Ab-initio investigation on mechanical properties of copper*

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Employing the *ab-initio* total energy method based on the density functional theory with the generalized gradient approximation, we have investigated the theoretical mechanical properties of copper (Cu) systematically. The theoretical tensile strengths are calculated to be 25.3 GPa, 5.9 GPa, and 37.6 GPa for the fcc Cu single crystal in the [001], [110], and [111] directions, respectively. Among the three directions, the [110] direction is the weakest one due to the occurrence of structure transition at the lower strain and the weakest interaction of atoms between the (110) planes, while the [111] direction is the strongest direction because of the strongest interaction of atoms between the (111) planes. In terms of the elastic constants of Cu single crystal, we also estimate some mechanical quantities of polycrystalline Cu, including bulk modulus B, shear modulus G, Young's modulus $E_{\rm p}$, and Poisson's ratio ν.

Keywords: copper, theoretical tensile strength, *ab-initio* method

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1. Introduction

The theoretical (ideal) tensile strength of metals is the stress required to force deformation or fracture in the elastic instability.[1] The theoretical tensile strength sets an upper bound on the attainable stress. The strength of a real crystal can be changed by the existing cracks, dislocations, grain boundaries, and other microstructural features, but its value can never be raised above the theoretical one.[1,2] The theoretical tensile strength is that a metal becomes unstable with respect to fracture by the spontaneous separation of atomic planes. The upper limit of tensile strength is interesting for strong solids in atomic models.[1,3–5] Those models were originally developed by Frenkel[6] and Orowon.[7]

By virtue of the development of the density-functional theory (DFT)[8,9] combined with the band-theoretical schemes and the rapid progress of modern computers, it becomes possible to perform the *ab-initio* computational tensile test (AICTT) to investigate the stress as a function of strain and obtain the theoretical tensile strength by deforming crystals to failure.[10] For single crystals, the theoretical tensile and shear strengths of Al, Mo, W, Nb, Fe, and NiAl have been published.[2,5,11–15] On the other hand, the theoretical strength can also be extended to the defective system containing only one defect, such as a point defect,[16] an interface, or a grain boundary.[17–23] The theoretical tensile strengths of a clean Al grain boundary (GB) and an Al GB containing Na, Ca, S, and Ga have been calculated to explore the impurity-induced intergranular embitterment.[19–23]

Copper (Cu) is regarded as one of the important transition metals which have a broad range of applications in material physics.[24–26] The stress as a function of strain and the theoretical strength (both tensile and shear) for Cu have been explored in the past few years. In the early study, Sandera *et al.* performed the three-axial tension (without considering the Poisson' effect) on a Cu single crystal using the linear muffin-tin orbital atomic sphere approximation (LMTO-ASA).[11] Recently, the *ab-initio* computational shear test (AICST) has been used to calculate the theoretical shear strengths in the $\{111\}\langle 112\rangle$ and the $\{111\}\langle 110\rangle$ slip systems.[5,14,27,28] Besides, Jahnatek *et al.* also investigated the shear deformation and the stacking fault formation in the $\{111\}\langle 112\rangle$ and the$\{111\}\langle 110\rangle$ slip systems for the face-centered cubic (fcc) Cu.[29]

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tal aspects underlying the mechanical properties for Cu remain poorly understood. Up to now, we find no reported relevant work employing the AICTT method to investigate the theoretical tensile strength and the structure deformation behavior of the fcc Cu under a uniaxial tensile strain considering the Poisson' effect. Such a study can help to understand the intrinsic interaction between atoms in Cu. The theoretical tensile strength of the fcc Cu has been provided by either a simple formula or theoretically from the semiempirical approximations, which enables us to make a full comparison. With this purpose in mind, in this paper, we perform the AICTT on the fcc Cu in the [001] and the [110] directions to explore its theoretical mechanical properties systematically.

2. Computational method

Our *ab-initio* calculations have been performed using the VASP code[30,31] based on the DFT. We use the generalized gradient approximation of Perdew and Wang[32] and the projected augmented wave (PAW) potentials.[33] A plane wave energy cutoff of 350 eV is found to be sufficient to obtain the converged total energy for the fcc Cu. For summation over the Brillouin zone, a uniform k-point grid is chosen according to the Monkhorst–Pack scheme[34] until the change of the total energy of the unit cell is less than 0.001 eV with further increasing number of k-points. The calculated equilibrium lattice constant is 3.63 Å for the fcc Cu, which is in good agreement with the corresponding experimental value of 3.61 Å.[35] It demonstrates the accuracy of the employed PAW potentials. Both supercell sizes and atomic positions are relaxed to the equilibrium, and the energy minimization is converged when the forces on all the atoms are less than 10^{-3} eV·Å^{-1}.

In the AICTT, a uniaxial tensile strain is applied to the chosen crystalline direction, and the corresponding stress is calculated according to the Nielsen–Martin scheme.[36,37] For the uniaxial tensile strain, the tensile stress σ is given by

$$\sigma_{ij} = \frac{1}{\Omega(\varepsilon_{ij})} \frac{\partial E_{\text{total}}}{\partial \varepsilon_{ij}}, \tag{1}$$

where E_{total} is the strain energy, and $\Omega(\varepsilon_{ij})$ is the volume under the given tensile strain. The ε_{ij} denotes the strain of the simulation cell, which is defined as

$$\varepsilon_{ij} = \frac{l - l_0}{l_0}, \tag{2}$$

where l and l_0 denote the lengths of the cell in the corresponding direction in the final and the initial structures, respectively.

Considering the Poisson's effect in the AICTT, we fix the tensile direction and let the other directions orthogonal to the tensile direction relax automatically at each strain step until all other stress components vanish except that in the tensile direction, i.e., it is indicated by those stress components orthogonal to the tensile direction being less than 0.1 GPa. The tensile stress for each strain step can be calculated, and thus the stress–strain relation and the ideal tensile strength can be obtained.

3. Results and discussion

3.1. Bulk properties of fcc Cu

The bulk properties of Cu single crystal are first examined. We know that there exist three independent elastic constants, C_{11}, C_{12}, and C_{44}, due to the cubic structure of the fcc Cu. In Table 1, we list the calculated results and the experimental values. We can see that C_{11} and C_{12} are consistent with the corresponding experimental values.[35] However, the value of C_{44} from the present calculation is about 8.06% smaller than the experimental value. Such a large error also occurs in calculating the elastic constants of some cubic metals, such as Fe.[15]

Table 1. Calculated and experimental elastic constants of fcc Cu single crystal.

	C_{11}/GPa	C_{12}/GPa	C_{44}/GPa
Cal.	174.5	125.3	75.2
Expt.[35]	176.2	124.9	81.8

3.2. Energy–strain and stress–strain relations of Cu single crystal

Three representative directions including [001], [110], and [111] are selected to perform the AICTT for the fcc Cu. The theoretical tensile strength in a certain direction is not determined by the size of unit cell, i.e., we can obtain the same tensile strength value using supercells of different sizes. For example, if 32-atom and 108-atom supercells are respectively chosen to perform the AICTT in the [001] direction, we will obtain the same theoretical tensile strength with the value from the present calculation with a 4-atom unit cell. In view of this, we thus try our best to choose relative smaller unit cells in the respective [001], [110], and [111] directions to perform the AICTT in order

to reduce the computational time. Three unit cells with different symmetries for the AICTT in different directions are shown in Fig. 1.

For the AICTT in the [001] direction, we use the fcc unit cell drawn from the fcc crystal, as shown in Fig. 1(b). The original unit cell exhibits the cubic symmetry. The symmetry will be changed and a tetragonal structure will be obtained in the tensile process along the [001] direction. Figure 2(a) shows the strain energy as a function of tensile strain. It can be seen that the strain energy increases with the increasing strain, exhibiting an inflexion at the strain of 36%. Correspondingly, as shown in Fig. 2(b), the stress increases with the increasing strain until it reaches a maximum of 25.3 GPa at the strain of 36%, after which the stress decreases. Thus, we can conclude that the theoretical tensile strength is 25.3 GPa in the [001] direction. For the [111] direction, we use the unit cell including 6 Cu atoms shown in Fig. 1(d). Similar to the [001] direction, the structure conversion does not occur in the tensile process. The stress reaches the maximum of 37.6 GPa at the strain of 38%. This corresponds to the inflexion at the energy–strain curve shown in Fig. 2(a). Therefore, the theoretical tensile strength is 37.6 GPa in the [111] direction.

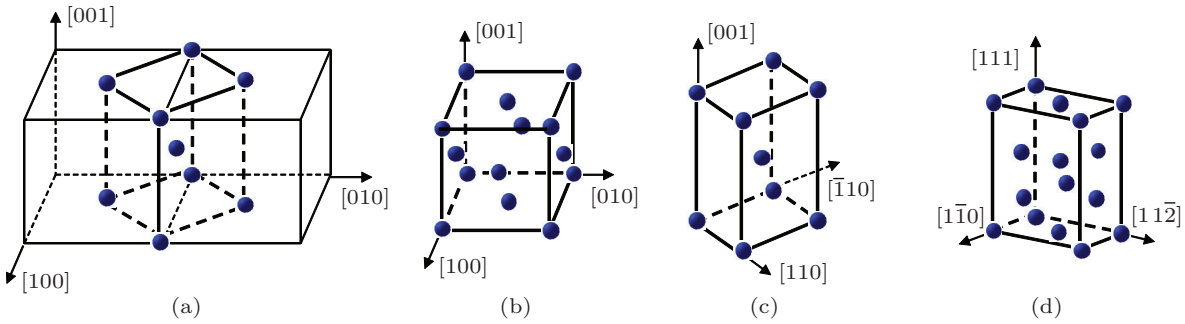


Fig. 1. (colour online) Geometric structures of tensile unit cells of fcc Cu in the [001], [110], and [111] directions. (a) Body-centered tetragonal (bct) unit cell inside fcc Cu, (b) general fcc unit cell of Cu with 4 atoms inside, (c) bct unit cell with 2 atoms inside drawn from panel (a), (d) unit cell contains 6 atoms. The unit cells in panels (b), (c), and (d) are employed to perform the AICTT in the [001], [110], and [111] directions, respectively.

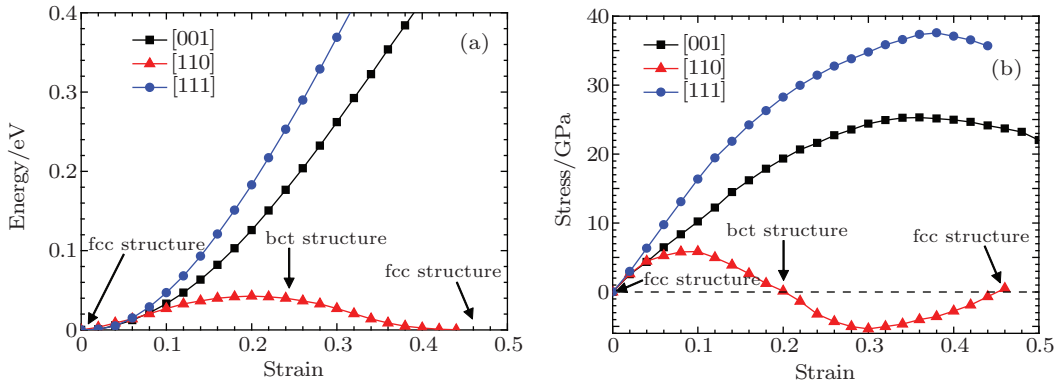


Fig. 2. (colour online) (a) Energies and (b) stresses in the [001], [110], and [111] directions for fcc Cu each as a function of tensile strain.

Compared with those in the [001] and the [111] directions, the stress–strain relation in the [110] direction differs obviously. The unit cell employed for this tensile direction is the body-centered tetragonal (bct) structure shown in Fig. 1(c). The strain energy as a function of strain is shown in Fig. 2(a). Similar to the [001] direction case, the energy increases first with the increasing strain, then reaches a maximum at the strain of 20%. However, different from the [001] direction case, the strain energy begins to decrease again until it reaches the zero point at the strain of $\sim 46\%$. The maximum or the minimum of the strain energy corresponds to the zero stress points in the stress–strain curve in [110]. As shown in Fig. 2(b), the stress exhibits one maximum of 5.9 GPa at the strain of 10%, and then reaches zero at the strain of

20%. Further strain increasing leads to a compressive stress, and the stress reaches a minimum of −5.3 GPa at the strain of 30%. Further, it reaches zero again at the strain of ∼ 46%. Therefore, the stress exhibits two saddle points (one maximum and one minimum) and three zero points in the tensile process.

In order to clarify such complicated energy–strain and stress–strain relations in the tensile process for the [110] tensile direction, we give a detailed analysis based on the structure transition. The zero-stress point in the stress–strain curve corresponds to a stress-free phase, which is generated in the tensile process. The initial zero-stress point corresponds to the initial bct phase, which is drawn from the fcc structure, as shown in Fig. 3(a). Here, a, b, and c are the lattice constants, while a_0 is the lattice constant of the fcc Cu. The ratio of $a : b : c$ for such a phase is $1 : 1 : \sqrt{2}$. With the strain increasing, lattice parameter a increases, while c decreases and b remains almost unchanged. Lattice parameter c is equl to a at the strain of 20%, where the stress reaches the second zero-stress point. At this strain point, a new bct structure is obtained with $a = c > b$ (Fig. 3(b)), which is different from the original one. This strain point corresponds to a saddle point of the energy maximum in Fig. 2(a), which suggests the new bct structure is an instable phase despite of its stress-free characteristic. Such a structure will evolve to the stable fcc phase even with a small perturbation. With the further increase of strain, lattice parameter c decreases continuously. The ratio of $b : c : a$ becomes $1 : 1 : \sqrt{2}$ at the strain of 46% (Fig. 3(c)), corresponding the third zero-stress point in the stress–strain curve. The present stress-free bct structure (i.e., fcc structure) is actually the same as the initial one (Fig. 3(a)), but with a rotation of 90°.

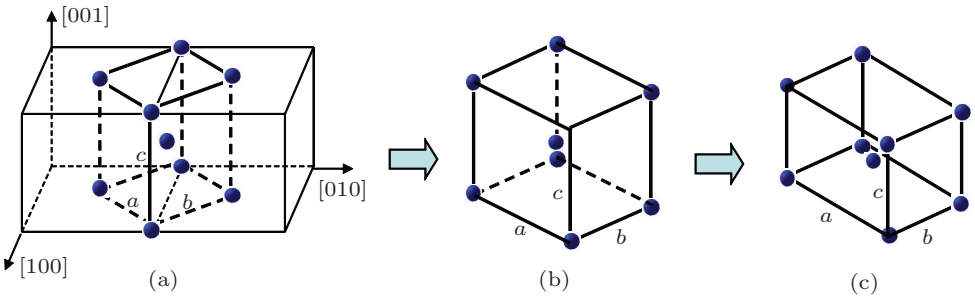


Fig. 3. (colour online) The evolution of structure of the unit cell for fcc Cu under the tension in the [110] direction. In panel (a), $a = b = \sqrt{2}/2a_0$, $c = a_0$, in panel(b), $a = c > b > \sqrt{2}/2a_0$, and in panel (c), $b = c = \sqrt{2}/2a_0$, $a = a_0$.

Based on the above results, [111] can be considered as the strongest direction, along which the theoretical tensile strength is above 37.6 GPa. However, it is important to note that [110] is the weakest direction with a tensile strength of only 5.9 GPa. This can be understood based on the following facts. For fcc metals, (111) is the most-closely-packed crystalline plane, which can lead to the strongest interaction of atoms between the (111) planes in comparison with that of the (001) and the (110) planes. This can make the theoretical tensile strength in the [111] direction higher than those in the [001] and the [110] directions. For the [001] and the [110] directions, the (001) plane is more closely-packed as compared with the (110) plane, resulting in the stronger interaction of atoms between the (001) planes, so the theoretical tensile strength in the [001] direction is larger than that in the [110] direction. Among the three directions, the [110] direction is the weakest direction due to the occurrence of structure transition at the lower strain and the weakest interaction of atoms between the (110) planes.

3.3. Comparison with experimental and other theoretical results

Table 2 shows the tensile strengths and the corresponding strains obtained from the present calculation and the previous studies, including experiment and theoretical values. In the present calculation, the theoretical tensile strength in the [001] and the [111] directions are 25.3 GPa and 37.6 GPa, respectively. These values are in good agreement with 25 GPa and 39 GPa estimated from the empirical formula[1] $\sigma_{\max} = \sqrt{\frac{E \cdot \Theta}{a_0}}$, which is based on the experimental values of surface energy Θ and Young's modulus E, and is only applicable to estimate the fracture strengths for ideal crystals. However, Sandera *et al.* also used the *ab-initio* method to perform the AICTT

on the [001] direction and obtained the strength value of 26.0 GPa,[38] which is consistent with the result of the present calculation. The semiempirical values in the [001] direction estimated from the polynomial approximation[39] and the self-consistent augmented spherical wave method[40] are 32.7 GPa and 32.0 GPa, respectively, which are much larger than the present result. For the [110] direction, the theoretical tensile strength is shown to be 5.9 GPa in the present calculation. Unfortunately, there is no other relevant data found for comparison. Thus, our result provides a quite useful reference to quantitatively understand the mechanical properties along the [110] direction for the Cu single crystal.

Table 2. The tensile strength $\sigma_{\rm m}$ and Young's modulus E obtained from our calculation and the other studies.

Direction	$\sigma_{\rm m}$/GPa					E/GPa		
	Calculation	Expt.[1]	Ref. [11]	Ref. [38]	Ref. [40]	Calculation	Expt.[1]	Expt.[35]
[001]	25.3	25	26.0	32.7	32.0	69.8	67.0	72.0
[110]	5.9					133.4		141.1
[111]	37.6	39				191.7	192.0	205.8

The theoretical tensile strength can also be determined from Young's modulus, which can be calculated from the elastic constants.[1] The Young's moduli for the [001], [110], and [111] directions can be given by

$$E_{[001]} = \frac{(C_{11}+2C_{12})(C_{11}-C_{12})}{C_{11}+C_{12}}, \tag{3}$$

$$E_{[110]} = \frac{4C_{44}(C_{11}+2C_{12})(C_{11}-C_{12})}{2C_{11}C_{44}+(C_{11}+2C_{12})(C_{11}-C_{12})}, \tag{4}$$

$$E_{[111]} = \frac{3C_{44}(C_{11}+2C_{12})}{C_{44}+(C_{11}+2C_{12})}. \tag{5}$$

According to the above equations, we can obtain Young's moduli of 69.8 GPa, 133.4 GPa, and 191.7 GPa for the [001], [110], and [111] directions, respectively. It can be seen that $E_{[001]}$ is consistent with the experimental values,[1,35] as shown in Table 2. However, $E_{[110]}$ and $E_{[111]}$ from the present calculation are about 5.4% and 6.8% smaller than the corresponding experimental values.[35] Such errors might partly stem from the fact that there is a relatively larger difference of C_{44} between the calculated and the experimental values.

By analyzing the elastic constants of Cu single crystal, we can further deduce some mechanical quantities of polycrystalline Cu. It is well known that the plastic properties of metal polycrystalline can be estimated from the elastic properties based on some empirical criteria originally proposed by Pugh.[41] In Pugh's criteria, the resistance to plastic deformation is proportional to the elastic shear modulus G and the burgers vector $v_{\rm b}$ for metals at the temperatures below one third of the melting point, i.e., the hardness is proportional to $Gv_{\rm b}$. The fracture strength of a pure metal is proportional to Ba_0, where B is the bulk modulus. On the other hand, the quotient of B/G can reflect the extent of the plastic range for a pure metal, so a high value of B/G is associated with ductility, while a low value is associated with brittleness. Thus, it is extremely important to deduce these mechanical quantities, including the bulk modulus B, the shear modulus G, Young's modulus $E_{\rm p}$, and Poisson's ratio ν for polycrystalline Cu.

Since C_{11}, C_{12}, and C_{44} are a complete set of elastic constants for a cubic metal system, B, G, $E_{\rm p}$, and ν for polycrystalline Cu can be calculated respectively from

$$B = \frac{C_{11}+2C_{12}}{3}, \tag{6}$$

$$G = \frac{3C_{44}+C_{11}-C_{12}}{5}, \tag{7}$$

$$E_{\rm p} = \frac{9BG}{3B+G}, \tag{8}$$

$$\nu = \frac{1}{2}\left(1-\frac{E_{\rm p}}{3B}\right). \tag{9}$$

Table 3 lists the mechanical quantities of polycrystalline Cu. The calculated bulk modulus B is in good agreement with the corresponding experimental value. However, the calculated G, $E_{\rm p}$, and ν exhibit 7.7%, 6.6%, and 3.1% differences in comparsion with the corresponding experimental values. The possible reason might be directly originated from the difference of C_{44} between the calculated and the experimental results. The B is not relevant to C_{44}, while G, $E_{\rm p}$, and ν contain C_{44} in the formulas. Therefore, we can conclude that C_{44} is crucial if the first-principles method or the other computational methods are used to pre-

dict mechanical quantities of polycrystalline Cu or the other metals.

Table 3. Bulk modulus B, shear modulus G, Young's modulus $E_{\rm p}$, and Poisson's ratio ν of polycrystalline Cu determined from the elastic constants.

	B/GPa	G/GPa	$E_{\rm p}$/GPa	ν
Calculation	141.7	54.9	145.8	0.33
Expt.[35]	142.0	59.3	156.1	0.32

4. Conclusion

We use the *ab-initio* total energy method based on the density functional theory with the generalized gradient approximation to investigate the theoretical mechanical properties of copper (Cu) systematically. The theoretical tensile strengths are calculated to be 25.3 GPa, 5.9 GPa, and 37.6 GPa for the fcc Cu single crystal in the [001], [110], and [111] directions, respectively. Among the three directions, The [110] direction is found to be the weakest one due to the formation of an instable body-centered tetragonal phase in the tensile process and the weakest interaction of atoms between the (110) planes in comparison with the (001) planes, while the [111] direction is the strongest direction because of the strongest interaction of atoms between the (111) planes. According to the elastic constants of Cu single crystal, we have also estimated the corresponding mechanical quantities of polycrystalline Cu, including bulk modulus B, shear modulus G, Young's modulus $E_{\rm p}$ and Poisson's ratio ν. We provide a quite useful reference to quantitatively understand the mechanical properties of Cu.

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