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Spin-polarized metastable-atom deexcitation spectroscopy: A new probe of the dynamics of metastable-atom–surface interactions

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Spin-labeling techniques, specifically the use of electron-spin-polarized metastable atoms coupled with spin analysis of the ejected electrons, are used to probe the dynamics of metastable atom-surface interactions. In particular, the data show that the electrons involved in Auger neutralization tend to have antiparallel spins and that secondary electrons can provide a significant contribution to the total ejected electron signal.

Experiments in several laboratories have demonstrated that metastable atom deexcitation spectroscopy (MDS) provides a valuable probe of surface electronic properties.[1] In MDS, a thermal-energy beam of rare-gas metastable atoms is directed at the surface of interest and the energy distribution of electrons ejected from the surface as a result of metastable atom deexcitation is measured. Because the internal energy of the incident metastable atoms is well defined, analysis of the ejected electron distribution provides information on the local density of electronic states at the surface. This spectroscopy is attractive because it is particularly surface specific and because the incident metastable atoms do not modify the surface either through sputtering or chemical reaction. Detailed interpretation of MDS data, however, requires a thorough understanding of the mechanisms that give rise to electron ejection. In the present work we demonstrate that use of spin-labeling techniques, specifically the use of electron-spin-polarized metastable atoms coupled with spin analysis of the ejected electrons, can illuminate directly the dynamics of metastable atom-surface interactions thereby increasing the value of MDS as a surface spectroscopy.

The present apparatus is shown schematically in Fig. 1.[2,3] A fraction of the atoms contained in a ground-state helium atom beam are collisionally excited to the $2\,^{1,3}S$ levels by a coaxial electron beam. The $2\,^1S$ atoms are removed from the beam by illuminating it with 2.06-μm radiation from a helium discharge which excites $2\,^1S \rightarrow 2\,^1P \rightarrow 1\,^1S$ transitions. A weak ($\sim$500 mG) magnetic field is applied perpendicular to the beam to preserve a well-defined quantization axis. Circularly polarized 1.08-μm $2\,^3S \rightarrow 2\,^3P$ resonance radiation from a high-power rf-excited helium lamp is incident along the magnetic field direction and is used to optically pump the $2\,^3S$ atoms to increase the relative populations in the $M_J(M_S) = +1$ or -1 magnetic sublevels. The resultant beam polarization[4] $P_z \sim 0.40$ is measured by a Stern-Gerlach analyzer. A mechanical chopper is used, in conjunction with time-of-flight techniques, to eliminate any possibility of effects due to photons or fast neutral atoms that might be produced in the source.

In initial experiments the electrons ejected from the target surface by metastable-atom impact were accelerated directly into a medium-energy (30-keV) Mott polarimeter[5] in which their average, energy-integrated polarization (relative to the quantization axis defined by the applied magnetic field) was determined by measuring the asymmetry in the count rates of electrons quasielastically scattered at ±120° from a gold film. More recently, improvements in Mott polarimeter technology have permitted incorporation of a retarding potential energy analyzer (as is illustrated in Fig. 1), thereby making possible energy-resolved polarization measurements.[6] The polarization of those electrons in a selected energy interval $E - \Delta E/2$ to $E + \Delta E/2$ is determined by switching the potential applied to the retarding grid in the analyzer between the appropriate limits and measuring the asymmetry in the resultant *changes* in the count rates of electrons scattered from the gold film. The apparatus also in-

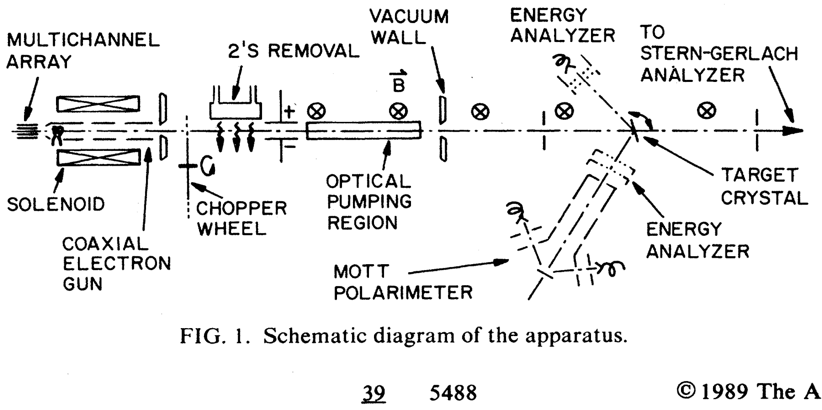

FIG. 1. Schematic diagram of the apparatus.

cludes a separate retarding potential-energy analyzer to permit direct measurement of ejected-electron energy distributions.

Ejected-electron energy distributions and energy-resolved polarizations (normalized to unit incident metastable atom polarization) measured for a chemically cleaned (but otherwise untreated) Cu(100) surface, an atomically clean Cu(100) surface, and a Cu(100) surface with a potassium adlayer are shown in Figs. 2(a), 2(b), and 2(c), respectively. The corresponding average, energy-integrated polarizations are presented in Table I together with results obtained from a variety of other surfaces.

The marked differences in the observed energy and polarization distributions evident in Fig. 2 suggest that in each case different ejection processes are operative. The electron-ejection processes that can occur when a He($2\,^3S$) atom is deexcited at a clean metal surface have been discussed by Hagstrum[7] and are illustrated schematically in the energy-level diagrams shown in Fig. 3. If the work function of the surface is sufficiently large, then an incident $2\,^3S$ atom first undergoes resonant ionization (RI) in which the excited $2s$ electron tunnels into an unfilled level above the Fermi surface in the metal, as indicated by the wavy arrow in Fig. 3(a). The resulting He^+ ion continues toward the surface where it is neutralized by a conduction electron from the metal, the released energy being imparted to a second (Auger) electron in the metal which may, if the energy transferred is sufficiently large, be ejected from the surface. This two-electron process is termed Auger neutralization (AN). At low work-function surfaces RI cannot occur because there are no vacant levels of appropriate energy within the metal. In this situation He($2\,^3S$) atoms are deexcited via the Auger deexcitation (AD) process diagramed in Fig. 3(b). In this process an electron from the metal tunnels into the helium ground atomic state and the energy released is communicated to the $2s$ electron which is ejected. The presence of adsorbed layers on a metal surface can also inhibit RI by preventing a good overlap between the $2s$ wave function and vacant states within the metal. In this situation deexcitation again occurs by AD. Because the electron tunneling to the helium ground state originates in the adsorbed layer, this process is similar to gas phase Penning ionization and is frequently termed surface Penning ionization (SPI).

Information as to the ejection processes operative under a particular set of surface conditions can be obtained from both the high energy cutoff and the form of the ejected electron energy distribution. For example, RI+AN results in a relatively structureless energy distribution that reflects, approximately, a self-convolution of the local density of electronic states at the surface whereas AD, a quasi-one-electron process, results in energy distributions that reflect more directly the local density of states and that can contain relatively sharp features. The ejection mechanisms can, however, be probed directly, as is evident from Figs. 3(a) and 3(b), by spin polarizing the incident He($2\,^3S$) atoms and measuring the polarizations of the ejected electrons. In RI+AN the ejected electron originates in the surface in which case, for nonmagnetic surfaces, any detected polarization is a measure of the correlation in spin orientation between the ejected and neutral-

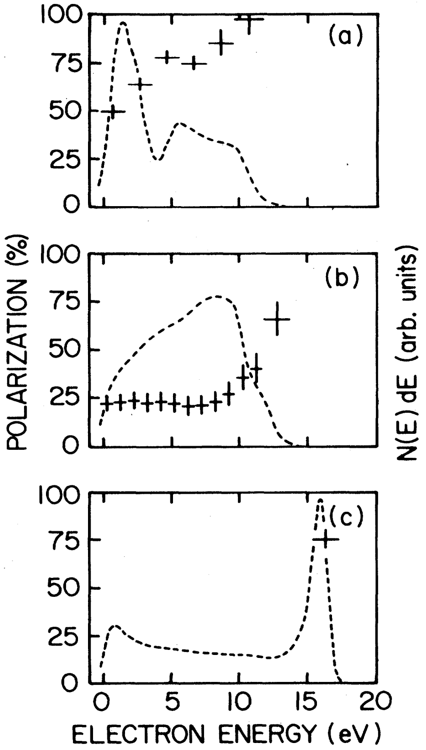

FIG. 2. Ejected-electron energy distributions (dashed lines) and energy-resolved polarizations (normalized to unit incident metastable atom polarization) for He($2\,^3S$) deexcitation at (a) a chemically cleaned Cu(100) surface, (b) a clean Cu(100) surface, and (c) a Cu(100) surface with a potassium adlayer.

TABLE I. Average polarization of ejected electrons produced by the deexcitation of polarized rare-gas metastable atoms at a variety of surfaces. The ejected-electron polarizations are normalized to unit incident metastable atom polarization.

	Chemically cleaned Cu(100)	Chemically cleaned Pd(110)	Atomically clean Cu(100)	Atomically clean Pd(110)	Cu(100) $(\sqrt{2}\times\sqrt{2})R45$O	Pd(110)/CO Saturation coverage
He($2\,^3S$)	0.74 ± 0.10	0.80 ± 0.10	0.22 ± 0.03	0.19 ± 0.03	0.25 ± 0.03	0.41 ± 0.05
Ne($^3P_2$)		0.61 ± 0.08		0.09 ± 0.02		
Ar($^3P_2$)		0.62 ± 0.08		0.12 ± 0.02		

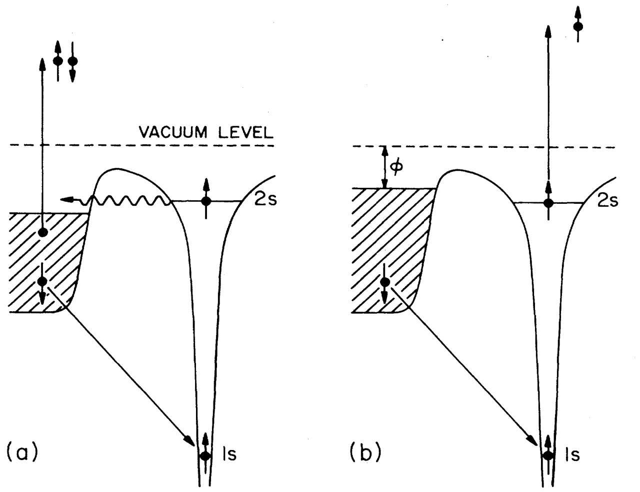

FIG. 3. Schematic diagram of the electron-ejection processes that can occur when He($2\,^3S$) atoms are deexcited at a clean metal surface.

izing electrons. In AD or SPI it is the 2*s* atomic electron that is ejected with polarization equal to that of the incident He($2\,^3S$) atom beam.

As noted in earlier flowing helium afterglow studies,[8] the average polarization of electrons ejected from chemically cleaned surfaces by polarized He($2\,^3S$) atoms is large [Fig. 2(a)] indicating that, as might be expected, electron ejection results from SPI. The ejected-electron polarization, however, is on average, less than unity and, at least for the copper surface, is energy dependent. This can be explained in terms of the generation of (unpolarized) secondary electrons by electrons produced in the metastable atom-surface interaction that are initially directed into the surface.[9] At the highest ejected-electron energies the measured polarization is close to unity, a characteristic of most gas-phase Penning ionization reactions[8] suggesting that the secondary-electron contribution is small. Because secondary-electron distributions peak at low energies, the relative importance of secondary electrons is expected to increase with decreasing ejected-electron energy, leading to a decrease in the net electron polarization. However, even at the lowest energies the measured polarizations are quite sizable indicating that the low-energy peak evident in the energy distribution is not due solely to true secondary electrons.

In contrast, the polarization of electrons ejected from clean metal surfaces is low. [The surfaces were prepared by repeated Ar$^+$ ion sputtering and annealing cycles. Low-energy electron diffraction (LEED) and Auger analysis indicated that, following this treatment, the surfaces were both well ordered and clean.] The low polarization suggests that deexcitation occurs via RI+AN, as expected for metal surfaces with large work functions. The measured polarizations are, however, nonzero and, given the possibility of secondary-electron production, must represent a lower bound to the true polarization of electrons generated in direct metastable atom-surface interactions. Thus, assuming that ejection results solely from AN with no contribution due to AD, the present results require that the two electrons involved in the AN process tend to have antiparallel spins, an effect that is most pronounced when both electrons originate near the Fermi surface, i.e., at the highest ejected-electron energies. The data are, however, consistent with the Pauli principle which suggests a higher probability for finding electrons of antiparallel spins in close proximity.

Deposition of a potassium adlayer (from an SAES dispenser) on a clean Cu(100) surface results in a marked decrease (measured as ~2.1 eV) in the surface work function and in the appearance of a sharp high-energy feature in the ejected-electron energy distribution [see Fig. 2(c)] that has been ascribed to the potassium 4*s* band.[10] The measured polarization of these electrons is large, indicating that they result from AD. Their polarization is, however, less than unity suggesting degradation due to secondary-electron production. (The other possibility, namely contributions from RI+AN, appears unlikely at these energies.) This would require that the secondary-electron production processes operative at the alkalated surface differ from those at a chemically cleaned surface because, for a chemically cleaned surface, the polarization approaches unity at the highest energies. One possible explanation is that at the alkalated surface there is a high density of unoccupied electron states immediately above the Fermi level. The availability of these states makes possible an electron scattering mechanism in which, in essence, a liberated helium 2*s* electron falls into one of these vacant states and the energy released excites a second electron, which may escape from the surface.

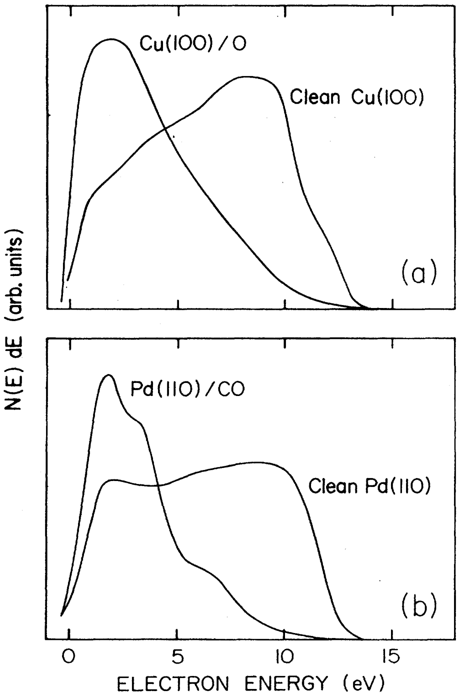

FIG. 4. Ejected-electron energy distributions for He($2\,^3S$) deexcitation at (a) clean and oxygen-covered Cu(100) surfaces and (b) clean and CO-covered Pd(110) surfaces.

Under appropriate conditions, this process can result in the ejection of secondary electrons with energies only slightly lower than the incident electrons, but of opposite spin.

Oxygen adsorbs dissociatively on a room-temperature Cu(100) surface.[11,12] Exposures of ~1500 L resulted in the appearance of a sharp LEED pattern characteristic of an ordered $(\sqrt{2}\times\sqrt{2})$ $R45$ adlayer which, as illustrated in Fig. 4(a), was accompanied by a marked change in the ejected electron energy distribution. The average polarization of the ejected electrons, however, remained essentially unchanged from its clean surface value (see Table I) indicating that, even for the adsorbate covered surface, RI+AN remains the dominant deexcitation mechanism. This suggests that the adsorbed atoms do not shield the incident metastable atoms from vacant metallic states above the Fermi surface. This is consistent with other studies of the Cu(100)/O system that point to the oxygen atoms occupying fourfold hollow sites on the surface essentially coplanar with the surface copper atoms. No significant increase in ejected electron polarization was observed even for exposures in excess of 10000 L.

CO adsorbs nondissociatively on Pd(110) and at saturation coverage results in the appearance of peaks in the ejected electron energy distribution [see Fig. 4(b)] that have been associated with AD (SPI) involving different occupied orbitals of the adsorbed CO molecules.[13] The corresponding average polarization of the ejected electrons, although somewhat higher than for a clean Pd(110) surface (see Table I), is, however, quite low. Even though secondary-electron production can dilute the overall ejected-electron polarization, it seems unlikely that their contributions alone would be sufficient to account for the low polarizations observed with the Pd(110)/CO surface. Energy-resolved polarization studies will be undertaken in hopes of better elucidating the dynamics of metastable atom deexcitation at the Pd(110)/CO surface.

Table I also includes preliminary data obtained using polarized Ne($^3P_2$) and Ar($^3P_2$) metastable atoms, i.e., atoms with $M_J=\pm 2$, $M_L=M_S=\pm 1$. The general characteristics of these data are the same as observed with He($2\,^3S$) atoms. The ejected electron polarizations are large for chemically cleaned surfaces (pointing to SPI) and small, but nonzero, for clean surfaces (indicating RI+AN). In both cases, however, the measured polarizations for Ne($^3P_2$) and Ar($^3P_2$) incident beams are significantly lower than for He($2\,^3S$) beams. This may result from differences in the secondary-electron contributions to the total electron signal, or from effects associated with the nonzero orbital angular momentum of the incident metastable atoms, since reorientation of the orbital moments during surface interactions could lead to a degradation in the spin polarization as a result of spin-orbit interactions. Nonetheless, the present data show that use of spin-labeling techniques can provide significant new information regarding the dynamics of metastable atom-surface interactions. This will permit more detailed interpretation of MDS data and will enhance the power of this spectroscopy as a probe of surface electronic and magnetic properties.

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