Theory of Ion Angular Distributions in Electron-Stimulated Desorption*

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The angular distribution of ions desorbing from the surface of a solid is studied theoretically. Specific calculations for oxygen adsorbed on the (100) face of tungsten are presented. The angular patterns result from the three-dimensional spatial variations in the ion-solid potential surface. Details of the pattern are found to vary sensitively with changes in the surface geometry.

The phenomenon of electron-stimulated desorption (ESD) has been the object of experimental[1] and theoretical[2] research for a number of years. Recent experiments[3] have revealed that ions desorbed from surfaces by electron impact are, in fact, emitted in sharp cones whose orientations are correlated to the substrate geometry. The purpose of this Letter is to offer an explanation for this effect and to show how valuable information concerning surface geometry and surface parameters may be extracted from studying such patterns.

Since previous theories[2] have been restricted to one-dimensional geometries they are not directly applicable to the problem at hand. However we adopt the basic philosophy of these theories and view ESD as a three-step process: (a) promotion of the atom-solid system to an excited electronic state (which is ionic in the large atom-surface separation limit), (b) propagation of of the ion away from the surface, and (c) competition with reneutralization processes (quenching of the ionic state). One might expect that anisotropies in the ground- and excited-state potential surfaces, in the quenching rate, or in the electronic-excitation rate could produce angular patterns. We shall show that, using reasonable values for the physical parameters, the patterns are explainable predominantly in terms of the spatial variation of the ion-solid interaction energy. For the sake of comparing theory with experiment our attention will be limited here to oxygen adsorbed on the (100) face of tungsten, although the methods we will develop will have more general validity. We show how one can use dynamical arguments to link the observed angular distribution patterns to details of the bonding of adatoms on surfaces.

The key to the dynamics is a knowledge of the function $\epsilon_+(r)$, the positive-ion–solid interaction potential. It is fortunately not as difficult to model as the atom-solid or negative-ion–solid potential, because of the absence of significant exchange, correlation, and Pauli repulsion effects. The compact nature of the positive ion makes it, in effect, a local probe of the electrostatic potential produced by the solid. This potential consists of the Hartree fields of the individual atoms, $V_{\rm H}$, plus the image potential, V_I. The possibility of electron tunneling, leading to reneutralization, is always there and is a perturbation on the model, but is neglected here. A numerical fit to detailed calculations leads to the approximate formula for the image potential $V_I = (4z + 1.16 + 1.34r_s - 0.04r_s^2)^{-1}$, where r_s is the usual screening radius. The image potential has a transverse variation due to the discrete nature of the ions of the solid which is not as severe as the variations in the Hartree potential, since the delocalized conduction electrons of tungsten are mostly responsible for the conductivity of the metal. In the present model transverse variations of the image potential are averaged over. We shall henceforth approximate $V_{\rm H}$ by a superposition of free atomic Hartree potentials[5] of the lattice atoms. The substrate will be taken to be rigid and unrelaxed. Furthermore recoil will be neglected. Despite these rather drastic assumptions we shall see that reasonable results ensue. If a more realistic potential were available the same program could be carried through.

We start by modeling the ground-state potential $\epsilon_0(r)$. Here we make a crude estimate for the spring constant (which is not known for the present system). We take the value for hydrogen on tungsten[6] and scale it down by the ratio of the square root of the atomic masses. The temperature was taken nominally to be 700°K. The [110] W-O bond length was determined recently[7] and we accept this value for the (100) face since we do not expect it to be much different. The anisotropy of the ground-state potential has been found to be of little consequence in our computer runs so is neglected. Points in phase space are ran-

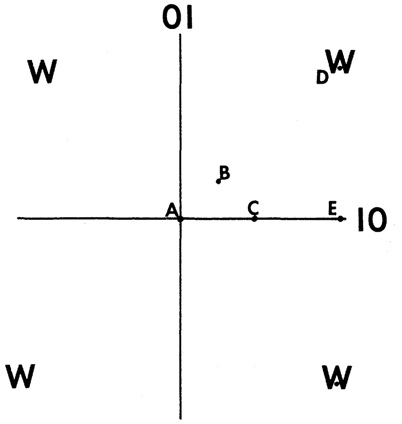

FIG. 1. Sketch of the (100) face of tungsten with several reference points labeled. W denotes the tungsten atoms.

domly selected according to a Maxwell-Boltzmann distribution. The atoms are converted to ions (by the excitation process) and follow an appropriate dynamic trajectory. The asymptotic direction of the ion is recorded and displayed in the figures to follow. For those cases where sharp cones occur, the effect of surviving the quenching process just leads to a constant-numerical-factor correction. Since we will not discuss absolute cross sections here but only the angular distributions, we will neglect such numerical factors. For those distributions which are broader in extent the effect of quenching will be to reduce sharply the flux of wide angle ions. This effect has been discussed in the literature[3] and has to do with the amount of time spent in the vicinity of the surface.

In Fig. 1 we present a sketch of the (100) surface of tungsten. Various points on the surface have been labeled for reference purposes. Let us start by examining the angular patterns produced by assuming a single adatom lies on the substrate. In Fig. 2(a) we present the spot pattern produced by assuming that the original atom was centered at point A at a distance of 1 Bohr from the surface. Figure 2(b) shows the spot pattern when the atom is located at position D a distance of 4 Bohr from the surface (both positions corresponding to realistic[8] W-O bond lengths). We see that the spot patterns do not have lobes. Positions A and D are high-symmetry points where the potential surfaces have approximate cylindrical symmetry. Thus there is no reason for preferred azimuthal emission directions to occur. A similar result has been found for the atom at point E, a distance of 3.0 Bohr above the surface. In the low-coverage phase (β_2 phase) it has been conjectured that the atoms go into position D and no sharp lobes have been found experimentally, although there appears to be a hint of a hazy cross pattern.[3]

In Fig. 3(a) we present the spot pattern associated with the atom lying originally at point B (coordinates $x=0.7a_0$, $y=0.7a_0$, $z=1.0a_0$, where $a=5.97a_0$ is the tungsten lattice constant). Here we see sharp islands appear. The angular patterns have a fourfold rotational symmetry and a fourfold reflection symmetry—resulting in a replication of the pattern of the first octant in the other seven octants. In Fig. 3(b) the spot pattern associated with point C ($x=1.4a_0$, $y=0$, $z=1.0a_0$) is presented. The pattern also displays sharp cones but rotated by an angle of $\pi/4$. In both

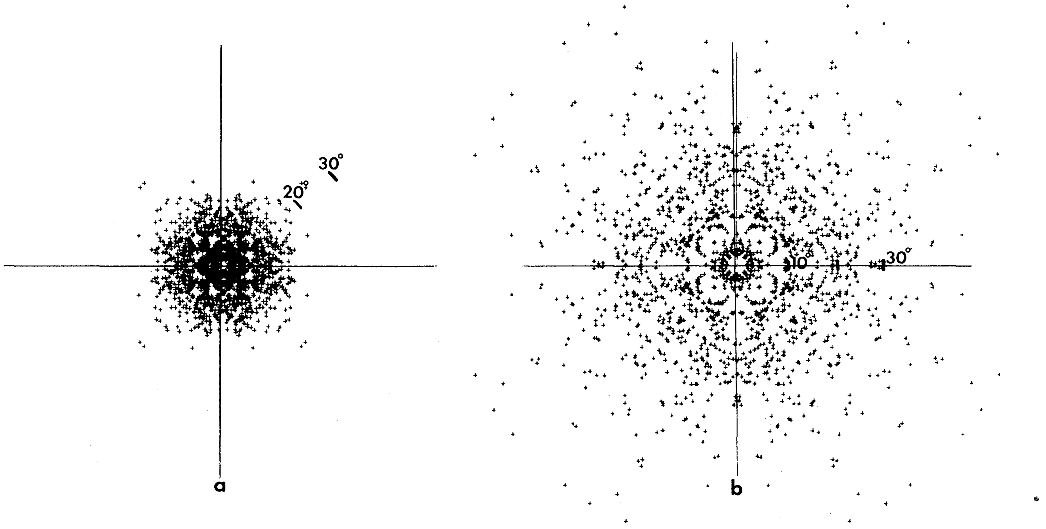

FIG. 2. Spot patterns corresponding to reference points A and D of Fig. 1.

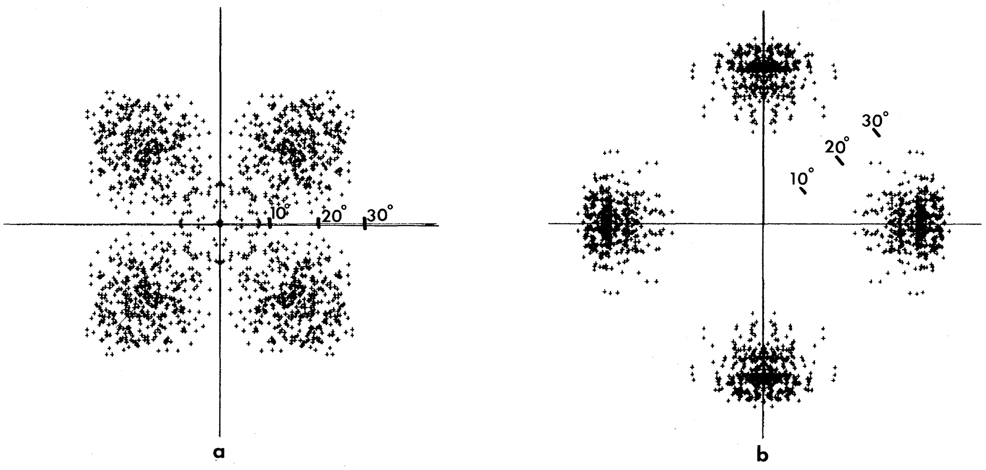

FIG. 3. Spot patterns corresponding to reference points B and C of Fig. 1.

cases the upper-state potential surface is highly anisotropic and thus the dynamical evolution of the trajectories could be expected to produce sharp angular patterns. The degree of angular divergence of the cones as well as their size depend on both the distance away from the surface and the distance away from symmetry points in the plane of the surface. Since we are using a rather crude ionic potential we shall not explore the systematics of the variation here. However if a more accurate ion-solid potential were available, one should be able to pin down the approximate location of the adatom.

One must emphasize that the spot patterns are not unique to the geometries cited above. If one now looks at situations where there are two adatoms (e.g., an O_2 molecule) adsorbed on the surface, it is possible that the second oxygen atom provides an asymmetric potential for the ion to be accelerated by. In Fig. 4(a) we show the spot pattern resulting from a molecule situated at point D with orientation parallel to the [10] direction. In Fig. 4(b) we have the molecule rotated by an angle of $\pi/4$ in the surface plane. The interatomic oxygen distance has been taken to be that appropriate to molecular oxygen. Since experimentally the cones are associated with the β_1 phase of adsorbed oxygen and since this phase is believed to involve molecular oxygen, we see that a reasonable explanation can be had in the context of such a model.

In summary we have shown that the angular patterns can be explained in terms of the dynamics of the ion-solid interaction. Two possibilities exist to explain the patterns. Both involve the three-dimensional spatial asymmetry of the potential seen by the oxygen ion when it is produced. The first situation involves a single atom located

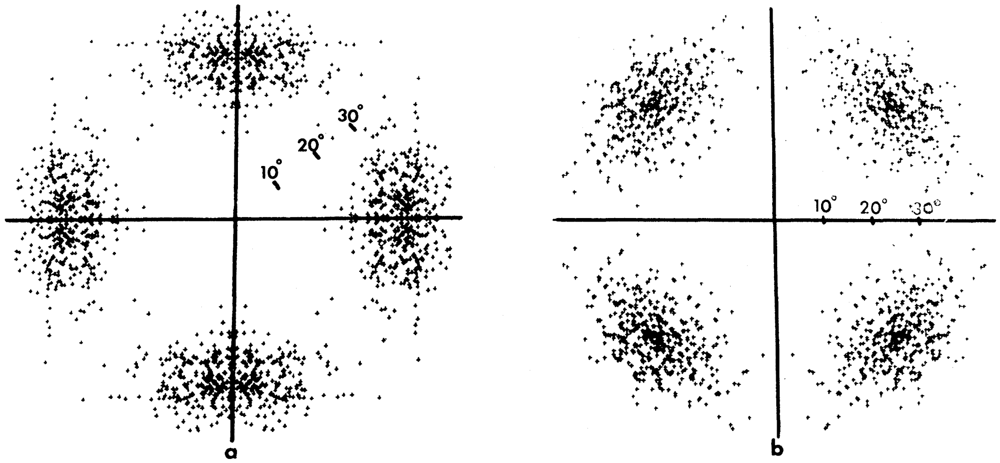

FIG. 4. Spot patterns corresponding to desorption from molecular oxygen.

at a nonsymmetry site. Such a nonconventional location could be brought about by subtle long-range interactions between oxygen atoms on the surface. The second situation involves an oxygen molecule pinned to a tungsten atom on the surface. The present theory is not able to differentiate between these cases. Thus further diagnostics and analysis are necessary. Currently we are investigating the possibility that vacancies in an oxygen overlayer could give rise to additional potential asymmetries.

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[1] For recent reviews see D. Menzel, Surf. Sci. 47, 370 (1975); T. E. Madey and J. T. Yates, Jr., J. Vac. Sci. Technol. 8, 525 (1971).

[2] P. A. Redhead, Can. J. Phys. 42, 886 (1964); D. Menzel and R. Gomer, J. Chem. Phys. 41, 3311 (1964).

[3] T. E. Madey, J. J. Czyzewski, and J. T. Yates, Jr., Surf. Sci. 49, 465 (1975), and Phys. Rev. Lett. 32, 777 (1974).

[4] J. I. Gersten, R. Janow, and N. Tzoar, Phys. Rev. B 11, 1267 (1975).

[5] We have used the Herman-Skillman wave functions to calcuate a rough estimate for these potentials.

[6] E. W. Plummer and A. E. Bell, J. Vac. Sci. Technol. 9, 583 (1972); F. M. Propst and T. C. Spicer, J. Vac. Sci. Technol. 4, 53 (1967).

[7] M. A. Van Hove and S. Y. Tong, Phys. Rev. Lett. 35, 1092 (1975).

[8] We use the bond length determined in Ref. 8.

Prediction of Strong Bonding Effects and an Anomalous Form Factor in Sc Metal*

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Field-induced magnetization densities of Sc metal determined from augmented plane-wave functions, including local density-of-states effects, were found to show a large spatial expansion of the 3*d* density and strong bonding effects. These result in an "anomalous" behavior of the neutron magnetic form factor which has been found in the experiments of Koehler and Moon.

Although the electronic energy band structure and the related properties of transition and rare-earth metals appear to be well understood, direct information about the nature of their wave functions has been difficult to obtain. Knowledge about wave-function-related phenomena is becoming increasingly important for the challenges presented to our theoretical understanding. Neutron magnetic scattering experiments allow the possibility of obtaining, through Fourier inversion of the measured magnetic form factor, detailed information about the spatial distribution of the magnetization density. In general, however, free-ion form factors have been found to give an excellent description of the magnetic scattering observed in transition metals and thus appeared to obviate the need for band theoretical calculations. Recently, the precise and detailed determination of Moon *et al.*[1] of the magnetic form factor of ferromagnetic Gd metal, which well illustrates the promise of the method, revealed a serious flaw in the predictions of the band theory approach to the magnetization density. In analyzing their results, Moon *et al.* separated the total form factor into a "local" part, representing the localized 4*f* electrons, and a remainder presumably due to the diffuse distribution of the polarized conduction electrons. The localized part of the form factor was found to be reproduced very precisely by the fully relativistic Dirac-Fock free-ion/atom calculations of Freeman and Desclaux.[2] However, the spin-polarized augmented plane-wave (APW) calculations of Harmon and Freeman[3] resulted in only qualitative agreement between the theoretical conduction-electron spin density and experiment, principally because of lack of agreement at the first of the several inner (*hkl*) reflections from which the spin density