Electron paramagnetic resonance of solid surfaces

A. B. Roĭtsin and V. M. Maevskiĭ

Institute of Semiconductors, Academy of Sciences of the Ukrainian SSR

The current state of studies of solid surfaces by EPR is reviewed. The methodological problems of theory and experiment that are specific or important for studying surfaces are examined. Concrete results are presented for most studied substances. Comparison of the levels of study of paramagnetic centers in the bulk and at the surface has shown that studies lag substantially in the latter case in comparison with the former. The reasons for this situation are analyzed and pathways for further studies are discussed.

1. INTRODUCTION

In recent years interest has grown in studying solid surfaces. A detailed exposition and explanation of this fact is contained in a series of publications, including monographs,[1–4] reviews,[5] and articles of programmatic[6] and popular[7] type. Yet in brief the fundamental reasons for the situation that has developed are: the development of a unique apparatus and high level of study of bulk properties have logically posed the question of using this baggage to study more complex systems, in particular, surfaces; the view of the surface as a special phase of matter from which we can expect a number of new phenomena; the important role of the surface in contemporary applied developments, in instrument design, adsorption and catalytic phenomena, mechanochemistry, and biomedicine.

One of the effective methods of studying a solid is electron paramagnetic resonance (EPR) and its associated methodology. The most substantial feature of the method is the possibility of determining the detailed structure (the nature) of a paramagnetic center (PC). These data can be chosen as a touchstone to estimate and compare the level of study of different substances (including their surfaces). In this regard we shall briefly discuss the achievements of the EPR method in bulk properties. On this background we shall try to evaluate the situation for the surface. At present most studies by the EPR method of the bulk of solids end with deciphering the spectrum and establishing the nature of the PCs. This has been facilitated by the following factors: accumulation of a vast experimental material since the discovery by E. K. Zavoĭskiĭ in 1944 of the EPR phenomenon[8,9]: development of the method of the generalized spin Hamiltonian and the development on its basis of the theory of the EPR spectrum, which has enabled, apart from an inversion operation, determining the local symmetry of the PC[10]; application of an external electric field in addition to the magnetic field, which made it possible to distinguish all 32 point groups of the PC[11,12]; application of electron-nuclear double resonance (ENDOR) and its varieties, which enabled establishing the configuration of atoms near a defect[11,13]; knowledge of the crystal structure of the bulk, which enabled adducing x-ray structural data to establish the site of a defect in the crystal[14]; the concentration of PCs in the bulk is usually such that the sensitivity of most radiospectrometers relatively easily enables detecting and studying EPR.[15]

At first glance, the surface "formally" differs in no way from the bulk from the standpoint of study by the methods of radiospectroscopy. However, the existence of numerous features only inherent in it leads to a qualitatively new situation that considerably complicates its study. These features are the following.

a) With a uniform distribution of defects, their concentration at the surface is considerably smaller than in the bulk ($\approx N^{2/3}$, where N is the concentration in the bulk). Moreover, the optimal filling area for the magnetic component of the UHF part of the resonator in which the specimen is placed is $\lesssim 1$ cm^2. Therefore the sensitivity of radiospectrometers can prove already insufficient for detecting the EPR signal. This leads to a need for studying finely dispersed systems in which the total area is considerably larger than for a whole crystal of equivalent volume (approximately by a factor of p, where a/p and a are the linear dimensions of a powder granule and of the original crystal, respectively). However, the use of powders qualitatively alters the EPR spectrum: instead of the angular distribution of a single narrow line inherent in a PC in a monocrystal, the orientationally broadened envelope of the line arises, as is inherent in a randomly oriented PC. *Per se* the broadening leads to a supplementary loss of sensitivity of the system, but the important point is that it is more complicated to extract from such a summation line the information on the nature of the defect than from the angular dependence of a single line. In crushing the crystal the danger also arises that the surface of a granule, owing to possible origin of new defects and to its infinitesimal dimensions, may not reflect the surface of a monocrystal.

b) The view of a surface as being an ideal cross section of the crystal would not correspond to reality. Even if isolated from the environment, this cross section is not a direct continuation of the structure of the bulk, but is strongly deformed owing to the so-called reconstruction and relaxation of the juxtasuperficial atoms (or ions).[7] To study atomically clean surfaces, all the contemporary methods have been employed, whereby considerable advances have been obtained in understanding its structure and properties. Thus it has been possible from low-energy electron diffraction spectra to establish the symmetry of the superstructures created by the rearrangement of the juxtasuperficial atoms. Intensive application of tunneling microscopy has begun. In addition, at present only the corresponding models of the surface structure are being discussed,[16] while data on the arrangement of atoms near such an ideal surface are lacking. The situation is even more complicated in the so-called real surface, i.e., a surface not isolated from the environment (gas, liquid, solid of differing composition). In the atmosphere many substances become covered with an oxide layer. This covering can be altered by the action of thermal, mechanical, chemi-

0038-5670/89/100891-20$01.80

cal, and other factors. All the more we do not possess exact information on the atomic configuration of such a surface, so that EPR studies on surfaces are actually conducted blindly.

c) Strictly speaking, the surface is not two-dimensional, but amounts to an extended transition layer from the bulk to another phase of matter (or the vacuum). PCs can be contained throughout this layer. Their characteristics will vary from bulk to boundary type. Therefore the EPR spectrum will be broadened in addition, while its decipherment will require knowing the distribution function of the defects in the interior of the crystal. Of course, one can extract the latter from experiment, but then this is a new parameter of the theory that complicates the analysis of the spectrum. Under certain conditions, e.g., under the action of ionizing radiation, a breakdown of the surface close to amorphization can occur, i.e., loss of long-range order. In this case, along with the depth distribution of defects, they undergo a deformation that leads to an additional broadening of the spectrum and a complication in deciphering it.

d) The properties of the surface, including the magnetic properties, are very sensitive to both the external conditions (technique of preparation, elemental composition of the gas environment and its pressure and temperature) and the internal conditions (structure of defects in the bulk, their migration, and temperature of the crystal). This gives rise to additional problems involving the difficult reproducibility of the results. Figuratively one can say: "new conditions—new specimen."

e) In studying surfaces by the EPR method and the usual (instrumental) methods are supplemented by the technological methods. Thus, to distinguish the surface centers, one etches the specimen layer by layer, while, to become convinced that the processes are taking place in a monolayer, one applies gas adsorption to compensate the effect of unpaired spins or some other agent on a parameter of the spectrum.

f) One must also overcome a psychological barrier arising from the fact that the problem lies at the boundary of two disciplines: physics and chemistry. Adsorption, catalysis, and other phenomena at the surface determine in many ways the structure and properties of PCs that arise in it. Therefore, the establishment of the nature of the latter involves elucidating the mechanism of all these phenomena, which unavoidably entails learning a new field of knowledge.

We see already from what we have said that the conditions of study of EPR at a surface are far more complex than in the bulk. To overcome the difficulties, the old methods have been refined and new ones developed. Considerable attention has been paid to increasing the sensitivity of the instruments, to determining the specific surface of powders and the concentration of PCs at the surface, to producing high vacuum, and to developing manipulators for different procedures under conditions of complete isolation from the external environment, to cleaning the surfaces, to the technique of admitting gases at different pressures, to doping the surface, to low- and high-temperature studies, and to combatting contamination of the surface and parasitic signals.

The number of factors that influence the EPR spectrum of a surface is larger than the corresponding number for the bulk. Therefore, for describing the results of an experiment studying the surface, a greater number of characteristics is required. For better perception of the existing wealth of data

and of their possible use for further studies and for examining the mutual influence of the different factors, it is convenient to classify all the data into the following four groups: the preparation and state of the specimen, the conditions of observation of the EPR spectrum, the parameters of the spectrum (the influence of the angular position of the specimen and the conditions of observation on them), and the derivable information and conclusions. We list in the first group: the method of preparation proper (crushing, polishing, cleavage, film deposition, irradiation); the medium in which the specimen is produced (vacuum, oxygen, air, and other gases at definite pressures); the temperature of preparation; subsequent annealing and etching; cooling rate; method and type of doping of the bulk and the surface; dimensions of granules; depth of penetration of radiation. We list in the second group—the means of observation, i.e., admission of different gases at a certain pressure; the temperature of the specimen during measurement; the sensitivity of the instrument and its other features. The third group includes the spin Hamiltonian (SH) that describes the spectrum and its parameters; the intensity of lines and concentration of unpaired spins; the line shape and width; the degree of homogeneity of the line; the relaxation time; and the stability of the signal. The fourth group includes comparison with other experiments, including EPR data on the bulk, and establishment of correlation with the latter; models of PCs and phenomena associated with them; theory; and microcalculations. All these problems are reflected in this review to some extent.

The number of papers studying surfaces by the EPR method has passed 400. All possible compounds are being studied, but mainly the simple ones–one- and two-component. The greatest number of studies has been devoted to silicon, germanium, silicon dioxide, and two-layer structures combining them ($Si–SiO_2$), ZnO, MgO, TiO_2, semiconductors of the $A^{II}B^{VI}$ and $A^{III}B^{V}$ types, and porous substances (zeolites and silica gels). The main stress has been put on identifying surface defects, the kinetics of their accumulation, establishing the correlation between PCs and the defects responsible for electrophysical, catalytic, and adsorptive properties. Under special doping of the surface with atoms of other elements (Mn, Cu, etc.) or admission of adsorbed gases (O_2, CO, CO_2, N_2O, etc.) leading to impurity PCs, the structure of the substrate is studied, and its role in formation of PCs and their effect on the parameters of the SH.

Some of these studies are reflected in the monographs of Refs. 1, 17 and review of articles of Ref. 18. The main stress in them is put either on studying a certain set of objects, on studying a concrete phenomenon or on using a certain method of study. This review aims to give an overall view of the current state of affairs, of the methods of study and the results, on the problem that arise, and as much as possible, to discuss the pathways for further studies. Space restrictions have not allowed citing all papers, but we hope that the fundamental content of the existing papers and their overall direction are reflected correctly. In reading the article the outlook of the radiospectroscopists cannot remain unremarked—we have endeavored to reveal to what extent such a unique method as EPR (and the methodology associated with it) is manifested in studying surfaces as compared with what it is capable of. The review includes papers up to April

892   Sov. Phys. Usp. **32** (10), October 1989

A. B. Roĭtsin and V. M. Maevskiĭ   892

1989. The sequence of presentation is: Secs. 2–4 treat the fundamental methodological problems of theory and experiment specific or substantial for studying surfaces by the EPR method. Then (Secs. 5–11) we present and discuss the concrete results of studies of surfaces of different objects. Finally Sec. 12 gives a general summary.

2. THE THEORY OF EPR SPECTRA OF SURFACE PARAMAGNETIC CENTERS

The overwhelming majority of studies on EPR of solid surfaces have been performed under conditions in which the specimens containing PCs amount to disordered systems. The disorder is manifested in the fact that all or certain parameters describing the EPR spectrum vary from PC to PC by some law that reflects the character of the distribution of PCs in the specimen. Consequently the line positions and their intensities for different PCs cannot coincide. The resultant line $F(H)$ will amount to a certain envelope, or superposition of individual lines corresponding to the different PCs. We can represent it in the form

$$F(H) = \sum_k f\,|H - H_p(t_k)|\, J(t_k). \tag{2.1}$$

Here f and J are respectively the line shape and the absorption intensity of the k th PC, t_k is the set of parameters of the SH and of angles characterizing the orientation of the magnetic field H, H_r is the resonance value of the magnetic field[1] as defined by diagonalizing the SH. If there are many PCs, we can transform from summation to integration. Let Δv_i be the volume element of the variables t_i in which all the Δn_i of the PCs have the same value of H_r (t_i). Correspondingly we shall rewrite (2.1) in the form

$$F(H) = \sum_i f(H - H_p(t_i))\, J(t_i)\, \Delta n_i. \tag{2.2}$$

Here $\Sigma \Delta n_i = n$ is the concentration of PCs, or

$$F(H) = \frac{n}{v} \int_v f(H - H_p(t))\, J(t)\, dv. \tag{2.3}$$

Usually the width of the EPR line of an individual PC proves to be considerably smaller than the width of the envelope of the spectrum caused by the spread in the parameters of the SH. In this case we can replace the function f in Eq. (2.3) with a δ function with sufficient accuracy.

The case is most frequent in which a monocrystal is converted into a powder to increase the surface, and each granule along with the PCs contained in it is oriented randomly. Here the angles θ, φ, and ψ (e.g., Eulerian angles) characterizing the local system of coordinates (associated with the PC) with respect to the main system, usually associated with the external fields, serve as the variables of integration. In this case Eq. (2.3) takes on the form

$$F(H) = \frac{n}{8\pi^2} \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} f(H - H_p(\theta, \varphi, \psi))\, J(\theta, \varphi, \psi) \sin\theta\, d\theta\, d\varphi\, d\psi. \tag{2.4}$$

One can find a treatment of the line shape of randomly oriented PCs for different forms of SH, both in the original literature and in the monograph literature (e.g., Refs. 8, 11, 19, and 20). The initial expression of the type of (2.4) for a certain form of the function f is usually analyzed numerical-

ly with a computer. Attempts to obtain preliminarily an analytic expression for $F(H)$ face fundamental difficulties and difficulties of technical character involving the unwieldiness of the calculations. In a number of cases,[8,19,20] one can eliminate these difficulties. Here we shall take up the simplest, and also most widespread case so as to illustrate the idea of the calculation and typical spectra, which will be discussed in the further treatment. However, we note preliminarily that, in the absence of electric fields, H_r does not depend on ψ.[11] All the studies cited below are distinguished precisely by this feature. Let the SH have the following form (axial symmetry of the PC):

$$W = \beta[g_\perp(H_x S_x + H_y S_y) + g_\parallel H_z S_z]. \tag{2.5}$$

Here H_i and S_i are respectively the components of the field intensity H and the spin operator S, $g_\perp$ and $g_\parallel$ are the components of the g factor, and β is the Bohr magneton. The resonance value of the magnetic field corresponding to (2.5) and the square of the matrix element (J) of the transition $M \to M - 1$ under the action of the UHF magnetic component (H_i) have the form

$$H_p = \frac{h\nu}{\beta g}, \quad J = c\left(1 + \frac{g_\parallel^2}{g^2}\right). \tag{2.6}$$

Here we have

$$g = [g_\perp^2 + (g_\parallel^2 - g_\perp^2)\cos^2\theta]^{1/2},$$
$$c = \tfrac{1}{8}\beta^2 H_1^2 g_\perp^2,$$

ν is the klystron frequency, θ is the angle between the z axis of PC and the vector H, and M is the quantum number of the operator S_z. Consequently, on the basis of (2.4) we have

$$F(H) = nc \int_0^{\pi/2} \left(1 + \frac{g_\parallel^2}{g^2}\right) f(H - H_p(\theta)) \sin\theta\, d\theta. \tag{2.7}$$

Upon transforming in (2.7) from the variable θ to the variable H_r according to (2.6) and using a δ function instead of f, we obtain

$$F(H) = nc H_\perp^2 H_\parallel (1 + H^2 H_\parallel^{-2})$$
$$\times [H^2 (H_\perp^2 - H_\parallel^2)^{1/2}(H_\perp^2 - H^2)^{1/2}]^{-1}. \tag{2.8}$$

Here we have $H_{\perp,\parallel} = h\nu/\beta g_{\perp,\parallel}$, with H varying within the range $H_\parallel \leqslant H \leqslant H_\perp$ if $g_\parallel > g_\perp$, and $H_\perp \leqslant H \leqslant H_\parallel$ if $g_\perp > g_\parallel$ [for other values of H, $F(H) = 0$]. The line shape of (2.8) amounts to an asymmetric curve, finite and discontinuous at $H = H_\parallel$, and asymptotically diverging to ∞ at $H = H_\perp$. The divergence involves the use of the δ function as the individual form of the PC line, and reflects the behavior of the curve for very narrow lines f. Actually the curve is smoothed at both edges, and its contour has a maximum shifted toward greater fields if $g_\parallel > g_\perp$, and in the opposite direction if $g_\parallel < g_\perp$. The parameters $g_\parallel$ and $g_\perp$ are determined from the characteristic boundary points.[2] In the more general case of orthorhombic symmetry, in which all the principal values of the g tensor are not equal to one another, the line shape can be represented (Fig. 1) as a combination of two curves corresponding to the case of axial symmetry. In the presence of hyperfine interaction (HFI), an additional hyperfine structure (HFS) appears in the spectrum, which is superposed on the fundamental line discussed above. One can decide from
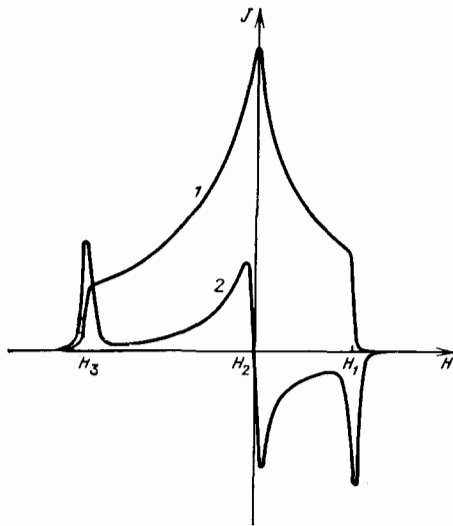
FIG. 1. Form of an absorption line (*1*) and its derivative (*2*) in the case of orthorhombic symmetry. The characteristic three-component spectrum is exhibited by many surface paramagnetic centers. $H_i = h\nu/\beta g_{ii}$.

the number of HFS lines on the magnitude of the spin l, and from their arrangement on the parameters of the HFI. The most general SH that is encountered in studies on EPR of solid surfaces has the form

$$W = \beta \, \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{H} + \sum_i \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}_i. \qquad (2.9)$$

Here $S = 1/2$ and A is the HFI tensor; the summation is performed over the close-lying nuclei having a nonzero magnetic moment. In certain studies, besides (2.9), an interaction is manifested with the intracrystalline electric field (if $S > 1/2$), but they as yet are not typical, and we note them in presenting the concrete material.

3. SPECIMEN PREPARATION

3.1. Atomically clean surface

We understand as atomically clean a solid surface void of impurities and structural defects.[3,21] At present several methods have been developed for preparing such surfaces, most of which employ annealing in a superhigh vacuum (better than 10^{-9} Torr). They include: 1) Cleaning the surface by heating in a superhigh vacuum (SHV). The most substantial defects are: nonuniversality of the method, segregation at the surface of impurities dissolved in the bulk, and breakdown of stoichiometry. 2) Reduction of the surface in a suitable atmosphere. This method employs reduction of surface oxides upon annealing in an atmosphere of hydrogen and carbon monoxide. Here the working temperatures are lower than in method 1), but other defects arise: solution of hydrogen in the material, impossibility of cleaning of atoms that do not form volatile compounds with H_2 or CO. 3) Cleavage in an UHV or in a neutral medium. This method, based on the existence of planes of cleavage in a number of crystals, lacks the defects of the first two methods, but is limited by the impossibility of obtaining a surface with an arbitrary orientation with respect to the crystallographic axes; moreover, cleavage is accompanied by formation of steps on the cleavage surface whose number depends on the purity and degree of perfection of the crystal. 4) The method

of epitaxial growth under UHV conditions; it yields good results and is promising for creating interphase surfaces. 5) The method of ion bombardment with annealing. The method is based on the ejection of atoms lying on the surface by ions of inert gases and annealing, which is necessary to liquidate the structural defects caused by the bombardment. The method allows one to remove material layer by layer and perform a chemical analysis of it. Its fundamental defects include diffusion of impurities from the bulk during annealing, as well as the increased microrelief of the surface owing to the dependence of the rate of ejection on the orientation of the crystal planes with respect to the direction of the beam of bombarding ions.

3.2. Comminution of specimens

To obtain powdered specimens, one must not only fragment the crystal and create granules of the needed dimensions, but also, depending on the purposes of the experiment, solve a number of supplementary problems. First of all is the maintenance of the purity of the surface upon comminuting the specimen and the transfer of it, now as a powder, into the instrument for measurements. It is also important to reduce to a minimum the damage to the surface upon crushing. Various devices[17] have been developed to attain these goals: vibromills, glass hammers, vacuum mechanical manipulators for removing chips. The powder of a brittle material is prepared by "scraping." The method is simple and is reduced to breaking off of granules without additional mechanical actions (as in a mortar or mill); it is also convenient for dosing a prepared powder. More complex devices[22–24] enable one to cleave off layers of a crystal in an UHV at room temperature and at low temperature (≈ 20 K), both directly in the resonator of an EPR spectrometer and with subsequent transport to the resonator.

3.3. Adsorption and desorption

These processes play an important role in doping a surface and cleaning it. They are the basis of the methods of the paramagnetic probe and the identification of surface PCs. Adsorption of gases[25] is widely employed. They either form PCs themselves, or they act on ones already existing on the surface. One applies also deposition of impurities from solutions[20,21,26,27] or by vacuum sputtering.[21,28] To observe ERP, the impurity must be paramagnetic. That is, after deposition on the surface it should have a quite definite charge state. An important factor also is its distribution on the surface, since coagulation of PCs leads to disappearance of the signal. The attainment of these conditions faces great difficulties, especially in obtaining isolated PCs from electrolytes.[20,26,27] The charge state of an impurity can be altered by choosing the composition of the electrolyte.[26] Yet the character of its distribution depends strongly on the state (ionic or atomic) in which it is deposited: atomic adsorbates manifest a great tendency to cluster formation.[21] In the doping of a surface with paramagnetic particles from solutions, other impurities contained in the solutions as contaminants can be adsorbed. Studies have shown that, even when they are present in microamounts (10^{-7}–10^{-5}%), the adsorption of each impurity can reach 10^{13}–10^{15} at /cm^2, which is close to a monolayer. This imposes high requirements on the purity of the reagents and can lead to the need of additional purification of the surface of undesired adsorbates. A number of methods

has been developed for desorption of impurities.[21] Yet we note only that the methods of removing most metallic impurities from the surface of silicon and germanium are based on using acids and complexing agents. Good results are obtained by using films with a desorbing composition. Thus, for desorption from the surface of silicon or impurities of different metals (Cu, Ag, Hg, Au, Zn, Fe), a complexing agent has been applied[29] in combination with a film-forming polymeric material. After drying off the solvent, the film was removed from the surfaces along with the adsorbate, which was almost fully removed.

3.4. Surface purity monitoring

Most of the monitoring methods are based on applying various probe particles[3,4]: electrons–in ionization electron spectroscopy, electron Auger spectroscopy, and x-ray spectroscopy; photons–in the method of photoelectron spectroscopy; ions–in the method of secondary-ion mass spectroscopy; phonons–in the method using surface elastic waves. Application of these methods enables one to probe the surface to a depth of 5–30 Å, and to conduct layer-by-layer analysis of the material of the surface. The detecting power of the most sensitive methods reaches 10^{-6}–10^{-5} of a monolayer. In many cases the surface being monitored remains undisturbed. In addition to the methods cited, to detect and analyze impurities existing at the surface, one can use chemical methods, ellipsometry, optical spectral analysis, radioactive isotopes, and electron and tunneling microscopy. As will be seen from the presentation below, the EPR method is effective for monitoring. In particular, it has been possible to use it to detect contamination of surfaces arising from the vapor of the oil of the vacuum pumps and from diffusion of impurities from the bulk upon annealing.

4. EXPERIMENTAL TECHNIQUE
4.1. EPR spectrometers and their sensitivity

The small amount of the PCs at the surface increases the demands on the sensitivity of the EPR spectrometers. Since the concentration of atoms at the surface of solids is of the order of 10^{14} cm^{-2}, to study isolated PCs, the concentration of the latter should be two or three orders of magnitude smaller. This implies that, with an area of the specimen ≈ 1 cm^2, the detecting power of the EPR spectrometer for observation of lines of width 10 G should be $\approx 10^{10}$ spins. The best contemporary EPR spectrometers have the appropriate sensitivity and can be successfully applied to study surface PCs. Combination of the spectrometers with such instruments as perfected synchronous detectors[30] and signal storage units can further enhance the sensitivity. Use of storage units is preferable,[15] since they ensure the same averaging of both the high- and low-frequency noise. Increased sensitivity can be attained by applying UHF radiation of shorter wavelength, by cooling the specimen, in a number of cases by going over to recording the dispersion,[22] and by using maser or parametric amplifiers in the input circuits of the spectrometers.[15] The problem of attaining high sensitivity becomes especially sharp when, in studying the angular dependences of an EPR spectrum one must work with an oriented surface, and it is impossible in principle to use powders. In this case one can enhance the signal by using a set of several identically oriented specimen plates.[31-33]

There are also other ways to increase the sensitivity. They consist in using the so-called spin-dependent effects that arise in measuring various physical quantities in the presence of a UHF field and a magnetic field. They include: 1) spin-dependent conductivity, which is manifested in the form of a resonance variation of the resistance of the specimen when the magnetic field passes through its resonance value[34,35]; 2) spin-dependent recombination (SDR), i.e., a variation in the rate of recombination of photoexcited carriers, together with a resonance variation in the concentration of the latter under EPR conditions[34-37] (one measures SDR from the dependence of the electric losses of UHF power in the resonator); 3) spin-dependent thermoemission of electrons from deep levels,[38] which is manifested in a resonance variation of the capacitance-spectroscopy signal (DLTS)[39] caused by EPR; 4) resonance variation of the Faraday rotation of the plane of polarization of laser radiation[40] and other resonance magnetooptical phenomena that serve as the basis of contemporary optical methods of detecting EPR. The listed methods enable one to increase the sensitivity of apparatus by a factor of 50–100 as compared with ordinary EPR.

4.2. Vacuum technique

One usually uses UHV to preserve the atomically clean surface. Estimates of the required degree of high vacuum show[3] that, to maintain the cleanness of the surface at the level of 0.1% of a monolayer for ten hours at room temperature and with an attachment coefficient of the residual gases equal to unity, one needs a vacuum of the order of 10^{-14} Torr. However, the low partial pressure of most of the residual atmospheric gases and the low adsorptive power of many materials reduce this limit to 10^{-10} Torr. Such a degree of vacuum can be obtained by using ion-sorption pumps. A typical block diagram of an apparatus includes a specimen chamber heated to 400 °C, an ion-sorption pump, a zeolite sorption forevacuum pump, and a system of valves. A merit of such a system is the absence of oil pumps, which are an additional source of contamination of the specimen. Yet oil diffusion pumps are applied rather broadly, both in instruments for obtaining atomically clean surfaces and in apparatus for admitting gases and annealing specimens.[23,24] In this regard, measures have been developed for preventing the oil vapors of these pumps from reaching the surface.

4.3. Temperature technique

Instruments have been developed[15,41] to study EPR over a broad temperature range. They can be classified into two fundamental types: 1) The studied specimen lies in a resonator having the same temperature as it has; 2) The specimen lies in a jet of admitted gas having the given temperature, while the resonator is thermally insulated from the specimen. These instruments are also used to study the surface at different temperatures. The specifics of the latter is manifested in a need for isolating it from the surrounding environment and observing measures of caution against side temperature effects (diffusion, adsorption, desorption).

4.4. Admission of gases

The necessity of admitting gases arises in the process of studying PCs on a surface. If high demands are imposed on their purity and dosage, diffusion-type flow regulators or

chemical reactions are used. Thus, e.g., in Refs. 42 and 43 oxygen was admitted into the measuring system through a silver diffusion flow regulator; in Ref. 44 oxygen was obtained by thermal decomposition of Cu_2O and water vapor by reduction of CuO in hydrogen, while hydrogen was admitted by using a palladium flow regulator. In simpler apparatus gases are admitted through special valves[21,45] or through the main pumping system.[42,43] To choose the optimal admission system, one must allow for the attachment coefficient of the contaminating gases.

4.5. Determination of the area of the surface

A number of methods have been developed for measuring the area of the surface,[45] among which the most universal and commonly used is the method of Brunauer, Emmet, and Teller (BET). The idea on which it is based consists in employing gas adsorption. Various methods are known of experimental realization of this idea.[22,46] The essence of the method consists in determining the number of molecules N of a gas required for continuous covering of the surface to be measured with a monomolecular adsorbed layer; then the area will be $N\sigma$, where σ is the known area covered by a single molecule. The BET method has a number of advantages over the others: the relative simplicity of the experimental technique, the universality, the high accuracy (about 20%). Moreover, the adsorption of the usually applied inert gases does not affect the surface after measurement.

4.6. Determination of the surface concentration of spins

In finding the surface density of spins by the EPR method, one determines the number of spins over the entire surface of the specimen and measures its area. Measurement of the total number of spins is performed by comparing the EPR spectrum of the studied specimen with the spectrum of a standard whose number of spins is known.[15,47] Here it is desirable to put the test and calibration specimens in the same resonator for simultaneous determination of the spectrum to eliminate the dependence of the result of comparison on the parameters of the spectrometer. One uses as a standard various tested materials: DPPH, ruby, MgO: Mn^{2+}, $CuSO_4 \cdot 5H_2O$. Analysis of the factors that influence the accuracy of measurement of the number of spins using EPR has shown that the relative error under optimal conditions amount to 20–30%.[48]

5. EPR OF THE SURFACE OF SILICON

We have begun with silicon and devote an entire section to it because the number of papers devoted to studying its surface by the EPR method considerably exceeds the number of studies on any other crystal. With the example of Si, which we shall discuss in greater detail, we can best understand the problem as a whole, which will facilitate the discussion of other materials, since many of the approaches to surface study are identical. It is precisely with silicon that EPR studies of surfaces began. An EPR line from it was first discovered fortuitously. The authors of Ref. 49, in studying the EPR of donors in silicon, observed in passing a single line with a g factor equal to about 2.006. They noted that the parameters of this line did not depend on the type of doping, but its intensity strongly depended on the degree of etching of the surface. Therefore the authors associated this line with

the surface, rather than the bulk. Subsequently also other lines were discovered at the surface, but the fundamental studies were concentrated on elucidating the nature of the line with $g = 2.0055$ (the value of the g factor according to recent data). Therefore we shall divide the presentation following below in this section into two subsections. The first will discuss the line with $g = 2.0055^{3)}$, and the second will discuss the lines of other types. Here and below we shall adhere mainly to this sequence of presentation of the concrete material: first information will be given on the methods of preparing and processing the surface, as well as the conditions for performing the experiment. Then, in treating the EPR spectrum, we shall discuss the influence of all these factors on some given characteristic of it. After this we shall draw conclusions on the nature of the PCs.

5.1. The line with g = 2.0055

5.1.1. Preparation and state of the specimen

A single EPR line with a g factor equal to 2.0055 arose under the following methods of treating the surface: polishing, treatment with a sandblasting apparatus,[50,51] crushing the specimen to a powder,[52–57] irradiation of the specimen with ions[58–66] and neutrons,[67] fast cooling of the specimen after heating,[68] creation of an amorphous film,[69–75] and creation of microcracks on the surface.[76] Contradictory data with respect to the EPR line exist for a method of surface preparation, so important for understanding its nature, as shearing part of the specimen. According to the data of Refs. 24 and 54, an EPR line exists, but not according to the data of Ref. 23. The authors of Ref. 23 consider that the signal observed in Ref. 24 involves a powder that arises upon shearing.

Usually the specimens have been prepared in air at normal pressure and at room temperature. Yet the need arose in a number of cases of changing these conditions. Thus, in certain studies[43,56,76,77] the specimens were crushed in gases of different composition and pressure, and also *in vacuo* (the pressure was reduced to $10^{-9} - 10^{-10}$ Torr); the crushing temperature was varied from 1.3 to 700 K.[57,67,77,78] The effect of annealing was studied in the temperature range 600–1300 K[44,58,79,80] with varying gas composition, pressure, and annealing time. Much attention was paid to the effect of doping of the bulk[55,57,77,81] and the surface.[82] For this purpose the type of doping and the concentration of impurities were varied, oxygen was specially introduced into the bulk in different amounts, while atoms of Au, Ag, and Mn were deposited on the surface. To determine the depth of occurrence of the PCs, the surface was etched layer by layer.[82,83] The effect on the EPR line of dimensions of the granules,[23,50,52,82] the size of the grains of diamond dust,[51] the depth of penetration into the bulk of PCs[50,58,60,82] and implanted ions,[58,60] their elementary composition,[58,59] and the energy of the ions and beam intensity have been studied.

5.1.2. Conditions of performing the experiment

The conditions of measurement have been determined by the temperature and the environment (some particular gas at a certain pressure) in which the specimen prepared by the above-described method was placed. The temperture of observation at which the measurements were performed in practically all studies was varied from liquid-helium[49,77,84,85]

896   Sov. Phys. Usp. 32 (10), October 1989

A. B. Roĭtsin and V. M. Maevskiĭ   896

to room temperature. Various gases have been used to establish the degree of activity and location of the PCs (air, O_2, H_2, Ar, Kr, CO, CO_2, N_2, H_2O, Cl_2, and complex organic compounds),[42,44,56,80,81] whose pressure was varied from 10^{-9} Torr to atmospheric pressure. Gas admission was usually alternated with subsequent evacuation or holding in air. An important factor characterizing the measurements is the sensitivity of the spectrometer, which in the given experiments reached values of $10^{10}-2 \times 10^{11}$ spins/G.[42,77]

5.1.3. Characteristics of the spectrum

Spin Hamiltonian. All the experiments discussed here could be described by the following simple spin Hamiltonian:

$$W = g\beta \, HS$$

with $S = 1/2$ and an isotropic g factor.[4] Remarkably, this characteristic was not influenced by the methods noted above of specimen preparation and conditions of performing the experiment. In magnitude it equals 2.0055 ± 0.0002. According to the data of Ref. 67, the scatter in values involves the different specimens, but there are no indications of any purposeful variation in the magnitude of the g factor. An exception is Ref. 61, in which a gradual transition was observed to amorphization upon ion irradiation of silicon. At first an anisotropic spectrum was observed in it, characterized by several components of the g tensor, but with $g_{av} = 2.0055$. As the irradiation dose increased, the spectrum became isotropic with $g = 2.0055$.

Line shape. According to the data of most studies, the line is symmetrical, while close to Lorentzian in shape. An exception is the report,[67] which notes that the line shape is either intermediate between Lorentzian and Gaussian (if observed at the frequency 9.3 GHz) or Gaussian (if the frequency is 18.5 GHz). However, no dependence of the line shape on the frequency of the measurement was observed in Ref. 58: over the range 9.4–35 GHz the line maintained a Lorentzian shape. No special studies of the influence of various factors on the line shape have been performed, although a change on it has been noted in a number of studies. Thus, a deviation from a Lorentzian shape has been discovered[74] and discussed[86] upon raising the temperature of the specimen above room temperature, while Ref. 75 indicated a dependence of the shape on the concentration of PCs. It has also been noted[67] that, upon crushing the specimen at 1.3 K, the line became an "asymmetric Lorentzian," but after heating to 300 K and subsequent cooling again to 1.3 K, the line became symmetrical. Upon crushing *in vacuo* or with heavy doping of the specimen,[81] a line more gradual than Lorentzian was observed, but on adding oxygen the line again acquired a Lorentzian shape.

Line width.[5] Most studies of the line width ΔH yield a value of 4–7.5 Oe, with a spread determined by the method of specimen preparation, while within the confines of a given method ΔH varies slightly from specimen to specimen. However, in a number of cases (upon neutron irradiation[67] or upon preparing a silicon film by sputtering[87]), the values of ΔH reach 15–18 Oe. The possibility is also noted of deliberate variation of ΔH. Thus, it was found[82] that, upon gradual etching of the surface or upon doping it with atoms of Au, Ag, or Mn, ΔH can vary from 4 to 16 Oe; an increase in the line width with increasing concentration of PCs,[75,88]

with temperature,[55,69,74,88] and klystron frequency[54,58,67] was noted.

Degree of homogeneity of the line. The number of studies that have yielded appropriate data is small, and there is no unity among them: according to the data of Ref. 50, 58, the line is broadened homogeneously, and according to the data of Ref. 72 it is inhomogeneous. In Ref. 67 the degree of homogeneity was associated with the line shape, which varied as a function of the frequency at which the signal was measured.

Relaxation time τ. Despite the fact that the number of studies on the measurement of the relaxation time is already rather large,[50,63,64,67,72,81,86,88,89] it is as yet difficult to compare them with one another and draw definite conclusions. This involves the fact that not all studies reported on concretely what time was considered (transverse or longitudinal), and how it was measured. Another reason is that τ is very sensitive to the method of specimen preparation and the conditions of experiment. It was found, e.g., that the relaxation time decreases with the temperature: according to the data of Refs. 63 and 88 it varies from 10^{-2} to 10^{-7} s upon varying the temperature in the range 4.2–300 K; according to other data[50] $\tau \approx 10^{-5}$ s, even at 1.25 K. Despite the existing disagreement, we can assume that at room temperature $\tau \approx 10^{-6} - 10^{-7}$ s.

Stability of signal. According to the data of Ref. 67, the signal does not vanish, at least during one year.

Concentration of spins. Line intensity. Historically it happened that the unit of measurement of concentration depended on the method of specimen preparation. For cleavage, polishing, and other forms of surface processing, and also for crushing of the crystal, the concentration has been defined as the number of spins per cm^2, since it was assumed in this case that the PCs lie strictly at the surface (within the limits of a monolayer). According to the data of most studies, this quantity is of the order of 10^{14} spins/cm^2, but deviations have been observed, both on the low[24] (10^{12} spins /cm^2) and high[44] ($\approx 5 \times 10^{15}$ spins/cm^2) sides. In the preparation of an amorphous film or upon ion (neutron) bombardment of the specimen, the concentration was measured as the number of spins per cm^3 (it was assumed that the PCs penetrate into the interior of the crystal). According to the data of Refs. 58, 60, 64, 69, 70, and 85, this quantity is of the order of 10^{20} spins/cm^3. To compare the concentrations expressed in different units, we shall take account of the fact that the depth of penetration of implanted ions[60] or the thickness of the amorphous film[23] is of the order of 200 Å. Then, when $n \approx 10^{20}$ spins/cm^3, we obtain 2×10^{14} spins /cm^2 for the surface density of the layer being discussed, which is close to the value given above.[6] While bearing in mind the discussion below of PC models, we note that silicon breaks most easily along the (111) plane. The density of atoms on this free surface (i.e., the maximum possible density of unpaired electrons) equals 8×10^{14} atoms/cm^2. This quantity considerably exceeds the surface concentration of spins according to EPR data.

The concentration of spins is subject in highest degree to the effect of various factors as compared with other characteristics. Therefore the values of n given above should be treated as those obtained under "normal" conditions (usually at room temperature in air), i.e., without the special action of any other factors on the specimen. In studying the

effect of the latter, one often does not distinguish between the concepts of "concentration" and "signal intensity" (J); it is assumed that these characteristics are proportional to one another. The most substantial influence on the line intensity is exerted by the following factors: the temperature of crushing T_{cr}, the temperature of preliminary annealing (T_{an}),[90] the temperature (T_m) and gaseous environment during measurement. It was found[57,77,78] that, in the range $T_{cr} = 77–700$ K, the intensity of the EPR line declines with increasing T_{cr}, and, in particular, $J_{77}/J_{700} \approx 100$. According to most of the data, J begins to decline beginning at about $T_{an} = 670$ K, and by $T_{an} = 1300$ K the line has practically vanished. As regards the effect of the gaseous environment, contradictory data exist on oxygen: according to Refs. 44, 55, and 80, addition of oxygen did not affect the intensity whereas in Refs. 42, 54, 56, and 81 oxygen led to decrease in J. Hydrogen[42,44,56] and chlorine[56] elevated J, whereas water vapor[42] decreased it, while the gases Ar, Kr, CO, CO_2, and N_2 had no effect at all on the line intensity. Also the following phenomenon was observed: whenever the line intensity was altered by the action of gases, subsequent holding in air or evacuation of the gas partially or completely restored the initial value of J.[42,44,56] The measurements were performed in the following temperature range: $T_m = 1.25–300$ K. In the papers specially studying the $J(T_m)$ relationship, a Curie law was observed ($J \sim 1/T_m$). An exception was Ref. 44, according to which $J_{77} \approx 100 J_{300}$. As shown in Ref. 42, the function $J(T_m)$ depended on preliminary annealing or on the environment of measurement. Thus, after annealing at 670–870 K or holding in oxygen, the intensity of the signal at 77 K increased only by a factor of two as compared with $T_m = 300$ K.

5.1.4. Correlation with other experiments

Ref. 42 noted a relationship between the temperature of restructuring the surface, observed at 880 K, and the behavior of the EPR line under the action of oxygen. Namely: at $T < 880$ K admission of O_2 enhances the signal, whereas at $T > 880$ K it decreases the signal. It was noted[54,56] that the gases O_2, H_2, and Cl_2 strongly affect such macrocharacteristics as the work function, the surface conductivity, and at the same time they weakly affect the EPR line. On the other hand, according to the data of Refs. 66, 69, 74, 81, and 85, there is a direct connection between the PCs and the surface centers responsible for the electrophysical properties, and between the disappearance of the EPR line and the appearance of features in the electric conductivity and in the optics. The behavior was compared[43] of the EPR line and the surface tension upon action on the specimen of various factors, since one could assume that stresses arise during the mechanical processing of the specimens. No correlation was found.

5.1.5. Models of paramagnetic centers

In proceeding to one of the most interesting and complex problems, to the problem of the nature of the PCs, we should state that we as yet not only do not know the structure of the PCs, but are forced to find more precisely their energy and certain other characteristics. In this regard let us examine the viewpoint of different authors. We have been able to single out a series of statements on the nature of the

PCs. They are systematized below, together with a short substantiation of them, given in parentheses.

On their location. 1) The PCs lie in a layer $\approx 10^{-4}$ cm (disappearance of the signal during etching).[50,82] 2) They can lie at the surface, in cracks, and on particles that arise during processing of the specimen. (Existence of a maximum on the curve of the dependence of the intensity of the EPR line on the size of the grains of diamond dust.)[51] 3) The EPR signal is associated with imperfections of the surface of the microcrack type. (The signal is extremely weak at a freshly cleaved surface. Artificial creation of microcracks elevates the line intensity. The weak influence of gases of the type of H_2, Cl_2, and O_2. Upon etching ΔH increases, which indicates a larger dipole–dipole interaction of PCs in the interiors of cracks.)[24,56,76,82,83] 4) The PCs that arise in processing of the surface lie in an amorphous layer, where they are localized in extended cavities. (There is no EPR at a freshly cleaved surface. The EPR signal arises from the powder formed during shearing. The similarity of the parameters of the EPR lines of PCs in amorphous silicon and those formed in crushing or polishing a specimen. The presence of cavities–a constituent part of the model of amorphous silicon.)[23,61,64]

On the energy structure and the electrophysical properties. 1) The levels belonging to the PCs lie in the forbidden zone deeper than the levels of the shallow donors. They lower the Fermi level. The electrons of the PCs are strongly delocalized. (The intensity of the line of PCs declines with increasing concentration of donors. The intensity of the EPR line of the shallow donors declines upon crushing the specimen. The homogeneous character of the broadening, the lack of an allowed HFS from ^{29}Si.)[67,84] 2) The levels belonging to the PCs lie in the conduction band, the electrons are strongly delocalized, and have a high effective mass. (Estimates of the behavior of the wave function from data on the line width and the g factor.)[42,54] 3) The PCs possess two discrete bands of width $\approx 10^{-4}$ eV. They can act as acceptors or donors in trapping or releasing electrons. (Assumption of the correctness of the model of Haneman (see below). The correlation between the behavior of PCs and the surface states responsible for the electrophysical properties of the surface.)[81,91] 4) The PC levels lie in the allowed band, and the electrons of the PCs are rather localized. The PCs and the centers responsible for the electrophysical properties of the surface differ in nature. (Differing temperature dependence of the intensity of the EPR line and the characteristics of the surface states. Independence of the parameters of the EPR line and the type of doping.)[77,80,92]

On models of the PCs. Either holes resonate, or local centers for which the shells are more than half filled with electrons ($2.0055 >$ the g factor of a free electron.)[67,84] 2) Oxygen enters into the composition of a PC, forming a complex of the type SiO_x. (Absence of an EPR line in ultrahigh vacuum; influence of oxygen on the intensity of the EPR line. The possibility of complete pairing of free bonds at the surface–double-bonded model.)[44,52,90] 3) At least two types of PCs exist. They can be: Si-A centers, amounting to a $V_{Si} + O$ pair and a $V_{Si} + O_3$ complex, where V_{Si} is a silicon vacancy. Similar centers also exist in the bulk. (Partial and complete disappearance of the EPR line at various annealing temperatures. Correlation between the behavior upon annealing of the line with $g = 2.0055$ and the cited bulk

898   Sov. Phys. Usp. **32** (10), October 1989

A. B. Roĭtsin and V. M. Maevskiĭ   898

centers.)[67,79,84] 4) The PCs amount to broken bonds at the surface.[7)] Here, owing to reconstruction of the latter, two types of atoms arise. One type contains shells mainly of s character, their orbitals overlap by 80%, while the atoms themselves are slightly raised above the "bulk" positions. The second group of atoms is lowered, the shells are of p character with complete compensation of spins. (According to low-energy electron diffraction data, a superstructure is formed at the surface of silicon with a 2×1 unit cell. the density of atoms at the free surface is 8×10^{14} atoms/cm^2 while the concentration of PCs is fivefold smaller.)[42,54] 5) PCs are based on boundary atoms with broken bonds. The cause of the localized states is the differing type of surface defects, whose concentration can reach 1–20% of the total number of surface atoms. (Data on the surface concentration of PCs.)[77,80,92] 6) The source of the appearance of PCs is the Anderson localization electrons in microcracks.[76] 7) PCs are clusters of defects. They can be formations of spin-uncompensated vacancies (VV-centers) of dimensions ≈22 Å. The interaction between them is dipole–dipole in type. (Estimates of the line width under the assumption of a dipole-dipole character of broadening. The assumption that dislocations are formed in the mechanical processing of the specimens, leading to vacancy formation.)[58,60,72,75] 8) The PCs in amorphous silicon amount to broken bonds at the surface of microcrystallites of dimensions 10–15 Å that are disoriented with respect to one another. (Assumption of the correctness of the Haneman model.)[69,70,72,85] 9) The PCs amount to spin-uncompensated bonds distributed in the specimen and possessing somewhat differing parameters (Modeling of the EPR spectrum with a certain choice of "seed" parameters of the SH and with the assumption of a random law of their distribution).[73,86,93]

We see from the presented list that not only do varied viewpoints exist on the nature and properties of the PCs, but some of them are diametrically opposite. Yet the fact draws attention that some models have common features. In this sense we can distinguish three groups: models based on the picture of the presence of broken bonds of the boundary atoms, on the existence in the composition of PCs of oxygen, and on the possible localization of electrons in cavities in the juxtasuperficial region.

There are as yet no theoretical studies on the calculation of the parameters of the SH or other characteristics of the spectrum. The fundamental reason is the lack of models of the PCs.[8)] Nevertheless, some microcalculations have been performed to confirm the presented models. Thus the author of Ref. 54 proposed the existence of broken bonds and compared the results of calculations by the MO LCAO method with the line-width data and its g factor, and drew the conclusion that the electrons responsible for EPR are strongly delocalized, lie in the conduction band, and have a large effective mass. Another study[92] based on quantum-chemical methods studied the overlap integral of the orbitals. In particular, it was shown that the surface orbital can change direction of its lobe to the opposite, and thus ensure a maximum overlap with other orbitals, together with explaining the weak activity of the PCs with respect to oxygen. Reference 94 was conducted on a somewhat different level. It paid attention to the fact that one cannot explain the EPR data in the Hartree-Fock approximation, which does not take into account in an appropriate manner the correlation of the elec-trons. Only taking account of this correlation, e.g., within the framework of the Hubbard model, allows one qualitatively to explain the features of behavior of the intensity of the EPR line.

5.2. Other lines

Along with the line at $g=2.0055$, also other lines are observed in the surface EPR spectrum if it is subjected to specific treatment (many-hour annealing, addition of certain gases, laser irradiation, doping with special impurities). The greatest number of studies of this set is devoted to the line characterized by an isotropic g factor, whose value is 2.0027 ± 0.0004. This line usually appears upon mechanical treatment of the surface in air with subsequent evacuation (to 10^{-5} Torr), and heating of the specimen at a temperature above 670 K for several hours. The line is characterized by a small width ($\Delta H\approx0.7$–2 Oe), a small relaxation time ($\tau\approx10^{-6}$ s) and shape intermediate between Lorentzian and Gaussian. Air and oxygen strongly affect the line intensity, decreasing it with increasing gas concentration. Moreover, oxygen simultaneously broadens the line. Diamagnetic gases do not affect the intensity of the line. The signal does not depend on the properties of the bulk (e.g., the type of doping). In the first studies[44,52,53,90,95-97] the nature of the PCs was associated with the oxygen content (complex of the type SiO_x). As was assumed, the signal was caused by broken bonds, while the small width arose from clusterization of the defects and narrowing by the exchange interaction. The broadening of the line under the action of oxygen was assumed to be caused by the dipole-dipole interaction of the PCs with an oxygen molecule physically adsorbed on the surface of Si. However, it was later found[58,72,98,99] that carbon compounds that arise as contamination are responsible for the line (e.g., arising from oil vapors from the vacuum system).

References 20 and 26 carried out a special doping of the surface of Si with atoms of elements of the iron group with the aim of producing PCs. A feature of these studies is that paramagnetic probes arise at the surface; one can use them to study the properties and structure of the surface. These structures recall the bulk PCs, which are usually obtained by doping the specimens. Atoms of Cu and Mn were chosen as the impurities, which were deposited on the surface from electrolytes. It was possible not only to record the spectrum from Cu^{2+} and Mn^{2+} ions, but also to resolve the hyperfine structure, and also to determine the fundamental parameters of the spectrum: the components of the g factor, the HFI constants, the fine-structure parameters, and the width of the individual line. And although the detailed nature of the centers as yet has not been established, the EPR data (the character of the anisotropy, the magnitude of the SH constants) confirm that the PCs are concentrated at the surface of Si.

The other PCs lying at the surface of silicon have been studied little and their nature has not been established, although we can suppose that most of them are intrinsic defects. Therefore we shall restrict the treatment only to listing the pertinent studies by their fundamental characteristic, the g factor:

$g=1.9995,$[44,58,100] $2.0011,$[53] $2.0024,$[80] 2.0043[101];

$g_\perp=1.92,$ $g_\parallel=2.22$[44];

$g_\parallel=2.0025,$ $g_\perp=2.0011;$ $g_\parallel=1.993,$ $g_\perp=2.002.$[36]

6. EPR OF SURFACES OF OTHER DIAMONDLIKE CRYSTALS

6.1. Germanium

Ge in many respects resembles silicon. Therefore we can expect that the characteristics of the EPR spectrum of its surface will resemble those of the surface of silicon. Actually such a similarity is observed. In this regard, despite the fact that the number of studies on the EPR of the Ge surface is rather large, we shall not take up these studies in detail, as we have done for Si, since the methods of specimen preparation, the conditions of measurement, and other general problems of study of the Ge surface are analogous. Moreover, germanium and silicon are usually studied jointly, so that one can find detailed data on Ge in the articles already discussed above. Here we shall take up mainly the special features of the results and certain supplementary data on Ge.

Since in the case of Si the greatest interest was drawn to the line with $g = 2.0055$, the question arises as to what is the corresponding line for Ge. Such a line has been found. Its g factor proved to be 2.023 ± 0.001. The other characteristics of this line are: $\Delta H = 35$ Oe, $n \approx 10^{13}$ spins/cm^2, while the relaxation time is about an order of magnitude smaller than for Si. A characteristic feature of this line was that in many studies it could not be detected if the crushing of the specimens was conducted at room temperature rather than at lower temperatures, e.g., liquid nitrogen. This involved the fact that the intensity of the EPR signal declines with increasing temperature of crushing.[57] According to the data of most studies, the dependence of J on the temperature of measurement obeys the Curie law, although Ref. 22 indicated a stronger decline in J than $1/T_m$. Apparently this involves the fact that, with increasing T_m, a considerable line broadening occurs simultaneously,[102] which masks the Curie law. In this regard it is interesting to note that, in the case of the EPR line of Si at $g = 2.0055$, ΔH depends weakly on T_m. Apparently the corresponding temperature region lies above room temperature, which would be interesting to verify.

Just as in the case of Si, a line was observed with $g = 2.0027$,[53,96,98,99,103] involving carbon compounds contaminating the specimens. A number of additional lines arose upon treating the specimens with gases. Thus, Refs. 55, 77, 104, and 105 used p-benzoquinone (p-BQ). The molecules of this gas have the property of capturing an electron and becoming converted into a radical, and thus becoming paramagnetic. According to the plan of the authors, this phenomenon enables one to study charge exchange between molecules and the adsorbent. In the cited studies, after adsorption on the surface of Ge of p-BQ, two EPR signals were observed with the following parameters: $g_1 = 2.002$, $\Delta H_1 = 3$–8 Oe, and $g_2 = 2.02$, $\Delta H_2 = 22$ Oe. The molecules of diphenylamine have been used for analogous purposes.[104] In contrast to the molecules of p-BQ, the molecules of the latter can capture a hole. An EPR signal has also been observed upon admitting oxygen,[22] and in the opinion of the authors, it is due to the O_2^- molecule. The models proposed in the studies for the PCs responsible for the main line ($g = 2.023$) coincide with those discussed for silicon.

6.2. Diamond, SiC, SiGe, and graphite

According to the data of Refs. 51, 57, 67, 69, and 85, after crushing diamond or SiC at room temperature, EPR lines appear with $g = 2.0027 \pm 0.0002$ and $\Delta H = 5.5$ Oe.

They are analogous to the silicon line with $g = 2.0055$. It was noted[106] that, with gradual increase of the concentration of C in $Si_{1-x}C_x$, the g factor varies from 2.0055 to 2.0027, while for $x < 0.3$ it depends weakly on x. No special study of these lines has been performed.

Data on the EPR of the surface of SiGe are reported in Refs. 22, 107, and 108. At an Si content $\geqslant 92\%$, the line has a g factor close to $g = 2.0055$, although somewhat differing (≈ 2.006). The width of the line at $T = 77$ K amounts to 9.2 Oe, while increasing at room temperature to 16 Oe. Two lines are observed at other Si concentrations. One–with $g = 2.016$ and $\Delta H = 40$ Oe–corresponds to the line of pure germanium (with $g = 2.023$ and $\Delta H = 30$ Oe. The other, narrower line has $g = 2.005$ and $\Delta H = 13$ Oe; its nature has not been established. The parameters of both lines are strongly altered under the action of oxygen. The EPR data on the surface of SiGe are correlated with the character of the rearrangement of the band structure and the behavior of the EPR spectrum of PCs in the bulk as its composition is varied. In the opinion of the authors, the obtained results confirm the model[54] of weak localization of surface electrons, since a large sensitivity of the parameters of the spectrum to small admixtures of Ge exists.

Graphite, owing to its structural features, differs from the other crystals of Group IV, primarily in the number of lines in the EPR spectrum after crushing.[67,77,109] Three lines were observed: $g = 2.007$, $\Delta H_1 = 10$ Oe; $g_2 = 2.0036$, $\Delta H_2 = 4$–45 Oe; $g_3 = 2.027$, $\Delta H_3 = 55$ Oe. The width and intensity of the lines strongly depended on the temperature of crushing and the subsequent action of gases (CO_2, H_2, D_2). The interpretation of the experimental data reduces mainly to the following. The breakdown of graphite occurs in all crystallographic directions. Only the prismatic faces are active, the fraction of which amounts to $\approx 1/18$ of the total surface. In crushing, σ-bonds are broken at the prismatic faces, which leads to the unpaired electrons responsible for the line with $g = 2.027$. Partially delocalized $\pi = $ electrons are responsible for the line with $g = 2.0036$. At high crushing temperatures (300 K), electrons are captured by the broken bonds, and the EPR signal is strongly suppressed. However, it can be manifested by holding the specimen in hydrogen or deuterium. Here a charge transfer occurs analogous to that observed at the surface of Ge under the action of p-BQ.

7. EPR OF THE SURFACE OF SiO$_2$

The surface of silicon dioxide is of interest not only with regard to structure. It is the object of intensive study in mechanochemistry: The freshly prepared surface has an increased adsorptive and reactive power. In particular, one assumes that the latter is involved in the occupational disease silicosis, which arises upon prolonged inhalation of quartz dust. For study one uses quartz (crystalline or fused), silica, silica gel, and other varieties of silicon dioxide that yield similar EPR spectra. The specimen is usually crushed to a powder (in vacuo, in air, or in a medium of inert or active gases). In a number of cases an amorphous film was used that was obtained by sputtering. The PCs detected on the surface can be classifed into two groups: intrinsic defects that arise in the process of preparing the surface,[67,110–117] and impurity defects that arise from adsorption of gases or deposition on the surface of ions from electrolytes.[116–121]

900   Sov. Phys. Usp. 32 (10), October 1989

A. B. Roïtsin and V. M. Maevskiĭ   900

Intrinsic defects are observed usually in the form of electron centers (g factor less than 2.0023), and considerably more rarely in the form of hole centers. In the most carefully performed experiments[111,116] it was shown that the shape of the EPR line of electron centers (E'$_s$ centers)[9] is asymmetric with $\Delta H = 3$ Oe. An analysis of it showed that the broadening and asymmetry involve the random distribution of the PCs, which are characterized by an individual line of width ≈ 1 Oe and an axially symmetric g factor ($g_{\parallel} = 2.0018, g_{\perp} = 2.0003$). An HFS also appeared in the spectrum, due to the interaction of the electron of the PC with the nuclei of the closest neighboring silicon ^{29}Si. The spin Hamiltonian of an E'$_s$ center has the form (2.9) and possesses axial symmetry; the summation over i implies summation over the different sites of the ^{29}Si nuclei.

In elucidating the model of the E'$_s$ center attention was paid to the fact that the parameters of the surface centers are close to those of the bulk centers that arise upon irradiating silicon dioxide with γ-quanta or neutrons.[122,123] Such bulk centers studied by the EPR method include the E'$_1$ and E'$_2$ centers. Both centers amount to O^{2-} ion vacancies with a localized electron and with equilibrium positions of the surrounding atoms altered in different ways; since the silicon atoms closest to oxygen are not equivalent, relaxation of the atoms has two pathways that lead to E'$_1$ and E'$_2$ centers. The relaxation associated with the E'$_2$ center is metastable, but it is stabilized by a hydrogen atom that enters the environment of the PC. Just as in the case of an E'$_1$ center, for an E'$_2$ center the unpaired electron is strongly localized at the closest Si atom on the broken bond. In agreement with the data on bulk centers, it was proposed that at the surface E'$_s$ centers amount to a structure of the type of $\equiv$Si$\cdot$–an electron localized near the Si at the broken bond (the dot). In other words, one assumes that the immediate environment of the E'$_1$, E'$_2$, and E'$_s$ centers is qualtitatively the same. Owing to the difference in configuration of the more remote environment, one observes a certain difference in the parameters of the spin Hamiltonian. In particular, one observes a somewhat greater value of the isotropic HFI constant of the E'$_s$ centers, which can be explained by the absence at the surface of atoms of the environment that "suck away" the electron cloud.

EPR study of molecules adsorbed on the surface of SiO_2 (O_2, CO, CO_2, N_2O, H_2, etc.) is of interest at least from two standpoints. First, one can draw inferences from the EPR spectra of molecules constituting rather independent entities concerning the structure and properties of the substrate on which they are distributed. The point is that the spectra of the corresponding free molecules are known, while the substrate only transforms this spectrum in a certain way. Second, by observing the change in the charge state of the adsorbed molecules, one can conclude on the properties of the surface states. Thus, for example, the interaction of CO_2 molecules with the $\equiv$Si$\cdot$ radical occurs with charge transfer by the scheme: $\equiv$Si$\cdot$ + $CO_2 \rightarrow \equiv$Si$^+$ + CO_2^-, and now the paramagnetic CO_2^- ion resonates. Its spectrum possesses orthorhombic symmetry (three components of the g tensor), and HFI is manifested with the isotope ^{13}C. The parameters of its SH somewhat differ from the corresponding parameters for the CO_2^- ion existing on other matrices.[124] As another example we note that in the breaking of the Si-O-Si bond, along with the $\equiv$Si$\cdot$ radical at the surface of SiO_2, a

radical of the form $\equiv$SiO$\cdot$ arises.[121] However, owing to the degeneracy of its ground orbital state, it is not directly observed (by the EPR method). Yet it interacts with certain gas molecules (O_2, CO) to form new radicals (SiOOO$\cdot$, SiOCO$\cdot$), whose EPR spectra can now be studied, so that one can decide on the state of the surface before and after adsorption of the gases.

One can obtain information analogous to that noted above by depositing heavier ions from electrolytes on the surface of SiO_2. The ions Cu^{2+} and VO^{2+} were studied.[118,119] It was established that the symmetry of their EPR spectra depends on the temperature, going from axial at 77 K to cubic at room temperature. Such a transformation of the spectrum was explained by the fact that PCs on the surface of SiO_2 amount to the so-called aquacomplexes, i.e., ions of Cu^{2+} and VO^{2+} lying in an environment of water molecules: $[Cu(H_2O)_6]^{2+}$ and $[VO(H_2O)_5]^{2+}$. In such complexes the position of the ligands can vary with varying temperature, which leads to a change in the local symmetry of the PC. Another characteristic feature of these complexes is their ability to exist under the action of external factors either in the form of singles or of sets, and in particular, of pairs, while manifesting an exchange interaction.

Just as in the case of Si, PCs have been detected on the surface of SiO_2[98,99] that arise from contamination with carbon compounds. And finally we note that, under certain technological treatments that lead to an amorphous state of the silicon oxide, spectra from SiO have been detected,[112,125] which resembled the EPR spectra from irradiated compounds of SiO_2 ($g \approx 2$). Data on the nature of these centers are not given, while only the existence of broken bonds is assumed.

8. EPR OF THE Si–SiO_2 INTERLAYER

A generalization of the concept of the surface of a solid as the boundary between the solid and the vacuum (air or another gas) is the boundary between two solids or a solid and a liquid. An example of such a formation is the layer between silicon and its dioxide. Both Si and SiO_2 enter as constituent elements of the combination metal-oxide-semiconductor, which has been widely applied in technology and has been increasingly studied by various physical methods. Of especial interest is the structure of the defects in the Si-SiO_2 interlayer, since precisely they determine the electrophysical properties of the entire system.

Study of them by the EPR method was begun[126] in 1966. Even the first studies[31,32,126,127] established the most characteristic feature of the defects that arise at the surface of silicon subjected to high-temperature treatment (1000 °C) in a medium containing oxygen (such a treatment gives rise to an oxide layer $\approx 10^3$-Å thick). It was established that three types of PCs arise near the Si-SiO_2 boundary, which were called ^{32}P$_a$, P$_b$, and P$_c$ centers. Their parameters have also been determined. Thus, in the case of the P$_a$ center the spread in the components of the g factor, which determines the anisotropy of the EPR spectrum, proved to be 2.000–2.010, while the line width was ≈ 6 Oe. It was shown that there is a direct connection between the concentration of P$_b$ centers and the electrophysical characteristics of the specimen. Thus, for example, the mobility of the current carriers rose with decline in the number of P$_b$ centers. And, although no models of the PCs were established, some

901   Sov. Phys. Usp. 32 (10), October 1989

A. B. Roĭtsin and V. M. Maevskiĭ   901

assumptions on their structure were stated. Thus, it was subsequently confirmed that the P_b center is based on a structure of the type $\equiv Si\cdot$, which indicates that the unpaired electron is localized on one of the broken bonds. Subsequent studies were aimed at establishing the nature of the PCs, at examining the influence on them of the method of preparing the oxide film, of light, and radiation treatment, and at developing new, more sensitive experimental methods of detecting paramagnetic-resonance adsorption. In the identification of the PCs the question arose of whether the interlayer PCs are analogs of the bulk PCs (i.e., existing previously in the bulk, but localized at the boundary and thereby somewhat transformed) or they are specific only for the Si-SiO_2 interlayer. Therefore an important methological point in determining the nature of the PCs was to compare the parameters of their spectra with those of the spectra of all known defects in crystals of Si and SiO_2 and spectra of impurity atoms in other crystals.

The greatest number of studies has been devoted to studying the fundamental PC of the interlayer of the P_b center. On the basis of numerous data[128-132] it was established that P_b centers can be of two types, depending on which surface of silicon is being studied. For a surface of the (111) type the P_b center amounts to an axially symmetric center with $g_\parallel = 2.0016$ and $g_\perp = 2.009$. It is based on a pyramid consisting of four silicon atoms lying at the boundary between Si and SiO_2 and oriented along the [111] direction. The atom at the vertex of the pyramid, which lies at the Si-SiO_2 boundary, is adjoined by a broken $Si = O$ bond at which the unpaired electron is localized (Fig. 2). The PC depicted in Fig. 2 can be denoted by the formula $Si_3 \equiv Si\cdot$. In the case of a surface of (100) type, the model is defined by the formula $Si_2 O \equiv Si\cdot$. The dependence of the concentration of P_b centers on a number of factors was studied (conditions of specimen preparation, electric field) and a correlation was established with the analogous concentration dependence of various charge states (measured by electrophysical methods). These measurements showed that P_b centers are electrically active centers (D_{it} centers[10]), which can capture both holes and electrons, and whose levels lie in the forbidden band. In connection with what we have said, we note that calculations of the electronic structure of these de-

FIG. 2. Model of an Si-SiO_2 interlayer at the (111) surface of silicon. a–Arrangement of the atoms at the boundary. b–Model of a P_b center (perturbed arrangement of atoms): near a relaxed silicon atom at the boundary an oxygen ion is missing. Hence a broken bond is formed, at which a single electron is localized, which is responsible for the EPR of the P_b center. A fragment of the type $\equiv Si\cdot$ with a broken bond is the basis of many intrinsic defects in Si and SiO_2 (which differ in the type and arrangement of the three atoms closest to silicon). Some authors assume that such a fragment is the basis also of the model of the paramagnetic center with $g = 2.0055$ (see Sec. 5). 1–oxygen, 2–oxygen vacancy, 3–silicon, 4–electron.

fects have been performed,[134] whose results qualtitatively agree with the experimental data. The conclusions drawn above on the nature of the P_b centers were obtained on the basis of studies of only the angular dependence of H_p associated with the anisotropy of the g factor. And only recently[135] was it possible to detect the HFI of the unpaired electron with the ^{29}Si nucleus lying at the vertex of the pyramid (see Fig. 2). As it turned out, the HFI tensor contains nonzero components $A_\perp$ and $A_\parallel$, confirming the axial symmetry of the P_b center.

We have already noted that in preparing the oxide layer on silicon one must heat the Si specimen at high temperature. Under such a treatment part of the impurities contained in the bulk can diffuse to the surface. This circumstance entered into the error of certain investigators who had proposed structures as models for the P_a and P_c centers involving lattice breakdown (intrinsic defects). Yet actually it turned out that the P_c centers are Fe^0 atoms implanted into the interstices of Si near the Si-SiO_2 boundary.[100,128] The situation is somewhat more complicated with the P_a centers, but here it is assumed that impurity atoms of phosphorous that replace Si atoms in the interlayer are resonating.[128,129,136] In this regard attention is drawn to Ref. 137, where it was shown that the atoms of phosphorus in silicon diffuse to the surface upon annealing. Another viewpoint[138] associates the P_a centers with silicon vacancies and oxygen. In the process of studying P_a, P_b, and P_c centers, an isotropic line was observed[128] with $g = 2.0055$, which was described in detail above in connection with the surface of silicon. The PCs corresponding to it lie in the silicon near its boundary with SiO_2 and have the same nature as silicon PCs proper. In these studies they were named P_d centers. P_d centers interfere with the observation of P_b centers, and they must be distinguished in a special way.[132]

In line with the fact that the Si-SiO_2 system has found widespread application in technology, it was important to establish the optimal technological regime of preparing it and the character of the influence of various external agents on it. In solving this problem, substantial help was offered by the EPR method, since the kinetics of accumulation of PCs formed in the interlayer proved to be a good indicator of the properties of the whole system. It was found[33,138-140] that the parameters of this system strongly depend on its conditions of formation, and in particular, on the temperature of oxidation. In this regard a low-temperature (< 600 °C) treatment at reduced pressures of the surrounding gas was proposed.[33,139] It was also established that irradiation of the specimens with light ($h\nu > E_g$–the magnitude of the forbidden band in Si) leads to the appearance of new centers[37,128,139,141] or intensification of the signal of the centers already known.[130,142,143] The nature of the new PCs is as yet unknown but, in the opinion of most authors, they involve OH groups that arise owing to the presence of water vapor during the preparation of the specimens. It proved essential also that photostimulated or photoenhanced EPR enables one to detect a smaller amount of PCs than ordinary EPR does. The mechanism of this phenomenon as yet has not been sufficiently elucidated, but it is assumed that it, as in the experiments of Ref. 89, involves spin-dependent recombination of charge carriers excited by light. Owing to this new methodology, it has been possible to detect PCs in the interlayer that are not observable in the ordinary way
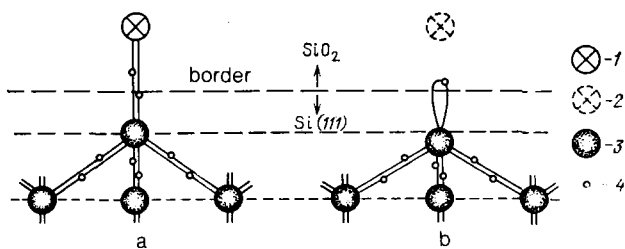
(e.g., E' centers[142]) and to establish that they are responsible for the electrophysical properties of the specimens. The cited set of studies, which mainly used white light, are adjoined by studies of PCs under the action of ultraviolet irradiation. It was noted that it can lead to a temporary weakening of the signal from the P_b centers[144] and to depletion of oxygen of the SiO_2 layer, i.e., to the appearance of E'$_1$ centers.[145]

Studies of the influence of γ-irradiation showed[146] that E' centers and hydrogen atoms arise in the SiO_2 layer, and P_b centers in the Si-SiO_2 interlayer. The distribution of the E' centers proved to be nonuniform: near the Si-SiO_2 boundary the concentration of E' centers proved to be considerably greater than at the boundary of the SiO_2 layer (by a factor of about four at a thickness of the layer $\approx 10^3$ Å). Also "oxygen-hole" centers were detected in the SiO_2 layer—holes localized near oxygen atoms. Under the action of ion irradiation (Ar^+, As^+, B^+, H^+, He^+, N^+, Ne^+, O^+, P^+) three types of centers arise,[147,148] which were identified as follows. In silicon near the interlayer P_d centers arose, and in the SiO_2 layer–E' centers and the so-called DI centers, associated either with O^- or with O_2^-. Study of the kinetics of accumulation of the various defects and their spatial distribution near the Si–SiO_2 boundary showed that one can monitor the process of implantation by the EPR method.

Reference 149 is especially noteworthy, in which information on the state of the surface was derived from the EPR spectrum of PCs existing in the bulk. In this case the Fe^0 atom was resonating. Usually the Fe^0 atom lies in a cubic environment, and having the spin $S = 1$, it yields a single isotropic line. Under the action of deformations that reduce the local symmetry, the EPR line splits in two. The authors of Ref. 149 created deformations by damaging the surface of silicon, and in particular, by deposition on it of a layer of SiO_2, which led to stresses. The study of the line splitting that arose here enabled them to derive information on the stress parameters.

9. EPR OF THE SURFACE OF $A^{II}B^{VI}$ COMPOUNDS

We shall classify this group of compounds into two parts, depending on the site occupied by the A^{II} element in the second column of the periodic table. The representatives of each part are the compounds ZnO and MgO, to which a number of studies have been devoted.

9.1. Crystals of the ZnO family

9.1.1. ZnO

Nonstoichiometric ZnO (with an excess of Zn ions) is an n-type semiconductor. Many of its physicochemical properties (as well as those of other semiconductors) involve the adsorption on its surface of molecules of electron-acceptor gases–such as oxygen, benzoquinone, fluoranil, and chloranil. ZnO, being subject to photolysis, is a typical photocatalyst on whose surface various chemical reactions can occur. ZnO powder has been applied as a thermal insulator for spaceships.[150,151] All this has caused heightened interest in studying its surface properties. The first studies were performed in 1961.[67,152] After crushing a monocrystal of ZnO, the authors[67] observed an EPR line with $g = 2.005$ and width $\Delta H = 8$ Oe. In Ref. 152, after irradiating the powder with ultraviolet radiation, a line was observed with $g = 1.957$. Subsequent studies were directed mainly at elucidating the nature of the line with $g \approx 1.96$, and also on dis-

covering and interpreting the lines that arise from adsorption on the surface of ZnO of various gases.

The line with $g \approx 1.96$ and width $\Delta H \lesssim 6$ Oe, as a rule having a Lorentzian shape, usually arises after heating the specimens at a temperature $T_o \geqslant 500$ °C in vacuo. The temperature of measurement is 77 K. This line is enhanced upon irradiating the specimen with light with a quantum energy exceeding the width of the forbidden band ($E_g \approx 3.435$ eV), and is weakened under the action of various gases adsorbed on the surface. Despite the large number of studies[150–171] devoted to elucidating the nature of this line, there is as yet no unambiguous model of the source of the resonance. In a number of cases doubt even remains with respect to whether this line belongs to a surface center. There are three viewpoints on the nature of the resonating spin: conduction electrons that arise in the conduction band or the impurity band[154–160]; electrons trapped at an oxygen vacancy (local centers of the type of F-centers[150,151,160–163]); or interstitial Zn^+ ions.[152,163–166] Without concretizing the type of defect, a localized character of the resonating electron has been indicated.[168–170] The most convincing proof of localization is the discovery of HFS.[160] Yet this same study noted that the very fact of localization of the electron depends on the concentration of defects and the temperature, so that also carriers can resonate at large n and T_u. It was noted[163] that with a certain thermal and gas-vacuum treatment the line with $g \approx 1.96$ can split into two lines (with $g_1 = 1.965$ and $g_2 = 1.961$). It is proposed that Zn^+ is responsible for the line with g_1 and an O^- vacancy for the line with g_2.

We should note that the ambiguous conclusions listed above on the nature of the resonance involve to a considerable extent the fact that the results substantially depend on the conditions of specimen preparation.

In studying the surface of ZnO, one of the methods used was the admission of various gases that influence the intrinsic defects and create new impurity centers via adsorption. In most studies oxygen was used for this purpose, but also CO,[170] H_2,[150,172] N_2O,[164,165] NO_2,[165,171] NO, Cl_2,[165] and more complex compounds (benzoquinone, anthraquinone, trinitrobenzene, fluoranil, chloranil, bromanil, tetracyanoethylene)[172–174] have been used. The most typical PC observed in many studies[158,159,163–167,175–178] was O_2^-, which arose upon capture by an O_2 molecule of an electron from the surface. It is characterized by orthorhombic symmetry with the following principal values of the g tensor: 2.051, 2.002, and 2.0088. In this PC HFI was detected[168] after enriching the oxygen with the isotope ^{17}O. The problem is discussed of the spectrum of the PC O^-,[156,162,164,167,176,177] yet the parameters of the SH ascribed to this center in different studies strongly differ from one another. Many lines have remained unidentified. They include, e.g., an isotropic line[154,159,165,168,170,171,175] whose g factor lies in the interval 2.013–2.019. Finally, in Ref. 99 a spectrum was recorded that arises from contamination of the ZnO surface with carbon compounds that yield parasitic signals ($g = 2.0024$–2.0027). In this regard we note that many unidentified lines or lines ascribed to other centers lie in the region $g = 2.002$–2.004.

9.1.2. Other crystals of the ZnO family

The surfaces of the following crystals have been studied: CdO,[67,157] CdS,[67,99,179–181] CdSe,[99,180–182] HgO,[67]

ZnS,[67,99,157,183–185] ZnSe.[180,183] The first attempts to detect an EPR signal of the powders after crushing crystals of CdO, CdS, HgO, and ZnS[67] were successful only in the case of ZnS. The EPR line observed with $g = 2.0031 \pm 0.0003$ was subsequently identified[185] as a line from an F-center (an S^{2-} vacancy that has trapped an electron). A number of studies on CdS, CdSe, and ZnS observed a narrow line with $g = 2.0027$, which was ascribed to intrinsic defects. However, it was established later[99] that it belongs to carbon compounds deposited on the surface of the crystals as contamination from the use of the vacuum technique. Measurements performed with special precautions[180] showed that intrinsic defects are not manifested on the surfaces of CdS, CdSe, and ZnSe. Admission of oxygen weakens the observed lines (including the line with $g = 2.0027$), while in the case of CdSe[180] it leads to an additional spectrum, which, however, has not been studied in detail. Somewhat apart from the cited studies is Ref. 183, in which the structure was studied of a ZnS film doped with Mn^{2+} ions that act as a paramagnetic probe. From the data of the EPR spectra of Mn^{2+} it was possible to establish the degree of ordering (crystallinity) of the film and the symmetry of the immediate environment of the Mn^{2+} ion.

9.2. Crystals of the MgO family

9.2.1. MgO

Crystals of MgO are a stoichiometric oxide, a dielectric with a width of the forbidden band of 8.7 eV. Without special treatment it is chemically weakly active. However, heat treatment, evacuation, ultraviolet, γ-, and neutron irradiation transform it into a strong adsorbent and catalyst. A substantial role in these phenomena is played by surface defects, which can be studied by the EPR method. The first experiments[67] showed that after comminution of MgO PCs arise, characterized by an easily saturated line with a g factor close to that of F-centers ($g = 2.0021 \pm 0.0001$, $\Delta H \approx 1.2$ Oe) that had been observed earlier[186] in the bulk after neutron irradiation of the specimen. The observation of HFI with the ^{25}Mg nucleus also indicated that structures of the type of F-centers can act as PCs. Consequently the conclusion was drawn that F-centers can be created also upon mechanical treatment of the specimens. Further studies were directed to elucidating the nature of the intrinsic defects in the juxtasuperficial layer, of the adsorbed gas particles on the surface, and studying the connection between the defect structure of the surface and catalysis.

The previously known F-centers[67,187–189] and their analogs arise under the action of neutron irradiation and mechanical treatment of MgO crystals. However, their distribution through the specimen proved to be nonuniform: the F-centers are mainly concentrated in a juxtasuperficial layer ≈ 35 Å thick,[188,189] while S-centers, which amount to a surface.[87,189–194] The electron of an S-center is not surrounded by six Mg ions, as in the case of an F-center, but by five. Consequently the symmetry of the PC proves to be axial ($g_{\parallel} = 2.0016$, $g_{\perp} = 2.0003$, $\bar{g} = 2.007^{11}$). In the case of an S-center the electron interacts mainly with the ^{25}Mg nucleus most remote from the surface. If one subjects to γ-irradiation a surface containing adsorbed hydrogen or deuterium, S_H-centers are formed,[192] which amount to S-centers having hydrogen (or deuterium) in the immediate environment.

S_H-centers manifest HFI both with ^{25}Mg and with H (or D);. S- and S_H-centers actively interact with oxygen, whereby the intensity of their lines is diminished up to complete disappearance. After special thermal treatment and ultraviolet irradiation, new centers arise—S'-centers. According to Refs. 175, 191, and 195, they amount to electrons localized at vacancies of the pair $Mg^{2+}O^{2-}$ ($g_x = 2.0015$, $g_y = 1.9990$, $g_z = 2.005$). An S'-center is analogous to an F_2-center, which had been previously observed in the bulk. Also V-like centers were detected (a hole localized at a cation vacancy)[189,194,196]; the g factor of these centers ($g_{\perp} = 2.038$, $g_{\parallel} = 2.003$) is close to the g factor of bulk V-centers.

Molecules (or atoms) of a gas adsorbed on the surface of MgO have been studied by the EPR method: O_2^-,[175,197–199] O^-,[193,199–201] O_3^-,[200,201] CO_2^-,[195,200] CO,[202] NO,[203,204] NO_2^-,[204] NO_3, NO_2,[203] benzoquinone, fluoranil, and other, more complex compounds.[173,174,205] The nature of PCs that arise owing to adsorbed molecules has been determined mainly by comparing their SH parameters with those of the corresponding free gas molecules. A substantial role in identifying them was played by using the isotope ^{17}O, which manifests HFS, and establishment of the correlation between the number of adsorbed particles and the concentration of the intrinsic defects measured by the EPR method. An important point in these studies was the elucidation of the mechanism of charge transfer to gas particles upon chemosorption. Here there is as yet no unified opinion. Most of the authors consider that the electron is captured from defects (e.g., a localized electron of an S-center is transferred to O_2 to form O_2^-), others admit the transfer of an electron from an O^{2-} ion contained in the MgO lattice. With this is associated and is discussed the question of the site of localization of the particles. Unfortunately there are as yet no direct radiospectrometric data that would allow answering all these questions.

It has also been noted[194,196,198] that, near a surface manifesting an EPR spectrum, an acceleration of chemical reactions (such as, e.g., $H_2 + D_2 \rightleftharpoons 2HD$) and isotope exchange between gas particles and particles already adsorbed on the surface occur. And finally we note that, in connection with the large number of PCs detected on the surface of MgO, a classification of them[200] has been proposed together with corresponding symbols for the PCs. Although the latter are unwieldy in comparison with the symbols adopted in the original articles (which we have maintained here), they can prove useful after most of the PCs have been identified more exactly.

9.2.2. Other crystals of the MgO family

Among this family also BaO,[173,188,206] BeO, BaS, CaS,[67] CaO,[67,188,190,192,197] and SrO,[67,188,190] have been studied. In the case of BaS it was not possible to detect a signal from surface centers. In the cases of BeO and CaS after crushing only an EPR line was detected. And only the crystals of BaO, SrO, and especially CaO have been studied on the same level as MgO, although to a considerably lesser degree. The parameters characterizing the PCs, or some phenomenon, differ from the corresponding parameters for MgO; yet on the whole the phenomena are analogous to those observed for MgO.

10. EPR OF THE SURFACE OF $A^{III} B^V$ COMPOUNDS

The first attempts[67] to discover an EPR signal from a freshly crushed specimen of GaAs were not successful. In subsequent studies it was possible to manifest a narrow ($\Delta H \approx 1$ Oe) line with $g = 2.0027$ in EPR spectra of crystals of GaAs, InSb,[53,96,207] and GaSb.[207] As it turned out, this line does not depend on the type of conduction, has a shape intermediate between Lorentzian and Gaussian, and broadens on adding oxygen. Etching off a thin layer makes it disappear. In the opinion of the authors of these studies, the line involves intrinsic surface electron states, while its broadening is due to the magnetic dipole-dipole interaction of the PC with O_2 molecules adsorbed on the surface. However, further study of this line in the spectra of GaAs,[98,99] GaSb,[98] and InAs[99] showed that it involves contamination with carbon compounds that arise in the vacuum technology. At the same time these[98] and other[208] studies manifested a new line in the spectra of GaAs and GaSb with $g = 2.0038$, which was also ascribed to intrinsic surface defects, but these data later[209] were not confirmed, so that the very fact of existence of the line with $g = 2.0038$ came under question.

Progress in studying the surface of $A^{III} B^V$ compounds by the EPR method was attained by using O_2^- as a paramagnetic probe. After admitting oxygen to the surface of powder freshly prepared *in vacuo*, an EPR signal was detected of the O_2^- ion on the surfaces of GaAs, AlSb, and GaP.[208–210] (Attempts to detect an analogous signal in InAs and GaSb[208] were not successful.) The SH of the O_2^- ion and its immediate environment has the form of (2.9). HFI was detected with the nuclei of the elements of the third group (Al,Ga). It turned out that the directions of the principal axes of the g and A tensors differ, which indicates that the symmetry of the PC is lower than orthorhombic. To elucidate the details of the structure of the PCs the authors of Ref. 210 studied the complex $Al(Ga)-O_2^-$. As the model of its wave function they chose a linear combination of the wave functions of the ground state of the O_2^- ion and of the atom Al (or Ga). On this basis they calculated the observable characteristics of the spectrum. Comparison of them with the EPR data enabled establishing the character of the binding of the electrons in the complex and the features of the reconstruction of the free surface of the $A^{III} B^V$ compounds in agreement with the low-energy electron-diffraction experiments. These studies amount to the first application of EPR to study the structure of the clean surface of crystals and is an example of use of a paramagnetic probe.

11. EPR OF THE SURFACE OF TiO_2, Al_2O_3, AND SOME OTHER CRYSTALS

11.1. TiO_2

Two varieties have been studied among the crystals of the TiO_2 family: rutile and anatase. Although their space groups differ,[211] they have a common important feature that enables explaining the experimental data from a unitary standpoint. This feature is the presence of $[TiO_6]$ octahedra. The parameters of the octahedra of rutile and anatase differ; this is taken into account in the qualitative interpretation of the EPR spectra, e.g., in order to understand the difference between the g factors. Yet the detailed difference in the structure of the two crystals at the surface, and as a consequence of this, in some of their physical properties, as yet

cannot be solved by the EPR method. Therefore we shall not draw a distinction between these two varieties of TiO_2 crystals below in discussing the EPR data.

The first attempt[67] to detect an EPR signal from the surface of TiO_2 after crushing led to observation of a broad ($\Delta H \approx 400$ Oe) line with $g \approx 2$. The subsequent measurements were performed after a special preliminary treatment of the specimen. The crystals were usually heated at $T_0 \approx 500$ °C in vacuo (10^{-5} Torr) for several hours. After this treatment a line was observed with $g = 1.95$–1.96 (according to more accurate data $g_\perp = 1.959$, $g_\parallel = 1.946$) and $\Delta H = 50$ Oe.[212–219] The EPR spectrum was axially symmetric. Most of the authors associate this line with the Ti^{3+} ion. However, no exact model of the center is yet known, and it is even unclear whether the Ti^{3+} lies at a node or an interstice. Some authors ascribe this line to an O^{2-} vacancy that has captured an electron, i.e., to a structure resembling an F-center. Independently of the nature of this line, the question was of interest of the character of the distribution of the PCs on the surface of TiO_2. If we assume that the PCs are distributed uniformly and calculate the width of the EPR line, then it turns out[213] that it is an order of magnitude narrower than the experimental curve. Hence the conclusion was drawn of a nonuniform distribution of the PCs, and in particular, of their clusterization.

Many studies have been devoted to studying the adsorption of oxygen[176,216–220] and other gases[174,212,214,216] on the surface of TiO_2. The aim of these studies was to establish a correlation between the adsorptive power of the surface, its catalytic activity, the electric conductivity of the specimen, and the EPR spectrum at different stages of treatment of the crystal. It was found that oxygen and certain other gases not only have acceptor properties, forming, e.g., O_2^- and O^-, but also donor properties, being converted to O_2^+ and O^+. The EPR data from studying the adsorption of O_2 containing the isotope ^{17}O are distinguished by great information content.[219] In this case it was possible to detect HFS and to show that the electron cloud is uniformly distributed between the two O atoms, and thus to establish that the O_2^- molecule is oriented along the surface. In the case of donor molecules, such as H_2O and NH_3,[212] adsorption occurs at sites of broken coordination and restores it.

11.2. Al_2O_3

The first study[67] reported that a broad EPR line was observed after crushing the specimen. Later[221] the question was discussed of the influence of the surface on the adsorption of organic compounds. Thus, after degassing the specimen at 400 °C in vacuo and admitting quinone, an EPR line was observed with $g = 2.00$ and $\Delta H \approx 10$ Oe. In the opinion of the authors an electron captured from the surface onto an adsorbed molecule is resonating. An analogous situation arises in adsorption of oxygen molecules, whereby it can be detected by the EPR method[199,222] in the form of the O_2^- ion. Al_2O_3 acquires enhanced catalytic activity after γ-irradiation,[222,223] with this activity being correlated with the PCs formed at the surface of Al_2O_3. References 118 and 224 are of a different character. They studied the EPR of ions of Cu^{2+}, Mn^{2+}, and VO^{2+} deposited from solutions onto the surface of Al_2O_3. Their spectra are characterized by axial symmetry and manifest HFI with the nuclei of Cu, Mn, and V. Under certain conditions these ions have a tendency to

905   Sov. Phys. Usp. 32 (10), October 1989

A. B. Roĭtsin and V. M. Maevskiĭ   905

aggregate into clusters. In the opinion of the authors, distorted water complexes of the type of $[Cu \cdot 6H_2O]^{2+}$ act as the PCs. As the surface is dehydrated, the coordination of water molecules decreases, which is revealed in the EPR spectrum in a change in the magnitudes of the components of the g tensor.

11.3. Alkali-halide crystals

An attempt[67] to detect an EPR signal by crushing KCl and LiF crystals to a powder was not successful. Another approach was adopted[27] in studying the surface of NaCl and KCl–doping with Mn^{2+} ions. This made it possible to detect EPR spectra of the Mn^2 ions and to determine the fundamental parameters: the g factor and the HFI constant. A model of the PCs was proposed: an Mn^{2+} ion in the neighborhood of six Cl^- ions lies in the juxtasuperficial region, whose properties differ strongly from the properties of the bulk. A charge compensator remote from the Mn^{2+} leads to inhomogeneous broadening of the EPR lines.

11.4. Other materials

Besides the compounds discussed above, others have been studied, albeit to a lesser extent. We shall restrict the treatment here only to listing them while indicating the appropriate references: $Ba(OH)_2 \cdot 8H_2O,$[225] $BaSO_4,$[110] $Bi_2Te_3,$ $CaCO_3,$ $CaF_2,$[67] CuO. $GaSe,$[226] $GeO_2,$[227] $La_2O_3,$[206] $Li,$[28] $MgO \cdot Al_2O_3,$[67] $MoO_3,$[217,228] $NiO,$[217] $PbS,$[76,180,229] $PbTe,$[67,180] $Si_2O_3,$[206] $Se,$[67] $SiN,$[230] $SnO_2,$[176,231] $Te,$[67] $Y_2O_3,$[206] and $ZrO_2.$[199] A special class of materials is constituted by porous materials, whose representatives are the zeolites and silica gels. They possess a relatively high surface owing to the characteristic cavities and consequently can serve as active sorbents of molecules. The corresponding processes have been studied by the EPR method, both in zeolites[232] and in silica gels.[233] However, we should note that the concept of surface for them is arbitrary, since the radius of curvature of the cavities is of the order of the distances of interatomic interactions. Therefore the processes occurring on such a surface will not be the equivalent to the phenomenon on surfaces of large radius of curvature.

12. CONCLUSION

EPR has proved to be a rather effective method of studying the surface of solids. Actually the study of surface defects began with the application of EPR. Success has been attained, both in establishing the nature of the defects and in elucidating the mechanisms of various processes associated with them. We should especially note the identification of P_b and P_c centers in the Si-SiO$_2$ interlayer, E'$_s$ centers in SiO$_2$, S-centers in MgO, O_2^- molecules and the Mn^{2+} ion on the surfaces of certain crystals, and the establishment of the correlation between the intensity of EPR lines and different electrophysical phenomena. Besides, if we compare these results with the analogous data for the bulk, we must state that the obtained results are as yet meager. In fact, even in the case of the advances noted above in identifying PCs, the question of the structure of the immediate coordination spheres remains open. As for the many other PCs, their nature has been treated ambiguously, while some lines as yet cannot be identified in any way. In this sense the line with $g = 2.0055$ from the surface of silicon is especially

noteworthy. Despite the vast number of studies devoted to it, the nature of the PCs corresponding to it remains actually unestablished.[12] Therefore we can conclude that, despite the advances attained in studying surfaces by the EPR method, as yet the accumulation of facts and the search for and development of new methods of study (including fundamentally new ones) is still proceeding. The level of study of surfaces by the EPR method to some degree is reflected in the style of the corresponding publications. Most of the studies are descriptive in character, they abound in a multitude of assumptions and discussions of general character, and they lack the rigor and brevity inherent in the studies of EPR of bulk PCs.

In connection with what we have said, let us take up some considerations. As it seems to us, taking them into account might substantially increase the information content of the studies.

a) There are as yet no studies of surfaces using such unique methods as ENDOR and application in EPR of external electric fields, despite the fact that the appropriate preliminary theoretical treatment has been carried out relatively recently.[235] Besides, as was noted in the Introduction, precisely these methods have made it possible to increase considerably the effectiveness of the EPR method. There is also no complete understanding of the mechanisms of spin-dependent phenomena, on the basis of which new methods have been developed for surface study.[35,236] This impedes the identification of PCs and the correct determination of certain of their characteristics. Therefore it seems expedient to develop further the theory of these phenomena.

b) Almost all studies on EPR of surfaces involve PCs for which the spin is $S = 1/2$. However, precisely this case is the least favorable for obtaining maximum information on the nature of PCs and the structure of the surface. Therefore it seems in order to use as paramagnetic probes the ions Mn^{2+}, Fe^{3+}, Eu^{2+}, and Gd^{3+}, etc., which have acquitted themselves well for bulk studies, and which are distinguished by high values of the total spin ($S = 5/2, 7/2$). Application of high-spin paramagnetic probes would enable determining the local symmetry of PCs with greater accuracy, and owing to its relation with the space groups[14]–the symmetry of the reconstructed surface as a whole. One of the features of the EPR of surfaces is that, in constrast to the bulk, here molecules (or atoms) of adsorbed gases (such as O_2) can act as probes. And although they have $S = 1/2$, study of the HFI with the intrinsic nuclei and the nuclei of the substrate can considerably enhance the information content of the EPR data. In this regard we note that enrichment of the elements with isotopes having a nonzero magnetic moment has justified itself.

c) Owing to the various factors (crushing to a powder, determination of the PCs near the surface, amorphization of the juxtasuperficial layer), the characteristics of the PCs will differ from one another. Therefore it seems expedient to develop further the theory of spectra of disordered systems. We bear in mind a more complete account taken in the SH of all the interactions and the derivation of exact analytic expressions for the line shape. In reducing the integral expressions for the line shape to elementary or special functions, the difficulties that arise are not only of fundamental character, but also involve various types of unwieldy, laborious calculations. The latter can be performed by using computers especially oriented to automation of algebraic calculations.[237]

d) Progress in studying surfaces by the EPR method is closely associated with advances in studying them by other methods that enable establishing the configuration of the surface, help in identifying defects, and determine their location and distribution. An important place is occupied by the technical methods of preparing and treating surfaces and the methods of producing PCs on them. We note also the role of theory, and in particular, quantum-chemical methods.[238] A knowledge of how to calculate the energy structure of a defect, and on its basis the SH parameters of the PC, would considerably facilitate establishment of the nature of the PC and the mechanisms of various processes at the surface involving EPR. Such calculations as yet are in the initial stage, although this involves to a considerable degree the absence of the source experimental data on the nature of the PCs. The study of the behavior of atoms (or molecules) on a surface is of independent interest. The point is that, in a number of cases, as was pointed out above, they have a tendency to clusterize, which substantially alters the EPR spectrum. The theoretical treatment of this problem has actually just begun.[213,239]

---

[1]We recall that in EPR it is not the frequency of the electromagnetic field that varies in passing through a resonance, but the external static magnetic field.

[2]EPR spectrometers are usually designed to detect the derivative of an absorption line, i.e., dF/dH, which enables one to reveal more distinctly the characteristic points of the $F(H)$ curves

[3]Generally the position of a line in a spectrum is determined not only by the g tensor, but also by other parameters of the SH. However, in the given case only one parameter, the isotropic g factor, proved to suffice.

[4]In Ref. 54 special efforts were undertaken to detect an angular dependence of the EPR spectrum of a freshly cleaved surface of silicon, but the position of the line did not vary within the limits of accuracy of the experiment.

[5]Distance between points of greatest steepness.

[6]In certain studies (e.g., Ref. 67), the concentration is expressed as the number of spins per gram. Transforming it into a bulk concentration is performed by dividing by the density of the material.

[7]The model described below is known in the literature as the Haneman model.

[8]Usually the parameters of the SH of bulk PCs are calculated after a model of the PC has been established experimentally on the basis of the phenomenological theory.

[9]E–electronic, s–surface, single prime–one unpaired resonating electron.

[10]On the terminology and classification of centers see Ref. 133.

[11]The value of the g factor at the point of intersection of the derivative of an absorption line with the scan line of the magnetic field.

[12]Recently it was possible to detect the HFI of an electron with an adjacent ^{29}Si nucleus for such PCs in hydrogenated amorphous silicon.[234] This allows us to hope for detecting HFI in PCs belonging to powders of pure silicon, and thus, to advance in understanding the nature of this line. We also note in this regard Ref. 135.

[1]V. F. Kiselev and O. V. Krylov, *Adsorption Processes on Semiconductor and Dielectric Surfaces*, Springer-Verlag, Berlin, 1985 [Russ. original, Nauka, M., 1978]; Adsorption and Catalysis on Transition Metals and Their Oxides (in Russian), Khimiya, M., 1981.

[2]F. F. Vol'kenshtein, *Physical Chemistry of the Surface of Semiconductors* (in Russian), Nauka, M., 1973; S. Morrison, The Chemical Physics of Surfaces, Plenum Press, N.Y., 1977 [Russ. Transl., Mir, M., 1980].

[3]B. A. Nesterenko and O. V. Snitko, Physical Properties of the Atomically Clean Surface of Semiconductors (in Russian), Naukova Dumka, Kiev, 1983.

[4]V. I. Nefedov and V. T. Cherepin, *Physical Methods of Studying the Surface of Solids* (in Russian), Nauka, M., 1983.

[5]A. Ya. Belenkiĭ, Usp. Fiz. Nauk **134**, 125 (1981) [Sov. Phys. Usp. **24**, 412 (1981)]; M. V. Gomoyunova, *ibid.* **136**, 105 (1982). [Sov. Phys. Usp. **25**, 58 (1982)].

[6]E. P. Velikhov, Nauka i Zhizn', No. 11, 2 (1981); A. P. Aleksandrov, *Science to the Land* (in Russian), Nauka, M., 1983, p. 114; V. L. Ginzburg, Physics and Astrophysics. *A Selection of Key Problems*, Pergamon Press, Oxford, 1985 [Russ. original, Nauka, M., 1973, 1979 and 1985, p. 45].

[7]L. V. Keldysh, Priroda, No. 9, 17 (1985).

[8]S. A. Al'tshuler and B. M. Kozyrev, *Electron Paramagnetic Resonance in Compounds of Transition Elements*, Wiley, N.Y., 1974 [Russ. original, Nauka, M., 1972].

[9]A. Abragam and B. Bleaney, *Electron Paramagnetic Resoance of Transition Ions*, Clarendon Press, Oxford (1970) (Russ. Transl., Mir, M., Vol. 1, 1972; Vol. 2, 1973).

[10]A. B. Roĭtsin, *Some Applications of Symmetry Theory in Problems of Radiospectroscopy* (in Russian), Naukova Dumka, Kiev, 1973; Phys. Status Solidi B **104**, 11 (1981).

[11]M. D. Glinchuk, V. G. Grachev, M. F. Deĭgen, A. B. Roĭtsin, and L. A. Suslin, *Electrical Effects in Radiospectroscopy* (in Russian), Nauka, M., 1981.

[12]A. B. Roĭtsin, Usp. Fiz. Nauk **105**, 677 (1971) [Sov. Phys. Usp. **14**, 766 (1971)]; W. B. Mims, *The Linear Electric Field Effect in Paramagnetic Resonance*, Clarendon Press, Oxford, 1976 [Russ. transl., Naukova Dumka, Kiev, 1982].

[13]V. G. Grachev and M. F. Deĭgen, Usp. Fiz. Nauk **125**, 631 (1978) [Sov. Phys. Usp. **21**, 674 (1978)].

[14]M. L. Meĭl'man and M. I. Samoĭlovich, *Introduction to the EPR Spectroscopy of Activated Monocrystals* (in Russian), Atomizdat, M., 1977.

[15]C. P. Poole, *Electron Spin Resonance; A Comprehensive Treatise on Experimental Techniques*, Interscience, N.Y., 1967) (Russ. transl., Mir, M., 1970).

[16]V. B. Timofeev, Poverkhnost', No. 2, 145 (1984) [Phys. Chem. Mech. Surf. (1984)]; D. Haneman, Rep. Prog. Phys. **50**, 1045 (1987); N. S. Maslova and V. I. Panov, Usp. Fiz. Nauk **157**, 185 (1989) [Sov. Phys. Usp. **32**, 93 (1989)].

[17]M. V. Vlasova and K. G. Kakazeĭ, *EPR in Mechanically Damaged Solids* (in Russian), Naukova Dumka, Kiev, 1979; S. I. Rembeza, *Paramagnetic Resonance in Semiconductors* (in Russian), Metallurgiya, M., 1988.

[18]D. Haneman, Jpn. J. Appl. Phys. Suppl., Vol. 2, Part 2, 371 (1974); V. V. Anisimov, Poverkhnost', No. 9, 5 (1984) [Phys. Chem. Mech. Surf. (1984)]; E. H. Poindexter and P. J. Caplan. Prog. Surf. Sci. **14**, 201 (1983).

[19]G. M. Zhidomirov, Ya. S. Lebedev, S. N. Dobryakov, N. Ya. Shteĭnschneĭder, A. K. Chirkov, and V. A. Gubanov, *Interpretation of Complex EPR Spectra* (in Russian), Nauka, M., 1975; M. G. Blazha and A. B. Roĭtsin, Phys. Tverd. Tela (Leningrad) **14**, 501 (1972); **16** 514 (1974) [Sov. Phys. Solid State **14**, 416 (1972); **16** 327 (1974)]; Ya. G. Kyava, *EPR Spectroscopy of Disordered Solids* (in Russian), Zinatne, Riga, 1988.

[20]V. M. Maevskiĭ, N. I. Vitrikhovskiĭ, E. V. Mozdor, and A. B. Roĭtsin, Poverkhnost', No. 8, 88 (1983); No. 10, 73 (1986) [Phys. Chem. Mech. Surf. (1983,1986)].

[21]A. S. Belanovskiĭ, *Adsorption and Desorption at the Surface of Semiconductors* (in Russian), M., 1969 (Reviews on Electronic Technique, Ser. Microelectronics, No. 58 (127)).

[22]J. Higinbotham and D. Haneman, Surf. Sci. **34**, 450 (1973).

[23]D. Kaplan, D. Lepin, Y. Petroff, and P. Thirry, Phys. Rev. Lett. **35**, 1376 (1975).

[24]B. P. Lemke and D. Haneman, *ibid.*, p. 1379.

[25]I. A. Kirovskaya, *Surface Properties of Diamondlike Semiconductors: Adsorption of Gases* (in Russian), A. A. Zhdanov State University, Irkutsk, 1984.

[26]A. G. Petrova, A. V. Rakov, V. P. Yarygin, E. N. Ivanov, and Yu. I. Pashintsev, Fiz. Tekh. Poluprovodn. **5**, 1140 (1971) [Sov. Phys. Semicond. **5**, 1002 (1971).

[27]V. M. Maevskiĭ, N. I. Vitrikhovskiĭ, N. N. Kolycheva, E. V. Mozdor, and A. B. Roĭtsin, *Radiospectroscopy* (in Russian), A. M. Gor'kiĭ State University, Perm', 1985, p. 192; Poverkhnost', No. 1, 128 (1989) [Phys. Chem. Mech. Surf. (1989)].

[28]A. A. Romanyukha, A. P. Stepanov, and V. V. Ustinov, Fiz. Met. Metalloved. **56**, 484 (1983) [Phys. Met. Metallogr. (USSR) **56**(3), 58 (1983)].

[29]A. G. Petrova and A. V. Rakov, Fiz. Tekh. Poluprovodn. **4**, 697 (1970) [Sov. Phys. Semicond. **4**, 591 (1970)].

[30]B. G. Ignatov and A. L. Aleksandrov, Prib. Tekh. Eksp. No. 1, **91**, (1983) [Instrum. Exp. Tech. **26**(1), 97 (1983)].

[31]A. G. Revesz and B. Goldstein, Surf. Sci. **14**, 361 (1969).

[32]Y. Nishi, Jpn. J. Appl. Phys. **10**, 52 (1971).

[33]J. Szuber, B. Salamon, and B. Dlugosz, Phys. Status Solidi A **53**, 289 (1979); **55**, K35 (1979); **56**, 111 (1979).

[34]G. Mend and D. Haneman, J. Phys. C **13**, 6737 (1980); **11**, L197 (1978).

[35]D. Haneman, Prog. Surf. Sci. **15**, 85 (1984).

[36]L. S. Vlasenko and V. A. Khramtsov, Pis'ma Zh. Tekh. Fiz. **11**, 909 (1985) [Sov. Tech. Phys. Lett. **11**, 376 (1985)].

[37]W. A. Martin and G. Hartung, Phys. Status Solidi A **44**, K159 (1977).

[38]M. C. Chen and D. V. Lang, Phys. Rev. Lett. **51**, 427 (1983).

907   Sov. Phys. Usp. **32** (10), October 1989

A. B. Roĭtsin and V. M. Maevskiĭ   907

[39]D. V. Lang, J. Appl. Phys. **45**, 3023 (1974).

[40]Laser Magnetic Spectrometer RÉ 1310, NTO AN SSSR, M., 1984 (Information sheet).

[41]A. A. Bagaĭ and V. M. Maksimenko, Prib. Tekh. Eksp., No. 4, 146 (1972) [Instrum. Exp. Tech. **15**(4), 1141 (1972)].

[42]M. F. Chung and D. Haneman, J. Appl. Phys. **37**, 1879 (1966).

[43]D. Haneman, M. F. Chung, and A. Taloni, Phys. Rev. **170**, 719 (1968).

[44]T. T. Bykova and I. V. Vinokurov, Fiz. Tverd. Tela (Leningrad) **7**, 2597 (1965) [Sov. Phys. Solid State **7**, 2103 (1966)].

[45]S. Brunauér, *Adsorption of Gases and Vapors*, Vol. 1, IL, M., 1948.

[46]G. A. Bootsma and F. Meyer, Surf. Sci. **18**, 223 (1969).

[47]R. S. Alger, Electron Paramagnetic Resonance Techniques and Application, Wiley, N.Y., 1968.

[48]Yu. N. Molin, M. M. Chibrikin, V. A. Shabalkin, and V. F. Shuvalov, Zavod. Lab. **32**, 933 (1966) [Industr. Lab. **32**, 1150 (1966)].

[49]R. C. Fletcher, W. A. Yager, G. L. Pearson, A. N. Holden, W. T. Read, and F. R. Merrit, Phys. Rev. **94**, 1392 (1954).

[50]G. Feher, *ibid*. **114**, 1219 (1959).

[51]A. Taloni and W. J. Rogers, Surf. Sci. **19**, 371 (1970).

[52]K. A. Muller, P. Chan, R. Kleiner, D. W. Ovenall, and M. J. Sparnaay, J. Appl. Phys. **35**, 2254 (1964).

[53]P. Chan and A. Steinemann, Surf. Sci. **5**, 267 (1966).

[54]D. Haneman, Phys. Rev. **170**, 705 (1968).

[55]G. B. Demidovich and V. F. Kiselev, Vestn. Mosk. Univ. Fiz. Astron. **14**, No. 2, 158 (1973).

[56]H. Iwasaki and S. Nakamura, Surf. Sci. **81**, L627 (1979).

[57]M. V. Vlasova and N. G. Kazakei, Solid State Commun. **47**, 255 (1983).

[58]N. N. Gerasimenko, A. V. Dvurechenskiĭ, and L. S. Smirnov, Fiz. Tekh. Poluprovodn. **5**, 1700 (1971) [Sov. Phys. Semicond. **5**, 1487 (1972)].

[59]B. L. Crowder, R. S. Title, M. H. Brodsky, and G. D. Pettit, Appl. Phys. Lett. **16**, 205 (1970).

[60]N. N. Gerasimenko, A. V. Dvurechenskii, L. S. Smirnov, and E. G. Shirokov, Cryst. Lattice Defects **2**, 125 (1971).

[61]S. Hasegawa, K. Ichida, and T. Shimizu, Jpn. J. Appl. Phys. **12**, 1181 (1973).

[62]F. Morehead, B. L. Crowder, and R. S. Title, J. Appl. Phys. **43**, 1112 (1972).

[63]A. A. Bugaĭ, I. M. Zaritskiĭ, A. A. Konchits, and V. S. Lysenko, Fiz. Tverd. Tela (Leningrad) **26**, 1939 (1984) [Sov. Phys. Solid State **26**, 1176 (1984)].

[64]K. Murakami, K. Masuda, K. Gamo, and S. Namba, Jpn. J. Appl. Phys. **12**, 1307 (1973).

[65]K. L. Brower and W. Beezhold, J. Appl. Phys. **43**, 3499 (1972).

[66]J. Stuke, in *Proc. Sixth Intern. Conf. Amorphous and Liquid Semiconductors* Leningrad 1975 (in Russian), Nauka, L., 1976, p. 193.

[67]G. K. Walters and T. L. Estle, J. Appl. Phys. **32**, 1854 (1961).

[68]S. N. Karyagin, A. V. Petrov, and I. M. Shtan'ko, Fiz. Tekh. Poluprovodn. **17**, 1900 (1983) [Sov. Phys. Semicond. **17**, 1217 (1983)].

[69]M. H. Brodsky and R. S. Title, Phys. Rev. Lett. **23**, 581 (1969).

[70]M. H. Brodsky, R. S. Title, K. Weiser, and G. D. Pettit, *ibid*. B **1**, 2632 (1970).

[71]N. N. Gersimenko, A. V. Dvurechenskiĭ, and L. S. Smirnov, Fiz. Tekh. Poluprovodn. **6**, 987 (1972) [Sov. Phys. Semicond. **6**, 862 (1972)].

[72]S. Hasegawa and S. Yazaki, Thin Solid Films **55**, 15 (1978).

[73]P. A. Thomas and D. Kaplan, Structure and Excitation of Amorphous Solids, American Institute of Physics, N.Y., 1976, p. 85.

[74]U. Voget-Grote, J. Stuke, and H. Wagner, *ibid*., p. 91.

[75]M. H. Brodsky and R. S. Title, *ibid*., p. 97.

[76]B. P. Lemke and D. Haneman, Phys. Rev. B **17**, 1893 (1978).

[77]G. B. Demidovich, V. F. Kiselev, and O. V. Nikitina, Dokl. Akad. Nauk SSSR **205**, 383 (1972) [Dokl. Phys. Chem. **205**, 598 (1973)].

[78]G. B. Demidovich and V. F. Kiselev, Phys. Status Solidi B **50**, K33 (1972).

[79]T. Wada, T. Mizutani, M. Hirose, and T. Arizumi, J. Phys. Soc. Jpn. **22**, 1060 (1967).

[80]G. B. Demidovich, S. N. Karyagin, and V. F. Kiselev, Phys. Status Solidi B **114**, 705 (1982).

[81]M. F. Chung, J. Phys. Chem. Solids **32**, 475 (1971).

[82]V. M. Maevskiĭ, V. E. Primachenko, O. V. Snitko, and H. G. Frolova, Poverkhnost', No. 1, 101 (1983) [Phys. Chem. Mech. Surf. (1983)].

[83]B. P. Lemke and D. Haneman, Surf. Sci. **81**, L325 (1979).

[84]G. K. Walters, J. Phys. Chem. Solids **14**, 43 (1960).

[85]M. H. Brodsky, J. Vac. Sci. Technol. **8**, 125 (1971).

[86]B. Movaghar, L. Schweitzer, and H. Overhof, Philos. Mag. Ser. B **37**, 683 (1978).

[87]Z. Z. Ditina, L. P. Strakhov, and Kh. Kh. Khelmz, Fiz. Tekh. Poluprovodn. **2**, 1199 (1968) [Sov. Phys. Semicond. **2**, 1006 (1969)].

[88]J. C. Gourdon, P. Fretier, and J. Pescia, J. Phys. (Lett.) **42**, L21 (1981).

[89]D. J. Lepine, Phys. Rev. B **6**, 436 (1972).

[90]H. Kasumoto and M. Shoji, J. Phys. Soc. Jpn. **17**, 1678 (1962).

[91]W. E. Spear, *Proc. 5th Intern. Conference on Amorphous and Liquid Semiconductors*, eds. J. Stuke and W. Brenig, Garmisch, West Germany, Taylor and Francis, London, 1974, p. 1.

[92]V. S. Kuznetsov, G. B. Demidovich, and V. F. Kiselev, Vestn. Mosk. Univ. Fiz. Astron. **16**, No. 2, 177 (1975).

[93]D. K. Biegelsen, *Nuclear and Electron Research Spectroscopies Applied to Materials Science*, eds. E. N. Kaufman and G. K. Shenoy, Elsevier, North-Holland, Amsterdam, 1981, p. 85.

[94]D. J. Miller, D. L. Heron, and D. Haneman, J. Vac. Sci. Technol. **9**, 906 (1972).

[95]P. Chan, K. A. Müller, A. Steinemann, and M. J. Sparnay, Helv. Phys. Acta **37**, 629 (1974).

[96]P. Chan and A. Steinemann, *ibid*. **38**, 359 (1965).

[97]C. Fletcher and G. Feher, Bull. Am. Phys. Soc. Ser. II **1**, 125 (1956).

[98]D. J. Miller and D. Haneman, Surf. Sci. **19**, 45 (1970).

[99]D. J. Miller and D. Haneman, *ibid*. **24**, 639 (1971).

[100]Y. H. Lee, R. L. Kleinhenz, and J. W. Corbett, Appl. Phys. Lett. **31**, 142 (1977).

[101]S. N. Karyagin, P. K. Kashkarov, V. F. Kiselev, and A. V. Petrov, Poverkhnost', No. 2, 113 (1984) [Phys. Chem. Mech. Surf. (1984)].

[102]G. A. N. Connell and J. R. Pawlik, Phys. Rev. B **13**, 787 (1976).

[103]J. Higinbotham and D. Haneman, Surf. Sci. **19**, 39 (1970).

[104]V. D. Kazaritskiĭ, S. N. Kozlov, V. F. Kiselev, and Yu. F. Novototskiĭ-Vlasov, Dokl. Akad. Nauk SSSR **195**, 115 (1970) [Dokl. Phys. Chem. **195**, 834 (1970)].

[105]S. N. Kozlov, Yu. F. Novototskiĭ-Vlasov, V. F. Kiselev, and V. M. Sharapov, Fiz. Tekh. Poluprovodn. **4**, 356 (1970) [Sov. Phys. Semicond. **4**, 292 (1970)].

[106]A. Morimoto, T. Miura, M. Kumeda, and T. Shimizu, J. Appl. Phys. **53**, 7299 (1982).

[107]D. J. Miller and D. Haneman, Surf. Sci. **33**, 477 (1972).

[108]A. Morimoto, T. Miura, M. Kumeda, and T. Shimizu, Jpn. J. Appl. Phys. **20**, L833 (1981).

[109]V. F. Kiselev and O. V. Nikitina, Dokl. Akad. Nauk SSSR **171**, 374 (1966) [Dokl. Phys. Chem. **171**, 736 (1966)]; A. Katayama and H. Kita, Chem. Soc.–Faraday Trans. **74**, 1963 (1978).

[110]P. Yu. Butyagin, A. A. Berlin, A. É. Kalmanson, and L. A. Blyumenfel'd, Vysokomol. Soedin, **1**, 865 (1959).

[111]G. Hochstrasser and J. C. Courvoisier, Helv. Phys. Acta **39**, 189 (1966).

[112]A. Razzaq, S. A. Hogarth, and K. A. K. Lott, Phys. Status Solidi B **141**, K61 (1987).

[113]V. E. Istomin, S. M. Koroleva, M. Ya. Shcherbakova, and T. S. Yusupov, Poverkhnost', No. 1, 118 (1984) [Phys. Chem. Mech. Surf. (1984)]; I. V. Kolbanev and P. Yu. Butyagin, Zh. Fiz. Khim. **48**, 1158 (1974) [Russ. J. Phys. Chem. **48**, 670 (1974)].

[114]R. I. Mashkovtsev, M. Ya. Shcherbakova, N. M. Lemina, G. N. Gusev, and L. S. Shumskaya, *Molecular Spectroscopy and X-ray Diffraction of Minerals* (in Russian), Nauka, Novosibirsk, 1981, p. 149.

[115]W. Wintruff, R. Herrling, and H. J. Tiller, Chem. Phys. Lett. **38**, 524 (1976); H. P. Henning, G. Boden, I. Ebert, J. Jedamzik, H. Geissler, and V. Steinike, Z. Chem. **20**, 388 (1980).

[116]G. Hochstrasser and J. F. Antonini, Surf. Sci. **32**, 644 (1972).

[117]H. J. Tiller and G. Rudakoff, Chem. Phys. Lett. **62**, 313 (1979).

[118]O. Cozar, V. Znamirovschi, and M. Gridan, Rev. Roum. Phys. **27**, 389 (1982).

[119]O. Cozar and V. Znamirovschi, Czech. J. Phys. Ser. B **33**, 1357 (1983).

[120]V. B. Kazansky, G. B. Pariisky, and V. V. Voevodsky, Disc. Faraday Soc., No. 31, 203 (1961).

[121]V. A. Radtsig, Kinet. Katal. **20**, 1203, 1206 (1979).

[122]Yu. N. Molin and V. V. Voevodskiĭ, Zh. Tekh. Fiz. **28**, 143 (1958) [Sov. Phys. Tech. Phys. **3**, 125 (1958)]; F. J. Feigle, W. B. Fowler, and K. L. Yip, Solid State Commun. **14**, 225 (1974).

[123]D. L. Griscom and M. Stapelbroek, Phys. Rev. B **20**, 1823 (1979); D. L. Griscom and E. J. Friebele, Radiat. Eff. **65**, 63 (1982).

[124]J. E. Bennett, B. Mile, and A. Thomas, Trans. Faraday Soc. **61**, 2357 (1965).

[125]J. P. Borel, Helv. Phys. Acta **32**, 448 (1959).

[126]Y. Nishi, Jpn. J. Appl. Phys. **5**, 333 (1966).

[127]Y. Nishi, K. Tanaka, and A. Ohwada, *ibid*. **11**, 85 (1972).

[128]P. J. Caplan, J. N. Helbert, B. E. Wagner, and E. H. Poindexter, Surf. Sci. **54**, 33 (1976).

[129]P. J. Caplan, E. H. Poindexter, B. E. Deal, and R. R. Razouk, J. Appl. Phys. **52**, 879 (1981).

[130]N. M. Johnson, D. K. Biegelsen, and M. D. Moyer, J. Vac. Sci. Technol. **19**, 390 (1981); K. L. Brower, Phys. Rev. **33**, 4471 (1986); Appl. Phys. Lett. **53**, 508 (1988); A. Stesmans, *ibid*. **48**, 972 (1986); Appl. Surf. Sci. **30**, 134 (1987).

[131]P. J. Caplan and F. H. Poindexter, J. Appl. Phys. **52**, 522 (1981).

[132]C. Brunström and C. Svensson, Solid State Commun. **37**, 399 (1981).

[133]B. E. Deal, J. Electrochem. Soc. **127**, 979 (1980).

[134]K. L. Ngai and C. T. White, J. Appl. Phys. **52**, 320 (1981).

[135]K. L. Brower, Appl. Phys. Lett. **43**, 1111 (1983); W. E. Carlos *ibid.* **50**, 1450 (1987).

[136]R. W. Barton, J. Rous, S. A. Schwarz, and C. R. Helms, *The Physics of MOS Insulators*, Pergamon Press, N.Y., 1980, p. 316.

[137]D. Langbaïn and E. Shelonin, Fiz. Tekh. Poluprovodn. **18**, 808 (1984) [Sov. Phys. Semicond. **18**, 504 (1984)]; A. A. Bugaï, V. A. Giriï, V. M. Maksimenko, and V. I. Shakhovtsov, *ibid.* **15**, 164 (1981) [Sov. Phys. Semicond. **15**, 96 (1981)]; A. Stesmans and J. Braet, Surf. Sci. **172**, 398 (1986); A. Stesmans, Solid State Commun. **58**, 299 (1986).

[138]D. I. Kropman and L. E. Pern, Poverkhnost', No. 11, 84 (1984) [Phys. Chem. Mech. Surf. (1984)].

[139]J. Ruzyho, I. Shiota, N. Miyamoto, and J. Nishizawa, J. Electrochem. Soc. **123**, 26 (1976).

[140]D. Kropman, L. Pirn, A. Sügis, and M. Vinnal, Phys. Status Solidi A **44**, K1 (1977).

[141]G. Mendz and D. Haneman, Solid State Commun. **33**, 657 (1980).

[142]B. Henderson, Appl. Phys. Lett. **44**, 228 (1984).

[143]N. S. Karyagin and A. V. Kurganskiï, Vestn. Mosk. Univ. Ser. 3, **22**, No. 6, 69 (1981).

[144]P. J. Caplan and E. H. Poindexter, J. Appl. Phys. **53**, 541 (1982).

[145]C. Fiori and R. A. B. Devine, Phys. Rev. Lett. **52**, 2081 (1984).

[146]P. M. Lenahan and P. V. Dressendorfer, J. Appl. Phys. **54**, 1457 (1983).

[147]R. A. B. Devine, A. Golanski, and M. H. Debroux, *ibid.*, 3833, 4197; A. Stesmans, J. Braet, J. Witters, and R. F. Dekeersmaecker. Surf. Sci. **141**, 255 (1984).

[148]B. I. Vikhrev, N. N. Gerasimenko, and G. P. Lebedev, Mikroelektronika **6**, 71 (1977) [Sov. Microelectr. (1977)]; A. A. Bagaï, I. M. Zaritskiï, A. A. Konchits, M. M. Lokshin, and V. S. Lysenko, Fiz. Tverd. Tela (Leningrad) **25**, 3192 (1983) [Sov. Phys. Solid State **25**, 1842 (1983)].

[149]W. Gehlhoff and K. H. Segsa, Phys. Status Solidi B **18**, 703 (1983).

[150]K. Hoffmann and D. Hahn, Phys. Status Solidi A **24**, 637 (1974).

[151]G. K. Born, A. B. Hofstaetter, A. O. Scharmann, G. M. Arnett, R. L. Kroes, and V. E. Wegner, *ibid.* **4**, 675 (1971).

[152]J. Schneider and A. Päuber, Z. Naturforsch. **16a**, 712 (1961).

[153]G. K. Born, A. B. Hofstaetter, and A. O. Scharmann, Z. Phys. **240**, 163 (1970).

[154]K. M. Sancier, Surf. Sci. **21**, 1 (1970).

[155]J. P. Bonnelle and M. Guelton, *ibid.* **27**, 375 (1971).

[156]R. J. Kokes, J. Phys. Chem. **66**, 99 (1962).

[157]K. A. Müller and J. Schneider, Phys. Lett. **5**, 288 (1963).

[158]K. M. Sancier, J. Catal. **9**, 331 (1967).

[159]J. O. Cope and I. D. Campbell, J. Chem. Soc. Faraday Trans. **69**, 1 (1973).

[160]A. Hausmann, Z. Phys. **237**, 86 (1970).

[161]P. S. Kasai, Phys. Rev. **130**, 989 (1963).

[162]É. V. Baranov, V. E. Kholmogorov, and A. N. Terenin, Dokl. Akad. Nauk SSSR **146**, 125 (1962) [Dokl. Phys. Chem. **146**, 619 (1962)].

[163]M. Codell, H. Gisser, J. Weisberg, and R. D. Iyengar, J. Phys. Chem. **72**, 2460 (1968).

[164]N. G. Wong, Y. B. Taarit, and J. H. Lunsford, J. Chem. Phys. **60**, 2148 (1974).

[165]R. D. Iyengar, S. V. V. Rao, and A. C. Zettlemoyer, Surf. Sci. **13**, 251 (1969).

[166]Y. Fujita and J. Turkevich, Disc. Faraday Soc., No. 41, 407 (1966).

[167]A. J. Tench and T. Lawson, Chem. Phys. Lett. **8**, 177 (1971); M. Codell, J. Weisberg, H. Gisser, and R. D. Iyengar, J. Am. Chem. Soc. **91**, 7762 (1969).

[168]K. M. Sancier, J. Catal. **5**, 314 (1966).

[169]C. H. Geisler and G. L. Simmons, Phys. Lett. **11**, 111 (1964).

[170]K. M. Sancier and T. Freund, J. Catal. **3**, 293 (1964).

[171]R. D. Iyengar and S. V. V. Rao, J. Am. Chem. Soc. **90**, 3267 (1968).

[172]T. Matsuzaki, T. Uda, A. Kususaka, G. W. Keulks, and R. F. Howe, *ibid.* **102**, 7511 (1980).

[173]V. Ya. Lodin, V. E. Kholmogorov, and A. N. Terenin, Dokl. Akad. Nauk SSSR **160**, 1347 (1965) [Dokl. Phys. Chem. **160**, 173 (1965)].

[174]Yu. D. Pimenov, V. E. Kholmogorov, and A. N. Terenin, *ibid.* **163**, 935 (1965) [Dokl. Phys. Chem. **163**, 584 (1965)].

[175]J. H. Lunsford and J. P. Jayne, J. Chem. Phys. **44**, 1487 (1966).

[176]J. H. C. Van Hoof, J. Catal. **11**, 277 (1968).

[177]M. Sedaka and T. Kwan, Bull. Chem. Soc. Jpn. **38**, 1414 (1965).

[178]L. V. Lyashenko, Ya. B. Gorokhovatskiï, L. N. Ganyuk, and I. A. Ustinov, Teor. Eksp. Khim. **8**, 840 (1972) [Theor. Exp. Chem. **8**, 696 (1972)].

[179]T. Arisumi, T. Misutani, and K. Shimakawa, Jpn. J. Appl. Phys. **8**, 1411 (1969); Z. Z. Ditina, B. A. Kazenov, and L. P. Strakhov, Fiz. Tekh. Poluprovodn. **1**, 1730 (1967) [Sov. Phys. Semicond. **1**, 1434 (1968)].

[180]J. Higinbotham and D. Haneman, Surf. Sci. **37**, 466 (1972).

[181]Z. Z. Ditina and L. P. Strakhov, Vestn. Leningr. Univ. Fiz. Khim., No. 4, 129 (1971).

[182]Z. Z. Ditina and L. P. Strakhov, Fiz. Tverd. Tela (Leningrad) **8**, 3089 (1966); **9**, 2539 (1967) [Sov. Phys. Solid State **8**, 2466 (1967); **9**, 2000 (1968)].

[183]J. Kreissl and W. Gehlhoff, Phys. Status Solidi A **81**, 701 (1984).

[184]H. Kasai and Y. Otomo, J. Chem. Phys. **37**, 1263 (1962).

[185]A. Räuber and J. Schneider, Z. Naturforsch. Teil A **17**, 266 (1962); Solid State Commun. **5**, 779 (1967).

[186]J. A. Wertz, P. Auzins, R. A. Weeks, and R. H. Silsbee, Phys. Rev. **107**, 1537 (1957).

[187]R. L. Nelson and A. J. Tench, J. Chem. Phys. **40**, 2736 (1964).

[188]R. L. Nelson and A. J. Tench, Trans. Faraday Soc. **63**, 3039 (1967).

[189]R. L. Nelson, J. W. Hale, B. J. Harmsworth, and A. J. Tench, *ibid.* **64**, 2521 (1968).

[190]R. L. Nelson, A. J. Tench, and B. J. Harmsworth, *ibid.* **63**, 1427 (1967).

[191]J. H. Lunsford and J. P. Jayne, J. Phys. Chem. **70**, 3464 (1966).

[192]A. J. Tench and R. L. Nelson, J. Colloid Interface Sci. **26**, 364 (1968).

[193]N. B. Wong and J. H. Lunsford, J. Chem. Phys. **55**, 3007 (1971).

[194]D. D. Eley and M. A. Zammitt, J. Catal. **21**, 377 (1971).

[195]J. H. Lunsford and J. P. Jayne, J. Phys. Chem. **69**, 2182 (1965).

[196]J. H. Lunsford, *ibid.* **68**, 2312 (1964); M. Boudart, A. Delbowille, E. G. Derowane, V. Indovina, and A. B. Walters, J. Am. Chem. Soc. **94**, 6622 (1972).

[197]A. J. Tench and R. L. Nelson, J. Chem. Phys. **44**, 1714 (1966).

[198]M. Che, B. Shelimov, J. E. Kibblewhite, and A. J. Tench, Chem. Phys. Lett. **28**, 387 (1974).

[199]V. A. Shvets and V. B. Kazansky, J. Catal. **25**, 123 (1972).

[200]A. J. Tench, T. Lawson, and J. F. Kibblewhite, Chem. Soc. Faraday Trans. **1**, 1169 (1972).

[201]N. B. Wong and J. H. Lunsford, J. Chem. Phys. **56**, 2664 (1972).

[202]J. H. Lunsford and J. P. Jayne, *ibid.* **44**, 1492 (1966).

[203]J. H. Lunsford, J. Colloid Interface Sci. **26**, 355 (1968).

[204]J. H. Lunsford, J. Chem. Phys. **46**, 4347 (1967).

[205]A. J. Tench and R. L. Nelson, Trans. Faraday Soc. **63**, 2254 (1967).

[206]A. Yu. Loginov, S. V. Kostikov, N. Krush, and K. V. Topchieva, Vestn. Mosk. Univ. Khim. **20**, No. 3, 216 (1979).

[207]T. Mizutani, K. Shimakawa, and T. Arisumi, Jpn. J. Appl. Phys. **9**, 1478 (1970).

[208]D. J. Miller and D. Haneman, Phys. Rev. **3**, 2918 (1971).

[209]G. H. Stauss and J. J. Krebs, Phys. Lett. A **50**, 49 (1974).

[210]D. J. Miller and D. Haneman, *ibid.* **60**, 355 (1977); Surf. Sci. **82**, 102 (1979); J. Vac. Sci. Technol. **15**, 1267 (1978).

[211]B. F. Ormont, *Structures of Inorganic Substances* (in Russian), Gostekhizdat, M., L., 1950, p. 458.

[212]L. I. Burbulyavichyus, Yu. A. Zarif'yants, S. N. Karyagin, and V. F. Kiselev, Kinet. Katal. **14**, 1526 (1973).

[213]Yu. A. Zarif'yants, S. N. Karyagin, and V. F. Kiselev, Vestn. Mosk. Univ. Fiz. Astron. **16**, No. 2, 237 (1975).

[214]R. D. Iyengar, M. Codell, and J. Turkevich, J. Catal. **9**, 305 (1967).

[215]K. M. Sancier and S. R. Morrison, Surf. Sci. **83**, 29 (1979).

[216]A. I. Mashchenko, V. M. Sharapov, V. B. Kazanskiï, and V. F. Kiselev, Teor. Eksp. Khim. **1**, 381 (1965) [Theor. Exp. Chem. **1**, 247 (1965)]; R. D. Iyengar, M. Codell, J. S. Karra, and J. Turkevich, J. Am. Chem. Soc. **88**, 5055 (1966).

[217]P. F. Cornaz, J. H. C. van Hooff, F. J. Pluijm, and G. C. A. Schuit, *ibid.* p. 290.

[218]A. I. Mashchenko, V. B. Kazanskiï, G. B. Pariïskiï, and V. M. Sharapov, Kinet. Katal. **8**, 853 (1967).

[219]C. Naccache, P. Meriaudeau, M. Che, and A. J. Tench, Trans. Faraday Soc. **67**, 506 (1971).

[220]I. D. Mikheïkin, A. I. Mashchenko, and V. B. Kazanskiï, Kinet. Katal. **8**, 1363 (1967); Y. Kera and Y. Matsukaze, J. Phys. Chem. **90**, 5752 (1986).

[221]A. K. Selivanovskiï, V. B. Golubev, E. V. Lunina, and B. V. Strakhov, Zh. Fiz. Khim. **52**, 2811 (1978) [Russ. J. Phys. Chem. **52**, 1617 (1978)].

[222]D. D. Eley and M. A. Zammitt, J. Catal. **21**, 366 (1971).

[223]G. J. K. Acres, D. D. Eley, and J. M. Trillo, *ibid.* **4**, 12 (1965).

[224]V. Hronsky and M. Rakos, Czech. J. Phys. Ser. B **30**, 1061 (1980); **33**, 1347 (1983).

[225]V. B. Golubev, Yu. M. Boyarchuk, and V. B. Evdokimov, Zh. Fiz. Khim. **34**, 696 (1960) [Russ. J. Phys. Chem. **34**, (1960)].

[226]R. Deen, P. I. T. Scheltus, and G. Vries, J. Catal. **41**, 218 (1976); S. S. Ischenko, *Double Electron-Nuclear Resonance in Dielectric and Semiconductor Crystals: Abstract of Doctoral Dissertation in Physical-Mathematical Sciences*, (In Russian), Kiev, 1988.

[227]S. N. Karyagin, P. K. Kashkarov, V. F. Kiselev, and S. N. Kozlov,

909   Sov. Phys. Usp. **32** (10), October 1989

A. B. Roïtsin and V. M. Maevskiï   909

Phys. Status Solidi A **37**, K17 (1967).

[228]B. Y. Taarit and J. H. Lunsford, J. Phys. Chem. **77**, 780 (1973).

[229]Yu. A. Zarif'yants and V. V. Kurilev, Fiz. Tekh. Poluprovodn. **7**, 598 (1973) [Sov. Phys. Semicond. **7**, 414 (1973)].

[230]T. Shimizu, S. Oozora, A. Morimoto, M. Kumeda, and N. Ishii, Phys. Status Solidi B **119**, 715 (1983).

[231]H. C. Van Hooff and J. F. van Helden, J. Catal. **8**, 199 (1967).

[232]E. Trig and A. Nicula, Phys. Status Solidi B **133**, 683 (1986); L. E. Iton, C. M. Brodbeck, S. L. Suib, and G. D. Stucky, J. Chem. Phys. **79**, 1185 (1983); I. D. Mikheĭkin, G. M. Zhidomirov, and V. B. Kazanskiĭ, Usp. Khim. **41**, 909 (1972) [Russ. Chem. Rev. **41**, 468 (1972)].

[233]I. P. Beletskiĭ, Yu. I. Gorlov, and A. A. Chuĭko, Teor. Eksp. Khim. **16**, 273 (1980) [Theor. Exp. Chem. **16**, 229 (1980)]; V. E. Shubin, V. A. Shvets, and V. B. Kazanskiĭ, Kinet. Katal. **19**, 1270 (1978); R. A. Zhitnikov and D. P. Peregud, Fiz. Tverd. Tela (Leningrad) **22**, 1956 (1980) [Sov. Phys. Solid State **22**, 1141 (1980)].

[234]D. K. Biegelsen and M. Stutzmann, Phys. Rev. B **33**, 3006 (1986).

[235]M. D. Glinchuk and M. F. Deĭgen, Fiz. Tverd. Tela (Leningrad) **4**, 2521 (1962) [Sov. Phys. Solid State **4**, 1848 (1963)]; A. B. Roĭtsin, *ibid*. **4**, 2948 (1963) [Sov. Phys. Solid State **4**, 2161 (1963)].

[236]D. Kaplan and M. Pepper, Solid State Commun. **34**, 803 (1980); R. A. Street, Adv. Phys. **30**, 593 (1981); V. S. L'vov, O. V. Tret'yak, and I. A. Kolomiets, Fiz. Tekh. Poluprovodn. **11**, 1118 (1977) [Sov. Phys. Semicond. **11**, 661 (1977)].

[237]V. P. Gerdt, O. V. Tarasov, and D. V. Shirkov, Usp. Fiz. Nauk **130**, 113 (1980) [Sov. Phys. Usp. **23**, 59 (1980)].

[238]Kh. Dunken and V. Lygin, *Quantum Chemistry of Adsorption on the Surface of Solids*, Mir, M., 1980.

[239]V. I. Gorchakov and É. L. Nagaev, Poverkhnost', No. 5, 47 (1986); V. I. Gorchakov, *ibid*., No. 4, 24 (1988) [Phys. Chem. Mech. Surf. (1986) and (1988)].

Translated by M. V. King

910   Sov. Phys. Usp. **32** (10), October 1989

A. B. Roĭtsin and V. M. Maevskiĭ   910