Auger-Electron Spectroscopy as a Local Probe of Atomic Charge: Si $L_{2,3}VV$

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Auger-electron spectroscopy is shown to measure something quite different from photoemission: the distribution of atomic (as opposed to overlap) charge populations across the valence bands. While matrix-element effects must be considered in *s-p* band materials, their inclusion in calculations still lead to poor agreement with experiment. Good agreement may be obtained, however, if one divides the electronic charge into atomic and overlap (bonding) LCAO components and notes that the latter does not contribute to the Auger current.

Previous theoretical work by Feibelman, McGuire, and Pandey[1] and Feibelman and McGuire[2] has shown that Auger matrix element effects cannot be neglected in *s-p* band materials such as silicon. Thus the naive theory of Auger core-valence-valence (CVV) line shapes, which uses the self-fold of the total valence-energy-band density of states (DOS), is inappropriate for these materials. However, the above theoretical work still failed to achieve good agreement with the experimental silicon $L_{2,3}VV$ or $L_1L_{2,3}V$ Auger line shapes. While the Auger matrix elements were shown not to vary appreciably with the Auger electron energy, they were shown to vary significantly as a function of the local angular momenta of the final-state holes. The matrix-element effects were shown to favor the *pp* over the *sp* or *ss* final states.[3] However, the analysis in Ref. 2 showed that the theory still predicts far too much *sp* character for the $L_{2,3}VV$. It has been experimentally observed for Li[4] and Al,[5] as well as for Si, that the CVV lines are almost purely self-folds of the *p* partial DOS (*p* PDOS) which may be obtained from *K*-shell x-ray emission experiments. The unanswered question that remains is, then, why the *ss* and particularly the *sp* contributions to these CVV Auger lines are almost nonexistent.

For covalent molecules[6] [where atomic orbital (AO) overlaps are comparable to silicon] the interatomic Auger matrix elements have been shown to be about 10^{-4} smaller than the intra-atomic elements.[7] This has been shown to be true for the Si $L_{2,3}VV$ transition by the present author. In the prototypical LCAO covalent (bonding) wave function between two atoms, $N[a(\vec{r}-\vec{R}_A) + b(\vec{r}-\vec{R}_B)]$, the charge density is usually analyzed in terms of atomic (N^2a^2 and N^2b^2) and bonding ($2N^2ab$) components.[8] However, since the bonding component is composed of the product of AO's from different sites, its contribution to the Auger current is intrinsically of the interatomic type shown to be negligibly small. Thus only atomic components (e.g., N^2a^2 if the core hole is on site *A*) contribute to the Auger line shape.

We expect then that the strength of a valence state's contribution to the Auger line will be inversely proportional to the square of its contribution to the bonding charge of the solid (see below). Examining the *s-p* band materials, in this case Si, we immediately note that such contribution is not uniform, but that the 3*s* AO in Si contributes considerably more to the bonding charge than the 3*p* AO's do.

This may be easily understood by considering the nature of the Bloch function normalization, $N_{\vec{k}}$, given by

$$N_{\vec{k}}^{-1/2} = \sum_{b}^{A} S_{ai,bi} \exp(i\vec{k}\cdot\vec{R}_b), \qquad (1)$$

where $S_{ai,bi}$ is the overlap integral between the *i*th AO's on atomic sites *a* and *b* and where the sum is restricted to the *A*th sublattice. Since the *s* functions are nondirectional and the overlap inherently positive, Eq. (1) is $\gg 1$ for the 3*s* AO; but for the directional *p* functions which often have negative overlaps, Eq. (1) is ~ 1 and is frequently < 1. Thus at the Γ point in the Brillouin zone (where the bands are purely *s*- or *p*-like and where the coefficients may be determined by AO overlaps and symmetry) the coefficient of the 3*s* AO is 0.42 (at Γ_1) while the 3*p* AO coefficients are 0.92 (at Γ_{25}').[9] Thus the 3*s* AO contributes an atomic charge (N^2 in the above notation) of $0.18/M$ electrons and a bonding charge of $0.82/M$ electrons (*M* is the number of unit cells). Each 3*p* AO, however, contributes $0.85/M$ atomic and only $0.15/M$ bonding electrons. While this effect is altered at other points in the Brillouin zone by the phase factor in Eq. (1) and by *s-p* mixing, the overall trend remains. If a Wannier basis were

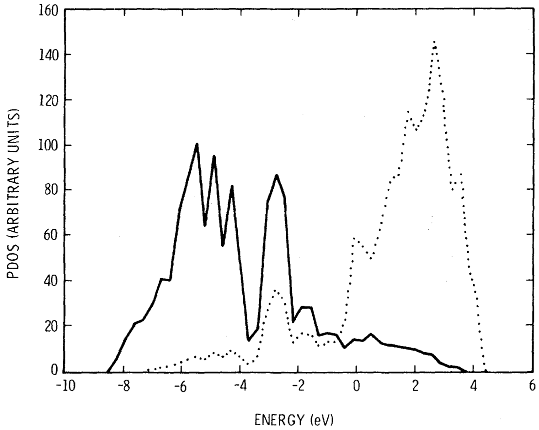

FIG. 1. The *s* (solid line) and p_x (dashed line) partial densities of states using a Hartree-Fock AO basis. Note the relative reduction of area under the *s* PDOS when compared to Fig. 2, illustrating the large contribution of the 3*s* AO to the bonding charge.

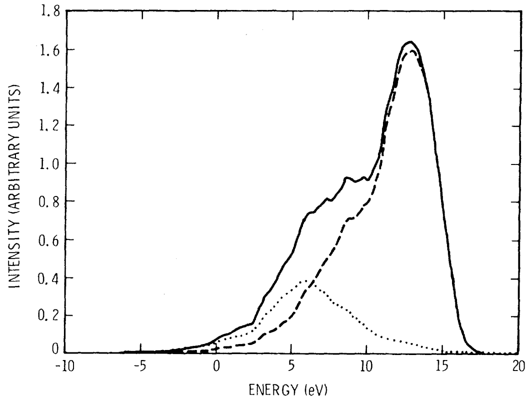

FIG. 3. The calculated Si $L_{2,3}VV$ Auger line broken into *sp* (dotted) and *pp* (dashed) components. The *ss* components are negligible and have been neglected. The energy scale is, of course, relative.

assumed (as was done in Refs. 1 and 2) instead of an AO basis, both coefficients would be 0.71. These differences are compounded by the fact that the product of the coefficients appears in the Auger matrix elements and that the contribution to the Auger line is given by the square of these elements (by first-order perturbation theory). Thus variation in the coefficients have a quartic effect on the Auger line shape.[10]

Feibelman and McGuire[2] noted the inconsistency in the theory, which made use of AO's in the calculation of the matrix elements but Wannier functions in the PDOS calculations. The present work shows that this is equivalent to a failure to divide the charge into atomic and bonding components, as the Wannier functions are by definition orthogonal and have no "bonding" charge. Since they were not explicitly determined by the empirical band theory of Pandey and Phillips,[11] they could not be used to calculate the Auger matrix elements.[1,2]

New PDOS for silicon using an AO basis[9] have been generated in the present work and these results (Fig. 1) may be compared to the Wannier PDOS (Fig. 2). Since the area under the PDOS corresponds to the amount of atomic charge con-

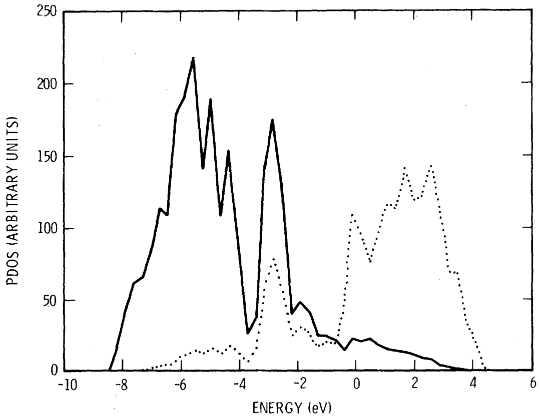

FIG. 2. The *s* (solid line) and p_x (dashed line) partial densities of states from the theory of Pandey and Phillips using a Wannier basis.

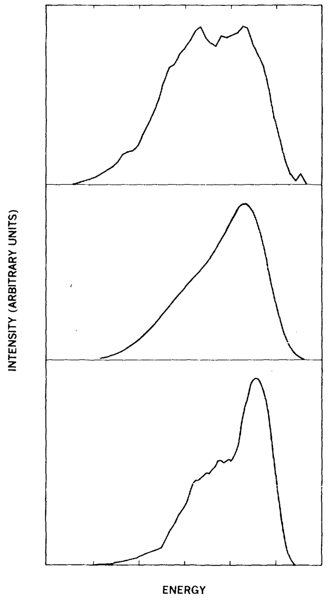

FIG. 4. A comparison of the theory of Ref. 2 (top) to the experiment (Ref. 14) and to the present theory (bottom). Broadening to the experimental resolution would improve the agreement further.

tributed by that basis function,[12] we see that the reduction in relative size of the *s* PDOS means the 3*s* function contributes more to the bonding charge than the 3*p* functions do, as expected.

A new Auger CVV line was generated using the formulas and radial matrix elements of Ref. 2,[13] but with the new AO PDOS that are consistent with these elements. Figure 3 shows that the *sp* portion of the new Auger line has been greatly reduced while the *ss* portion is so small that it has not been included. Comparison of the new results to experiment and to the older theory may be seen in Fig. 4.

It may thus be concluded that a consistent one-electron LCAO theory is indeed capable of agreement with the experimental CVV Auger spectrum of Si. The larger AO overlaps found in Li and Al imply that the effect in those metals will be even greater, and this fact is a probable explanation of the observed *pp* dominance in these materials.

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[1] P. J. Feibelman, E. J. McGuire, and K. C. Pandey, Phys. Rev. B 15, 2202 (1977). This work reports incorrect numerical results corrected by P. J. Feibelman and E. J. McGuire, Phys. Rev. B 17, 690 (1978).

[2] Feibelman and McGuire, Ref. 1.

[3] The notation of *ss*, *sp*, or *pp* refer to the local angular momenta of the final-state holes.

[4] H. H. Madden and J. E. Houston, Solid State Commun. 21, 1081 (1977).

[5] J. E. Houston, J. Vac. Sci. Technol. 12, 255 (1975).

[6] J. A. D. Matthew and Y. Komninos, Surf. Sci. 53, 716 (1975).

[7] "Interatomic" here means an Auger matrix element where any AO is not on the same center as the core orbital and the continuum wave function. The largest of these, when only one AO was on a different site, were called inter–intra-atomic in Ref. 6. The figure of 10^{-4} refers to this type.

[8] See, for example, Peter O'Doffenhartz, *Atomic and Molecular Orbital Theory* (McGraw-Hill, New York, 1970), p. 292, or any basic molecular theory text.

[9] This calculation was done by computing the overlaps for Hartree-Fock AO's for the neutral Si atom, transforming to the usual Bloch basis, and taking the *s*-*p* mixing to be that of K. C. Pandey and J. C. Phillips, Phys. Rev. B 13, 750 (1976). The details of this calculation will be reported soon.

[10] The analysis of Ref. 2 showed that the CVV Auger current may be analyzed in terms of folded PDOS's, and the square of the sum of a product of angular and radial matrix elements. The PDOS is given by $f_{ai,bj}(E) \equiv \sum_{(n\vec{k})} C_{ai,n\vec{k}}{}^* C_{bj,n\vec{k}} S_{ai,bj} \exp[i\vec{k}(\vec{R}_b - \vec{R}_a)]\,\delta(E - E_{n\vec{k}})$. The folding of these PDOS's, i.e., $(f \otimes g)_E \equiv \int dF f(F) \times g(E-F)$, produces the quartic dependence on the coefficients C.

[11] Pandey and Phillips, Ref. 9.

[12] This may easily be seen by writing the charge density in terms of the expanded Bloch functions, reversing sums, and integrating over real space. This expression for total charge is the same as that for a sum over all (including interatomic) PDOS's integrated over energy.

[13] See Eq. (12) and Table I of Ref. 2.

[14] J. E. Houston, G. Moore, and M. G. Lagally, Solid State Commun. 21, 879 (1977).