FIZIKA VOLUME 10 SUPPLEMENT 2, 1978
Proceedings of the VI Yugoslav Symposium of the Physics of Condensed Matter, Kruševac, September, 18-22, 1978

ELECTRONIC STRUCTURE OF METALLIC SURFACES

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INTRODUCTION

In recent years there has been a surge of interest in the electronic and structural properties of solid surfaces, stimulated in part by the development of new experimental methods which provide the description of the surface on a microscopic level, in part by the relevance of surface science to some practical problems of modern materials technology. These problems range from the areas such as heterogeneous catalysis, corrosion, solar energy conversion, to the variety of solid-state electronic devices. In the first part of this paper I shall briefly describe and discuss several experimental techniques that are especially suited for surface studies. In the second part I shall focus on the X-ray photoelectron spectroscopy (XPS) of core-levels near surfaces, in particular metallic surfaces, discuss in more detail the physical processes accompanying the photoionization event and their influence on the observed photoelectron spectra.

SPECTROSCOPY OF SURFACE STRUCTURE AND ELECTRONIC PROPERTIES

Various surface spectroscopies are described in order to furnish information about the following properties:

i) Chemical (elemental) composition, in particular surface cleanliness, depth profiling of different species in the surface region, etc. Some of the usual techniques, e.g. XPS or ALS, are shown in Table I.

ii) Geometry of surface layers: deviation of the substrate from the bulk properties (relaxation, reconstruction), structure of adsorbed monolayers and thin films. The most powerful technique is LEED (Low-energy Electron Diffraction), though ARPS (Angle Resolved Photoemission) and SEXAFS (Surface Extended X-Ray Absorption Fine Structure) can also give useful information. FIM (Field Ion Microscopy) gives direct pictures of surface atomic arrangements for some transition metals.

iii) Electronic structure of valence and core levels.Table I summarizes the most common experimental techniques that give information about local densities of electron states near surfaces, both extended (band) and localized atomic-like states, with their counterpart deep in the bulk, as well as the possible new phenomena, e.g. surface states and resonances (band-gap states) and adsorbate level resonances. Surface sensitivity in all these experiments arises from the strong Coulomb scattering of incoming and/or outgoing electrons or the short penetration depth of external static fields into the solid.

ELECTRONIC STRUCTURE OF CORE LEVELS

Now we shall restrict our consideration to the conceptually simplest experiment that probes core levels in the surface region, namely X-ray photoemission (XPS), which has become a powerful analytical tool in surface physics. By changing parameters of the experiment and assuming certain properties for the interaction of incoming photons and emitted electrons with

Table I: Valence and core-level surface spectroscopies

Spectroscopy	Probe (input)	Measurement (output)	Obtained information	Principal advantage	Principal disadvantage
Excitation types					
Ultraviolet photoelectron (UPS, ARPS)	monochromatic photon beam (2-150 eV)	photoelectron emission current vs. electron energy and/or angle	valence band states adsorbate energy levels, surface states	many variables (angles, polarization, etc.)	band structure, surface, matrix element and many-body effects important
X-ray photoelectron (XPS or ESCA)	monochromatic X-ray beam ($\gtrsim$1.5 keV)	photoelectron emission current vs. electron energy	elemental analysis, core-level energy shifts	non-destructive	complex spectrum (Auger, photoelectron and satellite peaks)
Core-level characteristic loss or ionization loss (ILS)	monoenergetic electron beam ($\gtrsim$1 keV)	derivative electron emission current vs. energy loss	elemental analysis	simple spectrum	weak signal
Soft X-ray appearance potential spectroscopy (APS, or SXAPS)	monoenergetic electrons (10-1000 eV)	derivative X-ray yield vs. incident electron energy	conduction band states	high resolution	insensitive to some elements
Field-emission energy distribution (FEED)	strong electric field ($\sim$0.2V/Å) applied to a metal tip	electron emission current vs. energy	valence and adsorbate electron densities	high resolution	limited range from E_{Fermi} few materials for tips
Recombination types					
Electron or X-ray excited Auger electron (AES)	electron or X-ray beam ($\gtrsim$3 keV)	derivative of electron emission current vs. emitted electron energy	elemental analysis	fast, high intensity	complex spectrum
Electron excited soft X-ray emission (SXE)	grazing incidence electron beam	X-ray emission intensity vs. energy	valence band states	high resolution	slow
Ion-induced X-ray (IIX)	high-energy ion beam ($\gtrsim$100 keV)	X-ray emission vs. energy	elemental analysis	insensitive to chemical environment	poor resolution
Ion neutralization spectroscopy (INS)	noble gas ion impinging upon surface	Auger electron current vs. energy	valence and adsorbate densities of states	local surface electronic structure	complex spectrum elaborate apparatus

the solid it is possible to vary the surface vs. bulk sensitivity in a controlled manner[1]. This interpretation of the photoelectron spectra is based on the assumption of strong electron ("extrinsic") scattering, i.e. very short and angle-dependent electron "escape depths", and it immediately links the quantitative analysis of spectra with the study of electron scattering processes near surfaces. In photoemission from localized initial states, the created hole also acts as a strong perturbation in the final state of the system, which leads to an additional structure ("intrinsic" effects) in the hole spectral function. However, in XPS, these two scattering mechanisms can interfere and partially cancel, which further complicates the theoretical analysis and requires a proper many-body approach to the photoemission process.

Here we shall analyze some features of the spectra of photoelectrons excited from localized levels of atoms near solid surfaces (which can be either substrate, impurity or adsorbed atoms), concentrating on the qualitatively new ideas and indicating the relevant literature. There are several aspects of this problem worth emphasizing. First, the surface plays an important role: it leads to the breakdown of translational symmetry, modification of the ground-state properties of the system and to the appearance of new excitation modes (e.g. surface plasmons). It also makes a theoretical treatment more involved, as it becomes essential to include spatial considerations. The localized character of the hole state leads to strong scattering effects, and ultimately to various relaxation shifts, and in a way gives the hole the properties of a classical source of perturbation. In addition, the adsorbed X-ray introduces into the system a relatively large energy which can be redistributed via a number of scattering processes until the system reaches its new N-1-body ground state. The initial transition triggering the subsequent scattering proceeds, therefore, very rapidly, and the adiabatic hypothesis cannot be applied, so it becomes necessary to include these dynamical aspects of the interaction into consideration.

Scattering processes

An exact description of the photoelectron current from the N-body interacting system can be given[2) in terms of the "3-current correlation function", which can be reduced into a more useful form[3) in the XPS region. The electron-hole pair is excited and propagates in time until the photoelectron gets decoupled from the system and detected, leaving the N-1-body fully interacting system possibly in some excited state. Some of the scattering mechanisms affecting the localized hole and the highly excited electron[4) in XPS are sketched in Table II. They may take place as single scattering events, but more often the spectrum contains electrons undergoing several inelastic events of different kinds.

In view of the enormous complexity of the photoemission process, it becomes necessary to consider possible simplifying procedures. The information contained in the spectra is related to the positions and intensities of the photoelectron peaks, their shapes and widths and the positions, strengths and shapes of their various satellites. Taking the no-loss peak as the reference and scanning the spectrum, we can restrict ourselves either a) to the large energy-loss region (Auger peaks, secondaries) or b) the "characteristic energy-loss" region, where the

Table II: Scattering mechanisms in XPS

	Core electrons	Valence electrons		Ion cores
		Single particle excitations	Plasmons	
Localized hole	Auger transitions	Auger transitions "Soft pairs": Infrared divergency	Bulk and surface plasmon excitation	Phonon excitation
Fast electron	Ionization losses	Secondary electron emission	Bulk and surface plasmon excitation	Elastic diffraction Phonon excitation

electron plasmon-like losses dominate or c) to the low-energy region, which modifies the shape of the main peak. We assume that each of these spectral regions can be considered separately, though in the final quantitative analysis they all have to be taken into account.

Bulk and surface plasmon excitation, spectral sum rules

This problem has been treated in several ways, using the Green´s function perturbation method5) or the Hamiltonian approach, with the semiclassical description for the fast photoelectron and the localized hole6) (which is almost exact for, say $E_{el}/\hbar\omega_{pl} \gtrsim 10$, as is usually the case). The main results are the following:

i) Each line in the spectrum is followed by a Poisson-like series of satellite peaks at energies $m\hbar_B+n\hbar\omega_S$ from the main peak, with strengths

$$J_{mn}(d) = \exp(-A_B-A_S)\, A_B^m\, A_S^n/(m!n!) \quad ,$$

which correspond to the excitation of m bulk and n surface plasmons. The factors $A_{B,S}$ depend on the distance d of the excitation point from the surface and the angle of the outgoing electron, and each of them is a sum of three contributions (Figs. 1a and b):

$$A = A^h + A^i + A^e = A^I + A^e \ .$$

A^e comes from the electron ("extrinsic") scattering, A^I is the "intrinsic" term, containing the hole (A^h) and interference (A^i) scattering.

ii) The observed spectrum has to be calculated by averaging over the "escape" region near the surface7,8). This amounts to taking into account other, mostly short-range processes which attenuate the electron beam. The strengths of plasmon satellites then deviate from the Poisson distribution, and it becomes impossible to separate exactly the "intrinsic" from the "extrinsic" effects9).

iii) The deviation of the total cross section $A_B(d)+A_S(d)$ from linear dependence on the distance d indicates the breakdown of the mean free path concept10) for long-range scattering near the surface7,11,12). This is due both to the finite size of the solid and to the effect of hole scattering.

iv) The appreciable strength of "extrinsic" effects casts doubt on the use of the "sudden approximation" in XPS from solids, which attributes all scattering to the final-state hole. As a consequence, the spectral sum rule connecting the inelastic scattering and the energy shifts13) may be modified3). Even for very high photoelectron energies the "sudden" limit is not reached, e.g. for the excitation on the surface, while the averaging over a large solid region would further emphasize the "extrinsic" terms8).

v) The analysis of experimental data8,14) indicates that in XPS from metals and adsorbates "intrinsic" effects are generally smaller than predicted by theory. This discrepancy can be removed by taking into account the dispersion and finite lifetime of plasmon modes15), because the dispersionless plasmon model becomes inaccurate for processes in the vicinity of metallic surfaces, especially for hole scattering.

In conclusion, we see from the many-body analysis of plasmon excitations in XPS that the interplay of electron and hole scattering can lead to some new phenomena. In particular, the dynamics

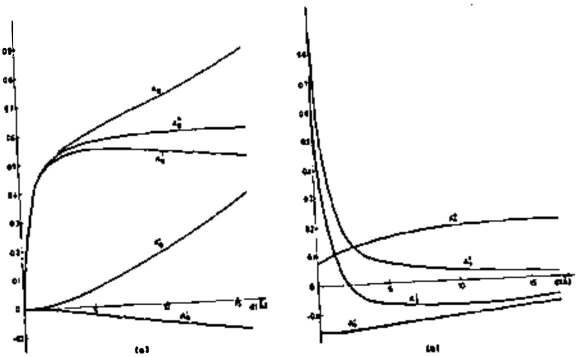

Fig.1. (a) Separate contributions to the strengths of bulk plasmon satellites in XPS from 2p level of Al. (b) Contributions to the strengths of surface plasmon satellites in XPS from 2p level of Al.

entering through the electron kinetics determines the shape of the spectrum. While the detailed quantitative analysis certainly awaits further improvements in the description of electronic excitations at realistic surfaces, even this simplified treatment illustrates some important problems of photoemission spectroscopy.

Core level lineshapes

With the present increase in the resolution of experiments it is becoming necessary to study many-body processes that modify core-level lineshapes, as they contain much information, e.g. about local scattering effects and about long-time relaxation, which is inaccessible with electron-scattering experiments. The excited electron contributions become less important in the immediate vicinity of the no-loss peak. Since the excited electron moves very rapidly (say in the keV region), its coupling to low-energy (slow response) excitations that can influence the lineshape is negligible, and its only effect is to trigger hole excitation processes.

This reduction of "extrinsic" effects in the core-line region also means that the surface plays a less important role than in the "intermediate" part of the spectrum, which is dominated by the long-range interaction. Actually, the core hole scattering in the first place reflects the atomic nature of the deep level and bulk properties of the solid, and the surface influences these effects mostly through the modification of the excitation spectrum for atoms near the surface. As mentioned before, the low-energy excitations involved are often local (short-range) and therefore only weakly surface-dependent.

Core hole spectra are broadened primarily due to their decay via Auger or radiative deexcitation, and these processes are supposed to give Lorentzian lineshapes$^{16)}$. These arise from the hybridization of the sharp core-hole line with the approximately constant tail of the energetically very distant, say, Auger peak in the spectrum.

The suddenly created localized hole in a metal singularly scatters the low-energy electron-hole pairs on the Fermi surface$^{17)}$ thus creating the divergent main peak and a low-energy tail in the photoelectron spectrum. When the finite hole lifetime is taken into

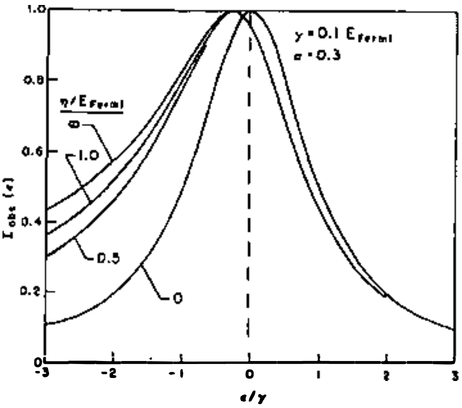

Fig. 2. A typical asymmetric XPS lineshape.

account, the obtained asymmetric lineshape[18] (Fig. 2) turns out to be one of the few real many-body effects that are indeed observed[19] according to theoretical predictions. Apart from this fundamental interest, very extensive quantitative studies of this phenomenon[20] have already provided a wealth of information about the scattering phase shifts of core-hole potentials in solids, and have also served to elucidate the problem of similar many-body phenomena in X-ray absorption and emission[21].

While these observed asymmetric lineshapes emphasize the importance of transient phenomena due to the sharp onset of perturbation in the solid, it would be nevertheless desirable to establish a link with the more usual adiabatic limit, and see the influence of some finite switching mechanism, which is obviously related to the removal of the core electron from the screening region and to the characteristic response of the surrounding medium. Calculations of the photoelectron lineshapes assuming a time-dependent potential of the form $V_{hole}(R,t)=V_{hole}(1-e^{-\eta t})\theta(t)$ lead to the theoretical results[22] indicating the sudden limit to be valid in most XPS spectra from bulk solids. However, soft X-ray and high UV excitation spectra may show the suppression of lineshape asymmetries[23]. This could be especially interesting in UV photoemission from localized surface states and adsorbed atom levels[24], where, however, it becomes necessary to take into account other considerations (partial hole mobility, modified excitation spectrum, etc.).

Another line-broadening mechanism in XPS from solids is multiple phonon excitation[25]. This mechanism has been recently studied in close analogy with the phonon broadening of impurity absorption spectra[26] or vibrational structures in photoemission from molecules[27]. The expected Poisson distribution of phonon peaks (often broadened and/or experimentally unresolved) would in the strong-coupling limit (large average number of excited phonons) give an overall Gaussian lineshape, with temperature dependence related to the phonon population of the ground state. However, the analogy with other similar situations should not always be taken too far, because hole-decay processes in this case may compete with phonon relaxation, and partially suppress it, indicating that the simple convolution procedure for the spectra (i.e. assumption of mutually independent processes) may be unjustified[28] It seems that the present study and the planned high-resolution studies of core-level spectra promise to revive close connections between solid-state physics and some ideas of atomic and molecular physics, and offer an exciting challenge to both experiment and theory.

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