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The Chemical Aspect of Exoemission

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The results of studies on exoemission employing various excitation procedures are examined from the single standpoint of physicochemical reactions on the surfaces of solids. The prospects for the application of exoemission in scientific research and in engineering are discussed.
The bibliography includes 164 references.

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I. THE PROBLEM OF EXOEMISSION

Exoemission is a new type of emission of negative charges—slow electrons and ions—together with thermal emission, autoemission, photoemission, and secondary emission. In contrast to the types of emission known previously, it appears after a solid has been subjected to various influences inducing the formation of excited states and exhibits an appreciable inertia. On subsequent heating in the pre-Richardson region, the emission exhibits a number of peaks characterising the energy spectrum of the charge localisation levels on the surface.

The emission may be excited either by physicochemical reactions in the surface layers accompanying adsorption (desorption), oxidation, corrosion, and catalytic processes, phase transformations, etc. or as a result of external influences—mechanical, radiation, etc. Since emission occurs at low temperatures, the emitting surface may be assumed to be in a thermodynamic non-equilibrium state and to retain the properties resulting from its previous history. This gives rise to the prospect of employing exoemission in the study of physicochemical processes on the surface.

Detailed investigation of this effect began with Kramer's studies in 1950.[1] Despite the publication of numerous reports, particularly in recent years[2], exoemission continues to remain a relatively little investigated phenomenon, which is considered only by a limited circle of physicists.

There is at present no theory whereby one could explain from a single standpoint the emission from metals and non-metallic crystals, semiconductors, and dielectrics. Kramer[1] suggested that mechanical influences on the surface of metals result in the formation of an amorphous phase (the Beilby layer) and that the emission is a consequence of the exothermic transformation during its recrystallisation. This hypothesis still stands, but the effect described by Kramer has been called "exoelectron emission" (The First International Symposium, Innsbruck, 1957).[3] Unfortunately there is a confusion in terminology and the individual types of manifestation of exoemission are referred to as "chemoemission",[4] stimulated emission[5], sorption emission[6], and low-temperature emission[7]. This situation merely complicates the development of a single mechanism of this phenomenon and hinders mutual understanding between teams of research workers concerned with the problem of exoemission.

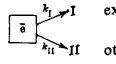
In order to explain exoemission from metals, a hypothesis has been put forward[8] according to which electrons are emitted as a result of the heat of adsorption of active gases and the peaks of the thermally stimulated emission correspond to centres with different adsorption potentials.

The problem of the nature of emission from ionic crystals—crystalline phosphors and coloured alkali metal halides for which electron energy level schemes have been developed fairly satisfactorily—has been investigated to the greatest extent. The majority of studies in this field are based on the experimental analogy between the phenomena of exoemission and luminescence and are directed to the investigation of the physical aspect of this phenomenon[1,9-12]. According to the most general Bohun-Nassenstein theory[10,12], the electrons entering the conductivity band on excitation are localised at shallow capture levels. After the removal of excitation, the trapping levels are gradually vacated owing to thermal energy with transfer of electrons via the conductivity band outside the limits of the crystal—afteremission is observed or, when the electrons enter activator levels, there is an afterglow (phosphorescence). Decaying afteremission frequently occurs only on stimulation with light and in this case the emission is said to be photostimulated. In a number of studies it has been assumed[13] that the thermally stimulated emission (TSE) and the photo-stimulated emission (PSE) are two different phenomena involving different mechanisms, which should be considered separately.

The afteremission phenomena are due to the relaxation processes of the excited states and in the general case can be described by a sum of exponential terms or by the empirical law $I \propto I_0 t^{-n}$, where $n \simeq 1$. When the temperature is increased uniformly, deeper levels are vacated—thermally stimulated emission is observed with a set of maxima corresponding to localisation levels of different depths. For the analysis of the energy spectrum of the capture levels, the mathematical procedures of the theory of luminescence developed by Randall and Wilkins[14] are used. In the mathematical treatment of exoemission kinetics, one usually calculates the depth of the localisation

levels (more precisely the activation energy for the release of electrons) and the pre-exponential factor. A very thorough critical review of studies concerning the kinetic analysis of exoemission phenomena has been published[15]. The authors note the deficiencies of the mathematical procedure of the luminescence theory (of Randall and Wilkins, Lushchik, etc.) and its modification in relation to calculations of the depth of the localisation levels of exoelectrons[14,16]. A method has been proposed for the analysis of the complex spectra of thermally stimulated emission when several unresolved peaks are superimposed. The possibility of resolving the TSE peaks and of determining their parameters has been demonstrated. Similar problems are being solved in the theory of thermal luminescence and in the analysis of thermal desorption spectra.

On the basis of "physical considerations", exoemission has been considered[15] as one of the possible channels for the relaxation of excited solids. The simplified relaxation mechanism proposed by the above workers is given below:



I exoemission or thermal luminescence

II other channels for relaxation involving the same capture centre.

The results of non-isothermal experiments undertaken in the study of thermally stimulated emission, thermal luminescence, etc. led to a method for the interpretation of experimental data[17] whereby one can determine the parameters of the two processes involved in the mechanism. Recommendations have been made for computer calculations on the kinetics of relaxation processes (programming). The authors note that the correct determination of the kinetic parameters by any of the methods described in the literature is then possible only when account is taken of the multichannel processes in relaxation. According to Burkhanova et al.,[15] the proposed mathematical models are of interest for the construction of a physical picture of the relaxation; they have been analysed in detail[15] and will therefore not be considered in the present review.

Thermally stimulated emission takes place as a result of the thermal liberation of negative charges in the pre-Richardson region when the energy of the electrons in the state of thermodynamic equilibrium is insufficient to overcome the surface potential. Photo-stimulated emission takes place under the influence of light with a wavelength exceeding the red limit of the photoeffect. Thus the phenomena considered are observed in the region of stimulating influences below the threshold values for thermal emission and photoemission and one of the central problems of the theory is the origin of the energy required for the release of electrons.

It has been suggested[18,19] that the energy required for the release of electrons is supplied by electron–hole recombination processes in transitions between the bands ("Auger recombinations"). This energy is transferred, for example, by the exciton mechanism, to the electrons localised at shallow capture levels near the surface. According to Bohun, only the high-energy component of the Maxwellian distribution of conductivity electrons is emitted (in the author's terminology[19], the "Maxwell tail theory"). It is noted that the "Auger mechanism" is valid only for dielectrics, where the width of the forbidden gap exceeds the electron affinity of the crystal, but does not explain the emission from semiconductors.

Assuming that TSE is a quasistationary process, Bohun[14] combines the equations of thermionic emission and thermoluminescence and obtains expressions describing the experimental data for emission from coloured or activated alkali metal halides.

The mathematical models for calculations on exoemission kinetics, based on the most general physical concepts, make it possible, according to Burkhanova et al.,[15] to determine the energy spectrum of the surface traps; the role of the surface potential in the exoemission phenomena is not discussed in this connection. The mathematical apparatus of Bohun's theory[14] represents the electron liberation processes as processes in which the surface potential is overcome. The role of the electron work function (electron affinity) has been considered theoretically also in a number of other studies[20], but the experimental results concerning the influence of the surface potential on the exoemission parameters are contradictory.

It has been established[21] that the intensity maxima of thermally stimulated emission from certain metals correspond to the minimum electron work functions and exoemission has been suggested[22] as a method for the determination of the surface potential. An unambiguous correspondence between the parameters of exoemission and the electron work function has not been found in recently published investigations[23,24]: the emission capacity can increase after both a decrease and an increase of the electron work function. The results make it necessary to approach with even greater caution the interpretation of the results of studies on exoemission from the standpoint of the band theory of solids. Analysis of the available data shows that the fundamental exoemission parameters (decay constants, the number and positions of the peaks on the temperature curves characterising the spectrum of the energy states on the surface) are not determined by the nature of the emitting substance—the width of the forbidden gap, the type of conductivity, the nature of the chemical bond, and whether or not the substances are semiconductors or dielectrics, metals, oxides, or salts[25].

In view of the presence of non-compensated bonds, the surface of a real solid is known to be always covered by adsorption layers, particularly water. Since emission takes place from shallow surface layers, the adsorption film should play a significant role in emission processes. A phenomenological theory of the origin of exoemission has been proposed[25]. It is based on the interpretation of the physicochemical processes accompanying the formation and relaxation of the excited states in surface layers in the presence of adsorption films.

The chemical aspect of exoemission is considered in the present review. Various types of manifestation of emission accompanying the physicochemical processes on the surface or arising as a result of external influences are discussed. The results are considered from the single standpoint of the physicochemical reactions accompanying the relaxation processes in the damaged surface layer.

II. EXPERIMENTAL METHODS FOR THE INVESTIGATION OF EXOEMISSION

In view of the low currents (10^{-17}–10^{-19} A), exoemission is studied under conditions where individual pulses are counted. Geiger counters or secondary electron multipliers (SEM) are used in combination with standard radiometric apparatus[26]. Since the exoelectron energies are small (from a few tenths of an electron-volt to several electron-volts), the electrons do not pass through the mica window and the emitter must be placed within the counter. The designs of special counters of this type have been described[27]. Some investigators use closed counters applying an accelerating potential before the inlet window[28]. Gas-flow counters are more convenient and reliable. The

working plateau (500 V) hardly changes when the temperature is raised to 400°C.[29] The application of an accelerating potential to the grid over the specimen constitutes a significant improvement to the operation of the counters; this not only increases the sensitivity but also reduces the scatter of the results.

In experiments with gas-filled counters, it is impossible to investigate the role in exoemission of physicochemical factors due to adsorption-desorption, catalytic, and other processes. The development of the chemical aspect of exoemission has become possible after secondary electron multipliers of the open type have been devised and high and ultrahigh vacuum techniques have been employed. The method of the physicochemical investigation of exoemission developed in a number of studies[25,30,31] involves special "cleaning" of the emitter in a high or ultrahigh vacuum and simulation of the emitting surface by the adsorption of the corresponding gases and vapours under controlled conditions.

The autoradiographic method, based on the familiar Russell effect[32,33], is used for the analysis of structural changes under mechanical influences. This method is not suitable for studies *in vacuo* and its sensitivity is low. An image of the structure of a high quality surface was obtained after the development of channel multipliers. Microchannel plates, consisting of a system of close-packed channel multipliers, make it possible to obtain directly the image of the emitting surface. An exoemission microscope has been developed on the basis of microchannel plates[34,35].

Studies *in vacuo* using a secondary electron multiplier with application of a deflecting magnetic field established the occurrence of the emission of negative ions together with that of electrons[36-38]; the ionic component was observed only in TSE measurements on substances containing adsorption layers. It therefore appears useful to replace the generally accepted term "exoelectron emission" by the term "exoemission".

Numerous studies dealing with the distribution of exoelectron energies have been published recently. The average energy of the electrons emitted after Emery powder has been ground is 0.65 eV.[39] The most probable energy of the electrons in the afteremission from BeO caused by electron bombardment is 0.1 eV.[40] A Maxwellian distribution of electrons, with average energies amounting to a few tenths of an electron-volt, has been found for photostimulated emission from K_2SO_4.[41] It was noted that the electron energy depends on the accelerating potential, the charge acquired by the specimen as a result of the emission, the optical stimulation energy, temperature, and the presence of adsorption layers. A study has been devoted[42] to special problems of the influence of the charging of the specimen surface, occurring both on excitation and as a result of emission processes, on the distribution of exoelectron energy.

The average energy of the emitted electrons in thermally stimulated emission from $BaSO_4$ (t_{max} = 160°C) was 1.1 eV, only 10% of the electrons had an energy of 2.7 eV, 1% had an energy of 5 eV, and the energy of 0.1% was greater than 8 eV.[43] The average exo-electron energies for TSE from ceramic BeO specimens were 0.5 eV.[44] The energy distribution depended on the technology of the manufacture of the ceramic; for t_{max} = 250°C, the maximum electron energy varied from 1.5 to 16 eV. Even higher energies (up to 80 eV) were found[45] for thermally stimulated emission from the surface of oxidised silicon. It is noteworthy that such high electron energies cannot be achieved, for example, as a result of exothermic chemical reactions, Auger recombination processes, or the emission of the high-energy component of the Maxwellian distribution, i.e. they cannot be understood on the basis of the available models of the origin of exoemission[18,19]. In order to account for the high electron energies, a theory was proposed[45] postulating the possibility of the acceleration of electrons in the strong field of the electrical double layer comprising the dielectric—the oxide covering the semiconductor. However, it is possible that the high electron energies observed by the authors are due to methodological errors.

A study of TSE from LiF specimens showed that a Maxwellian distribution of exoelectron energies occurs only at temperatures $\leq$ 100°C; with increase of temperature, deviations from the Maxwell law are observed. The authors note that the interpretation of the energy measurements in terms of the approximate equations of thermionic emission must be treated with caution. Studies on the distribution of the energies of exoelectrons from an aluminium surface (TSE)[47] also showed that the average energies and their temperature dependence are inconsistent with the exoemission models based on the band theory and the thermionic emission approximations.

III. EXOEMISSION ACCOMPANYING PHYSICOCHEMICAL PROCESSES

1. Emission in Adsorption and Oxidation of Metals

Studies under conditions of high and ultrahigh vacuum have now established that atomically clean metal and semiconductor surfaces lack exoemission capacity[48-50]. When active gases are admitted, particularly oxygen and water vapour, an intense emission of negative charges is observed. It has been established that the occurrence of the emission accompanying adsorption and oxidation requires photostimulation[48], but in some studies such emission has been observed in the dark[51].

A freshly formed layer of aluminium *in vacuo* ($p \simeq 10^{-7}$ mmHg) does not emit electrons. When oxygen is admitted ($p \simeq 10^{-5}$ mmHg), emission, decaying over a period of time, takes place[52]; in order to excite the emission, a continuous incidence of oxygen molecules on the surface is necessary. The emission in the adsorption of oxygen on a nickel film sputtered under ultrahigh vacuum conditions ($p \simeq 10^{-10}$ mmHg) has been studied[53]. Each successive admission of oxygen is accompanied by an emission flash, whose "yield" is 10^{-10} electrons per molecule. At room temperature the emission intensity initially decreases and then rises again, the number of emitted electrons depending strongly on the time interval between the successive doses of oxygen. The observed phenomena are explained by the gradual incorporation of the adsorbed molecules in the lattice, which terminates in several minutes; according to approximate estimates, two oxygen monolayers are sorbed. Similar processes occur when oxygen is sorbed by atomically clean tungsten and copper surfaces[53].

In some studies, an atomically clean metallic surface was formed as a result of the removal of oxide by milling[48,49,54]. The admission of oxygen at a specified pressure (5×10^{-5} mmHg) to a zinc surface cleaned with a steel brush gives rise to emission, whose intensity passes through a maximum[54]. A similar result was obtained for zinc and aluminium under ultra-high vacuum conditions[48].

The residual gas pressure has a significant influence on two factors: the time interval elapsed after cleaning the surface before the appearance of the maximum and the intensity of the latter (Fig. 1). After the maximum, the emission intensity diminishes exponentially; at a residual pressure $p \simeq 1 \times 10^{-8}$ mmHg, neither dark nor photostimulated emission was observed in the course of 10 min. Comparison of the time required for the appearance of the emission maximum (τ'_{max}) and the time required for the formation of a monolayer (τ'') showed that τ'_{max} exceeds τ'' by a factor of 10^3–10^4. The results were examined taking into account the Cabrerr–Mott mechanism of the oxidation of metals and it was concluded that the exoemission is not associated with the adsorption step but is due to a slower process—the initial oxidation stage. A shift of the limit of the photoeffect to the long-wavelength region in adsorption and oxidation takes place according to some investigators[48,49], owing to the decrease of the photoelectron work function of the oxide layer formed, although the corresponding measurements of φ were not made.

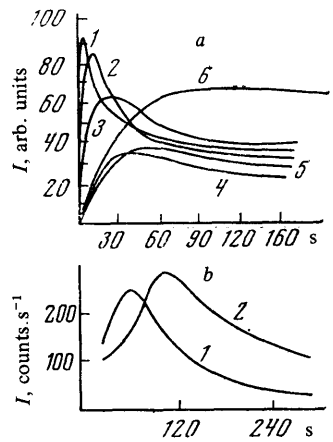


Figure 1. Time variation of the PSE intensity: *a*) from a zinc surface after cleaning at different residual gas pressures[49] [pressure (mmHg): 1) 5; 2) 3; 3) 2; 4) 1; 5) 0.7; 6) 0.2]; *b*) from an aluminium surface after mechanical treatment by impact[60] [time (min): 1) 1; 2) 4].

Simultaneous studies on photostimulated emission and the surface potential in the oxidation of metals have been made by Gel'man and Fainshtein[55]. The surface was cleaned in air and the emission was recorded by means of an open proportional counter. An increase of the surface potential φ corresponded to a fall of the PSE intensity I in the initial stage of oxidation; after a further growth of the oxide layer, the emission intensity increased and passed through a maximum and the correspondence between I and φ broke down. Since the experiments described were performed under non-controlled conditions, it is difficult to interpret the results, in particular it is impossible to take into account the role of the adsorbed water and oxygen.

Measurements of PSE and of the surface potential under controlled conditions with the aluminium surface cleaned in an ultrahigh vacuum were carried out by Linke and Born[56]. At a residual pressure $p < 10^{-5}$ mmHg, the emission intensity passed through a maximum after the surface had been cleaned, as in other studies[49,54]. In an ultrahigh vacuum ($p \simeq 10^{-10}$ mmHg), PSE was not observed even after a very vigorous mechanical treatment. Emission did not appear even after several hours following the admission of oxygen ($p \simeq 10^{-4}$ mmHg). It was found that the presence of adsorbed water is necessary for the appearance of PSE. Fig. 2 illustrates the variation of the "tribophotostimulated" emission from an aluminium surface in an atmosphere of water vapour and oxygen. In the former case, the emission intensity increased to a limit, falling after the next admission of oxygen. The authors[56] believe that, in the case of metals coated by adsorbed layers with a thickness of several angstroms, PSE represents photoemission of electrons from the metal; here the shift of the limit of the photoeffect occurs as a result of changes in electron work function in the presence of adsorbed molecules. This conclusion was confirmed by direct measurements of the photoelectron work function by Fowler's method. The admission of water reduced φ from 4.5 to 3 eV and led to the appearance of emission following illumination with red light.

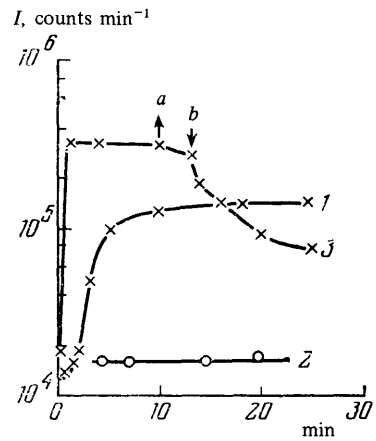


Figure 2. Time variation of the intensity of PSE from an aluminium surface after cleaning in different atmospheres: 1) H_2O (7.5×10^{-8} mmHg); 2) O_2 (8×10^{-8} mmHg); 3) H_2O (1×10^{-6} mmHg); *a*) evacuation; *b*) admission of O_2 (4×10^{-6} mmHg).[56]

The experiments described above led to a second fundamental conclusion[56]: the structural defects generated by mechanical treatment do not form emission centres in the absence of adsorbed layers. This postulate is consistent with Scharmann and Seibert's data[48] and demonstrates the lack of validity of the view of some investigators on the nature of exoemission from deformed metals, who failed to take into account the decisive role of the physical chemistry of the surface in exoelectron emission processes[57–60].

2. Thermally Stimulated Emission in Desorption

For the majority of substances investigated—metals, elementary semiconductors, oxides, and ionic crystals (salts)—the phenomenon of "self-excited" emission has been observed: when the initial specimens are heated without any preliminary external influences (excitation[3]), peaks appear on the temperature curves. These effects are manifested particularly clearly when the test substances are subjected to a preliminary treatment leading to the hydration of the surface. Intense TSE is observed after metals are wetted with water[61], semiconductors are etched[37], alkali metal halides are hydrated[36,62], etc.

The initial metals[61], which did not exhibit emission, were wetted with water, dried, and heated at a linear rate in air, while recording the charges with an open counter. The "self-excited" TSE curves (t_{max} = 295°C for Al, 225°C for Fe, and 225° and 270°C for Cu) were compared with the curves obtained for the same specimen after mechanical cleaning. A satisfactory agreement of the temperatures of the peaks was observed, but the intensity of the maxima was significantly higher for the metals wetted with water. For germanium specimens subjected to mechanical treatment and wetted with water, the temperatures of the peaks varied in the range between 240° and 360°C, depending on the duration of treatment with water, i.e. the degree of hydration. It was concluded[61] that the exoemission parameters are not constants of the substance, but are determined by the method used for the preliminary treatment. The processes occurring in the oxide film are responsible for the emission. On dehydration, structural changes take place in the oxide and lead to the formation of capture levels (emission centres).

Direct experiments *in vacuo* established[30,63-65] that, when highly hydrated oxides such as Al_2O_3, MgO, synthetic zeolites, etc. are heated, the increase in TSE intensity is accompanied by vigorous gas evolution at certain temperatures (140–160°, 280°, and 360°C). Later these results were checked and confirmed[15]. Simultaneous studies of thermally stimulated emission and thermal desorption accompanied by condensation or mass-spectrometric analysis led to the conclusion that the self-excited emission is caused by the desorption of water. Calculation showed that one electron is emitted for approximately 10^6 desorbed molecules. Fig. 3 presents the results of studies on TSE and the rate of thermal desorption from magnesium oxide[64]. The present author's special experiments[50] under ultrahigh vacuum conditions (10^{-8}–5×10^{-9} mmHg) showed that the observed effects are not a consequence of "parasitic" signals arising in the detector due to gas evolution, as suggested by Burkhanova et al.[15]

Bohun, who is the author of the most widely accepted theory of exoemission based on the band model[14], notes that some results do not fit within the framework of this concept. Thus distinct TSE peaks have been observed for initial alkali metal halides without colour centres in the range 230–430°C, particularly when the specimens were wetted with water, alcohol, etc.[62] It was suggested that reactions take place on the surface of the crystal coated by the adsorption film and result in the emission and desorption of both neutral and charged species. However, since the experiments were carried out in air and the emission was recorded with an open counter, the above postulates could not be subjected to an experimental test. Studies *in vacuo*, in which the emission was recorded with a secondary electron multiplier accompanied by mass-spectrometric analysis, showed[36] that the "self-excited" TSE from sodium chloride is due to the desorption of water (in the form of negative ions).

Thus it has now been established for substances of different classes—metals, semiconductors, and dielectrics—that emission occurs not only as a result of adsorption with liberation of energy but also accompanies desorption processes involving the absorption of energy. These phenomena could not be understood from the standpoint of the available hypotheses and were explained from the standpoint of the physicochemical mechanism of exoemission developed by the present author[25] (see also Section VI).

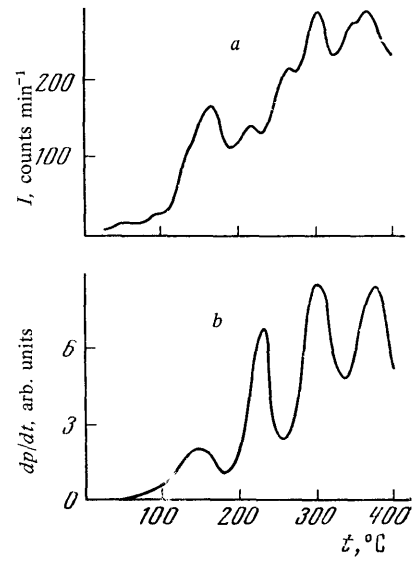


Figure 3. Temperature variation of the intensity of "self-excited" TSE (*a*) and of the rate of thermal desorption (*b*) from an MgO surface[64].

Desorption, which is an important stage in the activation of many adsorbents and catalysts, leads, according to the data examined above, to the formation of excited states with long relaxation times, which is important for the understanding of the processes involving the formation of an active surface.

3. Exoemission and Catalysis

According to modern ideas, heterogeneous-catalytic processes take place at active centres where electron exchange in the catalyst–substrate system is facilitated. Exoemission also occurs from a small fraction of the surface (active centres) where the binding of electrons is weakest; only approximately 10^{-6} of the surface atoms are capable of emission. Since such emission is observed over a wide range of temperatures, including the temperatures where heterogeneous-catalytic reactions occur (20–500°C), exoelectrons may participate in catalytic reactions. On the basis of these considerations, some workers pointed out a possible relation between emission and catalysis already in the early stages of this research[62,66]. Definite correlations were established between catalytic

activity and emission capacity for substances of different classes—metals, semiconductors, and adsorption catalysts[67-69] (Fig. 4). As in studies involving the application of the majority of physical methods, catalysis and exoemission were investigated in such research under different conditions and only indirect conclusions about the causes of the observed correlations could be made.

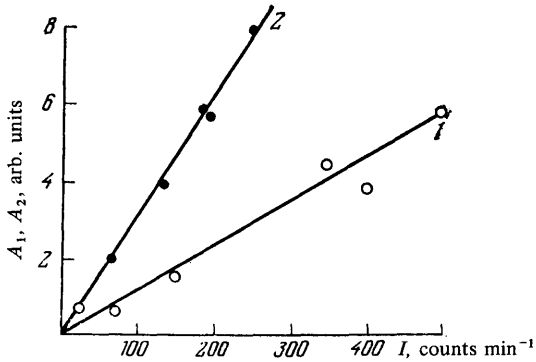


Figure 4. Relation between the emission capacity and catalytic activity: 1) Pt(SiO_2 with different platinum contents in the vapour-phase hydrogenation of cyclohexene[69]; 2) ZnS.Cu with different copper contents in the decomposition of methanol[68].

Studies have now been published where the heterogeneous-catalytic reactions were carried out directly in the chamber for the measurement of exoemission with simultaneous recording of the emitting charges. Exoemission from a silver catalyst in the course of the partial oxidation of ethylene has been investigated[70]. It was shown that the emission intensity in the range 150–210°C is proportional to the rate of formation of epoxyethane. At a constant temperature (250°C), non-decaying emission, accompanying the oxidation reaction, was observed. Exoemission under such conditions is regarded as thermal electron emission from a thin semiconductor oxide layer, for which the electron work function is reduced as a result of the adsorption of the epoxyethane formed. The authors support this view by the finding that exoemission is not observed during the reaction on copper, nickel(II) oxide, and iron(III) oxide, where only complete oxidation of ethylene takes place.

However, it is noteworthy that the authors[70] carried out experiments in which emission was recorded by a gas-filled counter and a component of the reaction mixture (ethylene) played simultaneously the role of the quenching gas. Under these conditions, the presence of oxygen and of water vapour (produced by the reaction) in the atmosphere of the quenching gas might have interfered with the operation of the counter and might have distorted the results of the measurements.

Another investigation[71] was undertaken to study the emission accompanying the catalytic oxidation reactions of CO, H_2, and NH_3 on a heated platinum wire. The experiments were performed *in vacuo* at partial pressures of the reacting gases of 10^{-6} mmHg. The authors attempted to discover whether exoemission is a necessary stage in the heterogeneous oxidation or whether it merely accompanies the catalytic reaction but has no influence on the latter. It was found that the increase or suppression of the emission capacity of the platinum catalyst when a negative potential is applied to it is accompanied by the simultaneous increase or decrease of the rate of catalytic oxidation. Hence it was concluded that exoelectrons are directly involved in heterogeneous-catalytic reactions. It is suggested that the observed correspondences are based on the same rate-limiting stage in both processes—the adsorption stage—which is believed[53] to be accompanied by intense emission.

However, the observed effects[71] can hardly be attributed to the involvement of exoelectrons in the reactions. This is indicated by two fundamental factors: the fairly high temperatures at which the emission and catalytic reactions take place ($\geqslant$ 800°C) and the fairly large currents ($\sim 10^{-8}$ A), which are not characteristic of exoemission. It is more likely that Richardson thermal emission from the platinum wire and the changes in its intensity owing to the increase or decrease of the thermal electron work function following the adsorption of oxygen, hydrogen, etc. are involved here.

The phenomenon of exoemission accompanying catalytic reactions in the adsorption layer at temperatures between 100° and 400°C, typical for catalytic reactions, has been observed and investigated[72,73]. A study was made of the catalytic oxidation and decomposition reactions on metals, oxide semiconductors, and ionic crystals. The experiments were formulated on the basis of the following initial postulates. The binding energy of oxygen in the surface layer of oxides is known to determine to a large extent their catalytic properties in oxidation reactions. Only "mobile" oxygen participates in reactions on specimens with inhomogeneously bound oxygen[74]. On the other hand, it has been shown that thermally stimulated emission processes are accompanied by the desorption of active gases and vapours[30,31]. Analysis of the results of comprehensive studies led to the conclusion that the emission and desorption centres are formed by mobile oxygen atoms on the surface layer of the oxide[25].

The oxidation of hydrogen and carbon monoxide has been studied[73] on oxides with hole (NiO) and electronic (ZnO) types of conductivity and on a metal (platinum black). The reaction was carried out in a cell for the measurement of exoemission with simultaneous recording of negative charges by a secondary electron multiplier. The catalyst was activated in oxygen (400°C) and hydrogen was then adsorbed. Emission, decaying with time, was observed for platinum black even at room temperature. The decay was found to be represented by the sum of two exponential functions with relaxation times $\tau_1 = 300$ s and $\tau_2 = 3700$ s. This was accompanied by the emission of not only electrons but also ions, the presence of which was detected by measurements in a deflecting magnetic field. Subsequent heating at a linear rate of both platinum and NiO led to the appearance of more or less distinct emission peaks at 130–150°, 180–190°, and 240–260°C. Repeated heating results in a change of the relative intensities of the peaks, which indicates the formation of active centres during the reaction (Fig. 5). The conclusion that catalytic reactions occur under the given conditions was confirmed by the results of thermal desorption analysis[73].

In conformity with the mechanism proposed by the present author[25] and later by Euler et al.[134] for exoemission from oxides, the TSE peaks are due to valence transformations in the layer of adsorbed oxygen, for example:

$$O_2(\text{ads.}) + e \underset{\text{stimulation}}{\overset{\text{excitation}}{\rightleftharpoons}} O_2^-(\text{ads.})$$

The same forms of oxygen are reactive in heterogeneous-catalytic oxidation[74]:

$$O_2 \rightarrow O_2^- \text{ (ads.)} \rightarrow O^- \text{ (ads.)} \rightarrow O^{2-} \text{ (ads.)}.$$

When charged forms of oxygen interact with the substance being oxidised, there is a reverse electron transfer to the catalyst according to Boreskov[74]. It follows from the data in Fig. 5 that the electrons liberated in the catalytic step can leave the surface ("exoemission"). A possible reaction mechanism is presented below[73]:

$$O^{2-} \text{ (ads.)} + H \text{ (ads.)} \rightarrow OH^- \text{ (ads.)} + e \text{ (loc.)} + Q_{rec}, \quad (1)$$

$$O^- \text{ (ads.)} + H \text{ (ads.)} \rightarrow OH^- \text{ (ads.)} + Q_{rec}, \quad (2)$$

$$OH^- \text{ (ads.)} + H \text{ (ads.)} \rightarrow H_2O^- \text{ (ads.)} + Q_{rec.} \rightarrow H_2O^- \text{ (gas)}, \quad (3)$$

$$e \text{ (loc.)} + Q_{rec} \rightarrow e\uparrow \text{ etc.} \quad (4)$$

Electrons are ejected outside the limits of the crystal as a result of the recombination energy of ions and radicals[25,73]. A similar oxidation mechanism, but without allowance for electronic transitions, has been proposed by Khasin and Boreskov[75].

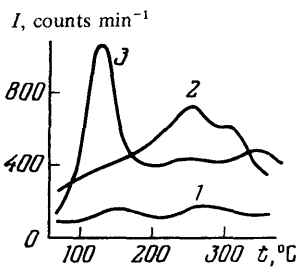


Figure 5. Thermally stimulated emission from an NiO surface: 1) before admission of reaction mixture; 2) after admission of reaction mixture (H_2–O_2); 3) after subsequent heating[73].

Analogous results were obtained in studies on the exoemission accompanying the catalytic decomposition in the adsorption layers of methanol (on Al_2O_3 and NaCl powders) and formic acid (on an NaCl single crystal).[72] It was established that the appearance of the most intense maxima at $t > 200°C$ is accompanied by the formation of decomposition products. The smaller low-temperature peaks are due to fluctuation processes in the adsorption layer (the "pre-catalytic" state). The emission of negative charges—electrons and ions—in catalytic decomposition processes in the adsorption layer is also explained from the standpoint of the radical mechanism of exoemission proposed by the present author[25]. The formation of radicals as intermediates in the catalytic decomposition of alcohols has been demonstrated experimentally[76].

It was found that the decomposition of methanol on a hydrated NaCl surface is accompanied by a shift of the most intense TSE peak to lower temperatures[77]. The products of the dissociative adsorption of water, particularly protons, can serve, by virtue of their high mobility, as energy transferring agents in surface migration and recombination processes; this in fact explains the promoting role of water. The surface diffusion of water plays a decisive role in many cases in chemisorption and catalysis[78].

4. Thermally Stimulated Emission in Phase Transformations

It was shown for the first time in 1950[1] that phase transformations are accompanied by the emission of negative charges. A sharp increase of emission was recorded in the solidification of Wood's alloy and in the allotropic transformations of chromium, selenium, etc. modifications. It was suggested that the emission is caused by exothermic processes. Later these studies were developed further[79–81]. Exoemission has been observed in the transition from the hexagonal to the cubic configuration of thallium[79], in the solidification of bismuth, cadmium, and their alloys[80], in the solidification of aqueous ammonia solutions[81], and in liquid gallium at the temperatures corresponding to structural transformations[82]. The emission was recorded with gas-filled or open counters. Studies on exoemission in phase transformations have already been reviewed in detail[83].

The authors[80–82] emphasise that the observation of exoemission from metals and alloys in their phase transformations requires photostimulation and suggest that the emission of charges is caused by deformations in the oxide film and not by its disruption.

Studies with a gas-filled counter led to the observation of the exoemission accompanying the solidification of lead ($t_{max} = 235°C$), tin ($t_{max} = 235°C$), and the lead–tin eutectic alloy ($t_{max} = 180°C$).[84] However, experiments showed[85] that *in vacuo* emission accompanying phase transformations is not recorded. The available data concerning the coincidence of the TSE peaks with the temperatures of allotropic transformations are also contradictory. Thus, in a study of the transformation of layers of the hexagonal modification of chromium obtained by an electrolytic method, a TSE maximum was observed at 230°C, while the phase transition temperature is 180°C. It is suggested[85] that the thermally stimulated emission is caused by oxidation processes.

In contrast to earlier investigations[84,88], peaks of exoemission from tin and lead were found[87] not only on solidification processes but also on fusion, and for bismuth the emission maximum was observed only on fusion. It was established that, in the absence of an oxide film, there is no emission and that the most intense TSE peaks are observed for an optimum thickness of the oxide layer. The authors[87] suggest that the phase transitions occurring on solidification lead to stresses in the oxide layers, which are removed by the migration of dislocations. The annihilation of dislocations carrying opposite charges leads to the release of phonons, whose energy is sufficient for the liberation of electrons from capture levels.

Despite the ambiguity of the results and of their interpretation, exoemission is recommended for the determination of phase transformation temperatures in those cases where they cannot be found by other methods, for example by thermal analysis. Rostovtsev[88] determined the limits of the solubility of zinc in aluminium (at 100–275°C), the emission being recorded with a gas-filled counter. It was established for a series of alloys of different compositions that TSE peaks correspond to the thermal decomposition temperatures of the solid solution (α) with formation of

crystals (β). The results agree with data for the solubility of zinc in aluminium obtained by other methods.

The ageing processes in the aluminium–magnesium–silicon alloy have been investigated[89]. The PSE decay curve at a constant temperature shows a maximum corresponding to the segregation of the excess of the Mg_2Si phase from the supersaturated solid solution. This emission flash is shown 60 min after the start of "ageing" and occurs at the instant of segregation of Mg_2Si found by other methods (for example by electron microscopy). It was concluded that exoemission is a simple and extremely sensitive method for the investigation of the technologically important alloy ageing processes.

Studies have been made on the exoemission in second-order phase transformations[90-93]. The exoemission method has been used to investigate the γ–ϵ transformations of the manganese austenite alloy and of the first- and second-order phase transformations in iron–manganese alloys of different compositions[91,93]. The emission was recorded *in vacuo* with the aid of a secondary electron multiplier. The TSE peaks occurring on heating and cooling were attributed to first-order ($\epsilon \rightleftharpoons \gamma$) and second-order (for example, the transition from antiferromagnetic austenite to paramagnetic austenite) phase transformations. The results were explained[92] by the increased mobility of dislocations at the phase transition temperatures. It is suggested that the intensity of the TSE peaks is associated with the "degree of completion of the phase transformation and the number of structural defects"[93] and the role of physicochemical processes in oxide and adsorption films is not taken into account.

The magnetic transformations in nickel, chromium, and the oxide films coating them have been investigated[92,94,95], the emission being measured with a gas-filled counter. The TSE maxima were observed under illumination at the temperatures corresponding to the Néel points for the oxides (NiO and Cr_2O_3) covering the metal and at the Curie point of the initial nickel. It was established that the fundamental parameters—the temperatures of the peaks and the emission intensity—are determined by the thickness of the oxide layer. It was concluded that the exoemission method can be used to investigate not only phase transformations but also the gas corrosion of metals and in the solution of the problem of the formation of protective coatings in the form of thin films of metals and dielectrics.

Exoemission on heating and cooling has been observed for $Fe_{1-x}S$ pyrite specimens cut out of a lump of the mineral[96]. The peaks and inflections on the curves were attributed to the polymorphic and magnetic transformations in microregions of the crystal with a different phase composition. The powdered specimens did not exhibit emission peaks under these conditions. The exoemission method was suggested for the study of the degree of homogeneity and composition of complex minerals in those cases where the phase transition points depend strongly on the stoichiometry.

The changes in emission intensity at the phase transition points are said[95] to be caused by processes occurring on the specimen surface, for example, the generation of stresses and cracks during plastic deformations in the oxide film owing to abrupt changes in the thermal expansion coefficients. The observed emission is accounted for by the possible local decrease of the electron work function owing to the displacement of dislocations onto the surface followed by adsorption (photosorption) or heterogeneous-catalytic processes when the emitter interacts with the quenching vapour of the counter, etc.[95]

Thus the data available at the present time for exoemission in first- and second-order phase transitions in metals and alloys are contradictory. Depending on the previous history of the specimen and the state of the surface, the TSE peaks may or may not coincide with the phase transition points; the emission observed on heating the specimens, i.e. in phase transformations involving absorption of energy, is difficult to interpret.

There are two views on the nature of the emission in phase transformations. The first is based on the consideration of physical processes only. The emission peaks observed on heating certain ferroelectric substances, for example, are regarded[97] as a result of the "filling of traps with electrons and the liberation of electrical energy in phase transitions". The second view, which takes into account the role of physicochemical factors, is based on the absence of exoemission from metals and alloys lacking an oxide layer, which has been firmly established experimentally[85,87]. A detailed analysis of the available data leads to the conclusion that the emission accompanying phase transitions is caused by a set of complex physicochemical transformations in the oxide and sorption films and can be understood on the basis of the physicochemical concept described below (see Section VI).[25]

In studies of the thermally stimulated emission accompanying the decomposition of certain salts, particularly hydrated salts, it was observed that heating of hydrated quinine sulphate gave rise to an intense emission at 75–100°C; the corresponding emission peak was also observed on cooling[1]. It is suggested that these phenomena are caused by the liberation and absorption of water[1]. Later these studies were repeated[98,99]. The emission and the accompanying luminescence phenomena were absent when quinine sulphate had been dehydrated beforehand.

More detailed studies of emission from hydrated sulphates, chlorides, carbonates, etc. were made by Hanle et al.[100] The charges were recorded *in vacuo* with the aid of a secondary electron multiplier. In all the cases investigated, the liberation of the water of crystallisation was accompanied by the emission of negative ions. The number of TSE peaks corresponded exactly under these conditions to the number of singular points associated with the decomposition of hydrates of different composition; however, the TSE maxima were somewhat displaced towards higher temperatures.

Exoemission was also observed in the decomposition of certain nickel compounds[101]. Thermally stimulated emission was recorded by a gas-filled counter under illumination. The TSE peaks corresponded to the decomposition temperatures of the initial compounds, which was confirmed by X-ray diffraction analysis. Repeated heating led to the observation for all the compounds of the same maximum at 230°C, which was attributed to a phase transition in nickel(II) oxide (the Néel point). The author[101] notes that the method described makes it possible to investigate the kinetics of the thermal decomposition of chemical compounds and to analyse the decomposition products.

IV. EXOEMISSION AND MECHANOCHEMISTRY

1. Metals

For metals, exoemission caused by mechanical influences is in fact of greatest interest. This is because of the possibility of employing exoemission in the study of

deformations, the processes involved in the mechanical treatment of machine components, the fatigue resistance of materials, etc. Studies in this field have been concerned with the emission caused by plastic and other deformations, friction, milling, sand-blasting, etc.[1,26,48,58,59,102]. In these excitation methods, dislocations and point defects (vacancies) and their diffusion and annihilation play a significant role. Secondary surface processes take place simultaneously—the disruption of the oxide film and desorption as well as adsorption and oxidation, these being largely caused by the migration of dislocations onto the surface.

On the other hand, the influence of the physical chemistry of the surface on the mechanical (plastic) properties of metals has been vigorously investigated recently. Deformations are known to be facilitated by adsorption, the effect having been explained by Likhtman et al.[103] The significant influence of oxide and other special coatings on the mechanical properties of metals has been demonstrated. Oxide and other surface formations lead to the generation of energy barriers, preventing the emergence of dislocations; the decrease of the height of these barriers on polishing, etching, and the adsorption of surfactants facilitates deformation.

There is experimental evidence showing also that adsorption processes are the cause of deformations in the surface layer: depending on the nature of the adsorbent–adsorbate system and on the degree of surface coverage, both expansion and contraction can take place[104]. It follows from the foregoing that exoemission, deformation, and adsorption (desorption) phenomena are indissolubly linked and that they should be considered simultaneously.

There exist at present two fundamental and in a certain sense contradictory views on the nature of exoemission from deformed metals. Some investigators[105-108] believe that the processes determining emission occur in oxide layers, while others[57-59] claim that the emission kinetics are determined by the diffusion of defects (dislocations, vacancies) and that emission occurs as a result of the decrease of the electron work function caused by deformations.

A quantitative correspondence between the degree of deformation and the intensity of exoemission has been found[105,106]. The following emission mechanism has been proposed[106]. Plastic deformations lead to the generation of mobile point defects (vacancies) which migrate towards the surface and form capture layers in the forbidden gap of the oxide. The defects produced behave as centres of photoemission and thermally stimulated emission. The significant role of the formation and migration of vacancies and dislocations has been emphasised also in other investigations[57-59,107-109]. It has been shown that the emission intensity $I \propto \epsilon^n$, where n is the degree of deformation. After carrying out experiments on emission from deformed aluminium coated by oxide films of different thickness, Sujak[107] concluded that the emission takes place from charged cracks in the oxide. This model is analogous to that proposed previously[110]. It has been shown[111] that the intensity of emission on deformation increases significantly in the presence of moisture in the atmosphere of the quenching gases of the counter. It is suggested that moisture neutralises the strong electric field arising across the cracks, which hinders the release of electrons. Results obtained with a Geiger counter were confirmed by experiments *in vacuo* using a secondary electron multiplier as the recording instrument[112].

In other studies[57-59], it was suggested that exoemission is determined by the proportion of defects and by the nature of the elementary deformation steps, which depend on the nature of the metal itself. The authors believe that the "deformation excitation" possesses definite specific features and that the emission of electrons accompanying it should be regarded as an independent type of emission. There are numerous experimental facts indicating the lack of validity of these claims. It is also difficult to justify theoretically the existence in a conducting metal of trapping levels giving rise to the prolonged relaxation times of the excited states responsible for exoemission[48,114]. For example, it has been shown[25,48] that exoemission parameters are independent of the method of excitation. On deformation, the emission intensity always increases to a certain limit, after which it falls exponentially (Fig. 1). A similar type of curve with a maximum occurs when an atomically clean metal surface is exposed to active gases[49] and is explained by adsorption and oxidation phenomena. In support of their view that the exoemission on deformation is caused exclusively by the formation of structural defects, the authors[113] present the results of experiments in an ultrahigh vacuum, where PSE was observed following the extension of an aluminium specimen and attribute fundamental importance to them. No account was taken of the fact that, under the conditions of treatment adopted (degassing at 400°C), an atomically clean surface is not obtained and that the observed emission is caused by the degradation of the oxide layer. It has been shown[48,56] that, in the case of an atomically clean surface, mechanical treatment under the conditions of an ultrahigh vacuum does not lead to the occurrence of either photoemission or thermally stimulated emission.

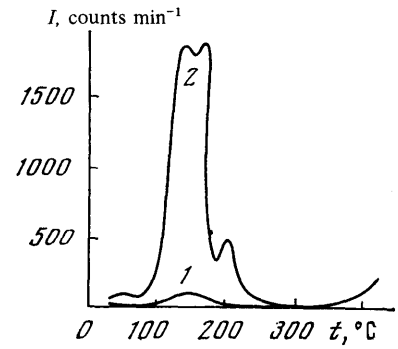


Figure 6. Thermally stimulated emission from a quartz specimen after vibromilling *in vacuo* (curve *1*) and in an atmosphere of oxygen (curve *2*).[125]

Depending on the thickness of the oxide layer, either PSE, which depends on the pressure of the residual gas (layer thickness $d \leq 45$ nm), or dark emission ($45 \leq d \leq 230$ nm) is observed on deformation by extension[114]. In the former case, PSE is analogous to that observed when the surface is cleaned[56] and is caused by the decrease of the electron work function owing to the adsorption of water. In the latter case exoemission is due to the disruption of the oxide film and occurs without photostimulation.

In calculations on the kinetics of exoemission from deformed metals, the authors[115,116] also took into account the cracking of the oxide film, the diffusion of vacancies to

the surface, and the interaction of the freshly formed surface with the gases in the surrounding medium followed by oxidation, in contrast to earlier views [57-59].

Exoemission on friction has been examined in detail by Evdokimov and Semov [102], who investigated emission under dynamic conditions during friction and after its cessation, in the absence and presence of lubricating materials. The photostimulated emission was recorded by an open counter in air. For different types of steel and cast iron, the PSE intensity after the cessation of friction passed through a maximum; for the chemically more reactive aluminium, emission whose intensity diminished exponentially was observed. These findings are analogous to those obtained on deformation [57,58] and on adsorption of active gases on freshly formed surfaces [48,56].

Thus the kinetics of exoemission on deformation of metals, friction, and adsorption of gases on freshly formed surfaces are determined by the physicochemical transformations which accompany the relaxation processes in a damaged surface layer.

2. Non-Metallic Crystals

For non-metallic crystals, emission decaying over a period of time has been observed after comminution and grinding [1]. Numerous minerals and inorganic and organic crystals have been investigated. It has been noted [1] that, on comminution *in vacuo*, the crystals acquire an appreciable charge, which plays a significant role in the observed effects. The formation of charges accompanying emission on heating single crystals (LiF) was recently confirmed by direct measurements [117]. The density of the elementary charges was 10^{10} cm^{-2}, but the charging mechanism is not clear. One of the possible explanations is based on the model involving the formation of a "triboplasma", arising when the crystal is cleaved. High energy levels of the emitted electrons were observed; the greatest number of electrons had an energy of 20 keV, while the maximum observed energy was approximately 120 keV. The field strength calculated from the formula $E = \sigma/\epsilon_0$ proved to be approximately 10^5 V cm^{-1}, so that the observed emission is not cold ("field") emission.

Independently of Kramer's study [1], the phenomena of the emission of negative charges in processes involving the dissociation of adhesion and cohesion linkages were investigated and described by Krotova [118], who observed the emission of fast electrons with energies of several keV. It was suggested that the high energies are caused by the acceleration of electrons in the strong fields of the electrical double layer arising following the breakdown of contacts. The phenomenon was called "mechanoemission". The mechanism of these processes is probably different from that of the exoemission of slow electrons. However, it must be emphasised that the after effects, consisting in the relaxation of the excited states arising following the breakdown of adhesion and cohesion contacts, are exoemission. This is indicated by the emission kinetics, which are the same as those observed after excitation by other methods, the low electron energies, and a number of other factors.

The significant role of dislocations in exoemission from ionic crystals has been noted. It has been established [119] that, when LiF is cleaved, mobile dislocations with a free path of several centimetres are formed. The hypothesis has been put forward that these dislocations transport the excitation energy generated by electron bombardment. The intensity of thermally stimulated emission from LiF caused by irradiation with X-rays increases with increase of the density of dislocations [120]. According to Knab and Urusovskaya [120], the observed effect is a consequence of the increase of the number of point defects owing to the interaction of dislocations. The thermal stability of the *F*-centres (the position of the TSE peak) is determined by the interaction of the point defects with dislocations of different types [121]. The authors do not take into account the possible processes involving radiation-induced and postradiation adsorption following the excitation of specimens in air and the recording of the emission by a counter. The conclusion concerning the lack of influence of adsorption layers on exoemission from deformed LiF crystals, reached in some investigations [122,123], are insufficiently justified, since the authors did not undertake special cleaning of the surface, although they recorded the emission under ultrahigh vacuum conditions.

It has been shown [124] that the cleavage of alkali metal halide crystals is accompanied by appreciable gas evolution. It was found that the structural defects generated by the vibromilling of quartz are capable of emission only in the presence of adsorbed oxygen (Fig. 6). [125] Under these conditions, the TSE peak ($t_{max} \simeq 150$°C) coincides with the maximum in the rate of desorption of oxygen from such oxides [126].

A detailed analysis of data for exoemission caused by mechanical influences on metals and non-metallic crystals leads to the conclusion that the presence of adsorption layers plays a decisive role under these conditions.

V. EXOEMISSION AFTER EXCITATION BY IONISING RADIATION

1. Metals, Semiconductors, and Oxides

Like mechanical treatment, ionising radiation does not excite exoemission from the atomically clean surfaces of metals and semiconductors [45,48]. It is therefore useful to examine emission only from real metals and semiconductors coated by an oxide layer. It has been established [127-129] that, independently of the nature of the metal, the thermally stimulated emission peaks occurring after excitation by X-rays are located in the same temperature ranges (140–160° and 260–280°C). The same peaks have been observed for aluminium [48] acted upon in other ways: milling and exposure to β-radiation. It was concluded that exoemission is excited from the capture levels in the oxide layer.

It has been established for the majority of powdered oxides, excited by electron bombardment, that the TSE peaks are located in the same temperature ranges as for metals [30,127] (Fig. 7). The number and relative intensities of the peaks are independent of the nature of the oxide (semiconductors with electron or hole conductivity as well as insulators), but are not determined by its previous history. The emission capacity of the oxide can be significantly reduced by vacuum heat treatment and increased as a result of the adsorption of active gases and vapours.

It has been established [130] that, following the adsorption of electron-donating gases (hydrogen), the emission capacity of Al_2O_3 excited by X-rays increases, while, on treatment with electron-accepting gases (N_2O, CO_2), it falls. It is suggested [131] that hydrogen adsorbed in the atomic form generates shallow donor levels and that hydrogen and deuterium atoms lead to the formation of donor levels of different depths (the "isotope effect").

The authors of the above investigations begin their interpretation with the concepts of the band model of exoemission and the electronic theory of chemisorption, assuming that the molecules (atoms) of the adsorbed gases generate donor (acceptor) levels, increasing (decreasing) the concentration of the conductivity electrons responsible for exoemission.

More detailed studies for more oxides showed that, in contrast to electrical conductivity, the emission capacity is not determined by the electron-donating or electron-accepting nature of the adsorbed molecules (atoms): the adsorption of oxygen, a typical electron acceptor, on the surfaces of silicon, ZnO, ZnS, SiO_2,[25,37,132,133] and BeO[134] leads to an increase of emission capacity. The band model, which takes into account the role of the concentration of conductivity electrons and of the surface potential in exoemission, cannot explain these results. It is suggested that thermally stimulated emission takes place directly from the capture levels generated by different forms of adsorbed oxygen[30,133,134].

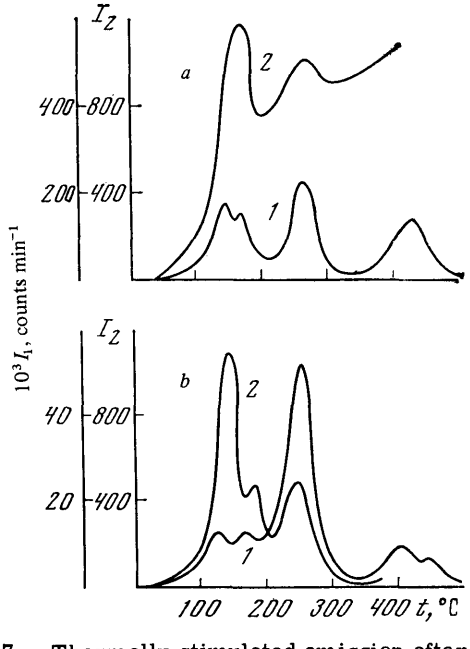


Figure 7. Thermally stimulated emission after excitation by electron bombardment: *a*) from aluminium[129] (curve *1*) and corundum[30] (curve *2*) surfaces; *b*) from nickel[129] (curve *1*) and nickel(II) oxide[73] (curve *2*) surfaces.

It has been established in a recently published study[132] that the surface states responsible for exoemission from oxidised silicon excited by low-energy electrons are generated by adsorbed oxygen (O_2^-). The physical model of the excitation and emission of exoelectrons is based on the potential curves for the excited state of the negatively charged form of adsorbed oxygen. It is concluded that the TSE method can yield valuable information about the state of the adsorbed molecules. This is of interest for both fundamental and applied research, particularly in the field of heterogeneous catalysis.

2. Ionic Crystals

For ionic crystals (crystalline phosphors and alkali metal halides), the commonest method of excitation is treatment with ionising radiation. The electronic energy level schemes for crystalline phosphors and coloured alkali metal halides have been deduced theoretically and investigated experimentally in considerable detail. An analogy has been found between exoemission and luminescence phenomena[1,9-11], which has in fact served as a basis for the development of the most widely accepted band model of exoemission. Like luminescence, exoemission can be excited by short-wavelength light and by high energy radiation (electronic and ionic bombardment, by X-irradiation and β-irradiation, by exposure to a glow discharge, etc.). After the removal of excitation, the decay of the afteremission and the afterglow are described by the same laws. Heat treatment frequently leads to the appearance of TSE peaks and thermoluminescence in the same temperature ranges. It is believed[11] that the analogy is based on common elementary physical processes. At the same time there are also differences between luminescence (bulk-phase effects) and exoemission (a surface phenomenon) phenomena. Luminescence is associated with the presence of activator atoms, while, according to the band scheme, exoemission should be independent of their presence.

Results which do not fit within the framework of the proposed model have been published. For example, it has been found that the intensity of the afteremission excited by electron bombardment depends on the activator concentrations[52]. Agreement between the numbers and temperatures of the exoemission and luminescence peaks is not always observed. The discrepancies between the results of different workers and the marked dependence of the thermally stimulated emission spectra on the technology of the preparation of the phosphors[135] led to the conclusion that surface states are involved in these phenomena; however, the nature of these states has not been considered.

The main objects of the fundamental investigations of exoemission and luminescence are sulphides, sulphates, and alkali metal halides. A correlation between the temperatures of the PSE and thermoluminescence peaks has not been observed for sulphides[136,137]. On the basis of the results of studies *in vacuo*, Behmenburg[136] suggested that in the case of zinc sulphide thermoluminescence is caused by the presence of capture levels in the crystal, while thermally stimulated emission takes place from trapping levels in the adsorption layer (for example, of oxygen). However, the nature of this layer was not investigated.

Exoemission from activated sulphides has been studied[67,138,139] using both a gas-filled counter and a secondary electron multiplier *in vacuo* as recording instruments. In the former case, it was found that the activator (Cu, Ag) has a significant influence on the absolute and relative intensities of the TSE peaks[67,138]. The observed direct relation between exoemission and catalytic activity permitted the conclusion that the emission centres (activator ions) are either the centres of the activated adsorption of methanol or the catalytic centres.

After electron bombardment, TSE peaks were observed for ZnS.Cu, ZnS.Ag, and ZnS.Al single crystals[139] in the same temperature ranges: at 120–140°, 160–180°, and 220°C. Vacuum heat treatment and heat treatment in hydrogen reduced significantly the emission intensity, while the adsorption of oxygen, water vapour, and methanol increased it. The adsorption of an electron-donating gas

is known to increase the concentration of conductivity electrons in a semiconductor and to reduce the surface potential, while the adsorption of oxygen acts in the opposite direction. These findings lead to the conclusion that, in contrast to the hypothesis of the band model, the exoemission from the sulphide surface takes place without the participation of the conductivity electrons and that the emission parameters are not influenced by the surface potential either.

Thermally stimulated emission from sulphates has been studied[1,9,11,135]. The emission intensity was measured using as recording instruments a counter after excitation with X-rays or a secondary electron multiplier *in vacuo* after excitation by electron bombardment. Data concerning the positions of the TSE peaks and their correlation with thermoluminescence (TL) are contradictory; the involvement of the activator in the formation of the electron localisation levels on the surface of sulphates is likewise controversial. These contradictions are associated with the differences in the technology of the preparation of the specimens[135], in the methods and duration of their storage[140], and in the methods of excitation and recording which have a significant influence on the state of the adsorption layers. Depending on its previous history, the temperatures of the TSE and thermoluminescence peaks for the same specimen can both coincide and diverge[141].

A correlation between the thermally stimulated emission and thermoluminescence phenomena is observed when gas and vapour molecules adsorbed during technological treatment, during excitation of the emission (radiation-induced adsorption), or during recording (postradiation adsorption of the quenching vapour of the counter) are involved in these processes. Luminescence is a bulk-phase phenomenon and the role of adsorbed gases is not usually considered in this connection, although in dispersed systems it can be considerable. Studies where it has been shown that the luminescence of a crystalline phosphor is stimulated as a result of adsorption, particularly of oxygen and water vapour, have been published only recently. The investigations of the comparatively new phenomena of adsorbo-[142] and radicalo-luminescence[143] are noteworthy.

The exoemission from alkali metal halides coloured by ionising radiation has been the subject of detailed research[19]. It is suggested that the TSE maxima correspond to the thermal decomposition of definite colour centres regardless of the method of their generation (additive electrolytic and photochemical colour generation). For example, the TSE peak for NaCl at 110°C has been explained by the thermal decomposition of the *M*-centres and that at 280–290°C by the decomposition of the *F*-centres. A detailed analysis of the available data has shown, however, that, for alkali metal halides too, the technology of the preparation, the method and duration of the storage of the specimen, and the method of excitation and recording (gas-filled counter, secondary electron multiplier *in vacuo*) play a much more significant role in the TSE phenomena than the presence of particular colour centres and the nature and concentration of activators.

It has been established[36] that the intensity of the fundamental peaks of the TSE from NaCl, which have been attributed to the thermal ionisation of colour centres, decreases appreciably as a result of vacuum heat treatment (at 400°C) and is restored after hydration of the specimens. The adsorption of active gases and vapours (hydrogen, carbon monoxide, oxygen, and water and alcohol vapours) on the NaCl surface excited by electron bombardment causes a marked activation of exoemission[144].

It follows from the foregoing that the defects arising under the influence of ionising radiation on alkali metal halides (colour centres) give rise to emission centres only in the presence of adsorption layers.

3. Principles of Exoemission Dosimetry

The proportionality between the emission intensity and the dose of the exciting radiation was established for the first time in 1957 for calcium sulphate[145]. The introduction of an activator (manganese) makes it possible to determine very low radiation doses (0.1 mrad). The first exoemission dosimeters, based on the recording of both photostimulated[146] and thermally stimulated emission[147], were developed using calcium sulphate. The following fundamental advantages of exoemission dosimetry have been noted: the possibility of wide variation of the emitting materials, their low cost, the lack of their sensitivity to light before exposure to the action of ionising radiation, the simple technology of their treatment, the possibility of their repeated employment, and their high sensitivity to the action of low-energy radiation.

Further studies on the scope of exoemission dosimeters and their commercial production were continued in 1966–1970. Sulphates, alkali metal halides, and particularly beryllium oxide, both in the initial state and activated by the addition of metals, have been used as the materials for the preparation of the dosimeters. The number of such studies has greatly increased in the last 3 years. TSE dosimeters based on BeO have been developed in the USA for specific applications and have undergone prolonged field tests[148]. These dosimeters have definite advantages over those usually adopted (for example, luminescence dosimeters) for the accurate measurement of small doses of low-energy radiation, particularly in mixed radiation fields. A detailed review of the problem of exoemission dosimetry has been published[149]. The main unsolved problems, preventing the commercial production of exoemission dosimeters, is the stability and reproducibility of readings. It has been found that the emission parameters (the number, temperatures, and intensities of the peaks) depend significantly on the technology of the preparation and methods of storage of the dosimeters[148].

The parameters of the thermally stimulated emission from $CaSO_4$ specimens, used as a basis for the development of TSE dosimeters in the USSR, have been investigated[141]. The "ageing" effect has been observed and investigated for the activated sulphates. Thus high-temperature emission peaks are characteristic of the initial $CaSO_4$ prepared by fusion; after prolonged storage in air, the "population" of the capture levels changes—the low-temperature peak (140–160°C), characteristic of all the metals and oxides investigated, predominates. Experiments on the influence of adsorption on the TSE spectrum showed that the "ageing" effect is a consequence of the adsorption of water.

Thus the problems of the stability of the operation of highly sensitive and promising exoemission dosimeters can be solved only by detailed investigation of the physical chemistry of the surface under storage and operating conditions.

VI. THE PHYSICOCHEMICAL NATURE OF EXOEMISSION

A phenomenological theory, permitting a description and an examination of exoemission from metals, semiconductors, and dielectrics from a single standpoint, has

been proposed[25]. As shown in Section I of this review, exoemission occurs as a result of the relaxation processes of the excited states and the study of its mechanism involves the analysis of the kinetic parameters—the quenching constants of the afteremission at a constant temperature and the activation energy and pre-exponential factors in the recording of thermally stimulated emission. A formal kinetic treatment of the emission processes and a mathematical model based on general physical considerations taking into account the band theory of solids have been described in a detailed review of these problems[15]. On the basis of the chemical aspects dealt with in the above review, we shall consider in this section the physicochemical picture of the exoemission phenomenon.

The emission of charges is the result of a complex set of physical and physicochemical processes in the damaged surface layer. Here the fundamental parameters are determined by the slowest stage of the reactions taking place. The coincidence of the TSE peaks for substances of different classes shows that the rate-limiting stage occurs in the surface layer whose nature is independent of the "support", for example it can be a layer of adsorbed oxygen[30,133,134].

The present author[25] believes that these layers are mobile ("quasi-insulated" from the support). In this case, the temperature of the peak, which in the general case determines the activation energy[15] of the emission processes, should depend only slightly on the nature of the adsorbent, which has been observed experimentally[25]. The mobile layer can be formed in the surface phase as a result of the adsorption of gases and vapours from the residual atmosphere *in vacuo* on excitation or heat treatment of the specimen, as suggested by Maenhout-Van der Vorst and Demuer[133], or on degradation of the oxide (adsorption) film present on the surface[150,151]. Hence it follows that the pressure and composition of the surrounding atmosphere during excitation and recording are of fundamental importance for the solution of the problem of the emission mechanism.

The fundamental emission parameters for metals, oxides, and ionic crystals (crystalline phosphors) have been compared using a counter (argon–alcohol atmosphere) as the recording instrument *in vacuo* (10^{-5} mmHg) with a residual air atmosphere and in an ultrahigh vacuum (10^{-8}–5×10^{-9} mmHg) with a residual hydrogen atmosphere[25,151]. It was found that for metals the fundamental parameters (the quenching kinetics and the positions of the TSE peaks) are independent of the method of recording, whereas for ionic crystals (phosphors) a significant discrepancy between the results is observed. This is associated with the possibility of the formation of stable radiation-induced defects in ionic crystals, stimulating the radiation-induced adsorption of gases from the surrounding medium, including the quenching gases of the counter. Experimental evidence in support of this phenomenon has been obtained in studies[139,144,152,153] where it has been shown that the radiation-induced adsorption of active gases and vapours has a significant influence on the number, temperatures, and intensities of the TSE peaks.

For excitation and recording *in vacuo*, the spectrum of the trapping levels characterised by the thermally stimulated emission is independent of the pressure and composition of the residual gases in the vacuum (air, $p \simeq 10^{-5}$ mmHg; hydrogen, $p \leqslant 10^{-8}$ mmHg) and of the presence of the lubricant vapour[151]. This implies that the "mobile" adsorption layer, responsible for the exoemission processes, is formed as a result of the degradation of the surface layer of the emitter on excitation.

It was shown above that exoemission takes place as a result of mechanical treatment, the action of ionising radiation, phase transformations, adsorption, desorption, and catalysis in adsorption layers. Fig. 8 presents the results of the study of TSE after exposure to different influences. The temperatures of the peaks are the same, so that the rate-limiting stage in the emission kinetics is determined by the same elementary processes regardless of the method used to generate the excited states. When mechanical influences are employed, the role of the formation of dislocations and vacancies as well as their diffusion and emergence on the surface is significant. Secondary processes take place at the same time—the disruption of the oxide film, adsorption, and oxidation, which take place primarily at the sites where dislocations and other defects emerge on the surface. Phase transitions are also coupled with the rearrangement of the structure, accompanied by the formation and degradation of the oxide layer; under these conditions, the mobility of the defects and the probability of their emergence on the surface increases and the adsorption and oxidation are activated. The adsorption and desorption processes are in their turn the cause of the deformations in the surface layer[104].

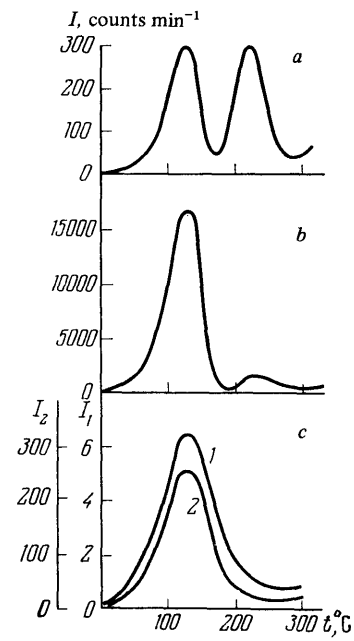


Figure 8. Thermally stimulated emission from a silicon single crystal: *a*) "self-excited" emission after etching[37]; *b*) after electron bombardment; *c*) after treatment with emery (curve *1*) and after polishing combined with exposure to X-rays[57] (curve *2*).

In constructing both the physical and the physicochemical model of exoemission, one of the central problems is the origin of the energy necessary for the release of electrons. The present author[25], who devised the physicochemical concept, believes that the source of this energy is the recombination reactions of the active species (ions and

radicals) in the damaged surface layer of the solid. In a recently published study[154], it was demonstrated by direct experiments that the recombination reactions of atomic hydrogen and oxygen on the surface of the solid (for example, activated sulphates) result in the emission of negative charges (electrons and ions). On subsequent heating, thermally stimulated emission is observed. This phenomenon has been called[154] "radicalo-recombination emission".

The formation of active species (radicals, radical-ions) is possible for all the methods of excitation of the solid described above, giving rise to exoemission. Mechanical, radiation, and other influences as well as phase transformations are known to lead to the same effects—the rearrangement of the structure and ultimately the dissociation of chemical bonds and the formation of free radicals (radical-ions) together with structural defects. It has now been established by electron spin resonance that radicals are formed under radiation-induced mechanical influences during adsorption and catalysis in the adsorption layer. Mass-spectrometric studies of gas evolution from the surface of oxides have shown that electron bombardment—one of the common methods of exciting emission—causes the degradation of the hydrate coating with formation of hydrogen and oxygen[150,151].

Data illustrating the physicochemical mechanism of exoemission, based on the above reactions in the surface layer, have been published[25,30,155]. Thermally stimulated emission is a result of the following set of processes: heat treatment, phase transformations in adsorbed surface compounds (for example hydrates), the formation of a mobile adsorption layer, desorption, the generation of stresses, the relaxation of stresses (deformations in the surface layer) and electron emission (the acquisition of a positive charge by the surface). The desorption step is preceded by surface migration (de Boer's migrating or "jumping" molecules)[156]. The recombination of ions, radicals, and other active species results in two-dimensional condensation. The recombination energy is consumed in the liberation of the electrons localised on the surface. The trapping levels can be produced either by surface defects such as colour centres or by adsorbed ions (O_2^-, O^-, OH^-, etc.). The active species are recombined near specific sites (defects), energetically insulated from the lattice, where the liberated energy is not dissipated in the form of phonons, but is consumed in the excitation of electrons. The probability of triple collisions (two active species colliding with a lattice defect) is low, and this accounts for the extremely low emission currents (10^{-17}–10^{-19} A). At the excitation temperature, only part of the radicals (ions) formed recombine—afteremission and gas evolution are observed. Subsequent heat treatment leads to the stepwise recombination of the active species—thermally stimulated emission and the accompanying thermal desorption take place. The experimental evidence for the simultaneous occurrence of the thermally stimulated emission and thermal desorption processes, thermally stimulated emission and catalysis in the adsorption layer, as well as examples of reactions illustrating the physicochemical mechanism of the exoemission phenomena described above (the "chemical mechanism of the processes") are described in Section III of the present review.

Thus, according to the concepts developed by the present author[25], exoemission is a consequence of the stepwise recombination of active species in the mobile adsorption layer arising during the excitation processes. The thermally stimulated emission peaks are caused by the valence transformations in the layer of adsorbed oxygen[132].

VII. THE PROSPECTS FOR THE APPLICATION OF EXOEMISSION IN SCIENTIFIC RESEARCH AND IN ENGINEERING

The above review of the phenomena accompanied by the low-temperature emission of negative charges shows that exoemission can serve as an extremely sensitive indicator of physicochemical processes in the surface layers of solids: adsorption, desorption, oxidation, corrosion, heterogeneous-catalytic reactions, etc. Studies have shown that thermally stimulated emission makes it possible to follow the formation of the active surfaces of catalysts and adsorbents during preliminary treatment (for example, dehydration) and their activation processes, to investigate the action of the individual components of the reaction and the reaction mixture on the "energy relief" of the surface, etc.[73]

Studies on TSE during catalysis permit conclusions concerning the mechanisms of certain reactions in both the adsorption layer[72,73] and in the gas phase[70,71]. A direct relation between catalytic activity and emission capacity has been established for certain deposited and promoted systems[67,69], so that the emission intensity can serve as the basis of a method for estimating the activities of catalysts, particularly when they are poisoned by admixtures in the starting material[157].

Since exoemission is extremely sensitive to radiation, the TSE method can be used to investigate the radiation-induced damage in semiconductors and dielectrics[37,158], the phenomena of radiation-induced adsorption and catalysis[159], and heterogeneous radiolysis[159]. A relation has been established between the exoemission parameters, the proportion of defects, and the "radiation stability"[157] of materials used as the elements of lasers. The author recommends the exoemission method for the quality control of the surfaces of the elements of solid-state lasers.

The adsorption layers formed during the technological treatment of the components and their storage or operation are known to determine in many instances the reliability of the apparatus in the electrovacuum industry and in semiconductor engineering. Exoemission, which is extremely sensitive to the presence of adsorption films, particularly those of water and oxygen, can serve as an effective method for the control of technological processing in many industries[37,160].

The "ageing" effects on active surfaces, for example those of catalysts, exoemission dosimeters, and crystalline phosphors, etc. are also associated with the formation of adsorption layers. The exoemission method makes it possible to follow the changes in the state of the surface during the storage of such systems exhibiting adsorption activity[140].

Exoemission was already suggested in the initial stage of research[26] for monitoring certain technical processes involving the treatment of metals, plastic deformations, etc. This applies particularly to processes employing lubricating materials, i.e. where the structure and mechanical properties of the surface of metals play an important role. For example, exoemission from the surface of a bearing under the conditions of prolonged working of a Mercedes-Benz goods truck has been investigated[1]. A study has been made of exoemission during the deformation of technically important materials and friction[58,59,102]. It was noted above that thermally stimulated emission is also recommended for the study of first- and second-order phase transformations in metals and alloys.

Exoemission has proved to be an effective method for the investigation of comminution and sintering processes

(for example in the paint and varnish industry and in powder metallurgy[28]). There is evidence for the possibility of employing exoemission in "photography"[1]. Exoemission microscopes, permitting a detailed study of the defect structures of metallic and non-metallic surfaces after mechanical, radiation, and other treatments, have been developed recently in the USA[35]. Exoemission microscopy has many advantages over electronic, thermionic, etc. microscopy. It makes it possible to reduce appreciably the temperature of the test specimens and to eliminate the activation of the surface (for example by barium, strontium, and caesium) necessary in thermionic emission from metals, and permits the investigation of semiconductors with a wide forbidden gap as well as insulators.

The likely usefulness of exoemission in biological research has been claimed recently[161]. There are publications concerning the thermally stimulated emission from certain aminoacids[162], kidney stone[163], etc. On the basis of the results obtained, the authors recommend exoemission for research in medicine and pharmacology. Mention should also be made of attempts to employ exoemission in radiological studies connected with the development of highly sensitive exoemission dosimeters for specific applications[149]. Exoemission from bone tissue, dental enamel, collagen, etc. after exposure to radioactive emission has been investigated[164].

Studies of heterogeneous-catalytic reactions have shown that oxidation processes are accompanied by spontaneous emission, particularly when they occur with proton or electron transfer. Presumably exoemission will serve as an effective method for the investigation of biochemical reactions, especially in the solution of problems such as those of photosynthesis and cell bioenergetics. These reactions are also known to include stages accompanied by the transfer of both electrons and protons.

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The above review of the results and their analysis have shown that exoemission is a complex physicochemical phenomenon and that the elucidation of its detailed mechanism is closely related to the problem of the physics and physical chemistry of the surface. Despite the fact that approximately 25 years have elapsed since the first studies by Kramer in this field, exoemission continues to be a relatively little investigated phenomenon, whose study is the concern of only a few scientists—physicists and metallurgists. However, it is known that the solution of the problems of chemisorption, catalysis, adhesion, mechanochemistry, surface phenomena in semiconductors, and the physics of thin films is closely related to the problem of exoemission and requires the joint efforts of physicists and chemists[164].

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