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Excited-Atom Deexcitation Spectroscopy using Incident Ions

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Outside a surface of sufficiently low work function, incident 10-eV He$^+$ ions convert to excited atoms which, in turn, eject electrons in the process of Auger deexcitation (Penning ionization). The electron spectroscopy thus demonstrated for He$^+$ incident on Ni(100) with adsorbed K$^+$ is the essential equivalent of that employing incident metastable atoms. Energy and wave-function considerations governing the partition between neutralization and deexcitation processes are discussed and evidence of the surface sensitivity of these processes is presented.

In this paper, it is demonstrated experimentally for the first time that a slowly moving ion incident on a metal surface of sufficiently small work function φ is resonance neutralized to an excited atom which, in turn, is deexcited with the ejection of an Auger electron. Thus, for a category of solid surface meeting certain energy and wave-function specifications, this two-stage, electron-ejection process provides an electron spectroscopy in which the energy distribution of electrons yields directly, without deconvolution, a transition density function approximating the local density of electron states outside the surface. Moreover, this spectroscopy, retains the properties of large beam intensity and particle-velocity variability characteristic of the incident ion beam.

The present experiment bears importantly on the questions now being discussed in the literature as to the conditions that determine when one- or two-stage processes of electron ejection from solid surfaces occur for either incident ions or incident metastable atoms.[1-4] In terms of the processes depicted in Fig. 1, we ask by which of two possible routes does either an incident ion or an incident metastable reach the neutralized, deexcited ground state. The possible component processes are resonance ionization (RI), resonance neutralization (RN), Auger neutralization (AN), and Auger deexcitation (AD). The present experiment also casts further light on the relative surface sensitivities of ultraviolet photomission spectroscopy (UPS) on the one hand and the neutralization and deexcitation spectroscopies on the other.

The present experiment was carried out in the apparatus that has been used for many years in the study of surfaces by means of ion-neutralization spectroscopy (INS) based on the AN process of Fig. 1.[5] He$^+$ ions of 10-eV kinetic energy were used. INS and UPS (He I, 21.2 eV) spectra were measured for the initially clean Ni(100) surface, for the surface after its work function had been reduced from 5.1 to 1.6 eV by adsorption of K$^+$ ions, and for the K$^+$-covered surface as it continued to adsorb gas from the background ambient in the apparatus. $\varphi = 1.6$ eV is achieved by K$^+$ adsorption on Ni(100) at a coverage of 0.2 monolayer.[6]

When the Ni(100) surface was clean and φ was

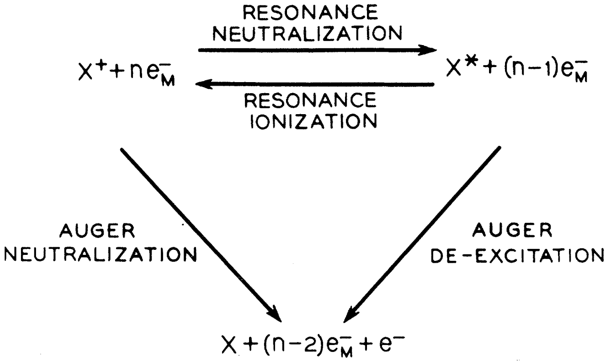

FIG. 1. Schematic diagram of possible electronic transition processes for incident ions (X^+) or excited atoms (X^*). ne_m^- denotes n electrons in the metal; e^-, a free electron.

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5.1 eV, the energy distribution of electrons ejected by the incident ion beam (curve 1 of Fig. 2) had the form of the self-fold of an initial, local state density and is thus characteristic of the AN process. When $\varphi = 1.6$ eV, the energy distribution of electrons ejected by 10-eV incident ions is given as curve 2 of Fig. 2. This does not at all resemble that expected if AN were constrained to occur at the K^+-covered surface (curve 3 of Fig. 2). The higher-energy portion of curve 3 should resemble that of curve 1 shifted to higher kinetic energy by $2\Delta\varphi$. Furthermore, for a Ni valence-band width of approximately 9 eV, curve 3 would be 18 eV wide and extend almost to $(E - E_{\text{vac}}) = 0$.

Curves 1 and 2 of Fig. 2 are plotted as curves 1 and 2 in Fig. 3 on the $E - E_F$ energy scale appropriate to the valence band of Ni. Here curve 1*a* is unfolded, by INS data reduction, from multirun digital data like curve 1.

After the conclusion of the K^+ adsorption, energy distributions of electrons ejected by incident He^+ ions and 21.2-eV photons were measured alternately (Figs. 3 and 4). Ion-beam retardation measurements and the $h\nu - \varphi$ widths of the photoelectron distributions agree in indicating that φ was increasing from its lowest value of 1.6 eV at a rate of 0.02 eV per minute.

Curve 2 of Fig. 3 and curves 2 and 3 of Fig. 4 each has a peak just below E_F as well as two deeper-lying orbital peaks near $E - E_F = -6$ and -10 eV. Because of this agreement, we conclude that curve 2 of Fig. 3 must result from a one-electron–ejection process that is the essential equivalent of photoemission. The only possibility is the two-stage RN + AD process of Fig. 1. As is then necessary the total width of curve 2 of Fig. 3 is close to the excitation energy of the metastable minus φ, $E_x' - \varphi \simeq 19.8 - 1.6 = 18.2$ eV.

The peak just below E_F in curve 2 (Fig. 3) and in curves 3 and 4 (Fig. 4) arises from the Ni *d* band. Note the agreement between curves 1*a* and 2 (Fig. 3). Thus metastables obtained by RN of 10-eV ions produce a *d*-band peak for Ni with adsorbed K^+, whereas 0.066-eV metastables incident on CO-covered Pd(111) eject no measurable electron current from the Pd *d* band [Figs. 2(b), and 2(c) of Ref. 4]. The reasons for this are (1) that the faster metastables from ions are deexcited closer to the surface and thus higher on the exponentially decaying tail of the *d*-band wave function outside the surface, and (2) that many of the incident metastables are Auger deexcited on interaction with CO orbitals that project about two atomic diameters from the Pd surface, whereas the K^+ orbital above E_F at the Ni surface is

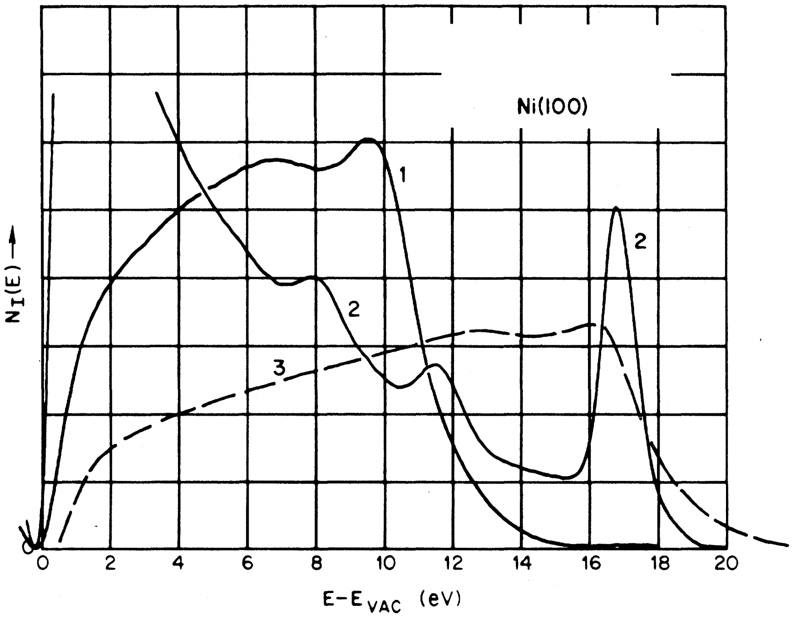

FIG. 2. Photographically reproduced plots of electron energy distributions ejected by 10-eV He^+ ions (full lines). Curve 1, clean surface; curve 2, K^+-covered surface. Curve 3, distribution for the hypothetical case of Auger neutralization at the surface with $\varphi = 1.6$ eV.

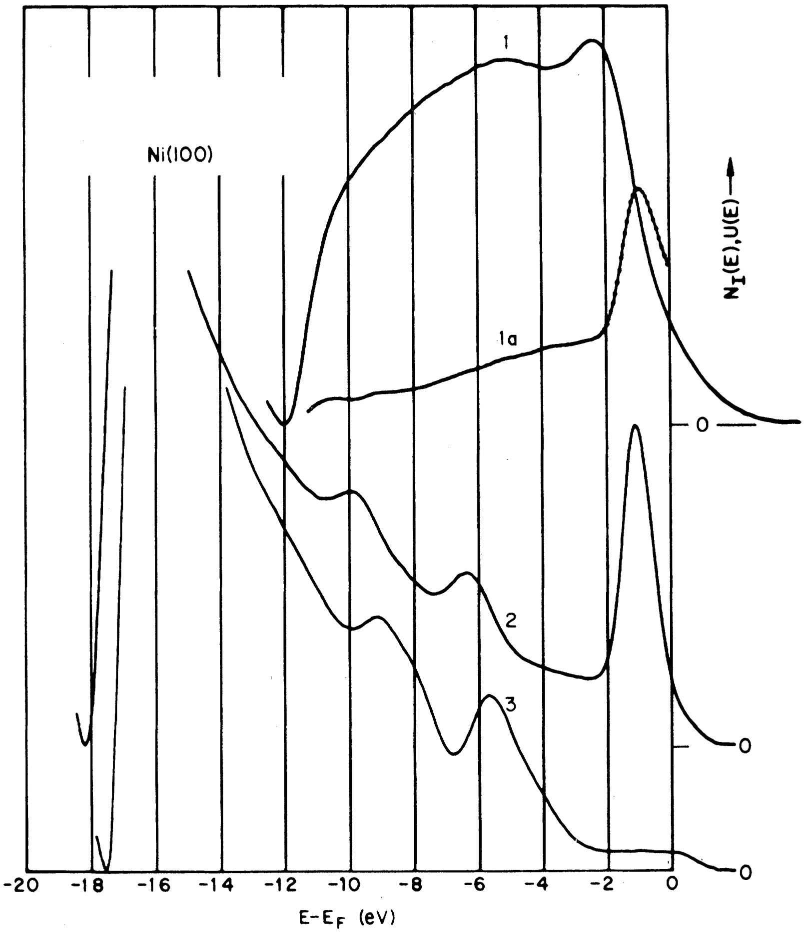

FIG. 3. Energy distributions of electrons ejected by incident 10-eV He$^+$ from the clean surface (curve 1) and from K$^+$-covered surfaces (curves 2 and 3). Surface work functions for curves 1, 2, and 3 were 5.1, 1.6, and 2.1 eV, respectively. Curves 2 and 3 were taken 2 and 27 min., respectively, after conclusion of K$^+$ absorption. Curve 1*a* is unfolded from curve 1.

not involved in the AD process. No attempt is made to interpret the two deeper-lying orbitals. Note, however, that they move toward E_F with increasing φ such that their ionization energies $(E_{vac}-E)$ are invariant.

The most spectacular effect of the continued adsorption of background gas after the conclusion of the K$^+$ exposure is the eventual disappearance of the d-band peak in the electron energy distribution for incident ions (curve 3, Fig. 3). Note that no such disappearance of the d-band peak occurs in the photoemission spectrum of curve 3 of Fig. 4 despite the fact that it was taken later than curve 3 of Fig. 3 (see captions). The surface adsorption that accounts for the 0.02-eV/min rise in φ has after 27 minutes obliterated almost all of the wave-function amplitude outside the solid due to the substrate d band and this fact is not, and cannot be, evident in the photoemission distribution.

It is now possible to state more precisely than has been possible heretofore the conditions that determine for metals whether one- or two-stage electronic transition processes occur for incident ions or metastable atoms. The two governing circumstances are (1) the energy levels near the surface of the excited states in the incoming atom relative to the Fermi level and (2) the relative transition probabilities of possibly competing resonance tunneling and Auger processes as determined by wave-function magnitude. In this discussion $E_n' - E_x'$, the difference between the effective neutralization energy of the ion and the effective excitation energy of the metastable near the surface, is the effective ionization energy of the metastable there. Let R be the total range of

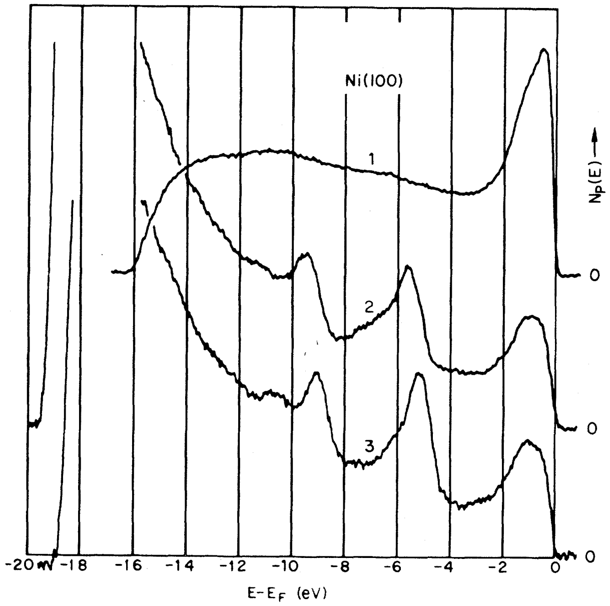

FIG. 4. Energy distributions of photoelectrons ejected by 21.2-eV light from the clean surface (curve 1) and two K$^+$-covered surfaces (curves 2 and 3). $\varphi = 5.1$, 1.9, and 2.3 eV for curves 1, 2, and 3, respectively. Curves 2 and 3 were taken 19 and 37 min, respectively, after conclusion of K$^+$ absorption.

atom-solid separation within which resonance tunneling or Auger processes can occur. The various possibilities will be stated in symmetrical form for incoming helium ions and metastables:

(1) AN (AD) is the only process possible for incident ions (metastables) if $E_n' - E_x'$ is less (greater) than φ throughout R.

(2) If $E_n' - E_x'$ is greater (less) than φ throughout R for incident ions (metastables) the possible processes are partitioned between AN (AD) and RN+AD (RI+AN). The partition is governed by the relative transition probabilities, as determined by wave-function overlap, of the competing Auger and precursor resonance tunneling processes. CO adsorbed on Pd(111) (Ref. 4) affords an example of a partition favoring a measurable component of AD for incoming metastables. Here the projection of the CO molecule from the Pd(111) surface provides at the position of the metastable the requisite wave-function magnitude of filled states below E_{F} relative to that of unfilled states above E_{F}. The relatively low probability of RI is in agreement with the relative inability of AD to detect the substrate *d* band. An example of the predominance of the two-stage process RN+AD for incoming ions ($E_n' - E_x' > \varphi$) is afforded by the present work and of RI+AN for incoming metastables ($E_n' - E_x' < \varphi$) by the clean Pd(111) results.[4] In this latter case the kinetic-energy distribution of ejected electrons has the form of a folded, initial-state, transition density. Unfolding by the INS data-reduction procedure of a smooth digital curve fitted to the data of Fig. 1(b) of Conrad *et al.*[7] yields an initial-state transition density that shows a peak in the range of the Pd *d* band observed by photoemission.

(3) If $E_n' - E_x' = \varphi$ in R, it is possible to vary the partition between one- and two-stage processes by varying the incident-atom velocity as is discussed for incident ions in Ref. 5.

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