Solid-surface electron spectroscopy

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Electron spectroscopy (ES) of the surface of a solid comprises a set of methods of studying its elemental composition, structure, electronic structure, and dynamics. The essence of almost all the methods consists in obtaining and studying the energy spectra and angular distributions of electrons emitted by the surface of the solid upon irradiation with fluxes of photons, electrons, or ions, or upon creating a strong electric field near it. Depending on the nature of the probe, one can distinguish photoelectron, secondary-electron, ion-electron, and field spectroscopy. Each of them is realized by several methods. In practically all the methods analysis of the characteristics that are obtained consists of singling out certain unitypical elementary events of interaction of the probe agent with the surface layers of the solid. As a rule, the depth of probing is determined by the mean free path of the electron with respect to inelastic interaction. In the electron energy range from tens to approximately hundreds of electron volts in various materials, it constitutes from one to several atomic layers. In determining elemental composition, the sensitivity of most of the ES methods is approximately equal to hundredths of a monolayer. One can employ a scanning probe to obtain the distribution of the elements over the surface of the specimen. Most of the ES methods have been invented in the past decade. At present the studies in the field of surface physics are intensively developing and have great scientific and important applied significance. This review briefly treats the physical fundamentals of the ES methods, their potentialities, classifies the methods, gives examples to illustrate them, and cursorily throws light on the fundamental technical means of realizing the methods.

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1. INTRODUCTION

In the past decade the solid surface has become one of the most important objects of physical studies. The steady attention of many prominent scientists working in various fields of science and technology has been fixed on it. The physics of the solid surface is entering its "golden age", similar to that experienced by atomic physics and the physics of bulk properties of solids.

The principal feature of the current stage of the study of surfaces consists in the atomic-molecular level of its investigation. The fundamental microscopic characteristics of a surface include: 1. The elemental (chemical) composition. 2. The geometric structure. 3. The electron structure, i.e., the energy spectrum of the states of the valence electrons and their spatial charge localization, together with the energy structure of the free electron states. 4. The dynamics of the surface, i.e., the data on its thermal vibrations.

What is the solid surface and why does it require special study? The interruption of translational symmetry in the direction perpendicular to the surface causes the atoms of the surface layers of a solid to exist under special conditions as compared with the bulk. The special conditions give rise to specifics of the properties of these layers that is reflected in the difference between their microscopic characteristics and the bulk characteristics. This subsurface region of a solid, i.e., its "envelope", which consists in various materials from about one to ten atomic layers, is identified in modern views with the solid surface.[1] Thus the surface is a special state of matter. Therefore the creation of a science of the surface is primarily a new stage in studying the structure of matter in the condensed state. This makes evident the vast significance of the development of this scientific field from the standpoint of obtaining fundamental knowledge.

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[1] The term solid surface is also employed with other meanings. In theoretical studies it is often employed to denote the two-dimensional boundary of a solid with another phase. In adsorption studies the solid surface usually denotes simply the upper layer of atoms of the solid.

The study of the surface is also extremely important for practical applications. The solid surface is widely employed in technology as the source of electron beams (electron-ray devices, electron multipliers, electron-beam melting, conversion of thermal energy into electrical, etc.). The solid surface is associated with numerous atomic processes—adsorption and desorption of atoms and molecules, dissociation of molecules, migration of atomic particles over the surface, diffusion into the bulk, reaction at the surface, etc. The level of understanding of these and many other surface phenomena now governs the progress in such important fields of technology as, e.g., heterogeneous catalysis and thin-film microelectronics. Also any interaction of a solid with the environment occurs via the surface. Therefore a knowledge of the properties of the surface is essential also in studying the changes undergone by the bulk characteristics of a solid, in particular, in corrosion and oxidation of metals.

The views of the solid surface as a boundary layer with special properties have also extended to the interphase boundaries of solids. Under certain conditions the processes occurring at these boundaries exert a decisive influence on the properties of the solid as a whole. For example, the segregation of certain impurities at grain boundaries in metals is accompanied by radical changes of many of their mechanical properties. Thus the development of solid-surface physics is necessary for solving important technical problems.

Although all four attributes of the surface are interrelated and give rise to one another, the starting point among them is the nature of the atoms. Yet the decisive influence on most properties of a surface is exerted by its electron structure, i.e., the state of the valence electrons.[2] Such a fundamental characteristic of a surface as the work function depends on the density distribution of valence electrons in the surface layers of the solid. The laws that many surface phenomena obey, and in particular, their energetics and the kinetics associated with it, are ultimately determined by the nature of the elementary events underlying them, while their essence consists in the interactions of the valence electrons of the atomic particles of the surface. The study of the microscopic characteristics of the surface, the establishment of their interrelations, and the construction therewith of an electron theory of the surface are now the first-rank problem of all solid-surface physics.

The diagnostics of the solid surface on the atomic-molecular level involves the development of an entire complex of new methods for studying it, including the solution of such problems as the creation and maintenance of superhigh vacuum, the preparation of monocrystalline specimens of macroscopic dimensions, the development of methods for cleaning their surfaces,

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[2] We recall that it is precisely the energy structure of the outer electron shells of atoms and molecules that determines many of their properties. In a solid also most of the bulk physical properties arise from the specifics of the states of the valence electrons. Their states undergo substantial changes when the atoms and molecules combine into a solid.

and the development of the methods themselves of obtaining the microscopic characteristics of the solid surface. Many of these problems had already been solved in the sixties. This enabled the development of broad, multilevel studies in the field of solid-surface physics. In turn, this has facilitated the creation and development of new methodologies with new potentialities.

Qualitative advances have also occurred in the theoretical studies of the solid surface. The theoretical views being developed at present enable one to model the surface and the various surface phenomena with a degree of accuracy that enables one to correlate the obtained results with experimental data. This became realized also only in the sixties, based on widespread application of computers.

One of the key positions among the spectroscopic solid-surface methods now belongs to the methods of electron spectroscopy (ES). The studies on the ES of the solid surface comprise an extensive field of physical studies of scientific and applied nature amounting to thousands of publications. The present review only briefly treats the general state of affairs in this new field, important to modern physics and technology. We pay major attention to presenting the fundamentals of the methods, their potentialities, and we briefly touch upon the main facets of the experimental technique.

2. CLASSIFICATION OF THE METHODS OF ELECTRON SPECTROSCOPY

All the experimental methods of studying the properties of the solid-surface are based on studying the results of interaction of some perturbing agent with the surface layers of the solid. One analyzes the changes, either those undergone by the probe itself, or those produced by it in the surface layers of the solid. As a rule, the perturbing agents are fluxes of particles or radiation, which are called the primary agents. Electric and magnetic fields, the thermal energy of the material (phonons), etc. are also used. The actions of the probes on the solid surface are often manifested in emission of fluxes of particles or radiation, called the secondary agents. To study them is the object of many of the forms of solid-surface spectroscopy. Thus one can classify all these methods by two fundamental features: 1) the nature of the exciting or primary probe; 2) the nature of the emitted secondary particles or secondary radiation.[1-3]

In ES the secondary particles are electrons.[4] As is shown by experiment and by theoretical treatment, the energy spectra and angular distributions of the electrons emitted by a solid surface under various perturbations contain practically all the needed information on its fundamental microscopic characteristics—composition, structure, electron structure, and dynamics.

At present four types of probes are applied in ES: photons, electrons, ions, and a probe in the form of a strong electric field. Hints have appeared of the expediency of employing metastable atoms of the inert gases.[5] Depending on the nature of the probes, solid-sur-
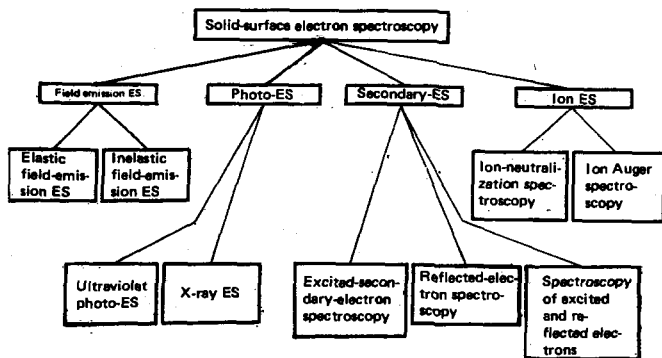
FIG. 1. Classification of the methods of solid–surface electron spectroscopy.

FIG. 2. Classification of the methods of solid–surface secondary–electron spectroscopy.

face ES can be classified into four types: photoelectron spectroscopy,[3,4,6-10] secondary–electron spectroscopy (it would be more correct to term it electron–electron spectroscopy),[3,4,9,11-13] ion–electron spectroscopy,[14] and field-emission spectroscopy.[15] Each of them is realized by several methods (Fig. 1). Field-emission ES has two variants: "elastic" and "inelastic". Photoelectron spectroscopy consists of x-ray, i.e., x-ray-electron[3] and ultraviolet electron spectroscopy. They differ in the energy of the radiation quanta employed, though the application of synchrotron radiation sources does not allow one to draw a sharp boundary between them.[17] Ion ES combines two methods: ion-neutralization spectroscopy,[18,19] which employs slow ions, and ion Auger spectroscopy,[20-22] in which the solid surface is irradiated with ions of medium or high energy.

The greatest number of methods is included in secondary-electron spectroscopy (SES).[11] This stems from the fact that the primary and secondary particles are identical in nature, and the spectrum of the electrons emitted by the solid surface contains both reflected primary electrons and true secondary electrons ejected from it. Both groups of electrons bear information on the properties of the surface. Therefore SES combines both possible methods of obtaining information on the surface and it includes the spectroscopy of the reflected electrons, that of the excited, true secondary electrons, and "mixed" spectroscopy, in which one studies these groups together. Figure 2 shows the classification of the methods of SES. Since the reflection of the electrons can be elastic, quasielastic, and inelastic, three groups of methods exist that employ these phenomena. The processes of elastic scattering of electrons are the basis of the methods of diffraction of slow and fast electrons.[9,23,25] There is a method that studies the fine structure of the energy-dependence of the total elastic reflection coefficient for electrons.[13,26-28] It belongs to the threshold methods. Vibrational ES is based on employing quasielastic reflection of electrons.[4,9,30-32] The spectroscopy of characteristic energy losses is concerned with studying the processes of inelastic scatter-

ing of electrons,[33,34] and, in particular, its variant: ionization ES.[35-37] The only "pure" spectroscopy of excited electrons is electron Auger spectroscopy.[3,9,11,38-40] The "mixed" methods include different variants of the threshold methods[13,41-43] and the spectroscopy of slow secondary electrons.[44-47]
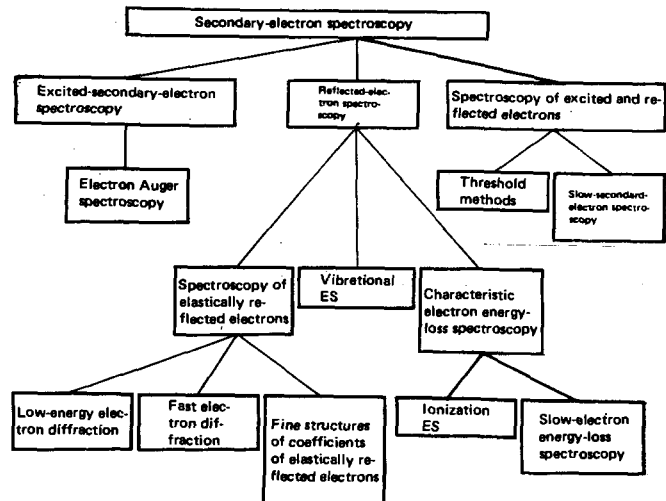
When studying the solid surface by ES methods, one must bear in mind that any perturbation of the object of study in the measuring process can alter it. If not taken into account, this can distort the results. For example, an electron beam can cause electron-stimulated desorption.[48,199] adsorption, diffusion, reaction at the surface, etc.[49,50] An ion beam, in ejecting atoms of the target, destroys it.[51] However, this effect is employed specially for obtaining data on the variation of the elemental composition of a solid with depth.[52,53]

3. ELEMENTAL COMPOSITION OF THE SOLID SURFACE

In studying the elemental composition of a solid surface, one must elicit some inherent property of the atoms that is conserved when they are converted to the condensed state. Such a characteristic of an atom, which is employed in solid-surface ES, is the set of binding energies E_i of the electrons of the inner shells (core electrons). It constitutes a system of discrete energy levels that are unambiguously fixed by the atomic number of the element, i.e., $E_i = f(Z)$. In contrast to the valence electrons, the states of the core electrons and their binding energy E_i are hardly altered when the atoms are combined into a solid. The observed small shifts in E_i, which depend on the electron state of the atom and also on its environment and the obtained values of the energy shifts ΔE_i are small in comparison with E_i. As a rule, they do not impede the identification of the atoms. We can assume approximately that in a solid the entire system of core levels of the atom is shifted only slightly, almost as a whole with respect to the vacuum levels. The nature of the

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[3] An older name of this method is electron spectroscopy for chemical analysis (ESCA).[16]

origin of the shifts ΔE_1 and their values are briefly treated in Sec. 4. We note that atoms of hydrogen and helium, which have no core electrons, cannot be detected by this method.

In a solid the binding energy of the core electrons is fixed with respect to the Fermi level, i.e. $E_i^F = f(Z)$. For the different faces of single crystals of a particular element, the work function $e\varphi$ differs, as well as the binding energy E_i^B of the core electrons, as referred to the vacuum level, i.e.,

$$E_i^V = E_i^F (Z) + e\varphi (Z, \{hkl\}) = f (Z, \{hkl\}). \tag{1}$$

Therefore it is usually measured from the Fermi level.

In order to find the E_i^F of the atoms of a solid surface, one excites its core electrons. The collection of information is based on studying either these excitation events directly or the relaxation processes that occur in the atoms after vacancies have been created in one of their inner levels. Several ES methods are suitable for these purposes: x-ray-photoelectron spectroscopy (XPS), three modifications of Auger spectroscopy (electron, x-ray, and ion), and ionization ES. One can also use threshold methods,[13] but they are as yet little employed. XPS and electron Auger spectroscopy (EAS) have received general recognition.

Figure 3 shows the energy diagrams that explain the methods of ES. Figure 3a illustrates the method of XPS, which is based on directly studying the events of excitation of core electrons. An arbitrary but fixed amount of energy equal to $h\nu$ is imparted to an electron, and the energy E of the photoexcited electron is measured after it emerges from the solid. We see from the diagram that E is determined by the relationship

$$E = h\nu - E_i^V = h\nu - E_i^F - e\varphi. \tag{2}$$

Consequently it allows one to determine the atom from which the photoelectron has emerged by comparing the experimentally found values of E_i^F with the tabulated values.[54-56] In the photoexcitation of the electrons from the various levels, their spectrum forms a system of discrete lines that reflect the energy structure of the electrons of the inner shells (Fig. 4). Many-electron processes and multiplet splitting of the lines can complicate the structure of the spectrum (see Sec. 5).

The second method of studying the events of excitation of the core electrons is realized in ionization ES.
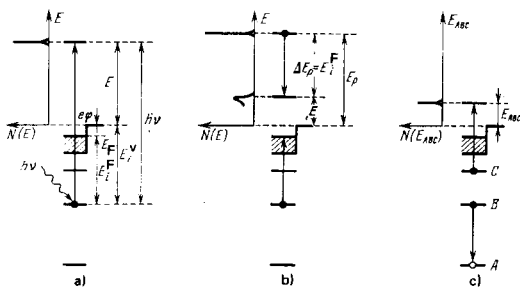
FIG. 3. Energy diagrams of the ES methods. a) XPS; b) ionization ES; c) Auger spectroscopy.
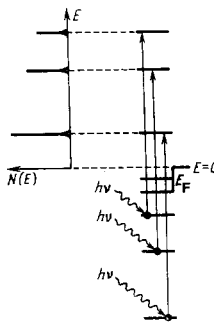
FIG. 4. Energy spectrum of x-ray photoelectrons at the instant of origin.

It consists in determining the minimal threshold energy losses ΔE_{thr} suffered by the electron probe in exciting the core electrons. For metals, e.g., as shown in Fig. 3b, we have $\Delta E_{thr} = E_p - E = E_i^F$, where E_p is the energy of the bombarding electrons. These losses are commonly termed the ionization losses, and hence the method of studying them is called ionization ES. We can easily see that the values of ΔE_{thr} are fixed with respect to the energy E_p of the primary electrons, which are the reference origin in this method for finding E_i^F.

The ES methods that employ the relaxation processes in atoms after vacancies have been generated in the inner shells are based on measuring the current of Auger electrons. As we know, states having a hole in the system of core electrons are unstable and the vacancies are rapidly filled by an electron from a higher level. The energy that is released is either emitted in the form of a quantum of the characteristic radiation $h\nu$, or it is transferred to another electron of the solid by a radiationless Auger process. This electron is called an Auger electron, and is emitted.[57] When the excitation energy does not exceed ~2 keV, the Auger process predominates. This is shown schematically in Fig. 3c. The energy E_{ABC} of the Auger electron directly depends on the binding energy of the electrons in the three levels A, B, and C that participate in the Auger process (A is the level in which the primary vacancy is created, B is the level from which the electron is taken to fill this vacancy, and C is the level from which the Auger electron is excited). Like the quantities E_i themselves, the energy of the Auger electron is also determined by the nature of the atom in which the vacancy was created. That is, we have $E_{ABC} = f(E_A, E_B, E_C) = f(Z)$. This enables one to identify atoms from the experimentally found values of the energy of the Auger electrons by comparing them with the tabulated data. Just like E_i, the quantities E_{ABC} vary somewhat in going from the atom to the solid. However, as a rule, these energy shifts ΔE_{ABC} are also inessential. In a solid the energy of the Auger electrons is fixed with respect to the Fermi level, and differs for different faces of monocrystals when referred to the vacuum level. Therefore it is also commonly measured from the Fermi level.

As compared with the photoelectron spectra, in which the ionization of each ith level corresponds in the zero-
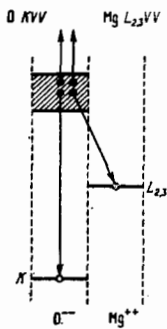
FIG. 5. Energy diagram of intraatomic and interatomic Auger transitions in MgO.

FIG. 6. Dependence on the energy E of the mean free path Λ of an electron for inelastic interaction.

order approximation to one line, the spectra of the Auger electrons have a more complex structure. Primarily this depends on the fact that the Auger process can involve different B and C levels in the ionization of the same A level. Consequently it is accompanied by emission of Auger electrons of different energies. Moreover, the removal of electrons from the B and C levels implies the appearance of new vacancies in the atom. Filling them also leads to emission of Auger electrons, but with a different energy. Thus the ionization of only one core level can be accompanied by the emission of an entire cascade of electrons. In the case of compounds, and also in the presence of adsorbed atomic particles on a surface or atoms of an impurity in the bulk of a solid, electrons that belong to different atomic systems can participate in the Auger process under certain conditions.[58] Figure 5 schematically shows interatomic Auger transitions using the example of MgO. Their energy depends here on combination of the levels of different atomic systems.

The calculated values of the energy of Auger electrons, and also the values found experimentally for all the materials studied, are given, e.g., in Refs. 55, 59–62.

Fluxes of photons, electrons, and ions are employed to generate vacancies in the inner electron shells of atoms. Thus there are three varieties of Auger spectroscopy—x-ray, electron, and ion. The latter is characterized by selectivity—the given ions can excite Auger electrons only in atoms of a certain type. The reason for the selectivity consists in the "exchange" mechanism of generating vacancies with an ion beam. The mechanism caused by direct Coulomb interaction with the core electrons of an atom, like the mechanism of electron-electron excitation, is realized only for the very lightest ions (H^+ and He^+). In the exchange mechanism, vacancies are generated by the interaction of the electron shells of the ion and the atoms of the target. It leads to shifts in their electronic levels. Under certain conditions it can be accompanied by isoenergetic transition of a core electron of the atom to the ion, which gives rise to a vacancy in the atom. The general status of the problem and the analysis of the prospects of this method are contained, e.g., in Ref. 21.
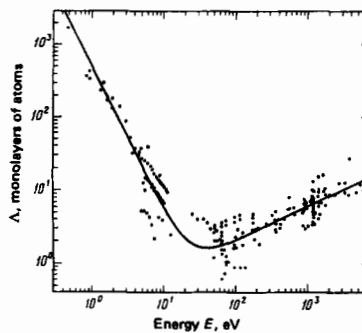
Thus the information on the elemental composition of the solid surface is contained in the energy spectra of the electrons excited (or reflected) by certain unitypical elementary processes of interaction of the probe with the core electrons of the atoms of the solid surface. But these electrons must now emerge from the solid. Here they can suffer different inelastic interactions that lead to loss of information. Its sole carriers are the electrons that have not undergone inelastic scattering. This can be realized only for electrons that emerge from depths that do not exceed the mean free path Λ for inelastic scattering. The quantity Λ approximately determines the thickness d_A of the surface layer that is analyzed by the methods of ES. The inelastic interactions play the role of a sort of filter that sifts out the information arising from the bulk.

The values of Λ depend on the energy E of the electrons. It is now well known that the $\Lambda(E)$ relationship for all materials is qualitatively depicted by a curve of universal type that has a broad minimum in the energy region 30–100 eV. The data on the free paths of electrons have been analyzed in Refs. 63 and 64. Figure 6 shows them for the elements.[64] We see that on the average the values of Λ differ for different materials by no more than severalfold. In the region of the minimum of the curve, they amount to 1–4 monolayers of atoms for most materials. Consequently, if the energy of the group of electrons to be analyzed corresponds to this minimum, the thickness d_A will be of the same order. Under these conditions one achieves the greatest sensitivity for the surface. The Auger electrons of many substances possess such an energy. By employing Auger electrons of different energies (whenever they exist), one can vary the thickness d_A. One can easily realize a continuous variation of the depth of probing in ionization ES by varying the energy of the primary electrons. This is an advantage of this method.[36,37] In XPS the energy of the photoelectrons is usually close to 1 keV, and we have $d_A \approx 5$–10 layers of atoms. In order to increase the sensitivity of the method specifically for the surface layers, one can resort to analyzing the electrons that emerge at small angles θ to the surface.[65] In this case, as is shown in Fig. 7, the thickness d_A is determined by the relationship $d_A = \Lambda \cos\theta$. One can vary the thickness d_A by varying the angle θ.
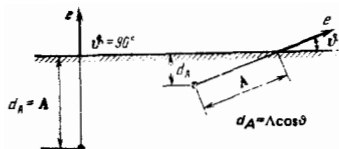
FIG. 7. Schematic diagram of the depth of emergence of an electron from a solid in emission along the normal and at a glancing angle.

FIG. 9. Energy spectrum $N(E)$ of secondary electrons from Ag and its derivative with respect to the energy.[52]

The electrons bearing information that we have been discussing are observed under the experimental conditions against a background of other electrons that emerge mainly from greater depths, and which mainly give shape to the general shape of the energy spectrum of the emitted electrons. This spectrum is continuous, and as a whole it reflects the statistical result of averaging the interaction of a large number of electrons over many elementary processes, including electron-multiplication cascades. The electrons that emerge from the layer of thickness d_A form only a fine structure on this curve. The detection and study of this structure constitutes the essence of the methods of ES. The structure is well marked in the x-ray photo- and Auger-electron spectra, where it exceeds the continuous background. This is schematically illustrated in Fig. 8 on the example of a metal from the second row of the periodic table. In the case electron and ion Auger spectroscopy as well as ionization ES, the structure is considerably weaker. For the most part, it amounts to only 10^{-1}–10^{-3} of the continuous background, and it takes a special technique to reveal it. Often this is done by the operation of differentiating the spectrum.[4] Figure 9 shows an example of the energy spectrum $N(E)$ of secondary electrons and its derivative with respect to the energy for Ag.[52]

The sensitivity of XPS and ionization ES amounts approximately to hundredths of a monolayer. For electron Auger spectroscopy it is higher, and often amounts to thousandths of a monolayer. With an optimal choice of the ion-atom pair, the sensitivity of ion Auger spectroscopy can be even an order of magnitude higher.[21]
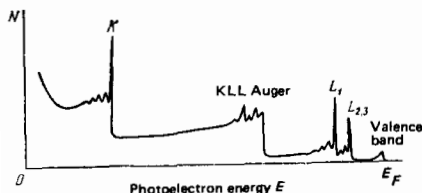

FIG. 8. Energy spectrum $N(E)$ of x-ray photoelectrons.

[4] Precisely its realization at the end of the sixties[39] actually led to the "birth" of electron Auger spectroscopy as a method of studying the elemental composition of the solid surface, although it was first proposed as early as 1954.[38] The development of the XPS of the solid surface mainly involves the recognition in the early seventies of the sensitivity of the method specifically for the solid surface.
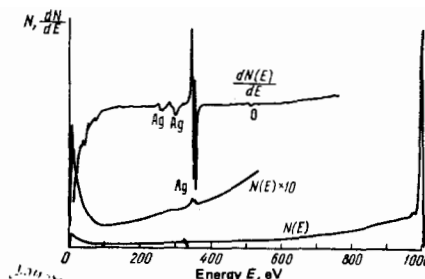
The methods of determining the elemental composition of a solid surface that we have been discussing have not yet been converted into analytical methods, and in most cases the studies have been performed on a qualitative or semiquantitative level. The problems of realizing quantitative analysis by the methods of XPS[66] and electron Auger spectroscopy[67,68] are currently being seriously discussed and developed. The greatest difficulties are to be overcome in creating a quantitative electron Auger spectroscopy. Mainly this involves the existence of two sources of generation of Auger electrons. They are, first, the direct flux of primary electrons propagating into the interior of the solid, and second, the backward flux of fast secondary electrons moving toward the surface, and consisting preferentially of inelastically scattered primary electrons. Both fluxes pass through the zone of emergence of Auger electrons and generate them. According to many experimental and theoretical estimates under different conditions, the backward flux can amount to up to ~50% of the Auger electrons.[69] Its contribution increases with increasing Z of the element. The accuracy of Auger analysis of homogeneous solids cited by the authors does not exceed tens of percent. In the case distributions of components inhomogeneous in depth, it can be substantially lower. In all the methods, roughness of the surface impedes the analysis.[70]

Additional complications arise in studying monocrystalline specimens. This involves the diffractive scattering of the electrons by the periodic potential of the lattice. Both the incident and the emerging electrons undergo this scattering. The first type of scattering, in particular, in electron Auger spectroscopy has the result that the number of emitted Auger electrons proves to depend on the orientation of the electron beam with respect to the axes of the crystal.[71-73] For example, when the {100} face of Mo is irradiated at an angle of 45° by a 1.5-keV electron beam, the current of Auger electrons varies by a factor of almost 1.5 as the azimuth of incidence is varied (Fig. 10).[73]

Diffraction of the electrons emerging from a crystal leads to anisotropy of the angular distributions. In the general case this must be taken into account in all the varieties of ES. The concrete manifestation of the effect depends substantially on the angle of collection of the electrons and on their energy. The angular distributions of Auger electrons have been studied, e.g., in
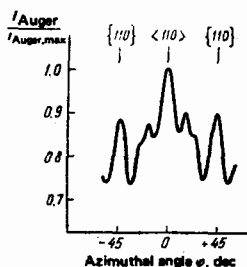
FIG. 10.. Relationship of the current of Auger electrons from Mo{100} to the azimuthal angle φ of incidence of the primary electrons of 1.5-keV energy (polar angle $\theta = 45°$).[73]

Refs. 74–77. As an illustration, Fig. 11 shows the data for Cu{100}[74] and Ni {100}.[75]

The discussed methods yield information on the elemental composition of the solid surface averaged, as a rule, over an area equal to the cross-section Φ of the probe. Since electron beams possess the smallest Φ, the most localized resolution is obtained by the EAS method. It amounts to about tenths of nanometers. It would seem that one could improve it substantially by decreasing the cross-section Φ. However, under standard conditions this cannot be realized because of the electron-scattering processes in the solid: the emerging electrons prove to be "smeared" over a larger area than the cross-section of the beam. As an illustration, Fig. 12 shows a picture obtained by the Monte-Carlo method of the pattern of penetration of 20-keV electrons into Al with normal and inclined incidence of a beam having an infinitesimally small cross-section.[77] We see that the smearing of the emitting area is governed by the depth of penetration d of the electrons. The region of the surface that emits Auger electrons "swells" correspondingly, though in smaller degree. The effect is inessential if $d \ll \Phi$. In order to weaken it when $d \gg \Phi$, it is expedient to operate at an energy of the electron beam close to the threshold for generating Auger electrons. However, this entails a loss in the sensitivity of the Auger analysis.

In order to study the distribution of elemental composition over a surface, one employs the variant of EAS with a scanning beam.[78,79] In this case the effect of electron scattering and the choice of optimal conditions have been discussed, e.g., in Ref. 80. The spatial resolution attained in this regime is lower than in local analysis, and amounts approximately to micrometers.
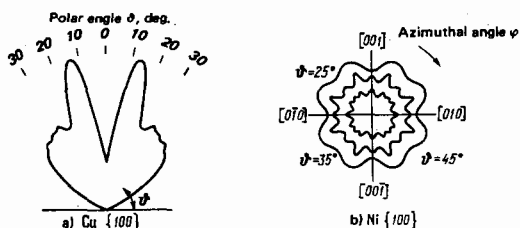

FIG. 11. Angular distributions of Auger electrons. a) Cu{100}, dependence on the polar angle θ[74]; b) Ni{100}, dependence on the azimuthal angle φ for different values of θ.[75]
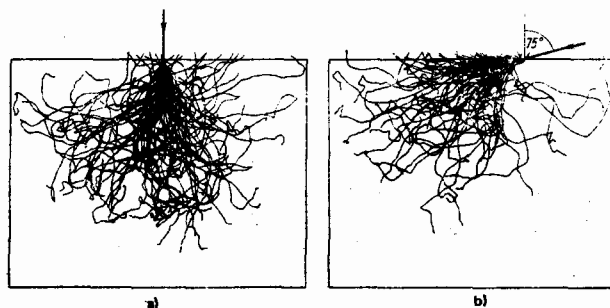

FIG. 12. Schematic drawing of the pattern of penetration of 20-keV electrons into Al.[77] a) Normal incidence; b) inclined incidence.

Owing to its large cross-section, an x-ray probe has not yet been used for scanning. A variant of scanning XPS proposed[81] for thin films is based on exciting x-rays within the film itself with the fast electrons with which it is being irradiated.

In order to get information on the depth distribution of elemental composition in the specimen within the limits of a layer of the order of micrometers, one can resort to layer analysis by successively removing the upper layers of the solid by ion etching.[52,53] In order to obtain correct data, one must allow for the possible differences in sputtering coefficients of the different components,[82,83] as well as that of a given component whose atoms exist in different electron states.[83] To demonstrate this combined method, Fig. 13 shows the "profiles" in depth of Au, Mo, and Si for an Au/Mo/Si system, as obtained immediately after sputtering Mo and Au onto Si, and after it had been heated to 450°C for 30 min.[84]

The ES methods that we have discussed are based on directly distinguishing certain unitypical elementary processes of interaction of probes with the core electrons of the solid surface. It is also proposed to study these elementary processes by threshold methods, not directly, but by studying their effect on the different characteristics of the phenomenon of secondary electron emission. The essence of the threshold methods
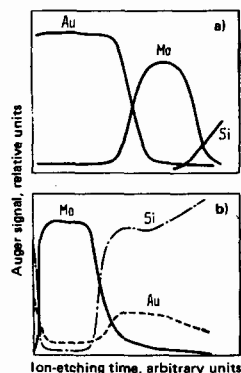

FIG. 13. Depth profiles of the content of Au, Mo, and Si for an Au/Mo/Si system.[84] a) After sputtering; b) after heating the system.

is that a new elementary process comes into play at $E_p = E_i$ as one raises the energy E_p of the primary electrons. This is the ionization of the ith level. As experiment shows, this leads to a nonmonotonicity at the given value of E_p in any integral or differential characteristic of the phenomenon. It has been proposed to use the dependence on E_p of the total secondary-electron-emission coefficient[41] and of the elastic reflection coefficient for electrons.[26]

4. STRUCTURE OF THE SOLID SURFACE AND ITS DYNAMICS

The same kinds of methods are employed to obtain information on the structure of a solid surface and on its dynamic characteristics. They are based on studying phenomena sensitive to the spatial arrangement of the atoms in the surface layers of the solid: electron diffraction and excitation by electrons of thermal vibrations of the solid surface. Just as in the other solid-surface spectroscopic methods, the information arising from the bulk is sifted out by the processes of inelastic scattering of the emerging electrons.

The fundamental diffraction method of structural analysis of the solid surface is low-energy electron diffraction (LEED). Although it has a history of more than 50 years,[85] its employment to study the solid surface began approximately in the sixties. Its physical foundations, potentialities, and the rich experimental material obtained with it have been repeatedly covered in the review literature.[9,23,24,86] There are monographs on LEED,[25,87] and we shall barely mention these problems here. We note only that LEED investigates the angular distributions of electrons with energies from ~10 to ~500 eV elastically scattered by a monocrystal when an almost paraxial electron beam is incident on its surface. The angular distributions that are obtained, or diffraction patterns, are governed by the symmetry and periods of the two-dimensional unit cells of the surface layers of the solid, and are the sources of this information. Studies of the relationships of the intensities of the individual diffraction maxima (diffracted beams) to the energy of the incident electrons enable one, in principle, to find the concrete arrangements of the atoms in the two-dimensional surface unit cells, their mutual orientation, and also the distances between them, by comparing these relationships with the results of theoretical calculations. This yields the total complex of data on the structure of the solid surface. The calculations needed here are complex and require large expenditures of machine time. As yet this limits the application of this method by restricting its studies to relatively simple systems.

The thermal vibrations of the atoms break down the strict periodicity of their arrangement in the surface layers of a solid. This decreases the intensity of the diffracted beams and gives rise to a continuous background between them of quasielastically scattered electrons. Studies of the effect of the temperature on the intensities of the diffracted beams allow one to estimate the rms deviation of the atoms of the solid surface in the thermal vibrations. Comparison with the data for

the bulk reveals the specific dynamics of the solid surface in particular.

Numerous LEED studies have established that the structure and dynamics of the surface are generally not the same as the bulk properties, while the degree of this mismatch can vary greatly. In the simplest case the change in the structure of the solid surface is expressed in a decrease or increase in the distance between the upper layer of atoms and the next as compared with the interplanar spacing in the bulk (relaxation of the surface). In the more general case, also the mutual arrangement of the atoms in this upper layer is altered. This leads to altered unit-cell periods of the two-dimensional lattice and to lowered symmetry. That is, the surface is reconstructed. The physical bases of these phenomena have been analyzed, e.g., in Ref. 88. The rms amplitudes of the thermal vibrations of the atoms of the upper layer are increased by a factor of 1.5–2. With increasing depth of the layers, these amplitudes decline and the differences vanish.

The structure of submonolayer films of adsorbate and phase transitions in them have been studied for many adsorption systems.[89] A relatively new feature is the use of LEED to study different types of defects in the solid surface.[90]

Fast-electron diffraction (FED) with glancing incidence of the beam is employed considerably more seldom than LEED for analysis of the structure of the solid surface. Application of FED is expedient in studying processes of growth of three-dimensional nuclei of a new phase when an adsorbate is being deposited on a foreign substrate. This method, also rather "old", is well known,[23] and we shall not spend time on it.

Recently[29] a new, relatively simple method of structural analysis of the solid surface has been described that doesn't require studying the angular distributions of the elastically reflected electrons, but is based merely on measuring the fine structure of the energy-dependence of the total elastic reflection coefficient for slow electrons at different angles of incidence on the crystal. Quasistationary states of the electrons above the vacuum level are responsible for the structure. These are the surface resonances, which are localized near the surface, and which arise in the region of the thresholds for appearance of new diffracted beams. As has been shown,[29] analysis of this structure enables one to obtain data on the two-dimensional periodicity of the surface.

New diffraction methods of structural analysis of the solid surface have also been proposed in recent years, based on the diffraction of photo-,[91-99] Auger,[100] and secondary electrons.[13,28,42,101] They are aimed preferentially at studying the deposition sites of adsorbed atomic particles. Their principal feature is that the sources of the diffracted electrons do not lie outside the solid, but are localized in its surface layers, and emit divergent fluxes of electrons, which are generally anisotropically distributed in space. Two types of diffraction processes are analyzed, and are schematically illustrated in Fig.
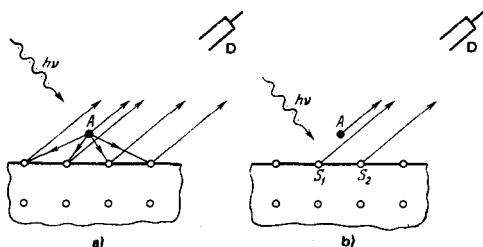
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FIG. 14. Schematic drawing of the diffraction of photoelectrons upon emerging from a solid. A —adsorbed atom, S_1 and S_2 nearest atoms of the substrate. a) The role of the final states; b) the role of the initial states.

14 with the example of ultraviolet photoelectron spectroscopy. Diffraction of the first type involves the initial states of the electrons being excited, and reflects the result of interference of the electron waves emitted directly into the vacuum (Fig. 14b).[91] Diffraction of the second type involves the final states and arises from scattering of already-excited electrons in the surface layers of the solid (Fig. 14a).[92] Both types of diffraction processes lead to anisotropic angular distributions of the electrons emerging without loss of energy from the solid. These distributions contain information on the structure of the solid surface and are the object of study. Generally diffraction of both types is manifested simultaneously and the situation here is more complicated than in the LEED method. However, analysis and search for the potentialities of realization of different experiments show that sufficiently correct results can be obtained under certain conditions also when one employs more simplified models. Several modifications of this method have already been developed up to now. In particular, in applying the methods of photoelectron spectroscopy to eliminate diffraction effects involving the initial states, it has been proposed to study the angular distributions of the photoelectrons excited from the core levels.[92] In order to determine the deposition sites of an adsorbate by this method, as has been shown,[99] one can, e.g., study the azimuthal angular distributions of x-ray photoelectrons emerging at glancing angles to the surface. A satisfactory model here for interpreting the results proves to be that of single scattering of the electrons by nearest neighbors in the Born approximation. The deposition sites of oxygen on Cu {100} shown in Fig. 15 have been determined specifically by this method.[99]
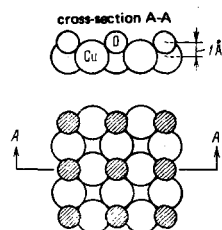

FIG. 15. Atomic structure of the {100} face of Cu and oxygen adsorbed on it to yield the structure $c(2 \times 2)$.[99]

The interpretation of the angular distributions of the photoelectrons is complicated when one uses a synchrotron source of radiation having an energy $h\nu$ of photons equal to tens of electron volts, for which the energy of the electrons being excited proves substantially smaller, and one must take account of multiple scattering. This requires one to adapt the apparatus already developed in the LEED method. As a number of examples have shown, it also allows one to obtain structural data on the adsorbate by starting with an analysis of the polar and azimuthal angular distributions of the photoelectrons.[94,95] The same type of approach is realized in studies of Auger electrons of the corresponding energy.[100]

Another approach that is becoming recognized to employing diffraction effects involving the final states consists in studying the dependence of the photoabsorption cross-section on the energy $h\nu$ beyond the absorption edge in the energy region of 100–300 eV.[94,96,97][5] The development of this method involves using a synchrotron radiation source, which allows one to obtain fluxes of photons with continuously variable energy.[17] The essence of this method is that the photoexcited core electrons scattered by nearest neighbors are "thrown" back at the atom that emits them. These scattered waves interfere with the waves emitted by the atom (Fig. 16).[96] The result of interference depends on the spatial distribution of the atoms surrounding the given atom and on the energy of the electrons associated with the energy $h\nu$. Therefore we can represent it in the form of a dependence of the photoabsorption cross-section on $h\nu$. By studying the latter we can obtain information on the structure of the surface. As has been shown, e.g., in Ref. 94, when we study the photocurrent in a narrow solid angle normal to the surface, relationships of this type are very sensitive to the adsorbate-substrate distance, and they allow one to determine it with a greater accuracy than by the LEED method. The dependence of the absorption cross-section on $h\nu$ can also be studied by measuring the current of Auger electrons emitted in the ionization of the given core level.[98] The diffraction effect that arises in the photo-
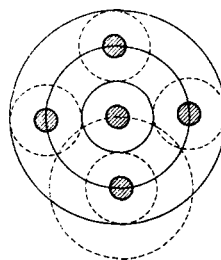

FIG. 16. Schematic diagram of the electron waves emitted by a given atom (solid curves) and those scattered by the nearest atoms (dotted curves).

[5] This method is a development and an application to studying the solid surface of a method of x-ray absorption spectroscopy, the EXAFS method, which is employed for bulk structural analysis.[96] This modification of the method is called SEXAFS.

excitation of the core electrons is also manifested in their excitation by electrons, which has also been proposed for use in structural analysis.[13,42,101]

The chief merit of the new diffraction methods is that the observed effects involve individual emission centers—atoms or molecules, and stem from the interference interaction of the electron waves, which are scattered mainly by the nearest neighbors. Therefore one can use these methods to study the deposition sites of an adsorbate at small coverages, i.e., actually for single adsorbed particles, and for disordered coverings. These potentialities reach beyond the limits of the LEED method. In the case of ordered coverings, one must take additional account of the mutual interference of the electron waves emitted by different emitting centers. This is important in studying their electron structure (see Sec. 5). In some cases the existence of long-range order even plays a negative role in structural analysis and complicates the studies.[13]

Vibrational ES, which is also called high-resolution low-energy electron energy-loss spectroscopy, has developed in very recent years,[102-108] although it was proposed as early as 1967.[38] The method consists in studying the energy spectra of the electrons quasielastically reflected from a solid surface, and which have suffered small characteristic energy losses of the order of tens or hundreds of meV in exciting thermal vibrations, generally those of adsorbed particles. The processes of excitation of thermal vibrations of clean surfaces have as yet been little studied. For effective excitation of vibrations, one needs slow electrons with energies of a few electron volts.

There are two mechanisms of exciting thermal vibrational modes of adsorbed particles with electrons—the long-range[31,107] and short-range (or impact) mechanisms.[104] In the former case the electrons excite the vibrational degrees of freedom of the adsorbed particles that correspond solely to the oscillations of the dipoles perpendicular to the surface. The interaction of the long-range field of the dipole with the electric field of the electron approaching the surface and its image are responsible for exciting them. Since this field is perpendicular to the surface, it interacts with the normal component of the dipoles. In excitations of this type the electron incident on the solid surface practically does not change its direction of motion, and suffers only a small energy loss. Therefore, in order to be reflected from the solid, it must also undergo elastic scattering. Consequently such electrons are concentrated in diffracted beams, and their loss spectrum reflects only the vibrational modes of the adsorbed particles normal to the surface.

The impact mechanism is based on the short-range interaction of an electron approaching the solid surface directly with the core of an adsorbed particle, similarly to what happens in the excitation of phonons by an electron moving in a solid. In this case the electron can excite all the vibrational degrees of freedom of the adsorbed particle and can suffer wide-angle scattering in addition to energy loss. Consequently these electrons are distributed throughout the entire hemisphere of re-

flection. The probability of this type of quasielastic scattering increases when the energy of the electron corresponds to a surface resonance, since under these conditions the "lifetime" of the electron near the surface increases. Therefore this mechanism is sometimes also called resonance scattering. It was discovered in 1978 in connection with the development of an angle-resolved variant of the method,[104] and it has substantially refined the methodology. The observation of only the vibrational modes normal to the surface had restricted the potentialities of the method, and often did not allow an unambiguous interpretation of the data.

The total spectrum of vibrational modes of an adsorbed particle is determined, first, by its structure, and is hence related to the number of atoms of which it consists, and second, to the point-group symmetry of its site of deposition. Therefore it contains in principle data on both of the factors. In the adsorption of molecules it proves possible to determine whether the adsorption is molecular or dissociative, and to find the sites of deposition of the adsorbed particles. If the adsorbate consists of molecules of complex composition with a large number of degrees of vibrational freedom, then substantial help in deciphering the spectrum and elucidating the nature of the adsorption is offered by comparing the obtained spectra with the spectra of these molecules in the gas phase.

Up to now already a large number of adsorption systems have been studied by vibrational ES, in particular adsorption on metals of molecules of the simple gases and of vapors of many organic compounds. Catalytic reactions at a surface are being studied intensively.[32,102-104] As an example, Fig. 17 shows the vibrational spectra of CO molecules adsorbed on W {100} for different times of exposure of the crystal to CO.[103] It shows that the spectrum contains only two loss peaks (68 and 78 meV) at small coverages, when only the β-phase of CO exists on the surface. The authors ascribe them to chemisorption on W via dissociative adsorption of CO as C and O atoms localized in the "pits" between four W atoms. When the surface also contains the α-phase of CO, the spectrum manifests two new losses (48 and 258 meV). The authors identify them
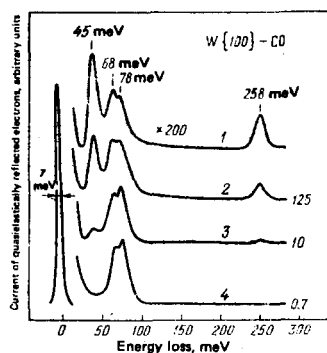

FIG. 17. Energy spectra of 5-eV electrons quasielastically scattered from the system W{100}/CO for different exposures. Langmuirs: 1—0.7; 2—10; 3—125; 4—equilibrium pressure $p_{CO} \sim 10^{-7}$ Pa.[103]

with the vibrational modes of CO molecules "sitting" on tungsten atoms.

Vibrational ES has been employed to a considerably smaller extent for studying clean solid surfaces, i.e., to obtain the spectra of surface phonons.[6] Slow electrons interact most effectively with the optical phonons, as was shown in the very first studies, in particular, on the example of ZnO.[31] It has recently been found in studying a stepped Pt {111} surface, i.e., a vicinal face, that it is characterized by vibrational modes supplementary to those of a smooth surface.[105] According to Ref. 106, they are localized in the regions of the steps and arise from the relaxation of the atoms at these sites.

Thus the method of vibrational ES possesses rich potentialities, especially in studying adsorption phenomena, and it undoubtedly faces a great future.

5. ELECTRON STRUCTURE OF THE SOLID SURFACE

We can classify somewhat arbitrarily the methods of studying the electron structure of a solid surface as "direct" and "indirect". The methods are called direct that obtain the energy spectra of the valence electrons emitted into the vacuum or of the reflected electrons that have lost energy in exciting them. The indirect methods, which we shall take up first, study the effect of the electron structure of the atoms and the electron environment on the binding energy E_i of the core electrons or the energy E_{ABC} of the Auger electrons. It can be found by measuring the energy shifts ΔE_i or ΔE_{ABC} when electrons are emitted from atoms of the same type, but existing in different states. It has also been proposed to study the effect of these states on the structure of the so-called satellite lines (see below). The indirect methods enable one to detect and establish the difference in the electron states of atoms. However, as a rule, they do not answer the question of what kind of state it is. The foreign literature uses the term "fingerprint" to denote this type of information. At present the potentialities of the indirect methods are expanding in connection with the intensive development of the theoretical foundations of ES.

Let us touch briefly on the nature of the shifts ΔE_i. Until recently two reasons for their appearance were considered: the chemical shift $\Delta E_{i,\mathrm{chem}}$ and the relaxational shift $\Delta E_{i,\mathrm{rel}}$, i.e., $\Delta E_i = \Delta E_{i,\mathrm{chem}} + \Delta E_{i,\mathrm{rel}}$.[109–116]

The chemical shift is the shift in the initial state of a core electron in the atom when its electron state is altered, i.e., upon any redistribution of the spatial localization of the valence electrons. It alters the screening action of the valence electrons on the core electrons. This is accompanied by a change in the binding energy E_i of the latter, i.e., the chemical shift. In particular, an increase in the effective charge of the atom diminishes the binding energy of the core electrons, while

conversely a decrease in the charge elevates the binding energy. The concept of the chemical shift had been introduced already in the study of the electron structure of molecules.[16] According to Ref. 111, a shift in the core level is observed also when the electron configuration of the atom alone is altered. The authors of Ref. 111 singled out this component and called it the configurational shift $\Delta E_{i,\mathrm{con}}$. Thus they proposed that ΔE_i consists of three terms.

In contrast to the chemical shift, the relaxational shift involves changes, not of the initial states, but the final states of the system of the atom, as well as of the electrons surrounding the given atom, as one of its core electrons is removed. The concept of the relaxational shift had already arisen in treating the binding energy E_i of the electrons in an isolated atom. According to the theorem of Koopmans,[112] the energy E_i is equal to the energy ε_i, with reversed sign, of an electron as calculated for the atom in the one-electron approximation: $E_i = -\varepsilon_i$. This equality presupposes an invariant, "frozen" state of the electrons of the atomic system as the electron is removed from it. However, as it is removed from the N-electron atom, the remaining system of $N-1$ electrons actually proves not to be at equilibrium. It undergoes relaxational rearrangements leading to a state of lower energy, and which hence are accompanied by release of the excess energy. It is carried away by the electron being removed from the atom[7] and is manifested as a decrease in its binding energy by the amount $\Delta E_{i,\mathrm{rel}}$ as compared with $-\varepsilon_i$. Thus the relaxational shift stems from the multielectron character of the atomic system. More exactly, the binding energy of the electron is determined by the relationship $E_i = E(N) - E(N-1)$. Here $E(N)$ and $E(N-1)$ are the energies of the atomic system with N and with $N-1$ electrons.[110]

An additional type of relaxation process arises in a solid: interatomic relaxation.[109,110] In metals it is manifested as a screening of the excess positive charge of the ionized atom by the valence electrons of the atoms surrounding the given atom. Here it plays the dominant role. Two mechanisms have been proposed of screening of a hole[56,62,109-111,113,114] (see below). In dielectrics the interatomic relaxation consists of polarization.[115] Figure 18 shows an example of the calculation of the shifts ΔE_i and their components upon forming the metals from isolated atoms.[111] It also shows the
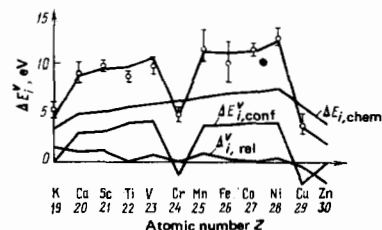
FIG. 18. Energy shifts ΔE_i and their components for the metals of the 4th row of the periodic table (solid curves). Circles—experimental data.[111]

[6]One can also use the concepts of surface phonons in analyzing the vibrations of ordered submonolayer and monolayer films when the lateral interactions between the adsorbed particles are substantial.[108]

[7]See below concerning more complex photoexcitation events.

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FIG. 19. Spectra of x-ray photoelectrons excited from the 2p level of V and from the 1s level of O for vanadium and its oxides.[116]

experimentally found shifts. By definition, the binding energy of the electrons in a solid must be measured from the vacuum level. We see that the agreement between theory and experiment is satisfactory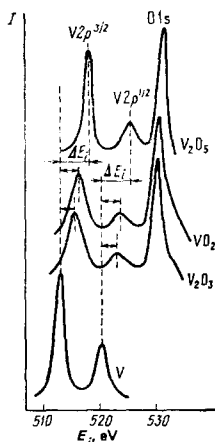. Shifts are also observed on comparing the binding energies of the core electrons contained in different solids. For example, it has been shown that the transition from the metal to the oxide gives rise to a shift ΔE_i in the core electrons of the metal and to a systematic increase with increasing oxygen content in the oxide. Figure 19 shows these data for vanadium and its oxides as obtained by excitation of x-ray photoelectrons from the 2p level of V and also from the 1s level of O.[116]

It is of interest for solid-surface physics to study the difference between E_i of the core electrons of atoms belonging to the bulk and to the surface. Although such attempts had been undertaken long ago,[117] only in recent years has it been possible actually to detect these shifts, in connection with the development of angle-resolved XPS. In particular, it has been shown that the binding energy of the 4f electrons of the surface atoms of gold is 0.4 eV smaller than in the bulk.[118]

Investigation of the shifts is widely used in studying adsorption phenomena.[8,117,119-121] As has been shown in many studies, ΔE_i is a reliable empirical characteristic of the electron state of an adsorbed atom and its environment. A correlation has been found between the shifts ΔE_i and the activation energy E_{des} of desorption of adsorbed particles.[120] When adsorbed atoms of a single element coexist on a solid surface, but in different adsorption states, the photoelectron spectra exhibit somewhat shifted lines.

Theoretical papers have paid much attention in recent years to the problem of the relaxational shifts of the core electrons in particles adsorbed on metals. Just as in the case of pure metals, two mechanisms of screening of a hole are discussed. According to the former, the hole is screened by the negative charge of the forces of the mirror image induced in the metal. To describe them, one employs the concept of superposition of sur-
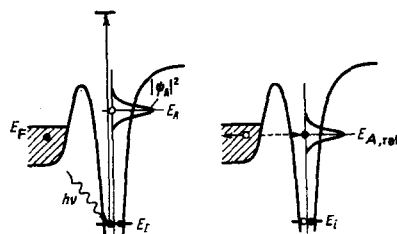

FIG. 20. Schematic diagram of screening of holes in an adsorbed particle.

face plasmons.[114,122] In the latter mechanism the metal is only the supplier of the screened charge localized on the adsorbed particle.[123] The appearance of a hole in the adsorbed particle shifts the electron energy levels associated with it. Here the first free orbital E_A of the adsorbed particle can prove to be lower than the Fermi level E_F of the metal. This causes it to become filled with a conduction electron of the metal, and thus the hole becomes screened (Fig. 20). In the general case, as has been shown in Refs. 124 and 125, both mechanisms coexist, and the contribution of each depends on the character of the binding of the adsorbed particle to the substrate. In physical adsorption, in which electronic exchange between the adsorbed particle and the metal is hindered, the mirror-image forces play the determining role. In the case of chemisorption the filling of the free orbital of the adsorbed particle predominates. The existence of the two mechanisms of hole screening can complicate the shape of the lines of the photoelectron spectrum, and in particular, cause them to be multiplets.[125,126] This effect must not be confused with the existence in the spectrum of several lines caused by the coexistence on the surface of atoms of a single given element, but existing in different states.

Multiparticle effects in the photoexcitation of the core electrons are also manifested in additional excitations caused by the interaction of the hole with the system of valence electrons surrounding it. Thus, conduction electrons having a continuous spectrum can be excited in metals. This gives rise to asymmetry of the line shape, with a slower decline of the photocurrent on the low-energy side. This effect has been found both for a solid,[127] and for atomic particles adsorbed on its surface.[126] Electron excitations can also have a characteristic energy, as, e.g., in generating plasmons in a solid, in interband transitions of the valence electrons, or in exciting electrons in an adsorbed particle.[128-130] All these processes are accompanied by the appearance in the spectrum of extra lines—"intrinsic" satellites, lying at certain distances from the main lines. Their structure is also a source of information on the electron structure of the adsorbed particle.[130,131]

Extra lines also arise in the spectrum when the photoexcited electrons emerging from a solid suffer characteristic energy losses—these are the "extrinsic" satellites. Since the excitations in both cases can have the same nature, it takes a special analysis to distinguish the satellites, as has been done, e.g., in Ref. 129.
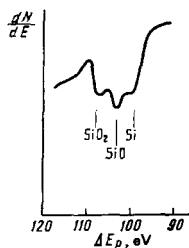
FIG. 21. Spectrum of ionization energy losses of electrons in partially oxidized silicon.[36]
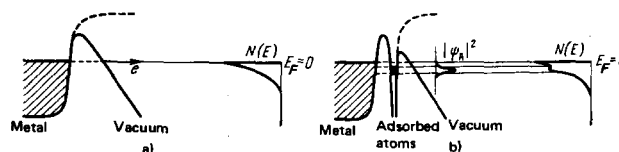

FIG. 22. Energy diagrams of tunneling of electrons out of a metal and the spectra of field-emitted electrons. a) Pure metal; b) metal + adsorbed layer.

As a rule, one finds the shifts and satellites by the XPS method. It would seem that the method of ioniza-tion ES would be ideally suited for this purpose, since the ionization energy losses that it determines are equal to E_i^F, and it does not require a knowledge of the work function of the specimen.[8] However, the line shape of these threshold energy losses on the low-energy side depends on the density distribution of free electron states near their boundary, i.e., in metals—near the Fermi level, and in semiconductors and dielectrics—near the bottom of the conduction band. Therefore if, simultaneously with the change of state of the atom, the structure of the allowed states near this boundary is altered, the form of the ionization losses will change, and this can distort the shift ΔE_i being measured. Ap-parently this situation is not very essential if one only needs to distinguish certain types of states. The meth-od is illustrated by the spectrum shown in Fig. 21 of the ionization energy losses of electrons in partially oxidized silicon.[36] We can clearly see three different energy-loss lines, which the authors attribute to three different states of the silicon atoms in pure Si, SiO, and SiO_2.

The dependence of the line shape of the threshold losses on the structure of the density of free electron states near the boundary, which hinders measurement of the shifts, allows one to study this structure per se. In this modification, ionization ES has been repeatedly applied to study the structure of the free states in semiconductors near the bottom of the conduction band, and also the free surface electron states above the Fermi level.[132]

As has been already noted, energy shifts are also ob-served for Auger electrons, where they are usually ex-pressed more strongly and have a more complex nature. The large shifts ΔE_{ABC} are mainly due to an enhanced role of relaxation processes involving the appearance of a doubly ionized atom in the Auger process.[133] One can find a theoretical treatment of the shifts ΔE_{ABC} in the studies devoted to calculating E_{ABC}, e.g., Ref. 62. Study of the shifts ΔE_{ABC} is also widely employed in studying adsorption phenomena.[133] Attention has been paid in recent years to the importance of determining

the shifts for the surface atoms of the substrate.[134] Multiparticle effects in the Auger process can also be manifested in asymmetry of the Auger lines and can give rise to "intrinsic" satellites.[135] It is also of inter-est to study them for solid-surface physics.

Let us proceed to the direct methods. Valance elec-trons can be emitted as a result of effects of two types. They can be emitted from the ground states when one creates a strong electric field near the solid surface. The field converts the potential threshold existing at the boundary of the solid with the vacuum into a potential barrier, which allows the valence electrons to tunnel.[136] This mechanism is realized in field-emission ES.[15] In the second type of effect, the valence electrons are pre-liminarily exicted to an energy level $E > 0$, and they exit from the solid above the barrier.[137] The application of photoelectron, secondary-electron, and ion-electron spectroscopy is based on this effect.

Figure 22a shows schematically the process of tun-neling of the valence electrons out of a metal and their energy spectrum $N(E)$ after emerging. Realization of field emission requires a field of the order of 3 GV/m. The spectrum $N(E)$ depends on two main factors, the flux $n(E)$ of electrons incident from inside the metal on the potential barrier, and their probability W of tun-neling. The flux $n(E)$ determines the upper bound of the spectrum for $E \approx E_F$. For $E < E_F$ the form of $N(E)$ is determined by the transparency W, which declines ex-ponentially with decreasing energy E. The influence of $n(E)$ in this region of E is weak, and it is manifested in terms of the factor preceding the exponential in the ex-pression for the current density of electrons. At the same time, this is precisely what expresses the elec-tron structure. In order to study it, one must eliminate from the treatment the stronger exponential relation-ship. One can do this by comparing the measured spec-trum $N(E)$ with $N_0(E)$ as calculated in the free-electron approximation for an emitter that has the same work function and the same field at the surface as in the studied $\{hkl\}$ face of the metal. Then the relationship $R(E) = N_0(E)/N(E)$ reflects the specifics of the electron-ic structure of the surface region of the metal ex-pressed in terms of the deviation from the free-elec-tron model. This is precisely the method by which the existence was first found of surface states in a metal on the example of the W$\{100\}$ face.[138] One can find an application of this method to studying semiconductors in Ref. 15.

One can also apply field ES to study the electronic structure of an adsorbate.[15,139,140] Figure 22b shows

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[8] Under the experimental conditions, owing to the existence of a contact potential difference between the specimen and the electrodes of the energy analyzer, one must know the work function of these electrodes, rather than of the specimen.

the energy diagram explaining this variety of the method. As we know, the change in the electronic structure of an atom upon adsorption can be described on the phenomenological level as a shift and smearing of the energy levels of its valence electrons that arises from its interaction with the metal.[141] The appearance of an allowed energy band of electron states in the former (before adsorption) forbidden band leads to an appreciable increase in the probability of tunneling from the metal at these energies—to the phenomenon of resonance tunneling.[142][9] It is manifested in the form of a structure (of maxima) in the energy spectrum of the field-emitted electrons, which allows one to study the electronic structure of the adsorbate. This is depicted schematically in Fig. 22b. The results of study of several adsorption systems are presented, e.g., in Ref. 140. The electrons tunneling through an adsorbed particle can excite in it vibrational degrees of freedom involving the normal component of its thermal motion. This gives rise to a corresponding fine structure in the energy spectrum. The variant of the method aimed at studying this structure is called inelastic field-emission ES. Examples of using it are described in Ref. 144. The main defects of field-emission ES are the small energy interval of probing, which usually does not exceed ~2 eV, and the need for preparing and studying the object in the form of a sharp point.

The methods are more universal that are based on preliminary excitation of the valence electrons. Just as in the excitation of the core electrons, the information is contained in the structure of the energy spectra of the electrons at the moment of excitation. In the general case these spectra reflect not only the structure of the initial, but also of the final states, as well as the probabilities of transitions among them as described by the corresponding matrix elements of the transitions. Therefore, in order to obtain data on the initial states, one must separate out this information. The role of each factor is determined by the mechanism of excitation of the valence electrons, which depends on the nature of the probe being employed, as well as on the energy of the particles or quanta comprising it. The effect of the probe can prove insubstantial only in the excitation of the valence electrons via relaxation processes. Just as in the other ES methods, the elimination of information arising from the bulk is due to processes of inelastic scattering of the excited electrons during emergence from the solid. The optimal conditions for studying specifically the solid surface are created when one excites the electrons to states having an energy E that corresponds to the region of the minimum of the $\Lambda(E)$ curve (see Fig. 6). If, however, this energy is considerably higher, then one must record the electrons that emerge at small angles to the surface (see Fig. 7).

Among the methods involving preliminary excitation for purposes of studying the electronic structure of the solid surface, the most suitable and most widespread is photoelectron spectroscopy (PS). Electron Auger spectroscopy is also widely used. Also other methods are

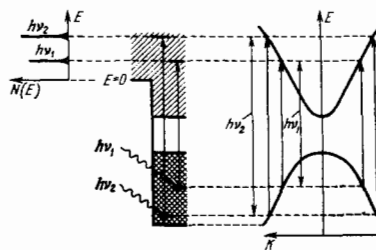[9]On the qualitative level this model was first proposed in Ref. 143.

FIG. 23. Schematic diagram of the photoexcitation of valence electrons in a one-dimensional model and the energy spectrum of the excited electrons.

employed—characteristic electron energy-loss spectroscopy, slow secondary-electron spectroscopy, ion-neutralization spectroscopy, etc.

The information contained in photoelectron spectra depends on the energy of the photons.[6,7] The energy $h\nu$ determines which one we "sense", the volume or the surface. For an $h\nu$ not exceeding 10–15 eV, the fundamental optical absorption in crystals obeys the optical selection rules, according to which the electrons can absorb photons only via direct interband transitions with conservation of the quasimomentum $\mathbf{K}$. As Fig. 23 shows with a very simple one-dimensional example, the energy spectrum of the photoexcited electrons under these conditions depends on the structure of both the initial and the final states, and perhaps, on the probabilities of the transitions between them. That is, it involves the band structure of the solid. Since the energy of the electrons excited at these values of $h\nu$ corresponds to the falling branch of the $\Lambda(E)$ relationship, where Λ amounts to about ten or more layers, the main contribution to the flux of electrons that emerge without energy loss comes from the bulk. It is precisely this region of small $h\nu$ that is widely employed for studying the band structure of solids.

With increasing $h\nu$, the energy of the electrons being excited increases, and the depth from which they emerge without energy loss declines. Consequently, when $h\nu = 40$–100 eV, the part of the spectrum corresponding to the most energetic electrons is formed mainly by electrons emerging from the surface layers. However, according to the uncertainty principle, the localization of the excitation of the electrons to this surface layer leads to an uncertainty in the component normal to the surface of the momentum of the electron being excited. This is equivalent to nonconservation of the vector $\mathbf{K}$ in photoexcitation. Under these conditions, the structure of the energy spectrum of the photoexcited electrons reflects mainly the density of electronic states in the surface layer of the crystal. This allows one to study the latter. In particular, this method allows one to detect the intrinsic surface states of a metal.[145]

PS is widely applied for studying the electronic structure of atomic particles adsorbed on a solid surface. In order to reveal better the structure of the spectrum caused specifically by the adsorbate, one usually employs difference curves, as is illustrated in Fig. 24
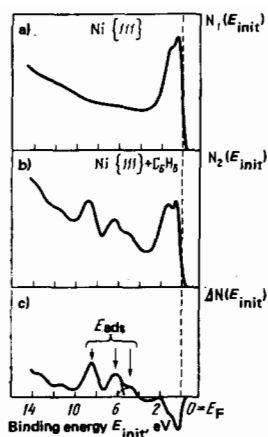
FIG. 24. Energy spectra of photoelectrons in the system Ni{111}/C_6H_6. a) $N_1(E)$—substrate; b) $N_2(E)$—substrate + adsorbate; c) $\Delta N(E) = N_1(E) - N_2(E)$.[146]

with the example of the system Ni {111}/C_6H_6.[146] [10)] The maxima found on the $\Delta N(E)$ curve are treated as electron states arising from the adsorbate, while the negative excursions are treated as changes in the electron states of the surface atoms of the substrate caused by adsorption. In many cases studies of this type enable one to determine the character of the adsorption— physical adsorption or chemisorption. In chemisorption one can find out whether it involves dissociation, or is molecular in type. In the case of the molecular form of adsorption, one can often reveal the orbitals that participate in forming the chemisorptive bonds to the surface. In order to do this, one must compare the obtained structure of the electron levels of the adsorbed molecules with the spectrum of electron levels for the same molecules as obtained in the gas phase. In the chemisorbed state the orbitals participating in bonding with the substrate prove to shift with respect to the levels that do not take part. This method is precisely how it has been shown[146] that the saturated hydrocarbons, e.g., C_2H_6 or C_3H_8, are physisorbed on Ni, whereas the unsaturated hydrocarbons, e.g., C_2H_2, C_2H_4, and C_6H_6, are chemisorbed, their π-orbitals being responsible for formation of the bond with the substrate. One can elucidate their role in adsorption by studying the relationship of the spectra to the degree of coverage of the adsorbate or to the crystallographic orientation of the substrate.

The goal-oriented application of the method of ultraviolet PS (UPS) for analysis of the solid surface dates back to the early seventies.[147] [11)] Up to now, the adsorption has been studied on metals and semiconductors of the molecules of many simple gases, vapors, and

also of various organic compounds. Many reviews have been published on this topic, e.g., Refs. 8, 49, and 149. It has also been treated in monographs,[4,7,10,150] while the most recent results have been treated in the proceedings of the recent conferences on solid-surface physics.[151] Catalytic reactions on a solid surface are being widely studied. The employment of the ES methods, including UPS, in catalysis, and the advances attained using them have been treated in Refs. 152 and 153.

New potentialities in studying the solid surface by UPS are opened up by using angular resolution. The study of the energy spectra of the photoelectrons that emerge at different angles to the surface in a fixed azimuthal plane and the detection in them of maxima arising from emission from surface states (surface resonances) allows one to study the energy structure of the bands of these states. That is, one determines the two-dimensional dispersion relationship $E(K_{\parallel})$ characterizing the surface of clean crystals.[154,155] One can do this because the component of the quasimomentum K parallel to the surface (i.e., $K_{\parallel}$) is conserved in the photoexcitation and emergence of an electron from the solid.[214,215] Two-dimensional energy bands on a solid surface can also be produced when one deposits atoms and molecules of foreign materials on a substrate in the presence of appreciable lateral interactions between the adsorbed particles. Studies along this line have been begun in recent years.[156,157,216]

The potentialities of angle-resolved PS expand substantially and enable us to raise the studies on the electronic structure of the solid surface to a qualitatively new level when we use polarized radiation.[158,159] The most developed source of this is synchrotron radiation.[17] By varying the spatial orientation of the vector potential A of the electromagnetic field and appropriately choosing the angle of exit of the photoelectrons, one can single out the processes of excitation of electrons from initial states having a certain symmetry and obtain thereby information on the spatial localization of the valence electrons. In view of the extremely great information content of this method, we shall examine it in somewhat greater detail.

As we know, in the simplest one-electron approximation, the matrix element M_{fi} of the optical transition of an electron from the initial state characterized by the wave function $|i\rangle$ to the excited state described by the wave function $\langle f|$ is $M_{fi} = \langle f|A\nabla|i\rangle$, where $A\nabla$ is the transition operator. In order to have $M_{fi} \neq 0$, the transition $i \rightarrow f$ must also satisfy, in addition to the optical selection rules, certain selection rules with respect to symmetry. In the general case it requires calculations of M_{fi} to take account of them. However, these rules are very simple for a certain geometry of experiment, and they enable one to obtain data on the symmetry of the initial states of the excited valence electrons solely from the qualitative form of a number of the experimental dependences of the photocurrent. In particular, this is realized when the system under study has a mirror symmetry plane (MSP) perpendicular to the surface of the crystal, and the electron detector lies in this same

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[10)]We note that, as a rule, photoelectron spectra are not drawn in the form of a function of their kinetic energy, but in the form of a dependence on the energy of the initial states. In particular, in metals the Fermi level is taken as the reference origin, as is denoted in Fig. 24.

[11)]Pioneer studies on the structure of the electron levels of adsorbed particles were also performed by the photoionization method.[148]

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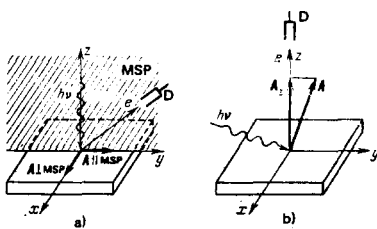
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FIG. 25. Schematic diagram of the relative orientation of the crystal, the vector A of the polarized radiation, and the photoelectron detector. a) Emission of electrons in the MSP; b) emission of electrons along the normal to the surface of the crystal.

plane, and also when one studies the emission of electrons emerging along the normal to the surface.[217] In the former case (Fig. 25a) if the vector A is perpendicular to the MSP, then we have a photocurrent $i_{ph} \neq 0$ only when the electrons are excited from states that are odd with respect to this plane. Conversely, when the vector A is parallel to the MSP and to the surface of the crystal, we have $i_{ph} \neq 0$ only for wave functions $|i\rangle$ that are even with respect to the MSP. When the emission lies along the normal and A is oriented parallel to it, as is realized when p-polarized radiation for the component A_z is incident on the crystal (Fig. 25b),[12] the initial state must be symmetric with respect to the operation of rotation about this normal. For the basal faces of cubic crystals, the initial states that satisfy this last requirement are given in Ref. 217. An application of them to study the symmetry type of surface states of a clean W {100} face and one covered with hydrogen has been described in Refs. 159 and 220.

Application of the symmetry selection rules is especially effective in studying the localization of the orbitals of the valence electrons in adsorbed molecules. It also allows one to obtain data on the orientation of the molecules themselves with respect to the substrate.[158] Let us demonstrate this with the example of study of adsorbed CO molecules. In the photoelectron spectra of these molecules adsorbed on the transition metals from the right-hand side of the periodic table, one usually observes two distinct maxima P_1 and P_2, as shown in Fig. 26.[221] To explain them, model concepts have been advanced of occupied valence orbitals of the CO molecule—4σ, 1π, and 5σ. It is assumed that the CO molecule "stands" on the substrate with the carbon atom directed toward the substrate. Adsorption weakly perturbs the 4σ orbital, which is localized preferentially near the O atom.[13] The 1π orbital suffers a stronger perturbation. The chemisorptive bond to the
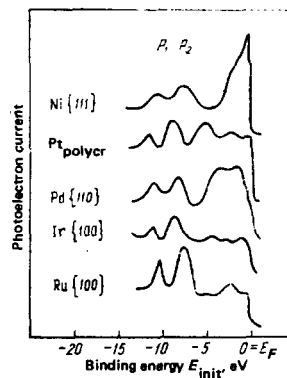

FIG. 26. Energy spectra of photoelectrons for metal/CO systems.[221]

surface of the metal arises mainly from the interaction of the 5σ orbital, which is directed toward the metal, and is concentrated mainly near the C atom. This causes it to shift appreciably in energy with respect to the weakly perturbed orbitals. Consequently it proves to overlap the 1π orbital. A contribution to forming the chemisorptive bond also comes from the first free orbital $2\pi^*$ of the CO molecule, which becomes partially filled with electrons from the metal. Within the framesork of this model, the maximum P_1 is due to excitation of electrons from the 4σ orbital, and P_2 to their excitation from the overlapping 1π and 5σ orbitals. The application of angle-resolved PS with polarized radiation to a number of metal-CO systems has proved the validity of these model concepts.[222-225]

If the CO molecule actually stands on the substrate, then if we take into account the fact that the 4σ orbital possesses cylindrical symmetry with respect to the axis of the molecule joining the nuclei of the C and O atoms, any plane drawn through this axis perpendicular to the surface is a mirror symmetry plane for the 4σ orbital. Therefore, if one places the detector for photoelectrons in such a plane (see Fig. 25a), then according to the stated selection rules, there should be no current of photoelectrons from the 4σ orbital for polarized radiation when the vector A is oriented perpendicular to this mirror plane, and a current should be observed when A is parallel to it. This has been found experimentally. Figure 27 shows these data for the
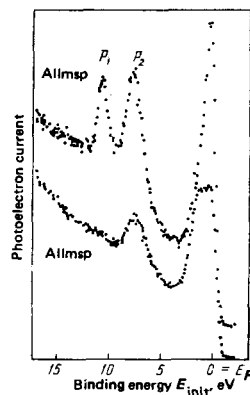
FIG. 27. Energy spectra of photoelectrons for the system Ni{100}/CO; the source of photons is synchrotron radiation.[224]

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[12] In determining A_z one must take into account the effects of refraction and reflection of the radiation at the boundary of the crystal with the vacuum. In particular, they substantially affect the dependence of A_z on the angle of incidence of the radiation on the crystal.[218,219]

[13] Lateral interactions arise at dense coverages of CO owing to the overlap of the orbitals of adjacent CO molecules. As has been shown, e.g., for the system Ni{100}/CO, these give rise to a dispersion of $E(K_{\parallel})$, even for the 4σ orbitals, which indicates the formation of bands of these states.[157]

system Ni{100}/CO.[224] A result agreeing with predictions has also been obtained upon measuring the photocurrent along the normal to the surface. In this case the photocurrent arising from excitation of electrons from the 4σ orbital existed only when a component of the vector A_z perpendicular to the surface existed, i.e., $A_z \neq 0$. It was zero for s-polarized radiation for which $A_z = 0$, i.e., A perpendicular to the axis of the molecule.[14] The polarization effects found in these experiments for the maximum P_2 also agree with the adsorption model being discussed. Emission from the $2\pi^*$ orbital has also been observed[159] for the Ni {100}/CO system for a certain geometry of experiment.

More complete theoretical distributions of photoelectrons with respect to their polar and azimuthal angles of emergence from oriented CO molecules for different orientations of the vector A with respect to the axes of the molecules have been calculated and discussed in Ref. 158.[15] These same studies have shown a valuable source of information on the orientation of the orbitals in adsorbed CO molecules to be the dependence on $h\nu$ of the current of photoelectrons emitted normal to the surface from different molecular orbitals for different orientations of the vector A with respect to them. The form of these dependences qualitatively differs for the different orbitals. In particular, the $h\nu$-dependence of the photocurrent from the 4σ orbital has a characteristic maximum near 30 eV due to a resonance enhancement of the amplitude of the wave function $\langle f |$ of the continuous spectrum in the vicinity of the CO molecule. This is not observed for emission from the 1π orbital. Studies of these relationships for CO on Ni {100}[223,224] and on Cu {100}[225] have also proved to agree with the proposed orientation of the CO molecules.

The results of experimental and theoretical studies of other adsorption systems have been described in Refs. 219 and 226.

Polarization effects that aid in determining the symmetry type of orbitals on a solid surface are manifested with unpolarized radiation, though in more complex fashion, as one varies the angle of incidence on the crystal, since this varies the component A_z.[218,227] Such effects can also be obtained by studying the photocurrent within the total angle of collection in going from s- to p-polarized radiation.[228]

Let us turn now to the x-ray region of the spectrum. Here, in photoexcitation of the valence electrons, the structure of the final states becomes inessential. Their energy distribution qualitatively reflects (to an accuracy of the constancy of the matrix elements of the transition) the curve of density of states of the valence elec-

FIG. 28. Energy-dependence of the density of electronic bulk and surface states in Au.[118]

trons. Since here the values of Λ amount to ~2 nm, the information contained in the spectra corresponds to the bulk density of the states, and is employed to study the latter. In order to elevate the sensitivity with respect to the surface, one analyzes the photoelectrons that emerge at small angles to the surface. In particular, this method has confirmed the small (~10%) narrowing predicted by the theory for the d-bands of Cu for the surface atoms.[229] Differences have been found[118] for Au in the local density of electron states between the bulk and the surface layers of the metal (Fig. 28). One can find the results of the theoretical studies that have been started on the specifics of the local density of states of the atoms of a solid surface, e.g., in Refs. 160 and 161. They are illustrated by Fig. 29, which shows the theoretical dependences for Nb {100} of the local density in the layers of atoms oriented parallel to the surface.[161] They vary up to about the fifth layer.
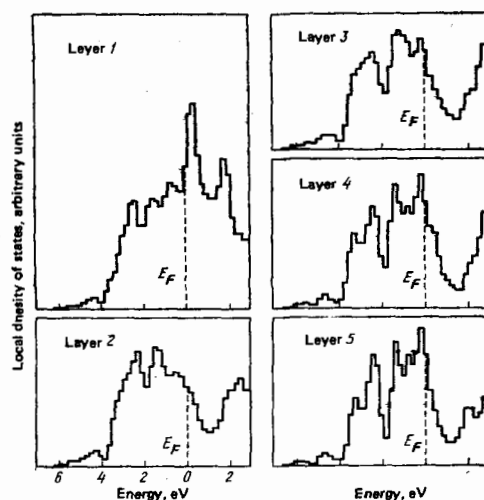
FIG. 29. Theoretical curves of the local density of electronic states in layers of atoms oriented parallel to the surface of the crystal Nb{100}.[161]

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[14] More detailed studies have shown that the axis of the CO molecule on Ni perhaps deviates from the normal by an angle $\lesssim 15°$, possibly owing to thermal vibrations.[224]

[15] Since diffraction involving the final states was not taken into account in Ref. 158, the presented data are most correct for describing the angular distributions of the electrons whose momenta in the photoexcitation are preferentially directed into the vacuum, as is realized for electrons excited from the 4σ orbitals.[158]
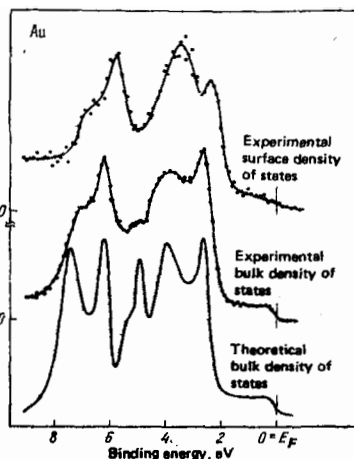
FIG. 30. Energy diagrams of Auger transitions involving valence electrons.

FIG. 32. $M_{4,5}N_{4,5}N_{4,5}$ Auger spectrum of tellurium.[183]

The collection of information on the electronic structure of a solid surface by electron Auger spectroscopy is based on studying the Auger processes in which valence electrons participate. These are the ABV or AVV transitions (Fig. 30). Especially many studies have been devoted to the AVV lines. At present one can speak of two levels of information obtained from these spectra. The first level is the "fingerprint", which only allows one to detect differences in the electron states of atoms and to systematize them. It is based on the experimental fact that a given element under different conditions exhibits AVV lines of different shapes. As a characteristic example, one can cite the widely known data for carbon, which are presented in Fig. 31.[162]

The second level involves studying the shape of the Auger lines and deciphering them. First of all it requires data on the true shape of the Auger lines, which presupposes eliminating the effect of the background and of satellite lines from the experimental spectra. This has thus far been done for a small number of substances, in particular for Al,[163, 164] Li,[165] Mg,[164] Si,[166] Cu,[167] and MgO.[164] Moreover, one must define more precisely the mechanism of the Auger process in order to decipher the spectra. Theoretical studies along this line have been conducted intensively in recent years.[168-175]
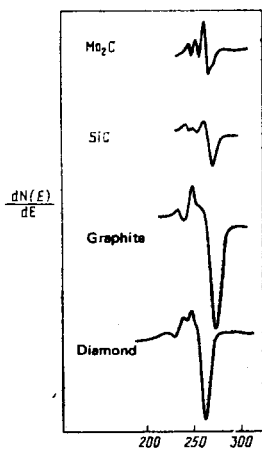
The shapes of AVV Auger lines are generally found to be quasiatomic ("atom-like")/or "band-like", and also can reflect features of both types.[174] In the former case the lines have the same structure as for the isolated atoms from which the solid is built. Hence it arises from the multiplet splitting of the line. The differences that are observed primarily reduce to broadening of the lines of the Auger electrons emitted by the solid. Quasiatomic spectra have been obtained for a number of metals, in particular for Cu,[177,179] Zn,[178,180] Cd,[181] Ni,[179] and also for certain dielectrics with a narrow valence band, e.g., for MgO.[182] To illustrate, Fig. 32 shows the Auger spectra for solid Te as well as the positions of the lines for gaseous Te.[183] In the case of band-like spectra, the shape of the Auger lines involves the curve of the density of electronic states of the valence band. This type of spectra has been observed for metals with almost free electrons, such as Li,[165] Al,[163,164] and Mg[164]; for semiconductors having a sufficiently broad band, e.g., for Si, whose spectrum is shown in Fig. 33a.[166] An empirical Auger energy parameter that allows one to predict the character of a spectrum has been proposed[184] from analyzing the data for the 3d-metals.

Although no complete theory of the shape of Auger lines arising upon excitation of valence electrons exists yet, a number of studies have revealed the factors that govern the shape of these lines on the basis of simplifed model concepts.[168, 169] The essential point is the relationship between the energy F of interaction of the two holes that arise in the valence band from the Auger process and the width W of this band.[169] When $F \gg W$,

FIG. 31. KVV Auger spectra of carbon atoms existing in different states on a surface.[162]
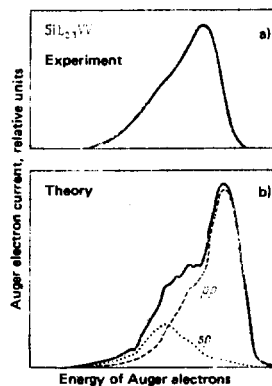

FIG. 33. $L_{2,3}VV$ Auger spectrum of silicon. a) Experimental curve; b) theoretical curve.[166]

the interaction of the holes plays the dominant role, the electrons "behave" as though in an isolated atom, and the spectrum proves quasiatomic. If, conversely, $F \ll W$, we can neglect the interaction of the holes and the probability of an AVV Auger process depends on the density of states in the valence band at the energy of the electrons participating in the Auger process. However, in order to obtain the shape of AVV Auger lines by using a convolution operation, we must take account of the matrix elements of the transitions.[170-174] Here, according to Refs. 172–174, we must bear in mind that the probabilities differ between Auger processes involving valence electrons localized near the core and collectivized electrons. Thus, in Si, in which the s-electrons are collectivized to a large extent, while the bonds are created preferentially by the p-electrons, the fundamental contribution to the Auger process comes from the transitions in which p-electrons participate. The s-p transitions play a smaller role, while we can totally neglect the s-s transitions. The spectrum of Si calculated under these assumptions, which is shown in Fig. 31b, gives the best agreement with experiment.[172] Considerations of the differing role of atomic and collectivized valence electrons in the Auger process have enabled the author of Refs. 172–174 to advance the proposal of the possible use of electron Auger spectroscopy to study the local density of states of the valence electrons near lattice nodes. One can find similar considerations on binary compounds in Ref. 171.

When the values of F and W are comparable, an AVV Auger spectrum consists of two components—quasiatomic and band-like.[169] An example of the classification of Auger lines into these two components is given in Ref. 174. The shape of the Auger lines can also depend on the interaction of valence-band holes with plasmons.[175] The shape of Auger lines reflecting transitions involving valence electrons[185] and particularly interatomic transitions[186] is also of great interest in studying adsorption and associated phenomena.

The method of energy-loss spectroscopy involving excitation of valence electrons has been employed to study the dispersion of surface plasmons[187]; for determining the optical constants of semiconductors (Si and Ge) and elucidating the effect of surface states on them[188]; and for detecting differences in the electronic structure of normal and reconstructed metal surfaces.[189] Many studies have been concerned with the electronic structure of adsorbed particles, e.g., CO on metals,[190-192] oxygen on metals,[190,192,193] and on semiconductors.[188,194] Reports have been published on the spectra of adsorbed molecules of organic compounds (see, e.g., Ref. 195). According to Ref. 196, one must take selection rules into account in interpreting the spectra of chemisorbed molecules. For systems of a metal on a metal, one can obtain valuable information on the electronic state of the adsorbed particles by studying the development of the plasmon spectrum of the adsorbate.[197]

In recent years total-current spectroscopy and angle-resolved spectroscopy of slow secondary electrons have been developing. These methods are aimed at studying the band energy structure of the bulk and surface states, and also at obtaining data on the density distribution of occupied and free states. One can find examples of their use in Refs. 43–47. Indications have appeared of the sensitivity of the method of slow secondary-electron spectroscopy for detecting long- and short-range order.[46] The method of ion-neutralization spectroscopy has not been used apart from the studies of its author.[18]

6. EXPERIMENTAL TECHNIQUES

The contemporary instruments designed for studying the solid surface usually enable one to employ several methods, and hence to obtain complex information on the surface. Along with the methods of ES discussed here, widespread application has also been made of secondary-ion mass spectrometry,[83,198] thermodesorption spectroscopy,[199] electron-stimulated desorption,[200] etc. At present about ten commercial firms produce more than thirty types of instruments for studying solid surfaces that employ different variants of combinations of the methods. In addition to the commercial types being used experimental apparatus specially built for this purpose is also employed.

Since the methods of ES reduce to analyzing in some form or other the energy spectra emitted by a solid surface under various perturbations, the instruments designed for such studies include as the basic elements a superhigh-vacuum measuring chamber with pumping of the system to a vacuum of 10^{-9}–10^{-8} Pa and means of cleaning the specimens under study; sources of the probes; an energy analyzer (several of them can be present in the instrument); and a recording apparatus. In studying active materials that do not permit contact with atmospheric air, and also in studying adsorption and associated phenomena, the instrument must include a system for introducing them. Often these operations, as well as the cleaning of specimens, are performed in an auxiliary chamber. The transfer of the specimen from the one to the other chamber, its study by different methods, operation with several specimens at the same time, and realization of angle-resolved spectroscopy, etc., require transmission into the vacuum of translational and rotational motions. This is performed with manipulators. Airlocks are used for rapid specimen change in the instrument without breaking the vacuum in the measuring chamber.

Let us present some brief information on the sources of the probes, energy analyzers, and measuring apparatus that involves the specifics of their employment in these instruments.

The operation of the photon sources is based on various phenomena, depending on the required range of energy $h\nu$. In UPS, where usually $h\nu = 16$–40 eV, one employs the resonance radiation of an arc discharge, in particular, in He and in Ne. The former source yields sufficiently intense lines at 21.2 and 40.8 eV, and the latter at 16.8 and 26.8 eV. Their nonmonochromaticity amounts to 10–50 meV. Since the source is usually directly connected to the measuring chamber, while a pressure of the order of tenths of a Torr is required to maintain the discharge, a capillary with dif-

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ferential pumping of the source is employed.[201] Recently, in connection with the heightened interest in polarized radiation, to obtain the latter from a gas-discharge source multiple reflection of the radiation at glancing angles from a solid has been employed.[202]

In the x-ray region the source of photons is characteristic x-ray radiation. The most widely employed lines are Al K_α ($h\nu = 1484.4$ eV) and Mg K_α ($h\nu = 1254$ eV).[16] The nonmonokineticity of the radiation amounts to ~1.2 eV. Supplementary monokinetization allows one to reduce $\Delta h\nu$ to ~0.2 eV.[203] In order to obtain softer or harder x-ray quanta one employs the characteristic lines of other elements, e.g., Y ($h\nu = 132.3$ eV)[110] and Ag ($h\nu = 2984$ eV).[204]

Synchrotron radiation has been applied ever more in recent years.[17] Its major merits consist in the possibility of exact determination of the flux intensity of photons, the continuous variation of their energy from the infrared to the x-ray region of the spectrum, and the high degree of polarization of the radiation. The isolation of fluxes of monochromatic quanta of radiation requires monochromators, whose characteristics determine the $\Delta h\nu$ of such a source.

The electron sources are electron guns having thermal cathodes or autocathodes. In the former case the nonmonokineticity ΔE of the electron beams is determined by the thermal spread. Depending on the type of cathode used, it lies in the range from several tenths of an electron-volt to ~1 eV. Autocathodes allow one to attain $\Delta E \sim 0.1$ eV. Moreover, their advantage consists in the possible shaping of high-density electron beams with small cross-sections. In vibrational ES, where ΔE must not exceed 5–20 meV, electron monochromators are employed (see below).

The obtaining of ions is usually based on ionizing atoms with electrons. Ion beams of the inert gases are most widely used at present. The development of ion beams is a substantially more complex problem than the production of electron beams.

The strong electric field near the solid surface required for field emission is attained by employing specimens in the form of a sharp point.

The energy analyzer or spectrometer is the "heart" of the instrument, since it is precisely what "sorts" the electrons with respect to energy. Electrostatic analyzers with a deflecting and retarding field are most widely employed in ES. Magnetic spectrometers are less widely employed for studying specifically the solid surface. The principles of operation of energy analyzers and the fundamental characteristics have been described in many studies, e.g., in Ref. 205. As applied to ES of the solid surface, they have been treated in Refs. 206 and 207.

Analyzers having a retarding field, which are usually designed in the form of quasispherical condensers with intermediate spherical grids, enable one simultaneously to analyze electrons emerging at different angles to the surface in any range of collection angles. Precisely this property renders them irreplaceable in

structural studies of the solid surface by the LEED method with visualization of the angular distributions of the elastically reflected electrons. The fundamental defects that restrict their sphere of application in ES are, first, the high noise level as compared with dispersive energy analyzers, and second, the need for differentiation of the "retardation curve" relationships directly obtained by experiment in order to get the energy spectra. Consequently such a spectrometer proves most suitable for revealing the structure of the spectrum when the extent of the latter is small, while the structure itself is clearly marked. This is roughly the situation in UPS, where this type of spectrometer was most widespread until very recent years. Now, in connection with angle-resolved ES, it has begun to be supplanted by dispersive-type spectrometers (see below). The conditions are also favorable in characteristic energy-loss spectroscopy in analyzing the region of the spectrum adjoining the elastically reflected electrons, which is also performed by the retarding-field method. This method has been applied in field ES, where it was realized with a small entrance angle. Thus the applications of the retarding-field method currently mainly involve either the study of the structure of a solid surface or its electronic structure. The resolution of these analyzers amounts to 0.2–0.3%.

It is preferable to use a dispersive energy analyzer for purposes of elemental analysis, where it is very important to have a low noise level to ensure as high a sensitivity as possible. The most widespread in these studies have been analyzers of the cylindrical-mirror type, as having the largest numerical aperture of ~0.1. Spherical deflectors (180° and sector) are also widely used and to a lesser extent, owing to their smaller light-gathering power, a cylindrical 127° Hughes-Rojansky condenser and an analyzer in the form of a plane mirror. Dispersive spectrometers have a small solid angle of entrance for electrons, and they are also used in various angle-resolved ES methods. Moreover, they are employed in vibrational ES for monokinetizing the electrons.[208] The energy resolution of spectrometers of this type amounts to about 0.1–0.2%.

The specifics of the recording apparatus employed in ES stems from the fact that the information on the solid surface is contained in the structure of the studied spectra as observed against a continuous background, and the problem consists in isolating and measuring it. Complications arise from the small signal/noise and signal/background ratios. In each method the stated quantities have their ranges of most characteristic values, and the problems that one must solve in developing apparatus for them differ from one another. For example, one of the difficulties that one must face in realizing electron Auger spectroscopy involves the small values of the signal/background ratio. As noted above, the problem consists of the need to improve it. In XPS the value of the signal-background ratio exceeds unity, but the signals themselves are very small, and it often takes recording of individual electrons to measure them.

The apparatus that has been developed employs both analog and digital techniques. In particular, a wide-

spread method in electron Auger spectroscopy for increasing the signal/background ratio is analog differentiation of the spectra using synchronous detection.[209] Methods have been proposed for complete removal of the background, as is necessary in detailed study of the shape of Auger lines.[210] Differentiation by the method of flux modulation is also applied.[211] As an example of the use of digital technique, one can cite the method widely used in XPS, based on using a multichannel analyzer operating in a multichannel-counter regime.[212] In order to isolate signals from a strong background in digital form, a method has been proposed, e.g., of "rectification based on smoothing".[213] The expansion of the application of digital technique in combination with a computer that has been observed in recent years apparently reflects the most promising pathways of development in the field of design of measuring apparatus.

7. CONCLUSION

Thus the methods of ES are an extremely informative and promising means of diagnostics of the properties of solid surfaces on the atomic-molecular level. They are already being widely applied in various fields of science and technology. For their most effective use, one must conduct complex investigations. Here it is expedient to choose one's own optimal variants of combination of the different methods for solving concrete problems. Fundamental scientific results in solid-surface physics have already been obtained with the methods of ES and important practical problems have been solved. The intensive development of the theoretical foundations of ES and of experimental techniques is continually expanding its potentialities, while enabling us to understand more deeply the properties of the solid surface and the nature of various surface phenomena. We can say boldly that further progress in the field of solid-surface physics and the solution of many technical problems are inseparably connected with the future of ES.

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