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Direct measure of surface impurity scattering by angle-resolved photoemission

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High-resolution angle-resolved photoemission experiments are reported which measure the scattering cross section σ of electrons in the zone-center surface state on Cu(111) off potassium surface impurities. The value (5.2 ± 2.0 Å), is discussed in terms of various surface processes, and the future possibilities of such experiments are investigated.

Small concentrations of surface impurities can lead to a variety of interesting chemical and physical effects, including catalytic enhancement and poisoning, large surface dipoles, and changes in electronic and elastic properties. A microscopic characterization of their effect on the substrate electronic structure is thus of considerable fundamental and practical interest. These high-resolution angle-resolved photoemission (ARP) experiments describe a direct measure of the scattering cross section of electrons bound in the zone-center surface state on Cu(111) off trace potassium surface impurities. The result indicates that the electronic structure is strongly perturbed over a range of ≈ 5 Å.

The approach adopted views the surface as a dilute alloy.[1-3] The impurities act as scattering centers, and endow the substrate valence electrons with a mean free path λ given by

$$\lambda = \Omega_0 / c\sigma \ , \tag{1}$$

where Ω_0 is the unit-cell area, c is the impurity concentration, and σ is the impurity-scattering cross section which has dimensions of length for scattering in two dimensions. These scattering events render the parallel crystal momentum of the surface-state electrons ill defined on a scale of

$$|\Delta \mathbf{k}_0| = 1/\lambda \ , \tag{2}$$

producing a scattering-induced inverse lifetime Γ_s of

$$\Gamma_s = v_{\parallel} \cdot \Delta \mathbf{k}_0 = \nabla E(\mathbf{k}_{\parallel}) \cdot \Delta \mathbf{k}_0 \ . \tag{3}$$

It is assumed in this simple system that the scattering is isotropic and elastic, so that

$$\Gamma_s = v_{\parallel} \Delta k_0 = v_{\parallel} c\sigma / \Omega_0 \ . \tag{4}$$

The surface state under consideration disperses parabolically about the center of the surface Brillouin zone with a nearly isotropic effective mass of $m^* = (0.42 \pm 0.01) m_e$.[2,4] This yields directly

$$v_{\parallel} = 16.5 k_{\parallel} \ \text{eV/Å}^{-1} \ . \tag{5}$$

A relatively small amount of momentum broadening (e.g., 0.01 Å^{-1}) yields an energy width Γ_s at $k_F = 0.22$ Å^{-1} which is easily measurable with currently available instrumentation.

The accuracy of these experiments is ultimately limited by both experimental and fundamental factors. Clearly, the value of Δk_0 cannot be determined much more accurately than the experimental momentum resolution Δk_e. This problem is exacerbated by the need to work in the dilute limit to avoid interactions between scatterers. The approach adopted here is effectively to measure the linewidth as a function of Δk_e and to extrapolate to zero to yield an estimate of Δk_0 for a particular surface preparation.[2,3] The effect of the experimental energy resolution ΔE_e is generally less severe since this contribution can be made fairly small and its effect on the observed width is constant. The fundamental limitation on these measurements is due to the contribution from the ARP final-state hole inverse lifetime Γ_h.[5,6] The observed linewidth is a convolution of these various contributions, and extraction of any one is difficult in the general case. By extrapolating results to the Fermi level E_F, the contribution from Γ_h can be made zero,[5,6] and the value of σ at E_F can be measured.

The procedure is as follows. The width Γ is measured as a function of $k_{\parallel}$. Assuming additive widths,

$$\Gamma(k_{\parallel}) = \Gamma_h(k_{\parallel}) + 16.5 k_{\parallel} \Delta k_{\parallel} + \Delta E_e \ . \tag{6}$$

The slope of these data at k_F yields an estimate of $\Delta k_{\parallel}$ containing both experimental and surface-preparation-dependent contributions. Extrapolating to zero experimental momentum resolution yields Δk_0. Finally, this is repeated over a range of impurity concentrations, and a plot of Δk_0 against concentration yields σ from Eqs. (1) and (2). In principle, a value for σ can be extracted from the decrease in the surface-state emission intensity rather than from the increasing linewidth. In the dilute limit used here, however, the intensity does not vary significantly, and observation of the linewidth is a more sensitive probe.

Experiments were performed at the National Synchrotron Light Source at Brookhaven National Laboratory. The toroidal grating monochromator and photoemission spectrometer have been described elsewhere.[7,8] In these experiments, the energy resolution was fixed as ~ 50 meV, while the momentum resolution was varied between ± 0.006 and ± 0.018 Å^{-1}. The quality of the extrapolations explained earlier yield an accuracy of ± 0.005 Å^{-1} in determining Δk_0.

The Cu(111) crystal was spark cut and mechanically polished to within $\frac{1}{2}°$ of the [111] axis. Electropolishing[9] yielded a lustrous surface finish with a small concentration of pits estimated to cover less than 1% of the surface. Following insertion into the vacuum system and cleaning by standard treatments, an excellent surface was obtained as determined by low-energy electron diffraction, Auger electron spectroscopy, and the ARP results below. Potassium was deposited from a getter source.[10] Surface coverages were measured by determining work-function changes.[11,12] While relative coverages of 0%–2% of a monolayer could be measured quite accurately by this technique, uncertainties in the absolute calibration yield an uncertainty of $\approx 10\%$ in

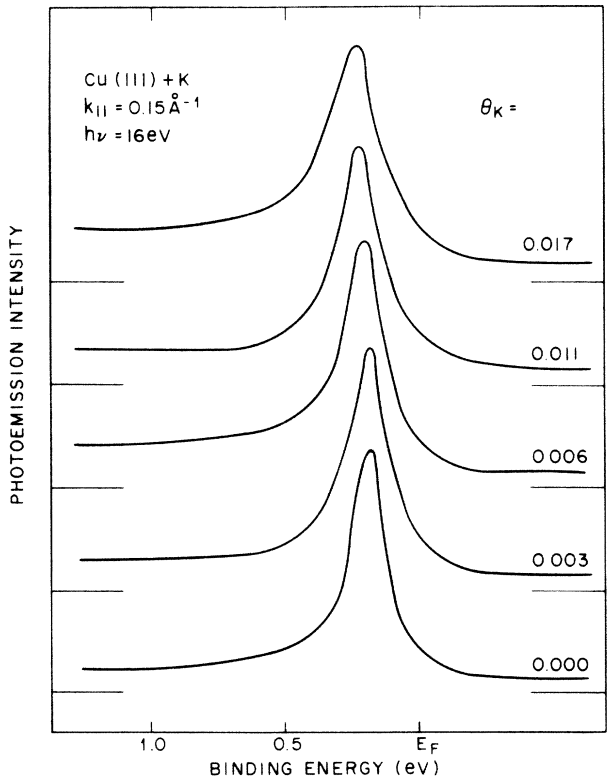

FIG. 1. ARP energy distribution curves of the Cu(111) $\bar{\Gamma}$ surface state at $h\nu = 16$ eV, $k_{\parallel} = 0.15$ Å^{-1} for various surface coverages of potassium Θ_K.

the value of σ. This is smaller than other contributions under the current constraints.

Figure 1 shows ARP energy distribution curves of the Cu(111) surface state near E_F at $k_{\parallel} = 0.15$ Å^{-1} for various potassium coverages. In accord with previous results,[11,12] the state is seen to move to slightly higher binding energy as the coverage is increased. This is directly related to the softening of the surface barrier induced by the decreasing work function.[13] The peak also broadens by nearly a factor of 2 over this small range of concentrations. This is the most direct observation of the scattering processes probed here.

The observed width is plotted as function of $k_{\parallel}$ in Fig. 2. Again, a dramatic broadening is observed as the potassium coverage is increased. More importantly, the slopes of these curves at k_F also increase significantly with coverage. On extrapolating Δk_e to zero, a value for Δk_0 is extracted. Figure 3 shows these results as a function of potassium coverage. The data are reasonably well fit by a straight line; using Eqs. (1) and (2), the slope yields a scattering cross section $\sigma = 5.2 \pm 2.0$ Å. These results were accumulated over a range of final-state energies of 6–14 eV with no systematic variation of σ. This rules out final-state scattering as the momentum-broadening mechanism.[5,6] The derived value of σ is reasonable for a metallic system; the range of the screened Coulomb scattering potential is of the order of one unit cell. The intercept at zero potassium coverage in Fig. 3 is nonzero. In accord with previous results,[2,3] this is attributed to residual defects and impurities on the surface. Part of the uncertainty in determining Δk_0 is due to the difficulty in preparing a reproducible surface prior to potassium depo-

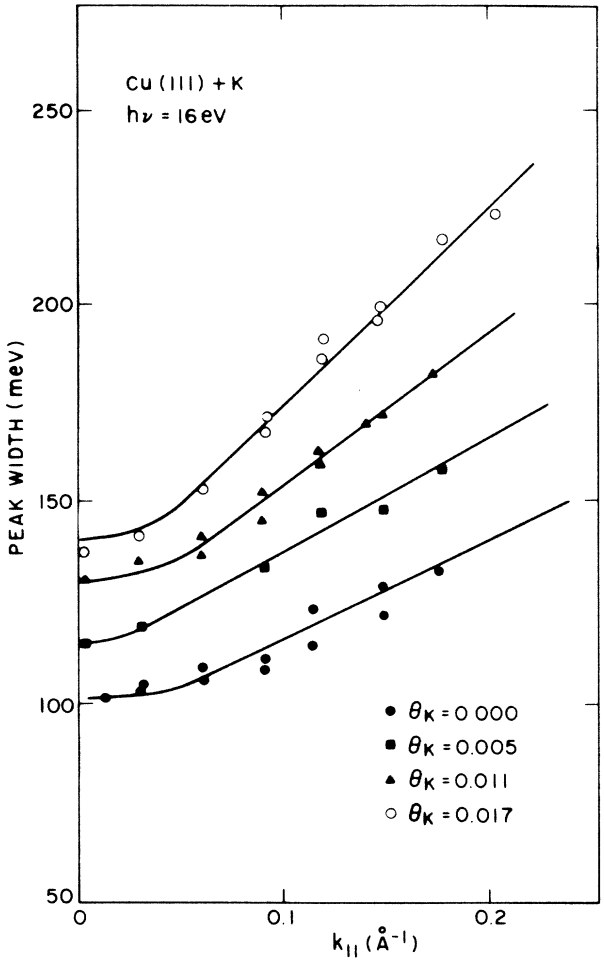

FIG. 2. Observed linewidth as a function of $k_{\parallel}$ for various potassium coverages at $h\nu = 16$ eV. The experimental momentum resolution is ± 0.08 Å^{-1}.

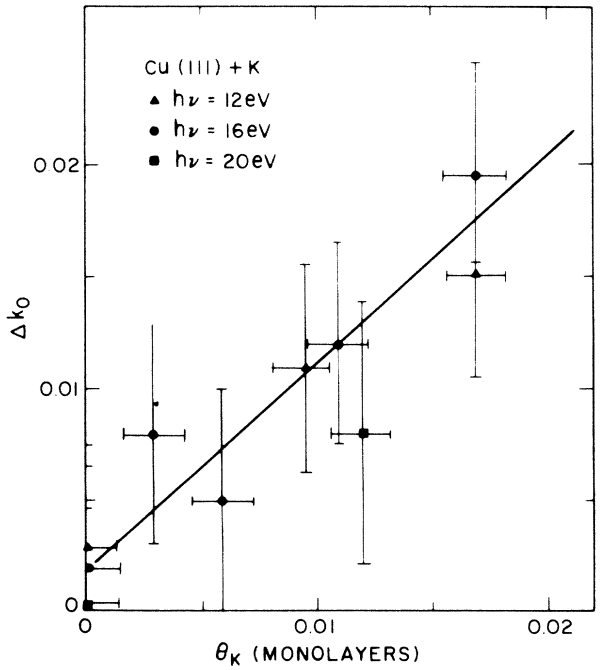

FIG. 3. Momentum broadening of the surface band at the Fermi level as a function of potassium coverage.

sition. Improvements in this respect along with improving the momentum resolution by a factor of 5–10 will allow a very precise measure of σ. Interesting correlations between σ and other observables (heat of adsorption, ionic radii, surface dipole, etc.) could then be drawn.

The data in Fig. 2 suggest that the scattering cross section is momentum dependent, increasing at lower $k_{\parallel}$. This would be roughly in accord with continuum scattering theory.[14–16] There is, however, an experimental difficulty in this analysis. The binding energy increases with increasing coverage so that the hole inverse lifetime Γ_h is coverage dependent. Much of the increase in the observed width near $\bar{\Gamma}$ can be explained without assuming a strongly momentum-dependent cross section. The scattering process involved here is probably not well described by simple continuum scattering theories since these are not truly continuum states and there is no reason to neglect the possibility of scattering from the two-dimensional surface state into the three-dimensional bulk continuum. A more complete theory of chemisorption in the dilute limit might shed light on these questions. The slightly asymmetric peak shapes observed in Fig. 1 suggest inelastic scattering processes. A large part of the asymmetry, however, is due to the proximity of the Fermi level and of a weak, but persistent density-of-states feature from bands near the $L_{2'}$ point of the bulk band structure. While inelastic processes cannot at present be ruled out, they appear to be of lesser importance than elastic scattering events.

Further experiments might probe other surface impurities. The advantages of the alkali metals lie in their tendency to spread randomly across the surface rather than forming islands, and the high sensitivity of work-function measurements to coverage. Other more weakly adsorbed impurities will require low-temperature adsorption to defeat the tendency to form clusters.

In summary, these ARP results have demonstrated a novel approach to measuring surface impurity scattering cross sections. The results for the K/Cu(111) system are in line with expectations of a metallic system. Future experiments will focus on even higher-resolution studies of more consistently prepared surfaces.

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