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Effect of An Electric Field on the Thermal Decomposition of Solids

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Studies on the thermal decomposition of solids subjected to the influence of an electric field (EF) are analysed and the effect of the electric field on the rate of decomposition is considered. Attention is drawn to the likely usefulness of the electric field in the study and control of the rates of the thermal decomposition of solids.
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I. INTRODUCTION

Advances in solid state chemistry (SSC) depend in many ways[1] on the extent of which the theory and experimental techniques of solid state physics (SSP) have been applied to it. The principal difficulty here is associated with the specific features of the problems in solid state physics and chemistry, which require not only a systematic treatment but also an analysis of the achievements of physics in relation to problems in solid state chemistry. This review is devoted to a partial solution of this problem: the analysis and systematic treatment of the scope of the applications of the electric field (EF) as a research technique and a method for controlling the rate of the thermal decomposition of solids. We neglect the magnetic component of alternating electric fields, since it is too small to influence significantly the physicochemical processes in solids.

II. EXAMPLES OF THE EFFECT OF AN ELECTRIC FIELD ON THE DECOMPOSITION OF SOLIDS

The paper of Bel'kevich and Osinovik[2] is apparently the first publication concerning a study of the thermal decomposition of solids in an electric field. The authors investigated by a volumetric method the thermal decomposition of silver oxalate *in vacuo* in the temperature range 105 to 120°C. The specimens were prepared by pressing and were clamped between metallic electrodes. Although the strength of the steady electric field was low (of the order of 3–4 V cm^{-1}) a clear effect of the field on the decomposition process was observed. In the absence of the field the specimens did not explode after attaining the maximum rate of decomposition in the given temperature range, while in the presence of the field an explosion generally occurred. The authors believe that the explosion is not associated with the electric breakdown of the specimens at the instant of the mutual approach of the silver particles, although this does appear to be most likely. The present authors also investigated[3,4] the thermal decomposition of silver oxalate in a constant 80 V cm^{-1} electric field. Three series of experiments were performed: decomposition in the absence of a field; decomposition in a steady field, and decomposition in a periodically applied field. The specimens were heated continuously at a rate of 0.5 deg min^{-1} to 90°C in a vaccum of 10^{-3}–10^{-4} torr. The cell was then disconnected from the pumps, heating was continued, and the amount of carbon dioxide formed before the detonation of the specimen was measured. During the decomposition in the absence of a field, the specimens exploded at 143°C, in a periodically applied field the detonation occurred at 130°C, and in a constant field it occurred at 122°C. Thus the field accelerated the attainment of the maximum rate of thermal decomposition of the specimen at which silver oxalate exploded. Simple calculation of the heat of decomposition rules out the explanation of the observed phenomenon as due to the heating of the specimen by the current.

Bowden and coworkers[5,6] investigated the behaviour of silver azide single crystals between -100° and 50°C in steady and alternating electric fields. At room temperature in a steady electric field weaker than 250 V cm^{-1} the crystals clamped between silver electrodes did not explode, while in higher fields detonation was observed. Before the detonation the resistance of the specimens fell sharply to 10^4 Ω and the crystals exploded approximately 45 s afterwards. The field strength necessary for the explosion of silver azide increased appreciably with decrease of temperature. Thus, whereas at 50°C 19 V was needed for explosion, at -45°C 125 V was already required and at -100°C more than 400 V had to be applied. Calculations showed that approximately 10^{15} electrons per second entered the crystals before detonation and that this was sufficient to heat them to the detonation temperature. It was established that the decrease of the resistence of the crystals before detonation is not caused by the formation of silver dendrites penetrating the crystal. It was suggested that the decrease of the resistance and the detonation of silver azide are due to the injection of electrons from the electrodes in the presence of an electric field. It was also stated[6] that similar results were obtained by Evans and Yoffe for copper azide, and by Berthold for silver acetylide. Subsequently Savel'ev and coworkers[7–9] established that a steady electric field accelerates the thermal decomposition of silver, lead, and barium azides and of silver oxalate. Studies of the effect of the electric field on the rate of thermal decomposition of azides confirmed the conclusion reached earlier using the method of homophase additives. The electric field influenced only the induction period in the decomposition of silver oxalate.

Sukhushin et al.[10] investigated the behaviour of lead, silver, and thallium azides in a strong steady and a pulsed electric field. The azides were found to decompose in the electric field with formation of gaseous and solid products, which was explained by a discrete development of electron avalanches and their chemical effect. Related results were obtained in a study[11] where an unexpected phenomenon,

hindering the investigation of the ferroelectric properties of potassium nitrate in a constant electric field, was observed: after the application of a 1 kV cm^{-1} electric field, a 1 V e.m.f. appeared between the platinum electrodes, which slowly decreased with time and did not disappear even after the specimens had been short-circuited. It was suggested that the phenomenon is caused by the partial decomposition of potassium nitrate in the electric field into potassium ions, nitrogen dioxide, and molecular oxygen with formation of an electrochemical battery. Kabanov and Zharova[12] studied the thermal decomposition of $KMnO_4$ at 220°C in a constant 250 V cm^{-1} electric field and in the absence of a field. The electric field was applied periodically (for 15 s at 5 min intervals) throughout the entire decomposition period. The maximum rate of decomposition of $KMnO_4$ was reached at 54% decomposition in the absence of a field and at 64% decomposition of the preparation under the influence of the electric field. The rate of decomposition of $KMnO_4$ was influenced by the electric field in different ways during different periods. During the first 25 min, the electric field did not affect the rate of decomposition at all, but afterwards the thermal decomposition was accelerated. In the range between 50 and 70 min from the start of the decomposition the electric field stabilised the rate. In the absence of the field there was a smooth increase of the rate of decomposition up to the maximum.

The studies examined above indicate the possibility of a marked influence of the electric field on the decomposition of solids. A common disadvantage of the published investigations is their superficiality, the main aim being to establish merely that an electric field affects the rate of thermal decomposition and yet they permit the conclusion that this rate can be controlled with the aid of the electric field. To develop further and extend studies of this kind, it is necessary to analyse the possible ways in which the electric field influences the rate of thermal decomposition and a systematic treatment of the achievements of solid state physics in this field with an indication of the scope of their applications to solid state chemistry is needed.

III. WAYS IN WHICH AN ELECTRIC FIELD INFLUENCES THE RATE OF DECOMPOSITION OF SOLIDS

The rate of thermal decomposition of solids is greatly influenced[13,14] by point and linear defects and also by the composition of the atmosphere. On the other hand, they give rise to many physical and physicochemical phenomena, which constitutes the basis for considering the ways of which the electric field influences the rate of thermal decomposition solids.

1. Properties of Crystals Grown in an Electric Field

The structure and habit of crystals play[13] a major role in the kinetics of their thermal decomposition. Therefore, by altering the conditions governing the formation of the crystals, it is possible to alter the rate of their thermal decomposition. The study of the influence of the electric and magnetic fields on various physicochemical properties of growing crystals is receiving increasing attention[15–17], since this method of controlling the properties of crystals is more convenient than the method based on the introduction of impurities during crystallisation. It has been established that the electric field has a significant influence on the formation of crystal nuclei and on crystallisation kinetics. Although the problem has been little studied, it is possible to distinguish three possible ways in which the electric field influences the formation of crystals: 1. By the alteration of the properties of water[18–21] (in growing crystals from aqueous solutions) under the influence of a variable electric field in combination with its magnetic component. 2. By the effect of the electric field on the habit and structure of the crystals formed[22–35]. 3. By the electric field[20] initiating a chemical reaction between the solvent and solute, which leads to the entrainment of various impurities by the growing crystals.

The contactless method of applying an electric field to solutions (via glass, air, etc.) is more popular[21,23] than the contact method. It yields more reproducible properties of the grown crystals. When an electric field is applied to the test substances, various types of polarisation arise in the prenuclear groups of atoms: electronic, ionic, and dipole-orientation. The orientation of polar molecules in the field does not occur instantaneously, which promotes the formation of crystals with polar species. In an electric field the number of crystallisation centres initially increases rapidly and then the growth slows down and finally stops completely, reaching saturation. The orienting effect of the electric field frequently entails structural changes in the solvent, which makes it more difficult to understand the mechanism of the influence of the field on the crystallisation process. The nature of the changes in the rate of formation of crystallisation centres under the influence of a variable field depends on temperature[23].

Melent'ev and Kozlovskii[24] studied the effect of an electric field on the crystallisation of lead sulphide from the gas phase. Lead sulphide was vaporised at 850–900°C and, after precipitation on a quartz support, crystallised in a steady electric field. A 2–3 kV cm^{-1} field influences significantly the habit and properties of the growing crystals. For example, Mohs' hardness of the crystals is appreciably lower for specimens grown in the absence of a field; this is associated with the influence of the electric field on dislocation density. Steady and alternating electric fields in supercooled betol, salol, and piperine melts lower [25] the temperature of the onset of crystallisation. The rate of migration of the layers in spiral-laminar crystal growth[26,27] from the gas phase can increase in a steady electric field, which affects the density of the dislocations produced. A change in the structure and catalytic properties of Cu_2O formed in an electric field at 1040°C was observed by Stadnik and Kuznetsov[28], who explained it by the formation of an interstitial solid solution with an excess of copper ions or oxygen.

The influence of an electric field on the crystallisation of amorphous selenium has been observed[29–35] and a number of interesting facts have been established. Thus Geller et al.[29] noted that electric fields up to 10 kV cm^{-1} at mains frequency increase the number of spherolites at 50 to 90°C in selenium specimens with an admixture of bromine and accelerate their growth due to the polarising effect of the electric field on selenium molecules. In a 180 to 360 V cm^{-1} steady electric field the rate of crystallisation of selenium usually[30,31] increases and in higher fields begins to decrease. The growth of spherolites[32,33] under the influence of the electric field takes place usually (but not always) along the lines of force of the field, since the direction of growth depends on the material of the support. On a mica support preferential growth of spherolites in opposition to the lines of force of the electric field is observed, while on a carbon support the growth takes place along the lines of force. A similar result was obtained by Odobescu[34], who investigated the influence of a constant electric field on the kinetics of the crystallisation of selenium from the amorphous and liquid states in the temperature range 150–190°C. He established that the rate of crystallisation of selenium depends

on the direction of the electric field, which exhibits an orienting effect and facilitates the crystallisation process. Bolotova et al. [35] observed the effect of the exposure of liquid selenium to an electric field on its subsequent crystallisation. On cooling in air melts which were not in an electric field, crystals of selenium were not observed.

2. Effect of an Electric Field on Electronic and Ionic Processes

The thermal decomposition of solids is accompanied by different[1,13,14,36,37] electronic processes: the excitation of ions with formation of excitons, polarons, or free electrons and the migration of the local excitation of the crystal with charge transfer, or with energy transfer alone, or with recombination of the excited electrons, which can lead to luminescence in self-activating systems[38]. Apart from luminescence, the above processes give rise also to other physical phenomena: a change in the electronic and hole conductivity[1,12–14,36,37–39], a change in the concentration of the colour centres[13,14], and a change in magnetic properties[40]. Chemical transformations of the initial substances involving the dissociation of old and the formation of new chemical bonds take place simultaneously with physical processes, which implies[41] a redistribution of charges, the transition of electrons from one state to another, or quantum-mechanical resonance.

A common method for altering the concentration of free electrons in the surface region of crystals is that of heterophase additives, the influence of which is explained[42,43] by the transfer of electrons into the substance with a higher work function. We believe[44] that at least two other evident possibilities have been neglected here; chemical interaction of the additive with the substance undergoing decomposition and the influence of the solid decomposition products of the initial substance on the catalytic activity of the additive. As in the method of heterophase additives, the electric field alters the concentration of free electrons in the surface region without changing the structure of the solids. We shall analyse examples of the influence of the electric field on various physical phenomena, which depend on point (in the given case electronic) defects. (The influence of the field on luminescence will be analysed separately).

A strong electric field can alter the state of solids[40] from antiferromagnetic to ferromagnetic by generating conduction electrons. This method is better than the introduction of impurities (homophase additives), since it does not distort the crystal lattice, does not alter the chemical composition of the substance and the nature of the distribution of electron density, and finally makes it possible to control readily and reversibly the concentration of conductivity electrons. The electric field can cause the dissociation of excitons with a large radius, as a result of which the exciton absorption bands are broadened. For example, Thomas and Hopfield[45] observed that the absorption lines corresponding to large-radius excitons in the spectrum of cadmium sulphide are broadened and merge in a field as low as 500 V cm^{-1}. Gross and Zakharchenya[46] observed a similar effect in copper(I) oxide, but in a field of 9 kV cm^{-1}. The difference in field strengths is consistent with the dimensions of the excitons: the exciton radius in copper(I) oxide is smaller by a factor of 2 than the radius of the analogous excitons (on the basis of the absorption spectrum) in cadmium sulphide and their bonding energy is higher by a factor of approximately 4. Consequently, the ionisation of excitons in copper(I) oxide requires an approximately 8 times higher field than in cadmium sulphide. The experimental data are qualitatively consistent with this rough estimate.

Kucherov et al. [47] and Lyashenko[48] established that the electrical conductivity of cadmium sulphide[47] and antimony sulphide[48] increases with time when an electric field is applied. This has been explained by the diffusion of the impurities and of the adsorbed gases in the direction of the field of which diminishes the concentration of the capture centres for free electrons and holes. Subsequently Cox and Tredgold[49] and also Kunin et al. [50] observed a change in the electrical conductivity and colour of $SrTiO_3$ single crystals in an electric field at an elevated temperature. During the first 1–2 min, the electrical conductivity diminished by an order of magnitude and then reached a value higher than at the beginning. It is suggested that the initial decrease of conductivity is caused by ionic polarisation and the subsequent increase is due to the increase of the concentration of V-type colour centres, formed under the influence of the electric field and altering the colour of the crystals. A sharp change in electrical conductivity during the application of the electric field (electric ageing) has been observed also for rutile single crystals[51] at 300°C, which has been attributed to the formation of new donor centres (defects) in the crystal lattice and a transition from p-type conductivity to n-type conductivity.

It has been established[52–54] that the potential barrier $\Delta\varphi$ (the difference between the electron work functions) of the metal–dielectric couple can be decreased with the aid of the electric field not only as a result of the Schottky effect but also owing to the penetration of the electrodes by the external electric field. Then, for low strengths E of the external electric field the condition $\Delta\varphi \propto \sqrt{E}$ holds and at high field strengths we have $\Delta\varphi \propto E$. The effect observed by the authors may predominate over the Schottky effect in high electric fields. It is useful to know this phenomenon in the study of the thermal decomposition of substances with a high-resistance additive in electric fields. The effect[55] observed in β-carotene and selenium is no less interesting. A transverse constant electric field superimposed on a longitudinal constant electric field causes periodic oscillations in solids at very low frequencies. The period of the observed current oscillations is influenced significantly by the strength of the transverse field, the intensity and length of the monochromatic light, the temperature of the specimen, and the composition of the atmosphere. The authors put forward two interesting hypotheses to account for the phenomenon.
1. In certain regions of semiconductors and probability of the localisation of charge carriers (electrons and holes) may increase with increase of the field strength and local unstable regions with a variable resistance may appear.
2. The cause of the observed current oscillations may be the formation of bulk-phase charges. The external field then disturbs locally the equilibrium current carrier density.

On the other hand, the application of a pulsed electric field and of illumination by flashes of ultraviolet light to a silver bromide photographic emulsion[56] induces physicochemical processes associated with the generation of a symmetry in the photoproducts and a decrease of the lifetime of the light-generated electrons. The intensity of these processes depends on the strength and duration of the application of the electric field.

In a strong electric field the long-wavelength limit of the intrinsic optical absorption of semiconductors (λ_g) must shift[57,58] towards longer wavelengths (the Franz–Keldysh effect). This can be explained by a definite probability of the migration of electrons from the valence band to the forbidden levels by a tunnel mechanism under the influence of the electric field. In other words, in a strong electric field the interaction of electrons with photons having a large

momentum can generate electron-hole pairs owing to the transition of some of the valence electrons to forbidden energy levels. In consequence of this process, electrons appear in the semiconductor above the valence band and their excitation to the conduction band requires a lower photon energy than for the electrons in the valence band. For this reason, a shift of λ_g towards lower energies is observed. By definition λ_g corresponds to the minimum energy of photons required for the excitation of electrons from the valence band to the conduction band of the crystal. The shift of λ_g for the semiconductor is observed also from absorption spectra and reflection spectra in constant and alternating fields. Seraphin and Bottka[59] proposed an analytical method for the interpretation of the electro-reflectance effect in semiconductors. The Franz–Keldysh theory has been extended to the majority of the field-induced changes in absorption and reflection spectra. The authors showed that the shift of λ_g in the field is not always towards longer wavelengths but only when the edge of the absorption (or reflection) band is parabolic. When the edge of the main band is saddle-shaped, the shift of λ_g is towards shorter light wavelengths. In degenerate semiconductors[60] (a high concentration of free charge carriers is characteristic of these) the electric field can shift λ_g much more owing to the "heating" of the charge carriers than at a concentration of carriers far from degeneracy. This additional shift of λ_g under the conditions of the field in degenerate semiconductors is called[61] the Burnstein shift. For example, in InSb for $n = 10^{19}$ cm^{-3} and 300 K the shift of λ_g is 0.50 eV via the Burnstein mechanism and 0.18 eV for a non-degenerate state.

The Franz-Keldysh effect has been frequently confirmed experimentally[62-66] for both atomic semiconductors (germanium and silicon) and for more complex substances with polar bonds: sulphides, selenides, tellurides, arsenides, and other typical semiconductors. For example, Moss[62] and Kireev et al.[63] measured the shift of the absorption edge in GaAs, CdS, and CdTe spectra by a 5 kV cm^{-1} electric field. The authors indicate a satisfactory agreement between the calculated and experimental shifts of λ_g. A difference was observed between the results for films and single crystals. There has been an interesting study by Dneprovskii et al.[64], who observed a shift of the absorption band in the spectra of mixed crystals of CdS_xCdSe_{1-x} semiconductors at liquid nitrogen temperature in electrostatic fields up to 30 kV cm^{-1}. The shift of λ_g for $CdS_{0.5}CdSe_{0.5}$ amounts to 30 Å in a somewhat weaker electric field than for $CdS_{0.7}CdSe_{0.3}$ crystals, which the authors attribute to a steeper absorption spectrum of the specimen. The most complete study of the shift of the intrinsic absorption band of a ZnTe single crystal in 60 kV cm^{-1} electric fields was that of Strel'tsov and Freidin[65]. The shift of λ_g is 0.004 eV. The effective mass of charge carriers $m^* = 0.16m_0$ was calculated from the shift, the result being in good agreement with the data obtained in other investigations. The shift of the absorption edge towards longer wavelengths leads to a change[66] of the absorption coefficient of PbI_2 single crystals in a 2.85×10^5 V cm^{-1} variable electric field, which is probably the result of the influence of the field on the transitions of excitons to the ground state.

One cannot rule out the possibility that the Franz–Keldysh effect also operates in non-classical semiconductors, which may be investigated in solid state chemistry. The determination[67,68] of the effective mass of free electrons and holes from the Franz–Keldysh effect is most important and promising: the energy of the shift of the long-wavelength absorption limit λ_g is inversely proportional to the reduced effective mass of charge carriers. It is also possible to obtain information about the structure of the valence levels and the levels of the conduction band involved in the electronic transitions. Knowing the effective mass of the majority charge carriers, it is possible to calculate[69,70] (using additional data for the thermo-e.m.f. and electrical conductivity) the concentration and mobility of the free charge carriers, which are needed to analyse the electronic processes in the thermal decomposition of solids. In a field of the order of 10^5 V cm^{-1} the minimum shift (in terms of energy) for semiconductors amounts to hundredths of an electron-volt[67], greatly exceeding the possible Stark effect[71], which also shifts λ_g. The method for the determination of the effective mass of charge carriers with the aid of the Franz–Keldysh effect is much simpler and no less accurate than the method of cyclotron resonance[72], which is the classical procedure.

While chemical bonds are redistributed by electronic processes, ionic processes are responsible for the transfer and redistribution of mass in the decomposition of solids. The ionic processes underlying[13,14] the formation and growth of the nuclei of the new phase are much slower than the electronic processes and for this reason they often constitute the rate-limiting stages in the thermal decomposition of solids. Naturally, the electric field, influencing the diffusion coefficient and mobility of ions, will influence also the thermal decomposition of solids. We shall analyse examples of this effect.

Geguzin and Solunskii[73] observed an effect of a constant 100 V cm^{-1} electric field on the kinetics of the development of diffusional porosity in alkali metal halide crystals at 650° C. It was suggested that the electric field, influencing the directed diffusion of charged vacancies, influences also the pore-formation process. Together with this phenomenon, the constant electric field can affect the phase composition of solid solutions. Thus Freimanis et al.[74] established that in ceramic specimens of barium niobate there exist two ferroelectric phases with orthorhombic and tetragonal symmetry. A 20–90 kV cm^{-1} electric field gives rise to phase transitions between the orthorhombic and tetragonal symmetry or conversely, depending on the orientation of the crystals. The magnitude of the effect depends on the field strength and the energy state of the specimens. The influence of the heat treatment of the specimens on electrical ageing has been studied by Harwood[75] for rutile. He established that the greatest changes in electrical conductivity occur when the field is applied along the *c* axis regardless of the direction in which the crystals are grown. It was suggested that the impairment of the dielectric properties of rutile as electrical ageing progresses is due to the drift of certain ions under the influence of the applied electric field. This experiment is important for the investigation of the anisotropy of the thermal decomposition of ionic crystals. The problem of the effect of the electric field on the alloying process is no less urgent in practice. Pavlienko et al.[76] observed that the rate of alloying of silicon by boron from the gas phase depends on the electric field, which causes an additional ionisation of boron at high temperatures in the gap between the electrodes and, when a positive potential is applied to the electrode, causes an accelerated diffusion of boron to silicon. The tracer atom technique makes it possible to investigate the rate of self-diffusion of various ions on the natural cleavage surfaces of single crystals in an electric field. Thus, it has been shown[77] that a field oriented along the surface of an NaCl single crystal can alter the rate of self-diffusion of sodium and chloride ions. On the other hand, a field oriented at right angles to the surface can influence the amount of the

"pumping away" of these ions, diffusing on the surface, into the bulk of the crystal.

The thermal decomposition of certain ionic salts, for example permanganates[78,79], is accompanied by intense cracking and atomisation of the crystals. The results of a study by Kononov et al.[80], who investigated the dust carried away from a fluidised bed furnace in the presence of an electric field in the working space of a reactor, are of interest for the investigation of the decomposition of such substances, with and without additives, in an electric field. The field reduced the amount of dust removed by a factor of 3–5 and caused the coagulation of dust particles whose size was between 40 and 80 μm.

The effect of the electric field on the physicochemical properties of silver bromide under illumination has been studied[81-83]. Although the aim was to investigate photolysis, the observation that the field influences ionic processes is useful also for the investigation of such processes in thermal decomposition. For example, Klein and Matejec[81] studied the formation and growth of silver nuclei on silver halide microcrystals (grains). When the silver halide grain is irradiated in a strong stationary field (of the order of 10 kV cm^{-1}) by ultraviolet light pulses lasting 10^{-2}–10^{-3} s, it is possible to accumulate photoelectrons on the anodic side and interstitial ions on the cathodic side, without the complete disappearance of these charge carriers in the remaining parts of the grain. As a result, better conditions are created on both the cathodic and anodic sides of the grain for the formation of nuclei compared with the rest of the grain. The formation of negative centres on pulsed illumination of a photographic emulsion based on silver bromide under the conditions of a pulsed electric field has been observed by Hamilton and Bready[82], who proposed a method for calculating the cationic conductivity. At room temperature the calculation yielded a conductivity differing only by an order of magnitude from the experimental value for silver bromide single crystals. The bulk-phase diffusion of cationic vacancies, arising in the photochemical decomposition, was also observed for the single crystals[83]. A semi-transparent metallic layer was deposited on the one side of the single crystal and a continuous silver layer, obtained by evaporation *in vacuo*, was deposited on the other side. The light intensity decreased by a factor e at a depth of 1.5 μm, but, owing to the electric field, a dark reaction took place on the other side of the single crystal, which resulted in a gradual increase of transparency of the silver layer and its final disappearance. This study was apparently the first in which the bulk-phase diffusion of cationic vacancies was observed experimentally. The problem of the diffusion of ions in an electric field is no less important. Thus, Arnikar and Chaure[84] studied the influence of γ-radiation and of the electric field on the diffusion of the tracer ions $^{45}Ca^{2+}$, $^{90}Sr^{2+}$, and $^{133}Ba^{2+}$ through calcite. The application of a 27–100 V cm^{-1} electric field increased the diffusion coefficients of all three ions in the direction of the field as well as in the opposite direction. This effect was explained by an increase in the probability of the diffusional jumps of the ions in the electric field. The authors' studies are of fundamental importance, since an increase of the rate of diffusion had not been observed previously in similar experiments[85,86] and an impression had been created that the electric field cannot influence the diffusion coefficients of ions.

All these observations are valuable and interesting for the development of a method for electrophysical studies on the thermal decomposition of solids in an electric field.

3. Influence of the Electric Field on Dislocations

The influence of dislocations on the rate of thermal decomposition of solids is well known[13,87,88]. The decomposition of solids usually begins from the surface at the point of emergence of dislocations and extends throughout the bulk of the substance. It is therefore necessary to know the influence of the external field on the behaviour of dislocations in solids. Sproull[89] investigated elastic deformation effects, arising as a result of the application of an electric field, in lithium fluoride crystals bent at 220°C. He established that the dislocations in lithium fluoride are charged and can migrate over distances which are not susceptible to measurement, and that a considerable proportion of the mechanical strain is electrostatic in nature. The migration of the dislocations caused by the electric field in lithium fluoride crystals reaches a maximum in the course of a fraction of a second. The excess of dislocations of the same sign in cubic NaCl type crystals can actually disturb the symmetry and can make the crystal anisotropic, which is extremely interesting for the investigation of the electrophysical properties and decomposition of crystals. The migration of dislocations under the influence of a steady electric field of up to 15 kV cm^{-1} leads to a decrease in the optical transmission by sodium chloride[90] at a wavelength of 220 nm. A strong electric field also intensifies the absorption of light in this optical region. The migration of charged dislocations in an 8 kV cm^{-1} electric field has been observed by following the migration of etching figures under the microscope in studies by Zagoruiko[91] and Shvidkovskii et al.[92] The minimum field in which the migration of dislocations was observed was found to have a strength of 2 kV cm^{-1}. It was suggested that the migration of dislocations is caused by electrostriction, by the direct action of electrical forces on the charged dislocation, or by the joint influence of both factors. Using a similar technique, Zuev and Turchinovich[93] studied the migration of dislocations in lithium fluoride crystals under the conditions of a constant electric field. The authors suggest that the electric field lowers the potential barrier to the thermal liberation of dislocations from fixation centres. The influence of the electric field on the structural changes in such solids has been studied by Trap and Stevels[94]. The authors observed in certain chalcogenide glasses a transition to two states with different electrical conductivities when the electric field was altered. The conductivities of these states can differ by many orders of magnitude (up to 7). The transition of the glasses from one state to the other took place in a period of about 10^{-6} s. Since the conductivities of solids are related solely to the concentration of charges and their mobility, it is easily understood that the electric field alters sharply in this case the conditions governing the occurrence of ionic and electronic processes.

4. Influence of the Electric Field on Luminescence

The initial stage in the thermal decomposition of solids may be accompanied by luminescence[38]. Despite the great possibilities which arise from the application of luminescence measurements, this method has not so far been used in the experimental techniques of solid state chemistry. We are not aware of any study of the thermal decomposition of solids employing the luminescence phenomenon. In investigations of the photolysis of solids there are examples of the use of luminescence measurement which are of interest also for the study of thermal decomposition. For example, Belous and Chibisov[95] used luminescence measurements to

study the photolysis of silver chloride. They established that, depending on their size, the silver nuclei can serve as traps for both electrons and holes. The hole traps are usually aggregates consisting of several atoms with precolloidal and colloidal degrees of dispersion. The thermal decomposition may be accompanied by luminescence in the following cases: 1. The thermal excitation of complex anions of self-activated[38,96] inorganic compounds, which usually contain transition metals with a partly filled 3*d* orbital. 2. The thermal decomposition of substances with homophase additives, which can serve as luminescence centres. 3. The thermal decomposition of substances in different gases, whose absorption may be accompanied by luminescence[97].

In view of the likely usefulness of luminescence measurements in the study of the mechanism of thermal decomposition, it is desirable to analyse the ways in which the electric field influences the luminescence process in solids. The electric field can be a source of a specific type of luminescence of solids — electroluminescence. Electroluminescence is observed when steady and alternating electric fields of several kV cm^{-1} are applied. The brightness of the glow then depends on the field strength, the field frequency, and the duration of application of the field. It is particularly characteristic of alternating electric fields. A few crystalline phosphors are capable of electroluminescence, but the mechanism of the generation of the glow has been by no means fully studied. Afanas'eva and Mikho[98] observed the electroluminescence of a microcrystalline alumina powder using a transparent electrode. The brightness of the luminescence is related exponentially to the exciting potential, which agrees well with the concept of an inhomogeneous distribution of the field in the specimen. The threshold potential for the occurrence of the electroluminescence of ZnCdS discs was reduced[99] when the specimens were irradiated with light in the spectral region corresponding to the excitation of the intrinsic or impurity photoconduction. In this way a relation was established between the electroluminescence and photoconductivity of the specimens. Electroluminescence was observed also in powdered tantalum pentoxide[100] on excitation by potential П-pulses lasting 2×10^{-3}–3×10^{-2} s. The hypothesis of an inhomogeneous distribution of the electric field in the specimens made it possible to explain the shape of the curves describing the development of the luminescence. The electroluminescence of cadmium selenide single crystals, arising on excitation by variable 5–25 kV cm^{-1} electric fields, was studied by Ivanchenko[101]. The electric field caused appreciable heating of the crystals and the electroluminescence was observed at a high temperature. It was noted that the free electrons generated in the electric field and to some extent thermal electrons pass from the conduction zone to ionised acceptor levels. Assuming that the luminescence is excited by the electrons displaced by the field, Henich[102] and Curevich[103] proposed a mechanism of the electroluminescence of ZnS with an admixture of copper and chlorine. The holes formed in this process are localised at the luminescence centres and the electrons are displaced from the excitation region and are captured by traps.

Apart from initiating electroluminescence, the electric field can also influence[104–109] the intensity of other types of luminescence: thermoluminescence photoluminescence, and radioluminescence. For example, this has been established for Cu_2O, ZnS, and alkali metal halide crystals with additives. Thus Peka[104,105] observed an effect of constant electric fields up to 10^6 V cm^{-1} on the photoluminescence of copper(I) oxide. The magnitude of the effect depended on the treatment of the surface, the strength and sign of the electric field, the surrounding gas, and the wavelength of the light exciting the luminescence. The author explains this dependence by a change in the conditions governing the annihilation of excitons with the depth of screening on the Cu_2O surface. Busca et al.[106] determined the temperature variation of the effect of the electric field on the thermoluminescence of ZnS with copper additives. It is suggested that the electric field influences the capture of electrons by recombination centres, which consist of copper atoms, and this alters the intensity of the thermoluminescence. The influence of the electric field on the X-ray luminescence of phosphors based on KI–Tl at low excitation intensities is contradictory[107]. At the instant of application of the field the glow is quenched, but after a time it is intensified. This complex behaviour of the luminescence is difficult to interpret, although the most likely mechanism of the increase of the luminescence intensity is a reduction by the electric field of the radiationless recombinations outside the luminescence centres. The results obtained by Denks[108] for alkali metal iodides activated by thallium are close to those of Pologrudov and Penzina[107], but in this case the electric field resulted merely in an instantaneous decrease in the intensity of the thallium luminescence without a subsequent increase in intensity. The influence of the electric field on radioluminescence and thermoluminescence has been studied most completely by Volkov et al.[109] in alkali metal halide scintillators. Both positive and negative effects of electric fields up to 50 kV cm^{-1} were observed. Various experimental findings enabled the authors to conclude that the effect of the electric field on radioluminescence and thermoluminescence reduces to a redistribution of the probabilities of radiative and radiationless processes. It follows from the studies quoted above that the most likely mechanism of the influence of the electric field on the intensity of the luminescence of solids is a shift of the cloud of quasifree electrons in the electric field, which reduces their concentration in the glowing region of the crystalline phosphor and diminishes the number of radiative recombinations. The influence of the electric field on luminescence can be used to study the recombination of electrons on the surface of crystals.

The possibility that an electric field quenches the photoluminescence, thermoluminescence, and radioluminescence of zinc sulphide with admixtures of copper and chlorine and also of alkali metal halide crystals has been studied[110–115]. Thus Vereshchagin et al.[110] observed the quenching of the luminescence of ZnS powder with an admixture of copper in constant and pulsed fields of the same polarity. The variable electric field led to a brief change in the brightness of the photoluminescence. Several possible mechanisms have been proposed for the quenching of photoluminescence: (1) in the region of electroluminescence the electric field accelerates free electrons: (2) weak electric fields cause the migration of holes, liberated from the emission centres by heat or light, to quenching centres; (3) strong electric fields ionise the luminescence centres.

The quenching by the electric field of the photoluminescence of a powdered ZnS phosphor with an admixture of chlorine[111] occurs differently with light corresponding to different spectral bands. It is suggested that the luminescence bands are caused by various luminescence centres differing from one another in their energy structure. The mechanism of the quenching of the photoluminescence is believed to involve the thermoelectric saturation of the luminescence centres by electrons ionised on photoexcitation. However, a similar mechanism can lead to an increased intensity of the photoluminescence due to the electric field when the electronic levels of the activator in the crystalline phosphor are above the middle of the forbidden gap. Andrianov and

Bogacheva[112] reviewed studies on the effect of the electric field on the thermoluminescence of activated zinc sulphide and noted three possible mechanisms for the quenching of the luminescence: (1) the field accelerates free electrons and holes; (2) the field displaces the charges to sites of radiationless transitions; (3) the field alters the potential barrier to the thermal liberation of the electrons and holes localised after excitation.

Denks et al.[113] and Grigor'ev et al.[114] applied the mechanism of the quenching of the ZnS luminescence in an electric field to alkali metal halide scintillators with an admixture of thallium, where a 10^5 V cm^{-1} electric field weakened the photoscintillation by 25%. The quenching of the luminescence of alkali metal halide crystalline phosphors by the electric field is of a general type and the authors believe it to be related to the separating effect of the field, which prevents the recombination of electrons and holes. An example of the quenching of the thermoluminescence of alkali metal halide crystals doped with thallium and indium by a 50 kV cm^{-1} electric field is provided by the study of Grigor'ev et al.[115] The field intensified the thermoluminescence after prolonged application and quenched it after brief application. The observed intensification of the thermoluminescence was attributed by the authors to the decrease in the potential barrier to the autolocalised holes.

5. Phase Transition in the Electric Field

Phase transitions are usually accompanied[116,117] by anomalies in the temperature dependence of the rate of decomposition and conductivity under the conditions for investigating the mechanism of the thermal decomposition of the material. To develop electrophysical methods[1] for the investigation of the thermal decomposition of solids, it is necessary to know how the electric field affects their phase transitions.

A semiconductor–metal phase transition has been observed in a number of transition metal oxides, such as vanadium oxides, and has been explained by the instability of the electronic excitation system[118–120]. Owing to the intense electron-phonon interaction, the crystal lattice of the oxide is then rearranged. Andreev et al.[121] observed a sharp jump in the conductivity of V_2O_5 (an increase by 5 orders of magnitude) in a 10^4 V cm^{-1} field, which indicated the appearance of metallic conduction. The electric field shifts the temperature of the phase transition. The thermal effect and the Poole effect do not then play a significant role. It has been suggested that the increase of conductivity is caused by the decrease of the width of the forbidden gap due to the piezoelectric effect, which is the main cause of the semiconductor–metal phase transition. Valiev et al.[122] observed a similar phase transition under the influence of the electric field in another crystalline vanadium oxide (VO_2) at $T < T_c$ (T_c is the temperature of the VO_2 phase transition). The authors attribute the phase transition to a change in the lattice parameters in the electric field (the reverse piezoelectric effect). The influence of the electric field on the ferroelectric phase transition in barium metatitanate has been studied[123] and a change in the phase transition temperature in the electric field has been demonstrated. The same problem was investigated by Zarembskaya et al.[124] in a study of the influence of a constant electric field on the temperature of the phase transition in triglycine fluoroberyllate. The ferroelectric phase transition was recorded on the basis of a maximum in the dielectric constant measured at a frequency of 1 kHz in the temperature range 40–90°C. The application of the electric field decreased the dielectric constant of triglycine fluoroberyllate and shifted the ferroelectric phase transition to higher temperatures.

6. Adsorption in the Electric Field

The thermal decomposition of solids is frequently carried out in different vapours and gases: for example, in water vapour[125,126], in ammonia vapour[127], in oxygen[128], and in carbon dioxide[129]. Such studies are performed either to establish an effect of different components of the atmosphere on the decompositon kinetics, or to investigate the autocatalytic influence of the gaseous decomposition products of the initial substance, or to investigate the electronic stages of the decomposition process. In view of this and also bearing in mind the development of electrophysical methods[1] for the investigation of the thermal decomposition of solids, it is necessary to formulate clearly the specific influence of the electric field on the adsorption of gases.

The Fermi level can be regarded[130] as the regulator of the chemisorption properties of the semiconductor surface. The position of the Fermi level fixes the concentration of the electron and hole gas on the semiconductor surface. The surface and bulk phase of the semiconductor have a common Fermi level at equilibrium. The chemisorption of gases entails the charging[130,131] of the semiconductor surface, which causes the bending of the energy bands at the surface. This alters the position of the Fermi level in the energy spectrum of the crystal on the surface compared with the bulk phase. Factors which shift the Fermi level in the bulk of the crystal (which corresponds to a change in conductivity) shift it also on the surface, altering the catalytic activity of the semiconductor. However, under certain conditions[130] the position of the Fermi level on the crystal surface is independent of its position in the bulk phase (the case of a quasi-isolated surface).

Vol'kenshtein and coworkers[130,132–134] predicted theoretically the possible changes in the electronic properties of the surfaces of semiconductors under the influence of the electric field. If a semiconductor plate is placed between the plates of a planar air condenser, then a positive charge will be induced on one side of the semiconductor and a negative charge on the other. The semiconductor as a whole remains electrically neutral, but the adsorption capacity of its sides is altered. Vol'kenshtein's theoretical predictions have been frequently confirmed experimentally. For example, Stadnik and coworkers[135–140] demonstrated the influence of a constant electric field on the rate of liberation of various products of heterogeneous catalytic reactions, one of the stages of which is adsorption. For instance, studies have been made on the oxidation of the propane–butane mixture in the presence of platinum with formation of peroxides, aldehydes, and acids, the oxidation of methanol to formaldehyde on zinc oxide and a zinc oxide (60%)–copper(II) oxide (40%) mixture, the oxidation of various alcohols on silver, and the oxidation of sulphur dioxide to the trioxide on a platinum catalyst. The field can influence only the electronic stages of heterogeneous catalytic reactions and therefore its influence on the rate of reaction leads to the converse conclusion that electronic processes take place and play a significant role in the given heterogenous process. In the examples quoted the catalysts are metals. This does not contradict the previous conclusions reached for semiconductors, since the catalytic activity of metals is due to the presence of a very thin layer of oxides, which are semiconductors[130,141].

The gas–solid interaction, which frequently accompanies thermal decomposition, gives rise to the adsorption phenomenon. The adsorption of gases alters[142] various electrophysical parameters of the surface of solids, primarily their conductivity. A decrease of the concentration of charge carriers as a result of chemisorption at the points of contact between the particles in "sintered" specimens can give rise[131] to "blocking" layers due to the migration of the gas along the pores. These layers cause a particularly marked change in the conductivity of semiconductors. The adsorbed gas species can themselves behave as electron donors and acceptors if they react with the solid. The activation energy for chemisorption on semiconductors is in most cases considerable. The adsorbed gas molecules charge the semiconductor surface[130] and a potential difference, the value of which can be very high, is established between the surface and the bulk phase. For example, in the chemisorption of oxygen on zinc oxide[131] a 10^6 V cm^{-1} field is established between the surface and the bulk phase. The impurity ions can diffuse into the bulk phase under the influence of the electric field. The surface potential can be altered by the field effect and adsorption methods. Under certain conditions, both effects can operate simultaneously. Thus in very high fields and in measurements in a high vacuum the adsorption—desorption equilibrium can be displaced by the electric field, i.e. electroadsorption and electrodesorption is possible. In measurements in a vacuum of the order of 10^{-5}–10^{-6} torr, for a field strength less than 10^6 V cm^{-1}, the electroadsorption effect does not influence the field effect[142]. Unfortunately the electrodesorption effect has so far been studied only on classical semiconductors.

Flitner[143] investigated the effect of the field on germanium under the condition of the adsorption of oxygen, ozone, and water vapour. He established that ozone increases the number of fast states. Slow energy states arise on the surface of germanium in the adsorption of oxygen. A moist atmosphere influences the fast states, but does not alter the charge of the slow states. The author believes that this indicates the formation of germanium oxide on the germanium surface. Lyashenko and coworkers[144,145] observed the influence of the electric field on the desorption of gases from a germanium film. The resistance of the film increased following the desorption of gases. It is interesting that an increase of gas pressure in the system was observed only after the first application of the electric field. When the desorbed gas is evacuated, a repeated application of the field within the same limits does not alter the gas pressure. However, after the readsorption of the gas the electrodesorption process is again observed. The change of pressure in the system and of the resistance of germanium are due to the same cause—the change in the surface charge of the semiconductor. The gas contained hydrogen, hydrocarbons (oil from the pump), nitrogen, and nitric oxide. Mainly nitrogen was electrodesorbed. In the case of a negative potential on germanium this phenomenon was not observed. The external field reduced the negative charge on the surface of germanium, which led to the desorption of the gas. The electrodesorption effect was not observed on germanium films with a thickness greater than the screening radius. The studies by Mikheeva and Keier[146–148], who investigated the influence of a constant transverse electric field on the chemisorption properties of *n*-type germanium in relation to methanol and oxygen, constitute a logical continuation of studies on the adsorption capacity of germanium in the electric field. The field, leading to an increase in the surface potential, which is positive on germanium, and to an upward bending of the bands), resulted in the appearance of charged chemisorbed methanol species. In the absence of the field under these conditions (at 27°C and a pressure of 10^{-2} torr) methanol was not adsorbed. It was established that a transverse electric field disturbs the electronic equilibrium between the surface and bulk-phase bands. After the application of this field, the equilibrium between the surface and the bulk phase was restored in 1.5 to 2.0 h. When a field is applied, there is a possibility of side effects associated with the ionisation, polarisation, and orientation of the molecules in the gas phase. Therefore measurements must be made at a pressure of the order of 10^{-2}–10^{-3} torr. It was also established that the change in the adsorption properties of germanium in the electric field is caused by the change in the position of the Fermi level and the filling of the surface energy levels with electrons. The influence of the field on the adsorption of oxygen was observed only following the application of a negative potential to germanium, which decreases the electron work function. By measuring the relaxation of the conductivity of germanium when the field was switched on and off *in vacuo* and in an atmosphere of oxygen, it was shown that oxygen does not form new acceptor centres and that adsorption takes place on the existing surface acceptor centres. It was suggested that the active adsorption centres on germaium are slow donor states for methanol and slow acceptor states for the adsorption of oxygen. It was concluded that the adsorption properties of semiconductors are determined by the chemical state of the surface and the presence of active adsorption centres. Similar studies on the effect of a steady electric field on the adsorption of CO_2 were carried out by Ivankiv and coworkers[149,150] using thin tellurium films. Electrodes (silver, aquadag) for the measurement of the resistance were located along the edges of the film and a field electrode was placed on the other side of the support. Simultaneously measurements were made of the CO_2 pressure, and of the film resistance. The experiment on the electrodesorption of CO_2 from the tellurium film was performed in a vacuum of 5×10^{-9} torr in a 10^5 V cm^{-1} field. Under these conditions, with a positive potential on the semiconductor, CO_2 was electrodesorbed. At a negative potential a slight adsorption of CO_2 was observed on the film. The same workers[151,152] investigated the adsorption of oxygen and water vapour in an electric field on epitaxial β-HgS films with *n*-type conductivity. The adsorption was investigated on the basis of the changes in film conductivity. The application of a positive potential to the film increased the degree of adsorption of donor molecule and decreased the degree of adsorption of acceptor molecules, while at a negative potential the opposite effect was observed. The removal of the field restored the conductivity of the previous value owing to intense chemisorption on certain sections of the film. It was concluded that the chemisorption of oxygen on mercury sulphide is enhanced following the application of the electric field.

The conductivity of potassium permanganate single crystals has been investigated in water and ethanol vapours[153]. Single crystals, clamped between graphite electrodes, were alternately placed in desiccators [sic] containing water or alcohol and in a desiccator with phosphorus pentoxide. A 100 V cm^{-1} electrostatic field acted constantly or was applied periodically (at the instant of measurement of the conductivity). As potassium permanganate was made moist under the conditions of a briefly applied field, its conductivity steadily increased, tending to saturation. On the other hand in a steady field the conductivity passed through a maximum after the first moistening process. Due to the repeated drying and treatment of the crystals in water

and ethanol vapours, residual effects appeared in the changes of the conductivity of the single crystals, which were accounted for by the influence of the field on the chemisorption of the polar vapours.

7. The Change in the Properties of the Surfaces of Solids under the Influence of the Electric Field.

Since the thermal decomposition of solids begins as a rule from the surface[13,14], the state of the surface plays a major role in the development of the decomposition process. There is usually a complete system of discrete and continuously distributed energy levels on the surface of crystals[142,154–159], which may have different origins. These may be Tamm levels, arising on the surface as the result of the termination of the crystal lattice, and also energy levels associated with impurities or due to surface defects in the crystal lattice. Finally surface levels may be associated with the adsorption of molecules from the surrounding gas. The local energy levels on the surface and the associated surface charge lead to the bending of the energy bands near the surface, which is reflected in a significant change of the electron field work function and photoelectric and other properties. Often the state of the surface largely determines the course of the physical processes associated with the bulk phase of the crystal. Thus the surface levels can behave as recombination centres and can influence the lifetime of the non-equilibrium charge carriers in the specimen. Owing to the presence of the potential "well" near the semiconductor surface, the migration of the charge carriers in the surface region differs significantly from their migration in the bulk phase. This leads to a change in the mobility of the carriers owing to the additional scattering of the electrons and holes on the surfaces. The change in the energy state of the surface is attributed to a change in a particular surface parameter of the substance—the surface potential φ_S. This quantity can be determined as the difference between the potential energy of the electrons in the bulk phase and on the surface of the crystal. There are many experimental methods for the measurement of the surface potential, the most convenient of which is the field effect method.

The field effect is characteristic of semiconducting substances and consists in a change of the conductivity of the semiconductor following the application of a potential difference at right angles to its surface (and to the direction of the current). The field effect was first observed on copper(I) oxide by Schockley and Pearson[154]. It can be interpreted as follows. If one assembles a condenser one plate of which consists of the specimen and the other of a metal, using an intervening layer of an insulator with a high dielectric constant, and an electric field is applied to the condenser, then a space charge is created near the semiconductor surface, neutralising the charge on the metallic plate. Thus Lashkarev and Lyashenko[155] continued the study of the field effect on copper(I) oxide and defined rigorously the semiconductor surface as a layer with a thickness equal to the free path of the charge carriers. The surface charge constitutes an obstacle to the imposition of an external electric field on the semiconductor. If a negative potential is applied to the metallic plate of the condenser, the semiconductor plate becomes positively charged. This charge is localised in the bulk phase and on the surface of the semiconductor and the neutrality of the latter is disturbed, the energy bands being bent upwards relative to the Fermi level. The decrease of the degree of filling of the surface level by electrons (which corresponds to an upward bending of the bands) leads to the appearance of an additional surface charge, i.e. to the screening of the external field. As a result of the field effect, the electron work function of thin layers of copper(I) oxide is greater than that of thick layers by 0.13–0.15 eV. Thus a considerable proportion of the charge induced by the electric field is captured[142,155–157] by the surface states and the bulk phase of the semiconductor is electrically neutral. If the metallic plate is positively charged, a negative charge is induced on the surface of the semiconductor and the surface region of the bulk phase of the conductor is positively charged. The thickness of the layer screening the external charge in the semiconductor is inversely proportional to the square root of the equilibrium concentration of its charge carriers outside the limits of the space charge. The bulk-phase charge carriers near the surface contribute to the conductivity of the specimen, in contrast to the stationary carriers in the surface energy levels[158]. By measuring the resistance of the specimen along the surface layer for different electric field strengths, it is possible to determine the change in conductivity associated with the applied field. To increase the accuracy of the measurements, the specimen should be made fairly thin, so that the change in the surface resistance constitutes an appreciable proportion of the total resistance of the specimen. The field effect can be investigated[158] in steady and alternating fields at frequencies up to 10^8 Hz. In an alternating field the degree of screening of the surface from the bulk phase is reduced at higher frequencies, and it becomes constant from 10^3 Hz up to 10^7 Hz. The thickness of the charged region near the surface of semiconductors is usually[159] of the order of 10^{-4}–10^{-6} cm and the mobility of the charge carriers in this layer depends on the thickness of the semiconductor. When the field effect method is used to measure the surface potential, the density of the surface states does not change, in contrast to the absorption method. When a transverse electric field is switched on, an induced charge is initially created at the surface and then equilibrium is established between the conduction band, the valence band, and the fast surface states with a time constant of 10^{-7}–10^{-4} s, as a result of diffusion, capture, and recombination. After this, an equilibrium degree of filling of slow surface states is established during a period from several seconds to 1 h. Ultimately the concentration of surface levels remains unchanged during the measurements and only the degree of their filling is altered. A continuous variation of the surface potential within fairly wide limits up to the minimum in the surface conductivity of the crystal can be readily achieved by the field effect method.

The type of surface conductivity and the relation between the degree of bending of the bands and the applied potential can be determined, the charge in the region near the surface can be discovered, and the mechanism of the surface recombination of charge carriers can be investigated by measuring the field effect under steady-state conditions[142,160–166]. Finally the field effect method makes it possible to determine whether or not the energy spectrum of the surface levels is continuous or discrete and their concentrations and energy positions can be determined. The study of the kinetics of the field effect (non-steady-state case) makes it possible to calculate the relaxation time of the surface levels and to elucidate the mechanism of the exchange of charge carriers between the bands in the bulk phase and the surface energy levels. A theory of the field effect has been devised for band semiconductors, but, as shown by Sandomirskii and Pyasta[160], it is applicable also to

polaron semiconductors with jump conductivity. In particular potassium permanganate, a classical system in solid state chemistry, is a polaron semiconductor[37]. The field effect has been observed[166] also in organic semiconductors. Thus Petrova and Rozenshtein[166] observed the field effect in a number of organic semiconductor films obtained by vacuum sublimation. The authors determined the sign of the conductivity of the test substances and observed the enrichment and depletion of the specimens in charge carriers under the influence of the electric field. It was concluded that slow states are characteristic of organic semiconductors. Consequently the type of chemical bond in solids does not play a decisive role in the manifestation of the field effect.

Measurement of the field effect using an alternating current yields information about the time characteristics of the surface traps, which measurements with a direct current fail to do. Whereas the field effects measured using a direct current are frequently masked by slow states, with an alternating current they are clearly manifested. Mathematical treatment of the frequency characteristics of the field effect yields quantitative data on the distribution of surface states with different time constants. Frolov et al.[167], who studied the influence of the thickness of silicon oxide on the field effect in silicon, observed a correlation between the thickness of the surface oxide layer and the concentration of surface electronic states in etched silicon specimens. It was shown that the nature of the fast surface states is determined by the structural defects at the semiconductor–oxide boundary. By studying the relation between the surface conductivity of silicon and the strength of a variable transverse field, Einspruch[168] showed that, under the experimental conditions, most of the charge induced by the field is captures by surface layers. Esaki et al.[169] studied the influence of the field effect on the conductivity of the contact layer in germanium–gallium arsenide heterojunctions. The mobilities found in the contact layer proved to be constant for fields in the range 2×10^4–5×10^5 V cm^{-1}. This case permits a simple investigation of the surface conductivity of semiconductors. The field effect in a high-resistance zinc oxide powder mixed with a silicone resin[170] showed that its magnitude and time constant in such specimens depend more on the associated charges than on the free charges, in contrast to low-resistance semiconductors. The rate of recombination of free electrons and the concentration of electron traps were calculated from the change in photoconductivity as a function of the transverse electric field.

Using the classical method[171] for the investigation of the field effect on zinc oxide single crystals, it was established that the surface potential of zinc oxide is negative and the specific conductance of the specimen increases rapidly with increase of the applied potential. It has been suggested that there are acceptor oxygen levels on the surface of zinc oxide to which electrons are withdrawn from the region of the bulk phase near the surface under the influence of the field. As a result, the layer of the bulk phase near the surface is depleted in electrons and their concentration on the surface increases. At a high concentration the acceptor levels on the surface of the ZnO crystals may be split off[172] as a band, which leads to an increase in the surface conductivity with increasing electric field strength. The bulk-phase specific conductance of the specimen then diminishes. For anisotropic semiconductor crystals[173], the relation between the transverse and longitudinal alternating currents is linear. This makes it possible to control the current in anisotropic semiconductors.

A steady influence of a constant electric field on surfaces has been established in a number of studies.[174–176] Thus Costa and Murphy[174] observed a persistent internal polarisation of a sulphur single crystal due to the operation of the electric field, the removal of which requires the application of external energy. It was established that the relation between this energy and the decrease of the polarisation is exponential. In amorphous selenium the phenomenon of residual polarisation, which decays exponentially as a function of time, was observed by Nasledov and Malyshev[175]. The mechanism of this phenomenon has not so far been elucidated, although it has been stated that the electrons get "stuck" within or on the surface of selenium. CdS single crystals placed between the plates of a charged condenser are quasineutral[176]. However, owing to the inhomogeneous bulk-phase conductivity of CdS, the charges are polarised and the polarisation may persist for a long time. It is suggested that in a strong electric field there is an injection of electrons at the cathode and not a limitation of the space charge.

The problem of the preparation of specimens for thermal decomposition is no less urgent. Ziman[177] reviewed studies on methods for the elimination of solid impurity particles from surfaces by the application of a high steady electric field. The initial specimen is earthed and exposed to the field via an air gap. The material of the field electrode does not affect the degree of purification of the dust-covered surface of solids. It is suggested that the dust particles are removed as a result of their becoming charged in the electric field. An electrical interaction then arises between the particles and the electrode, which tends to abstract the particles from the support.

In studies on the electrophysical properties of semiconductors and dielectrics attempts are made to carry out measurements in the region where Ohm's law holds. This is done to eliminate side effects: contact resistances and the Poole effect. However, it is not always possible to avoid the side effects and it is necessary to formulate clearly the influence of the field on these effects. The Poole effect[178,179] can be observed only for high-resistance substances in fields of 10^3–10^4 V cm^{-1}. The electrical breakdown of a layer of dielectric thicker than 10^{-5} cm occurs in fields of $(1–5) \times 10^6$ V cm^{-1}, which increase with decrease of the thickness. As the field increases, there is a rise in the concentration of charge carriers and not an increase of mobility[179]. Injection of charge carriers from the electrodes is one of the causes of the Poole effect, consisting in a rapid increase of the current with potential, which follows from Ohm's law. The knowledge of the relation between the field effect and the properties of the point contact is no less important in experimental studies. Nesmelova[180] stated that near the point contact the electric field has both normal and tangential components in relation to the surface. The presence of the normal component leads to the bending of the energy bands, similarly to the field effect, and hence to a change in the conductivity of the specimen. Then the dependence of the conductivity of the specimen on the applied potential should be minimal. Guerci and coworkers[181,182] observed the influence of a steady transverse electric field on the lag of the photocurrent in CdS crystals behind the instant when light is switched on. This lag was proportional to the electric field applied at right angles. They suggested that the transverse field disturbed the ohmicity of the contact and consequently reduced the current through a cadmium sulphide crystal. The same field induced oscillations in the photocurrent within the specimen, which made it possible to separate the surface and bulk-phase components of the photoconductivity.

Thus the study of the field effect yields important information about the electronic processes on the surfaces of solids, which can be used to understand the influence of the field on the development of the decomposition process.

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The examples analysed leave no doubt about the great but hitherto incompletely utilised scope of the electric field as the foundation of a method for the investigation of the mechanism of thermal decomposition and as a procedure for stimulating the thermal decomposition of solids. Electrophysical studies of the thermal decomposition of solids constitute an effective means of comprehending the essential physical nature of the elementary stages in the decomposition reactions and the mechanisms of the electronic and ionic processes whereby the initial substance is converted into the reaction products. These problems constitute the corner stone of solid state chemistry.

REFERENCES

1. A. A. Kabanov, Uspekhi Khim., 40, 2029 (1971).
2. P. I. Bel'kevich and E. S. Osinovik, Izv. Akad. Nauk Beloruss. SSR, No. 5, 149 (1955).
3. A. A. Kabanov, Candidate's Thesis, Tomsk State University, Tomsk, 1967.
4. Yu. A. Zakharov, A. A. Kabanov, and A. M. Trubitsyn, Izv. Vys. Ucheb. Zaved., Khim i Khim. Tekhnol., 8, 529 (1965).
5. F. Bowden and A. McLaren, Proc. Roy. Soc., A246, 197 (1958).
6. F. P. Bowden and A. D. Yoffe, "Fast Reactions in Solids" (Translated into Russian), Inostr. Lit., Moscow, 1962, p.162.
7. G. G. Savel'ev, Yu. A. Zakharov, and V. V. Spitsa, Izv. Tomsk. Politekh. Inst., 151, 32 (1966).
8. G. G. Savel'ev and V. P. Greben', Izv. Vys. Ucheb. Zaved., Ser. Fiz., No. 3, 38 (1967).
9. Yu. A. Zakharov and G. G. Savel'ev, Izv. Tomsk. Politek. Inst., 176, 35 (1969).
10. Yu. N. Sukhushin et al., Khim. Vys. Energii, 7, 261 (1973).
11. Ishibashi Yoshihiro et al., Japan J. Appl. Phys., 8, 812 (1969).
12. A. A. Kabanov and L. A. Zharova, Zhur. Fiz. Khim., 49, 719 (1975) [Russ. J. Phys. Chem., No. 3 (1975)].
13. V. V. Boldyrev, "Vliyanie Defektov Kristallov na Skorost' Termicheskogo Razlozheniya Tverdykh Veshchestv" (The Influence of Crystal Defects on the Rate of Thermal Decomposition of Solids), Izv. Tomsk. Gos. Univ., Tomsk, 1963, pp.87–225.
14. D. A. Young "Decomposition of Solids" (Translated into Russian), Izd. Mir, Moscow, 1969, pp.194–253.
15. H. E. Buckley, "Crystal Growth" (Translated into Russian), Inostr. Lit., Moscow, 1954, pp.20–38.
16. E. V. Khamskii, "Kristallizatsiya iz Rastvorov" (Crystallisation from Solutions), Izd. Nauka, Leningrad, 1967, pp.89, 90.
17. E. V. Khamskii, Symposium, "Kristallizatsiya i Svoistva Kristallicheskikh Veshchestv" (Crystallisation and the Properties of Crystalline Substances), Izv. Nauka Leningrad, 1967. p.9.
18. G. Piccardi, "The Problem of Relationship between Special and Terrestrial Phenomena Chemical tests, Publicazioni dell Instituti Nazional de Offica, ser. IV, 1961, p.344.
19. V. L. Chernobai, Symposium, "Kristallizatsiya i Svoistva Kristallicheskikh Veshchestv" (Crystallisation and the Properties of Crystalline Substances), Izd. Nauka, Leningrad, 1967, p.57.
20. M. Jose Lima-de-Faria, Compt. rend., 233, 252 (1951).
21. I. N. Plaksin, Dokl. Akad. Nauk SSSR, 168, 152 (1966).
22. L. T. Prishchepa, Symposium, "Mekhanizm i Kinetika Kristallizatsii" (The Mechanism and Kinetics of Crystallisation) (Edited by N. N. Sirota), Izd. Nauka i Tekhnika, Minsk, 1969, p.375.
23. L. T. Prishchepa, Symposium, "Mekhanizm i Kinetika Kristallizatsii" (The Mechanism and Kinetics of Crystallisation) (Edited by N. N. Sirota), Izd. Nauka i Tekhnika, Minsk, 1969, p.380.
24. I. I. Melent'ev and M. I. Kozlovskii, Symposium, "Mekhanizm i Kinetika Kristallizatsii" (The Mechanism and Kinetics of Crystallisation) (Edited by N. N. Sirota), Izd. Nauka i Tekhnika, Minsk, 1969, p.341.
25. B. I. Soldatov, Symposium, "Mekhanizm i Kinetika Kristallizatsii" (The Mechanism and Kinetics of Crystallisation) (Edited by N. N. Sirota), Izd. Nauka i Tekhnika, Minsk, 1969, p.333.
26. M. I. Kozlovskii, Kristallografiya, 12, 1099 (1967).
27. M. I. Kozlovskii, Doctoral Thesis, The State University, Kishinev, 1967.
28. P. M. Stadnik and S. T. Kuznetsov, Ukrain. Khim. Zhur., 36, 1117 (1970).
29. I. Kh. Geller et al., Izv. Akad. Nauk SSSR, Neorg. Materialy, 8, 1005 (1972).
30. G. B. Abdulaev, A. I. Odobesku, and A. Yu. Kon, Kristallografiya, 14, 1108 (1969).
31. G. B. Abdulaev et al., Izv. Vys. Ucheb. Zaved, Ser. Fiz., No. 10, 117 (1970).
32. S. A. Belan, I. E. Bolotova, and L. I. Komarova, Symposium, "Nekotorye Voprosy Sferolitnoi Kristallizatsii" (Some Problems of Spherolitic Crystallisation), Izv. Inst. Narodnogo Khozyaistva, Sverdlovsk, 1970, p.16.
33. S. A. Belan et al., Izv. Vys. Ucheb. Zaved., Ser. Fiz., No. 6, 106 (1971).
34. A. I. Odobesku, "Sbornik Trudov Molodykh Uchenykh Kishinevskogo Politekhnicheskogo Institute" (Collected Papers by Young Scientists at the Kishinev Polytechnic Institute), Izv. Akad. Nauk Mold. SSR, Kishinev, 1969, p.128.
35. I. E. Bolotova, G. N. Kleptsova, and L. I. Komarova, Symposium, "Nekotorye Voprosy Sferolitnoi Kristallizatsii" (Some Problems of Spherolitic Crystallisation), Izv. Inst. Narodnogo Khozyaistva, Sverdlovsk, 1970, p.25.
36. V. V. Boldyrev, and A. A. Kabanov et al., Zhur. Fiz. Khim., 41, 1783 (1967) [Russ. J. Phys. Chem., No. 7 (1967)].
37. A. A. Kabanov, Izv. Akad. Nauk SSSR, Neorg. Materialy, 7, 26 (1971).
38. A. A. Kabanov, E. M. Zingel', L. A. Zharova, and T. G. Chutchikova, "Vliyanie Predystorii Preparata na Skorost' Termicheskogo Razlozheniya $KMnO_4$" (Influence of the Previous History of the Preparation on the Rate of Thermal Decomposition of $KMnO_4$), VINITI, No.2661–74 (Dep. from 10th October, 1974).
39. A. A. Kabanov, "Elektrofizicheskie Svoistva $KMnO_4$" (Electrophysical Properties of $KMnO_4$), VINITI, No. 2158–74 (Dep. from 1st August, 1974).

40. A. A. Berdyshev, Fiz. Tverd. Tela, 8, 1382 (1966).
41. G. M. Shvab, Uspekhi Khim., 36, 1660 (1967) [Russ. Chem. Rev., No. 9 (1967)].
42. V. F. Komarov, A. A. Kabanov, and V. T. Shipatov, Kinetika i Kataliz, 8, 550 (1967).
43. Yu. A. Zakharov, Candidate's Thesis, Tomsk Polytechnic Institute, Tomsk, 1963.
44. A. A. Kababov and S. V. Degtyareva, Kinetika i Kataliz, 16, No. 1 (1975).
45. R. S. Knox, "Theory of Excitons" (Translated into Russian), Izd. Mir, Moscow, 1966, p 83.
46. E. F. Gross and B. P. Zakharchenya, Zhur. Tekh. Fiz., 28, 231 (1958).
47. I. Ya. Kucherov et al., Fiz. Tverd. Tela, 4, 1376 (1962).
48. V. I. Lyashenko, Ukrain. Fiz. Zhur., 6, 202 (1961).
49. G. Cox and R. Tredgold, Brit. J. Appl. Phys., 16, 427 (1965).
50. V. Ya. Kunin, A. N. Tsykin, and N. A. Shturbina, Fiz. Tverd. Tela, 11, 749 (1969).
51. V. V. Kunin et al., Fiz. Tverd. Tela, 5, 2771 (1963).
52. J. Simmons, Phys. Letters, 16, 233 (1965).
53. F. Ullman, J. Appl. Phys., 35, 265 (1964).
54. C. Mead, E. Snow, and B. Deal, Appl. Phys. Letters, 9, 53 (1966).
55. A. Madjid et al., Phys. Status Solidi, 3, 209 (1970).
56. J. Hamilton and L. Bready, J. Appl. Phys., 30, 1902 (1959).
57. W. Franz, Z. Naturforsch., 13A, 484 (1958).
58. L. V. Keldysh, Zhur. Eksper. Teor. Fiz., 34, 962 (1958).
59. B. Seraphin and N. Bottka, Phys. Rev., 145, 628 (1966).
60. M. Shur, Phys. Letters, 29A, 490 (1969).
61. E. Burstein, Phys. Rev., 93, 632 (1954).
62. T. Moss, J. Appl. Phys., 32, 2136 (1961).
63. P. S. Kireev et al., Fiz. Tverd. Tela., 7, 1271 (1965).
64. V. S. Dneprovskii and V. I. Parygin, Vestnik Moskov. Gos. Univ., Ser. Fiz. i. Astr., No. 3 128 (1966).
65. L. N. Strel'tsov and M. M. Freidin, Izv. Akad. Nauk SSSR, Neorg. Materialy, 4, 990 (1968).
66. P. I. Petrov, L. A. Avdeev, and M. I. Elinson, Fiz. Tverd. Tela, 11, 541 (1969).
67. V. S. Vavilov, "Deistvie Izluchenii na Poluprovodniki" (The Effect of Radiation on Semiconductors), Fizmatgiz, Moscow, 1963, pp.27–32.
68. E. Gitsche and H. Lange, "Phys. semiconduct. Compt. rend., 7, Congr. internat., Paris", Dunod, 1964, p.129.
69. A. A. Kabanov, Izv. Tomsk. Politekh. Inst., 199, 20 (1969).
70. A. A. Kabanov, A. M. Trubitsyn, and G. I. Kurdanov, "Trudy Tomskogo Institute Radioelektroniki i Elektronnoi Tekhniki" (Transactions of the Tomsk Institute of Radioelectronics and Electronic Engineering), 1967, Vol.5, p.91.
71. V. A. Gadzhiev et al., Fiz. Tverd. Tela, 12, 1350 (1970).
72. R. H. Bube, "Photoconductivity of Solids" (Translated into Russian), Inostr. Lit., Moscow, 1962, p.251.
73. Ya. E. Geguzin and V. I. Solunskii, Dokl. Akad. Nauk SSSR, 156, 644 (1964).
74. V. Freimanis et al., Izv. Akad. Nauk SSSR, Ser. Fiz., 35, 1976 (1971).
75. M. Harwood, Brit. J. Appl. Phys., 16, 1493 (1965).
76. A. N. Pavlienko, D. A. Sechenov, and Yu. D. Chistyakov, Izv. Akad. Nauk SSSR, Neorg. Materialy, 7, 1253 (1971).
77. Ya. E. Geguzin, Yu. S. Kaganovskii, and A. A. Rivlin, Symposium, "Poverkhnostnaya Diffuziya i Rastekanie" (Surface Diffusion and Spreading) (Edited by Ya. E. Geguzin), Izd. Nauka, Moscow, 1969, p.91.
78. E. Prout and F. Tompkins, Trans. Faraday Soc., 40, 488 (1944).
79. P. Herley and E. Prout, J. Inorg. Nuclear Chem., 16, 16 (1960).
80. N. G. Kononov, T. M. Gordon et al., Tsvetnye Metally, No. 1, 31 (1968).
81. E. Klein and R. Matejec, Z. Elektrochem., 63, 883 (1959).
82. J. Hamilton and L. Bready, J. Appl. Phys., 30, 1893 (1959).
83. F. Hamm, J. Appl. Phys., 30, 1468 (1959).
84. H. Arnikar and B. Chaure, Proc. Chem. Symp. Chandigarh., 2, 144 (1969).
85. M. Chemla, Annalen Phys., 13 (1), 959 (1956).
86. R. Friauf, J. Appl. Phys. Suppl., 33, 494 (1962).
87. J. Jach, Nature, 196, 827 (1962).
88. J. Jach, Nature, 196, 830 (1962).
89. B. Sproull, Phil. Mag., 5, 815 (1960).
90. N. N. Vishnevskii et al., Fiz. Tverd. Tela, 13, 2762 (1971).
91. N. V. Zagoruiko, Kristallografiya, 10, 81 (1965).
92. E. G. Shvidkovskii et al., Kristallografiya, 7, 471 (1962).
93. L. B. Zuev and G. E. Turchinovich, Fiz. Tverd. Tela, 10, 2811 (1968).
94. H. Trap and J. Stevels, Verres et réfract., 25, 176 (1971).
95. V. M. Belous and K. V. Chibisov, Dokl. Akad. Nauk SSSR, 156, 121 (1964).
96. M. A. Konstantinova-Shlezinger, "Khimiya Lampovykh Geterodesmicheskikh Luminoforov" (The Chemistry of Heterodesmic Lamp Phosphors), Izd. Nauka, Moscow, 1970, pp.3–20.
97. V. A. Sokolov and A. N. Gorban', "Lyuminestsentsiya i Adsorbtsiya" (Luminescence and Adsorption), Izd. Nauka, Moscow, 1969, p.44.
98. L. A. Afanas'eva and V. V. Mikho, Izv. Vys. Ucheb. Zaved., Ser. Fiz., No. 10, 119 (1971).
99. A. A. Gol'dman, A. I. Proskura, and A. M. Krichevets, Zhur. Prikl. Spektrosk., 17, 269 (1972).
100. L. A. Afanas'eva et al., Izv. Vys. Ucheb. Zaved., Ser. Fiz., No. 11, 102 (1972).
101. L. A. Ivanchenko, Tekhniki i Fizika Poluprovodnikov, 2, 1175 (1968).
102. H. K. Henich, "Electroluminescence" (Translated into Russian), Izd. Mir, Moscow, 1964, pp.195–208.
103. A. M. Gurevich, "Vvedenie v Fizicheskuyu Khimiyu Kristallofosforov" (Introduction to the Physical Chemistry of Crystalline Phosphors), Izd. Vysshaya, Shkola, Moscow, 1971, p.50.
104. G. P. Peka, Fiz. Tverd. Tela., 4, 1118 (1962).
105. G. P. Peka and Yu. I. Karkhanin, Fiz. Tverd. Tela, 4, 3618 (1962).
106. G. Busca et al., Lett. Nuovo cim., 2, 769 (1971).
107. V. V. Pologrudov and E. E. Penzina, Izv. Akad. Nauk SSSR, Ser. Fiz., 29, 497 (1965).
108. V. P. Denks, Fiz. Tverd. Tela, 8, 1479 (1966).
109. N. G. Volkov and V. A. Grigor'ev et al., Symposium, "Radiatsionnaya Fizika" (Radiation Physics), Izd. Akad. Nauk Latv. SSR, Riga, 5, 79 (1967).

110. I. K. Vereshchagin, E. A. Serov, and I. V. Khomyak, Zhur. Prikl. Spektrosk., 17, 81 (1972).
111. A. S. Andrianov et al., Izv. Vys. Ucheb. Zaved., Ser. Fiz., No. 7, 149 (1972).
112. A. S. Andrianov and L. S. Bogachev, Izv. Vys. Ucheb. Zaved., Ser. Fiz., No. 1, 135 (1973).
113. V. P. Denks, Ch. G. Lushchik, and T. A. Soovik, Fiz. Tverd. Tela, 11, 44 (1969)
114. V. A. Grigor'ev, V. K. Lyapidevskii, and I. M. Obodovskii, Fiz. Tverd. Tela, 11, 2996 (1969).
115. V. A. Grigor'ev, V. K. Lyapidevskii, and I. M. Obodovskii, Fiz. Tverd. Tela., 11, 1042 (1969).
116. W. E. Garner and A. Bircumshaw, Symposium, "Khimiya Tverdogo Sostoyaniya" (Solid State Chemistry) (Translated into Russian), Inostr. Lit., Moscow, 1961, p.328.
117. G. G. Savel'ev, Yu. A. Zakharov, A. A. Kabanov, and V. A. Budkov, Izv. Vys. Ucheb. Zaved., Khim i Khim. Tekhnol., 10, 735 (1967).
118. D. Adler and H. Brooks, Phys. Rev., 155, 826 (1967).
119. D. Adler, Rev. Mod. Phys., 40, 714 (1968).
120. A. G. Aronov and E. K. Kudinov, Zhur. Eksper. Teor. Fiz., 55, 1344 (1968).
121. V. N. Andreev, A. G. Aronov, and F. A. Chudnovskii, Fiz. Tverd. Tela, 12, 1557 (1970).
122. K. A. Valiev et al., Fiz. Tverd. Tela, 13, 421 (1971).
123. B. Jiemenoz et al., Electron y fis. Appl., 12, 21 (1969).
124. T. A. Zarembskaya et al., Izv. Akad. Nauk Beloruss. SSR, Ser. Fiz. -Mat. Nauk, No. 3, 97 (1971).
125. M. Stammler et al., Nature, 192, 626 (1961).
126. M. M. Pavlyuchenko, Dokl. Akad. Nauk SSSR, 5, 256 (1961).
127. J. Davies et al., Trans. Faraday Soc., 63, 1737 (1967).
128. Z. Szabo and E. Biro-Sugar, Z. Elektrochem., 60, 869 (1956).
129. J. Doremieux et al., Compt. rend., 250, 3184 (1960).
130. F. F. Vol'kenshtein, "Elektronnaya Teoriya Kataliza na Poluprovodnikakh" (Electronic Theory of Catalysis on Semiconductors), Fizmatgiz, Moscow, 1960, pp.91–147.
131. H. J. Engel, Z. Elektrochem., 66, 617 (1962).
132. F. F. Vol'kenshtein and V. B. Sandomirskii, Dokl. Akad. Nauk SSSR, 118, 980 (1958).
133. F. F. Vol'kenshtein, Probl. Kinetiki i Kataliza, 8, 201 (1955).
134. V. G. Baru and F. F. Vol'kenshtein, Symposium, "Metody Issledovaniya Katalizatorov i Kataliticheskikh Reaktsii" (Methods for the Investigation of Catalysts and Catalytic Reactions), Izd. Sibir. Otd. Akad. Nauk SSSR, Novosibirsk, 1965, p.238.
135. P. N. Stadnik, Zhur. Fiz. Khim., 28, 577 (1954).
136. V. P. Fentsik and P. M. Stadnik, Dokl. i Soobshch. Uzhgorodsk. Univ., Ser. Khim., No. 3, 16 (1960).
137. P. N. Stadnik, E. Yu. Sekeresh, and V. V. Grodziskii, Dokl. i. Soobshch. Uzhgorodsk. Univ., Ser. Khim., No. 4, 25 (1961).
138. P. N. Stadnik and V. P. Fentsik, Kinetika i Kataliz, 2, 562 (1961).
139. V. P. Fentsik and P. N. Stadnik, Symposium, "Poverkhnostnye i Kontaktnye Yavleniya v Poluprovodnikakh" (Surface and Contact Phenomena in Semiconductors), Izd. Tomsk. Gos. Univ., Tomsk, 1964, p.190.
140. P. M. Stadnik and K. G. Stetskovich, Symposium, "Kataliz i Katalizatory" (Catalysis and Catalysts), Izd. Naukov Dumka, Kiev, 1965, p.94.
141. S. Z. Roginskii, Dokl. Akad. Nauk SSSR, 67, 97 (1949).
142. G. P. Peka, "Fizika Poverkhnosti Poluprovodnikov" (The Physics of Semiconductor Surfaces), Izd. Kiev. Univ., Kiev, 1967, pp.54–86.
143. H. Flitner, Annalen Phys. (DDR), 3, 414 (1959).
144. V. I. Lyashenko, A. A. Serba, and I. I. Stepko, Dokl. Akad. Nauk Ukrain. SSR, 3, 350 (1962).
145. V. I. Lyashenko, A. A. Serba, and I. I. Stepko, Kinetika i Kataliz, 7, 1094 (1966).
146. E. P. Mikheeva and N. P. Keier, Kinetika i Kataliz, 5, 748 (1964).
147. E. P. Mikheeva and N. P. Keier, Symposium, "Metody Issledovaniya Katalizatorov i Kataliticheskikh Reaktsii" (Methods for the Investigation of Catalysts and Catalytic Reactions), Izd. Sibir. Otd. Akad. Nauk SSSR, Novosibirsk, 1965, Vol.3, p.181.
148. N. P. Keier and E. P. Mikheeva, Kinetika i Kataliz, 10, 287 (1969).
149. L. I. Ivankiv and E. V. Solyanik, Ukrain. Fiz. Zhur., 13, 852 (1968).
150. L. I. Ivankiv et. al., Ukrain. Fiz. Zhur., 14, 1227 (1969).
151. L. I. Ivankiv, Vestnik L'vov. Univ., Ser. Fiz., No. 3, 67 (1968).
152. L. I. Ivankiv and A. M. Muzychuk, Zhur. Fiz. Khim., 42, 424 (1968) [Russ. J. Phys. Chem., No. 2 (1968)].
153. A. A. Kabanov and E. M. Zingel', Izv. Akad. Nauk SSSR, Neorg. Materialy, 10, 487 (1974).
154. W. Schockley and G. Pearson, Phys. Rev., 74, 232 (1948).
155. E. V. Lashkarev and V. I. Lyashenko, "Sbornik Posvyashchennyi 70-letiyu Akad. A. F. Ioffe" (Symposium Commemorating the 70th Birthday of Academician A. F. Ioffe), Izd. Akad. Nauk SSSR, Moscow, 1950, p.535.
156. A. V. Rzhanov, Trudy Fiz. Inst. im. Lebedeva, 20, 29 (1963).
157. Ya. A. Fedotov, "Osnovy Fiziki Poluprovodnikovykh Priborov" (Fundamentals of the Physics of Semiconductor Devices), Izd. Sov. Radio, Moscow, 1964, pp.86–90.
158. G. E. Pikus, "Osnovy Teorii Poluprovodnikovykh Priborov" (Fundamentals of the Theory of Semiconductor Devices), Izd. Nauka, Moscow, 1965, pp.94 to 108.
159. R. Green, Symposium, "Poverkhnostnye Svoistva Tverdykh Tel," (The Surface Properties of Solids) (Edited by V. F. Kiselev), Izd. Mir, Moscow, 1972, pp.109–114.
160. V. B. Sandomirskii and Ya. A. Pyasta, Symposium, "Voprosy Plenochnoi Elektroniki" (Problems of Film Electronics), Izd. Sov. Radio, Moscow, 1966, p.324.
161. V. F. Kiselev, "Poverkhnostnye Yavleniya v Poluprovodnikakh i Dielektrikakh" (Surface Phenomena in Semiconductors and Dielectrics), Izd. Nauka, Moscow, 1970, p.271.
162. K. V. Shalimova, "Fizika Poluprovodnikov" (The Physics of Semiconductors), Izv. Energiya, Moscow, 1971, pp.246–251.
163. H. K. Henisch, W. N. Reynolds, and P. M. Tipple, Symposium, "Elektrofizicheskie Svoistva Germaniya i Kremniya" (Electrophysical Properties of Germanium and Silicon), Izd. Sov. Radio, Moscow, 1956.

164. M. L. Petrova and P. N. Zanodzorov, Fiz. Tverd. Tela, 14, 826 (1927).
165. G. E. Pikus, Symposium "The Physics of the Surfaces of Semiconductors" (Russian Translation edited by G. E. Pikus), Inostr. Lit., Moscow, 1959, pp.5–30.
166. M. L. Petrova and L. D. Rozenshtein, Fiz. Tverd. Tela, 13, 2325 (1971).
167. O. S. Frolov et al., Ukrain. Fiz. Zhur., 11, 146 (1966).
168. N. Einspruch, J. Electrochem. Soc., 108, 1164 (1961).
169. L. Esaki, W. Goward, and J. Heer, Appl. Phys. Letters, 4, 3 (1964).
170. W. Ruppel, Z. Phys., 152, 235 (1958).
171. I. T. Drapak, "Tezisy Dokladov XXII Nauchnoi Sessii, Sektsiya Fizicheskikh i Matematicheskikh Nauk" (Abstracts of Reports at the XXII Scientific Session, The Section of Physical and Mathematical Sciences), Chernovtsy State University, Chernovtsy, 1966.
172. G. Heiland, Z. Phys., 148, 28 (1957).
173. V. A. Misnik and E. A. Arinshtein, Fizika i Tekhnika Poluprovodnikov, 2, 991 (1968).
174. S. Costa and V. P. Murphy, Anals Acad. brasil ciẽns., 35, 159 (1963).
175. D. Nasledov and E. Malyshev, Zhur. Tekh. Fiz., 16, 1135 (1945).
176. K. Böer and U. Kümmel, Annalen Phys. (DDR), 2, 217 (1958).
177. A. D. Ziman, "Adgeziya Pyli i Poroshkov" (Adhesion of Dust and Powders), Izd. Khimiya, Moscow, 1967, pp.311–326.
178. M. I. Elinson and G. F. Vasil'ev, "Avtoelektronnaya Emissiya" (Autoelectron Emission), Fizmatgiz, Moscow, 1958, pp.183–224.
179. A. F. Ioffe, "Fizika Poluprovodnikov" (The Physics of Semiconductors), Izd. Akad. Nauk SSSR, Moscow–Leningrad, 1957, pp.99–151.
180 L. I. Nesmelova, Fiz. Tverd. Tela, 5, 3023 (1963).
181. J. Guerci et al., "Internat. Lumenesz. Cympes. Phys. und Chem. Czintillator., München, 1966, pp.460 to 465.
182. J. Guerci et al., Phys. Letters, 18, 243 (1965).

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