Resonant Photoemisson in Nickel Metal

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A strong resonance effect has been observed for the first time in photoemission: This happens on a metallic nickel (100) surface when the photon energy is close to that of the $3p$ energy level. The effect is interpreted as the autionization of an excited quasidiscrete atomic configuration into a continuum of excitations with two holes in the $3d$ shell.

X-ray (XPS) and ultraviolet (UPS) photoemission spectra[1-3] of a clean Ni(100) surface show a weak structure at approximately 6 eV below the Fermi level. The interpretation of this feature has been quite controversial. The XPS core-level spectra ($2s$, $3s$, $3p$) have also a satellite structure about the same energy, which has been attributed to a localized many-body effect in the final state.[4] It has been suggested[2] that the XPS valence-band feature might be analogous to this because of the strongly localized character of the d bands in nickel.

However, in recent experiments with synchroton radiation between 23 and 40 eV, Smith *et al.*[3] have concluded that this weak structure is consistent with a simple band picture for an electronic transition originating from the s-p band, Δ_1. It should be emphasized that this is not consistent with the fact that this kind of satellite is observed only in metals like Fe, Co, and Ni, with partially filled d bands, but not in Cu.

We have studied this structure experimentally in photoemission from Ni for photon energies, $\hbar\omega$, ranging from 40 to 100 eV. We observe a strong resonance enhancement for $\hbar\omega$ in the neighborhood of the $3p$ energy levels ($E_{p_{3/2}} = 66$ eV; $E_{p_{1/2}} = 67.6$ eV). Off resonance the structure is still visible, both on the high- and low-energy side, but with rapidly falling intensity, especially on the low-energy side. The asymmetric line shape[5] is suggestive of resonant interaction between an excited quasidiscrete level ($3p^5 3d^{10} 4s$) and an ionized continuum ($3p^6 3d^8 4s$ plus emitted electron): This is the model that we choose to interpret our data.

The experiments, which are not discussed here in detail, were performed at the Orsay ACO storage ring. The energy analyzer was a 127° cylindrical type, with an acceptance angle of (1° $\times$ 2°), and was operated at an energy resolution ranging between 100 and 250 meV. Above 60 eV the experimental resolution is limited by the monochromator which is a small (0.3 m) Jobin-Yvon monochrometer[6] based on a simple rotation of a toroidal holographic grating. With our experimental setup a resolution of less than 1 Å was achieved with 100 slits. The photon beam was focused to a size of 0.5×0.7 mm^2 at the exit slit of the monochromator, with the light at 45° from the normal and strongly p polarized. Throughout the experiment, outgoing electrons were collected normal to the nickel single crystal (100) surface. This was prepared by the usual methods: ion bombardment and annealing under ultrahigh vacuum (less than 2×10^{-10} Torr). The surface was monitored by low-energy electron diffraction and Auger spectroscopy and care was taken to avoid oxygen contamination, since the oxygen $2p$ orbitals give by themselves a peak at about 6 eV below the nickel Fermi level.

Experimental results are shown in Fig. 1 for twelve different incident photon energies, between $\hbar\omega = 63$ and $\hbar\omega = 83$ eV. For $\hbar\omega = 63$ eV the photoemission spectrum consists of two main

features: a sharp peak structure A at about 1.5 eV below the Fermi level, due to the $3d$ bands of nickel, and the much weaker structure B at 6 eV below E_F. The structure B shows strong resonant behavior as $\hbar\omega$ is tuned through the energy corresponding to the $3p$–to–conduction-band transition (see $\hbar\omega = 67$ eV curve in Fig. 1). On the high-energy side of B, for $\hbar\omega \geq 69$ eV, a new peak appears: This is a well-characterized Auger transition (an $M_{2,3}M_{4,5}M_{4,5}$ process in which two $3d$ electrons scatter into a $3p$ hole and an unbound state) and it is indicated by an arrow on Fig. 1. The area under the structure B as a function of $\hbar\omega$, i.e., the line shape of the experimental resonance curve, is plotted in Fig. 2. It shows a marked asymmetry which leads naturally to an interpretation of the phenomenon as a Fano resonance.[5]

The transition-metal character of nickel, i.e., its metallic properties and the narrowness of its d-electron conduction band, is traditionally a source of difficulty in the interpretation of experiments. The correlation (localized, atomic) aspects of its electronic structure are always comparable in importance to the one-electron (itinerant, metallic) properties. Considered from the atomic point of view, each Ni atom in the metallic ground state of nickel can be thought of as being, from the electronic point of view, in a coherent superposition of various configurations, but mainly of $3d^9 4s$ and $3d^{10}$. It is the former which is responsible for the effect we find. The absorption process,

$$3p^6\, 3d^9\, 4s + \hbar\omega \rightarrow 3p^5\, 3d^{10}\, 4s\,, \qquad (1)$$

produces a quasidiscrete state which, through a Coulomb (autoionizing) interaction V_E, is hybridized with a continuum

$$3p^5\, 3d^{10}\, 4s \longleftrightarrow 3p^6\, 3d^8\, 4s + \text{unbound electron}. \qquad (2)$$

The kinetic energy of the unbound electron is in this case that of the difference between $\hbar\omega$ and the ionization energy of a $3d$ state (i.e., approximately the "Fermi energy") to which the excitation energy of the Ni^+ leftover ion should be subtracted (~6 eV in our case).

This Fano-type interaction,[5] with its characteristic asymmetric line shape, has been suggested to be the physical origin of the structure

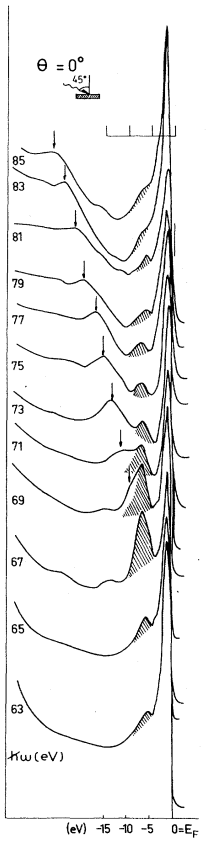

FIG. 1. Photoemission spectra of a clean Ni(100) surface for photon energy $\hbar\omega$ between 63 and 85 eV. The peak A corresponds to the d bands; B (dashed area) is the structure located at 6 eV from the Fermi level. The arrows indicate the Auger transition.

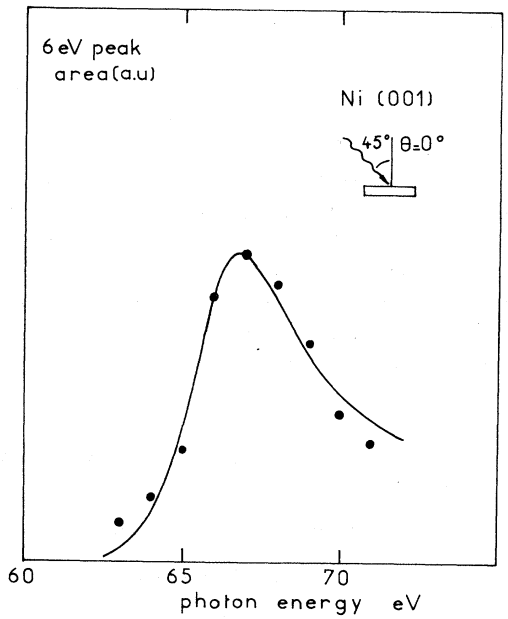

FIG. 2. Plots of the area of the B peak structure vs the photon energy in the vicinity of the $3p$ levels. The points are experimental. The full line corresponds to the values given by Eqs. (3)–(6) with the following parameters: $\Gamma = 2$ eV, $q = 2.5$, and $E_0 = 66$ eV.

observed in soft-x-ray absorption[7,8] and in electron energy-loss spectra[9] for nickel metal. The Fano interaction yields a spectral line with its typical resonance-antiresonance features and described by the simple formula

$$I=(q+\epsilon)^2/(1+\epsilon^2), \tag{3}$$

where

$$\epsilon\equiv(\hbar\omega-E_0)/\Gamma; \tag{4}$$

$$\Gamma\equiv\pi|V_E|^2 \tag{5}$$

is the spectral half-width of the autoionized state, and

$$q\equiv(3p|r|3d)/\pi V_E(\epsilon f|r|3d). \tag{6}$$

In these formulas E_0 is the displaced energy for the transition (1), r indicates dipole matrix elements, and $|\epsilon f)$ is the f partial wave of the unbound electron.[9,10]

We have fitted our experimental data to Eq. (3) and, as shown in Fig. 2, we find good agreement for $q=2.5$, $\Gamma=2.0$ eV, and $E_0=66$ eV. Our value for q is considerably larger than those obtained from either energy-loss spectra[9,11,12] ($q=0.9$ and 1.3) or theoretical calculations[9,13] ($q=1.8$). The values of Γ and E_0 are in excellent agreement with previous values.[9,13]

It should be emphasized that because of the experimental resolution and uncertainties, and the atomic model and simplifying assumptions,[10] a fit better than the one obtained and quoted above can only be considered fortuitous. The metallic character cannot be completely ignored in our interpretation. The itinerant, band-structure properties of the d electrons and their hybridization with s and p states produces in essence a spreading out of the $3d^9 4s$ configuration over a range of energies of the order of the one-electron—band widths. Interpreted in the one-electron picture the absorption process (1) can be described as

$$E(3p)+\hbar\omega\rightarrow E(\text{unfilled } d \text{ state}) \tag{1'}$$

while the Coulomb interaction (2) produces a mixing of states

$$E_1(\text{conduction band})+E_2(\text{conduction band}) \longleftarrow E(3p)+\text{unbound electron}. \tag{2'}$$

In (2') two conduction electrons in the narrow d band, with energies E_1 and E_2, scatter each other into the $3p$ hole and an unbound state. From this point of view the process (1') has a low-energy cutoff, reached when the photon has enough energy to promote the electron from the $3p$ state to the Fermi level.[14] On the high-energy side, on the other hand, there is no sharp cutoff and the process should continue as long as the oscillator strength for the transition (1') does not vanish. Equation (2'), moreover, states that the observable structure should be restricted to energies at which the density of occupied electron states (E_1 and E_2) is high, i.e., for E_1 and E_2 in the region of the narrow d band. Therefore the structure B should be asymmetric and should continue to exist for values of $\hbar\omega$ several tens of eV beyond its threshold value. This is what is observed, as shown in Fig. 1. This band-structure effect contributes substantially to the asymmetry of the line shape. It should be remarked, however, that a purely itinerant uncorrelated picture is incapable of yielding the sharpness of the features shown in Figs. 1 and 2.

The lack of an antiresonance in Fig. 2, which is predicted[5] by Eq. (3), is a consequence once again of this mixed atomic and itinerant character of the electron states in nickel metal, and of the many scattering channels[15] into which the quasi-discrete state may decay.

It should be also pointed out that the persistance at lower frequencies[14] of the feature at 6 eV below E_F cannot be explained by this resonant mechanism and requires a different physical origin: The $3p$ "deep" hole cannot participate at energies lower than the $3p\rightarrow 3d$ threshold. The energy of the final state (an unbound electron and an excited Ni^+ ion with two $3d$ holes) is such, however, that it is easily accessible, and if such state could be excited by whatever means, its presence in the photoemission spectrum should be felt.

It should be of considerable interest to study the photoelectron spectrum of atomic Ni in the same range of energies. A comparison with our present experiments would then yield information on the relative contributions of the one-electron band structure and of the electron-electron atomiclike correlations in metallic Ni.

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