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Fong, C.Y.

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C. Y. Fong and Marvin L. Cohen

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Energy Band Structure of Copper by the
Empirical Pseudopotential Method

C. Y. Fong

Inorganic Material Research Division

Lawrence Radiation Laboratory, Berkeley, California.

Department of Physics, University of California

Davis, California*

Marvin L. Cohen^{†, **}

Department of Physics and Inorganic Materials Research Division

University of California

Berkeley, California

* Present address.

[†] Professor, Miller Institute for Basic Research in Science, 1969-70.

** Supported in part by the National Science Foundation.

Abstract

The electronic band structure of copper is calculated using the Empirical pseudopotential method (EPM). A nonlocal d-wave potential with a damping factor is used to provide the potential for the d-electron. The results agree well with the available experimental data and with theoretical band calculations using other methods. It is anticipated that the EPM can be used for other noble metals and even extended to noble metal compounds, transition metals, and transition metal compounds.

Pseudopotentials obtained from experimental data have been extremely valuable in yielding information about the electronic structure of solids.¹ Fermi surface data has been used for metals, and optical properties have yielded a vast amount of information about the potentials appropriate to semiconductors and insulators.^{1,2} This later method has been called the Empirical Pseudopotential Method (EPM) and very accurate band structure calculations have resulted³ from its application. It has even been possible to associate the pseudopotentials with the atoms in a semiconductor compound and to use these potentials in different crystal structures or different compounds.⁴ It was this possibility which motivated the present work. An EPM scheme for the noble metals could allow band calculations of noble metal compounds. We also anticipate that the present work could result in an EPM for transition metals and would allow calculations of transition metal compounds which are currently the objects of intensive study.

Because of the strong s-d interaction⁵ between the $(4s)^1$ and $(3d)^{10}$ electrons, and the fact that the $(3d)^{10}$ electrons experience a strong core potential, a local pseudopotential calculation is not possible. This is what has motivated some authors to try new schemes, and some very successful analysis of the electronic properties of Cu⁶ have been done based on schemes⁷ which involve

the mixing of the tight-binding method for the d-bands and a pseudopotential-like method for the s- and p-bands. We have been able to treat the d-bands without resorting to the tight-binding method by using an $\ell = 2$ non-local potential. This method was also used by Lee and Falicov⁸ for potassium and by Fong and Cohen⁹ for KCl

The experimental information required for our calculations are given by Spicer,¹⁰ Gerhardt¹¹ and Fadley and Shirley.¹² Spicer, used photoemission data to derive the width of the d-bands and the gap of the p-band at $L(L_{2'})$ to the Fermi level. The values for these gaps are 2.8 eV and 0.35 eV respectively. Gerhardt measured the piezoreflectance of Cu for different crystal orientations. He obtained energy gaps between the filled d-bands and the vacant p band at X as well as the gaps between the filled p band and the vacant s band at L. The values he obtained are $E(X_5 \rightarrow X_{4'}) = 4.0$ eV and $E(L_{2'} \rightarrow L_1^u) = 4.5$ eV, where u refers to the upper L_1 band. Fadley and Shirley determined the width of the d-bands to be 3.0 eV by x-ray spectroscopy. We will compare these values with the theoretical values after we describe the theoretical calculation.

The crystal structure of copper is f.c.c. with lattice constant $a = 3.61 \text{ \AA}$.¹³ There is one atom per unit cell; we set the origin of the coordinate system at a Cu atom. The pseudopotential

Hamiltonian has the form

$$\mathcal{H} = -\frac{\hbar^2}{2m} \nabla^2 + V_L(\vec{r}) + V_{NL}(\vec{r}) \quad (1)$$

where $V_L(\vec{r})$ is the local pseudopotential and $V_{NL}(\vec{r})$ is the non-local pseudopotential which has been constructed to act on the d-electron states. The potential $V_L(\vec{r})$ is expanded in the reciprocal lattice

$$V_L(\vec{r}) = \sum_{|\vec{G}|} V(\vec{G}) e^{i\vec{G}\cdot\vec{r}}, \quad (2)$$

where \vec{G} is a reciprocal lattice vector in units of $(2\pi/a)$; $V(\vec{G})$ is the pseudopotential form factor and Ω is the volume of the unit cell. We have truncated $V(\vec{G})$ at $|\vec{G}|^2 \geq 12$. The periodic part of the wavefunction is expanded in a plane wave set to solve the secular equation corresponding to Eq. (1). For energies, $|\vec{k} + \vec{G}|^2 \leq E_1$ in units of $(2\pi/a)^2$ the Hamiltonian is treated exactly. For $E_1 < |\vec{k} + \vec{G}|^2 \leq E_2$ the states are treated using the Löwdin¹⁴ perturbation scheme as modified by Brust.¹⁵

The form of the d-like nonlocal pseudopotential is^{3,4}

$$V_{NL}(\vec{r}) = \sum_j P_2^\dagger V_2(\vec{r} - \vec{R}_j) P_2 \quad (3)$$

where \vec{R}_j is the lattice vector. P_2^\dagger and P_2 are projection operators. They act on the two wavefunctions respectively when the matrix elements of the V_{NL} are calculated and project out the $\ell = 2$ component only.

$$\begin{aligned} V_2(\vec{r} - \vec{R}_j) &= A_2 \quad \text{for } |\vec{r} - \vec{R}_j| \leq R_s \\ &= 0 \quad \text{otherwise} \end{aligned} \quad (4)$$

A_2 and R_s are treated as disposable parameters. In order to obtain good convergence for the energy of the d-bands, we use a \vec{k} -dependent damping factor similar to the one given by Jacobs.¹⁶ The matrix elements of the V_{NL} then take the following form:

$$\begin{aligned} \langle \vec{k} + \vec{G} | V_{NL} | \vec{k} + \vec{G}' \rangle &\rightarrow \quad (5) \\ e^{-\alpha \left\{ \frac{1}{2k_F} [|\vec{k} + \vec{G}| - \kappa] \right\}^2} &\cdot \langle \vec{k} + \vec{G} | V_{NL} | \vec{k} + \vec{G}' \rangle \cdot e^{-\alpha \left\{ \frac{1}{2k_F} [|\vec{k} + \vec{G}'| - \kappa] \right\}^2} \end{aligned}$$

where α and κ are treated as parameters and k_F is the Fermi momentum of copper in the free electron approximation. We neglect the contribution of V_{NL} for $E_1 < |\vec{k} + \vec{G}|^2 \leq E_2$. Even with the above damping factor, we still require $E_1 = 26.1$ and $E_2 = 50.1$ in order to have the convergence of the few important energy gaps at Γ , X and L to be within 0.1 eV. The size of the matrix is of the order of 140×140 .

The numerical values for the parameters are: $V(111) = 0.0131$ Ry, $V(200) = 0.0189$ Ry, $V(220) = 0.0162$ Ry, $V(311) = 0.0014$ Ry,

$A_2 = -9.9044$ Ry, $R_s = 0.814 \text{ \AA}$, $\alpha = 0.433$ and $\kappa = 2.63(2\pi/a)$.

If a continuous curve is fitted to the local pseudopotential form factors, the first zero is at $k = 1.9 k_F$. The corresponding value given by Harrison¹⁷ is at $1.76 k_F$. The value of R_s is smaller than the radius of the free Cu^+ ion which is 0.96 \AA .¹⁸ The value of κ is set roughly equal to the average length of the vector \vec{G} contributing to the band X_5 for $|\vec{G}|^2 \leq E_1$. In this way, we get the best convergence for the energies of the d-bands. Because of the time consumed in diagonalizing a matrix of size 140×140 , we have calculated the band structure only for 46 points in 1/48th of the Brillouin zone. The band structure is plotted in Fig. 1. The width of the d-bands can be specified roughly by the energy gap of $X_1 \rightarrow X_5$. For the present case, the gap is at 3.29 eV which agrees reasonably well with the experimental value of 3.0 eV. The calculated energy gap $X_5 \rightarrow X_4$ is 3.95 eV and the gap of $L_2 \rightarrow L_1^u$ is 4.26 eV. These agree well with the corresponding values determined by Gerhardt of 4.0 and 4.5 eV respectively. The density of states derived from the band structure is compared with the one given by Spicer in Fig. 2. The large density of states region starts at - 1.8 eV (all energies measured with respect to the Fermi surface E_F) and ends up at - 5.2 eV; the corresponding measured

results by Spicer are - 2.1 eV and - 5.44 eV. The peak positions in the calculation are - 2., - 3.4 and - 4.3 eV. The experimental results are - 2.1, - 3.62 and - 4.66 eV. the agreement is quite good. The height of the first two peaks do not agree with the experimental results. This discrepancy also appears in the calculations by Snow.¹⁹

It is interesting to compare our present results with a few representative calculations^{5, 19, 20} by various methods. We compare the results in Table I by listing the values of the important energy gaps along with the experimental data.

The agreement between the EPM and the other first-principles calculations is very encouraging, and we believe that these results should encourage EPM calculations for other noble metals, noble metal compounds, transition metals, and transition metal compounds.

Acknowledgement

Part of this work was done under the auspices of the United States Atomic Energy Commission.

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TableCaption

Table I. Comparison of present results with a few representative calculations by various methods and the experimental data.

Figure Captions

Figure 1. Band structure of copper.

Figure 2. The density of states derived from the band structure and from experiment (Spicer, ref. 10).

Table I.

Energy gaps (eV) Symmetry	Authors Segall ⁵ (Green's function)	Snow ¹⁹ (APW) Slater=5/6	Butler, etc. (MOPW) ²⁰	Gerhardt ¹¹ (exp.)	Spicer ¹⁰ (exp.)	Fadley ¹² Shirley (exp.)	Cohen Fong
$\Gamma_{25'} \rightarrow \Gamma_{12}$	1.03	0.73	0.79				0.8
$\Gamma_1 \rightarrow \Gamma_{25'}$	4.47	4.94	5.41				4.99
$X_1 \rightarrow X_5$	4.12	2.96	3.45		2.8	3.	3.29
$X_3 \rightarrow X_5$	3.6	2.51	3.01				2.96
$X_5 \rightarrow X_{4'}$	4.69	4.18	3.92	4.			3.95
$L_{2'} \rightarrow L_1^{u*}$	5.74		4.6	4.5			4.26
$L_3^{l*} \rightarrow L_{2'}$	3.6	3.06	2.95				3.24
$L_{2'} \rightarrow E_F$	0.63	0.35			0.35		0.35
$E_F \rightarrow X_{4'}$	2.39	2.26					2.29

* The subscripts
 u means the upper L_1 band.
 l means the lower L_3 bands.

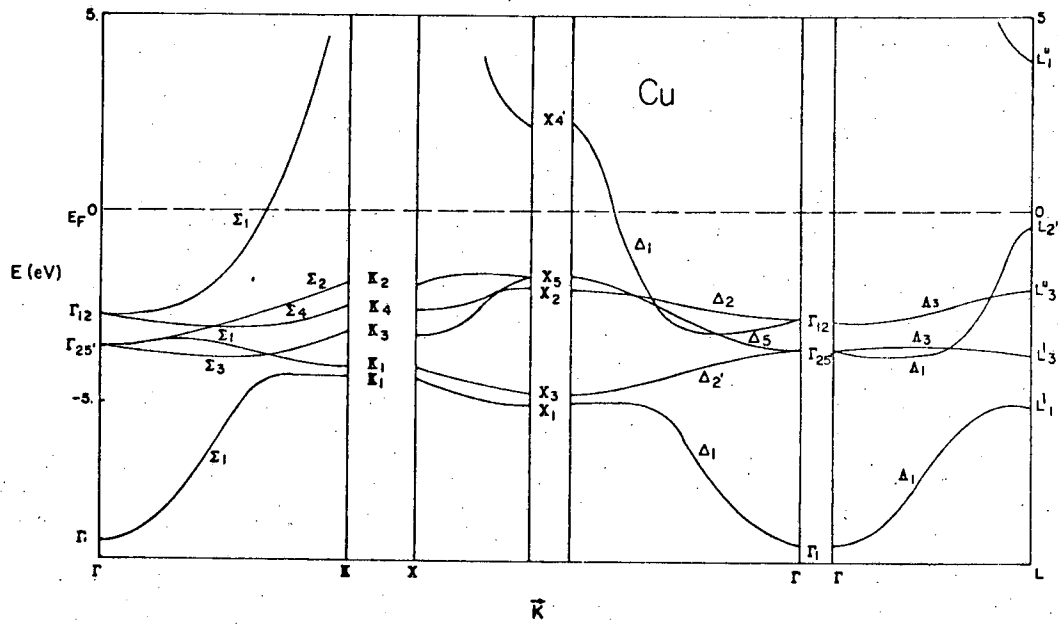


Fig.1

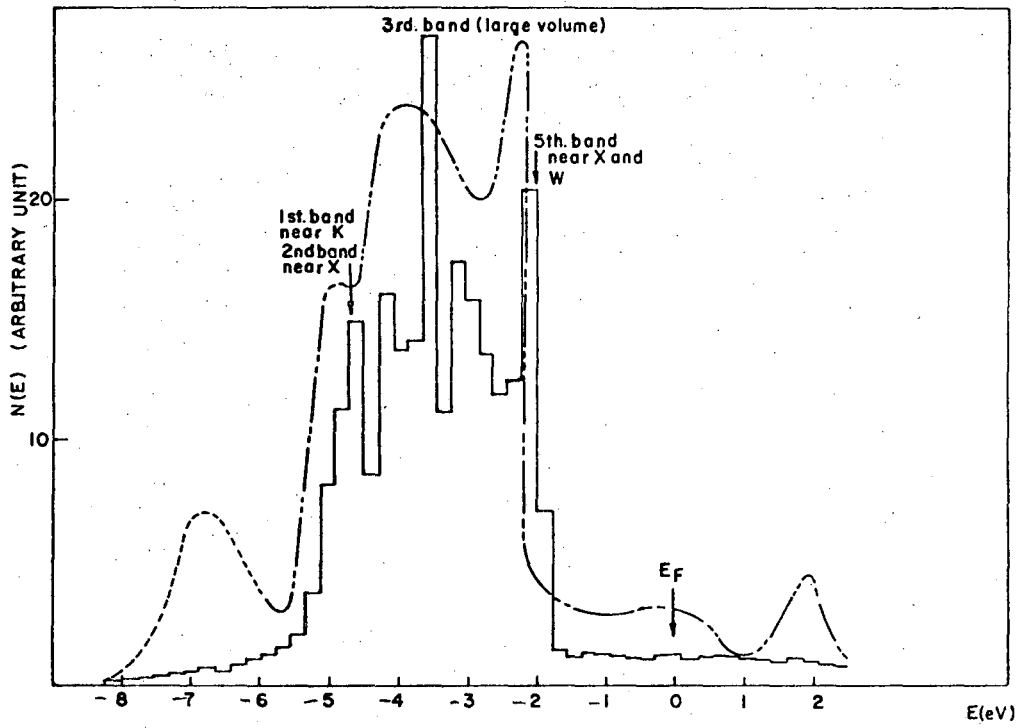


Fig.2

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