PHYSICAL REVIEW B VOLUME 8, NUMBER 12 15 DECEMBER 1973

Total Energy as a Function of Lattice Parameter for Copper via the Self-Consistent Augmented-Plane-Wave Method*†

E. C. Snow

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544

(Received 9 July 1973)

The $X\alpha$ exchange approximation was used in self-consistent augmented-plane-wave calculations on metallic copper. The value assigned to α (0.7225) was chosen to yield zero pressure at the experimentally determined lattice spacing, and the calculations were carried out for six different lattice parameters. The total energy as a function of lattice parameter, resulting from these calculations, was used to determine pressure as a function of lattice parameter, cohesive energy, and compressibility. The cohesive-energy calculation gave 0.286 Ry, which is within 11% of the experimental value of 0.257 Ry. The compressibility, as calculated for two sets of calculated pressure as a function of lattice parameter, was found to agree with the experimental value to within 7% for one set of pressures and to within 4% for the other.

I. INTRODUCTION

With the development of large fast computers, many methods of determining the electronic structure of solids have become feasible. Such methods employ various approximations that simplify the calculations, but with minimal loss of accuracy. In two of these methods, namely, the nonrelativistic and the electrostatic approximations, the Hamiltonian operator for a crystal can be written as

$$H_{\text{op}} = -\sum_{\mu} \frac{\hbar^2}{2M_\mu} \nabla_\mu^2 - \sum_j \frac{\hbar^2}{2m_0} \nabla_j^2 + V(X_\mu, x_j),$$

where the first term is the kinetic energy associated with the motion of the nuclei of masses M_μ, the second term is the kinetic energy associated with the motion of the electrons of masses m_0, and the last term is the potential energy, which includes nuclear-nuclear, electron-nuclear, and electron-electron Coulomb interactions, plus the electron-electron exchange interactions. In the Born-Oppenheimer approximation, which is based on the assumption that the electronic motion can be treated separately from the nuclear motion since $M_\mu \gg m_0$, the first term in the above equation vanishes, yielding the electron Hamiltonian as

$$H_{\text{op}} \simeq -\sum_j \frac{\hbar^2}{2m_0} \nabla_j^2 + V(X_\mu, x_j).$$

The Schrödinger equation for the system is then given as

$$\left(-\sum_j \frac{\hbar^2}{2m_0} \nabla_i^2 + V(X_\mu, x_j)\right) U(X_\mu, x_j) = E(X_\mu) U(X_\mu, x_j),$$

where the energy $E(X_\mu)$ depends on the positions of the nuclei X_μ only as a parameter. $E(X_\mu)$ is the total energy considered in this calculation as a function of lattice parameter.

Recently, considerable effort has been concentrated on developing for the crystal Hamiltonian an approximation to the electronic-exchange-interaction term that can be used with reasonable accuracy to determine the electronic states of a solid. The purpose of the work described here was to apply one such exchange approximation in evaluating the energy bands of metallic copper, through use of the self-consistent augmented-plane-wave (APW) method, and to determine the total energy as a function of lattice parameter. These results were then used to obtain pressure as functions of lattice parameter, compressibility, and cohesive energy.

The $X\alpha$ exchange approximation, as used in this work, is the outgrowth of the $\rho^{1/3}$ approximation originally proposed by Slater.[1] Later, when Gaspar[2] and Kohn and Sham,[3] using a slightly different approach, derived a $\rho^{1/3}$ exchange approximation that differed from Slater's by a constant multiplier of $\frac{2}{3}$, it became evident that a reasonable exchange approximation could be obtained by multiplying the Slater exchange by an adjustable parameter α, which led to the $X\alpha$ method. Many other exchange approximations, both local and nonlocal, have been suggested, but the use of several of these on the energy bands of copper by Boring and Snow[4] failed to produce results that were significantly better than those obtained from the less complicated $X\alpha$ method.

Copper was chosen for the present work for several reasons. The author has done considerable work on the energy bands of copper,[5,6] and thus has a background of experience with that metal. The many calculations[7-12] and experimental results[13-16] on copper that are available in the literature provide useful comparisons. The author has also presented calculations on silver[17] and aluminum,[18] but copper has a lower atomic number than does silver, and, therefore, copper is less likely to be affected by relativistic effects, which were not considered in the present work; and aluminum has been studied in great detail by Ross and Johnson.[19] Furthermore, copper has a large number of d-like electrons in a nearly filled d band that is especially sensitive to small changes in the exchange potential used in the present calculations, whereas the broad sp band in aluminum is affected very little by such changes.

II. METHOD OF CALCULATION

The present calculations employ the APW method[20] for determining the energy bands. In this method, the "muffin-tin" approximation to the potential, which has been found to give very good results in energy-band calculations of this type, is used. In the "muffin-tin" approximation, the electronic potential-energy function is considered to be spherically symmetric within nonoverlapping spheres centered at each lattice site and constant in the region between spheres. DeCicco[21] has found that the "non-muffin-tin" terms should have very little effect in a energy-band calculation of an fcc metal like copper, and therefore, these terms are not considered in the present calculations.

The self-consistent calculation is started with a potential that is generated by the superposition of atomic potentials centered at each lattice site. This potential is then used in the APW calculation to determine the energy bands and corresponding charge density of the filled Bloch states. The energies and charge densities of the core states are determined in a manner similar to that used in the Herman and Skillman[22] atomic calculations with the appropriate boundary conditions. The total charge density, core plus energy band, is then used to generate a new potential for use in the next iteration of the self-consistent process. This iterative process is continued until there is no significant difference between the one-electron energies obtained in two successive iterations. The details of the APW method of determining the energy bands are presented in an article by Mattheiss, Wood, and Switendick[23] and will not be repeated here.

This self-consistent method is used for calculations at various lattice parameters so that the total energy as a function of lattice parameter can be determined. Pressure, compressibility, and cohesive energy can then be determined and compared to experimental results and the results of previous calculations.

These calculations are all done for an appropriate value of the parameter α of the $X\alpha$ method, the choice of α still being somewhat of a question. In a recent paper, Schwarz[24] describes three methods for determining α in atomic calculations. In the first, suggested by Lindgren,[25] α is chosen so that the Hartree-Fock total energy, determined from the $X\alpha$ orbitals, is a minimum. This α, called $\alpha_{\min}$, has been evaluated for several elements by Kmetko[26] and Wood.[27] The second method, suggested by Berrondo and Goscinski,[28] is based on the quantum-mechanical virial theorem and recommends that the α_{vt} should be chosen so that the virial coefficient η, given by

$$\eta = \langle E_{\mathrm{PE}} \rangle / 2 \langle E_{\mathrm{KE}} \rangle ,$$

where $\langle E_{\mathrm{PE}} \rangle$ and $\langle E_{\mathrm{KE}} \rangle$ are the average potential and kinetic energies, respectively, calculated from the Hartree-Fock expression using $X\alpha$ orbitals, be equal to 1. The third method chooses α, called α_{HF}, so that the statistical total energy of the $X\alpha$ method equals the Hartree-Fock average energy of configuration[29–31] for the ground state of the atom. Schwarz has determined the values of α_{vt} and α_{HF} for the first 41 elements in the periodic table and has found that they differ by less than 0.0008 in every case except hydrogen. Slater and Wood[32] have recommended using α_{HF} in a solid calculation. Energy-band calculations similar to the one presented here, but using values of α given by Schwarz, have been done by Averill[33,34] and Hattox.[35]

The α used in the present calculation was determined to be the one that would yield a virial coefficient equal to unity at the experimentally determined equilibrium lattice constant for 0 °K. This was done by evaluating the pressure for a series of self-consistent APW calculations, each for a different value of α. The pressure as a function of α for these calculations was then plotted, and the α determined that would yield zero pressure. The pressure for each calculation was determined by

$$P = \frac{1}{3V} \left(2 \langle E_{\mathrm{KE}} \rangle + \langle E_{\mathrm{PE}} \rangle \right) ,$$

where V is the volume, and $\langle E_{\mathrm{KE}} \rangle$ and $\langle E_{\mathrm{PE}} \rangle$ are the same average energies used in the virial coefficient described above. Averill[36] has shown that this expression for pressure can be derived from the virial theorem for the $X\alpha$ method in the "muffin-tin" approximation. Obviously, the α that yields zero pressure also yields unity for the virial coefficient.

III. RESULTS

A. Determining α of the $X\alpha$ Method

Each self-consistent calculation used a 500-point linear radial mesh (for integration of the radial Schrödinger equation) and was done for 2048 points in the first Brillouin zone. The self-consistency criterion used in these calculations was that the resulting pressure vary by less than 1 kbar between two successive iterations. This generally required from 8 to 10 iterations, with each iteration taking about 4 min of computer time on the

TABLE I. Pressure, potential energy, kinetic energy, total energy, and cohesive energy for four self-consistent APW calcaultions on copper, with different values of α.

α	Pressure (kbar)	E_{PE} (Ry)	E_{KE} (Ry)	Total energy (Ry)	Cohesive energy[a] (Ry)
0.70000	33.70	−6553.880469	3276.967354	−3276.913115	0.2798
0.70635	24.35	−6556.226508	3278.132847	−3278.093661	0.2814
0.72000	3.64	−6561.271765	3280.638812	−3280.632953	0.2850
0.77000	−60.34	−6579.806760	3289.854829	−3289.951931	0.2967

[a] Experimental value of cohesive energy is 0.257 Ry (Ref. 37).

CDC 7600. It is of interest to note that the variation in total energy between two successive iterations was about 10^{-6} Ry when the pressure criterion was satisfied.

The resulting pressures for four values of α, calculated at the experimentally determined lattice parameter ($A_0 = 6.8086$ a.u.), are given in Table I, along with the kinetic, potential, total, and cohesive energies. Pressure as a function of α is plotted in Fig. 1, while total energy as a function of α, for the same four calculations, is given in Fig. 2. The total energy is very nearly a linear function of α, as it is in atomic $X\alpha$ calculations, but the pressure is not. However, the smooth curve drawn through the average of these data points on the pressure-vs-α plot in Fig. 1 predicts an α of about 0.7225 for zero pressure. This value of α was used to evaluate the total energy as a function of lattice parameter, the cohesive energy, and the compressibility.

Figure 3 is a plot of the cohesive energy as a function of α for the same four calculations. Again, the total energy for both solid and atomic calculations is very nearly a linear function of α. However, the nonlinearity of the cohesive energy indicates that the linear dependence of total energy on α cannot be carried too far. Even so, the cohesive energy is a smooth function that increases with increasing α.

If the cohesive-energy curve given in Fig. 3 is extended to intersect the experimental value of 0.257 Ry,[37] the intersection will occur at a value of α somewhat below 0.64. This value of α would give Fermi-surface "necks" that are too large in radius and a pressure of well over 100 kbar at the experimentally determined lattice spacing, both of which conditions would be in very poor agreement with experimental results. This indicates that the $X\alpha$ method (using a single α, as in the present calculations) does not simultaneously give cohesive energy, pressure, and a Fermi surface that are in the best possible agreement with experiment. However, the calculated values of cohesive energy differ from the experimental value by less than 16% throughout this range of α. This difference is small when we consider that the cohesive energies given in Table I are the difference between two calculated energies, each of the order of 3200 Ry. It is quite possible, that better precision in the present calculations could reduce the differences between the calculated and experimentally determined cohesive energies.

B. Total Energy, Cohesive Energy, and Compressibility

Calculations were made for six values of the lattice parameter A of fcc copper, each with $\alpha = 0.7225$. The lattice parameters chosen corresponded to that of the experimentally determined Wigner-Seitz cell volume V_0 and to 10% and 20%

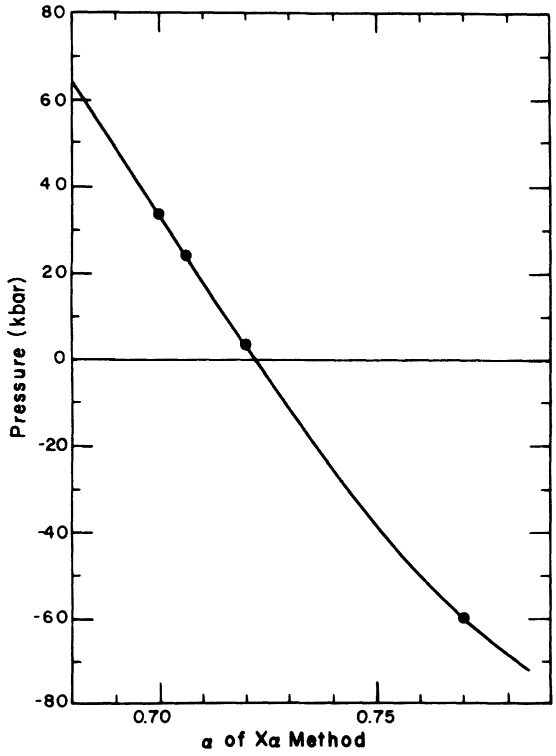

FIG. 1. Pressure vs α of the $X\alpha$ method, for copper ($A = A_0$).

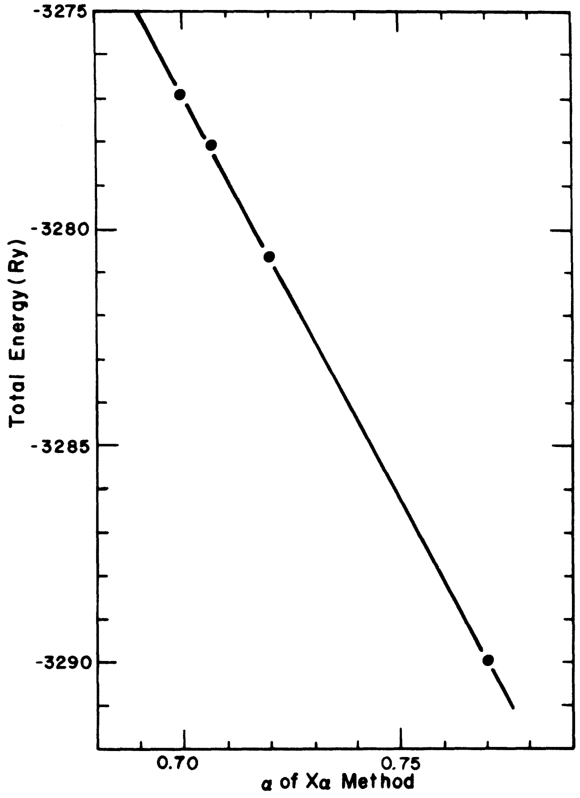

FIG. 2. Total energy vs α of the $X\alpha$ method, for copper ($A = A_0$).

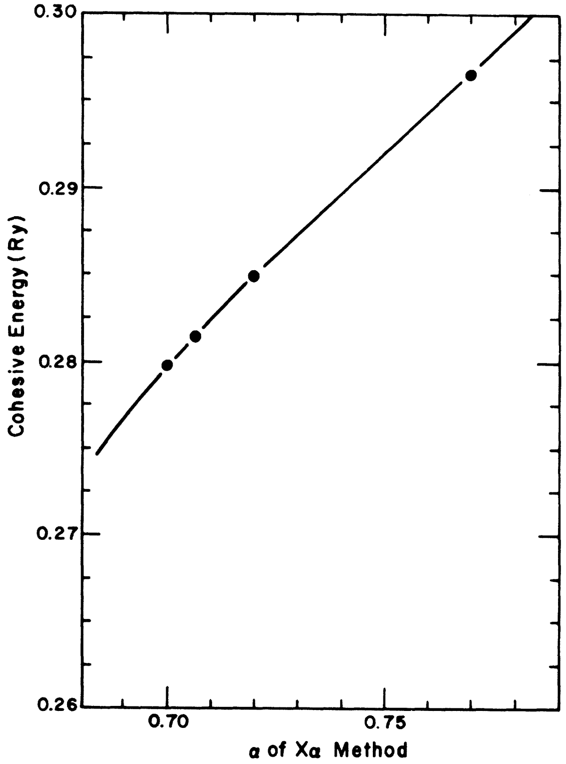

FIG. 3. Cohesive energy vs α of the $X\alpha$ method, for copper ($A = A_0$).

reductions and 10%, 20%, and 60% expansions of that volume. Each calculation, with the exception of the 60% expansion, was converged until the pressure, as determined by using the virial theorem, varied by less than 1 kbar between two successive iterations. This usually took from 10 to 15 iterations, at 5 min per iteration on a CDC 7600 computer. As in the calculations discussed in Sec. III A, when this convergence criterion was met, the change in total energy was about 10^{-6} Ry between two successive iterations. The calculation corresponding to 60% volume expansion was converged so that the total energy varied by less than 10^{-4} Ry between successive iterations. Each calculation was done for 2048 points in the first Brillouin zone and used in 500-point linear radial mesh.

The total energies resulting from these calculations are given in Table II. Also given are the volume in cubic atomic units and the lattice parameters in atomic units. These data are plotted in Fig. 4, showing the total energy as a function of lattice parameter. This curve shows a definite minimum near the experimentally determined lattice parameter A_0, as predicted by the results given in the Sec. III A.

The cohesive energy was determined as the difference between the total energy, at the minimum of the energy-vs-lattice-parameter curve in Fig. 4, and the statistical total energy for the atomic calculation using the same value of α. The atomic calculation for the ^2S ground state was a non-spin-polarized Herman-Skillman[22] calculation using the $X\alpha$ exchange approximation. These total energies are approximately -3281.098 and -3280.813 Ry for the metallic and atomic calculations, respectively. This gives a cohesive energy of 0.286 Ry, compared to the experimental value[37] of 0.257 Ry. The fractional difference between this calculated value and the experimental value of cohesive ener-

TABLE II. Total energy for six values of the lattice parameter for copper ($\alpha = 0.7225$).

V/V_0	Volume (V) (a.u.^{3})	Lattice parameter (A) (a.u.)	Total energy (Ry)
0.80	63.125 6584	6.320 5563	−3281.074 352
0.90	71.0163 639	6.573 6434	−3281.093 786
1.00	78.907 0739	6.808 6129	−3281.098 246
1.10	86.797 7809	7.028 3957	−3281.094 903
1.20	94.688 4870	7.235 2308	−3281.087 333
1.60	126.251 3250	7.963 4021	−3281.044 053
∞ (free atom)	∞	∞	−3280.812 553

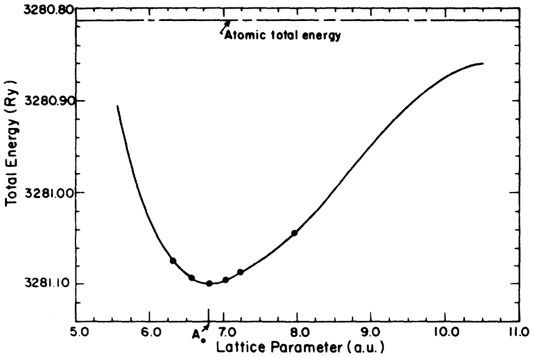

FIG. 4. Total energy as a function of lattice parameter for copper ($\alpha = 0.7225$).

gy is 0.112 or about 11%. This is fairly good agreement, considering that the calculated value of cohesive energy is about 0.00001 of the total energies used to determine it.

The bulk modulus was determined by

$$B = V \frac{d^2E}{dV^2} \bigg|_{V=V_0}$$

and was found to be 1396.6 kbar, as compared to the experimental value[37] of 1335.0 kbar. This calculated value differs from the experimental value by about 4.5%.

C. Energy Bands

The energy bands for five calculations of copper, for the lattice parameters corresponding to the experimental value and to 10% and 20% volume expansion and contraction, are given in Fig. 5. The energy bands in this figure are shown in the direction of high symmetry in the first Brillouin zone of the fcc structure. The value of α used for all five calculations was 0.7225.

Energy differences, for these calculations, that represent the bandwidths and relative locations of the bands with respect to each other and with respect to the Fermi energy are given in Table III. The energy differences identified as $\Gamma_{25'} - \Gamma_1$ and $X_5 - \Gamma_1$ give the relative location of the d band with respect to the bottom of the sp band, while the differences $E_f - X_5$ and $E_f - L_3$ locate the top of the d band with respect tothe Fermi energy. The energy differences $X_5 - X_1$ and $X_{4'} - \Gamma_1$ give the bandwidths of the d band and sp band, respectively. The difference $E_f - L_{2'}$ represents the location of the high-symmetry point having an eigenvalue nearest the Fermi energy. This energy difference also gives a measure of the "neck" radius of the copper Fermi surface.

Similar sets of energy differences for experimental results and results of previous calculations are given in Refs. 5–17 but are not included in Table III.

The relative movements of the bands and the changes in bandwidth as the lattice parameter is increased are expected; namely, both the d band and the sp band narrow and the d band moves toward the bottom of the sp band. If the lattice parameter were to continue increasing, the d band would continue to become narrower and would eventually drop completely below the sp band, approaching the $3d$ atomic state in the limit of infinite lattice parameter. The Fermi energy "follows" the d band, moving toward the bottom of the sp band faster than does the energy of the $L_{2'}$ point, resulting both in a decrease in the energy difference $E_f - L_{2'}$ and a decrease in the "neck" radius of the copper Fermi surface.

The only experimental results that can be considered for comparison with the results given in Table III are those for the experimental lattice parameter $V/V_0 = 1.0$. Such comparison with the results of photoemission studies[13–15] shows that the calculated d band appears to be too broad and too

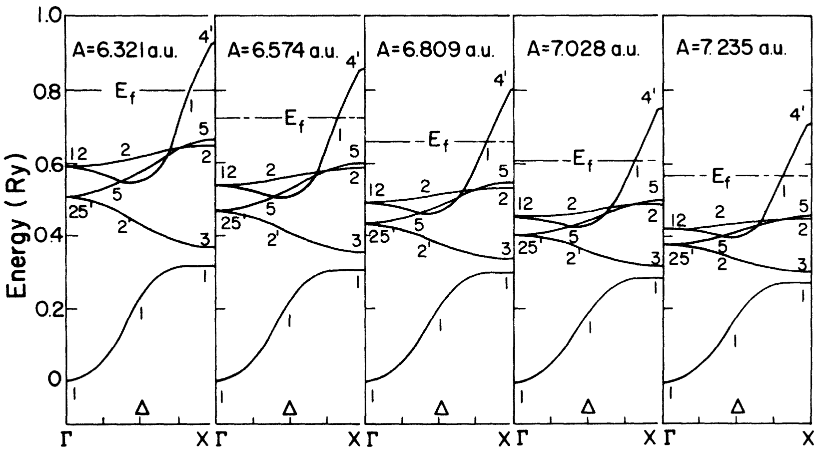

FIG. 5. Energy bands for fcc copper as a function of lattice parameter ($\alpha = 0.7225$).

TABLE III. Energy differences (in Ry) for states that indicate position and widths of the *sp* band and *d* band (Ry) ($\alpha = 0.7225$).

V/V_0	$\Gamma_{25'}-\Gamma_1$	$X_5-\Gamma_1$	X_5-X_1	$X_{4'}-\Gamma_1$	E_f-X_5	E_f-L_3	$E_f-L_{2'}$
0.8	0.507	0.688	0.356	0.926	0.132	0.152	0.120
0.9	0.469	0.603	0.297	0.857	0.121	0.138	0.088
1.0	0.435	0.549	0.252	0.801	0.114	0.127	0.063
1.1	0.405	0.504	0.217	0.754	0.108	0.119	0.041
1.2	0.379	0.465	0.189	0.715	0.103	0.113	0.024

close to the Fermi energy. The $E_f - L_{2'}$ energy difference also appears to be too large, as compared to the results of Spicer[13] or Lindau and Wallden.[16] The merit of such comparisons is questionable, but the value of $E_f - L_{2'}$ given here as 0.063 Ry is only slightly larger than the 0.061 Ry calculated by Janak *et al.*[12] as the value that gives a "neck" radius in good agreement with experiment.

IV. DISCUSSION

The main purpose of this work was to evaluate the $X\alpha$ exchange approximation as used in self-consistent APW calculations for a metal, viz. metallic copper. To achieve this end, the total energy as a function of lattice parameter was determined, and the results were used to determine cohesive energy and compressibility. Comparison of the calculated quantities with experimental results gives a measure of the accuracy of the calculations and indicates the worth of the method employed. Of course, a complete evaluation of a method would involve a large number of calculations on a variety of materials; other calculations similar to the present one have already been done by Averill[33,34] and Hattox.[35]

To evaluate the results of the present work, we first consider the method proposed to determine the α that was used in the $X\alpha$ exchange approximation. As pointed out above, the α that should give zero pressure at the experimentally determined lattice spacing was found to be 0.7225. The calculated pressure at the experimental lattice spacing resulting from the use of this value of α was 1.3 kbar instead of zero. However, the 1.3 kbar represents a difference in the potential energy, and in twice the kinetic energy, of only approximately 0.002 Ry. This is a very small fraction (on the order of 3×10^{-7}) of 6562 Ry, which is the approximate magnitude of each of the two energies. The virial coefficient, defined as the ratio of the negative of the potential to twice the kinetic energy, was 0.999 999 7 for this calculation, or very nearly 1.0, the desired value.

The total energy as a function of lattice parameter, as one would expect for this calculation, has a minimum very close to the experimentally determined lattice parameter, as shown in Fig. 4. The first derivative of the total energy as a function of volume evaluated at V_0, found to be about -4×10^{-5} in atomic units, indicates that the minimum occurs slightly outside the experimental value.

The cohesive energy obtained from the calculation at the experimental lattice spacing with $\alpha = 0.7225$ was 0.286 Ry. This value is within 11% of the experimental value of 0.257 Ry, and is probably within the experimental accuracy of determining the cohesive energy at 0 °K.

The calculated energy bands agree reasonably well with the results of photoemission studies, though such direct comparisons are somewhat questionable. However, the $E_f - L_{2'}$ energy difference of 0.063 Ry agrees very well with 0.061 Ry value that Janak *et al.*[12] give as corresponding to a "neck" radius of the copper Fermi surface, in agreement with experiment.

A significant result achieved in the present calculations is the agreement between the calculated and experimentally determined values for the bulk modulus, which differ by only about 4.5%. Indications are, however, that the calculated value would not change by a significant amount if a slightly different value of the exchange parameter α had been used in these calculations.

V. CONCLUSIONS

From the foregoing, one concludes that the $X\alpha$ method, as applied here, can be used to obtain, the total energy as a function of lattice parameter, the cohesive energy, and the compressibility, that are in good agreement with experimental values. However, the agreement with experiment would have been just about as good, if the α that satisfied the virial theorem for the atomic calculations ($\alpha = 0.70635$) had been used in the present calculations, even though this minimum of the energy-vs-lattice-parameter curve would then have been approximately 0.5% outside the experimentally determined lattice parameter. Consequently, this indicates that, from a practical point of view the value of α that satisfies the virial theorem is probably the best one to use in a calculation of this type, as was also shown by the calculations of Averiall[33,34] and of Hattox.[35]

*Work performed under the auspices of the U. S. Atomic Energy Commission.

†Based in part on the dissertation presented by E. C. Snow to the Dept. of Physics and Astronomy, University of Florida, in partial fulfillment of the requirements for the Ph. D. degree.

[1] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[2] R. Gaspar, Acta Phys. Hungary **3**, 263 (1954).

[3] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[4] Michael Boring and E. C. Snow, Phys. Rev. B **5**, 1221 (1972).

[5] E. C. Snow and J. T. Waber, Phys. Rev. **157**, 570 (1967).

[6] E. C. Snow, Phys. Rev. **171**, 785 (1968).

[7] B. Segal, Phys. Rev. **125**, 109 (1962).

[8] G. A. Burdick, Phys. Rev. **129**, 138 (1963).

[9] L. F. Mattheiss, Phys. Rev. **134**, A970 (1964).

[10] Shinya Wakoh, J. Phys. Soc. Jap. **20**, 1894 (1965).

[11] J. S. Faulkner, H. L. Davis, and H. W. Joy, Phys. Rev. **161**, 656 (1967).

[12] J. F. Janak, A. R. Williams, and V. L. Moruzzi, Phys. Rev. B **6**, 4367 (1972).

[13] C. W. Berglund and W. E. Spicer, Phys. Rev. **136**, A1044 (1964).

[14] A. H. Lettington, Phys. Lett. **9**, 98 (1964).

[15] D. E. Eastman and J. K. Cashion, Phys. Rev. Lett. **24**, 310 (1970).

[16] I. Lindau and L. Wallden, Solid State Commun. **8**, 1147 (1971).

[17] E. C. Snow, Phys. Rev. **172**, 708 (1968).

[18] E. C. Snow, Phys. Rev. **158**, 683 (1967).

[19] M. Ross and K. W. Johnson, Phys. Rev. B **2**, 4709 (1970).

[20] J. C. Slater, Phys. Rev. **51**, 846 (1937).

[21] P. D. De Cicco, Doctoral thesis (M.I.T., 1965) (unpublished).

[22] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J., 1963).

[23] L. F. Mattheiss, J. H. Wood, and A. C. Switendick, in *Methods in Computational Physics*, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic, New York, 1968), Vol. 8, p. 63.

[24] K. Schwarz, Phys. Rev. B **5**, 2466 (1972).

[25] I. Lindgren, Phys. Rev. Lett. **19**, 382 (1966); Ark. Fys. **31**, 59 (1966).

[26] E. A. Kmetko, Phys. Rev. A **1**, 37 (1970).

[27] J. H. Wood, Int. J. Quantum Chem. **35**, 747 (1970).

[28] M. Berrondo and O. Goscinski, Phys. Rev. **184**, 10 (1969).

[29] T. M. Wilson, J. H. Wood, and J. C. Slater, Phys. Rev. A **2**, 620 (1970).

[30] J. C. Slater, T. M. Wilson, and J. H. Wood, Phys. Rev. **179**, 28 (1969).

[31] J. C. Slater, *Advances in Quantum Chemistry* (Academic, New York, 1972), Vol. 6.

[32] J. C. Slater and J. H. Wood, Int. J. Quantum Chem. **4S**, 3 (1971).

[33] Frank W. Averill, Phys. Rev. B **4**, 3315 (1971).

[34] Frank W. Averill, Phys. Rev. B **6**, 3637 (1972).

[35] T. M. Hattox, Doctoral thesis (University of Florida, 1972) (unpublished).

[36] Frank W. Averill, Doctoral thesis (University of Florida, 1971) (unpublished).

[37] Karl A. Gschneidner, Jr., in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. 16.