu. The solution is considered to be self-consistent when the difference between the total energies in two successive iterations is less than 0.5 mRy.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the calculated total energy curves of bcc-Cu ($c/a=1$) as a function of lattice constant obtained by using LMTO-ASA in both LDA (solid line) and GGA (dash line), respectively. There is only one minimum in each curve. The equilibrium lattice constants are $a=2.85$ Å for using the Hedin-Lundqvist potential in LDA and $a=2.90$ Å for using the PW91 exchange-correlation potential, respectively. Our result is in good agreement with experiment[1,2] and supports the conclusion in Refs. 5 and 6, i.e., no double minimum in the total energy curve.

By fixing $a=2.75$ Å and varying value of c in a range of $1.0<c/a<1.27$, the total energy curves of bct-Cu had been given in Fig. 1(b). The equilibrium lattice constant $c=3.00$ Å obtained by using the Hedin-Lundqvist potential in LDA does not close to the experimental measurement of $c=3.24$ Å. It is well know that the calculation in LDA is used to underestimate the value of the lattice constant. However, the lattice constant $c=3.24$ Å calculated by us in the GGA approach is in accurate agreement with the measurement.

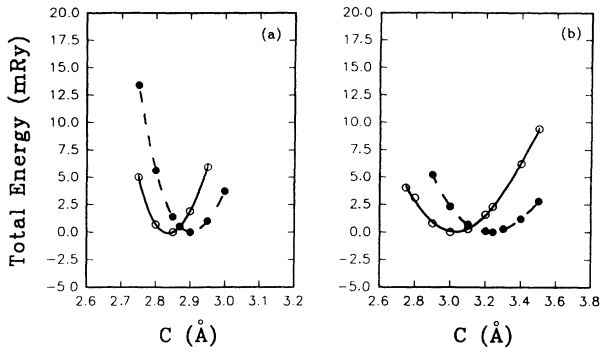

FIG. 1. Calculated total energy with respect to its minimal value as a function of lattice constant. Solid and dash curves represent the LDA and GGA scheme, respectively. (a) bcc-Cu ($a=c$) and (b) bct-Cu ($a=2.75$ Å).

Besides the success of the calculating lattice constants of both existing bcc-Cu and bct-Cu, we explored the possibility of epitaxial growth of the hexagonal-close-packed (hcp) structure Cu. Assuming to choose the cobalt crystal as a substrate for epitaxial film ($a=2.51$ Å and $c=4.07$ Å for hcp-Co), the calculated equilibrium lattice constants should be $a=2.51$ Å and $c=5.80$ Å when using the Hedin-Lundqvist potential, but $c=6.10$ Å when using the PW91 potential. However, the mismatch between the values of lattice constants $a=2.51$ Å of hcp-Co and $a=2.55$ Å in $\langle 111 \rangle$ of fcc-Cu is as small as 1.8% only, then the possibility of the epitaxial grown of a fcc-Cu in the $\langle 111 \rangle$ direction along the c axis of hcp-Co would exist. In our calculation, there is no equilibrium

TABLE I. Comparison of equilibrium lattice constants of metastable crystal Cu between theoretical calculation and experiments, in units of Å.

Crystal		Calculations					Experiments
		AIPP[a]	PPLO[b]	LAPW[c]	LMTO-ASA (ours)		
Type	Axis				LDA	GGA	
bcc ($a=c$)	a-	2.82	2.87	2.84	2.85	2.90	2.87 in Cu/Fe{001}[d] 2.89[e] in Cu/Ag{001}[f]
bct	a-	2.76			2.75	2.75	2.75[e] in Cu/Pd{001}[g]
					2.78	2.78	2.78[e] in Cu/Pt{001}[h]
	c-	3.09			3.00	3.24	3.24 in Cu/Pd{001}[g]
					2.95	3.20	3.24 in Cu/Pd{001}[h]
hcp	a-				2.51	2.51	
	c-				5.80	6.10	

[a]Reference 5.
[b]Reference 7.
[c]Reference 6.
[d]Reference 1.
[e]fcc-Ag, Pd, Pt, with cubic lattice constant a_0 equal to 4.09, 3.89, and 3.93 Å, have a square mesh on its {001} faces with side an equal to 2.89, 2.75, and 2.78 Å, respectively.
[f]Reference 2.
[g]Reference 3.
[h]Reference 4.

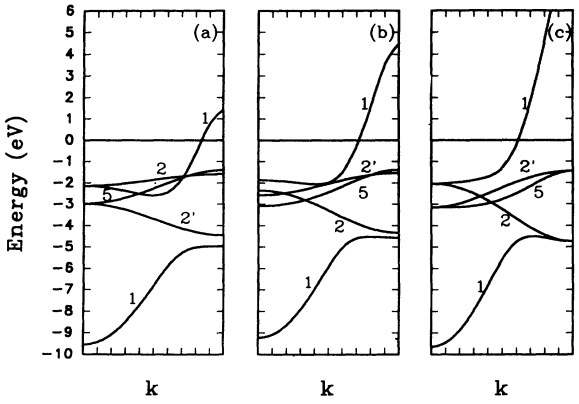

FIG. 2. Calculated band structure along the direction normal to the {001} plane of Cu with differential crystal symmetry: (a) fcc, (b) bct, and (c) bcc lattices. Energies are in eV measured relative to the Fermi level. The numbers of 1, 2, 2', and 5 indicate the bands of Δ_1, Δ_2, Δ_2', and Δ_5, respectively.

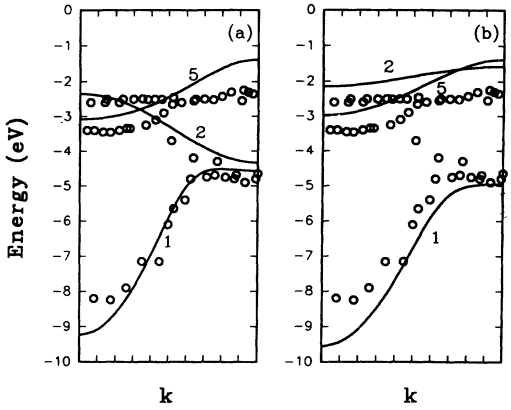

FIG. 3. A comparison between experimental band structure (circles) of bct-Cu along the direction normal to the {001} plane and calculated one. The solid curves are calculated for bulk (a) bct-Cu and (b) fcc-Cu. The numbers of 1, 2, and 5 indicate the bands of Δ_1, Δ_2, and Δ_5, respectively.

position in total energy curves for $a > 2.60$ Å. The task of searching for a suitable single-crystal substrate for epitaxial grown hcp-Cu is still open.

Summarizing the above facts, the equilibrium lattice constants obtained from experimental researches and theoretical calculations have been listed in Table I. It shows that our calculated results are in more accurate agreement with measurements.

An elegant experiment, angle-resolved photoemission with synchrotron light, was used to determine the band structure of a thin-film of bct-Cu grown epitaxially on Pd{001} and on Pt{001}.[4] Li *et al.*[4] pointed out that the experimental band structure of these films should be similar to the band structure calculated for bulk fcc-Cu without a detailed explanation of this finding due to the absence of a calculated band of bct-Cu at that time. Here, we give a calculation of the bct-Cu band structure which possesses the character of bcc-Cu rather than fcc-Cu.

To elucidate the relation between the band and crystal structures, we first give a comparison of calculated bands of these similar phases as fcc-, bct-, and bcc-Cu. The wave vector of these bands is along the direction normal to the {001} plane. A calculated band of fcc-Cu has been repeated and shown in Fig. 2(a). At Γ point, the higher band Γ_{12} is doublet including two singlet Δ_1 and Δ_2, and the lower band Γ_{25}' is triplet including a singlet Δ_2' and a doublet Δ_5. There is a confluence between the Δ_2 and the Δ_5 bands located at about three fourths of Γ-X axis. Meanwhile, the theoretical band structure of bct-Cu has obtained based on the LMTO-ASA calculation which is shown in Fig. 2(b). The main feature is that there is a crossover of the Δ_2 and the Δ_5 bands located at near one third of the Γ-X axis rather than a confluence at a higher k value as in fcc-Cu bands. The calculated band structure of bcc-Cu has also been shown in Fig. 2(c). One can find the following fact that the main character of the bct-Cu band is similar with the one of the bcc-Cu band rather than the one of the fcc-Cu band, especially for the characteristic Δ_2 band with the x^2-y^2 state and the Δ_2' band with the xy state.

Based on our calculations, we will explore the detail of experiment and theory in the following. The experimental data of the bct-Cu epitaxial film from Ref. 4 was put into the calculated band-structure curves of bct-Cu in Fig. 3(a). In the photoemission measurement, there are three binding energy values (Δ_2 Δ_5, and Δ_1 bands) corresponding to each k value from Γ through Δ to the X point. Taking all of these experimental points together into account, the profile of the Δ_2 and Δ_5 bands is closer to the feature of crossover but not confluence. In addition, the calculated k value at crossover of Δ_2 and Δ_5 bands of bct-Cu is in agreement with the experimental measurement. As a comparison, the same measurement data of the bct-Cu film were put into the calculated dispersion curves of fcc-Cu in Fig. 3(b). It is easy to find the discrepancy in features and characters.

The authors of Ref. 4 pointed out that a stronger emission occurs at -4.6 eV which is probably due to emission from the Δ_2' band, but the limited resolution of their monochromator did not allow them to decompose this peak into its components. If it is true, more experimental and theoretical research should be expected in the near future.

IV. CONCLUSION

In summary, the calculation of the energy band for metastable phases of bcc-Cu and bct-Cu in LMTO-ASA has been performed to elucidate the relation between crystal structure and electronic states. The more accurate equilibrium lattice constants and band structure in k space have been obtained. The new metastable phase is still expected. More measurements and complete calculations are still needed.

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