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1994 J. Phys.: Condens. Matter 6 L613

(http://iopscience.iop.org/0953-8984/6/40/002)

J. Phys.: Condens. Matter 6 (1994) L613–L618. Printed in the UK

LETTER TO THE EDITOR

Surface states as probes of buried impurities

S Crampin
Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK

Received 26 July 1994

Abstract. Shockley surface states at metal surfaces decay exponentially into the crystal, typically penetrating several interplanar spacings. Within this distance defects such as impurity atoms will scatter the surface state electrons and give rise to characteristic standing wave patterns in the local density of states outside the surface, similar to those recently detected with the STM due to scattering by adatoms. A multiple-scattering theory is developed to model this situation and applied to impurities near the Cu(111) surface. The results are discussed within a two-dimensional scattering model and the prospects for observation with the STM considered.

Common features of many surfaces are electrons in surface states, confined normal to the surface between the vacuum barrier and a crystal band gap [1]. Surface state wavefunctions decay exponentially into the solid with a decay length dependent upon the magnitude of the band gap, often extending in several interplanar spacings, and within this distance a defect such as an impurity will perturb the electron wavefunction. Two factors make this a potentially useful effect. Firstly, the surface state is separated in momentum from the continuum of bulk levels which also occur at a metal surface. Electron states will scatter off the impurity incurring a phase, and for the continuum states these phases will largely interfere and so leave the primary variation in the local density of states (LDOS) that due to the surface state. Secondly, surface states which occur near the centre of the surface Brillouin zone (BZ) decay least rapidly into the vacuum, and hence provide the dominant contribution to the LDOS well outside the metal surface—precisely the regime of operation of the STM which can measure (approximately) the LDOS. Standing wave patterns due to the scattering of surface state electrons by adatoms have been observed with the STM by Crommie *et al* [2, 3] and Avouris *et al* [4]. In this letter I consider to what extent the finite penetration depth into the solid allows the surface state to be used as a well defined probe, carrying information regarding the impurity through the surface and out where it may be interrogated by the STM. A multiple-scattering theory is developed for the LDOS outside a metal surface in the presence of a buried impurity, and applied to the Cu(111) surface with various impurities.

The LDOS is obtained from the single-particle Green function $\mathbf{G}$ evaluated at energy E (unless otherwise stated, Hartree atomic units assumed): $n(\boldsymbol{r}; E) = -(1/\pi)\Im\mathbf{G}(\boldsymbol{r}, \boldsymbol{r}; E)$. I determine $\mathbf{G}$ outside the metal surface ($z < 0$) in the region where the potential is constant, equal to the vacuum level W, from [5]

$$\mathbf{G} = \mathbf{G}_0 + \mathbf{G}_0\mathbf{T}\mathbf{G}_0 \tag{1}$$

where $\mathbf{G}_0$ is the free electron Green function, and $\mathbf{T}$ the transition operator for the crystal. By comparison with the corresponding equation for the wavefunction outside the surface

0953-8984/94/400613+06$19.50

$\psi = \psi_0 + \mathbf{G}_0\mathbf{T}\psi_0$, with ψ_0 a wave travelling toward the surface, the matrix elements of $\mathbf{G}$ may be expressed in terms of the reflection matrix $R_{gg'}(k, k')$ which relates, at energy E, a wave of parallel momentum $g + k$ (g a reciprocal lattice vector, k within the first BZ) incident upon the surface to the scattered component of parallel momentum $g' + k'$. The $\mathbf{T}$ matrix has a multi site expansion in scattering path operators (SPO) $\mathbf{T} = \sum_{ij} \tau^{ij}$ [5], and the SPOs of the crystal+defect may be related to those of the unperturbed crystal [6]. This allows the crystal reflectivity to be expressed as a sum of clean surface (R^c) plus impurity-induced contributions, $R_{gg'}(k, k') = \Omega\delta(k - k')R^c_{gg'}(k) + \Delta R_{gg'}(k, k')$, and similarly the Green function as the clean surface Green function $\mathbf{G}_c$ plus correction:

$$\mathbf{G}(r, r'; E) = \mathbf{G}_c(r, r'; E) + \frac{1}{A}\sum_{gg'}\int_\Omega \frac{dk}{\Omega}\int_\Omega \frac{dk'}{\Omega}\exp(-iK^+_{g+k}\cdot r)\frac{1}{\gamma_{g+k}}\Delta R_{gg'}(k, k')\exp(+iK^-_{g'+k'}\cdot r'). \tag{2}$$

A is the area of the unit mesh, $\Omega = (2\pi)^2/A$ the BZ area and $K^\pm_k = k \pm i\gamma_k\hat{z}$ where $\gamma_k = \sqrt{2W - 2E + k^2}$ is the decay constant into vacuum of the electron wavefunction. ΔR is found by evaluating $A^+_{g\mu}(k)$ ($\tilde{A}^-_{\mu g}(k)$) which relates a plane wave incident upon (emitted from) the surface to a partial wave (ℓ, m) emitted from (incident upon) site n, with $\mu = (\ell, m, n)$, including all possible scattering paths. These may be evaluated by conventional layer coupling algorithms of layer KKR theory [7, 8]. Then

$$\Delta R_{gg'}(k, k') = \sum_{\mu\mu'} A^+_{g\mu}(k)\left[(\mathbf{m} - \mathbf{m}_d)^{-1} - \tau\right]^{-1}_{\mu\mu'}\tilde{A}^-_{\mu' g'}(k') \tag{3}$$

where τ, $\mathbf{m}$ and $\mathbf{m}_d$ are the SPO and inverse $\mathbf{t}$ matrices of host and defect respectively in the site partial wave representation.

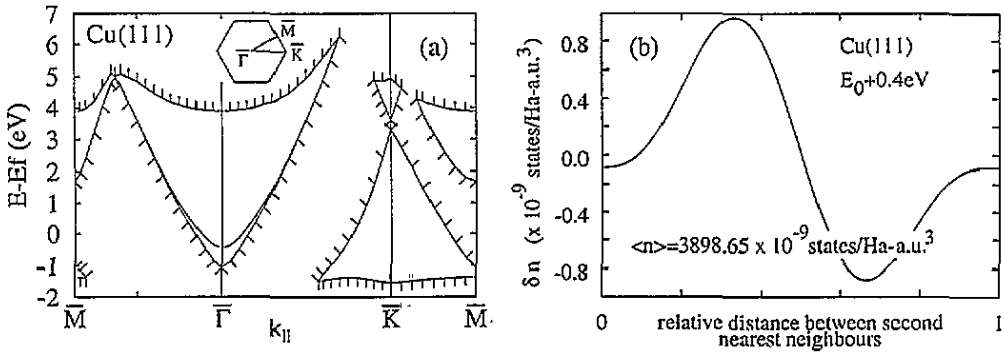

Figure 1. (a) Projected band structure for Cu(111) given by the potential described in the text. (b) Variation in the LDOS $n_c(r; E) = \langle n_c(z; E)\rangle + \delta n_c(r; E)$ at $E = E_0 + 0.4$ eV and $z = 5$ Å above the clean Cu(111) surface, along the $[\bar{2}11]$ direction.

In the present study the crystal potential is treated in the atomic sphere approximation neglecting relaxation at the surface and using a step potential barrier. The dispersion of the Shockley surface state (figure 1(a)) in this case, $E = E_0 + k^2/2m^*$ with $E_0 = -0.46$ eV and $m^* = 0.34$, is in good agreement with experiment [2] and fully self-consistent layer KKR calculations [9]. The impurity perturbation is considered in the single-site approximation

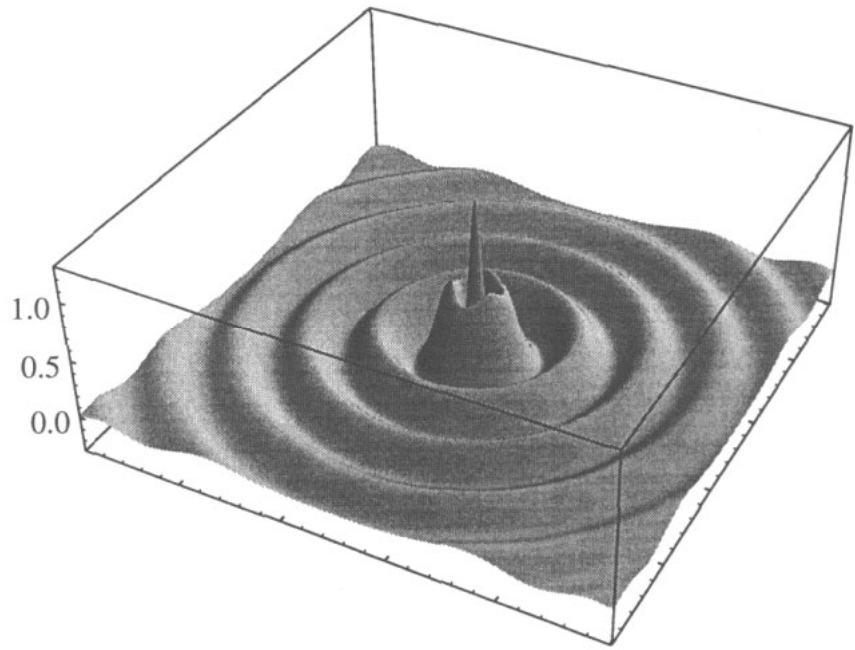

Figure 2. Impurity induced LDOS (10^{-7} states Ha^{-1} au^{-3}/spin) at 0.06 eV binding energy 5 Å above the Cu(111) surface due to substitutional Al in the surface layer (area 250×250 au^2).

using a site independent potential taken from scalar relativistic self-consistent calculations for impurities in bulk Cu. These approximations can be relaxed should accurate experimental results become available. At present they lead to significant savings in computational complexity and effort. Stacking algorithms used for evaluating half-space reflectivities require finite adsorption for convergence [7]. $\Im E = 1$ meV has been used corresponding to a decay length about 1000 times the intrinsic decay length of the Cu(111) Shockley state. The calculations use 19 $\boldsymbol{g}$ vectors, partial waves to $\ell = 4$ [10] and 27 648 $\boldsymbol{k}$-points (using special directions) for the BZ integrals.

Expressing the LDOS from (2) as clean surface (figure 1(b)) and impurity induced contributions, n_c and Δn respectively, figure 2 shows a typical example of Δn, due to an Al impurity in the Cu(111) surface layer. The LDOS is dominated by circularly symmetric oscillations decaying radially, and the wavelength of ~30 au indicates the long-range variation is due to scattering of the surface state. The phases incurred by scattered continuum states interfere, resulting in a negligible contribution to Δn a few wavelengths from the impurity. Locally, though, phase cancellation is incomplete and specific structure results. This interpretation is verified by omitting from the BZ integrals in (2) a narrow annulus around the surface state momentum $\boldsymbol{k}_0$, in which case the long range structure vanishes but large-amplitude features near the defect remain. Results for several impurities are shown in figure 3, illustrating a variety of amplitudes and structure. Of particular note are strong spin asymmetry in scattering by Fe (the only impurity considered with a local moment) and the similarity between Mo and Fe(↓). The latter indicates species identification may not always be possible working at a single energy—although it is here, due to the spin polarization of Fe. The results in figures 2 and 3 are qualitatively similar to the adatom

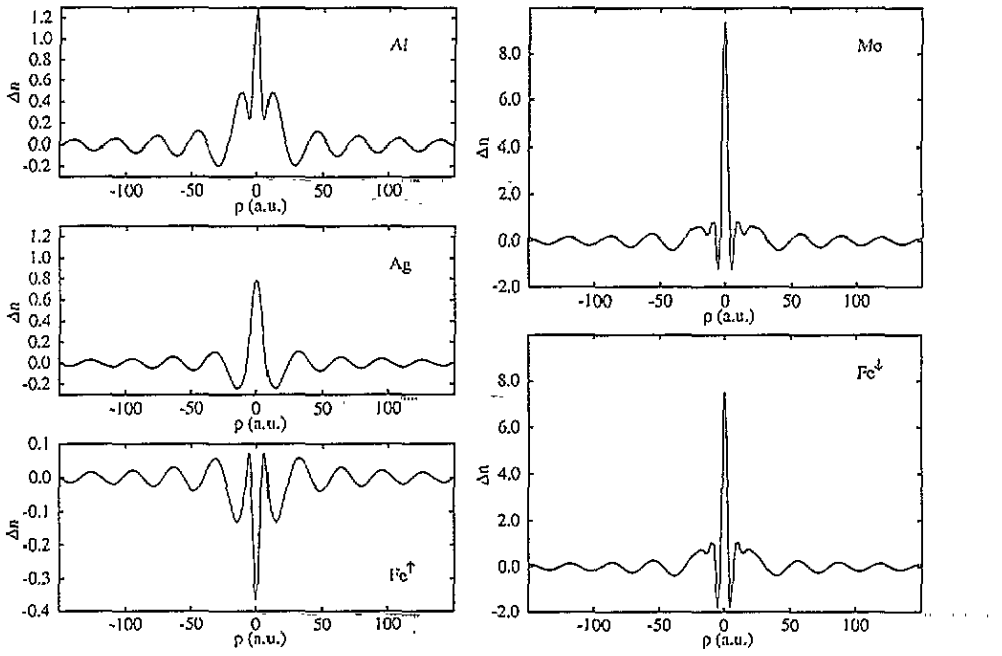

Figure 3. As figure 2 for various impurities, evaluated in the $[1\bar{1}0]$ direction.

results reported in [2, 3].

As a simple phenomenological model for the results consider a two-dimensional scattering treatment, as employed by various authors in discussing surface states interacting with adatoms, steps and pits [2, 3, 11–14]. The single-particle Green function in two dimensions outside a circular potential may be derived and from it the long-range LDOS oscillations:

$$\Delta n(\varrho)/\langle n_c\rangle = \Re\sum_M \left[H_M^2(\kappa\varrho)\mathbf{T}_M\right] \xrightarrow{\varrho\to\infty} \frac{2}{\pi\kappa\varrho}\Re\sum_M\left[(-1)^M \exp(\mathrm{i}\,(2\kappa\varrho+\delta_M))\sin\delta_M\right]. \quad (4)$$

Here, $\langle n_c\rangle$ is the LDOS in the absence of the defect, $\kappa = \sqrt{2m^*(E-E_0)}$ and $\mathbf{T}_M$ is the $\mathbf{t}$ matrix of the circular potential, related to the scattering phaseshift δ_M by $\mathbf{T}_M = \mathrm{i}\sin\delta_M \exp \mathrm{i}\delta_M$. A consequence of projecting from three dimensions to two is that no current conservation rules apply and so the phaseshifts are complex. A satisfactory fit of the data to equation (4) is possible with a single phaseshift (RMS error ~5%), representing a convenient quantity for experimental determination.

These are given in table 1. Unfortunately there appears no simple manner in which δ_M may be related quantitatively to the electronic structure of the impurity. Indeed, using a single phaseshift is questionable. Because of the exponential decay with increasing momentum, in equation (2) it is an excellent approximation to only consider $g, g' = 0$ and to replace the BZ by a circle. Then Δn may be written

$$\Delta n(r; E) \simeq \Im\int_0^{k_c} k\,\mathrm{d}k \int_0^{k_c} k'\,\mathrm{d}k' \sum_{MM'} \mathrm{e}^{-\mathrm{i}M\phi} J_M(k\varrho) G_{MM'}(k, k'; z) J_{M'}(k'\varrho)\mathrm{e}^{\mathrm{i}M'\phi}. \quad (5)$$

Table 1. Complex phaseshifts obtained by fitting equation (4) to calculated LDOS oscillations between 25 and 75 Å away from the defect. The impurity resides in layer N_l, with $N_l = 1$ the surface plane. Fe data are spin-averaged.

	$N_l = 1$	$N_l = 2$	$N_l = 3$
Al	(−0.049, −0.015)	(−0.030, −0.003)	(−0.017, −0.000)
Ag	(+0.030, −0.010)	(+0.019, −0.004)	(+0.012, −0.003)
Rh	(+0.012, −0.035)	(+0.006, +0.003)	(+0.010, +0.002)
Mo	(+0.093, +0.153)	(+0.100, +0.008)	(+0.048, +0.003)
Fe	(+0.026, +0.071)	(+0.034, +0.013)	(+0.014, +0.008)

In this form, only terms with $M, M' = 0, \pm 1$ are found to make sizeable contributions—the important states have large wavelengths and are pushed further away from the defect with increasing $|M|$, becoming less perturbed. Circular symmetry arises because symmetry restricts $M - M'$ to $0, \pm 3j$ for integer j. Only including G_{00} gives a good approximation for the large-ϱ behaviour with Al, Ag and Fe(↑) (which has a full d resonance), although the local structure, which includes contributions from continuum levels of shorter wavelength, is poorly represented. The transition metal impurities generally result in large perturbations in three-dimensional angular scattering, including $\ell, m = 2, \pm 2$ states which only enter $G_{MM'}$ for $|M|, |M'| \geqslant 1$. For these $G_{11} (= G_{-1-1})$ must also be included even for the long-range LDOS oscillations, and so two phaseshifts should be used in fitting to (4). However, over a restricted radial range such a fit is not particularly unique, and this will be even more true with any experimental noise.

What are the prospects for observing these LDOS oscillations? There are, in fact, indications that they have been observed [15] in the case of Pb impurities at the Cu(111) surface and unidentified impurities (possibly oxygen) subsurface. Pb is beyond the treatment here, due both to relativistic effects and to the size mismatch, the latter possibly giving rise to a larger perturbation and stronger LDOS oscillations. For the impurities considered here, since both n_c and Δn (at least for large ϱ) decay like $\exp 2\gamma_{k_0} z$ it is a simple matter to converted from LDOS at fixed height as calculated here (figure 3) to the variations in height $\delta z(r_\parallel)$ which produce constant LDOS, corresponding to topological scans with the STM at constant current for low bias and small amplitude [16]. For the clean surface the variation in $n_c(r; E)$ (see figure 1) corresponds to amplitudes $\delta z \sim 0.0002$ Å , well below the resolution of the STM. Calculated peak to trough corrugation amplitudes due to some impurities in the first two layers of the Cu(111) surface are tabulated in table 2. As is to be expected δz decreases with depth and the values are somewhat smaller than those reported for adatom scattering. However, with the resolution reported in [2, 3] standing waves for some of the impurities should be observable. Even when this is not the case, species identification may be possible due to the characteristic local structure in Δn (within ~30 Å) which produces larger tip height variations.

Table 2. Characteristic peak to trough corrugation amplitudes (Å) predicted for the STM operating in constant current topographic mode at small bias, 30–60 Å away laterally from substitutional impurities near the Cu(111) surface. The impurity resides in layer N_l, with N_l=1 the surface plane. Fe data are spin averaged.

N_l	Al	Ag	Rh	Mo	Fe
1	0.0040	0.0023	0.0025	0.0083	0.0037
2	0.0021	0.0013	0.0010	0.0065	0.0022

Finally, the theory presented here is equally applicable to adatoms and adatom arrays, which have recently received experimental [2–4] and theoretical [11, 17] attention and it is hoped to consider these cases in future work. The local environment surrounding an adatom is sufficiently different from a buried impurity for direct transfer of observations made here—importance of $|M| = 1$ states and lack of simple relationship between phaseshift and electronic structure—to be unreliable. However, it does seem reasonable to expect that the adatoms which will act as strongest scatterers will be those with narrow d resonances near the relevent energy, with strong scattering by both spin channels obviously important.

The author wishes to thank G Hörmandinger for bringing to his attention the work of P Varga and coworkers, to P Avouris and P Varga for informative communications and to J E Inglesfield and G Makov for some useful comments.

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