Electron structure of surfaces of nontransition metals

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An account is given of the current status of research on the energy band structure and some physical properties of crystalline surfaces of nontransition metals: alkali and alkaline earth metals, those with the hcp structure, and aluminum. The characteristics and properties of the surface states and resonances, which can be used to distinguish them from the bulk energy spectrum both in experimental investigations and in calculations by various methods, are described. The results of calculations of the work function and surface energy are presented in summary form. The problems concerning relaxation of the surfaces are discussed.

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1. INTRODUCTION

Progress in catalysis, chemisorption, contact and other phenomena depends largely on our knowledge of the electron structure of clean perfect surfaces of solids. Investigations of this topic go back to the work of I. E. Tamm¹ who showed that the boundary of the crystal lattice is a source of new electron states localized at the surface. Work on the electron structure of surfaces has become particularly intense after the development of the technique of spectral measurements, when experiments have become possible on wellprepared single-crystal surfaces, after progress has been made in the theoretical methods, and the computer efficiency has been increased. The history of the topic can be followed on the basis of a number of reviews.²⁻⁶ In these reviews the attention has been concentrated, apart from general aspects, on crystalline surfaces of semiconductors and of transition metals. The properties of the surfaces of nontransition metals, which are simpler from the theoretical point of view, have been considered mainly employing the jellium model in which the crystal potential is replaced by a homogeneous positive background and the band structure effects are ignored. In the last few years new results have been obtained on the electron structure of crystalline surfaces of nontransition metals and this has made it possible to analyze their physical properties on a more realistic basis than the widely used jellium model. The fairly extensive experimental and theoretical data already accumulated on crystalline surfaces of nontransition metals make it possible to review the subject and the results should be of interest also outside the class of nontransition metals. Simple metals are good "testbed" materials because one can use simpler models and make fewer calculations in order to observe a number of tendencies and properties which can be extended to other materials.

The purpose of the present review is to consider the progress made in studies of the electron structure of crystalline surfaces of nontransition metals. In addition to experimental studies, we shall give serious attention also to calculations of electron spectra, work function, and surface energies of alkali metals (sodium, lithium, potassium), alkaline earth metals (calcium, barium, strontium), and also aluminum, lead, and metals with the hcp structure (beryllium, magnesium, scandium, and zinc). We shall discuss relaxation of the atomic structure of the surface, which represents changes in the positions of the surface atoms which occur without disturbing the lattice symmetry (surfaces of simple metals do not undergo reconstruction), and its relationship to the electron structure. Such important, for the physics of surfaces, theoretical topics as an analysis of the feasibility to describe the electron-electron interaction within the framework of the one-electron formalism, the density functional and other methods, and also a detailed analysis of the principal techniques for the calculation of the electron spectra of the surface will not be considered. Moreover, we shall not deal with the methodological aspects of the theory of electron surface (Tamm) states (they are discussed in detail in the review by A. Ya. Belen'skii in the present jour nal^4) and the extensive work⁷⁻²⁰ carried using the jellium model. However, for the purpose of consistency and clarity of presentation, we shall recall in this introduction the main methodological aspects of the theory and consider briefly

the principal results obtained in the jellium model.

The presence of a surface disturbs the periodicity of a crystal at right-angles to the surface and introduces new solutions of the wave equation which do not satisfy the condition that the electron wave vector k_{\perp} (i.e., the component perpendicular to the surface) should be real. These solutions exist for energies in the band gap and are matched at the boundary of a crystal to the exponentially decaying wave functions in vacuum giving rise to localized surface states. The wave functions of these states decay monotonically in vacuum away from the crystal, but they decay in an oscillatory manner, because k_{\perp} is complex, inside the crystal. The periodicity along directions parallel to the surface is retained because electron states form bands along the surface and are characterized by a two-dimensional Bloch wave vector k_{\parallel} $(k_{\parallel}$ is naturally real), which is defined uniquely in a twodimensional surface Brillouin zone (TSBZ). Their appearance and the number of the surface states, their dispersion $E(k_{\parallel})$, and the degree of localization depend on the nature of the potential in the surface region. In earlier investigations the free surface has been considered as a sharp boundary between the bulk of a crystal and vacuum. In such an approach the surface represents practically an independent subsystem. In reality the effective potential experienced by an electron varies continuously from its value in the bulk of a crystal to zero in vacuum and the surface region extends over several atomic layers.

Surface states appear in the gaps of the bulk energy band structure and, therefore, it is convenient to project this structure onto a TSBZ. The projection procedure is described in detail in the literature (see, for example, Ref. 4) and it involves selection of a new unit cell in the reciprocal lattice corresponding to the plane of the surface and to the calculated energy band structure. Then, for each value of k_{\parallel} there is a continuous range of allowed energies in which there are bulk states and there are also gaps where there are no such states. Depending on the discontinuities in the energy spectrum in the three-dimensional band structure, a gap may be retained in the projected structure throughout the whole TSBZ. Even when a gap in the bulk band structure exists only in a certain range of wave vectors and not over the whole Brillouin zone, the gap may be retained on projection ("absolute gap") or it may disappear. In the latter case the range of energies corresponding to a discontinuity of any branch of the spectrum contains states from other branches and the gap is called relative. True surface states appear in the range of forbidden energies for a given value of k_{\parallel} and represent pure damped waves localized at the surface. In addition to well-localized states, there is another possible type of surface states which are resonances that appear when the energy of a surface state lies within a region of the quasicontinuous spectrum. For example, this is possible when a surface state lying below an extremum of one band is located inside another band. Hybridization of a state localized at a given symmetry point of the TSBZ because of overlap with a band of a different symmetry also gives rise to a resonance. An admixture of the bulk component reduces localization of the wave functions of surface resonances and slows down the decay in the bulk of a crystal. Surface resonances can exist even in a continuous spectrum above zero in vacuum. These main concepts of the theory of electron surface states will be illustrated in greater detail by specific examples in Sec. 2 and

in the Introduction we shall briefly review the main progress made using the jellium model in which, at least in principle, surface states cannot be obtained.

In 1970 Lang and Kohn⁷ calculated in a fully self-consistent manner the work function and the surface energy of simple metals in the jellium model using the method of a density functional. Their main assumptions were the local approximation in respect of the electron density, allowance for the pseudopotential corrections to the jellium potential regarded as small quantities in perturbation theory, and onedimensional nature of the problem. The results of Lang and Kohn had subsequently been refined mainly in three respects. First of all, an allowance has been made for nonlocal effects in a system of noninteracting electrons in various models: an analysis has been made of long- and short-wavelength contributions to the exchange-correlated interaction⁸; an allowance has been made for terms of higher orders in the gradient expansion of the exchange-correlated term in the energy functional⁹; a model correlated charge density of a system of interacting particles has been introduced¹⁰; Hartree-Fock calculations have been made for an inhomogeneous electron gas.¹¹ Secondly, the perturbing influence of the lattice introduced by Lang and Kohn as a correction of the first order in the pseudopotential has been allowed for by employing the variational approach in the first¹² and second¹³ orders. Thirdly, three-dimensional changes in the electron density have been introduced into the calculations by the density matrix method¹⁴ and also allowing for the pseudopotential corrections in the second order of perturbation theory.¹⁵ The jellium model provides a simple method for the description of the integral characteristics of the surfaces of simple metals and it continues to be used.¹⁶⁻¹⁸ In particular, the majority of the currently available results on the surface relaxation processes have been obtained in the jellium model with first- and second-order corrections to the discrete potential of the crystal lattice. Nevertheless, this model is ineffective when the parameter of the electron gas density is $r_s \leq 2$ $(4\pi r_s^3/3 = 1/\rho_0$, where ρ_0 is the average density of electrons in a crystal).^{11,16} This is due to the fact that also in the case of simple metals the correction for the perturbing effect of the lattice is large even in the second order.¹⁹ The average value of a perturbation in the bulk does not alter ρ_0 , but its decrease to zero in the surface region has a considerable influence on the kinetic energy and, consequently, on the charge density near the surface. An incorrect allowance for the contribution of the kinetic energy in the jellium model gives rise to negative values of the surface energy.11 Various corrections for the nonlocal nature of the exchange-correlation interaction near the surface and the perturbing influence of the crystal structure of the lattice make it possible to obtain values of the work function and surface energy of simple metals which are close to those found experimentally, but then the jellium model loses its simplicity and convenience in calculation procedures. Therefore, not only the surface states but also the work function and the surface of energy of a real crystal can be calculated correctly only if we take into account the real threedimensional structure.

The present review is organized as follows. Section 2 describes experimental investigations of electron surface states with the attention concentrated on the ability to identify surface states and resonances in the observed energy

spectra. Section 3 provides an analysis of the results of theoretical calculations of the electron spectra of the surfaces of nontransition metals. The work function and surface energy are discussed in Sec. 4 and some topics in the subject of relaxation of surfaces are considered in Sec. 5.

Atomic units are used throughout. All the energies of the surface states listed in tables are in electron volts relative to the Fermi energy.

2. EXPERIMENTAL INVESTIGATION METHODS

The method of ultraviolet spectroscopy with angular resolution (USAR) is the most widely used and the most successful technique for the experimental investigation of the electron structure of the surfaces of nontransition metals. The surface states of metals exist only in a certain part of the TSBZ and the dispersion of these states can be determined only by the USAR method. However, this is not the only complication that arises in the work on the surfaces of simple metals and it is these complications that have held up progress until the last three years.

First of all, the photoemission yield includes a considerable contribution from the damping of surface plasmons, which is not negligible even in secondary electron emission and which is enhanced by surface irregularities. There are also other sources of photoemission apart from surface states and resonances. Four of them have been identified in a study of the (111) surface of Al by the USAR method²¹: direct bulk transitions; enhancement of the density of states at the edges of gaps in the projection of the bulk band structure on the TSBZ; an increase in the density of states at the bottom of a band (giving rise to wide low-energy peaks interpreted as indirect transitions involving the surface potential); an increase in the density of states near $E_{\rm F}$. It has been found that peaks of this kind induce other peaks and affect each other so that, for example, near the band edge it is not possible to identify the dispersion of a surface state.⁷⁴ There is as yet no method for direct separation of the bulk and surface contributions to photoemission²² so that surface states in the structure of the spectrum can be identified only on the basis of a number of indirect criteria, each of which is necessary but not sufficient.

The initial energy of an emission peak of a surface state should be constant when the energy of the incident photons $\hbar\omega$ is varied (Fig. 1a): this makes it possible to separate surface states from direct transitions in the reduced bulk Brillouin zone. The energy of direct transitions shifts toward the Fermi energy on reduction in $\hbar\omega$, passes through a minimum at a high-symmetry point, and rises again.²³ However, a constant energy (for varying $\hbar\omega$) is exhibited also by peaks of plasma oscillations, but the latter can be distinguished because, firstly, their amplitude depends on $\hbar\omega$ much more strongly than the amplitude of surface state peaks and, secondly, the formation of surface plasmons is insensitive to the polarization and angle of incidence of light.²⁴ On the other hand, the dependence of the photoemission yield of a surface state on the polarization depends both on the symmetry of the surface state and on the mechanism of electron excitation.²² For example, an investigation of the wave functions of the state of the (111) surface of Al at the point \overline{K} has shown²¹ that this state has a mirror symmetry relative to a plane parallel to $(11\overline{2})$. Consequently, in accordance with the selection rules, the photoemission from this state should



FIG. 1. a) Spectra of normal emission of electrons from the (001) surface of Al recorded for different photon energies: 1) direct transition; 2) surface state. The peaks due to the direct transitions are shown shaded. b) Geometry of illumination of a sample with s-polarized light, AlRP (top part of the figure) and with p-polarized light, AlRP (lower part of the figure). Here, RP is the reflection plane of the sample, A is the vector potential, \hat{n} is the normal to the surface; θ_i is the angle of incidence of light; the emission plane (EP) is shown shaded.

be suppressed on illumination with s-polarized light (by a beam lying in the same plane, see Fig. 1b), as indeed found experimentally.

The most important criterion demonstrating that a photoemission peak is due to a surface state is the position of its energy within a gap in the projection of the bulk energy band structure. However, even this criterion is insufficient since the energy gap may be crossed by a dispersion curve of direct optical transitions in the bulk.²⁵ These two contributions can be separated using the inversion symmetry of the surface relative to the center of the TSBZ (in the case of those structures for which such symmetry is absent in the bulk): for a surface state function, $E(k_{\parallel})$ should be symmetric relative to the point $\overline{\Gamma}$, whereas the dispersion of direct optical transitions in the bulk does not have this symmetry.²⁵

Another criterion of a surface state is the dependence of the photoemission yield on the contamination and disorder of the surface, which can be utilized to separate photoemission due to the surface states from that due to the band edges.^{21,22} Several layers of oxygen on the surface or bombardment with argon ion suppress completely the emission peaks of the surface states,^{24,26} but do not affect the yield of photoelectrons from the edges of the bulk energy bands.

An additional test has recently become popular: this test represents determination of the dependence of the photoemission intensity of a peak on k_1 of the final state (or on $\hbar\omega$). A surface state has an oscillatory intensity with its maximum near a high-symmetry point in the bulk Brillouin zone.⁷⁴ This is due to the fact that (in the model of direct transitions) a considerable part of the photoemission corresponds to a certain value of k_1 , which is governed by the relationship $E(k_1) - E_s = \hbar\omega$, where E_s is the energy of a surface state. If we expand the wave function φ_s of a surface state in terms of bulk wave functions ψ_n for the same value of k_{\parallel} , $\varphi_s = \Sigma k_{\perp,n} a_n(k_1) \psi_n$, we find that the intensity I_s of

emission from the surface state at a given energy $\hbar\omega$ is pro-

portional to $|\sum_{k_{\perp},n} a_n(k_{\perp})M_b(n)|^2$, where *n* is the energy band number, M_b is the matrix element of the transition for the bulk bands, and $a_n(k_{\perp})$ is the coefficient in the expansion. Consequently, I_s oscillates, since $|a_n(k_{\perp})|^2$ is a narrow peak at that value of k_{\perp} where the bulk band is closest in energy to the surface state and the frequency dependence of the bulk intensity is a smooth function.⁷⁴

The USAR method has been used to obtain also the dependences of the width of photoemission peaks on k_{\parallel} . Studies of this dependence⁷⁴ have revealed that broadening of the peaks due to surface states for the (001) and (111) faces of Al cannot be explained by the presence of only two known mechanisms: the finite lifetime of a photohole and the dispersion of k_{\parallel} due to surface defects. It has been shown that broadening includes also a contribution from the interaction of surface state peaks with the bulk continuum (the effect of this mechanism has been revealed also in calculations of the electron structure on the surface of Ca; see Sec. 3).

In contrast to the USAR method, which gives the maximum information on the filled states, the method of integral emission spectroscopy makes it possible to determine only the energy of a photoemission peak obtained from the region of a gap in the TSBZ.²⁷ The surface contribution to the photoemission can be separated from the bulk contribution by altering the angle of analysis θ of the photoemission field relative to the surface (the angle θ differs by 90° from the polar angle of electron emission θ_e). Suitable materials for such investigations are alkaline earth metals since the gap in the projected energy band structure of these metals is located at a minimum of the density of states formed as a result of hybridization of the s and p bands and the d band, and the surface states within the gap do not become mixed with the states in the bulk spectrum (see Sec. 3).

The methods described here are used to obtain information on filled surface states. Equally interesting are the vacant states on the surface, particularly in the case of alkali metals because there are then no filled surface states. In the last few years the method of bremsstrahlung spectroscopy (inverse photoemission)²⁸ has become popular for the investigation of states with energies in excess of E_F . It differs from the other similar methods (optical spectroscopy, electron energy loss spectroscopy, and image potential spectroscopy) by the fact that it does not create a hole when an electron is excited and, consequently, it does not distort the spectrum. The physics of this method can easily be understood if we compare it with ultraviolet spectroscopy.²⁸ In the course of



FIG. 2. Schematic representation of the photoemission and inverse photoemission processes.

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photoelectric emission a photon of monochromatic radiation $\hbar\omega$ is absorbed by valence electrons of initial energy E_i , resulting in transfer of these electrons to the final state $E_f = E_i + \hbar\omega$. The velocity of the emitted electrons is then determined as a function of E_f and the probability of occupancy of the initial state E_i is then calculated. Bremsstrahlung is the inverse process (Fig. 2). The initially free electron of energy E_i undergoes a radiative transition emitting a photon $\hbar\omega$ and drops to another vacant state E_f . By analogy with photoemission, it is possible to determine the intensity of emission of optical quanta of energy $\hbar\omega$ as a function of the energy of the final state $E_f = E_i - \hbar\omega$. Therefore, these two processes differ by the interchange of the initial and final states.

Photoemission can be regarded as a three-stage process²⁹: optical excitation of an electron from an occupied valence band to an empty conduction band; transfer of a hot electron to the surface; electron emission from the surface. The emission of bremsstrahlung can be regarded similarly: optical damping of an electron (with the momentum conserved or altered) to a vacant final state $E_i - \hbar\omega$; transfer of the resultant photon in a solid, including the probability of scattering and absorption; emission of the photon from the solid into vacuum.

We shall assume that J_e is the number of electrons per unit energy and per unit solid angle, corresponding to one photon emitted as bremsstrahlung and J_p is the number of bremsstrahlung photons emitted by the surface per unit solid angle per electron. The number of electron states per unit solid angle is

$$\frac{\Omega}{(2\pi)^3} |\mathbf{k}^2| \cos \theta_{\mathbf{e}} = \frac{\Omega}{(2\pi)^3} \cdot 2E \cos \theta_{\mathbf{e}}, \qquad (2.1)$$

where Ω is the volume of the system and E is the electron energy. The number of photon states per unit solid angle is

$$\frac{\Omega}{(2\pi)^3} |\mathbf{Q}|^2 \cos \varphi = \frac{\Omega}{(2\pi)^3} \frac{\omega^2}{c^2} \cos \varphi, \qquad (2.2)$$

where **Q** is the photon momentum, c is the velocity of light, and φ is the polar angle of photon emission. It follows from Eqs. (1.1) and (1.2) that

$$\frac{J_{\rm p}}{J_{\rm e}} = \frac{\omega^2}{2Ec^2} \frac{\cos\varphi}{\cos\theta_{\rm e}} , \qquad (2.3)$$

i.e., the emission of photons is c^2 times weaker than the emission of electrons. It has been estimated that the photon flux from the surface is $3 \times 10^6 \text{ sec}^{-1}$ when the band width is 0.1 eV and the incident electron current is 100 mA; this estimate has been confirmed experimentally.³⁰

Bremsstrahlung spectra can be observed in the x-ray range and in the ultraviolet region by two methods (in the xray region they give the same result³¹): direct observation of a spectrum by dispersion for a fixed energy of the incident electrons and "isochromatic" observation when the intensity of radiation with a fixed wavelength is measured for different energies of the incident electrons (isochromat-bremsstrahlung radiation). The method of inverse photoemission has been applied so far only to the surfaces of transition metals, semiconductors, and adsorbates.^{28,32–34}

The atomic crystal structure of surfaces of nontransition metals has been investigated less than the electron structure. Atomic modification of the surfaces of simple metals

has not yet been observed experimentally, but it is known that relaxation can be quite considerable.³⁵ The most widely used method for the study of the surface geometry is still low-energy electron diffraction (LEED). The method involves theoretical calculation of the electron diffraction spectra for several atomic layers closest to the surface and a comparison with the experimentally determined spectra.³⁶ Calculations are carried out employing the Korringa-Kohn-Rostocker (KKR) layer method, which combines the KKR method for the calculation of the band structure in order to determine the scattering properties of one atomic layer with the matrix approach that allows for multiple scattering between the layers. The main difficulties encountered in the interpretation of the results of experimental investigations are associated with the fact that such interpretation is based on an analysis of models which include not only structural variables, but also nonstructural ones, such as the intrinsic crystal potential, the energy-dependent mean free path, phase shifts due to scattering, the dynamic response function, etc. The best agreement between the calculated and measured values in the LEED method requires variation of the structural and nonstructural parameters, which can be mutually interdependent. The analysis turns out to be fairly complex and not free of ambiguities in respect of the uniqueness of determination of the structure.³⁷ Precision experimental results are not yet available on the relaxation of the (111) surface of Al. The LEED method has been used to establish³⁸ that such relaxation is positive (i.e., the last interplanar distance is greater than in the bulk) and its magnitude is 2.2%. The same method was used elsewhere³⁵ to show that this surface does not relax, whereas an investigation of the fine structure of electron transitions in the course of absorption of x rays³⁹ has shown that relaxation is negative and amounts to about 8%. Another method-involving calculation of the atomic structure of the surface on the basis of the experimentally determined diffraction intensities³⁷---also gives a negative value of the relaxation amounting to 3%. In this method an expansion of the diffraction intensities as a Fourier series gives a convolution of the function of the required structural parameters with Fourier transforms of the atomic form factors; this is followed by the inverse transformation to find the structural and nonstructural contributions. The method makes it possible to vary the parameters fully, but provides a more approximate approach to the process of diffraction which is limited to single scattering.

The relaxation of the (011) surface of Al is not fully understood either: the LEED method has been used to show in some cases that the relaxation is negative and amounts to 10-15% (Refs. 35-40). However, the same method was used recently⁴¹ to show that the relaxation process is oscillatory: for the first layer the relaxation is -8.6%, and +5.0% and -1.6% for the second and third layers. Only in the case of the (001) surface of Al do all the experimental methods produce the same result, which is the absence of relaxation.

The relatively low sensitivity of the LEED method, which according to Ref. 42 is 0.1 Å, is clearly insufficient to detect weak relaxation of light alkali and alkaline earth metals. The method is mainly suitable for the determination of the atomic structure of thin films of these metals⁴³ and for the precise orientation of samples in the USAR experiments.^{22,44}

3. ELECTRON SURFACE STATES. CALCULATION METHODS AND RESULTS

In the case of a crystal with a surface as well as for an unbounded crystal the electron spectrum is found by solving the wave equation with suitable boundary conditions. In the adiabatic one-electron approximation the problem reduces to the solution of the self-consistent system of equations

$$\{-\nabla^{2} + V_{eff} [\rho(\mathbf{r})] - E\} \psi_{E}(\mathbf{r}) = 0, \ \rho(\mathbf{r}) = \sum_{E < E_{F}} |\psi_{E}(\mathbf{r})|^{2},$$

$$V_{eff} [\rho(\mathbf{r})] = V_{e1}(\mathbf{r}) + V_{xe} [\rho(\mathbf{r})],$$

$$\nabla^{2} V_{e1}(\mathbf{r}) = 4\pi \left[\sum_{i} \rho_{i} (\mathbf{r} - \mathbf{R}_{j}) - \rho_{e}(\mathbf{r})\right],$$

$$\int \left[\rho_{e}(\mathbf{r}) - \sum_{i} \rho_{i} (\mathbf{r} - \mathbf{R}_{j})\right] d^{3}\mathbf{r} = 0;$$

$$(3.1)$$

here, $\rho_{\rm e}({\bf r})$ and $\rho_{\rm i}({\bf r} - {\bf R}_{\rm j})$ are the electron and ion densities, respectively; $V_{\rm ei}({\bf r})$ is the potential of the electron-ion interaction in the Hartree approximation; $V_{\rm xc}[\rho({\bf r})]$ is the exchange-correlation potential. If the potential is divided arbitrarily into the bulk (b) and surface (s) parts:

$$V_{\text{et}}(\mathbf{r}) = V_{\text{et}}^{\text{b}}(\mathbf{r}) + V_{\text{et}}^{\text{s}}(\mathbf{r}), \quad V_{\text{xc}}(\mathbf{r}) = V_{\text{xc}}^{\text{b}}(\mathbf{r}) + V_{\text{xc}}^{\text{s}}(\mathbf{r}),$$

it becomes clear that the classical analog of $V_{\rm ei}(\mathbf{r})$ is the dipole potential of a double layer and the analog of $V_{\rm xc}^{\rm s}(\mathbf{r})$ is the image potential, which should decrease at large distances from the surface in accordance with the 1/4 z law. A self-consistent microscopic calculation based on Eq. (2.1) with a self-consistent effective potential should allow for both classical contributions.

The methods used to calculate the electron spectrum of the surface differ in respect of the selection of the effective potential, representation of the wave function, and specification of the boundary conditions. Practically all the methods for the calculation of the energy band structure of bulk crystals have been used also in the case of surfaces; they include the tight-binding,^{44,45} orthogonalized plane wave,⁴⁶ linearized augmented plane wave (LAPW),^{47,48} and pseudopotential^{49–55} methods with surface boundary conditions which are different for different calculation models. The selection of the method is determined by the nature of the object and the purpose of the investigation. In the case of nontransition metals the pseudopotential method is the most effective.

Formulation of the boundary conditions which allow for the surface is not a trivial task and therefore various models have been proposed in which the authors tend to reduce these conditions to the familiar schemes of a semi-infinite crystal,^{49,50} a film,^{51,53} a "synthetic" crystal,^{52,54} and solution of the integral Schrödinger equation by numerical methods.55 The electron surface states in the model of a semiinfinite crystal are found by solving the wave equation in three regions: in the bulk, in the surface region, and in vacuum; the solutions are then matched at the appropriate boundaries.^{49,50} The model is inconvenient mainly because of the difficulties due to the complexity of the wave vector: it is necessary to allow for damped waves in the bulk of a crystal. Appelbaum and Hamann⁴⁹ carried out a self-consistent calculation by the pseudopotential method for the (001) surface of Na without allowance for the damped solutions in the bulk and found no surface states. Hardy and Allen⁵⁰ allowed

TABLE I. Energies of electron states on (001) and (111) surfaces of alkali metals.

Metal	Surface	Symmetry point of TSBZ	Calculated val- ues
Sodium Lithium	(001) (001) (111)	$\begin{vmatrix} \overline{X} \\ \overline{X} \\ \overline{X} \\ \overline{K} \end{vmatrix}$	2,24 ⁵⁵ , 1,97 ⁵⁰ 3,8 ⁵⁵ , 2,95 ⁵¹ , 3,0 ⁵⁰ 2,72 ⁵⁵ , 3,34 ⁵⁵

for the damped waves and found states localized on the (001) surfaces of Na and Li (Table I). Moreover, this model suffers from problems related to the arbitrary nature of the selection of the plane of matching of the solutions and the inability to apply the standard technique for solutions of the secular equation. The models which admit the solid-state formalism are those of a single film and a film repeated periodically in space at equal vacuum intervals, i.e., a "synthetic" crystal. In the model of a film there is a packet of atomic planes oriented perpendicularly to the z axis and symmetric relative to z = 0. The film thickness should be sufficient to reproduce the bulk states; then the boundary planes of the film can be regarded as the surfaces of the crystal.⁵¹ In the "synthetic" crystal model the repeated films make it possible to carry out calculations in a supercell extended along the zaxis. The wave functions used in this model are characterized by a three-dimensional Bloch wave vector and can be expanded in terms of plane waves. The calculations therefore reduce to the usual energy band problem with cyclic boundary conditions for a crystal in which the unit cell contains several atoms. The size of the matrix of the Hamiltonian can then exceed 200×200 . The convergence deteriorates on increase in the vacuum gap, which is introduced to prevent interaction between neighboring films.

The method based on the numerical solution of the integral Schrödinger equation⁵⁵ also reduces to the film and "synthetic" crystal models; in this case the size of the supercell is not selected in advance, but is dictated by the requirements of the precision and by the size of the matrix of the Hamiltonian.

The eigenvalues obtained by diagonalization of the matrix are electron levels in a crystal film. However, the discrete spectra do not give a full picture of the energy structure of a surface. As the number of layers in a film is increased until an infinite crystal is formed, the levels behave in different ways: the majority shift strongly along the energy scale, broaden, and form a continuous spectrum. However, the energies of some of the levels located in band gaps change only very slightly. Since in the calculations we cannot increase the number of layers in a film too much, the presence of such levels is deduced by fitting the energy band structure of a film to the projection of the band structure of an ideal crystal on the two-dimensional surface Brillouin zone (TSBZ) at the same high-symmetry points and directions as in the calculation of the energy levels of a film. The projection is constructed by calculating the electron energies for an ideal crystal with a three-dimensional wave vector, when two coordinates of this vector vary along a selected direction in the TSBZ, whereas the third is along the direction of projection.

Electron levels of a film which fall within a gap when the energy structure of the film is made to fit the projection differ from those which are found in the projection region of the continuous spectrum firstly because their energy (within the limits of the calculation errors) is independent of the number of layers in the film and of the vacuum interval and, secondly, the charge density for these levels exhibits stronger oscillations near the surface. These are the localized states which are the true surface states. Surface resonances can also fall within a gap, but the amplitude of oscillations of their density rises near the surface much less than that of a surface state and it decays more slowly inside a film.

In spite of the large size of the matrices of the Hamiltonian, the calculation procedure is simpler in the case of the film model than in the case of a semiinfinite crystal and this is why the majority of the subsequent calculations have been carried out in the model of a film or a "synthetic" crystal using the pseudopotential method.^{51–55}

In the nonself-consistent calculations there is always a problem of the behavior of the potential on the surface. Superposition of atomic (pseudo)potentials which gives good results in the calculation of the bulk properties is unsuitable for the surface: firstly, in this region the Fourier components with low values of \mathbf{k} , compensated in the bulk, play an important role; secondly, in the case of low charge densities the importance of the exchange and correlation increases so that the crystal potential changes to its vacuum value very slow-ly.⁵³ In Ref. 53 this problem is solved by the replacement, in the surface region, of the crystal potential obtained by superposition of atomic pseudopotentials with the potential of aluminum calculated by Lang and Kohn⁷ in the jellium model.

This problem does not arise in self-consistent calculations, but there is a difficulty associated with the poor convergence of long-wavelength components of the potential and charge density, which gives incorrect values of the ionization potential of the work function, but does not affect very greatly the relative positions of the energy bands and the surface states. The first self-consistent calculation of the properties of the (111) surface of Al was made by Chelikowsky *et al.*⁵⁴ by the pseudopotential method using the "synthetic" crystal concept.

The use of pseudopotentials simplifies calculations, but creates its own problems, such as charge transfer, nonlocal behavior, orthoholes, and precision. The advantages and shortcomings of the pseudopotential calculation methods were discussed by Schlüter.⁵⁶ Simple methods for checking the precision of some of the pseudopotentials used in the calculation of the electron structure of the surface were discussed by A. Zunger⁵⁷ in the density functional formalism.

Among other techniques for the calculation of the electron structure of the surfaces of nontransition metals the most popular are the LAPW^{47,48} and the linear combination of the Gaussian orbitals (LCGO)^{44,45} methods. The properties of the (001) and (111) surfaces of Al were calculated in Refs. 47 and 48 using the film model. The (001) surface states and resonances found in this way had the same degree of localization near the surface, although the resonances were broadened because of the interaction with the states in the free spectrum.

The tight-binding methods have been used least in the calculation of the surface properties of nontransition metals. The LCGO method was used in Ref. 44 to calculate the electron structure of the (111) surface of Al in the film model. The boundary conditions were introduced by supplementing

surface atoms with additional s and p orbitals and plane waves. In Ref. 45 calculations of the (001) surface of Al were made by the LCGO method used in conjunction with the Green function formalism. A free surface was assumed to form as a result of removal of one or more layers of atoms. Formally, this was manifested by exclusion from the interaction matrix of diagonal elements for the interaction of the removed atomic layers with the remaining ones.

The tight-binding methods are effective in the calculations of the electron energy and density of states, but they cannot give the density of the charge of the electron levels and cannot be used to identify surface states in resonances. Moreover, the potentials constructed from atomic orbitals should clearly allow for the core shifts of the levels near the surfaces, which, as is known, can be significant not only for the d electrons in the case of transition metals,⁵⁸ but also for the valence levels of simple metals. In particular, measurement of the photoemission spectra⁵⁹ has shown that 2p electron states of the (001) surface of Al are shifted toward lower energies¹⁾ by 0.057 eV and the results of LAPW calculations accurate to within 10^{-3} of a rydberg (Ry) reported in Ref. 60 revealed a shift of these states for a surface layer on the same face of Al by 0.12 eV and by 0.05 eV for the next layer. Shifts of this kind have not yet been allowed for in the calculations of the electron structure of surfaces.

We shall now discuss in detail the results of calculations of the electron structure of the surfaces of simple metals.

3.1. Alkali metals Na, Li, and K

The properties of the surfaces of alkali metals have been investigated quite extensively. Calculations have been carried out by the pseudopotential method using the models of a semiinfinite crystal^{49,50,61,62} and of a film.^{51,55} It follows from these calculations that in projections of the bulk band structure on the planes of the (001) and (111) surfaces there are gaps located above the Fermi level and the parameters of these gaps (Ry) at the point \overline{X} for the (001) surface are as follows: 0.281–0.316 (Na), 0.186–0.201 (K), 0.364–0.486 (Li). At approximately two-thirds of the distance between the points \overline{X} and \overline{M} (Figs. 3 and 4) the gaps of a projection on



FIG. 3. Electron structure of a ten-layer film of Na with the (001) surface. The dashed curves represent the gaps in the projection of the bulk band structure.

(001) overlap in the case of alkali metals so that the bottom of the upper band is located in this region higher on the energy scale than the top of the lower band. In the region $\overline{\Gamma}$ - \overline{X} the gap in the projection includes some of the electron levels of the band structure of a crystal film (Figs. 3 and 4), but none of them can be regarded as a surface state because the density of their charge is not characterized by an enhanced oscillation amplitude near the surface. In the region \overline{X} - \overline{M} the gap of the projection for Na and Li includes a state (Table I) which is observed until the gap is closed and throughout this region the amplitude of the charge density and wave function oscillations for this state^{51,55} is higher at the surface (Figs. 5a and 5b). There are no surface states in the narrow gap in the projection obtained for potassium. The level closest to the gap coincides, within the limits of the calculation error (0.01 Ry), with the bottom of the band and the density of its charge exhibits a resonance (Fig. 5c).

In the projection of the bulk band structure on the plane of the (111) surface of alkali metals there are gaps in the region of the point \overline{K} of the two-dimensional surface Brillouin zone.⁵⁵ The largest gap in the projection obtained for



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FIG. 4. Electron structure of a ten-layer film of Li with the (001) surface. The dashed curves represent the gaps in the projection of the bulk band structure.



FIG. 5. Charge density of surface states: a) sodium, point \overline{X} on the (001) surface; b) lithium, point \overline{X} on the (001) surface; c) potassium, surface resonance, point \overline{X} on the (001) surface; d) lithium, point \overline{K} on the (111) surface. The black dots are the atoms in planes parallel to the surface.

Li is 0.414-0.522 Ry: it extends about three-quarters to the point $\overline{\Gamma}$ and about half the distance to the point \overline{M} . The gaps in the projections for the metals Na and K are narrower: 0.315-0.348 and 0.207-0.222, respectively. They extend to about five-eighths of the distance to \overline{M} and by one-sixth to $\overline{\Gamma}$. Everywhere else the gaps overlap. The gap in the projection for Na includes partly the film electron level (Fig. 6). The density of the charge of this level is localized more strongly at the surface than the density of the charge of the state on the (001) surface of potassium. However, this level cannot be regarded as a surface state because variation of the number of layers in a film shows that different electron levels fall within the gap, i.e., there is no stability in respect of the geometric parameters in the calculation. Therefore, in Ref. 55 this level is attributed to surface resonances. The (111) surface of potassium exhibits a similar resonance. The gap of the projection for the (111) surface of Li includes two states (Fig. 7), which are localized fairly strongly near the surface (Fig. 5d): the amplitude of the oscillations of the density of the charge of these levels in the last layer of the atoms rises approximately twofold compared with the amplitude at the center of the film. Moreover, these states have a constant energy in the gap when the number of layers in the film is varied and, therefore, they are attributed to surface states.

Calculations and identification of electron levels of the (001) and (111) surfaces of alkali metals reported in Refs. 51 and 55 thus show that Na has a surface state at the point \overline{X}

for the (001) surface, Li has a surface state at the point \overline{X} for the same surface, and also two states at the point \overline{K} for the (111) surface. The (001) and (111) surfaces of potassium and the (111) surface of sodium exhibit resonances (Table I). These conclusions are in conflict with recent results^{61,62} in which the pseudopotential method was used in the semiinfinite crystal model to find the levels for the surface of Na: according to these results such levels are not within the gap of the projection but below the bottom of a band, which is difficult to account for physically.

There have been no published calculations for the (110) crystal surface of alkali metals. This may be due to the fact that the low symmetry of this surface requires much computer time for the calculation of its properties.

Experimental investigations of the surfaces of alkali metals have consisted mainly of determination of the optical absorption by films of these metals deposited on quartz substrates,^{63–65} determination of the dependence of the photoelectric work function of the thickness of a film of an alkali metal deposited on a refractory metal,^{66–69} and determination of the photoemission and electron energy loss spectra at an interface between an alkali metal and a transition metal.^{70,71,75}

A determination of the optical absorption in Na has established⁶³ that the dependence of the absorption of light on the photon energy has two maxima (Fig. 8). This has led to the hypothesis⁶¹ that the second absorption maximum at



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FIG. 6. Electron structure of a ten-layer film on Na with the (111) surface. The dashed curves represent the gaps in the projection of the bulk band structure.

FIG. 7. Electron structure of a ten-layer film of Li with the (111) surface. The dashed curves represent the gaps in the projection of the bulk band structure.

higher energies is due to the presence of a surface state of the Tamm type. A determination of the energy of the state required measurement of the dependence of the photoelectron yield I on $\hbar\omega$ and this was used to plot the theoretical Fowler curve and to find the work function Φ of a thin film deposited on a quartz substrate: $\Phi = 2.3 \pm 0.04$ eV. Then, the discrepancy between the experimental points and the theoretical curve was determined in the high-energy part of $I(\hbar\omega)$ and it was used to plot a second Fowler curve and once again the work function $\Phi = 3.45 \pm 0.04$ eV was determined. This value made it possible to locate a surface state below the Fermi level in the bulk band structure of Na (Ref. 72).

The following objections can be raised against this procedure. Firstly, the surface states can be attributed only to a two-dimensional projection of the bulk band structure, since this structure is formed as a result of loss of the translational symmetry in one direction. Secondly, in the projection energy band of Na below the Fermi level there is only a region of continuous states, whereas the surface state should lie within a gap. Thirdly, irrespective of whether the surface state is located above or below $E_{\rm F}$, it does not affect the work function of metals. The nature of the dependence $I(\hbar\omega)$ was explained in Ref. 73. At energies $\hbar\omega$ below 1.2 eV the absorption is described in the approximation of a free electron gas, whereas in the range $\hbar \omega > 2.5$ eV it is attributed to direct electron transitions from the conduction band to higher vacant states. The middle minimum, which is attributed to a surface state in Ref. 61, is explained by M. H. Cohen⁷³ by the formation of exciton pairs in Na.

3.2. Metals with the HCP structure Mg, Be, Sc, and Zn

The surfaces of light alkaline earth metals Mg and Be were investigated recently by Karlsson et al.22,44 by the method of ultraviolet spectroscopy with angular resolution. The relatively small value of the bulk potential of Mg made it possible to determine the photoemission spectra of the excitation of the surface by photons of energy below the energy of plasma oscillations. Studies were made of the surface states along the $\overline{\Gamma M}$ and $\overline{\Gamma K}$ lines (Fig. 9) in the twodimensional projection on the plane of the (0001) surface. Two photoemission peaks A and B with the angle of incidence $\theta_i = 45^\circ$ and the angle of emission 0° were observed for this surface: their energies were constant when the photon energy how was varied (Fig. 10a). A study of the dependence of the photoemission on the polar angle θ_e showed that the peaks exhibited a symmetric dispersion relative to ΓA and crossed $E_{\rm F}$ at the emission angles $\theta_{\rm e} = 33^{\circ}$ and 25°, respectively (Fig. 10b). At higher polar angles $53^{\circ} < \theta_{e} < 80^{\circ}$ there were two other structures C and D (Fig. 10c). The peak C

FIG. 8. Optical absorption spectrum of Na at 20 °C.

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FIG. 9. Bulk (a) and surface (b) Brillouin zones for hcp structure.

FIG. 10. Experimental curves of the distribution of electron emission from the (0001) surface of Mg: a) at a constant energy $\hbar\omega$; b) for different polar angles varying in the ΓAL plane when $\hbar\omega = 10.2 \text{ eV}$; c) at high polar angles in the ΓAL plane with $\hbar\omega = 10.2 \text{ eV}$; d) dispersion of the peaks A (points), B (circles), and C (crosses); the projections of the bulk band structure are unshaded.

shifted on increase in θ_e toward lower energies of the initial state, whereas the peak D remained constant within 0.1 eV. When the energies of the initial states of the peaks A, B, and C were plotted as a function of the vector k_{\parallel} (Fig. 10d), it was found that A and C were within the gaps of the twodimensional projection and extended over the whole gaps. The peak B was emitted from the region of continuous states near the upper edge of the gap and the peak D from a similar region at the point \overline{M} near $E_{\rm F}$. In accordance with the criteria of the surface states, the two photoemission peaks A and C were interpreted as due to the surface states: the first at the point $\overline{\Gamma}$ had an energy -1.7 eV relative to $E_{\rm F}$, whereas the second at the point M had the energy -1.1 eV. The peak B was interpreted as the surface photoemission from the higher (Δ_2) of the two bands surrounding the gap where the peak A was located. The peak B reflected the initial bulk density of states, as confirmed by the stability of its initial energy for all values of $\hbar\omega$. Moreover, when the energy of the initial state of the peak B was represented by the function $E(\bar{k}_{\parallel})$, the dispersion was similar to the band edge profile. This raised the following question: if the peak B reflects the states near the upper edge, why is the density of states not high near the lower edge of the band? One of the possible explanations is that the lower edge of the band is smoothed out too much for electron lifetimes of this order of magnitude. This depends critically on the redistribution of the charge between the lower edge and the surface states, i.e., it depends on how much charge in the surface layer corresponds to the peak A.

The peak D is due to emission from the electron state near the point \overline{M} in the two-dimensional surface Brillouin zone (Fig. 9). In the vicinity of this point the overlapping third and fourth bands are located well below $E_{\rm F}$, have flat edges, and form a region with a high density of the occupied states. The peak D may favor a strong photocurrent also because its position is near the direct transitions.

These results thus revealed that there are two (0001) surface states in the case of Mg: at the point $\overline{\Gamma}$ with the energy -1.7 eV and at the point \overline{M} with the energy -1.1 eV. Both these states are localized in narrow gaps, which is an indication of a low sensitivity of the wave functions of these

TABLE II. Energies of electron states on (0001) surfaces of simple metals with HCP structure.

Metal	Symmetry point	Calculated values	Experimen- tal values
Magnesium	Ē	_	1,7 22
	\overline{M}		-1,1 22
Beryllium	Γ	l —	-2,8 44,84
Scandium	\overline{M}	2; 2,878	
	K	2,8 78	
Zinc	$\overline{\Gamma}$	-3,279	3,6 77
	\overline{M}	-8 979	
		-1,979	
	<u> </u>		

FIG. 11. Experimental curves of the distribution of electron emission from the (0001) surface of Be: a) at a constant energy $\hbar\omega$; b) for different polar angles; c) electron structure of an ideal Be crystal along the ΓA direction (on the left) and electron structure of the (0001) surface of Be in the $\overline{\Gamma M}$ direction (on the right). The dashed curve is the dispersion of the surface state.

states to the surface potential (Table II).

Among the simple metals, beryllium is the "most complicated" 44: the bonds between the close-packed Be planes are almost covalent and large gaps are expected in the structure. The largest gap in the bulk energy structure is located in the vicinity of the point $\overline{\Gamma}$ and its energy is close to $E_{\rm F}$ for Be. The intensity of the photoemission yield obtained on illumination incident normally on the surface exhibits a peak with an initial state at the energy $E_i = -2.8 \text{ eV}$ (Fig. 11), which is not affected by variation of the photon energy $\hbar\omega$. In addition to this peak there is only the $E_{\rm F}$ edge, which is much less prominent than in the case of Mg. The dispersion of this peak has been investigated in the ΓALM plane along the ΓM direction (Fig. 9) in the course of variation of the photoemission yield obtained for different polar angles (Fig. 11b): an increase in the polar angle causes the peak to approach E_F and to cross the Fermi level at $\theta_e = 23^\circ$ becoming even steeper. The experimental results indicate that the - 2.8 eV peak lies within a gap in the two-dimensional projection of the band structure on the two-dimensional Brillouin zone formed by the first Δ_2 bands along the ΓA line; the dispersion of the peak is almost parallel to the lower edge of the band. These two criteria (constant energy of the peak and its location within the gap) and the fact that its intensity falls strongly as a result of contamination of the surface allow us to attribute the peak to emission from a surface state (Fig. 11).

The symmetry of the surface state is similar to the symmetry of the wave functions of Δ_1 and Δ_2 (Ref. 44), so that transitions to the final states are possible to the bands Δ_1 and Δ_2 . This is due to the fact that the wave function of the surface state can be constructed by superimposing the bulk wave functions at the same value of k_{\parallel} , but for whole sets of values of the perpendicular component k_1 : it is the existence of all possible k_1 vectors in the wave function that account for the stability of the energy of the initial state when the photon energy $\hbar\omega$ is varied; for a given value of the initial energy E_i the transition to a surface state is possible for any fixed vector k_{\parallel} .

Direct transitions are not observed in the case of normal emission. The low intensity at the E_F edge is also explained by the electron structure of Be along ΓA : near E_F there are no states accessible to normal emission and all the transitions observed at E_F are due to indirect excitation processes with scattering by the final state.

It therefore follows that on the (0001) surface of Be there is a surface state with the energy -2.8 eV at the point $\overline{\Gamma}$ (Table II).

The authors are not aware of theoretical calculations of

the electron properties of the Mg and Be surfaces. However, calculations were made^{78,79} of the electron structure of the (0001) surface of two d metals with the hcp structure: Sc and Zn; investigators of the surface properties regard these two metals as simple because their d shells are located well below $E_{\rm F}$ and it is assumed that they do not affect strongly the s-p nature of the surface states.⁷⁸ In both cases a parametrized method of tight binding in the "synthetic" crystal model was used. The calculation of the surface electron structure of Sc was made⁷⁸ by introducing corrections to the bulk potential to account for the presence of the surface. However, these corrections have little effect on the result. so that in Ref. 79 the corrections were ignored. The planes parallel to the (0001) surface have the hexagonal symmetry of the atoms in these two metals, so that the two-dimensional Brillouin zone is exactly the same as for the (111) surface in the fcc structure. The gaps of the projection for the (001) surface of Sc have an occupied surface state only in the vicinity of the point \overline{M} and its energy is approximately -1 eV(Fig. 12). Above E_F there are two bands of surface states with the energies 3 and 3.5 eV near \overline{M} . The upper band at the point $\overline{\Gamma}$ overlaps the continuous spectrum. The surface structure below $E_{\rm F}$ is not very pronounced and, therefore, as in the case of alkali metals it would be more interesting to investigate experimentally the vacant bands above $E_{\rm F}$ by employing suitable methods.

A filled surface state showing damping over a considerable region was found by the method of ultraviolet spectroscopy with angular resolution⁷⁷ on the (0001) surface of Zn at the point $\overline{\Gamma}$ and it was identified as having the s-p nature. The energy of this state is -3.6 eV. A calculation reported in Ref. 79 in the model of multiple films consisting of 23

FIG. 12. Electron structure of the (0001) surface of Sc. The dashed curves are the surface states in the gaps of the projection of the bulk band structure and the dotted curves are surface resonances.

FIG. 13. Calculated energy band structure of a 23-layer film of Zn with the (0001) surface. The dashed curves represent the surface states in the gaps of the projection of the bulk band structure.

atomic layers was in good agreement with the experimental results (Fig. 13) and it revealed a surface state at the point $\overline{\Gamma}$ with the energy -3.2 eV (Table II). Moreover, in the calculated energy band structure at the point \overline{M} there was a state with the energy -1.9 eV which was not very extended and which rapidly degenerated to the bulk spectrum. The level at $\overline{\Gamma}$ in the first (surface) layer of atoms had 25% density of its charge and the wave functions were damped out in the seventh layer. The surface nature of this state disappeared and it degenerated to the bulk spectrum away from $\overline{\Gamma}$, again in agreement with the experimental results. All the discrepancies between the calculated and measured values were attributed to the approximation involving calculation

TABLE 111. Energies of electron states on (001) and (111) surfaces of alkaline earth metals and aluminum (experimental results for polycrystalline samples of alkaline earth metals were taken from Ref. 52).

Metal	Surface	Symmetry point	Calculated values	Experimental values
Calcium	(001)	Ē	$-0,1^{55}$ $-0,1, -2,5^{52}$	
		X	$-1,42, -1,28^{55}$ $-1,4^{52}$	-1,6
	(111)	T	-0,9 ⁵⁵ -0,5, -2,5 ⁵²	-0,6
		K	-0,3 52	2,5
Barium	(001)	X	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	-0,35
	(111)	$\vec{\Gamma}$	-0,67, -2,16	1,8
		\overline{M}	-0,94,1,51	-0,65
Strontium		\overline{K}	-1,3, -1,63	0.5
Aluminum				-1,4 -2,3
Aluminum	(001)	Г	2,83 ⁵⁵ 2,97 ⁴⁷ 2,92 ⁴⁵	2,80 ²⁶ 2,75 ²³
	(111)	Γ	4,68 44 4,49 54	-4,6±0,047±
		\overline{K}	-2,4, -0,58 ⁴⁸ -2,0, -0,95 ⁵⁴	-0,51,0 ^{21,81} -0,7 ⁷⁴

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FIG. 14. Electron structure of the (001) surface of Ca. The dashed curve represents the surface states in the gaps of the projection of the bulk band structure.

of the surface states by the bulk potential and to limitations imposed by the bulk calculations.

3.3. Alkaline earth metals Ca, Sr, and Ba

The fullest investigation of the electron structure of the surfaces of alkaline earth metals was reported in Ref. 52: the method of integral x-ray spectroscopy revealed electron emission peaks in the region with a mainly surface contribution (see Sec. 2) and a theoretical self-consistent calculation was made by the pseudopotential method using the "synthetic" crystal method. Similar results were obtained also in calculations made by the same method⁵⁵ using the film model.

The gap in the projection of the bulk energy band structure on the (001) surface of Ca (Fig. 14) which may contain filled surface states extends from $\overline{\Gamma}$ to \overline{X} and then approximately to seven-eighths of the distance from \overline{X} to \overline{M} ; it is then overlapped and reappears at half the distance between \overline{M} and

FIG. 15. Density of the charge in surface levels of Ca: a) at the point \overline{X} on the (001) surface; b) at the point $\overline{\Gamma}$ on the (001) surface; c) at the point $\overline{\Gamma}$ on the (111) surface. The black dots are atoms in planes parallel to the surface.

 $\overline{\Gamma}$. The parameters of the gap are (Ry): 0.338–0.353 ($\overline{\Gamma}$), 0.241–0.278 (\overline{X}). The gap contains electron states unaffected by changes in the geometric parameters of the calculations, extending over a considerable part of the gap, and with energies that agree with the energy of the maximum of the electron yield found experimentally (Table III). The calculations reported in Ref. 52 revealed one surface state at the point \overline{X} , whereas those reported in Ref. 55 revealed two states with similar energies: in the experiments they were indistinguishable because of the error of + 0.1 eV. The localization of the density of the electron charge carried by these states near the surface is very strong⁵⁵: it is much stronger than the localization of surface levels near $E_{\rm F}$ (Fig. 15a). This can be explained if we bear in mind that the density of states in an ideal Ca crystal not only has a minimum near $E_{\rm F}$ ($E_{\rm F} = 0.347$ Ry), as already pointed out (see Sec. 2), but exactly the same minimum (5-6 states/atom) in the energy range 0.2-0.25 Ry (Ref. 80), as shown in Fig. 16. Between them lies the first maximum of the density of states amounting to 15 states/atom. The lower part of the gap in the projected band at the point \overline{X} of the (001) surface coincides with the minimum of the density of states in the region 0.2-0.25 Ry and the surface states located in this part of the gap at 0.105 and 0.09 Ry (1.42 and 1.28 eV) below $E_{\rm F}$ can be revealed in their pure form without the admixture of states from the free spectrum, which lowers the degree of localization of the surface levels. It is probably this fact that enabled Caruthers et al.⁵² to detect by the method of integral spectroscopy a band of surface states in the region of 1.6 eV below $E_{\rm F}$.

At the point $\overline{\Gamma}$ of the (001) surface of Ca there is also a surface level which is localized less strongly (Fig. 15b) in spite of the fact that it is also located at a minimum of the bulk density of states. This occurs because the density of its charge is affected strongly by the states in the free spectrum of electrons.

FIG. 16. Dependence of the density of states on the energy in an ideal Ca crystal.

The gaps in the projected energy band on this (111) surface of Ca extend from the point $\overline{\Gamma}$ by 0.241–0.278 Ry to three-quarters of the distance between \overline{M} and \overline{K} , and from \overline{K} by 0.320–0.345 Ry to one-eighth of the distance between \overline{M} and $\overline{\Gamma}$ (Fig. 17). It was found in Ref. 52 that a second small gap lies largely above $E_{\rm F}$ and the surface state within the gap is not filled. In Ref. 55 the major part of the gap below $E_{\rm F}$ and the corresponding level are filled (Table III). The gap of the projection at the point $\overline{\Gamma}$ for the (111) surface has the same position relative to the energy axis as the gap of the projection of the (001) surface at the point \overline{X} , i.e., the lower half in both gaps lies within the same minimum of the densities of states of an ideal crystal at 0.2-0.25 Ry. However, the states at the point \overline{X} located in the lower half of the gap and at the point $\overline{\Gamma}$ for the (111) surface are located in the upper half and do not correspond to the minimum. This can account for the different nature of the density of the charge of the surface levels: the states at $\overline{\Gamma}$ for the (111) surface are localized less strongly near the surface than at the point \overline{X} for the (001) surface (see Fig. 15c), the amplitude of the oscillations of the density of the charge for the former case increases by one-third at the surface, whereas at \overline{X} it increases by a factor of almost 5. The maximum value of the amplitude at $\overline{\Gamma}$ for

FIG. 17. Electron structure of the (111) surface of Ca. The dashed curves represent the surface states in the gaps of the projection of the bulk band structure.

the (001) surface is six times less than at X for the same (001) surface.

These results make it clear how strongly the density of the charge of the surface states and the degree of their localization are affected by the positions of the gaps and of the levels themselves in the gaps relative to the minima and maxima of the density of states in an ideal crystal, and also by the amplitudes of these maxima.

Experimental investigations of the photoelectric properties of the Ca surface were carried out^{82,83} by the same method as that employed⁶¹ in the determination of the properties of Na, i.e., the photoelectric yield of electrons and the work function were determined, and the deviation of the behavior of the work function from that calculated theoretically was used to draw the conclusion about the influence of the surface states on the work function. The work function of a Ca film evaporated on quartz was 2.87 ± 0.06 eV and constant when the thickness of the film was reduced to 10μ . For smaller thicknesses the work function had two minima (at 2.5 and 5.5 μ) and a maximum between them with its amplitude amounting to $3.72 \pm 0.06 \, \text{eV}$; a further reduction of the thickness enhanced this maximum. The maximum was attributed to the presence of a surface state located, according to the calculations of these authors, at 0.85 eV below $E_{\rm F}$. This approach was again based on the incorrect hypothesis that the surface states affect the work function of metals. Moreover, it is not clear why the surface state begins to affect photoelectric properties when the film thickness is less than 10 μ . Calculations of the surface properties in any model show that 50 Å is sufficient for the formation of a structure of an ideal crystal in the middle layers of a film: a further increase in the thickness reduces the relative contribution of the surface region where the influence of the surface states is significant and measurements of any integral characteristic (without separation of the purely surface contribution to electron emission), particularly of the work function, give not the surface but the bulk properties.

An attempt has been made to calculate the surface electron structure of Ba by the pseudopotential method. The energies of the surface states located within wide gaps of the projections differ considerably from the experimental values (Table III), which is explained by some errors in the calculation of the energy structure of heavy metals by the pseudopotential method without relativistic corrections.

To the best of our knowledge there have been no theoretical investigations of the surfaces of Sr.

3.4. Aluminum

This metal is the one which has been studied more than other metals both theoretically and experimentally. The first calculations of the electron structure of the (001), (111), and (011) surfaces of Al were made by Caruthers *et al.*⁵³ by a nonself-consistent pseudopotential method using the film model. The first self-consistent calculations of the (111) surface of Al were made by Chelikowsky *et al.*⁵⁴ using the pseudopotential method and the "synthetic" crystal model. The results of experimental investigations of the Al surfaces were published in 1978 and these were probably the first in which the method of ultraviolet spectroscopy with angular resolution was used.^{24,26} Subsequently, Al became a "test-bed" metal for checking various methods for the calculation of the electron structure of the surface: Krakauer *et al.*⁴⁷ used the

1.4

FIG. 18. Electron structure of the (111) surface of Al. The shaded regions are the gaps in the projection of the bulk band structure. The dashed curve represents the surface states in the gaps of the projection of the bulk band structure.

nonself-consistent LAPW method for the investigation of the (001) surface of aluminum; Jona et al.³⁸ calculated the energies of the states on the (001) surface by the scattering matrix method (layer-by-layer KKR method allowing for multiple scattering), which is employed mainly in connection with the LEED investigations (see Sec. 2); the (111) surface was investigated by the self-consistent LAPW method⁴⁸ and by the self-consistent LCGO method.^{44,45} The results of these calculations are ambiguous: there are differences not only in respect of the energies of the electron states within a gap, but also in the numbers of these states: ranging from five (filled) states at the point \overline{K} and two at the point $\overline{\Gamma}$ for the (111) surface⁴⁴ to complete absence of the surface states (only resonances were identified) on the same surface.⁵⁵ This difference is due to the fact that the projections of the bulk energy band structure on the (111) surface of Al have very narrow gaps (Fig. 18). It was pointed out in Ref. 55 that the positions of the electron levels of a film relative to the gaps of the projection depend strongly on the number of atomic layers in a film: when the number is altered, different electron levels fall within the gap. The density of their charge then behaves like a resonance and, therefore, they have been attributed to surface resonances. Chelikowsky et al.54 did not vary the number of layers in a film and the energies of the electron levels were compared with the energies of the gaps taken from the calculations of the other authors, and no allowance was made for the dispersion of the levels relative to the gap. Nevertheless, these calculations revealed two states in the gap at the point \overline{K} and one at the point $\overline{\Gamma}$ for the (111) surface (Table III). A very large number of surface states is obtained by a calculation carried out using the LCGO method,44 but this result does not agree with the experimental data.

Hansson *et al.*²⁴ found experimentally a photoemission peak in the region of the gap at the point \overline{M} (at the energy $\hbar\omega = 10.2$ eV for $\theta_i = 45^\circ$) and attributed it to a surface resonance. This interpretation was rejected in Ref. 25 because surface states or resonances have no quantum number k_{\perp} , so that they should appear in the spectrum as a fixed structure when the directions of the incidence of light and of the electron emission are varied so that \overline{K}_{\parallel} remains constant (Sec. 2). This condition is not satisfied by the emission peak

46.4

FIG. 19. Experimental dispersion of the surface state on the (111) surface of Al at the point \overline{M} on the reflection plane (110). The dots represent the results from Ref. 25 ($\hbar\omega = 11.7 \text{ eV}$, $45^\circ < \theta_i < 52.5^\circ$); the open circles are the results from Ref. 24 ($\hbar\omega = 10.2 \text{ eV}$, $\theta_i = 45^\circ$). The dashed line is the calculated dispersion of direct transitions. The shaded region represents projections of the gap along the $\overline{\Gamma M}$ direction in a two-dimensional surface Brillouin zone.

in question. Moreover, a surface resonance energy band should have an inversion symmetry relative to the point $\overline{\Gamma}$ in the two-dimensional Brillouin zone (Fig. 19), whereas the dispersion on both sides of the normal to the surface does not have this symmetry. According to Grepstad and Slagsvold,²⁵ the observed emission peak can be interpreted with a high degree of accuracy by the dispersion calculated on the assumption of simple optical transitions in the bulk, including the reciprocal lattice vectors \mathbf{G}_{002} and \mathbf{G}_{220} , from occupied initial states to a final state in the free spectrum with the vectors $\mathbf{k} + \mathbf{G}_{111}$. Therefore, at the point \overline{M} there are no energy bands of surface states or resonances. At high angles, $45^{\circ} < \theta_{i} < 52.5^{\circ}$, near E_{F} , there is an electron emission peak showing weak dispersion and it cannot be explained by the kconserving bulk transitions. The energy of this peak is ~0.4-0.7 eV less than $E_{\rm F}$ (Ref. 25) and its vectors $\bar{k}_{\parallel} \approx 9.75 (\overline{\Gamma} - \overline{M})$ are close to the values -1.05 eV and 0.75 eV, obtained in calculations of Wang et al.,48 i.e., it is concluded in Ref. 25 that at three-quarters of the distance from the point $\overline{\Gamma}$ to the point \overline{M} there is a localized band of surface states. However, careful classification of the photoemission peaks obtained for the (111) surface of Al made in Ref. 21 has led to the conclusion that this band of surface states represents simply the emission from the edge of the relative gap of the projection of the bulk band structure on the two-dimensional Brillouin zone. On the other hand, the same investigation revealed a peak satisfying all the criteria of photoemission from a surface state (see Sec. 1) located at

FIG. 20. Electron structure of the (001) surface of Al. The dashed curve represents surface states in the gaps of the projection of the bulk band structure.

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FIG. 21. Experimental dispersion of a state on the (001) surface of Al: 1) results from Ref. 26, $\overline{\Gamma X}$ direction; 2) results from Ref. 24, $\overline{\Gamma X}$ direction; 3) results from Ref. 24, $\overline{\Gamma X}$ direction. The dashed curve is the calculated dispersion of free electrons.

the point \overline{K} at 0.5–1.0 eV below $E_{\rm F}$. An investigation by the method of ultraviolet spectroscopy of high angular resolution confirmed the presence of this state,⁷⁴ gave a more accurate value of its energy (-0.7 eV, in agreement with that calculated in Refs. 48 and 54), and showed that it is fairly strongly localized. At the point $\overline{\Gamma}$ in the same investigation it was found experimentally in a narrow range of energies that there was a slowly damped (in the coordinate space) surface state with an energy of -4.6 eV (close to the calculated results of Refs. 44 and 54), and it was pointed out that it was very close to a resonance. Nevertheless, the authors attributed it to a surface state and they showed that the large width of the peak is a consequence of weak splitting of this state of the (111) surface by the crystal potential, which results in a strong interaction with the states in the continuum. Therefore, the agreement between the theory and experiment in the case of the (111) surface of Al demonstrated the following: at the point $\overline{\Gamma}$ there is a surface state of energy $-4.6 \,\mathrm{eV}$ and at the point \overline{K} there is another state with the energy -0.7 eV.

In the case of the (001) surface the theory and experiment give the same result: in a wide gap (of width 0.1 Ry) extending to about half the separation from $\overline{\Gamma}$ to \overline{M} and from $\overline{\Gamma}$ to \overline{X} there is a surface state which has the energy -2.75eV at the point $\overline{\Gamma}$, according to Ref. 23 (whereas according to Ref. 45 the energy is -2.8 eV), as shown in Fig. 20. Its experimental dispersion is shown in Fig. 21. Theoretical calculations give similar energies (Table III). When this gap is overlapped, the surface state in question becomes a surface resonance.

3.5. Lead

The published data are available only for the (111) surface of this metal. The method of ultraviolet spectroscopy with angular resolution was used in Ref. 85 and it was found that in the case of normal emission from the region of the s-p gap there are no surface state peaks, at least in the energy range $18 < \hbar\omega < 55$ eV. Since calculations of the electron structure of the surface have not yet been carried out, this absence of the surface states has not yet been explained.

4. WORK FUNCTION AND SURFACE ENERGY

The work function is the minimum energy required for the transfer of an electron from the Fermi level to vacuum. The work function is governed by two contributions, the bulk contribution equal to the Fermi energy measured from vacuum zero for an ideal crystal and the surface contribution (dipole barrier) due to a redistribution of the electron charge density on the surface; in the calculations these contributions are usually not distinguished. The work function varies little from one metal to another,⁶ but it is fairly sensitive to a redistribution of the electron density at the surface and this accounts for its dependence on the crystallographic orientation of the surface.

In a model of a semiinfinite crystal the work function is calculated as the difference between the self-consistent potential at infinity and the Fermi energy. In the film and "synthetic" crystal models, when we are dealing with packets of atomic planes, the work function of the crystal surfaces is governed by the energy of the upper filled electron state measured from vacuum zero.

In comparing the results of calculations of the work function of crystalline surfaces carried out using different methods and different models it is found that values agreeing poorly with experiments are obtained when the calculations are self-consistent. This may be explained by the poor convergence of the long-wavelength component of the crystal potential (Table IV). There are some discrepancies between the trends of the anisotropy of the work function calculated by the jellium model and that found by the pseudopotential method. Following the rule of R. Smoluchowsky, the work function should rise on reduction of the denity of packing of ions on the surface. Self-consistent calculations carried out in the jellium model,⁸⁹ including corrections for the perturbing influence of the lattice and for changes in the self-consistent field, yielded the following work functions (in electron volts) for the (001) and (111) surfaces: 2.84 and 2.76 (sodium) and 4.25 and 4.27 (aluminum). Investigations of the anisotropy of the work function in the pseudoatom model⁹⁰ also gave values in agreement with the Smoluchowsky rule: 2.72 and 2.44 (sodium) and 4.05 and 4.57 (aluminum) for the (001) and (111) surfaces, respectively. The values of the work function of crystalline surfaces calculated by the pseudopotential method and also in some cases by the jellium model^{7,91} obeyed the same Smoluchowsky rule only in the case of bcc metals, whereas the reverse trend was observed in the case of fcc metals. Two experimental investigations of single-crystal aluminum surfaces revealed both anisotropy trends.^{87,88} The absence of experimental data on the work function of single-crystal surfaces of other metals makes it impossible to draw reliable conclusions on the validity of the Smoluchowsky rule and on theoretical calculations.

It is necessary to point out some discrepancies between the experimental results and the calculated dependences of the work function on the film thickness or the size of crystalline particles. Firstly, a reduction in the number of atomic layers forming a film (in the film or "synthetic" crystal model) is possible right down to the film thickness of about 40-50 a.u. (Ref. 55). When the thickness is less, we can no longer ignore the mutual influence of the surfaces, which gives rise to interference effects that shift the electron levels toward higher energies and which increases the density of electrons at the middle layers of the film and reduces the work function correspondingly. A somewhat higher minimum size of the crystal particles amounting to 100-120 a.u., down to which the work function is independent of the size, is obtained in Ref. 124. Experimental investigations of the dependence of the work function on particles size show that the function remains constant and equal to the work function of an "infinite" crystal when the particle size is reduced to 0.5-2.5 μ (Ref. 125), which is a value an order of magnitude greater. Secondly, a further reduction in the size in the experimental investigations increases the work function which tends to the limit set by the ionization potential. However, calculations predict a strong reduction in the work function. This discrepancy is a consequence of the adopted calculation models. In these models not only we cannot go over from the work function of an infinite crystal to the ionization potential, but there is no allowance for the changes which occur in the surface region and the relative thickness of this region increases on reduction in the number of layers (relaxation, reconstruction of the surface). This reduces the particle size at which the bulk properties are still retained.

The surface energy σ can be calculated as the work lost in the formation of a unit area of the new surface as a result of splitting of a film into two halves along a plane parallel to the

TABLE IV. Values of work function (eV) for (001) and (111)	surfaces of some simple metals
(values in the third column are taken from Ref. 57).	•

	Surface	rface Calculated values		Experimental (photoemission)		
Metal	Surface			polycrystals	single crystal	
Sodium Lithium	(001) (111) (001)	2,8 2,6 3,6	2,71 49 3,71 ⁵¹	2,7 ⁷ 2,32; 3,1 ⁷		
Potassium	(111) (001) (111)	3,58 2,5 2,47				
Barium	(001) (111) (001) (111)	3,2 2,3 3,37 3,13	2,9 82 3,4 82 —	2,87 82		
Aluminum	(1001)	4,42	4,49 4 ³	4,197	$4,20\pm0,03^{87}$ $4,41\pm0,03^{88}$	
Lead	(111)	4, <i>3</i> 0 —	3,2, 4,27, 4,73		$4,26\pm0,03$ * $4,24\pm0,02$ ** 3,8 *5	

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surface. This work is determined by the change in the energy of the electron-ion system of a crystal as a result of such splitting of a film. Therefore, the energy σ includes two contributions: the ion contribution σ_1 and that due to electrons σ_2 . The former is due to the change in the electrostatic energy of the interaction of the lattice ions with one another (Madelung energy) because of the formation of a metalvacuum interface. The electrostatic contribution was calculated in Refs. 7, 91, and 92:

$$\sigma_1 = \alpha z_0 \rho_0, \tag{4.1}$$

where z_0 is the valence and α is a coefficient dependent on the surface geometry.

The second contribution represents a change in the energy of the electron subsystem when a surface is formed. In the film model it amounts to

$$\sigma_{2} = \frac{\gamma}{2H} \left(\sum_{i}^{2p} \varepsilon_{i} - 2 \sum_{i}^{p} \varepsilon_{i} \right), \qquad (4.2)$$

where H is the area of a unit cell obtained by projection of the structure on the surface plane; $p = Nz_0$; N is the number of atomic layers in a film; γ is a coefficient governed by the number of representative points in the summation over the two-dimensional Brillouin zone; ε_i are one-electron eigenvalues deduced by solving the system (4.1). The doubled sum of one-electron energies of the film with the number of layers N given by Eq. (4.2) is greater than the corresponding sum for a film twice as thick, because in the former case two "extra" surfaces are allowed for. The corrections for the double inclusion of the electron-electron interaction in each term are compensated.

Determination of the surface energy of solids is a complex task. Firstly, a surface always carries some surface-active inclusions which reduce the value of σ . Secondly, it is difficult to identify the actual surface contribution to the energy of a solid. The most widely used method for the determination of the energy of a surface of a solid is the zero-creep method.⁹³ In this method a thin sheet or wire of a metal is compressed by the surface tension close to the recrystallization temperature. We can find a load which balances this effect and stops deformation, which provides us with a measure of the surface energy. However, several incorrect assumptions in the theory of this method are pointed out in Ref. 94, particularly that the equation underlying the method is unstable. Moreover, the method can be used only in the case of plastic metals with a high melting point. The method is subject to an error of 200–400 erg/cm^2 .

For comparison with the experimental results we included in Table V the values of σ at absolute zero obtained from the data on the surface tension of a molten metal at the melting point.⁹⁵ These results can be compared with the calculations of σ carried out for specific crystallographic surfaces only approximately, but it is assumed that the surfaces of a metal with the closest packing can be approximated by the surface of a liquid at absolute zero.^{7,97} Table V gives also the results of a calculation⁹⁶ carried out by applying the pseudopotential method and the film model to the (001) and (111) surfaces of some simple metals. The values of σ_1 were taken from Ref. 7. These calculations were subject to an error of 100 erg/cm².

An investigation of the dependence of the surface ener-

TABLE V. Values of surface energy σ (erg/ cm²) for (001) and (111) surfaces of some simple metals.

Metal	Surface	Calcula- ted va- lues ⁹⁶	Experi- mental values ⁹⁵		
Sodium	(001)	216	234		
Lithium	(001)	397	472		
Potassium	(111) (001)	485	129		
Calcium	(001)	569	425		
Barium	(111) (001) (111)	544 682 348	326		
Aluminum	(001)	1176	1020		
Aluminum*)	(111)	906			
*)Calculated allowing for surface relaxation.					

gy on the film thickness was reported in Ref. 96. A reduction in the thickness to about 40–50 a.u. does not affect the surface energy σ as long as we can ignore the interaction between the two faces of a film. Interference effects may increase the kinetic energy of electrons considerably in such a way that the difference in Eq. (4.2) increases. For example, the surface energy of a four-layer aluminum film is 3 times greater than that of an eight-layer film. This conclusion is in qualitative agreement with the calculations⁹⁸ carried out using the jellium model.

The values of the surface energy reported in Ref. 96 agree with the experimental results (Table V) and the anisotropy trend is the same as in the calculations carried out using the jellium model^{7,12,16} with the exception of Ba, which can be explained by incorrectness of the calculation of its properties using the pseudopotential method with a local Animalu-Heine-Abarenkov potential. The calculations of Ref. 96 underestimate almost twofold the contribution of σ_1 for the (111) surface of bcc structures. The Madelung constants were refined in Ref. 99 and it was found that in the case of this surface the constant in question is approximately twice as large as that given in Ref. 7. On the other hand, determination of the electron contribution σ_2 not from the density of electrons found by a variational procedure, as is done in the jellium model, but by summing one-particle energies is in a sense more precise because the value of σ is more sensitive to the nature of the charge density distribution near the surface than to the charge density itself. As pointed out already, the jellium model gives an incorrect estimate of the contribution of the kinetic energy and exaggerates the correlation effects. Moreover, the pseudopotential method is used in Ref. 96 without restrictions typical of the jellium model and no use is made of perturbation theory because it is invalid near a metal-vacuum interface.

5. SURFACE RELAXATION

Recent investigations of the properties of the surfaces of metals have exhibited a trend to pay more attention to the geometry of the distribution of ions near the surface layer, because this geometry may differ considerably from that in the bulk of a metal and this can alter the physical properties

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TABLE VI. Relaxation of surfaces of simple metals (*i* and *j* are numbers of atomic layers, counting from the surface) in percent relative to bulk interplanar distance (the minus sign corresponds to a reduction in Δ_{ij} and the plus sign corresponds to an increase).

		Surface Δ_{ij} Calculated values from Ref. 114 other wo	Calculated values		Experimental values
Metal	Surface		other work		
Na(bcc)	(001) (011)	$\begin{array}{c} \Delta_{12} \\ \Delta_{23} \\ \Delta_{12} \\ \Delta_{23} \end{array}$	$\begin{array}{c} -2,7\\ 0,7\\ -0,2\\ 0,1 \end{array}$	<u>_2 115</u> 	 0 121
Li(bcc)	(111) (001)	$egin{array}{c} \Delta_{12} \ \Delta_{23} \ \Delta_{34} \ \Delta_{12} \end{array}$	$ \begin{array}{c} 8 \\ 29 \\ 23 \\ \end{array} $	$15,5^{99}, -20^{116}, -16,3^{110}$	
Al(fcc)	(001)	$\Delta_{12} \\ \Delta_{23} \\ \Delta_{12}$	0 0 14	$-1,4^{99}, 2^{122}$	$\begin{array}{r} 0^{108}, 5^{24} \\$
Mg(hcp)	(111) (0001)	Δ ₂₃ Δ ₃₄ Δ ₁₂ Δ ₂₃ Δ ₃₄ Δ ₁₂	-10 4 1,6 0,1 0	1,2 ⁹⁹ , 0 ¹²²	$\begin{array}{c} & & & & +5,0 \ 104 \\ & & & +5,0 \ 104 \\ & & -1,6 \ 104 \\ 2 \ ^{38}, \ -3 \ ^{37}, \ -8 \ ^{39}, \ \pm 5 \ ^{35} \\ & -1 \\ & & -11 \ ^{108} \end{array}$

of the surface. As pointed out already, in experimental studies of the relaxation of surfaces it is usual to employ the LEED method (Sec. 2) and the methods of ion scattering^{100,101} and fine structure of the x-ray absorption spectra of surfaces.^{23,102} In the majority of cases (including both simple and transition metals) there is a reduction in the last interplanar separation Δ_{12} on the surface compared with the bulk value¹⁰³⁻¹⁰⁷ in the case of bcc and fcc structures (Table VI) and the reduction depends on the orientation of the surface. Some experiments on the (111) surface of Al have indicated^{24,108} an increase in Δ_{12} although the situation is not quite clear because this surface also reveals a reduction in Δ_{12} (Refs. 23 and 115) including that on the (011) surface of Al.

The problem of theoretical calculations of the surface relaxation meets with the difficulty of the need for self-consistent determination of the minimum of the energy of a system of interacting ions and electrons. In the case of a real metal with a crystal potential the problem is complicated by the poor convergence of the long-wavelength components of the potential and also because a large volume of calculations is needed. On the other hand, attempts to carry out calculations by the methods of static lattices with a pair empirical potential deduced from the calculations of the bulk properties have given results in direct conflict with the experiments: it is predicted that Δ_{12} should increase.¹¹⁰ This is due to the fact that in the usual interatomic interaction potential there is no allowance for the change in the distribution of conduction electrons at the surface giving rise to forces that tend to reduce Δ_{12} . It is also known¹¹¹ that all the interatomic potentials of the classical type (Morse, Lennard-Jones, and others) generally predict, by their very nature, an increase in the interplanar distance at the surface, which is quite understandable from the physical point of view because the minima of these potentials are located in such a way that the force exerted on an ion by the second and third neighbors is attractive. When a surface is formed, an ion in the last layer is subject only to an attractive force acting along the normal to the surface in the direction of the bulk of a crystal. This ion can achieve an equilibrium only if we assume that it can be displaced a little out of the crystal. The shortcomings of the model of pair potentials can be corrected by introducing a many-body interaction: it is shown in Ref. 112 that if an allowance is made for the three-body interaction of ions, the values of Δ_{12} and the dependence of relaxation on the stacking density of ions on the surface agree with the experimental results.

The largest numbers of theoretical calculations of the relaxation have been carried out by minimization of the surface energy σ in respect of the relaxation parameter^{99,100} and minimization of the forces acting on the ions in the surface layer.^{99,113–116} The lattice contribution to σ (Madelung energy) is calculated from Eq. (4.1), whereas the electron contribution

$$\sigma_2 = \frac{1}{2H} \left(2E\left[\rho_{\rm s}\left(\mathbf{r} \right) \right] - E\left[\rho_{\rm b}\left(\mathbf{r} \right) \right] \right)$$
(5.1)

is calculated by the density functional method where $E[\rho(\mathbf{r})]$ is the functional of the total energy of a system of electrons and ions: for an infinite space (index b) and a semiinfinite space (index s); H is the surface area. The charge density $\rho_{\rm s}(\mathbf{r})$ is either calculated self-consistently in the jellium model or it is described parametrically by a model profile. We shall now consider the most serious difficulties encountered in such calculation methods.⁹⁹ Firstly, the gradient expansions of the kinetic energy require the simplest possible expressions for the electron density profile, which limits greatly the precision of the results; moreover, there are certain indeterminacies in the convergence of the expansion. Secondly, from the point of view of the exchange and correlation it is not clear what is preferable: the approximation of a local density, the gradient approximation, or the dynamic calculation of the correlation contributions (contributions of surface plasmons).

The approximations adopted in the calculations differ basically in respect of the number of the contributions included in the interaction energy of the electron-ion system. The fullest analysis is given in Ref. 114, where an allowance

is made for five components of the total energy: 1) the intrinsic energy of the system with the jellium potential; 2) the Madelung energy found by summation over the planes (this method is described in detail in Ref. 92); 3) the energy of a dipole layer which appears when a surface is formed; in this case the interaction of point ions with a homogeneous density of electrons is replaced by their interaction with the jellium density (exhibiting characteristic Friedel oscillations); 4) the Hartree contribution (in which the point ions are replaced with the pseudopotential), representing the difference between the energies of the interaction of the density of electrons in the jellium model with point ions, on the one hand, and the model pseudopotential with finite range, on the other; 5) the energy of the band structure, which is a consequence of an allowance for the interaction of the electron density of a given ion with the pseudopotentials of other ions. The contributions 3) and 4) are first-order corrections, whereas the contribution 5) is a second-order correction. The equilibrium configuration of ions is determined by minimizing the surface energy in respect of the relaxation parameter and in this case each contribution to the energy tends to zero. We can check the importance of the role played by each contribution if we calculate charge densities of different types: 1) a truncated step on the surface (which allows for the first and second contributions to the energy); 2) the jellium model density (first, second, and third contributions); 3) point ions were replaced with the pseudopotential (the fourth contribution to the energy was added); and 4) second-order corrections were taken into account. In the first case a large negative relaxation (reduction in Δ_{12}) is predicted for the surfaces of simple metals with low-index faces and with either the fcc or bcc structure. Inclusion of the dipole layer and the pseudopotential in the calculations strongly reduces the relaxation, which approaches the experimental value. The second-order corrections generally alter Δ_{12} only slightly. This shows that the surface energy and the relaxation of the surface depend most on the charge density and on the potential near the surface.

A similar conclusion is reached in Ref. 99, where a detailed comparison is made of the advantages and shortcomings of the familiar approximations made in the calculations of the quantity Δ_{12} , based on the use of the electron densities of different types. In particular, it is pointed out that adiabatic calculations must be carried out: it is necessary simultaneously to minimize the surface energy with respect to the relaxation parameter and to optimize the model profile of the electron density using the variational parameter β . This takes into account how the influence of the change in the positions of the ions on the surface affects the distribution $\rho(\mathbf{r})$, which is ignored in the calculations even in the most complex case when use is made of the self-consistent charge density obtained in the jellium model for the potential of an unrelaxed distribution of ions. The greatest error is made in the calculations carried out using the "frozen-in" density profile, i.e., using a constant parameter β , as has been done in the calculation of Δ_{12} in the simple electrostatic model¹¹⁰ in which the electrostatic potential is determined by summing over the planes, and the energies and forces exerted on a given ion by all the other ions are calculated using the exponential charge density, as well as the charge density calculated by Lang and Kohn. The advantage of this calculation method is the use of a very effective and rapidly converging technique for the summation over planes in determination of the electrostatic potential. Clearly, the relaxation of the surface could be found most rapidly and accurately by combining this method with the calculation of the density of the surface charge for a real metal with the crystal potential.

In spite of the shortcomings of the methods used to calculate the surface relaxation, they have provided qualitatively important results.¹¹⁶ Firstly, it is now possible to determine which forces and along which direction they act on ions in the surface plane: in the absence of relaxation the electrostatic Madelung forces tends to shift the surface into the crystal, whereas the electron forces tend to shift it into vacuum. If the distance Δ_{12} is reduced sufficiently, these forces act in the opposite direction. The real value of Δ_{12} is obtained when these forces balance out. Secondly, important conclusions are obtained on the strong influence of the screening by the electron density on the equilibrium positions of the ions, on the need to allow for the adiabaticity of the relaxation process, and on serious shortcomings of the calculations with a "frozen-in" profile of the charge density. Thirdly, the general trend of the relaxation anisotropy is known: the surfaces with closer packing relax less. Fourthly, it has been shown that several layers in the lattice may participate in the relaxation process. This has been observed experimentally by a variety of methods applied to the surfaces of both simple and transition metals.^{101,103,104,107,117,118} Multilayer relaxation is oscillatory (the first interplanar distance Δ_{12} is usually reduced, whereas the second Δ_{23} is increased relative to the bulk value) and the oscillation period is equal to the period of stacking of the layers parallel to the surface (Table VI).²⁾ It is due to the three-dimensional nature of the forces acting in the electron-ion system, the complex interlayer structure, and the shift of ionic stacking layers relative to one another.¹¹⁴ Another important conclusion then follows: it is necessary to allow for the three-dimensional change in the potential and in the charge density. The jellium model was used to allow for the three-dimensional charge density¹¹⁵ based on the density matrix formalism. The calculated values of σ and Δ_{12} agreed with the experimental data and with other calculations. However, the selection of the range of the pseudopotential was difficult and it was introduced as a firstorder correction ignoring its three-dimensional nature.

All the shortcomings of the jellium model are avoided if calculations are made of the properties of the surface of a real metal using the crystal potential. However, the large volume of the calculations has hindered self-consistent adiabatic calculations of the geometry of the distribution of ions near the surface. Only one attempt has been made to determine the change in the energy of the (111) surface of Al as a result of a shift of the surface layer into a crystal and into vacuum (see Table VI and Ref. 96). The shift was based on the experimental data: +2% was reported in Ref. 38 and -8% in Ref. 39. It was found that the electron contribution to σ decreased on reduction of Δ_{12} for this surface and increased on increase in this quantity. A similar reduction in σ (within the limits of 10%) on compression of Δ_{12} is predicted by the calculations reported in Ref. 120, which were carried out using the jellium model in which a negative relaxation was introduced by a variational parameter. However, in this case it is not clear how the electrostatic potential contribution to σ behaves and, therefore, we cannot say anything definite

about the change in σ due to the relaxation of the surfaces of real metals. We can only postulate that the relaxation trends and relationships deduced in the jellium model are valid also in the case of crystalline surfaces.

Investigations of the influence of relaxation of the (111) crystal surface of Al on the work function were reported in Ref. 55. It was found that a change in the work function was within the limits of the calculation error both on reduction and on increase in Δ_{12} . A similar result was obtained earlier in the jellium model.¹²⁰

6. CONCLUSIONS

We shall summarize this review by stressing once again that the attention has been concentrated on factual data for a specific class of materials, and on the progress in the experimental and theoretical studies that have provided more realistic quantitative estimates of the electron structure of crystal surfaces of nontransition metals. The relationships and trends typical of the surfaces of simple metals are shared also by other materials. However, in spite of the considerable progress in experimental investigations and theoretical methods for the calculation of physical properties of crystal surfaces of simple metals, some problems still remain. The absence of data on the bremsstrahlung spectra makes it impossible to compare the calculated parameters of surface states located above E_F in alkali and other metals with the experimental results. Trends in the anisotropy of the work function and surface energy of crystal surfaces of simple metals are not vet clear and this requires a more rigorous analysis of the redistribution of the electron density at the surface and corresponding modifications in the electron interaction contributing to the work function and surface enegy. It is not clear what is the influence of the relaxation of the surface on the electron spectrum and physical properties of the surface; it is necessary to find experimentally more accurate values of the shift of the surface layers (not only in aluminum but also in other metals), whereas from the theoretical point of view it is desirable to carry out more rigorous self-consistent calculations allowing for the adiabaticity and multilayer relaxation of the electron and lattice contributions to the surface energy of crystals.

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¹⁾A similar measurement was made¹²⁶ for the 1s level of Be.

²⁾It is interesting to note that the oscillatory nature of the relaxation was revealed also by calculations of the dependence of the total energy of a cluster of Li atoms on the interatomic distances, carried out using the Hückel method. 119 Two basis systems of functions 1s2s and 1s2sp were used in these calculations. It was found that the relaxation is characterized by alternate changes in the lattice period which penetrate far into the crystal. The equilibrium shifts vary from -10 to +23%.

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