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WAVELENGTH MODULATION SPECTRUM OF COPPER

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Wavelength Modulation Spectrum of Copper

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ABSTRACT

The wavelength modulation spectrum of Cu is presented at 7 ^{o}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 measurements[2] of the electroreflectance of Ag and Au, but there is some uncertainty[3] associated with the interpretation of these results. Thermoreflectance and piezoreflectance have yielded[4] valuable information about noble metal band structure and in the case of piezoreflectance 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 ^{o}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 Gerhardt[4] 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 Spicer[9] and by Smith[10] 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 $\mathring{A}^{-1}$. The measured values by Shoenberg[11] are 1.40, 1.38 and 0.28$\mathring{A}^{-1}$.

The imaginary part of the dielectric function, $\epsilon_2(\omega)$, (constant dipole matrix elements are <u>not</u> 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 Phillips[18] and by Animalu and Harrison[19]. Our treatment is different from theirs in that the core contributions are explicitly included. The actual wavefunction of the conduction electron is

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

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 $Z_{eff} = 13.5$ 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 is[14]

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

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 Schulz[15] 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 Phillips[18]). 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 Phillips[20] 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 Phillips[18] 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.

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Table Caption

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

Figure Captions

Figure 1 The measured $R'(\omega)/R(\omega)$ at $T = 7\ ^{o}K$ 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→6, 4→6) and all the transitions from 5-th band to the Fermi surface.	2.1	Osculating point* Osculating points
Large (5→6)(4→6) transition region inside the BZ near X and the Fermi surface	3.2	Volume effect
$\Sigma_1 \rightarrow \Sigma_1$ (3→6)	3.7	Osculating point
Large(5→6)(4→6) and (3→6) transition region inside BZ near X and the Fermi surface.	3.7	Volume effect
$X_5 \rightarrow X_4'$ (4→6)(5→6)	3.96	M_1
$L_2' \rightarrow L_1^u$(6→7)	4.25	M_0
$\Sigma_1 \rightarrow \Sigma_1$ (1→6)	4.38	Osculating point
Large (5→6), (4→6) and (3→6) transitions inside BZ near the Fermi surface.	4.5	Volume effect
Large (2→6) (1→6) transitions inside BZ near the Fermi surface.	5.0	Volume effect

*follow the definition in Ref. 18.

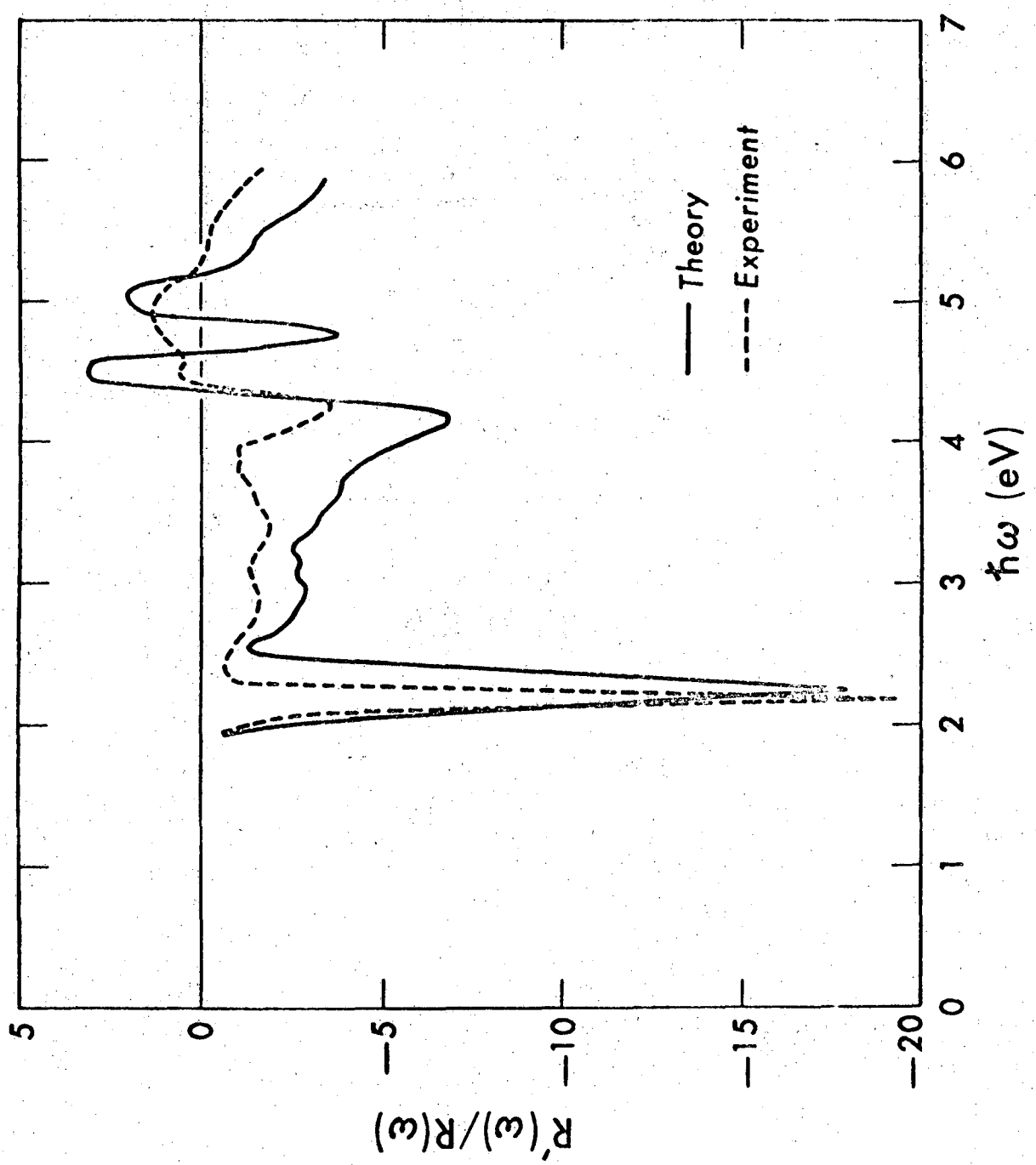

Figure 1

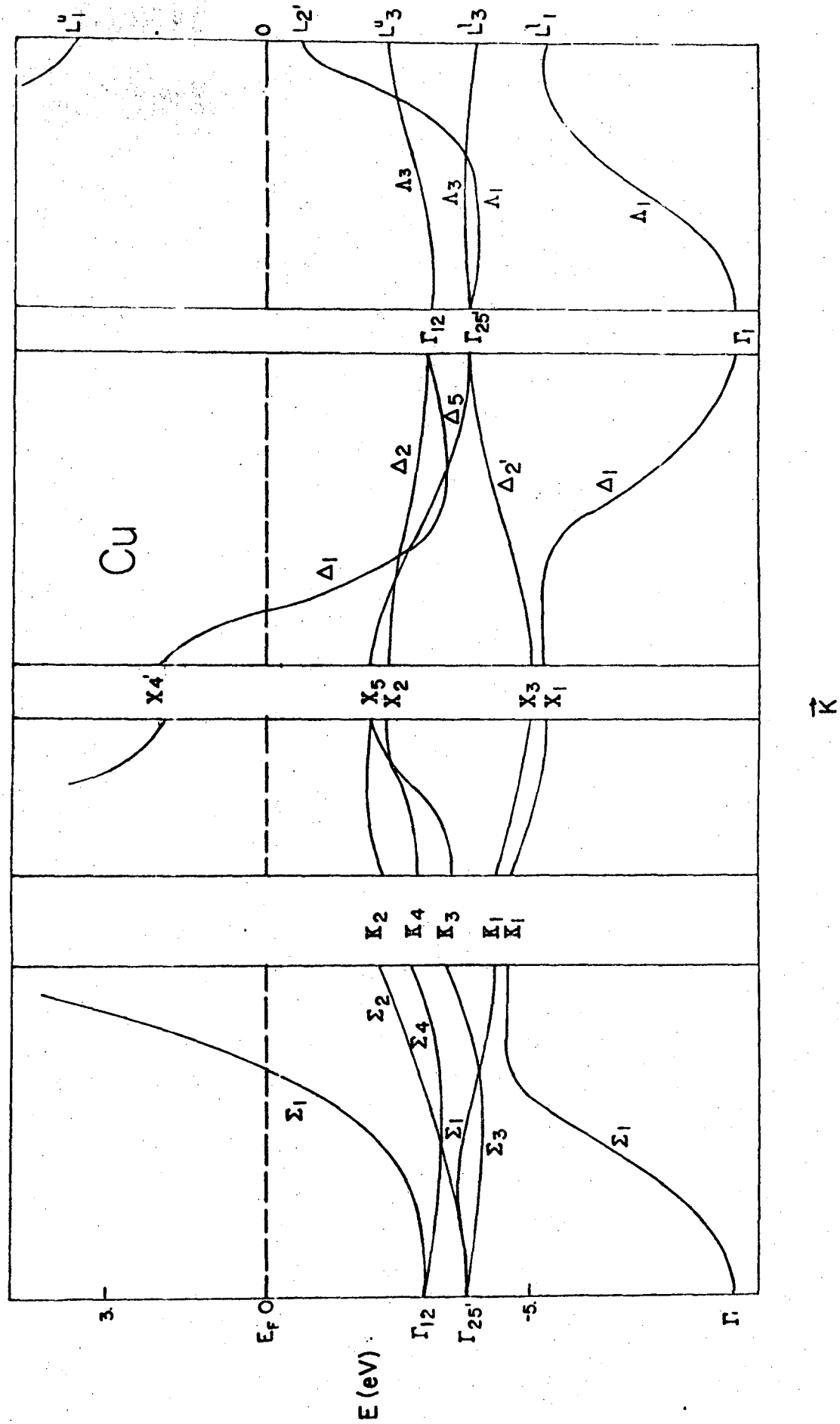
Cu
E (eV)
3
E_F 0
-5
Γ_{12}
$\Gamma_{25'}$
Γ_1
$\vec{K}$
Σ_1
Σ_2
Σ_4
Σ_3
K_2
K_4
K_3
K_1
X_4'
X_5
X_2
X_3
X_1
Δ_1
Δ_2
Δ_5
Δ_2'
Λ_3
Λ_1
L_1^u
L_2'
L_3^u
L_3^l
L_1^l

FIG. 2

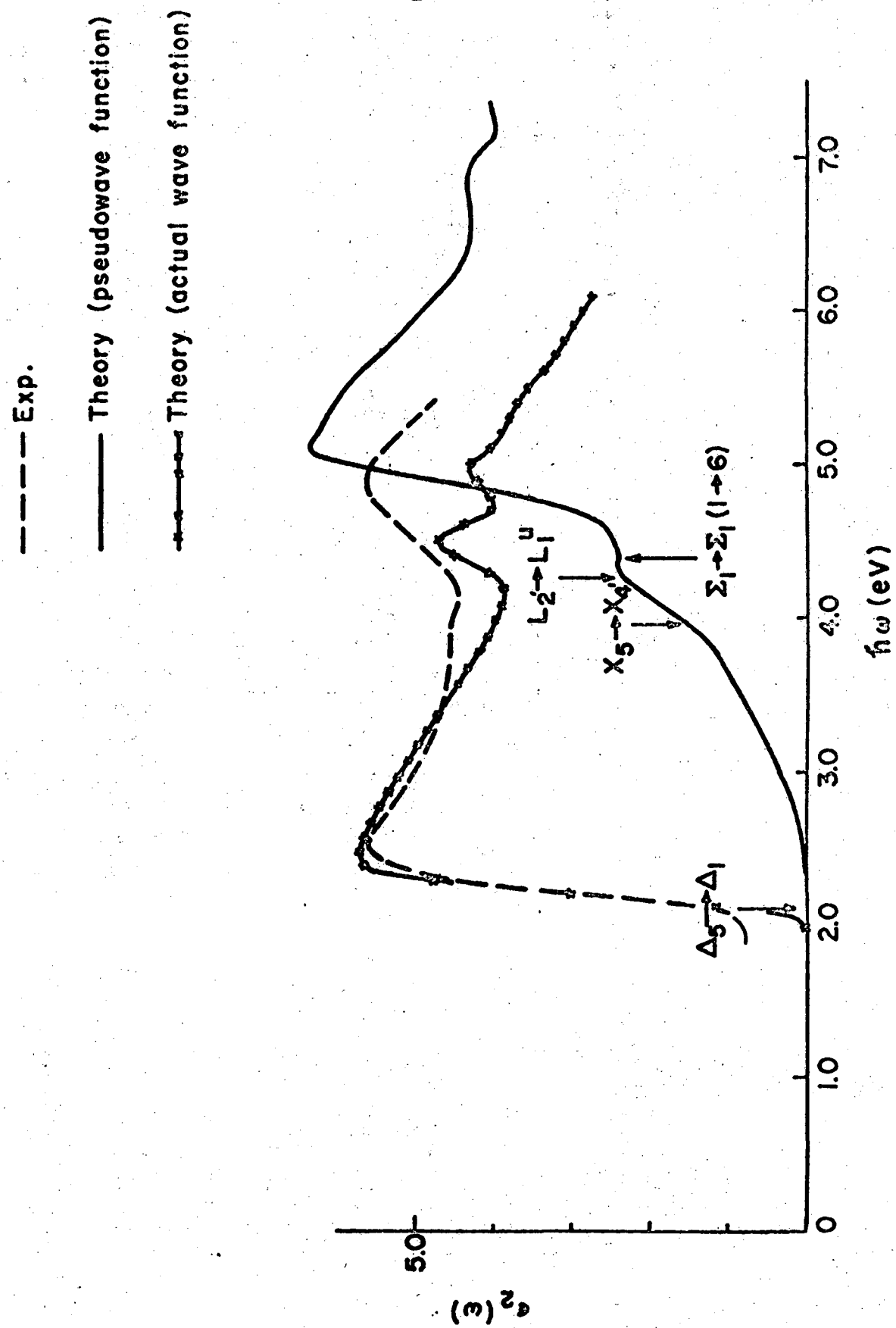
Exp.
Theory (pseudowave function)
Theory (actual wave function)
$\Delta_5' \to \Delta_1$
$L_2' \to L_1^u$
$X_5 \to X_4'$
$\Sigma_1 \to \Sigma_1 (1 \to 6)$
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
$\hbar\omega$ (eV)
5.0
$\epsilon_2(\omega)$

Fig. 3

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