[1] See, for example, P. M. Platzman and P. A. Wolff, *Waves and Interactions in Solid State Plasmas*, Suppl. No. 13 to *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1973).

[2] V. F. Gantmakher and E. A. Kaner, Zh. Eksp. Teor. Phys. 48, 1572 (1965) [Sov. Phys. JETP 21, 1053 (1965)].

[3] S. Schultz and G. Dunifer Phys. Rev. Lett. 18, 283 (1967); P. L. Platzman and P. A. Wolff, Phys. Rev. Lett. 18, 280 (167).

[4] F. J. Dyson, Phys. Rev. 98, 349 (1955).

[5] A detailed account of this work will be published elsewhere.

[6] In tilted magnetic fields, even for electrons with equal v_H, interference between electrons at different positions of their momentum-space orbits occurs. Electrons with maximum v_H usually have the smallest orbit radius and are expected to give the dominant contribution.

[7] In this expression T_2 does not appear since the tail of the ESR is damped by the phase spread of electrons diffusing through the sample in different times and not by relaxation. We assume $\tau < T_2$.

[8] P. Monod and A. Janossy, to be published.

[9] R. B. Lewis and T. R. Carver, Phys. Rev. 155, 309 (1967).

[10] S. Schultz and C. Latham, Phys. Rev. Lett. 15, 148 (1965).

[11] T. G. Phillips, G. A. Baraff, and P. H. Schmidt, Phys. Rev. B 5, 1283 (1972).

[12] A. Janossy and P. Monod, in *Proceedings of the Ninth International Conference on Magnetism, Moscow, U. S. S. R., 1973* (Nauka, Moscow, U. S. S. R., 1974), Vol. 5, and Solid State Commun. 18, 203 (1976).

[13] D. Lubenz, M. R. Shanabarger, and S. Schultz, Phys. Rev. Lett. 29, 1387 (1972).

[14] M. R. Halse, Philos. Trans. Roy. Soc. London, Ser. A 265, 507 (1969).

[15] The present analysis ignores possible Fermi-liquid effects. See Ref. 3.

Direct Observation of Wave-Function Variation Outside a Solid Surface

Homer D. Hagstrum and Toshio Sakurai
Bell Laboratories, Murray Hill, New Jersey 07974
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In an extension of its capabilities, ion-neutralization spectroscopy is used to determine transition density functions corresponding to ion neutralization at different ion positions. This provides the first direct measurement of the relative variation in the local density of states outside a solid surface. It is shown that the *d* orbitals of Hg adsorbed on Si are a minor component of the total wave function at the ion position and decay more rapidly with distance outside the solid than does the Si *p* component.

An important static characterization of a solid surface is the local density of electronic states in the surface region. Another is the spatial variation of the local density of states throughout the surface region. In this paper we present the first direct experimental determination of the relative variation of a distinguishable component of the local density of states outside a solid surface. This has been achieved by extending the capabilities of ion-neutralization spectroscopy (INS).[1] Indirect evidence concerning the variation of the local density of states outside a surface was presented by Appelbaum and Hamann who fitted ion-neutralization electron energy distributions by folding together theoretical local densities calculated at different positions in the surface region.[2]

The transition probability of the ion-neutralization process depends upon the magnitude of the wave function at the ion position and thus on the local density of states there. Although we need not know the exact functional dependences involved in order to interpret our experimental results, understanding of the phenomenon is made easier if we present it in terms of approximate functions. We know that the transition rate function $R_t(s)$, the rate at which ions are neutralized if held at the distance s from the surface, will have a major exponential component since wave functions fall off exponentially outside the surface. Corresponding to an idealized exponential rate function, $R_t(s) = A\exp(-as)$, the probability that a single ion fired at the surface with velocity v will be neutralized in ds at s is the sharply peaked function[3] $P_t(s,v)\,ds = (A/v)\exp[-(A/av)\times\exp(-as)-as]\,ds$. The shape and width of $P_t(s,v)$ are independent of v but its peak at $s = s_m$ moves closer to the surface with increasing v according to the equation[3] $s_m = (1/a)\ln(A/av)$.

The principal results of neutralization closer to the surface are two: (1) greater energy broadening of the measured kinetic energy distribution,

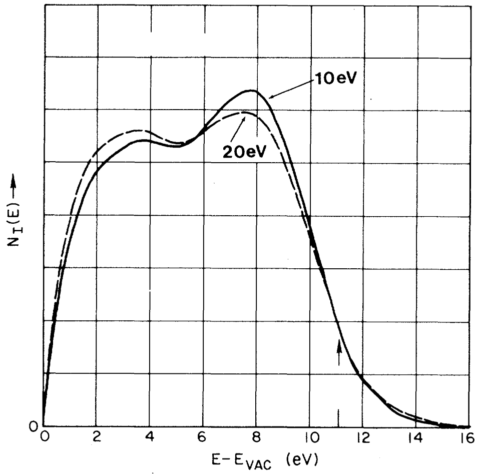

FIG. 1. Kinetic energy distributions, $N_I(E)$, obtained using 10- and 20-eV He^+ ions at a Si (111) surface with adsorbed Hg.

$N_I(E,K)$, of electrons of energy E ejected by ions of kinetic energy K,[4] and (2) relative changes within $N_I(E,K)$ and hence in the unfold function $U(E)$ derived from it, as a result of changes in the relative magnitude at different energies of components of the wave function at the ion position.[5,6] Both of these effects are evident in Fig. 1. Since $\int_0^\infty P_t(s,v)\,ds$ is close to unity,[3] we expect the total electron yield to vary little with ion velocity, $v \propto \sqrt{K}$, as can be seen from the fact that the $N_I(E)$ functions of Fig. 1 and the $U(E)$ functions of Fig. 2 have nearly the same area.[5,6]

The experimental data we present in this paper are for Hg adsorbed on Si (111). Here we expect the d wave functions of the $5d_{5/2}$ and $5d_{3/2}$ orbitals to be mixed with the p orbitals of the degenerate p band of the silicon substrate. Both INS and ultraviolet photoelectron spectroscopy (UPS) (Fig. 2) indicate that the s orbital of the Hg atom is so delocalized in energy as to be "invisible" by either method. This is also true for Hg adsorbed on Ni (100).[7,8] We may get some feeling for how p and d wave functions fall off outside a solid by considering the atomic case. At larger distances from the nucleus an atomic wave function has the form $f(s)\exp[-(2mE_i/\hbar^2)^{1/2}s]$, where E_i is the ionization energy of the state and $f(s)$ is a function of the principal and angular momentum quantum numbers of the state.[5] $f(s)$ is such that it causes a p wave function to have greater value at a given point in its exponential tail than does a d wave function having the same E_i.

For p and d states having different ionization energies we expect the ratio of the squares of the magnitudes of d to p wave functions to be $r = [f_d(s)/f_p(s)]^2\exp[-2(2m/\hbar^2)^{1/2}(E_{id}{}^{1/2}-E_{ip}{}^{1/2})s]$. At distances from the atom where the exponential predominates $f_d(s)/f_p(s)<1$. Taking the atomic case to be an approximation to the conditions prevailing outside a solid surface, we are led for the case $E_{id}\sim 2E_{ip}$ to expect (1) that the d component in the local density of states is considerably smaller than the p component at a given distance from the surface, and (2) that the d component will increase exponentially relative to the p component as distance from the surface is decreased. We emphasize that we are presenting experimental results whose validity is independent of the simplified functional forms used in presenting the phenomena involved.

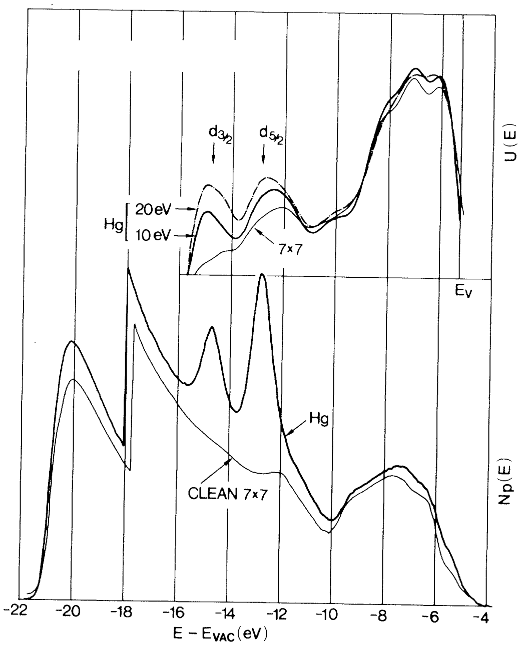

FIG. 2. Top: unfold functions, $U(E)$, for 10- and 20-eV He^+ ions incident on the Hg-covered Si (111) surface and for 10-eV ions incident on the Si (111)7×7 clean surface; bottom: UPS spectra, $N_p(E)$, for the clean and Hg-covered Si (111)7×7 surfaces.

The experimental demonstration of relative wave-function variation outside a surface requires an extension of the data handling procedures used in INS.[1,9] These have involved, first, the determination of a "debroadened" electron energy distribution, $N_I{}^0(E)$, from the experimentally determined distributions, $N_I(E,K)$. This has been followed by division by a probability of escape, change of variable from electron kinetic energy $(E-E_{vac})$ to band energy $(E-E_V)$, and a sequential deconvolution to produce the unfold function $U(E)$.[1] Here E_{vac} is the vacuum level and E_V the level of the top of the valence band. Since the present work involves a modification of the first or debroadening step it is essential to distinguish between what we shall call the "two-curve" method we have used and the "one-curve" method we are now proposing. Both methods grow out of Van Cittert's extrapolative debroadening procedure.[10] There is a considerable literature in which this procedure is used, for example, for the removal of instrumental broadening of spectral lines or diffraction lines, the effect of antenna smoothing in radio astronomy, and the sharpening of observational data on the darkening of the solar limb. In each of these cases an experimentally determined function Y_1 is related to an unbroadened "parent" function Y_0 by convolution with a *known* broadening function $B(\epsilon)$. Thus $Y_1(E)=\int_0^\infty B(\epsilon)Y_0(E-\epsilon)\,d\epsilon=B*Y_0$. Van Cittert broadened Y_1 with $B(\epsilon)$ to obtain $Y_2=B*Y_1$, took the incremental function Y_1-Y_2 as a first-order approximation to the desired incremental function Y_0-Y_1, and obtained $Y_0=Y_1+(Y_1-Y_2)=2Y_1-B*Y_1$ as a first-order approximation to Y_0. In INS we do not know $B(\epsilon)$ *a priori* and therefore must devise means of getting around it.

The two-curve method of debroadening in INS uses the equation[1]

$$N_I^0(E)=N_I(E,K_1)+R[N_I(E,K_1)-N_I(E,K_2)], \quad (1)$$

where $N_I(E,K)$ are experimental distributions of electrons ejected by ions of kinetic energies $K=K_1$ and K_2 $(>K_1)$. Earlier work[4] has shown that broadening varies proportionally to ion velocity $v\propto\sqrt{K}$, from which a value for the factor R can be calculated. The two-curve method is appropriate when broadening, not the wave-function change, is the dominant reason for the difference between $N_I(E,K_2)$ and $N_I(E,K_1)$. A test for this condition that we have consistently applied is to observe whether $N_I(E,K_2)$ has a form consistent with a simple broadening that leaves the curves for K_1 and K_2 stationary at their points of inflection.

If the wave-function variation is the dominant cause of the variation of $N_I(E,K)$ with K, or if we wish to observe the relative variation of a small wave-function component relative to the principal one, the two-curve method is inappropriate. Analysis shows that its use actually depresses the evidence in the unfold function $U(E)$ of a small wave-function component that decays more rapidly with distance from the surface than does the principal component. Our proposed one-curve method of debroadening is based on the equation

$$N_I^0(E)=N_I(E,K)+R\Big[N_I(E,K)-\int_{-\infty}^{\infty}B(\epsilon)N_I(E-\epsilon,K)\,d\epsilon\Big], \quad (2)$$

in which only one measured electron energy distribution for a single ion kinetic energy K is used. Here we generate an incremental function N_I-B*N_I by broadening $N_I(E,K_n)$ with a broadening function $B(\epsilon)$ whose breadth is small, say 0.5 eV. We have shown that the *form* of this incremental function will be relatively independent of the exact form of $B(\epsilon)$ used, be it Gaussian or Lorentzian, for example, provided its breadth is small. The *magnitude* of the incremental function needed to get the first-order debroadened $N_I^0(E)$ is determined by the factor R whose value is, to be sure, dependent on the breadth of $B(\epsilon)$ that we use. We use R in the form $R_1-R_2(E_V-E)$. R_1 is determined so that $N_I^0(E)$ crosses zero at that energy which puts the origin of the unfold $U(E)$ at the energy of the top of the valence band E_V as determined by UPS. R_2 is determined so that the one-curve method gives the same result as the two-curve method for the clean surface. It is required because the actual broadening decreases in magnitude deeper in the band.

The debroadening procedure of Eq. (2) has been applied to each of the $N_I(E,K)$ distributions of Fig. 1 using a Lorentzian $B(\epsilon)$ of width 0.5 eV.[2] The remainder of the INS data reduction procedure proceeds as before[1] and yields the $U(E)$ functions labeled 10 and 20 eV at the top of Fig. 2. Here we see that the Hg $5d$ peaks in $U(E)$, which appear at the energies $E-E_{\text{vac}}\sim-12.9$ and -14.8 eV where they are observed by UPS, behave exactly as expected. First, they are quite small relative to the p band of Si. Second, their contribution increases relative to that of the p band, as suggested by the exponential term in the wave-function ratio r discussed above. Note that the p contribution is almost constant in $U(E)$ even though ion neutralization occurs closer to the surface where the p wave functions are also greater in magnitude. This results from the normalization of the $U(E)$ curves to about the same area by virtue of the normalization of the area under the $P_t(s,v)$ probability distribution to one excited Auger electron per incident ion as discussed above. Thus our ability in INS to vary the position at which ion neutralization occurs by varying ion velocity has enabled us to observe the relative change of a distinguishable component in the electronic wave function outside a solid surface. This feature is unique to INS among the electron spectroscopies used to determine surface electronic structure.

Because the effective neutralization energy of the ion is ~ 2 eV less than the free-space value,[5] we can estimate the distance s_m where neutralization occurs. Equating $\Delta E_n = 2$ eV to the principal interaction term, namely the image interaction (3.6 eV Å)/s_m, we obtain $s_m \sim 1.8$ Å as the distance of the ion from the image plane. This simple image interaction has been shown to hold with good accuracy to 1.5 Å.[11] From the equation $s_m = (1/a)\ln(A/av)$ given earlier we obtain $\Delta s_m = (1/a)\ln(v_2/v_1)$ as the difference in neutralization distances for ions of velocities v_1 and v_2. The parameter a that specifies the rate of exponential falloff of $R_t(s)$ is taken as 2λ, where $\exp(-\lambda s)$ is the rate of decay outside the surface of a p wave function at $E - E_{\text{vac}} \sim -7$ eV, the principal determinant of where neutralization occurs. From $\lambda = (2mE_i/\hbar^2)^{1/2}$ with $E_i = 7$ eV we obtain $a = 2.8$ Å^{-1}. This estimate agrees closely with the variation of charge density outside the Si surface calculated by Appelbaum and Hamann.[12] Adding the 2-eV image acceleration to the experimental ion energies we obtain $v_2/v_1 = (\frac{22}{12})^{1/2} = 1.35$ and $s_m \sim (1/2.8) \times \ln(1.35) \sim 0.1$ Å. Hence the relative change in the Hg $\boldsymbol{d}$ orbital components that we see in the $U(E)$ functions of Fig. 2 occurs over a distance increment of ~0.1 Å at an ion-surface separation of ~2 Å.

The observed changes in the Hg d orbital intensity have only relative significance. The absolute magnitude cannot be determined because we do not know *a priori* either the electron escape probability function or the factor R_2 used in the one-curve method.

We conclude that ion-neutralization spectroscopy using our new one-curve debroadening procedure yields information about the relative variation of wave-function components outside a surface. We believe this to be a significant addition to the capabilities of electron spectroscopies because we expect it to help us understand the intensity differences of orbital resonances in chemisorption systems as observed by INS and UPS. This, in turn, should yield information about the wave-function character of particular orbital resonances.

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[1] H. D. Hagstrum, Phys. Rev. 150, 495 (1966).

[2] J. A. Appelbaum and D. R. Hamann, Phys. Rev. B 12, 5590 (1975).

[3] H. D. Hagstrum, Phys. Rev. 96, 336 (1954).

[4] H. D. Hagstrum, Y. Takeishi, and D. D. Pretzer, Phys. Rev. 139, A526 (1965).

[5] H. D. Hagstrum, Phys. Rev. 122, 83 (1961).

[6] H. D. Hagstrum and G. E. Becker, J. Chem. Phys. 54, 1015 (1971).

[7] H. D. Hagstrum, J. Vac. Sci. Technol. 12, 7 (1975).

[8] H. D. Hagstrum and G. E. Becker, in *The Physical Basis for Heterogeneous Catalysis*, edited by E. Drauglis and R. I. Jaffee (Plenum, New York, 1975), p. 173.

[9] H. D. Hagstrum and G. E. Becker, Phys. Rev. B 4, 4187 (1971).

[10] P. H. Van Cittert, Z. Phys. 69, 298 (1931).

[11] J. A. Appelbaum and D. R. Hamann, Phys. Rev. B 6, 1122 (1972).

[12] J. A. Appelbaum and D. R. Hamann, private communication.

Model for the Low-Temperature Lattice Anomaly in $SrTiO_3$ and $KTaO_3$†

A. S. Chaves, F. C. S. Barreto, and L. A. A. Ribeiro
Departmento de Física, Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil

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The low-temperature anomaly in the lattice dynamics of $SrTiO_3$ and $KTaO_3$ is described as resulting from an anharmonic coupling between an optical and an acoustic branch. The numerical calculations performed for ω_{TO} at the center of the Brillouin zone give an excellent fit to the available data from 4 to 300 K. It is shown that the ferroelectric phase transition in $SrTiO_3$ is prevented by the zero-point fluctuations of the acoustic mode.

Strontium titanate and potassium tantalate are incipient ferroelectrics. Their static dielectric constant follows a Curie-Weiss law down to about 50 K. Below this temperature, however, although continuously increasing to such values as 3×10^4 for $SrTiO_3$ and 5×10^3 for $KTaO_3$, the dielectric