

why superfluidity of solids, if it does exist, has failed to manifest itself, although it should be noted that so far there has been no explicit attempt to measure ρ_s/ρ_0 in solid He⁴.

I would like to acknowledge helpful discussions with G. V. Chester, R. A. Guyer, W. P. Kirk, A. K. McMahan, D. G. Naugle, and L. H. Nosanow

¹A. J. Leggett, Phys. Rev. Lett. **25**, 1543 (1970).

²I believe that the Fermi system of solid He³ may more easily violate the Landau criterion than the Bose system of solid He⁴. Therefore, I consider solid He⁴ as my prototype. Since solid He³ is more "quantum" than solid He⁴, this errs on the pessimistic side.

³See R. A. Guyer, Phys. Rev. Lett. **26**, 174 (1971), for a tunneling analogy which lowers ρ_s/ρ_0 to $O(10^{-6})$.

⁴J. F. Fernandez and M. Puma, J. Low Temp. Phys. **17**, 131 (1974). Their calculation was done for superflow along the hexagonal *c* axis. These authors employ the important observation that Leggett's variational solution gives the exact value of a lower limit on ρ_s/ρ_0 .

⁵C. N. Yang, Rev. Mod. Phys. **34**, 644 (1962); D. Sher-

ington and W. Kohn, Rev. Mod. Phys. **42**, 1 (1970).

⁶For a recent summary see D. J. Bergman, B. I. Halperin, and P. C. Hohenberg, Phys. Rev. B **11**, 4253 (1975).

⁷The fact that ρ_s/ρ_0 deviates from unity only for strongly localized systems makes it likely that no correction for this effect need be made for superconducting electrons flowing in a metal.

⁸This value is consistent with the representative calculations of L. H. Nosanow, Phys. Rev. **146**, 120 (1966); C. Ebner and C. C. Sung, Phys. Rev. A **4**, 269 (1971); J. P. Hansen and E. L. Pollock, Phys. Rev. A **5**, 2651 (1972). It is also consistent with the "experimental" estimate of the rms displacement $\langle r^2 \rangle^{1/2} = \frac{3}{2} \hbar (mk_B \Theta_D)^{-1/2}$, where Θ_D is the experimental Debye temperature, as obtained by D. O. Edwards and R. C. Pandorf, Phys. Rev. **140**, A816 (1965). See R. A. Guyer, Solid State Phys. **23**, 413 (1969).

⁹M. H. W. Chan, A. W. Yanof, and J. D. Reppy, Phys. Rev. Lett. **32**, 1347 (1974); T. E. Washburn, J. E. Rutledge, and J. M. Mochel, Phys. Rev. Lett. **34**, 183 (1975).

¹⁰M. Kriss and I. Rudnick, J. Low Temp. Phys. **3**, 339 (1970).

¹¹W. M. Saslow, to be published.

¹²A. F. Andreev and I. M. Lifshitz, Zh. Eksp. Teor. Fiz. **56**, 2057 (1969) [Sov. Phys. JETP **29**, 1107 (1969)].

Tight-Binding Calculation of a Core-Valence-Valence Auger Line Shape: Si(111)†

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The shape of the $L_{2,3}VV$ Auger line has been calculated for a Si(111) surface and found to be in excellent agreement with the data of Houston and Lagally. By contrast, the experimental line shape scarcely resembles the self-fold of the occupied Si density of states, a fact which the calculation shows to be the result of matrix-element angular momentum dependence and *not* of "many-body" effects.

This Letter reports the first complete one-body calculation (i.e., including matrix elements) of a core-valence-valence Auger line shape for a solid. The case treated, the ($L_{2,3}VV$) line associated with Auger emission from Si $2p$ core holes through a clean Si(111) surface, is of particular interest because (see Fig. 1) the experimental line shape¹ is in rather poor agreement with the weighted self-fold of the occupied density of states (WSFDOS) for this surface (the weighted SFDOS is calculated by summing the self-fold of the occupied local DOS for each crystal layer

times a factor² which accounts for inelastic damping of the Auger electrons). Until now it has not been known whether such a discrepancy is an indication of "many-electron effects" or, more simply, of a variation across the valence band of one-electron model Auger matrix elements,³ because neither of these effects has heretofore been studied quantitatively. In fact, our results show for Si(111) that the simpler explanation is correct, i.e., that apart from the absence of a sharp dangling-bond surface-state peak in the data,⁴ the discrepancy can be largely explained as a conse-

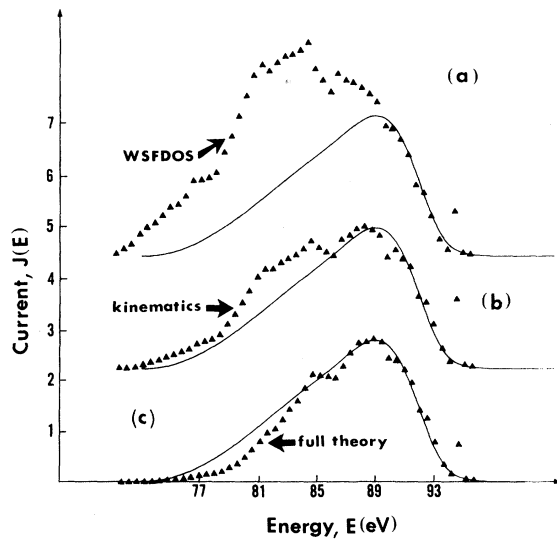


FIG. 1. Comparison of experimental Si(111), $L_{2,3}VV$ Auger line shape of Ref. 1. (solid lines) with curve *a*, the WSFDOS (see Ref. 2 for definition), curve *b* the full theoretical curve with all matrix elements not forced to equal zero by selection rules set equal to 1, and curve *c* the full theoretical curve with the actual matrix elements. The scale on the *y* axis is for the "full theory" curve *c* and is expressed in $4\pi \times 10^{-4} \hbar^{-1}$ (particles/energy \times time). Units for the other curves are arbitrary. All the theoretical curves were computed for a 7-Å mean free path. E_c was taken to equal its x-ray-edge value of -99.5 eV relative to the valence-band maximum; thus, no "relaxation" energy shift was necessary to obtain agreement between data and theory.

quence of a strong angular momentum dependence in the Auger matrix elements of a one-electron band model [see Fig. 1, curve *c*, for the quality of the agreement].

The substantial difference between the WSFDOS and one-electron-theory curves can be reduced, to an extent, by accounting properly for the relative numbers of final partial-wave states allowed by angular momentum and parity conservation (see the "kinematics" curve in Fig. 1). Final-state counting is, of course, completely ignored in comparing the WSFDOS, an initial-state prop-

erty,⁵ to experiment. However, a much closer agreement is found between the theoretical line shape and the weighted self-fold of the *p*-like component of the DOS. In fact, the agreement is so close that we have not plotted this curve in Fig. 1. This result is a consequence of the dominance of certain of the Auger matrix elements in the one-electron band calculation, for which both valence electrons must be *p*-like.⁶ Thus the discrepancy between the WSFDOS and experiment is a "matrix-element" and not a "many-body-effect" (apart from the dangling-bond peak⁴).

Our calculation was carried out for a twenty-layer Si film with unreconstructed (but relaxed⁷) (111) surfaces, by using a linear-combination-of-atomic-orbitals description of the Si valence bands^{8,9} to reduce the Auger matrix element to a linear combination of atomic Auger matrix elements. These atomic elements were then evaluated using a set of self-consistent atomic Si orbitals.¹⁰

Multiple scattering in the final-electron wave function was ignored on the assumption that it would have little effect on the total number of Auger electrons to escape the solid and would therefore not affect the angle-integrated Auger line shape. Thus the final electron was represented by an incoming Coulomb-like wave function¹¹ calculated for a single Si^{++} ion. The Si inner potential, $V_0 \approx 17.5$ eV, was included by evaluating the final electron wave function at an energy equal to $E + V_0$, where E is the Auger electron energy referenced to the vacuum level. The effect of the inelastic mean free path $\lambda(E)$ was incorporated by multiplying the matrix element for emission of an Auger electron from depth D ¹² inside the film, at exit angle θ ,¹³ by the damping factor $\exp[-D \times \sec \theta / \lambda(E)]$.

These approximations, together with the neglect of all interatomic contributions to the Auger matrix element and the assumption of a uniform spatial distribution of $2p$ core holes within a few $\lambda(E)$ of the surface, lead to a general expression for a core-valence Auger current of the form

$$J(E) = \sum_{iL_1L_1',L_2L_2'} \int d\omega F_{L_1L_1'}(E - \omega, Z_j) F_{L_2L_2'}(E_c + \omega, Z_j) W_{L_1L_1',L_2L_2'}(E, Z_j), \quad (1)$$

where E_c is the core level energy, Z_j is the depth of the *j*th layer of atoms, and where, for *s-p* valence bands, the angular momentum indices $L = (l, m_l)$ range over the four values $\{(0,0), (1,0), (1,\pm 1)\}$. The quantities $F_{L,L'}(E, Z_j)$ are occupied local density-of-states matrices defined by

$$F_{L,L'}(E, Z_j) \equiv \sum_n \int \frac{d^2k''}{(2\pi)^2} f(E_{\vec{k}''n}) \delta(E - E_{\vec{k}''n}) c_L^n(\vec{k}'', Z_j) c_{L'}^{n*}(\vec{k}'', Z_j), \quad (2)$$

where $E_{\vec{k}''n}$ is the valence-band energy associated with surface wave vector \vec{k}'' and band *n*.⁸ $c_L^n(\vec{k}'', Z_j)$

is the amplitude of the atomic orbital of angular momentum L in the j th layer, and $f(E\vec{r}_{j,m})$ is a Fermi function. The quantity $W_{L_1 L_1' L_2 L_2'}(E, Z_j)$ in Eq. (1) is given by¹⁴

$$W_{L_1 L_1' L_2 L_2'}(E, Z_j) = \frac{4m}{3\hbar^3} \sum_{m^{(i)}, m^{(f)}} \sum_{l_1^{(f)}, l_2^{(f)}} A_{l_1^{(f)}, l_2^{(f)}, m^{(f)}}(E, Z_j) \{ M_{L^{(i)}, L_1 L_2, l_1^{(f)}, m^{(f)}} \times [M_{L^{(i)}, L_1' L_2', l_2^{(f)}, m^{(f)}}]^* - \frac{1}{2} M_{L^{(i)}, L_2' L_1', l_2^{(f)}, m^{(f)}}]^* + L_1, L_1' \rightleftharpoons L_2, L_2' \}, \quad (3)$$

where

$$A_{l_1, l_2, m}(E, Z_j) \equiv \left[\frac{2mE(2l_1+1)(2l_2+1)(l_1-m)!(l_2-m)!}{\hbar^2 (l_1+m)!(l_2+m)!} \right]^{1/2} \int_0^1 dx \exp[-2Z_j/\lambda y(x)] P_{l_1}^m[y(x)] P_{l_2}^m[y(x)], \quad (4)$$

with $y(x) \equiv [(Ex^2 + V_0)/(E + V_0)]^{1/2}$. The $P_l^m(y)$ in Eq. (4) are associated Legendre polynomials. Finally, the atomic matrix elements $M_{L^{(i)}, L_1 L_2, l^{(f)}, m^{(f)}}$ in Eq. (3) are given by

$$M_{L^{(i)}, L_1 L_2, l^{(f)}, m^{(f)}} \equiv \int d^3r_1 d^3r_2 \psi_{L^{(i)}}^*(\vec{r}_1) \psi_{L_1}(\vec{r}_1) \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \psi_{L_2}(\vec{r}_2) \psi_{L^{(f)}}(\vec{r}_2). \quad (5)$$

In Eq. (5), $\psi_{L^{(f)}}(r_2)$ is the partial-wave component of the (incoming¹¹) final electron wave function corresponding to $L^{(f)} \equiv (l^{(f)}, m^{(f)})$.

In order to recover the usual assumption that $J(E)$ is proportional to the WSFDOS it is clear from Eq. (1) that $W_{L_1 L_1' L_2 L_2'}(E, Z_j)$ must be proportional to $\delta_{L_1 L_1' L_2 L_2'}$. However, cf. Eqs. (1)–(4), it is hard to see what choice of the $M_{L^{(i)}, L_1 L_2, l^{(f)}, m^{(f)}}$'s could yield this result. Thus, in general for s - p valence bands such as those of Si, one should expect $J(E)$ to be not the WSFDOS, but rather a sum of the 256 different folds of the sixteen components of the density-of-states matrix $F_{L, L'}(E, Z_j)$. The marked difference between the WSFDOS and one-electron theory curves in Fig. 1 illustrates this fact dramatically.

On the other hand, there is an approximation involving "neglect of matrix element variation" that predicts $J(E)$ somewhat better than the WSFDOS. Specifically, setting all the $M_{L^{(i)}, L_1 L_2, l^{(f)}, m^{(f)}}$ equal to 1 apart from those required to vanish by the angular momentum and parity selection rules, $m_1 + m_2 = m^{(i)} + m^{(f)}$, $|l^{(f)} - l_2| \leq 1 + l_1$, and $l_1 + l_2 + l^{(f)} = 1, 3, \text{ or } 5$, one obtains the curve labeled "kinematics" in Fig. 1. Notice that this curve still has too much weight on the low-energy side, but does resemble the data more closely than the WSFDOS. The reason for this improved agreement is that the "kinematics" curve includes the fact that the selection rules (cf. above) allow decay into more final partial-wave channels [i.e., values of $(l^{(f)}, m^{(f)})$] when either or both of l_1 and l_2 equal 1 than when both of them are zero. As a consequence, the p -like region of the Si DOS (i.e., the upper part of the valence band) is enhanced relative to the s -like part. Since this final-state counting argument is quite general, we anticipate its possible usefulness in inter-

preting Auger spectra from materials other than Si.

We conclude with a discussion of the two main differences between the $J(E)$ calculated via Eqs. (1)–(5) and the experimental line shape¹ as seen in Fig. 1, curve c . The first difference, the presence in the theoretical curve of a sharp peak at ~ 95 eV, is a consequence of our neglect of the Coulomb repulsion between valence electrons. The 95-eV peak, that is, can be easily shown to represent an Auger event in which both valence electrons are initially localized in a single Si dangling bond. In a theory which included Coulomb correlations, the probability of finding two electrons in such a configuration would be much smaller (i.e., by a factor ~ 50)¹⁵ than in the present uncorrelated theory. Thus the absence of the 95-eV peak in the experimental line shape is a true "many-body effect."

The other main difference between the calculated and observed Auger line shapes is the fact that the main peak in the former is split, while in the latter it is not. This discrepancy may be due to one of our approximations, e.g., the neglect of final-state multiple-scattering or of many-body effects, or it may be due to the fact that the data of Ref. 1 were obtained from a rather imperfect Si(111) surface. This latter possibility is being checked at present.

In summary, the differences between the experimental and theoretical line shapes are relatively small. Thus, we conclude that the $L_{2,3}VV$ Auger transition for Si(111) can be understood largely within a one-electron-band picture of Si; many-electron effects need only be invoked to explain the observed suppression of the calculated dangling-bond peak. This result suggests the

following studies for the future:

(1) Equations (1)–(5) yield an absolute number for the total yield of Auger electrons per core $2p$ hole, given the electron mean free path. Thus one should measure the Si $L_{2,3}VV$ Auger intensity absolutely, which would permit a determination of λ given the $2p$ ionization cross section, or vice versa.

(2) The $L_{2,3}VV$ line shape should be measured for Si(111) covered by an adsorbed monolayer. One would hope to see a surface-state peak appear due to this state's being doubly occupied.

(3) Comparison of complete one-body calculations and data should be undertaken for a variety of materials, not only for the Auger spectra, but also for ion-neutralization¹⁶ and appearance-potential¹⁷ spectra. The theories of both of these latter experiments are similar to that of Auger spectra. Thus they should also be subject to significant matrix-element effects.

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¹J. E. Houston and M. G. Lagally, to be published.

²The WSFDOS is defined to equal the sum on j of the self-fold of the local DOS for the j th crystal layer times the factor $f_j \equiv \int_0^1 d\nu \exp(-2Z_j/\lambda\nu)$, where Z_j is the depth of the j th layer and λ is the Auger-electron inelastic mean free path. In Fig. 1 we used $\lambda = 7 \text{ \AA}$. The specific form of f_j was chosen to account approximately for the number of Auger electrons which can escape from depth Z_j , including the effect of increased path length for escape at an angle off normal.

³See, e.g., C. J. Powell, Phys. Rev. Lett. **30**, 1179 (1973); also J. E. Houston, J. Vac. Sci. Technol. **12**, 255 (1974), and references cited therein.

⁴As is discussed below, the absence of this peak is a many-electron effect. See also J. A. Appelbaum and

D. R. Hamann, Phys. Rev. B **12**, 5590 (1975).

⁵The WSFDOS measures how many valence electrons are available to participate in the Auger event, given that energy is conserved.

⁶The large matrix elements are those for which each of two p -like valence electrons is coupled to zero angular momentum, one with the initial ($2p$) core hole and the other with a final p -like Auger electron.

⁷The outer to second layer distance was taken as 0.58 times the value it would have been in bulk Si.

⁸K. C. Pandey and J. C. Phillips, Phys. Rev. Lett. **32**, 1433 (1974), and Phys. Rev. B **13**, 750 (1976).

⁹In the calculations reported here, two-dimensional Brillouin zone integrals were done on a mesh of 66 points in the irreducible $\frac{1}{12}$ of the zone, and the histogram box size used to calculate densities of states was 0.3 eV.

¹⁰E. J. McGuire, Phys. Rev. A **3**, 587 (1971).

¹¹We used a wave function appropriate to a Si^{++} rather than to, e.g., a partially neutralized Si because in the time τ required for valence holes to diffuse away from a Si^{++} , $\sim \hbar/12.5 \text{ eV}$ (12.5 eV being the valence band width), the final Auger electron moves to a distance $r \geq \tau(2E/m)^{1/2}$ from the ion which is sufficiently large that the Coulomb potential there, $2e^2/r$, is $< 5\%$ of E . Thus by the time the Si^{++} starts to be neutralized, the effect of the Coulomb potential on the Auger electron is small. The necessity of using an incoming-wave final state is well known. See P. J. Feibelman and D. E. Eastman, Phys. Rev. B **10**, 4932 (1974), and references cited therein.

¹²The outermost layer was assumed to be at a depth equal to $\frac{1}{2}$ the bulk Si bond length.

¹³Measured from the normal, inside the film.

¹⁴The factor $\frac{1}{3}$ represents the average over initial $2p$ states. The subtracted terms in the square brackets arise from exchange symmetry, after spin summation.

¹⁵See Appelbaum and Hamann, Ref. 4.

¹⁶H. D. Hagstrum, Phys. Rev. **96**, 336 (1954), and **122**, 83 (1961).

¹⁷R. L. Park and J. E. Houston, J. Vac. Sci. Technol. **11**, 1 (1974).