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Grazing-ion-surface interaction as a probe of surface states

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We propose a simple theoretical model for the study of the electronic structure of surface bands by the measurement of resonant charge transfer between localized surface electrons and grazingly incident projectiles. We present an analytic expression for the parallel velocity dependence of the scattered charge-state fraction, and show how it can be used to estimate the Fermi level and width of the surface band. [S0163-1829(97)06427-8]

The velocity dependence (both parallel and perpendicular) of scattered charge fractions has been intensively studied for projectiles grazingly interacting with metal targets[1–3] for a number of years already, and more recently with some insulators as well.[4,5] For projectile velocities in the range of 0.05 to 0.6 a.u. and incidence angles of the order of a degree, grazing ion-surface collisions are characterized by two different characteristic time scales, the first being the very slow motion normal to the surface plane, which defines the time scale at which resonant electron transfer occurs with the surface within the adiabatic regime, and the second being the fast motion parallel to the surface, which determines which target electrons can be accessed in the rest frame of the projectile (‘‘kinematic resonance’’[6]). The latter manifests itself in the parallel velocity dependence of the resonant electron transfer process. In general, resonant electron transfer occurs during interactions of ions or atoms with solid surfaces if the projectile's ground state lies close to the Fermi level of the target. The final charge fraction of scattered projectiles, as determined by resonant electron transfer between projectile and target under grazing conditions, can provide some information about the surface electronic structure of the target, since under such conditions the transfer occurs above the surface, and only target electrons at the surface have wave functions of sufficient spatial extent to have significant overlap with the relevant projectile atomic level.

There are two different types of electronic states at the surface, bulk states and surface states. Bulk states are extensions of bulk electronic states at the surface, whereas surface states are truly localized at the surface with energies lying inside the bulk band gap. In metal or semiconductor targets, surface states are usually very close to the conduction band or valence bands. As a result, the electronic states involved in resonant electron transfer come dominantly from bulk states rather than surface states. Studies have been carried out for a number of years that have investigated the velocity dependences of scattered neutral fractions[7,8] for alkali projectiles grazingly interacting with metal or semiconductor targets. Due to the complicated dependence of the transition probability on the $\vec{k}$ vector of the electron, only a limited amount of information on the three-dimensional (3D) band structure can be extracted from charge-transfer measurements. On the other hand, if true surface states are involved in the resonant electron-transfer process, for which the target electronic motion is two dimensional (2D) in nature, it is possible to extract detailed information about the band structure from the dependence of the scattered projectile charge-states on velocity. In this paper, we describe a simple theory by use of which the parallel velocity dependences of scattered projectile charge state distributions can be used to probe the electronic properties of surface states. Such an approach could complement other probes of surface states, such as angle-resolved photoemission,[7,8] inverse photoemission,[8] and electron scattering.[9]

Some theoretical treatments of charge transfer[10,11] during grazing interactions with metal surfaces have used a two-state classical rate equation approach, in which initial and scattered charge states are coupled by a transition rate given by the 3D wave-function overlap weighted by the number of initial available resonant electronic states of the metal target. The rate equation is solved along the outgoing trajectory assuming an exponential dependence of the transition rate on above-surface distance. Beyond some distance termed the ‘‘freezing distance,’’[10,12] the transition probabilities become negligible, and the rate of change of the scattered charge distribution goes to zero, at which point the final charge states are essentially determined. Within such a framework, the charge-state distribution is determined as the equilibrium solution of the rate equation describing the coupling of the atomic level with the Galilei-shifted Fermi sphere. Under various simplifying assumption, the charge-state fraction can be written in terms of a Saha equation[3]

$$P(v)=\{1+(g^{-}/g^{+})\exp[f(v)]\}^{-1} \tag{1}$$

with

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$$f(v)=(\Delta+v^2/2)/v_c v, \tag{2}$$

where Δ is the ''energy gap,'' i.e., the difference between the Fermi level and the energy of the atomic level including the effective energy shift ΔE_a of the atomic level (including image shift) at the ''freezing distance'' and is given by $\Delta=\Phi-|E_a+\Delta E_a|$, with Φ the work function of the target. The characteristic velocity v_c is a fit parameter related to an ''effective nonthermal temperature''[11] of the target electron Fermi-Dirac distribution, and g^-/g^+ is the ratio of statistical weights of the initial and final atomic levels. Because of the underlying assumption of equilibration, the explicit dependence on transition rates has disappeared. However, the dependence of the transition rate on the freezing distance and on the parallel and perpendicular velocity of the transfered electrons is implicitly contained in the fit parameters. If additional information is available on the energy shift ΔE_a as a function of the distance from the surface, the fit to Eq. (1) can provide information on the freezing distance. However, information on the band structure, in particular the Fermi energy, is difficult to extract. As shown below, for the case of charge transfer with a 2D surface band, the situation is simplified considerably.

The present model for resonant charge transfer involving occupied surface states relies on the properties of the surface state wave function above the surface $(z>0)$. Using the expression in terms of a nearly-free-electron (NFE) approximation, the surface-state wave function above the surface $z>0$ with reduced wave vector $\vec{k}$ parallel to the surface and energy E can be written as the following sum over the surface reciprocal lattice $\vec{g}$:[13,14]

$$\Psi_{E(\vec{k})}(\vec{r},t)=\sum_{\vec{g}} b(\vec{k},\vec{g})\exp[-\gamma(\vec{g},\vec{k})z]\exp[i(\vec{k}+\vec{g})\vec{r}] \times\exp[-iE(\vec{k})t], \tag{3}$$

where the decay constant of the evanescent wave into the vacuum is given by

$$\gamma(\vec{g},\vec{k})=\sqrt{2m^*[V_0-E(\vec{k})]+(\vec{k}+\vec{g})^2} \tag{4}$$

for energies $E(\vec{k})$ of the surface band in the band gap and m^* is the effective electron mass of the surface band. The Galilei transform of Eq. (3) $T(\vec{v}_p)$ to the frame of the projectile moving with velocity $\vec{v}_p$ parallel to the surface,[15–17]

$$\begin{aligned}T(\vec{v}_p)\psi_{E(\vec{k})}(\vec{r},t) &=\sum_{\vec{g}} b(\vec{k},\vec{g})\exp[-\gamma(\vec{g},\vec{k})z]\exp[i(\vec{k}+\vec{g}-m^*\vec{v}_p)\vec{r}]\\ &\times\exp\{-i[E(\vec{k})-m^*\vec{v}_p(\vec{k}+\vec{g})+\tfrac{1}{2}m^*v_p^2]t\},\end{aligned} \tag{5}$$

enters the description of charge transfer in terms of a kinematic resonance. One key observation is now that under the assumption of a narrow surface band $k_F \ll g$ (or $\epsilon_F \ll g^2/2m^*$) the exponential damping of the evanescent wave [Eq. (4)] is governed by the magnitude of reciprocal lattice vectors. Note that k_F and ϵ_F of the surface band are different from the corresponding bulk quantities. Accordingly, at typical distances of the projectile from the surface where resonant charge transfer is expected to take place (''freezing distance''),[12,16] the term $\vec{g}=0$ in Eq. (3) dominates. In this limit, translation invariance is approximately restored and Eq. (5) becomes

$$T(\vec{v}_p)\psi_{E(\vec{k})}(\vec{r},t)=\psi_{E(\vec{k}-m^*\vec{v}_p)}(\vec{r},t). \tag{6}$$

In other words, near the freezing distance the effect of corrugation is of minor importance. The condition for resonant charge transfer into a projectile-centered atomic level with energy E_a is given by

$$E(\vec{k}-m^*\vec{v}_p)=E_a. \tag{7}$$

Using a locally quadratic dispersion of the band $E(\vec{k})=E_b+k^2/2m^*$, Eq. (7) can be simply written as

$$(\vec{k}-m^*\vec{v}_p)^2=K_a^2, \tag{8}$$

with $K_a=(2m^*|E_a-E_b|)^{1/2}$. We note in passing that Eqs. (5) and (6) can, under otherwise identical assumptions, also be derived from a tight-binding ansatz for surface states. For a 2D surface band, the density of occupied surface states satisfying the resonance condition [Eq. (8)] is proportional to the geometrical overlap between a circle of radius K_a and the Fermi ''disk'' of radius k_F, representing the surface band, Galilei shifted into the frame of the projectile. The geometrical overlap $\mathcal{F}$ is given by

$$\mathcal{F}=\arccos\left(\frac{\Delta+\frac{1}{2}m^*v_p^2}{K_a v_p}\right)\Big/\pi \tag{9}$$

with Δ the energy gap as defined above. For a surface band the charge exchange probability can be assumed to be directly proportional to the density of occupied states in kinematic resonance [Eq. (9)]. This is different from a bulk band due to the fact that the Fermi sphere is compressed to a disk. Dispersion effects in the z direction that lead to strong variations of the transitions matrix elements over the resonance surface for capture[18] are absent. If the dispersion of the surface band deviates from a purely quadratic behavior [Eq. (8)], the corresponding overlap function must be calculated numerically.

The resulting velocity dependence of the scattered neutral fractions for incident projectiles can now be easily visualized by reference to the diagrams shown in Fig. 1. For $K_a<k_F$ (i.e., atomic level below the top of occupied surface band), the overlap with occupied states is complete. The neutral fraction will decrease monotonically with increasing parallel velocity starting at a threshold of ionization $v_{\text{th}}=(k_F-K_a)/m^*$, falling to zero above $v_{\max}=(K_a+k_F)/m^*$. On the other hand, for $K_a>k_F$ (i.e., atomic level above the top of the occupied surface band), the neutral fraction will start to increase from zero when the surface band electrons are first brought into resonance at a threshold velocity of $v_{\text{th}}=(K_a-k_F)/m^*$, reach a maximum, and then decrease as the overlap decreases again. At a velocity $v_{\max}=(K_a+k_F)/m^*$ the overlap, and therefore the neutral fraction, goes to zero. The total width of the resonance peak is twice the Fermi velocity, while the mean of v_{th} and $v_{\max}$ gives K_a. These two parameters, which specify the

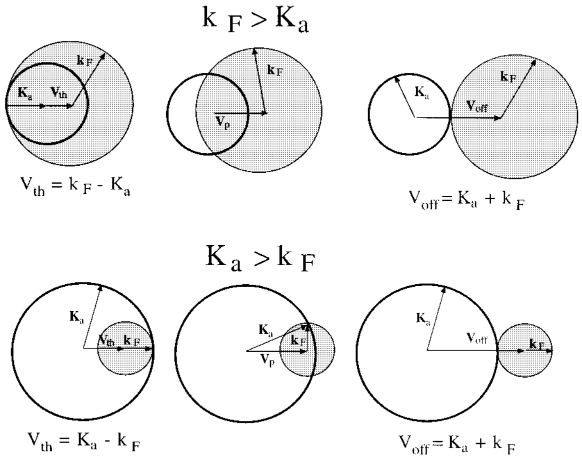

FIG. 1. Schematic diagrams of the geometric overlaps of occupied surface states (represented by Fermi disk of radius k_F) in resonance with projectile atomic level (represented by the circle with radius of K_a as defined in the text) for different projectile velocities.

position of the surface band in relation to the projectile level into which transfer occurs as well as its width, can be readily determined from the gross features of the experimental data. A more precise determination can, of course, be obtained by fits of the data to Eq. (9). By contrast, for a NFE band in 3D such a simple extraction of the band-structure parameters is not possible because of the complicated dependence of the decay constant γ on both k_z and $k_\parallel$.

Figure 2 illustrates the scaled velocity dependence of the overlap function [Eq. (9)], expected for the different conditions described above, when plotted as a function of the dimensionless projectile velocity $v_p^*=v_p/v_F$, for a range of values of $K_a^*=K_a/k_F$. With this variable transformation and setting $m^*=1$, Eq. (9) takes the following form:

$$\mathcal{F}=\arccos\left(\frac{K_a^{*2}-1+v_p^{*2}}{2K_a^* v_p^*}\right)\Bigg/\pi. \qquad (10)$$

The velocity dependence displayed in Eq. (10) is universal in the sense that it only depends on two scaled variables v_p^* and K_a^*. Values of K_a^* greater than 1 correspond to positive ''energy gaps'' (i.e., atomic level lies above the top of the surface band), while those less than 1 correspond to negative ''energy gaps'' (i.e., atomic level lies energetically within the surface band). The following limitations of the present description should be pointed out: the magnitude of the scattered neutral fraction is known only to within a scale factor. The latter does not influence, however, the extraction of the band-structure parameters. Furthermore, as is the case for the 3D model [Eq. (1)] we have assumed equilibration and that transition matrix elements do not feature any additional velocity dependence beyond the Galilei shift incorporated in Eq. (9).

We have demonstrated that the parallel velocity dependence of scattered neutral or negative ion fractions can provide direct information on the location of the top of an occupied surface band in relation to the relevant shifted projectile level as well as on ϵ_F, the effective width of the occupied surface band. In practice, the observation of surface states in grazing incidence charge exchange collisions requires either that surface states are energetically well separated from the bulk valence and conduction band or that their strong localization at the surface induces a propensity for capture. The most promising candidate for the former case would appear to be a metallized surface of a wide-band-gap material. In the latter case, surface states whose local density of states strongly dominates over bulk states near the freezing distance are likely candidates.

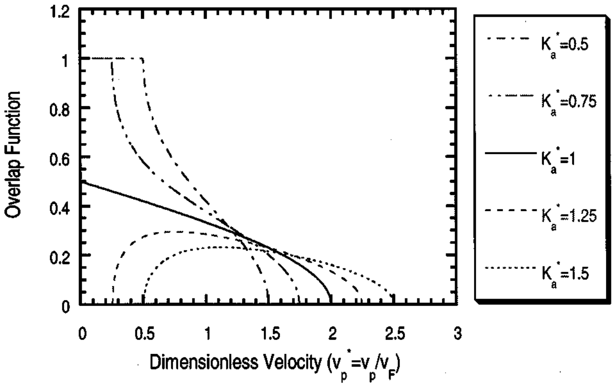

FIG. 2. Scaled neutralization fraction for surface band (overlap function $\mathcal{F}$) as a function of scaled parallel velocity $v_p^*=v_p/k_F$. The curves are calculated using Eq. (10) for different values of $K_a^*=K_a/k_F$.

A third possibility exists in the area of thin films. In this case the electronic motion in the direction of the surface normal is quantized and the electronic structure at the surface consists of an ensemble of 2D surface bands attached to the different quantized levels in the z direction. A recent ''coupled anglar mode'' (CAM) calculation for charge trans-

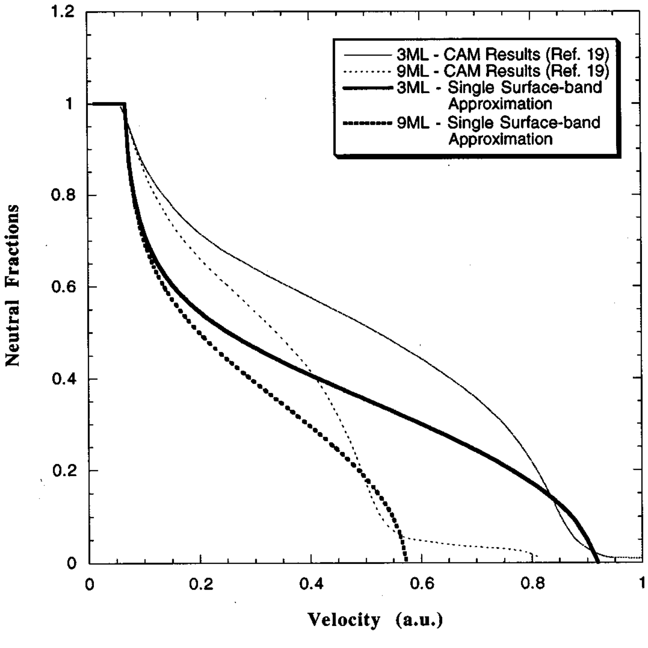

FIG. 3. Comparison between fitted neutralization fractions using overlap function $\mathcal{F}$ [Eq. (10)] and calculation for proton scattering on Al films 3 and 9 ML thick (Ref. 19) as a function of the parallel velocity v_p. The fit parameters obtained suggest dominance of topmost occupied surface band in the projectile neutralization.

fer in grazing incidence collisions with an Al film[19] displays, indeed, a velocity dependence that markedly differs from the corresponding semi-infinite aluminum surface. Even though the applicability of the present theory to this problem is not obvious since the theoretical data of Ref. 19 correspond to the superposition of many subbands, the results can be described reasonably well (Fig. 3) with the simple universal function [Eq. (10)]. Following the prescription given above, the relevant parameters for the surface band, $K_a \approx 0.25$ and $k_F \approx 0.32$ (or $\epsilon_F \approx 1$ eV), are obtained for the 9-ML case, while $K_a \approx 0.42$ and $k_F \approx 0.49$ are the parameters determined for the 3 ML thick film. Both sets of parameters are completely consistent with the assumption that the surface band attached to the quantized level immediately below the respective Fermi edges of the two films (as given in Ref. 19) dominates the neutralization probability. Since the spatial distribution of this band extends furthest out into the vacuum, it is plausible that its contribution dominates the charge transfer process at the freezing distance.

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