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Independent electron calculation of $L_3M_{4,5}M_{4,5}$ and $M_{2,3}M_{4,5}M_{4,5}$ Auger line shapes for Cu metal*

Peter J. Feibelman and E. J. McGuire
Sandia Laboratories, Albuquerque, New Mexico 87115

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We have calculated the L_3VV and $M_{2,3}VV$ Auger line shapes of Cu metal, within an independent-electron tight-binding model. The calculated line shapes do not show the sharp features which are seen experimentally, a result which lends further credence to the validity of the "quasiatomic" picture of these Auger lines. We describe two possible mechanisms which might underlie the presence of the "quasiatomic" spectral features.

I. INTRODUCTION

Until recently, Auger-electron spectra from solids have been obtained primarily in order to identify the atoms present. However, now that high-resolution, loss-, and background-corrected Auger spectra are available for a number of materials,[1,2] it is of interest to attempt to extract from them whatever further information they may contain. Specifically, one may hope to derive surface (or bulk, depending on the Auger electron energy) electronic-structure information from valence-band[3] Auger line shapes.

The fundamental feature of valence-band Auger line shapes that makes their analysis a subject for the theorist, is that such line shapes seem rarely, if ever, to conform to the predictions of simple density-of-states (DOS) models.[4] Thus it is necessary, in most cases, to take account of matrix-element variation across the band. *A priori* it is not known, for a given material, whether such variation is principally the result of band-structure effects, in which case an independent-particle description of the Auger line should be sufficient, or whether many-electron phenomena, such as the repulsion between the two holes in the final state, might he dominant. In the case of the $L_{2,3}VV$ lines of Si(111) and Si(100) it has recently been shown[5,6] that band-structure effects in themselves are sufficient to explain the discrepancy between observed line-shapes and corresponding DOS models. The present work represents an attempt to see whether a similar simple picture (i.e., an independent-electron model) can also explain the surprising valence-band Auger spectra of Cu metal, which have been the focus of much recent work.[2]

On the basis of the excellent agreement for Cu between ultraviolet-photoemission-spectroscopy data[7] and band-theory calculations,[8] one might anticipate equally good agreement between valence-band Auger spectra and band theory. However, as is shown in Fig. 1, for example, the L_3VV Auger spectrum of Cu metal is found to be a series of sharp lines (~1-2 eV wide), not at all what one would predict on the basis of a simple DOS model. Other valence-band Auger lines for Cu ($L_3M_{2,3}M_{4,5}$,[2(e)] $M_1M_{4,5}M_{4,5}$,[2(a)] and[2(a)] $M_{2,3}M_{4,5}M_{4,5}$) also show more and/or sharper structure than the corresponding DOS models.

To date the main progress that has been made toward an understanding of the Cu valence-band Auger spectra has been the recognition that the number and positions of the features seen in them can be interpreted reasonably well on the basis of a comparison to the corresponding Auger spectra of *atomic* Cu.[2(b)-2(d),9] Thus the number and energy separations of the peaks seen are attributed to the various possible two-hole con-

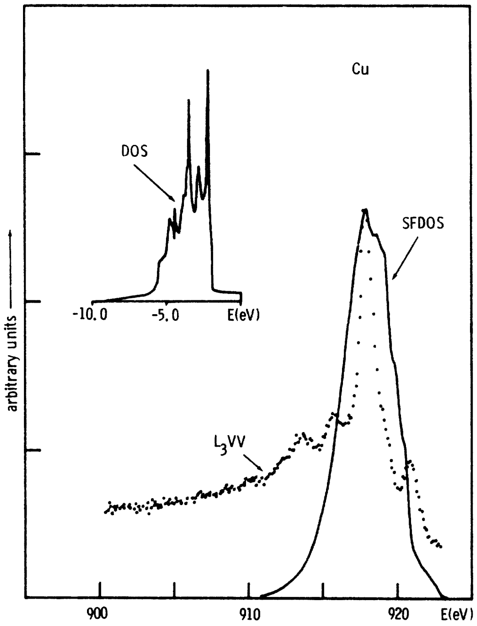

FIG. 1. Comparison of measured Cu L_3VV Auger spectrum (dots), after Ref. 2(b), with the self-convolution of the Cu DOS (curve labeled SFDOS). The Cu DOS itself, taken from Ref. 8, is shown in the inset.

figurations left behind in atomic Cu Auger decays and to the hole-hole repulsion energies for each of these configurations.

Although the atomic interpretation of the Cu-metal Auger spectra has apparently been quite successful, it is as yet an incomplete one in that the reason why it should work is not known. Specifically, if the atomic model is valid it should be possible to calculate the widths of the features seen in the metal spectra and to show why they are so sharp despite the fact that the *d* bands in Cu are ~3.5 eV wide, and would therefore appear to permit valence-band holes to migrate away from the site of an Auger decay quite rapidly. At the same time, there has not yet been an attempt to see whether a full-scale independent-electron calculation might not also provide an adequate, as well as more easily understood, interpretation of the Cu Auger data. One would not expect matrix-element variation with orbital angular momentum to play the same role in Cu as it did in Si.[5,6] In this latter case the discrepancy between the $L_{2,3}VV$ Auger spectrum and the DOS model was found[5,6] to be due to the dominance of matrix elements involving valence *p* electrons over those involving *s* electrons; in Cu we expect (cf. below) only one orbital angular momentum value, $l=2$, to be important in the L_3VV and $M_{2,3}VV$ spectra. However, it is still conceivable that the matrix elements involving electrons from the various *d* subbands, might conspire to cause structure in the Cu Auger spectra that is not present in a simple DOS model.[4]

Thus despite the apparent success of the atomic picture we have calculated the L_3VV and $M_{2,3}VV$ spectra of Cu metal on the basis of a band-structure model. As in Ref. 6 for Si we have carried out the calculation by combining a linear-combination-of-atomic-orbitals (LCAO) parametrization of the band structure of a Cu film[10] [with (001) surfaces] with Auger matrix elements calculated using Hermann-Skillman[11] atomic orbitals. Unfortunately, as is shown in Figs. 2 and 3, the resulting L_3VV and $M_{2,3}VV$ line shapes are in very poor agreement with the data. Thus since we believe that the LCAO band-structure model we have used should be adequate to predict at least the qualitative features of the Auger spectra [particularly of the L_3VV spectrum, which, by virtue of its being at ~900 eV, should be relatively free of uncertainties associated with our lack of knowledge of the Cu (001) surface], we are led to conclude that the atomic interpretation of these spectra is likely to be correct.

The remainder of this paper is divided into two parts. In Sec. II we present a brief description of our LCAO calculation. In Sec. III we recapitulate our conclusions and speculate on how a theory underlying the atomic model of the Cu Auger spectra might be constructed.

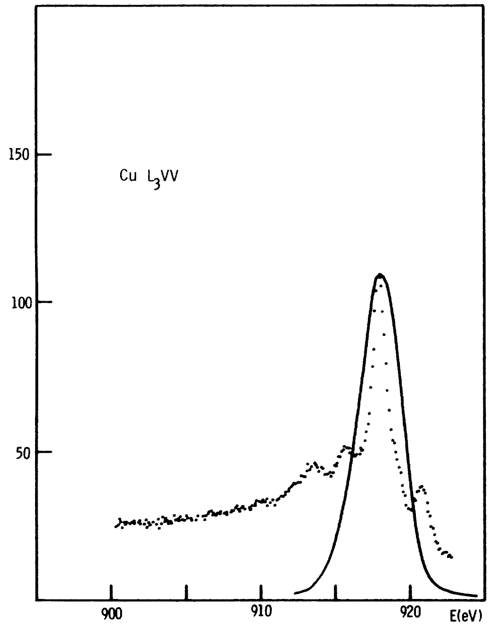

FIG. 2. Comparison of measured Cu L_3VV Auger spectrum (dots), after Ref. 2, with calculated Auger line shape (solid line). The energy of the core level in the theory was shifted down 2.7 eV from its x-ray value in order to make the major peaks in the two curves agree. The theoretical curve was also folded with a Lorentzian of width 0.7 eV to account roughly for lifetime broadening of the L_3 hole. The units on the ordinate are for the theoretical curve and are $4\pi \times 10^{-4}\hbar^{-1}$ (particles/energy × time).

II. LCAO CALCULATION OF THE CU L_3VV AND $M_{2,3}VV$ AUGER LINE SHAPES

This section contains a brief description of the calculation which leads to the theoretical Auger spectra of Figs. 2 and 3. The theoretical development is discussed only sketchily here because it parallels closely that which is given in Ref. 6 in considerable detail.

Our calculation was carried out for a 17-layer Cu film having ideal (100) surfaces, by using the LCAO description of the valence bands given by Sohn *et al.*,[10,12] to reduce the Auger matrix elements for Cu metal to a linear combination of atomic Auger matrix elements. These atomic elements were evaluated using self-consistent atomic orbitals.[11]

As in Ref. 6, multiple scattering in the final-electron wave functions was ignored on the assumption that it would have little effect on the number of Auger electrons to escape the film, and would therefore not affect an angle-integrated

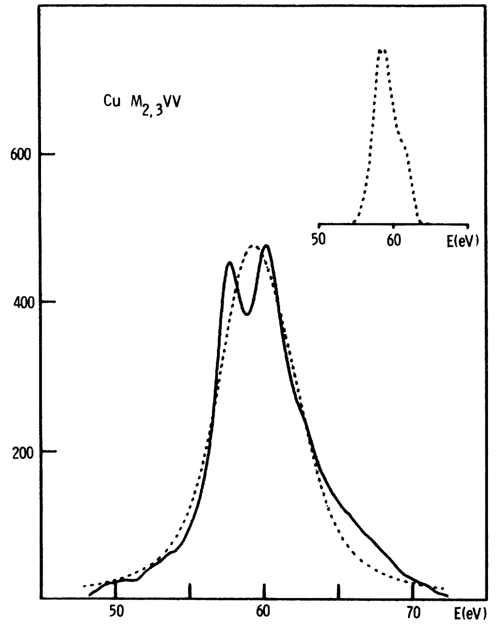

FIG. 3. Comparison of measured Cu $M_{2,3}VV$ Auger spectrum (solid line), after Ref. 2(a), with calculated Auger line shape (dashed curve). The theoretical curve was obtained by assuming a 2.4-eV splitting between the M_2 and M_3 levels [see Ref. 2(a)], with the relative numbers of M_2 and M_3 holes assumed to be in the ratio 1:2. The curve shown also includes the effects of a Lorentzian broadening of 3.5 eV for both the M_2 and M_3 levels. This value was chosen in order to give a reasonable fit of the overall width of the theoretical curve to the experimental. In fact, if the independent electron picture were valid, we would expect the M_2 and M_3 levels to have widths closer to 6 eV. Units on the ordinate are for the theoretical curve and are $4\pi\times 10^{-4}\hbar^{-1}$ (particles/energy $\times$ time). Inset: theoretical $M_{2,3}VV$ spectrum with no core-hole-lifetime broadening included. This curve shows that the M_2VV and M_3VV spectra are sufficiently broad in themselves that the M_2-M_3 spin-orbit splitting does not yield a line with two resolved peaks.

Auger line shape. (At the energy of the L_3VV line, ~900 eV, multiple-scattering effects should not be particularly large anyway.) Thus the final Auger wave function was calculated as though the electron were to emerge from an isolated Cu^{++} ion. The Cu inner potential $V_0 \approx 1$ Ry was incorporated into the calculation by evaluating the final-electron wave function at an energy $E+V_0$, where E is the Auger electron energy referenced to the vacuum level. The inelastic mean free path λ,[13] was included by multiplying the matrix element for emission from depth Z in the film, at exit angle θ from the normal, by the damping factor $\exp(-Z/\lambda\cos\theta)$.

With these assumptions and approximations, as is shown in detail in Ref. 6, we find the following general expression for the current $J(E)$ of Auger electrons having energies between E and $E+dE$:

$$J(E)=\sum_j \sum_{L_1,L_2,L_1',L_2'} \int d\omega\, F_{L_1,L_1'}(E-\omega,Z_j) \times F_{L_2,L_2'}(E_c+\omega,Z_j) \times W_{L_1,L_1',L_2,L_2'}(E,Z_j). \tag{2.1}$$

Here E_c is the core level energy, Z_j is the depth of the jth atomic layer, and the $L\equiv(l,m_l)$ are angular-momentum indices, which for copper include $l=0$, 1, and 2. The quantities $F_{L,L'}(E,Z_j)$ in Eq. (2.1) are occupied local density-of-states matrices given by

$$F_{L,L'}(E,Z_j)\equiv\frac{1}{N}\sum_{n,\vec{k}''} f(E_{\vec{k}'',n})\delta(E-E_{\vec{k}'',n}) \times c_L^n(\vec{k}'',Z_j)c_{L'}^{n*}(\vec{k}'',Z_j), \tag{2.2}$$

where $E_{\vec{k}'',n}$ is the valence-band energy associated with surface wave vector $\vec{k}''$ and band n, $c_L^n(\vec{k}'',Z_j)$ is the amplitude of the atomic orbital of angular momentum L in the jth layer, N is the total number of two-dimensional unit cells, and $f(E_{\vec{k}'',n})$ is a Fermi function. The quantity $W_{L_1,L_1',L_2,L_2'}(E,Z_j)$ in Eq. (2.1) is given by[6]

$$W_{L_1,L_1',L_2,L_2'}(E,Z_j)=\frac{4m}{\hbar^3}\frac{1}{2l_i+1}\sum_{m_{l_i}=l_i}^{l_i}\sum_{m_f,l_{f_1},l_{f_2}} B_{l_{f_1},l_{f_2},m}(E,Z_j) \times[M_{l_{f_1},m_f;L_i,L_1,L_2}(M^*_{l_{f_2},m_f;L_i,L_1',L_2'}-\tfrac{1}{2}M^*_{l_{f_2},m_f;L_i,L_2',L_1'})+L_1,L_1'\rightleftarrows L_2,L_2'], \tag{2.3}$$

where

$$B_{l_1,l_2,m}\equiv\frac{1}{2}\left(\frac{2mE}{\hbar^2}\,\frac{(2l_1+1)(2l_2+1)(l_1-m)!\,(l_2-m)!}{(l_1+m)!\,(l_2+m)!}\right)^{1/2}\int_0^1 dx\exp\left(\frac{-2Z}{\lambda y(x)}\right)P_{l_1}^m(y(x))P_{l_2}^m(y(x)). \tag{2.4}$$

In Eq. (2.4), the $P_l^m(y)$ are associated Legendre polynomials, and $y(x)\equiv[(E+V_0x^2)/(E+V_0)]^{1/2}$. Finally the atomic matrix elements $M_{l_f,m_f;L_i,L_1,L_2}$ in Eq. (2.3) are given by

$$M_{l_f,m_f;L_i,L_1,L_2}\equiv\int d^3r_1\,d^3r_2\,\psi^*_{L_i}(\vec{r}_1)\psi_{L_1}(\vec{r}_1)\frac{e^2}{|\vec{r}_1-\vec{r}_2|}\psi_{L_2}(\vec{r}_2)\psi^*_{L_f}(\vec{r}_2), \tag{2.5}$$

where $\psi_{L_f}(r)$ is the partial-wave component of the final-electron wave function corresponding to $L_f = (l_f, m_f)$. Incidentally, note that Eqs. (2.1)–(2.5) are valid whether the quantum numbers of our initial core hole are assumed to be its total angular momentum j_i and corresponding z component, m_{j_i} (averaged over), or alternately its orbital and spin angular momentum z components, respectively, m_{l_i} and m_{s_i} (both averaged over). This fact follows from the assumption that spin-orbit coupling in the valence bands of our solid, and in the final-electron state, is negligible.

A priori the numerical evaluation of Eq. (2.1) would appear to involve quite a lengthy computer calculation. However, a number of properties of Cu reduce the amount of computation considerably. First, one notes that principal features of both the L_3VV and $M_{2,3}VV$ spectra (cf. Fig. 1) cover only about 9–10 eV, which is about twice the d-band width of Cu and not twice the Fermi energy ($2E_{\text{Fermi}} \sim 18$ eV). This fact, together with the narrowness of the various features in the L_3VV and $M_{2,3}VV$ spectra, suggests that we need not concern ourselves with Auger processes involving other than valence-band d electrons; and thus at the outset we can delete the sums on l_1, l_1', l_2, and l_2' of Eq. (2.1), and set all of these l's equal to 2.

The second fact which reduces the amount of computation necessary is, given that $l_i = 1$ and $l_1 = l_2 = 2$, the atomic matrix elements [cf. Eq. (2.5)] for which $l_f = 3$ are typically several times as large as those for which $l_f = 1$ or 5, the other allowed values.[14] Thus in Eq. (2.3) we can eliminate the sums on l_{f_1} and l_{f_2}, setting both of these l's equal to 3.

Incidentally, the fact that l_f can only equal 1, 3, or 5 follows directly from angular-momentum and parity conservation.[14] In the past a number of theoretical calculations of the angular distribution of Cu $M_{2,3}VV$ Auger electrons have appeared in which, as a convenient way of looking purely at the effects of final-state multiple scattering, the final Auger electron was assumed to emerge from a Cu atom as an s electron.[15] However, having assumed that the transition involved is predominantly an $M_{2,3}M_{4,5}M_{4,5}$ (i.e., $3p3d3d$) Auger decay, this assumption is in direct conflict with parity conservation, and thus leads to results of doubtful significance.

III. DISCUSSION

We have shown in Figs. 1–3 that the predictions of the independent-electron model for the L_3VV and $M_{2,3}VV$ Auger line shapes of Cu fail to describe the experimental data. Thus we are forced to conclude that it is the atomic picture of these Auger decays which is essentially correct. In what follows we propose two mechanisms which may account for the success of the atomic model.

In the atomic picture the features seen in an Auger spectrum (e.g., the L_3VV spectrum) are identified with the states one can construct by coupling the angular momenta of two final-state holes in all possible ways. Thus in order to explain the energy separations of the features seen, one must calculate the differences between the hole-hole repulsion energies of the various two-hole states. To explain the widths of the features, one must calculate the lifetimes against neutralization of the Cu^{++} states to which they correspond.

The main issue that needs to be addressed is how the lifetime of a Cu^{++} state can be long enough to give rise to features in the Cu Auger spectra whose widths are ~1–2 eV, when the width of the Cu d bands, which determines the hole diffusion time in a band theory picture, is ~4 eV. The answer must evidently be that when the effects of hole-hole interaction are taken into consideration the decay times of the Cu^{++} final states become considerably longer.

We must therefore ask how the hole-hole interaction, which is *repulsive*, can prolong the life of a two-hole state. We can envision at least two possible mechanisms:

(i) Let us first recall the facts that at the bottom of a band, the effective mass of a hole is negative, and that the effect of a repulsive force on a negative mass particle is similar to that of an attractive force on one of positive mass. Thus we propose, as one potential explanation of the resonances in the Cu Auger spectra, the idea that they are aligned in energy with the d-like subbands of Cu in such a way that for a hole to diffuse away from a Cu^{++} it must go into a negative mass state, and thus it must surmount the effective attraction it feels due to the presence of the second hole. In order to see whether this idea is capable of predicting the Auger resonances of Cu as well as the presence or absence of analogous resonances in other materials[16] one must presumably carry out a Hubbard-model-like calculation,[17] i.e., a calculation which in addition to a tight-binding description of the d-bands includes the correlations due to Coulomb repulsion for two carriers on the same atomic site. Such a calculation will assuredly be a difficult one.

(ii) A second consideration which may lead to long two-hole state lifetimes[18] is that if the repulsion energy associated with having two holes on a single atom is appreciably larger than the Cu $3d$ bandwidth, then two holes initially formed on the same site are forced to remain together by virtue of energy conservation.[19] That is, in order for the holes to separate spatially they must give up their mutual repulsion energy, and if the $3d$ bandwidth is too small they cannot simply convert it to kinetic energy. Rather they must lose their repulsion energy by exciting electrons into the $4s$ and $4p$ bands, or by creating phonons or photons. The inverse lifetimes for these hole decay processes should not, in general, be governed by the $3d$ bandwidth but rather might be expected to be considerably smaller.

Note added in proof. This second mechanism, we have discovered, has also been suggested and discussed by E. Antonides, E. C. Janse, and G. A. Sawatzky, Phys. Rev. B, (to be published).

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[1] See, e.g., J. E. Houston, J. Vac. Sci. Technol. 12, 255 (1975), Al; H. H. Madden and J. E. Houston (unpublished), Li; M. G. Lagally, J. E. Houston, and G. Moore (unpublished), Si.

[2] Auger spectra for Cu have been reported by a number of groups. See (a) D. M. Zehner, J. R. Noonan, and H. H. Madden (unpublished); (b) D. Roberts, P. Weightman, and C. E. Johnson, J. Phys. C 8, L301 (1975); (c) S. P. Kowalczyk, R. A. Pollack, F. R. McFeeley, L. Ley, and D. A. Shirley, Phys. Rev. B 8, 2387 (1973); (c) L. I. Yin, I. Adler, T. Tsang, M. H. Chen, D. A. Ringers, and B. Craseman, *ibid.* 9, 1070 (1974), Cu; also, e.g., C. J. Powell and A. Mandl, *ibid.* 6, 4418 (1972), Cu, Al, and Ni.

[3] A valence-band Auger transition is one in which one or two of the electrons involved belongs to the valence band.

[4] A DOS model calculation is one which assumes the independent-particle model to be valid and in which matrix element variation across the valence band is taken to be negligible.

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[9] For Zn, whose L_3VV Auger spectrum is similar to that of Cu, a vapor-phase spectrum has been published by S. Aksela, J. Väyrynen, and H. Aksela, Phys. Rev. Lett. 33, 999 (1974).

[10] K. S. Sohn, D. G. Dempsey, L. Kleinman, and E. Caruthers, Phys. Rev. B 13, 1515 (1976).

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

[12] We performed our calculations for a 17-layer film using a mesh of 55 points in the irreducible $\frac{1}{8}$ surface Brillouin zone to carry out surface wave-vector integrals.

[13] For the $M_{2,3}VV$ line we used $\lambda = 6$ Å, while for the L_3VV case we chose $\lambda = 25$ Å. Note that because λ is so large in this latter case, the Auger current contains substantial contributions from deeper layers of the Cu. In order to take this effect into account for the L_3VV line we added to the current from the first nine layers of our 17-layer film a "bulk" contribution in which the contributions of layers ten and greater were taken to equal that of layer nine, with appropriately modified damping factors.

[14] That $l_f = 1, 3$, or 5 are the only possibilities can easily be demonstrated using the angular momentum and parity selection rules given in Ref. 6.

[15] H. L. Davis and T. Kaplan, Solid State Commun. 19, 595 (1976); L. McDonnell, D. P. Woodruff, and L. H. Jenkins, *ibid.* 18, 483 (1970).

[16] See, e.g., C. J. Powell, Phys. Rev. Lett. 30, 1179 (1973); J. M. Burustrand and G. G. Tibbets (unpublished); M. H. Chen, B. Crasemann, L. I. Yin, T. Tsang, and I. Adler, Phys. Rev. A 13, 1435 (1976); P. Weightman, J. Phys. C 9, 1117 (1970).

[17] J. Hubbard, Proc. R. Soc. A 276, 238 (1963).

[18] This idea arose in a conversation with Dr. P. Pincus and Dr. W. J. Camp.

[19] Note that if two holes are bound to one another they can still delocalize, together. However, the characteristic inverse time for this second-order hopping process is smaller by the bandwidth divided by the hole-hole repulsion [t/U in Hubbard-model language (Ref. 17)] than the $3d$ bandwidth itself. This result follows because each of the two hole hops is governed by a matrix element proportional to the bandwith (t) while the intermediate-state energy (which appears in the denominator) is just the Coulomb repulsion energy (U), i.e., the energy missing after the first hole has hopped but before the second one does.