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Electronic and structural properties of elemental copper: A pseudopotential–local-orbital calculation

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We have examined the electronic and structural properties of elemental copper using pseudopotentials and a local-orbital basis consisting of Gaussians. We find we can use a much weaker ionic pseudopotential to describe accurately the measured band structure, cohesive energy, lattice constant, and compressibility of copper than previous pseudopotential work. Our potential should be more amenable than existing ones to momentum-space evaluations of the total crystalline energy. In addition, we have examined the equation of state for copper in both the fcc and bcc structures. Unlike a recent pseudopotential–mixed-basis calculation, we find that the energy-versus-volume curve for copper in the bcc structure does not exhibit a double minimum.

I. INTRODUCTION

One of the most challenging applications for pseudopotential descriptions of solids involves elements which have "loosely bound" core shells. For example, the noble metals (Cu,Ag,Au) have a filled outer *d* shell which can strongly influence the chemical and structural properties of these metals, yet owing to its filled-shell character does not participate directly in the formation of chemical bonds.[1–3] Another example involves the element zinc. If one computes the structural properties of zinc-blende semiconductors, e.g., ZnSe, without including the effects of the Zn 3*d* shell, the lattice constant can be typically 10–20% too small.[4]

The pseudopotential method can, of course, handle such situations by considering the *d* shell as part of the valence shell and not part of what is usually treated as the "chemically inert" ion core. However, if this procedure is followed, some of the advantages of the pseudopotential method are lost. For example, the effective valence (z) of a noble metal such as copper becomes $z=11$, not $z=1$. The concurrent ionic pseudopotential is much stronger as it now must bind eleven electrons instead of a single electron. Consequently, the basis must not only be capable of replicating the loosely bound Cu 4*s* state, but the highly localized Cu 3*d* states. One approach to this problem is to employ a mixed basis which combines plane waves with localized functions.[1,2] However, one of the most efficient methods for evaluating the total electronic energy of a solid is to use a momentum-space formalism.[5] This formalism usually expresses the total energy in terms of Fourier transforms of the potential and a plane-wave basis. If the potential of interest is very strong, then a large number of Fourier coefficients and plane waves must be used to describe the total energy.

In this paper we wish to demonstrate that local orbitals alone, i.e., Gaussians, can be used as an effective basis for Cu and that one can construct a much weaker ionic pseudopotential than has been used in the past without sacrificing any significant accuracy. Also, we have examined the structural properties of copper in both the fcc and bcc structures. A recent pseudopotential calculation for copper in the bcc structure yielded an intriguing suggestion that the total-energy–versus–volume curve contained a double minimum.[1] Since calculations for other metals do not exhibit this behavior,[6] we felt another calculation using a somewhat different approach would be in order.

II. CONSTRUCTION OF THE COPPER IONIC PSEUDOPOTENTIAL

Within the local-density method[7] for handling exchange and correlation one can construct an ionic pseudopotential from an atomic-structure calculation. Typically, one solves an all-electron calculation for an isolated atom. This calculation generates energy levels and wave functions for both core and valence electrons. By taking the valence energy levels from such a calculation and by suitably modifying the valence wave functions, one can then invert Schrödinger's equation and obtain an ionic pseudopotential which will, by construction, accurately reproduce only the valence energy levels and modified valence wave functions.[8] Normally, one modifies the atomic valence wave functions by altering their behavior in the core region. For example, within a specified distance of the core, one might smoothly continue the wave function to the nucleus and by so doing remove the nodal structure.[9]

For copper we used the procedure as outlined above following the method proposed by Kerker.[9] The resulting ionic copper pseudopotential binds only the 4*s* and 3*d* states. The Cu 4*s* states present no particular problem; however, the Cu 3*d* states are very localized with the radial–wave-function maximum occurring at 0.6 a.u. (1

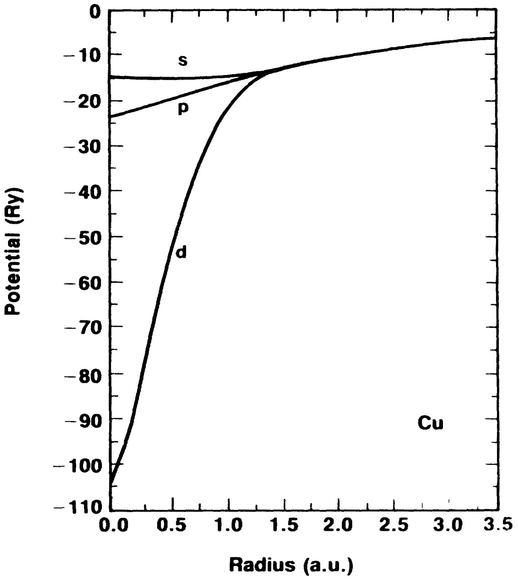

FIG. 1. *Ab initio* ionic pseudopotential for copper.

a.u. = 0.529 Å) from the nucleus. In constructing the copper potential we noted that the Wigner-Seitz–cell radius is about 2.67 a.u. for elemental fcc copper. Thus, we felt it was not necessary to preserve the shape of the d-wave function within a radius several times that of the radial–wave-function maximum. In the spirit of the pseudopotential approach, we only demand an accurate valence wave function in the bonding region. We chose the following core sizes for the s, p, and d states: 1.7 (s), 2.0 (p), and 1.8 (d) a.u. The corresponding radial–wave-function maxima for the all-electron case are at 2.3 (s), 3.5 (p), and 0.6 (d). The atomic configuration used to construct the ionic pseudopotential was $s^{0.9}p^{0.1}d^{10}$. The results are very insensitive to the details of the atomic configuration.[8,9]

Although the d-potential component of our ionic pseudopotential is not expected to do well within the core region, the radial–wave-function maximum is only off by ~20% and outside a distance of ~1.4 a.u. the all-electron and pseudopotential $3d$ wave functions are essentially identical. Thus, we would expect our copper pseudopotential to reproduce accurately all those properties which are dependent on the wave functions outside the core, e.g., cohesive energy, lattice constant, structural parameters, etc. The ionic pseudopotential is illustrated in Fig. 1.

III. COMPUTATIONAL DETAILS

The most difficult aspect of the calculation, after the ionic pseudopotential is constructed, is determining an accurate basis. The form of the basis and details of this issue have been presented elsewhere.[10] Here we will give a brief outline of our procedure. Our basis consists of a polynomial times a Gaussian with the polynomial having s, p, and d character. For grouping purposes we consider sets of basis functions characterized by an exponential decay constant. Each set consisted of two s-, three p-, and five d-symmetry polynomial-Gaussian orbitals. Typically, for a transition metal three or four decay constants are used for a total basis of 30 or 40 orbital functions per atom.[10] However, for copper we found this set to be inadequate. Specifically, we found the bulk modulus to be quite sensitive to the number and values of the decay constants.

In order to optimize the basis, we systematically varied the largest and smallest decay constants and allowed the intermediate decays to be determined by demanding the distribution correspond to even-tempered Gaussians.[10] By even tempered we mean the decay constants λ_i's are such that $\lambda_i = (\lambda_{i+1}\lambda_{i-1})^{1/2}$ (see Ref. 10). We then calculated the total energy by increasing the number of decays. With six decays, the total energy was converged to ~0.5 eV. We further optimized the basis by adjusting each decay individually, i.e., relaxing the constraint of being even tempered. The energy was converged to within ~0.1 eV. The final set of exponential decay constants was 0.25, 0.6, 1.0,1.6, 4.0, and 10.0 a.u.$^{-2}$.

The total energy of the system was evaluated using a momentum-space formation.[5] This procedure involves sums over **k** points in the Brillouin zone and over reciprocal-lattice vectors. The number of **k** points was taken to be 44 **k** points for the bcc structure and 60 **k** points for the fcc structure. This is probably the minimum number of **k** points for obtaining an accurate

TABLE I. Band energies at high-symmetry points for fcc copper. The energy (in eV) is relative to the Fermi level, i.e., $E_F - E(\mathbf{k})$. Theoretical calculations are using the Korringa-Kohn-Rostoker (KKR) method (Ref. 11), the linearized augmented-plane-wave (LAPW) method (Ref. 12), a mixed-basis–pseudopotential (MB) method (Ref. 1), and a Gaussian-orbital–pseudopotential (GO) method (present work). Also listed are experimental values from angle-resolved photoemission. The band-structure calculations are done at the experimental lattice constant of copper.

Symmetry point	KKR[a]	LAPW[a]	MB[c]	GO	Expt.[d]
Γ_{12}	2.41	2.40	2.45	2.46	2.85
Γ'_{25}	3.24	3.20	3.27	3.35	3.65
Γ_1	9.42	9.47	9.88	10.26	
X_5	1.62	1.64	1.70	1.74	2.05
X_2	1.82		1.89	1.91	
X_3	4.68		4.69	4.76	4.50
X_1	5.27	5.07	5.18	5.23	5.20
L'_2	1.14		0.98	0.81	0.90
L_3	1.78	1.80	1.86	1.90	2.25
L_3	3.29		3.32	3.39	3.65
L_1	5.25	5.23	5.41	5.46	
$\Gamma_{12} - \Gamma'_{25}$	0.83	0.80	0.82	0.89	0.80
$X_5 - X_1$	3.65	3.43	3.48	3.49	3.15
$L_3 - L_1$	3.47	3.43	3.55	3.56	

[a] Reference 11.
[b] Reference 12.
[c] Reference 1.
[d] Reference 14.

structural energy difference between the total energies of the fcc and bcc structures. We also tested grids ranging with as few as eight **k** points and found, as expected, that these grids are too coarse to distinguish between the total energies of the fcc and bcc structures.

One of the most difficult issues is that involved with the summations over reciprocal-lattice space.[5] We used a final cutoff of 16 a.u.$^{-1}$, i.e., the largest reciprocal-lattice vector, $G_{\max}$, had a kinetic energy of 128 hartrees associated with it. This corresponds to about 5500 waves. With this cutoff the total energy was converged to within $\sim$0.05 eV. We tested cutoffs as large as $G_{\max}=20$ a.u.^{1}, which corresponded to approximately 11 000 plane waves in the summations required. Using a much stronger copper potential, Kang *et al.*[1] used a cutoff which required about 12 000 reciprocal-lattice vectors.

With respect to other parameters, the required overlap integrals and three-center integrals were neglected for site distances which exceeded 10 a.u. For example, at the known equilibrium distance for fcc copper, 58 neighbors were included. When the volumes of the bcc and fcc structures were changed, we rescaled this cutoff along with the reciprocal-space cutoff. This procedure ensures that we will be treating different volume states with the same "effective" cutoff.

IV. BAND STRUCTURE OF fcc AND bcc COPPER

To compare the accuracy of our work with previous calculations of fcc copper,[1,11,12] we present in Table I a comparison of the energy bands at high-symmetry points. In Fig. 2 we also present the energy bands along high-symmetry directions. These results were obtained at the experimental lattice constant of fcc copper ($a_0=6.82$ a.u.).[13] Given the differences in bases, potentials, and various other approximations, it is very gratifying that the energy levels agree so well. The largest discrepancy is bandwidth, i.e., $E_{\mathrm{BW}}=E_F-E(\Gamma_1)$, which the pseudopotential calculations obtain as 9.88–10.26 eV, whereas the Korringa-Kohn-Rostoker[11] (KKR) and linearized augmented-plane-wave[12] (LAPW) methods yield a narrower width of 9.42 and 9.47 eV, respectively. We speculate that this may arise from the pseudopotential approximation given that our Gaussian-orbital–pseudopotential and the mixed-basis–pseudopotential calculations[1] yield similar results.

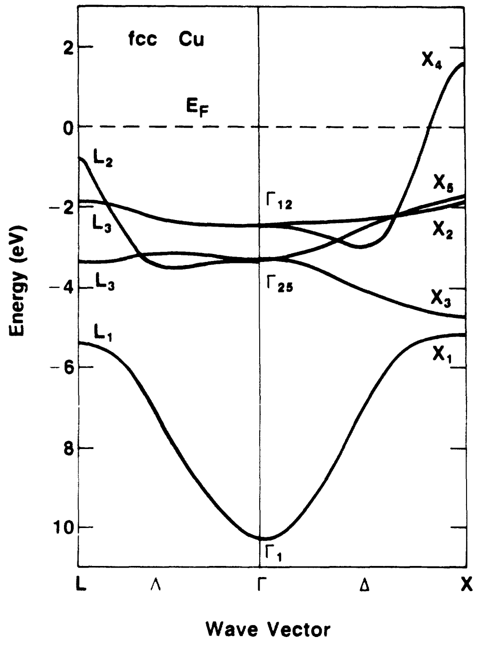

FIG. 2. Band structure for fcc copper at the experimental lattice constant. Energies are in eV measured relative to the Fermi level.

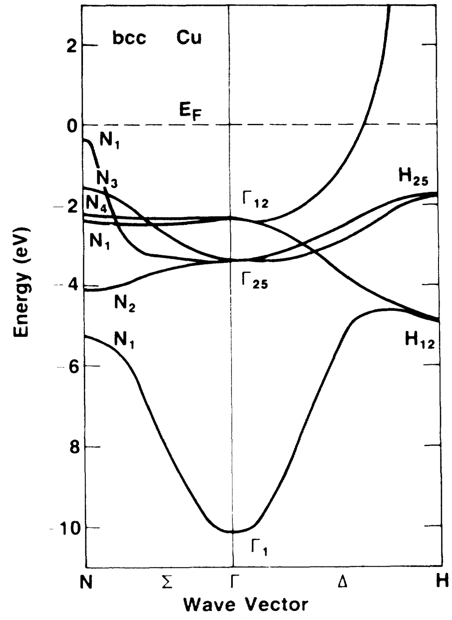

FIG. 3. Band structure for bcc copper at a lattice constant of $a=5.42$ a.u. Energies are in eV measured relative to the Fermi level.

Another issue is how accurate one might expect the local-density approximation to be. As noted in the previous work,[1] the local-density band structures are slightly more dispersive than indicated by angle-resolved photoemission measurements.[14] Typically, the discrepancy is on the order of $\sim$0.2–0.3 eV. It would be an interesting exercise to include the effects of dynamical screening and local fields on the placement of the energy bands.[12,15,16]

In Fig. 3 we present results for the energy bands of copper in the bcc structure. The lattice constant of the bcc structure was taken to be such that the atomic volume of the bcc and fcc structures is identical. As with the case of fcc copper, our band structure is nearly identical to the mixed-basis–pseudopotential work of Kang *et al.*[1] Given that we have a considerably weaker pseudopotential than the mixed-basis calculation, it is reassuring that the results agree so well for the both structures.

V. GROUND-STATE PROPERTIES OF fcc AND bcc COPPER

In Fig. 4 we present the total energy of copper as a function of the atomic volume. The energy zero was taken to be that of an isolated copper atom. Using the same

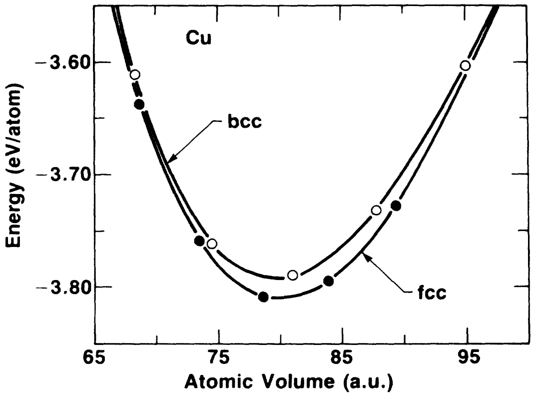

FIG. 4. Calculated total energy of bcc and fcc copper as a function of atomic volume. The solid line represents a Murnaghan equation-of-state (Ref. 26) fit to the calculated energy-vs-volume point.

ionic pseudopotential as for bulk copper, which was fitted by Gaussians, we find the total energy of an isolated Cu "pseudoatom" to be −1272.55 eV. This value includes an estimated spin-polarization correction of 0.23 eV.[17] The energy per atom for our calculated equilibrium fcc structure is −1276.38 eV, leading to a cohesive energy of about 3.83 eV.

For both the bcc and fcc structures we calculated five energy-versus-volume points and fitted an equation-of-state curve to the calculated points. Also, in Tables II and III we present the resulting cohesive energies, lattice constants, and bulk moduli. In Table II we compare our work to experiment[13,18] and other calculations[1,11,19] for fcc copper. We find the best agreement for the lattice constant with all calculations within 0.02 Å of experiment. This is a typical local-density-approximation (LDA) result, i.e., the lattice constant is the most accurate property obtained. The LDA cohesive energies tend to overestimate the experimental values. This appears to be a general result, as evidenced by a number of LDA calculations.[10,11] As a guideline we feel an underestimate of the cohesive energy could be indictive of an inadequate basis. We found the bulk modulus to be the most difficult property to reproduce. With 40 orbitals per atom we found a bulk modulus of ~2.6 Mbar. By increasing the basis to 60 orbitals per atom, we found that the bulk modulus was reduced by ~30%. We feel most of the remaining discrepancy in Table II with respect to bulk modulus would be removed by assuming a larger basis. [Also, the cohesive energy might be increased to the values given by the KKR and augmented-spherical-wave (ASW) methods.]

TABLE III. Ground-state properties for bcc copper as calculated using Gaussian orbitals with *ab initio* pseudopotentials.

Property	Theor.
Cohesive energy (eV)	3.81
Lattice constant (Å)	2.87
Bulk modulus (Mbar)	1.85

In Table IV we compare our results to other all-electron calculations[20] and to experiment[21] for the equation of state of fcc copper. We have not included zero-point pressure corrections and the experiment is not at zero temperature. Nonetheless, the agreement is satisfactory. Our pseudopotential result predicts a slightly higher pressure as a function of volume owing to the larger bulk modulus we find as compared to experiment. Again, we feel this is a result of our basis and not an intrinsic problem with the pseudopotential.

With respect to bcc copper, we find very similar properties. Within our computational accuracy, about the only difference we find is a small upward shift of the energy-versus-volume curve. Given results for other metals, e.g., Mo and W, in which the fcc and bcc curves have similar properties, perhaps our results are not too surprising.[22] We may also compare to other theoretical estimates for the fcc-versus-bcc energy difference. A linear combination of muffin-tin orbitals (LMTO) calculation by Skriver[23] gave the energy difference between fcc and bcc copper, at the known equilibrium volume for fcc copper, to be about 15 meV, which is in good accord with our work, which yields a value of about 20 meV. Other estimates are higher, e.g., the Kang *et al.*[1] value of 75 meV and a generalized pseudopotential calculation by Moriarty,[24] which estimated a value of 49 meV.

With respect to a possible fcc→bcc transition under pressure, from Fig. 4 we estimate that the volume for such a transition would have to be less than ~65 a.u., which corresponds (Table IV) to a pressure greater than ~500 kbar. Experimentally,[25] there is no evidence for a

TABLE II. Comparison of ground-state properties of fcc copper with other theoretical calculations and experiment. ASW corresponds to augmented-spherical-wave method. See Table I for other notations.

Property	KKR[a]	ASW[b]	fcc copper MB[c]	GO	Expt.[d]
Cohesive energy (eV/atom)	4.09	4.05	3.35	3.83	3.50
Lattice constant (Å)	3.58	3.60	3.62	3.62	3.60
Bulk modulus (Mbar)	1.55	1.29	1.50	1.88	1.42

[a] Reference 11.
[b] Reference 19.
[c] Reference 1.
[d] References 13 and 18.

TABLE IV. Comparison with other theoretical calculations (notation as in Table II) for the equation of state of fcc copper. The volume is normalized to the experimental equilibrium volume of copper of 79.2 a.u., and the pressures are in in Mbar.

V_0/V	APW[a]	LMTO[a]	GO	Expt.[b]
1.0	−0.04	−0.08	0.00	0.00
1.1	0.13	0.09	0.20	0.16
1.2	0.37	0.32	0.46	0.39
1.3	0.67	0.63	0.77	0.69
1.4	1.06	1.01	1.14	1.07
1.5	1.54	1.49	1.55	1.56

[a]From Ref. 20.

[b]From Ref. 21.

fcc→bcc transition up to 770 kbar, which is consistent with our calculation.

In contrast to our work is the mixed-basis–pseudopotential calculation of Kang *et al.*[1] These workers find a bcc copper phase which is unusually stable at 6% volume contraction compared to a fcc phase, although still above the fcc phase in energy. They also found another metastable phase at a 7% expansion. This double minimum is not reproduced in our calculation. At present, we are unable to account for this discrepancy. However, we are not convinced that the energy difference can be accounted for by charge-density arguments given by Kang *et al.*[1] While it is clear that "symmetry" breaking of the *d* charge density can occur, it is not clear as to why this should have a "sudden onset" at a particular volume which would produce the double minimum they observe. Additional, independent calculations on the differences between fcc and bcc copper should prove very interesting.

VI. CONCLUSIONS

We have examined the ground-state properties of copper using *ab initio* pseudopotentials[8,9] constructed within a local-density approximation[7] and a basis of localized orbitals, i.e., Gaussians. We find that by using a core site which includes the Cu 3*d* radial wave function, we can still obtain accurate results, i.e., our 3*d* wave function is only valid in a region far outside the radial–wave-function maximum. This procedure is consistent with the pseudopotential philosophy that only the wave function in the bonding region is important, but it is different than the procedure normally followed. Usually, one demands the wave function be accurate outside a point between the outermost node and the radial–wave-function maximum.[8,9] However, copper is special in that the Cu 3*d*-state radial–wave-function maximum is so far removed from the Wigner-Seitz radius. By using a procedure which allows a larger core size than normally allowed, we were able to construct a weaker pseudopotential than normally used. Such a potential allows a plane-wave formalism[5] to determine the total energy to be more readily implemented without loss of accuracy.

A second point to be made, in summary, is that we do not reproduce the double minimum in the energy-versus-volume curve of bcc copper obtained elsewhere.[1] Our results yield a bcc copper energy-versus-volume curve which is very similar to the fcc curve, i.e., contains only a single minimum.

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