Lawrence Berkeley National Laboratory

Recent Work

Title

WAVELENGTH MODULATION SPECTRUM OF COPPER

Permalink

<https://escholarship.org/uc/item/1588k7sk>

Authors

Fong, C.Y.
Cohen, Marvin L.
Zucca, R.R.L.
et al.

Publication Date

1970-10-01

c.2

RECEIVED
LAWRENCE
RADIATION LABORATORY

NOV 13 1970

LIBRARY AND
DOCUMENTS SECTION

WAVELENGTH MODULATION SPECTRUM OF COPPER

C. Y. Fong, Marvin L. Cohen, R. R. L. Zucca,
J. Stokes, and Y. R. Shen

October 1970

AEC Contract No. W-7405-eng-48

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

3 | LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

UCRL-20364

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Wavelength Modulation Spectrum of Copper

by

C. Y. Fong

Department of Physics, University of California
Davis, California 95616

and

Marvin L. Cohen^{*}, R. R. L. Zucca[†], J. Stokes, and Y. R. Shen
Department of Physics, University of California,
Berkeley, California 94720

and

Inorganic Materials Research Division,
Lawrence Radiation Laboratory
University of California,
Berkeley, California 94720

^{*}Supported in part by the National Science Foundation.

[†]Fellow, Consejo Nacional de Investigaciones Cientificas y Tecnicas,
Argentina.

ABSTRACT

The wavelength modulation spectrum of Cu is presented at 7 °K in the range of $2.0 \leq \hbar\omega \leq 6.0$ eV. The band structure of Cu calculated by the empirical pseudopotential method is used to compute the imaginary part of the dielectric function $\epsilon_2(\omega)$ and the logarithmic derivative of the reflectivity, $R'(\omega)/R(\omega)$. Good agreement between theory and experiment is obtained at the absorption edge and at higher energies using the one-electron approximation if dipole matrix elements are calculated from wavefunctions including core contributions rather than the pseudowavefunctions. The transitions causing the structure in $R'(\omega)/R(\omega)$ are identified.

Recent advances in optical derivative spectroscopy have helped significantly in obtaining detailed knowledge about the band structure of semiconductors.¹ Applications of this technique to metals, however, have been scarce. There have been measurements² of the electroreflectance of Ag and Au, but there is some uncertainty³ associated with the interpretation of these results. Thermorelectance and piezorelectance have yielded⁴ valuable information about noble metal band structure and in the case of piezorelectance the deformation potentials of Cu were measured. In this letter, we present the wavelength modulation spectrum of Cu from 2.0 to 6.0 eV taken at 7 °K. To our knowledge, this is the first application of wavelength modulation spectroscopy to metals at low temperatures. Our derivative spectrum of Cu shows clearly better resolution than those

obtained by other methods. The experimental set-up was described briefly elsewhere.⁵ The Cu sample used in our measurements was the same single crystal used in cyclotron resonance experiments by Kip et al.⁶ After electropolishing the surface, the sample was quickly transferred to the low-temperature dewar to avoid surface contamination. The sample temperature could be varied easily from 7°K to 300°K. Here, for the sake of clarity, we present in Fig. 1 only the Cu derivative spectrum taken at 7°K. We have also measured the normal reflectivity spectrum of Cu which agrees well with that of Gerhardt.⁴

The origin of most of the structure in the measured derivative spectrum of Cu can be determined using the theoretical band structure of Cu, calculated by the empirical pseudopotential method.⁷ In the calculation we used four form factors for the local pseudopotential and four other parameters relating to a nonlocal pseudopotential with $\ell = 2$. These eight parameters are determined by fitting to the optical data obtained by Gerhardt⁴ and the photoemission data of Spicer.⁸ Because of the complication in defining the parameters for the nonlocal pseudopotential, we give only the local form factors: $V(|\vec{G}|^2 = 3) = 0.0131$, $V(4) = 0.0189$, $V(8) = 0.0162$ and $V(11) = 0.0014$ Ry. (In Ref. 7, $V(4)$, $V(8)$ and $V(11)$ were inadvertently omitted.) The parameters related to the nonlocal pseudopotential are defined and their values are given in Ref. 7. The lattice constant of Cu is 3.61 Å. The resulting band structure is shown in Fig. 2. We have shifted the Fermi level upward by 0.25 eV compared to the results given in Ref. 7. In this way, the first peak relative to E_F of the density

of states for the d-bands is at - 2.25 eV. Most of the structure in the density-of-states agrees with more recent photoemission data by Krowlikowski and Spicer⁹ and by Smith¹⁰ to an accuracy of 0.1 eV. The radii of the Fermi surface along [100], [110] and [111] are 1.41, 1.32, and 0.29 Å⁻¹. The measured values by Shoenberg¹¹ are 1.40, 1.38 and 0.28 Å⁻¹.

The imaginary part of the dielectric function, $\epsilon_2(\omega)$, (constant dipole matrix elements are not assumed; they are computed directly from the pseudowavefunctions) is calculated by the method described in Ref. 12 with a mesh of 89-points in 1/48-th of the Brillouin zone. The results are shown in Fig. 3, accompanied by the experimental curve measured by Gerhardt.⁴ The agreement between theory and experiment near the 5 eV region is good. However, this $\epsilon_2(\omega)$ is about an order of magnitude less than the experimental results near 2.0 eV. This suggests either that the dipole matrix elements used in the calculation are not accurate or some kind of enhancement is present in that region.

An enhancement (e.g. indirect processes) involving the product of valence and conduction band density-of-states is excluded. As shown in Ref. 7 there is virtually no structure in the conduction band density-of-states. The valence band has structure at - 2.25, - 3.8 and - 4.5 eV, measured with respect to the Fermi surface. The largest peak is at 3.8 eV. The product of valence and conduction band density-of-states would rise sharply at $\hbar\omega = 2.25, 3.8$ eV. However, the slope of the product with respect to the photon energy would be positive because of the structureless character of the conduction band density-of-states. The corresponding

$R'(\omega)/R(\omega)$ would therefore have a positive value instead of negative value as obtained by the experiment between $2.0 \leq \hbar\omega \leq 4.0$ eV.

Our matrix elements can, however, be inaccurate because the pseudowavefunctions with s and p character are not orthogonal to the inner core states. The importance of using wavefunctions including core contributions instead of pseudowavefunctions to calculate the dipole matrix elements in metals has been recognized by Muller and Phillips¹⁸ and by Animalu and Harrison¹⁹. Our treatment is different from theirs in that the core contributions are explicitly included. The actual wavefunction of the conduction electron is

$$\psi(\vec{r}) = \frac{1}{N} \left\{ \varphi(\vec{r}) - \sum_b \varphi_b \langle \varphi_b | \varphi \rangle \right\} \quad (1)$$

where $\varphi(\vec{r})$ is the pseudowavefunction. The φ_b 's are the wavefunctions for the core states, and N is the normalization constant. In this work, we take φ_b to be tight-binding wavefunctions of 3s and 3p states. The 3s and 3p states are approximated by hydrogenic wavefunctions with effective atomic number, Z_{eff} , equal to 13.5. The $\epsilon_2(\omega)$ with matrix elements calculated using $\psi(\vec{r})$ is shown in Fig. 3. It is in excellent agreement with the experimental result. The value of $Z_{\text{eff}} = 13.5$ roughly corresponds to the minimum value of Z such that the overlap between neighboring cells for the tight-binding wavefunctions can be neglected. The agreement between theory and experiment for $\epsilon_2(\omega)$ at the absorption edge is so encouraging that one may be motivated to use this approach to resolve the discrepancies between theory and experiment in the optical spectra of alkali metals.

To calculate $R'(\omega)/R(\omega)$, we use the interband $\epsilon_2(\omega)$ in Fig. 3 calculated using the $\psi(\vec{r})$ wavefunctions and add to this the free electron Drude contribution as discussed by Ehrenreich and Cohen.¹³ The free electron contribution to the dielectric function, $\epsilon^f(\omega)$, calculated from Drude theory is¹⁴

$$\epsilon^f(\omega) = 1 - 4\pi n e^2 [m^* \omega(\omega + \frac{i}{\tau})]^{-1} \quad (2)$$

where n , e and m^* are the density, charge and effective mass of the free electrons respectively. We use $m^* = 1.42 m_0$ which is estimated at the belly using the matrix elements of the / present calculation; the measured value by Schulz¹⁵ is $1.45 m_0$, where m_0 is the bare electron mass. τ is the relaxation time and its value is approximately 2.0×10^{-14} sec.^{14, 16} With the quoted value of τ , we can neglect the imaginary part of $\epsilon_2^f(\omega)$.

The $R'(\omega)/R(\omega)$ is then calculated by the method described in Ref. 17 and is plotted in Fig. 1. The general structure of the calculated and the experimental $R'(\omega)/R(\omega)$ agrees very well. There is some discrepancy in the magnitude of the two results. The interband transitions start at 2.1 eV. Most of the transitions near this energy come from $\Delta_5 \rightarrow \Delta_1$ ($5 \rightarrow 6$, $4 \rightarrow 6$) and all transitions from the 5th-band to the Fermi surface. We shall refer to these points in $\vec{k}$ -space as osculating points (using the nomenclature of Mueller and Phillips¹⁸). The structure near 3.2 eV arises mainly from a large volume effect of $5 \rightarrow 6$ and $4 \rightarrow 6$ transitions. The corresponding contours of the energy difference between the 6th band and the 4th and 5th bands are roughly parallel to the Fermi surface. The contour will intersect along Δ very close to X. The calculated $R'(\omega)/R(\omega)$ shows some small structure

at 3.7 eV; the measured curve has a twin peaks structure at 3.8 and 3.95 eV. The contribution to this structure comes from an osculating point $\Sigma_1 \rightarrow \Sigma_1$ ($3 \rightarrow 6$) and a large volume effect from $5 \rightarrow 6$, $4 \rightarrow 6$ and $3 \rightarrow 6$ transitions with energy contours close to the Fermi surface. The effect of a critical point with M_1 symmetry at 3.96 eV from $X_5 \rightarrow X_4$ transition does not show up clearly in the calculated $R'(\omega)/R(\omega)$ but does show up in the calculated $\epsilon_2(\omega)$. We associate it with the upper structure of the twin peaks in the experimental results. The first zero in the calculated $R'(\omega)/R(\omega)$ is at 4.37 eV which is in excellent agreement with the experimental value of 4.4 eV. Both $R'(\omega)/R(\omega)$ curves in Fig. 1 show two structures for photon energy $4.0 \leq \hbar\omega \leq 5.5$ eV. The lower energy structure starts with $L_{2'} \rightarrow L_1^u$ transitions at 4.25 eV resulting from an M_0 singularity and $\Sigma_1 \rightarrow \Sigma_1$ ($1 \rightarrow 6$) transition at 4.38 eV which is an osculating point. These critical points contribute structure over a background caused by a large volume effect which is mainly from $(5 \rightarrow 6)(4 \rightarrow 6)$ and $(3 \rightarrow 6)$ transitions in the region near the Fermi surface inside the BZ. The contribution to the upper energy structure comes mainly from the volume effects of $1 \rightarrow 6$ and $2 \rightarrow 6$ transitions near the Fermi surface. This composite structure ends at 5.3 eV experimentally. The calculated $R'(\omega)/R(\omega)$ has a corresponding zero at 5.2 eV. The two zeroes agree very well. Our results strongly support the comment made recently by Phillips²⁰ that the 5.0 eV peak in the measured $\epsilon_2(\omega)$ consisting of a threshold at 4.3 eV coming from $L_{2'} \rightarrow L_1^u$ and a shoulder at 4.8 eV corresponding to d band to Fermi surface transitions. However, our identification for the upper structure shows that it is mainly a volume effect

and is not from osculating points. The identifications are summarized in Table 1.

In conclusion the agreement between the theoretical and experimental $R'(\omega)/R(\omega)$ and $\epsilon_2(\omega)$ enables us to confirm: (a) the optical transitions in Cu are direct as concluded by Smith;¹⁰ (b) the identification of $X_5 \rightarrow X_4$ agrees with the result given by Mueller and Phillips¹⁸ and the comments on the composite nature of the 5.0 eV peak in $\epsilon_2(\omega)$ by Phillips.²⁰ However, the upper energy structure arises from volume effects. (c) Strong many-body effects are not necessary to obtain agreement between experiment and theory near the absorption edge. (d) The volume effect contributions to the optical properties of Cu are more important than the critical points at the symmetry points and along the symmetry lines. In addition, our present approach to the dipole matrix elements may be used to resolve the discrepancy between theory and experiment at the absorption edge for alkali metals.

ACKNOWLEDGMENT

We would like to thank Professor A. F. Kip for making the copper crystal available to us. Thanks are due to Dr. J. C. Phillips for a very helpful discussion during a crucial stage of the calculation. We would like to thank Professor L. M. Falicov for helpful discussions. We also thank J. P. Walter for the use of his program in calculating $R'(\omega)/R(\omega)$. Part of this work was done under the auspices of the United States Atomic Energy Commission.

REFERENCES

1. See, for example, M. Cardona, Solid state physics, (Suppl.) 11 (1969).

2. J. Feinlieb, Phys. Rev. Letters 16, 1200 (1966). W. N. Hauser and A. Prostack, Phys. Rev. 174, 500 (1968).
3. B. J. Parson, Phys. Rev. 182, 975 (1969).
4. U. Gerhardt, D. Beaglehole and R. Sandrock, Phys. Rev. Letters 19, 309 (1967). U. Gerhardt, Phys. Rev. 172, 651 (1968).
5. R. R. L. Zucca and Y. R. Shen, Phys. Rev. B1, 2668 (1970).
6. A. F. Kip, D. N. Langenberg and T. W. Moore, Phys. Rev. 124, 359 (1961).
7. C. Y. Fong and M. L. Cohen, Phys. Rev. Letters 24, 306 (1970).
8. W. E. Spicer, in International Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 13-16 September 1965. Proceedings, edited by F. Abeles (North-Holland Publishing Co., Amsterdam, 1966).
9. W. F. Krowlikowski and W. E. Spicer, Phys. Rev. 185, 882 (1969).
10. N. V. Smith, (to be published).
11. D. Shoenberg, Phil. Mag. 5, 105 (1960).
12. W. Saslow, T. K. Bergstresser, C. Y. Fong, M. L. Cohen and D. Brust, Solid State Comm. 5, 667 (1967).
13. H. Ehrenreich and M. H. Cohen, Phys. Rev. 115, 786 (1959).
14. H. Ehrenreich and H. R. Phillip, Phys. Rev. 128, 1622 (1962).
15. L. G. Schulz, Suppl Phil. Mag. 6, 102 (1957).
16. See for example: C. Kittel, Introduction to Solid State Physics, 3rd edition, p. 228, John Wiley and Sons, Inc., (1966).

17. J. P. Walter and M. L. Cohen, Phys. Rev. 183, 763 (1969).
18. F. M. Mueller and J. C. Phillips, Phys. Rev. 157, 600 (1967).
19. A. C. E. Animalu and W. A. Harrison, Bull. Amer. Phys. Soc. 12, 415 (1967).
20. J. C. Phillips, Phys. Rev. 187, 1175 (1969).

Table Caption

Table 1. Identification of the important interband transitions of Cu.

Figure Captions

- Figure 1 The measured $R'(\omega)/R(\omega)$ at $T = 7^\circ\text{K}$ and the calculated $R'(\omega)/R(\omega)$.
- Figure 2 Band structure of Cu.
- Figure 3 The measured $\epsilon_2(\omega)$ and the calculated $\epsilon_2(\omega)$.

Table I.

Identification of the Important Interband Transitions of Cu

Transitions	Energy (eV)	Symmetry	
$\Delta_5 \rightarrow \Delta_1$ (5 $\rightarrow$ 6, 4 $\rightarrow$ 6) and all the transitions from 5-th band to the Fermi surface.	2.1	Osculating point* Osculating points	
Large (5 $\rightarrow$ 6)(4 $\rightarrow$ 6) transition region inside the BZ near X and the Fermi surface	3.2	Volume effect	
$\Sigma_1 \rightarrow \Sigma_1$ (3 $\rightarrow$ 6)	3.7	Osculating point	
→ Large(5 $\rightarrow$ 6)(4 $\rightarrow$ 6) and (3 $\rightarrow$ 6) transition region inside BZ near X and the Fermi surface.	3.7	Volume effect	
$X_5 \rightarrow X_4'$ (4 $\rightarrow$ 6)(5 $\rightarrow$ 6)	3.96	M_1	
$L_2' \rightarrow L_1^u$ (6 $\rightarrow$ 7)	4.25	M_0	
$\Sigma_1 \rightarrow \Sigma_1$ (1 $\rightarrow$ 6)	4.38	Osculating point	
Large (5 $\rightarrow$ 6), (4 $\rightarrow$ 6) and (3 $\rightarrow$ 6) transitions inside BZ near the Fermi surface.	4.5	Volume effect	
Large (2 $\rightarrow$ 6) (1 $\rightarrow$ 6) transitions inside BZ near the Fermi surface.	5.0	Volume effect	

* follow the definition in Ref. 18.

Figure 1

FIG. 2

Fig. 3

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or*
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.*

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

TECHNICAL INFORMATION CENTER ON
LAWRENCE R. HARRIS, A. H. HARRIS
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720