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Electric charge in irradiated dielectrics, and their properties

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Abstract. The formation of a space charge in dielectrics under the influence of ionising radiation (one of the fundamental effects stimulated by the irradiation of solids) is discussed. An increasing interest in this problem has been generated by the wide use of powerful sources of ionising radiation in both science and technology. Radioactive dielectrics, i.e. highly resistive solids of various natures (glasses, crystalline compounds, ceramics, etc) containing a permanent source of ionising radiation (radionuclides) occupy a special place in this field of study. These materials are used, for example, for the treatment and consolidation of nuclear waste in atomic technology. It has been experimentally established that the properties of irradiated dielectrics are affected not only by the presence of space charge resulting from the permanent self-irradiation but also by the form of the charge distribution in the volume of the dielectric. Examples of the relationship between the volume charging of radioactive and of irradiated dielectrics and the characteristics of the materials such as their dissolution kinetics, mechanical and electrophysical properties, redistribution of the energy absorbed from the ionising radiation, etc, are discussed. The bibliography includes 42 references.

I. Introduction

The formation of substantial space charges in solids during their interaction with ionising radiation (radiation charging) was first recognised as an independent physical phenomenon during studies of radioactive salts. In 1900 Pierre and Marie Curie published the results of their study of the formation of space charge in radioactive preparations of $Ba(Ra)Cl_2$.[1] The chosen experimental method allowed them to establish the sign but not the magnitude of the stationary space charge†, since only the current of ionising species from the sample was monitored. Unfortunately, no other studies of the charging of radioactive samples were published at the time.

Almost the whole of the later work in this field was aimed at solving the fundamental technical problem of creating 'radioactive current sources' (atomic batteries). Some current sources of this type operate on the principle of collecting the charges on a collector separated from the radioactive preparation by an insulating layer.[2] Their operation is very closely associated with the accumulation and redistribution of charges in a heterogeneous medium consisting of a source of radiation, a dielectric interlayer, and a collector.

Similar effects have been noted in the interaction of accelerated electrons, γ quanta, and other ionising species with various solid materials. Even the irradiation with electrons having an energy of 50 – 100 keV, in an electron microscope, stimulates the explosive breakdown[3] of crystals such as $BaSO_4$ and KCl as a result of the accumulation of electric charges in the bulk of the crystals. Explosions due to the internal charging of the lead walls of protective chambers used in operations with a ^{60}Co γ source (several hundreds of curies) have had disastrous consequences.[4]

'Radiation charging' can also affect the properties of solids.[5] The catalytic activity of solids, their dissolution and vaporisation kinetics, and their electrochemical and other properties are all extremely sensitive to radiation charging. Thus, any solid having an electric resistivity greater than $10^{12}\ \Omega$ m passes into the 'electret state' after lengthy irradiation.[6] For example, in ordinary window glass the space charge produced by electron irradiation decreases two-fold[7] after ~100 h.

In general the following changes take place in all dielectrics exposed to ionising radiation: the formation of primary and secondary radiation-induced defects (excited and ionised particles, localised holes and electrons, displaced atoms, etc); local disordering of the dielectric structure (thermal cracks, recrystallisation); radiation-chemical decomposition (degradation) of the material, characteristic of complex organic

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† The term stationary space charge denotes the maximum charge (in equilibrium under the stated conditions) found in the sample during irradiation.

molecules, followed by the evolution of volatile radiolysis products; strong local heat evolution (especially during irradiation with powerful beams of accelerated electrons), accompanied by the formation of large thermal stresses in a region of radius equal to one-third the penetration (range) of electrons in the substance, possibly leading to the evaporation of the substance by a microexplosion; the accumulation of electric space charge, often up to levels where spontaneous electric discharges can take place, leading to the breakdown of the material.

All these processes affect the properties of dielectrics, and in particular they degrade the radiation stability of electric insulators, enhance their electric conductivity, lower their mechanical strength, etc.

Irrespective of the formation conditions of the electric space charge (external irradiation, or self-irradiation in the case of radioactive materials) the formation mechanisms of the radiation-induced charge exploit the following basic processes: the retardation of the charged particles in the bulk of the irradiated uniform material (for example, in a heterogeneous system) and the appearance of electric charging as a result of the gradient (in space) of the flow density of ionising radiation.

In all these systems we observe a macroscopically nonuniform distribution of charge density over the volume of the solid, which in the case of radioactive dielectrics (ceramics, glasses, salts) is retained almost indefinitely as long as radionuclides remain in the sample. Because of the accumulation of space charge, conditions favourable to local electric discharges may be produced. This phenomenon, together with the formation of radiation-induced damage, should be interpreted as one of the fundamental effects associated with the action of ionising radiation on solid dielectrics. Under these conditions the energy needed to break down the material radiation-electrically is very much smaller than the energy needed for the purely radiation-mechanical degradation.

II. Analysis of the space charging process. Microscopic approach. Irradiation with electrons

The most thorough analysis of the models that have been proposed for the dynamics and the kinetics of the formation of space charge can be found in the work of Tyutnev et al.[8] and Evdokimov.[9] The following are the main propositions underlying the general approach to the solution of this problem: the dielectric contains both free and trapped charge carriers of different signs (electrons and holes); the action of the ionising radiation on the medium produces, in addition to excess (thermalised) electrons, also carriers of each sign, in equal amounts, as a result of the ionisation of the medium; a loss of carriers is produced by their recombination and drift towards the sample surface under the influence of the space-charge field; the irradiation acts on the trapping centres, i.e. the degree of filling of the traps by carriers may depend on the radiation dose; carriers of both signs contribute to the charge transfer; the diffusion component of the current of carriers is ignored; the charge transfer obeys Ohm's law. The polarisation of the dielectric under the influence of the space charge is indirectly allowed for in the analysis of the charge dynamics by postulating the presence of deep as well as of shallow traps. Furthermore it is assumed that the dielectric is isotropic in its properties, though this stipulation is valid only for amorphous materials. However, the assumption allows us to write the kinetic equations in a one-dimensional variant, which simplifies the solution:

$$\frac{\partial n}{\partial t} - \mu_n \frac{\partial (En_0)}{\partial x} = G + G_n - k_1 n_0 p - k_2 n p_0 , \tag{1}$$

$$\frac{\partial p}{\partial t} - \mu_p \frac{\partial (Ep_0)}{\partial x} = G - k_1 n_0 p - k_2 n p_0 , \tag{2}$$

$$\frac{\partial n_T}{\partial t} = k_{3,n} n_0 [M_n(\xi) - n_T] - \nu_{0,n} \exp\left(-\frac{\xi}{kT}\right) n_T - k_2 p_0 n_T , \tag{3}$$

$$\frac{\partial p_T}{\partial t} = k_{3,p} p_0 [M_p(\xi) - p_T] - \nu_{0,p} \exp\left(-\frac{\xi}{kT}\right) p_T - k_1 n_0 p_T , \tag{4}$$

$$n = n_0 + \int_0^\infty n_T \, d\xi ; \qquad p = p_0 + \int_0^\infty p_T \, d\xi ; \tag{5}$$

$$\frac{dE}{dx} = e \frac{p - n}{\varepsilon \varepsilon_0} , \tag{6}$$

where e is the electronic charge; n is the total concentration of electrons in the dielectric, equal to the concentration of holes; n_0 is the concentration of mobile quasi-free electrons having a mobility μ_n; G is the rate of injection of free electrons and holes into the volume during the irradiation of the dielectric; k_1 and k_2 are the rate constants of the bimolecular recombination of the carriers; k_3 is the rate constant for the capture of the quasi-free carriers; n_T and p_T are the densities of trapped (thermalised) electrons and holes respectively for the trap energy range $\xi \rightarrow (\xi + d\xi)$; ξ is the energy depth of the traps, measured from the bottom of the conduction band; $M_n(\xi)$ is the energy density of the distribution of electron traps; ν_0 is the frequency factor; G_n is the rate of the volume injection of electrons; the symbol p refers to holes (everywhere); E is the field generated by the space charge; k is Boltzmann's constant.

The functions of the carrier sources $G(x,t)$ and $G_n(x,t)$ depend on the irradiation conditions, on the type of radiation, on the thickness of the sample, and on the strength of the electric field produced by the space charge (i.e. they depend also on the local absorbed dose rate). The latter dependence makes the system of equations (1)–(6) strongly nonlinear. Therefore special cases of the solution are usually considered separately.

To make the discussion specific we shall examine only one variant, very often met in practice: the irradiation of a plate having end faces covered with a conducting layer, i.e. a short-circuited flat dielectric of thickness h. The system of equations (1)–(6) must now be supplemented by

$$\int_0^h E(x,t) dx = 0 . \tag{7}$$

The most difficult step in the solution of this problem is the evaluation of the source functions $G(x,t)$ and $G_n(x,t)$. It is often convenient to use the Monte Carlo method in the continuous retardation of the injected electrons approximation, to rely on semiempirical dependences, or to determine these functions by direct measurements.[8-11]

Case 1. The dielectric is irradiated with fast electrons whose depth of penetration exceeds the thickness of the sample. These conditions produce a uniform distribution of the absorbed dose and of the sources of thermalised electrons over the sample volume, i.e. they give a uniform primary distribution of space charge. Furthermore it is assumed that only the electrons behave as mobile charge carriers. Under these conditions the solution of the system of equations (1)–(7) takes the form

$$\bar{n}_0 = \left[\frac{(G + G_n) \sin \alpha\pi}{k_1 M_0 \alpha\pi}\right]^{\Delta} \left(\frac{\nu_0}{k_{3,n}}\right)^{\alpha/(1+\alpha)} , \tag{8}$$

where $\bar{n}_0$ is the stationary concentration of electrons; M_0 is the stationary distribution of the trap energy density; $\Delta = (1 + \alpha)^{-1}$; α is the dispersion parameter, equal to T/T_1 [where T is the temperature of the sample and T_1 is the distribution parameter of $M(\xi)$].

For the distribution of the electric field strength we can write

$$E(x) = -\frac{G_n}{\mu_n \bar{n}_0} x , \tag{9}$$

and the maximum value of the field is $G_0 h / 2\mu_n \bar{n}_0$. It follows from Eqn (9) that the field created by the space charge is proportional to the rate of injection of the carriers and inversely proportional to their loss rate. The conditions of space charge accumulation for

which $n \gg p$ are called the 'space charge current regime', whereas with $n \approx p$ we are in the 'plasma injection regime'. Thus, in this regime of space-charge accumulation the charge distribution is determined mainly by functions of the carrier sources in the bulk of the given sample, i.e. $G(x,t)$ and $G_n(x,t)$.

Case 2. The conditions specified above are supplemented by the assumption that both electrons and holes are mobile in the dielectric, and furthermore that $\mu_n = \mu_p$, $v_{0,n} = v_{0,p}$. For the stationary regime the space charge ($\bar{n}_0$) can be calculated by the equation

$$\bar{n} = \frac{\bar{n}_0}{(\bar{p} + \gamma_i \bar{n}_0)^{1-\alpha}} \left(\frac{k_3}{v_{0,n}}\right)^{\alpha} \frac{\alpha\pi}{\sin \alpha\pi} M_n \gamma_i^{1-\alpha}, \tag{10}$$

where γ_i is the radiation-induced electric conductivity of the dielectric. The stationary concentration of holes is

$$\bar{p}_0 = \left(\frac{G \sin \alpha\pi}{2M_p k_2 \alpha\pi}\right)^{\Delta} \left(\frac{v_{0,p}}{k_3}\right)^{\alpha/(1+\alpha)} (1+\gamma_i)^{(1-\alpha)/(1+\alpha)}. \tag{11}$$

An important aspect of this approach to the solution of the problem of space charge formation is that the final expressions contain microscopic characteristics of the dielectric such as $M(\xi)$, μ_n, μ_p, and α. Therefore it should be possible to find the microscopic parameters of the carrier migration from the experimentally determined macroscopic parameters which characterise the space charge.

III. Formation of an electric space charge. Total current model

In the present approach to the analysis of the formation of a space charge only the macroscopic (averaged) characteristics of the dielectric are taken into account: its electric conductivity (γ_0); its dielectric permittivity (ε), and the effective mobility of its carriers (μ), treated as a phenomenological quantity.[6-12] The most important component of the electric conductivity of a dielectric being irradiated (or previously irradiated) is its radiational component γ_i, which cannot be calculated by existing theoretical methods. Therefore it is usually determined either experimentally or from empirical relationships.

In the analysis of the formation of space charge in terms of the macroscopic approach an expression for the total current can be obtained in the one-dimensional variant. It is often called the total current integral:

$$J = \varepsilon\varepsilon_0 \frac{\partial E(x,t)}{\partial t} + \gamma_i(x,t)E(x,t) + j(x,t), \tag{12}$$

where all the currents are assumed to be calculated for unit area of the irradiated surface; ε_0 is the dielectric permittivity of a vacuum (equal to 8.85×10^{-14} F cm^{-1}); γ_i is the radiation-induced electric conductivity, depending on the local dose rate during irradiation (and in general on the density of the majority carriers, i.e. on the distribution of the space charge). Furthermore, in dielectrics $\gamma_i \gg \gamma_0$; $j(x,t)$ is the current density of the injected carriers. The first term in Eqn (12) corresponds to the displacement current, the second to the 'leakage' (or conduction) current; $E(x, t)$ is the field generated by the space charge. As before, the diffusion component of the conduction current is assumed to be negligibly small. Let us use Eqn (12) to examine different cases of the formation of space charge.

By adopting the total current model it is relatively simple to find the time dependence of the space charge density, i.e. $\rho(t)$. Thus by assuming that in the stationary regime (charge accumulation $\leftrightarrow$ leakage) discharge takes place mainly through the irradiated part of the dielectric we arrive at the following expression from Eqn (12)

$$\rho(x,t) = \frac{j(x,t)\varepsilon\varepsilon_0}{S\gamma_i}\left[1 - \exp\left(-\frac{t}{\tau_i}\right)\right], \tag{13}$$

where $\tau_i = \varepsilon\varepsilon_0/\gamma_i$; S is the surface area of the sample. This expression clearly shows the change in space charge with irradiation time for a material having purely electronic conduction. It was first obtained empirically.[6] It should not be forgotten that under our irradiation conditions the stationary space charge ρ_{st} (for $t \to \infty$) is given, according to (13), by

$$\rho_{st} = \frac{j_i(x)\tau_i}{S}, \tag{14}$$

i.e. it is limited only by the values of j_i and τ_i. With large injection currents j_i electric breakdowns can take place in the dielectric even before the formation of a space charge ρ_{st}. This suggests that the accumulation of space charge is limited by the dielectric strength of the material. Therefore electric breakdown occurs under the condition

$$j_i > j_1, \tag{15}$$

where j_1 is the leakage current in the given sample during the irradiation, and the time changes of the space-charge field (at every point of the dielectric being irradiated) are described by an expression analogous to formula (13).

IV. Charging processes during the irradiation of dielectrics by γ quanta

In contrast to the widely investigated aspects of the formation of a stationary charge as a result of the action of fast electrons on dielectric materials the charging of highly insulating solid samples in a field of γ radiation has been poorly investigated, even though the first publications in both these fields appeared at about the same time. This state of affairs probably arose because the use of accelerated electrons to inject electric space charge into a dielectric is experimentally more convenient than the use of γ rays.

γ Quanta are not electric charge carriers, and in this case the charging is a secondary process induced by the ionisation of the irradiated material and by the redistribution of the resulting carriers (mainly Compton electrons) over the volume of the dielectric. From this standpoint there is a great deal in common between charging by the interaction of electrons with the material and charging by γ radiation.

Even the earliest experiments with γ-irradiated dielectric materials detected undeniable charge effects. Thus, it was shown that a substantial amount of electric charge can accumulate in borosilicate glasses under the influence of γ quanta.[13] The following experimental technique was used. After being irradiated in a cobalt source [absorbed dose 4×10^4 Gy (4 Mrad)] the glass samples in the form of disks fitted with pressure ohmic contacts were heated at 300 °C while maintaining a temperature difference of 30–50 K between the contacts. As a result of the heat treatment the injected charge leaked to the external circuit, producing a current of 10^{-12} A. The charge leaking to the contact which was held at the higher temperature was always negative, denoting a correlation between the direction of the thermal current through the irradiated glass and the direction of the temperature gradient. As the heating and discharge proceeded, the current in the external circuit gradually decreased, and the dark yellow colour produced by the irradiation disappeared. A small current could be detected even after the complete bleaching of the glasses.

In the qualitative experiments described above the accumulated charge could not be calculated even approximately. Nevertheless the presence of a space charge following γ irradiation was established beyond doubt.

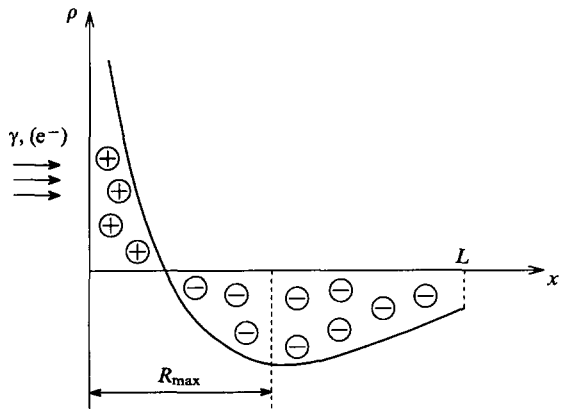


Figure 1. Charge distribution in a γ-irradiated dielectric with linear dimension L.[14] The ordinate axis coincides with the surface of the sample; ρ is the bulk density of the charge; the abscissa axis coincides with the direction of the γ quanta; the maximum penetration of the Compton electrons is R_{max}.

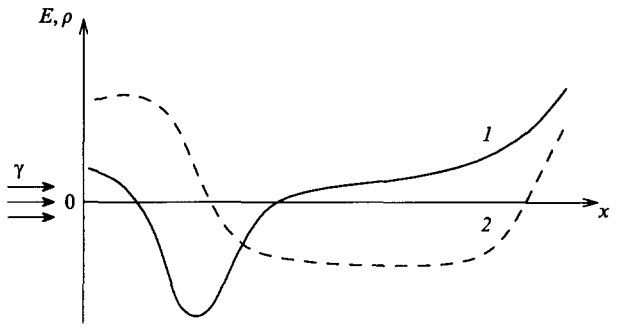


Figure 2. Distribution of space charge density (ρ) and of internal field (E) in a lead glass irradiated with γ quanta.[16] The abscissa axis coincides with the flow direction of the γ quanta: (*1*) charge; (*2*) field.

The magnitude, sign, and distribution of the charge are strongly affected by the irradiation conditions. For example, when the sample is not in electronic equilibrium and the Compton electrons leave the surface layer and move in the direction of the primary γ quanta the surface layer is positively charged, and the charge vanishes at a given depth (Fig. 1). If secondary electrons from the surroundings fall on the sample with the stream of γ quanta the charge can be negative as a whole and reside mainly near the irradiated surface. Experiments with irradiated paraffin wax[14] and Lucite‡[15] were satisfactorily consistent with these concepts.

The formation of large electric space charges by exposure to γ radiation leads to spontaneous internal discharges, as in the case of electron irradiation. The phenomenon was observed in experiments with large ^{60}Co sources in chambers shielded by thick lead walls,[7,16] the glasses being gradually broken down by spontaneous electric discharges. In some types of lead glass discharge formation was noted for doses of radiation higher than 5×10^5 Gy (5×10^7 rad).

It was established experimentally that a perturbation of the electronic equilibrium in the system is a necessary condition for the generation of radiation-induced charge by γ quanta. In other words, the number of electrons dislodged from the dielectric should be markedly different from the number of electrons arriving from the surroundings with the flux of γ quanta. If electronic equilibrium is established an excess of electric charge is not formed in the bulk of the dielectric during the irradiation: of course, this conclusion is valid only for isotropic solids.

The flux of γ quanta passing through the substance generates a flux of Compton electrons almost parallel to the γ flux. This is because the electrons are struck off mainly in the direction of motion of the γ quanta. For example, in Plexiglas exposed to a flow of γ radiation of 25 Jm^2s the average density of the accompanying electron flow was found[17] to be 1.37×10 A m^{-2}. A space charge is generated by the trapping of the Compton electrons as they travel through the material.

An empirical formula has been proposed[17] for the amount of charge accumulated in lead glass:

$$\rho = 4.4 \times 10^{-5} S\left[1 - \exp\left(-\frac{t}{\tau}\right)\right], \qquad (16)$$

where t is time (h), and τ is the relaxation time, equal to 64.1 h.

‡Lucite, Mylar, and Plexiglas are trade names of the same product: poly(methyl methacrylate) (PMMA).

If the dielectric experiences only the action of γ quanta, not accompanied by a flow of electrons from the surroundings, the charge distribution in the medium will be similar to that shown schematically in Fig. 2. If secondary electrons enter the medium simultaneously with the flow of γ quanta the distribution of charge in the depth of the sample can have an entirely different form. The absence of charge effects is certainly not guaranteed by the presence of an electronic equilibrium in the interaction of the γ quanta. Thus, even with an initially uniform distribution of positive and of negative carriers in the sample we can find a gradual separation of charges of opposite sign caused by the difference in their mobility in the solid matrix.

A simplified variant of the analysis of the accumulation of charge during the γ irradiation of dielectrics gives the following expression for the dependence of the total stored charge on the parameters of the sample and on the irradiation conditions:[6]

$$\bar{\rho} = S\frac{j_k(0)\varepsilon}{\mu_\gamma h\bar{\gamma}}\left[1 - (1 + \mu_\gamma h)\exp(-\mu_\gamma h)\right], \qquad (17)$$

where S is the surface area of the sample; h is its length; $\bar{\gamma}$ is the average electric conductivity; μ_γ is the linear absorption coefficient of the γ radiation; $j_k(0)$ is the current of Compton electrons near the sample surface. It is assumed that an equilibrium between the charge accumulation and the leakage currents was established during the γ irradiation.

To describe the charging process more correctly we need to allow for the appearance of a radiational component of the electric conductivity. A stricter derivation of formula (17) has been obtained[17] in the light of these considerations. In fact, the theory has been tested only for the region of linear charge accumulation, i.e. for the early stage of the irradiation. In lead glasses the charge accumulation in the initial stage has been shown to be satisfactorily described by these formulae.

In spite of this satisfactory agreement with experiment the above model of the charging of dielectrics in a field of γ radiation is not free from defects. In particular, many workers consider that the Compton electrons are trapped in the sample almost completely, and that their scattering can be ignored (thus ignoring the effect of the field from the charge on the path followed by the electrons and the spatial change in polarisation).

A commonly found case (the irradiation of an isotropic dielectric by a collimated monoenergetic beam of γ quanta) has been examined theoretically.[18] Under these conditions the charge becomes localised along the boundary between the irradiated and the nonirradiated part of the sample (Fig. 3). Charge formation is determined by the scattering of the Compton electrons. To simplify the treatment it was assumed (as in the work of Gross[17]) that the ratio of the dielectric permittivity to the conductivity is invariant during the exposure of the sample to γ quanta. It was

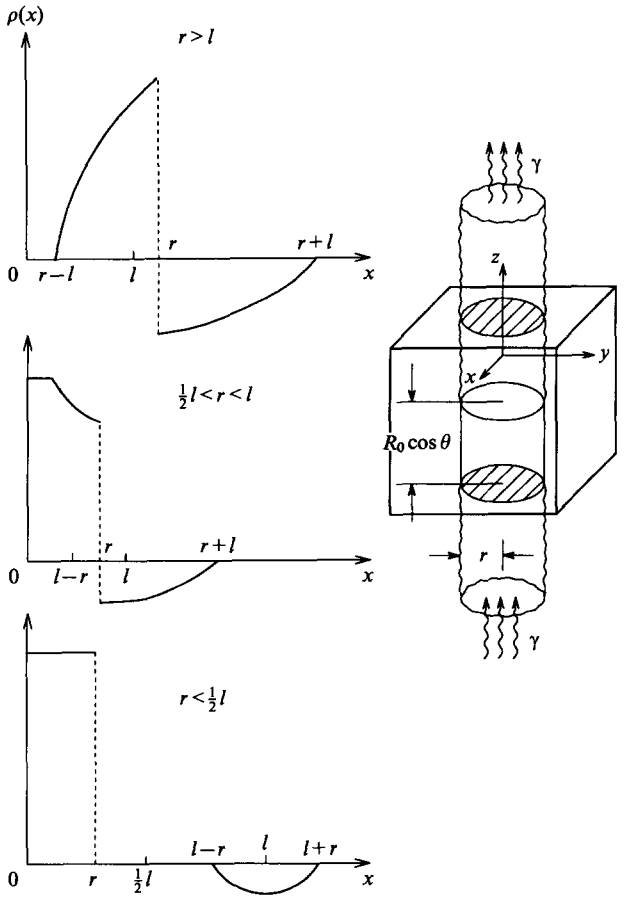


Figure 3. Distribution of charge density during the irradiation of a dielectric with a cylindrical stream of γ quanta for various ratios between the radius of the beam r and the deviation l of the Compton electrons from the direction of the γ quanta.[18] The orientation of the beam and of the sample relative to the chosen system of coordinates is shown on the right: θ is the average divergence angle, R_0 is the average path of the Compton electrons.

also assumed that the flux of particles incident on the surface consists only of γ radiation without any secondary Compton electrons from the surroundings, and that the suppression of the flux of electromagnetic radiation can be ignored.

If a cylindrical beam of γ quanta of radius r is used the charge distribution under stationary conditions is defined by the function f:

$$\rho(x) = ebf = ebj_\gamma \frac{1}{\pi} \arccos\left(\frac{x^2 - r^2 + l^2}{2lx - 1}\right), \qquad (18)$$

where l is the distance by which the Compton electron deviates from the direction of motion of the γ quanta; b is a coefficient which defines the link between the flux densities of the γ quanta (j_γ) and of the Compton electrons (with $r > l$). If $x > r$ the law for the dependence of $\rho(x)$ on x becomes

$$\rho(x) = ebj_\gamma \frac{1}{\pi} \arccos\left(\frac{x^2 - r^2 + l^2}{2lx}\right). \qquad (19)$$

The orientation of the sample and of the beam of γ quanta relative to the system of coordinates is shown in Fig. 3. The charge distribution is given for the xy plane.

A calculation shows that three special cases are possible.

1. $r > l$. In the region of $0 \leqslant x < r-l$ the sample does not become charged, since $f = 0$, and in the region of $r-l < x < r$ the charge density is proportional to f [see formula (18)]. Thus the centre of the irradiated cylindrical region is not charged. The density of positive charge to the left of the $x = r$ boundary is greater than the absolute density of negative charge outside the cylinder of radius r.

2. $\frac{1}{2}l < r < l$. Under these conditions the irradiated part of the sample is charged positively in the region of $0 < x < l-r$. For $l-r < x < r$ the charge is determined by the value of the function f according to formula (18), and for $x > r$ according to formula (19).

3. $r < \frac{1}{2}l$. In this case the whole of the dielectric enclosed in the cylinder of radius r is positively charged, and the charge density is proportional to $f = -ebj_\gamma$; the region between r and $l-r$ is uncharged, and in the region of $x > l-r$ the negative charge varies according to the expression (19).

We also note that on the side of the irradiated surface the region $r > l$ shown in Fig. 3 (a cylinder of radius r and height $R_0 \cos\theta$) becomes positively charged, as is also found in practice (compare with Fig. 2).

Under practical conditions the charge distribution is a superposition of all the cases which we have discussed. Therefore a discontinuity in the function f at the point $x = r$ should probably not be expected. However, the region outside the beam ($r < x < l-r$) should always be negatively charged.

In conclusion we should dwell briefly on the mechanism of the electrification of dielectrics by γ radiation. The effect is based on the difference between the rates of retardation and of generation of Compton electrons upon passing from one medium into the other, i.e. it can be realised in heterogeneous media in which the components have different absorption coefficients for the ionising radiation and different cross-sections for the formation of Compton electrons. A general discussion of this problem for systems composed of two media has been given by Lenchenko.[19]

V. Electric charge of radioactive substances

Radiation-induced charges were first observed, and then studied and used under practical conditions, in radioactive materials.[1,2,5] However, a reasonably complete theory of this phenomenon was developed only by abandoning to some extent the requirement of direct practical application and the existing theory of charging from external sources of ionising radiation. Unfortunately, even the present stage of development of the theoretical study of charge formation in radioactive materials cannot be taken as conclusive. Nevertheless, we now have some reasonably good theoretical models which can be used to establish an unambiguous relationship between the experimental results on the charging of radioactive materials and the properties of these materials.

One of the simplest and most effective methods of studying the electric properties of the surface of ionic crystals is to decorate the samples with charged particles of metallic sols.[20] The basis of the method is the fixing of the charged particles of the metallic sol on the appropriately charged regions when deposited on the surface. Experiments of this type have been carried out[5] with radioactive crystals of K_2SO_4* (containing ^{35}S, a β^- emitter).

It was established that individual sol particles are deposited, irrespectively of their charge, on elements of the surface topography (hillocks, growth steps, etc.). Thus, the negatively charged particles of a silver sol in methanol covered almost uniformly the whole surface of cleavage faces in radioactive crystals of potassium sulfate, which must obviously carry a positive charge. On the other hand, if the radioactive crystal was decorated with a nickel salt the metal particles were deposited only on surface nonuniformities. This is a direct proof that a stationary positive charge exists on the surface of β^- emitters.

One of the most characteristic features of radioactive dielectrics is the formation of a charged surface layer with a thickness equal to the maximum path length of the charged particles emitted by the radionuclide (if the linear dimensions of the sample are $L > R_{max}$), as was first reported by the present writer.[21]

In high-resistance radioactive materials the space charge can be so large that the electric field in the near-surface layer reaches the breakdown level. This assumption was tested by special experiments with a radioactive glass.[22]

The resistivity of the prepared glass blocks was $\sim 10^{22}$ Ω m. After solidification the samples began to darken and became opaque in a few minutes owing to the strong self-irradiation. According to tentative calculations the electric field intensity in the charged near-surface region of these glasses reached breakdown values ($\sim 10^8$ V m^{-1}). However, in order to stimulate electric discharges we need to create mechanical stresses by pressing a glass or a metallic rod on the surface of the radioactive glass block. A spark was seen in the charged layer beneath the pressure point. In most cases the discharges took place at the beginning of the experiment. The sparking then ceased, showing that the charge in the near-surface layer had become exhausted. After several days' storage of the blocks a new charge had accumulated, and the experiments on spark formation could easily be reproduced.

In contrast to irradiated materials a charge is always present in radioactive dielectrics: this is one of their most characteristic properties. The field generated by this charge can also extend beyond the dielectric, unless the charge is compensated by that of carriers drifting towards the surface of the radioactive sample from the surroundings. The charge accumulated in radioactive materials is most clearly detected in 'hot' aerosol particles, i.e. in solid formations whose specific radioactivity reaches ~ 10 Ci g^{-1} (3.7×10^{11} Bq g^{-1}) in particles of about micrometre size, so that the radioactivity of each aerosol particle is $\sim 10^{-8}$ Ci (or 200 Bq).[23]

VI. The charging of radioactive samples

The general theory of the formation of charge in radioactive solids has now been fully developed.[5,6,21,24] Two basic assumptions are made in the analysis of this phenomenon: Ohm's law is obeyed in the solid sample and the properties of the material are isotropic. In this case we can easily obtain a general expression which describes the dynamics of the charging both of radioactive materials (in which the radiation sources are located within the sample) and of materials irradiated from external radiation sources. Under these conditions the electrophysical properties of the system are characterised by macroscopic parameters such as γ (electric conductance) and ε (dielectric permittivity). It is also stipulated that charge neutralisation processes between charges of opposite sign can take place only on the surface. By allowing for these conditions we arrive at the following expression:

$$\rho(x,t) = \exp\left(-\frac{\gamma}{\varepsilon\varepsilon_0}t\right)\left[\int_0^t f(x,t)\exp\left(\frac{\gamma}{\varepsilon\varepsilon_0}t\right)\mathrm{d}t\right], \qquad (20)$$

where x is the coordinate of the reference point; $f(x,t)$ is the function of the charge sources (whose physical significance is to define the change in the charge density per unit time); γ is the electric conductance of the dielectric.

If the source of charged particles acts for a finite time (short-lived radionuclide) we can see from formula (20) that after the 'switching off' of the source the space charge density relaxes to zero with a time constant $\tau = \varepsilon\varepsilon_0/\gamma$. When the source of radiation acts for a long time with constant intensity (long-lived nuclide), i.e when f is independent of time, the solution of Eqn (20) takes the form

$$\rho(x,t) = \frac{\varepsilon\varepsilon_0}{\gamma}\left[1 - \exp\left(-\frac{\gamma}{\varepsilon\varepsilon_0}t\right)\right]f(x). \qquad (21)$$

Two special solutions of Eqn (21) are of interest.

1. Small electric conductance (dielectrics). By expanding the exponent into a Taylor series in powers of γ we obtain

$$\rho(x,t) = f(x)t.$$

Therefore, up to time t,

$$t \ll \frac{\varepsilon\varepsilon_0}{\gamma},$$

the charging will take place by a linear law, and at long times the charge ρ will tend towards the stationary value

$$\rho_{st} = \frac{\varepsilon\varepsilon_0}{\gamma}f(x). \qquad (22)$$

2. Large electric conductance (conductors), small relaxation time. Under these conditions the charge ρ immediately reaches the value ρ_{st} defined by Eqn (22), from which it follows that ρ depends only on the intensity of the sources of charged particles and on the electrophysical properties of the material.

At this stage of the solution the expressions obtained still retain their generality: they are valid also for an external source of radiation acting on the dielectric. The whole of the 'significance content', which allows ρ to be obtained in an explicit form for different particular conditions, is included in the 'source function' $f(x)$.

A strict derivation of the general form of the charge sources function for a uniform distribution of the radionuclide over the sample volume (when the specific radioactivity Q is independent of x) has been reported,[24] and also partial expressions for $f(x)$, which can be used to calculate the $\rho(x)$ values at various points in the radioactive sample. For example, for a radioactive preparation in the form of a sphere of radius r under stationary conditions we can write

$$\rho_{st} = b_n\int_0^x F_w(b_nR+1)\,\mathrm{d}R + \frac{b_n}{2}\int_x^{R_{max}} F_w\left(1+\frac{2Rx-x^2-R^2}{2R(r-x)}\right)\left(b_nR+1\right)\mathrm{d}R - 1, \qquad (23)$$

where ρ_{st} is expressed in relative units and is equal to

$$\rho_{st} = \frac{f(x)}{Q_0 e}$$

or

$$\rho_{st} = \rho\left(Q_0\frac{\varepsilon\varepsilon_0}{\gamma}\right)^{-1};$$

b_n is a constant, proportional to the concentration of electrons in the sample; Q_0 is the initial specific radioactivity; R is the range of β^- particles in the given material; x is the coordinate; F_w is a function which defines the form of the β^- spectrum. For a monoenergetic spectrum of β^- particles Eqn (23) simplifies to

$$\rho_{st} = 1 - \frac{1}{2}\left[1+\frac{2rx-x^2-R^2}{2R(r-x)}\right]. \qquad (24)$$

The results of a calculation of the charge distribution by using formula (23) for β-radioactive samples in the form of a plate or a sphere are shown in Fig. 4. As can be seen, in the radioactive samples the charge is accumulated in a near-surface layer of thickness R_{max}. Depending on the geometry of the sample the following cases are possible (for a sphere):

1. $r > R_{max}$; the central region of the sphere $(r-R)$ is uncharged.

2. $r < R_{max}$; the whole sphere is charged, but its near-surface layers have a charge density higher than in the central part.

3. $r \ll R_{max}$; the whole sphere is uniformly charged. This variant corresponds to hot aerosol particles.

Calculations by formula (24) give a qualitatively similar charge distribution, though some details of the changes in charge density over the volume of the radioactive sample are lost.

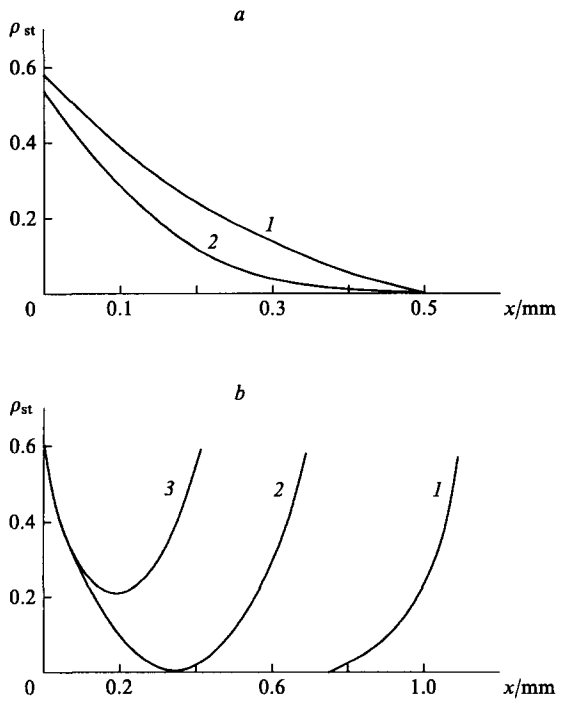


Figure 4. Changes in the charge density $\rho(+)$ of β^--radioactive samples of different size and shape. Maximum energy of β^- particles assumed to be 3 MeV, with a continuous emission spectrum; range R_{max} = 0.5 cm; (*a*) radioactive sphere, the ordinate axis coincides with the surface of the sphere, curves *1* and *2* correspond to sphere radii of 1 and 0.5 cm; (*b*) flat infinite layer, the ordinate axis coincides with the coordinate of one of its surfaces, layer thickness (cm): *1*, 1.1; *2*, 0.7; *3*, 0.4.

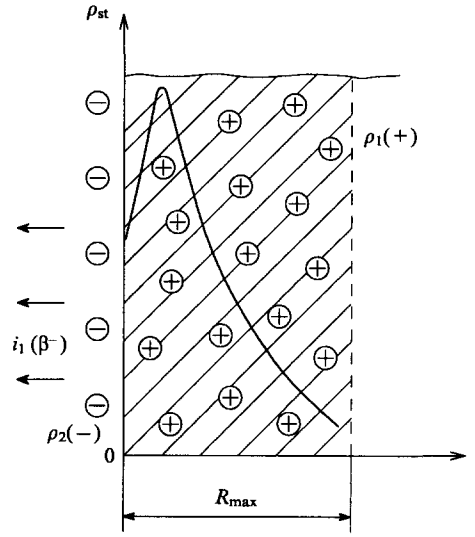


Figure 5. Charge distribution in a dielectric containing a β^- emitter and surrounded by a conducting medium (the ordinate axis coincides with the coordinate of the dielectric surface). i_1 is the flow of β^- particles emitted from the surface of the sample.

These calculations can account for the distribution of the charge expressed in relative units. To obtain the absolute values of ρ we must know the relationship between the change in γ and the dose rate of the ionising radiation, but at present only empirical formulae are available. This is one of the weaknesses of the theory in its present state of development.

Depending on the values and on the ratio of the conductivities of the radioactive material and of the surrounding medium, we may find different distributions of charge in the radioactive sample. For a β^- emitter in a conducting medium the distribution is shown in Fig. 5. The cross-hatched region corresponds to a positively charged near-surface region. Negative charge $\rho(-)$, created by ions from the surroundings, is localised on the surface. As can be seen from the figure, it is useful to distinguish between the total (positive) charge $\rho_1(+)$, distributed in a volume limited by a layer of thickness R_{max}, and the charge ρ_2, equal to the difference between $\rho_1(+)$ and the absolute value of $|\rho(-)|$.

The values of ρ_1 and ρ_2 can be calculated fairly accurately if the electrophysical parameters and the geometry of the radioactive sample and of the surrounding medium are known. By treating the formation of ρ_2 as a competition between the accumulation of charge ρ_1 (formed by the emission of β^- particles from the surface, which determines the current i_1) and the discharges in the surface layer resulting from the recombination with carriers of the opposite sign, i.e. by solving in a simplified variant the system of equations

$$\frac{d\rho}{dt} = i_1 - \frac{\rho_1}{\tau_{ef}}, \qquad \frac{di_1}{dt} = -\lambda t, \tag{25}$$

where λ is the disintegration constant and τ_{ef} is the effective relaxation time of the charge in the given system, we arrive at the expression

$$\rho_{t(2)} = \rho_{st\ (2)}\left[1 - \exp\left(\lambda t - \frac{t}{\tau_{ef}}\right)\right]\exp(-\lambda t)\,. \tag{26}$$

In the case of a time-invariant source intensity (i.e. for $\lambda = 0$) Eqn (26) simplifies to

$$\rho_{t(2)} = \rho_{st\ (2)}\left[1 - \exp\left(-\frac{t}{\tau_{ef}}\right)\right], \tag{27}$$

where $\rho_{st(2)} = i_1\tau_{ef}$. However, formula (27) gives no information on the distribution of charge in the bulk of the dielectric.

For practical purposes it is important to know not only the magnitude of the uncompensated (residual) charge of the radioactive sample ρ_2, but also the total charge ρ_1 distributed in the surface region. In the case of a spherical sample[5] these calculations can easily be made by using the following formula:

$$\rho_1 = \frac{b_1 emQ\varepsilon\varepsilon_0 f(\mu, r)}{4\pi r\gamma_1}, \tag{28}$$

where b_1 is a constant§; γ_1 is the electric conductivity of the sample (allowing for the radiational component). The function $f(\mu, r)$, which defines the fraction of the β^- particles leaving a sphere of radius r, is given in the form

$$f(\mu, r) = \frac{3}{4\mu r}\left[\frac{(2\mu r + 1)\exp(-2\mu r) - 1}{2\mu^2 r^2} + 1\right], \tag{29}$$

where μ is the linear absorption coefficient of the β^- particles in the given substance.

Thus, calculations for crystals of radioactive strontium sulfate containing ^{35}S ($\gamma \approx 10^{-16}$ S m^{-1}, r = 0.1 cm, ε = 5, μ = 840 cm^{-1}), showed that the charge averaged over the volume of a near-surface layer 8×10^{-3} cm thick for Q = 1 Ci g^{-1} (3.7×10^{10} Bq g^{-1}) is 3×10^{-3} C cm^{-1}, and the internal field in the charged layer is $10^3 - 10^4$ V cm^{-1}, $\tau \approx 5 \times 10^2$ s.

§ If the sample is an α emitter, the constant b_1 should include a factor for calculating the yield of δ electrons defining the magnitude and sign of the stationary charge.

These results agree tolerably well with experimental determinations, and they show convincingly that a fairly large charge with a corresponding electric field gradient exists in the near-surface layer of radioactive dielectrics, even if electrically neutral overall (the space charge is compensated though not neutralised).

A stationary distribution of electric charge should be established also at the boundary between two media (a radioactive and a nonradioactive solid dielectric).[25] Let us examine these cases.

Case 1. In a nonradioactive isotropic material we have a region containing a uniformly distributed β^- emitter. If this region is a sphere of radius r the volume density of electric charge at the point x can be found from the expression

$$\rho = \frac{eQ\varepsilon\varepsilon_0}{\gamma_0 - \varepsilon\varepsilon_0\lambda}\left(\frac{r^2 - R^2 - x^2}{4xR} \pm \frac{1}{2}\right)B(t)\,, \qquad (30)$$

where Q is the specific radioactivity; ε is the dielectric permittivity of the medium; λ is the disintegration constant; R is the range of the electrons emitted by the given radionuclide (it is assumed that all the β^- particles have the same energy, i.e. that the spectrum of the radiation is monoenergetic); γ_0 is the electric conductivity;

$$B(t) = \exp(-\lambda t) - \exp\left(-t\frac{\gamma_0}{\varepsilon\varepsilon_0}\right).$$

Eqn (30) defines the dependence of the bulk charge density upon the radioactivity of the dielectric, its electrical parameters, and the coordinate and time. In the region of $x \leqslant r$ (β^- emitting sphere) the term 1/2 of Eqn (30) takes the plus sign, and in the region of $x > r$ (nonradioactive dielectric) it takes the minus sign. Fig. 6 shows the 'coordinate part' of the dependence of the bulk charge density G:

$$G = \frac{r^2 - R^2 - x^2}{4xR} \pm \frac{1}{2}$$

for the case of $R < r$.

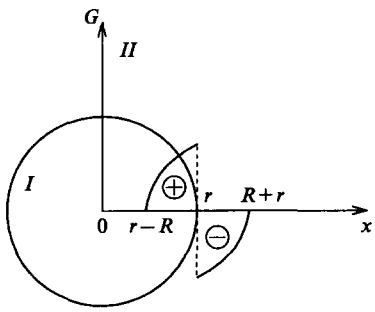


Figure 6. Plot of the 'coordinate part' of the charge density (G) for dielectric half-spaces with different radioactivities. R is the range of electrons in regions I and II; the plus and minus signs correspond to the sign of the space charge.

It should be noted that in every case the whole of the radioactive region (or part of it) becomes positively charged while the nonradioactive region is negatively charged; the $x = r$ boundary defines the charge separation zone. Furthermore 'radiative' electric charging does not take place at any point within the radioactive dielectric at a distance equal to or greater than R from the zone boundary (where $\rho = 0$).

A similar result is seen at the flat interface between the radioactive and the nonradioactive region of a dielectric: the near-surface region of the radioactive dielectric is charged positively, and that of the nonradioactive dielectric is charged negatively.

Case 2. In dielectric materials containing a uniformly distributed β^- emitter with a monoenergetic spectrum we can distinguish regions with different physical properties (i.e. two radioactive materials of different nature but with identical and uniformly distributed radionuclides, which produce an interface). Calculations have shown that the region with the higher electron density becomes negatively charged, and that with the lower electron density positively charged. For example, for a radioactivity of 10^{13} Bq m^{-3} and a conductivity of approximately 10^{-13} $(\Omega\text{m})^{-1}$ the charge at the phase boundary is ~ 1 C m^{-3}, which corresponds to electric fields of flashover magnitude ($\sim 10^8$ V m^{-1}).

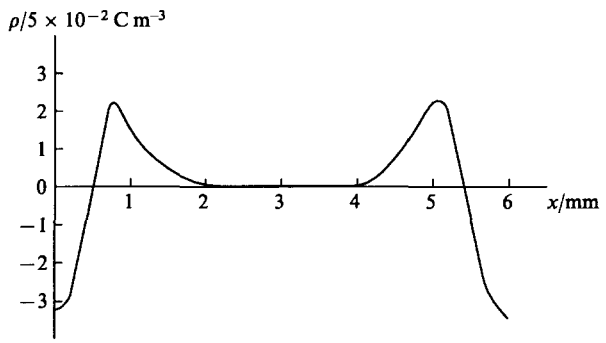


Figure 7. Distribution of electric charge in monocrystals of $Y_3Al_5O_{12}$ (yttrium-90 specific radioactivity 4×10^8 Bq g^{-1}).

The most correct experimental test of the theory of the distribution of space charge in the bulk of radioactive dielectrics was carried out by the acoustic probing method.[26] Thus, in the case of yttrium aluminium garnet ($Y_3Al_5O_{12}$) crystals irradiated with neutrons it was shown that the charge is not uniformly distributed on the surface of flat specimens (Fig. 7). Neutron irradiation of garnet crystals produces the β^- emitter yttrium-90.

It is clear from Fig. 7 that at the centre of the sample with $R < h$ (where h is the thickness of the sample and R the range of the β^- particles from yttrium-90) the charge is zero, whereas in the near-surface regions of thickness R we find an accumulation of positive charge. Narrow negatively charged layers are formed on the surface by the drift of carriers of opposite signs from the surroundings.[26,27]

VII. Charge and properties of solids

Many workers have noted the appearance of spontaneous electrical discharges during the irradiation of dielectrics, leading to the mechanical breakdown of the samples. For example, borosilicate glasses distintegrated when exposed to a flux of 10^{13} electrons cm^{-2} and a current density of $\sim 10^{11}$ electrons cm^{-2} s^{-1} (electron energy 1 – 2 MeV).[28] Discharges can occur in glasses even during lengthy storage (two weeks or more).

Some workers[29] associate the mechanical properties of irradiated glasses with the presence in those glasses of space charges, responsible for the production of internal mechanical stresses. It was pointed out[30] that the mechanical strength of a dielectric is decreased by charging. This effect can probably be attributed to an increase in the ponderomotive forces in a charged dielectric, since their bulk density increases linearly as charge is accumulated in the material.

The internal electric field of the space charge can also have a marked influence on the bleaching of the colour centres in transparent dielectric materials. For example, in glasses of composition $6B_2O_3.Na_2O$ the application of an external electric field of 7×10^7 V m^{-1} was found to break down the

radiation-induced colour centres. It was suggested that the internal 'cold' emission of trapped electrons into the conduction band is responsible for this process.[31]

According to both a theoretical analysis[32-35] and experimental determinations radiation-induced charging strongly decreases the penetration of electrons. The effect was observed visually[32] as a change in thickness of the luminescent layer in poly(methyl methacrylate) which had been irradiated with accelerated electrons with an energy of 1.3–1.7 MeV. This surface layer is a region of electron retardation and accumulation of space charge. The results of these studies are shown in Fig. 8.

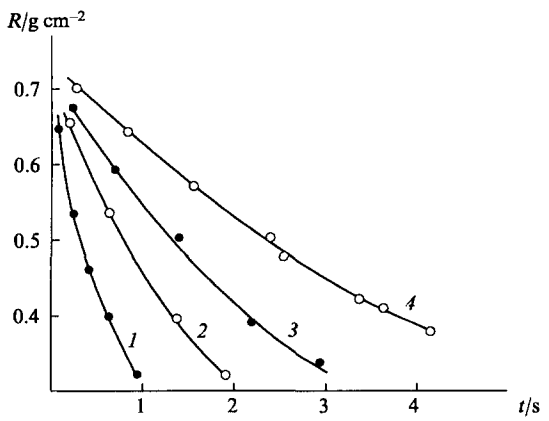


Figure 8. Plots of the range of electrons in poly(methyl methacrylate) against the time of irradiation.[32] Current density of electrons with an energy of 1.7 MeV in the beam (μA cm^{-2}): (*1*) 2.7; (*2*) 1.0; (*3*) 0.8; (*4*) 0.5.

It can be seen that the depth of penetration decreases with time (i.e. it decreases as space charge accumulates). Furthermore R tends towards a limiting value from which the maximum strength of the electric field generated by the space charge can be determined. According to the theory which has been proposed for this phenomenon the energy U_e of the electrons which reach the boundaries of the luminescence region is given by the nonlinear equation

$$\frac{dU_e}{dx} = -w(U_e) - eE(x), \tag{31}$$

where x is the coordinate of the motion of electrons in the materials; $w(U_e)$ is the stopping power of the material; $eE(x)$ is the force acting on an electron at a depth x from the field created by the space charge. Numerical solution of Eqn (31) for an initial electron energy of 1.3 MeV gives the maximum value of $eE(x)$ in poly(methyl methacrylate) as 3.4 MeV cm^{-1}.

Th existence of a relationship between the space charge field and the range of the electrons in irradiated dielectrics produces another interesting effect: the redistribution of absorbed energy.[36,37] In calculations of the profile of absorbed energy (which is very difficult to determine experimentally) it is assumed that some fixed distribution of electric field exists in the bulk of the dielectric. Therefore we need additional experimental definitions of the $E(x)$ or $\rho(x)$ dependences, which complicates the solution of the problem. However, at least when the thickness of the dielectric exceeds the range of the electrons, the required information on the distribution of absorbed dose can be obtained if a family of distributions calculated for a uniform electric field is available.[36] The method of calculation relies on a kinetic equation which describes the transport of electrons on the assumption of continuous retardation. The calculations were carried out for uniform dielectrics with $z_{ef} = 6$ and 14 (where z is the atomic number of the element). Some results of these calculations for a uniform field within the dielectric are shown in Fig. 9.

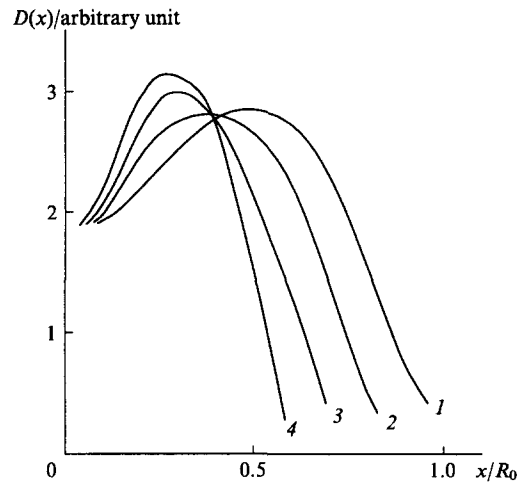


Figure 9. Distribution of the absorbed energy D for different values of the force $eE(x)$ acting on the electrons of energy 1 MeV injected into a dielectric ($z = 6$) from the side of the space charge field (MeV cm^2 g^{-1}): (1) 0; (*2*) 0.5; (*3*) 0.8; (*4*) 1.1.

The calculations show that as the interaction of the space-charge field with the electrons injected into the sample is increased the absorbed energy maximum moves towards the surface of the irradiated dielectric. This conclusion is of direct relevance to the study of the mechanical and optical properties of dielectrics exposed to a flux of charged particles. Allowance for this phenomenon should probably also be made in the measurement of radiation-chemical yield, which must also be varying over the thickness of the sample. Estimates[43] of the local values of the density of radiation-induced defects allowing for the space-charge field have confirmed this assumption.

The presence of large electric fields in irradiated dielectrics and semiconductors affects the yield of Compton electrons.[33] The change is characterised by the quantity δ, defined as the difference between the quantum yield in the electric field and without the field, and depending on the field intensity as follows:

$$\bar{\delta} = \int_0^R E(x) f(x) dx, \tag{32}$$

where $f(x)$ is the sensitivity function [$f(x) = \alpha x$], α is a constant, and R is the range. Integrating Eqn (32) by parts, and assuming that the electric potential is $V(x) = 0$ at $x = R$, we obtain

$$\bar{\delta} = 2\frac{\bar{\delta}_0}{ER}\int_0^R V(x)dx,$$

where $\bar{\delta}_0$ is the change in the quantum yield in a uniform electric field E. This result is strict in relatively weak fields. As the experiments show, $\bar{\delta}$ increases as E decreases. For example, in poly(methyl methacrylate) $\bar{\delta}$ increases almost 5-fold as the field strength is increased from 0.2 to 1.2 MV cm^{-1}.

Some published results[37] describe the formation of a powerful (explosive) emission from the free surface of dielectrics irradiated with strong beams of accelerated electrons in a pulsed regime. Unlike the previously known explosive emission from metallic samples this process is initiated by an internal (not by an external) electric field. It is observed in many dielectric materials —organic compounds, dielectric glasses, ionic crystals, and ceramic materials. It has been established that as soon as the intensity of the beam of bombarding electrons exceeds the threshold value characteristic of the particular material a powerful emission is produced, leading to a vacuum discharge [the experiments were carried out at a pressure of $10^{-6}-10^{-3}$ Torr, electron energy 0.35 MeV, pulse length $(2-30)\times 10^{-9}$ s, current density $(0.01-1.5)\times 10^3$ A cm^{-2}].

Threshold electron beam densities for various materials are shown below (10^{-5} cm^{-2} pulse^{-1}):

LiF	3
NaF	4
NaCl	6
KCl	7
Polyethylene	1
Teflon	3
Quartz glass	8

The strong explosive emission carries away from the dielectric, together with the ejected ion plasma, a charge ~100 times greater than the charge injected by the electron beam. This phenomenon could find practical applications in connection with the use of dielectrics excited by powerful electron beams as cut-off cathodes and commutators for high-current beams.

VIII. Dissolution kinetics of charged crystalline substances

The electrification of solids and the formation of electrical space charge in solids exposed to an ionising radiation have been studied reasonably widely, as has also the effect of the space charge on various physicochemical processes.[6]

We shall examine some examples in which the relationship between changes in the rates of dissolution and of electrification of the irradiated compounds can be monitored. We should point out first of all that the space charging of the dielectric is accompanied by its polarisation. Therefore when the substance is dissolved the transfer of ions (or of dipolar molecules) from the solid to the liquid phase takes place in an electric field.

In the dissolution of irradiated salts it is very difficult to separate the effects of one among several factors, such as charging, radiation-induced defects of the electronic type, displaced atoms, or structural surface changes. We shall discuss the changes in the dissolution rate constant k_v of irradiated crystals which may be attributed to radiation charging.

In crystals of $SrSO_4$ exposed to γ radiation or to accelerated electrons defects such as SO_4^- and SO_3^- ion radicals are produced, as well as e_{st}^- and others. At temperatures below −100 °C in the case of interaction with γ radiation (or at room temperature in the case of irradiation with electrons having energies of 1–3.5 MeV) only ion radicals and trapped electrons are formed. In Fig. 10 we show the changes in the rate of dissolution of crystals of natural celestine ($SrSO_4$) irradiated with fast electrons.

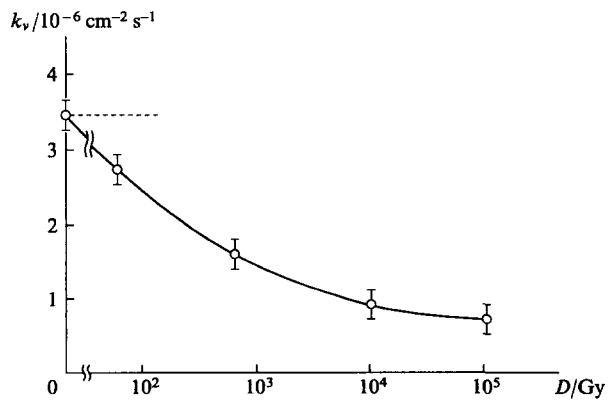


Figure 10. Dependence of the rate constant for the dissolution of a monocrystalline substance in water at 298 K on the dose of radiation. Crystals irradiated with accelerated electrons; energy 3.5 MeV; the broken line shows the value of k_v for nonirradiated crystals.

The experiments were carried out as follows. The crystals were irradiated at 20–30 °C (which produced only SO_4^- radicals and e_{st}^-) and immediately after the irradiation they were dissolved in distilled water at 20 °C. The outer layer of the crystals, damaged by the radiation, was removed by partial dissolution. Under these conditions a change in k_v could be attributed only to the radiation charging and to the formation of electronic defects. As can be seen from Fig. 10 the crystals of celestine freshly irradiated with 3.5 MeV electrons dissolve more slowly than the nonirradiated samples. In this effect the dominant role is played by the radiation charging, which nullifies the action of the radiation-induced defects.

When the crystals were stored (for several months) the charge produced by the irradiation decayed to some extent, and k_v increased, approaching the rate constant of the dissolution of the nonirradiated sample. We note that the concentration of SO_4^- fell slightly during storage, and SO_3^- ion radicals were formed instead. After heat treatment, which removed all the defects, the properties of irradiated and nonirradiated crystals became identical. This is confirmed by the results of experiments with polarised samples of $SrSO_4$ (Fig. 11). In this case the k_v value also gradually decreased as the polarisation field strength was increased.

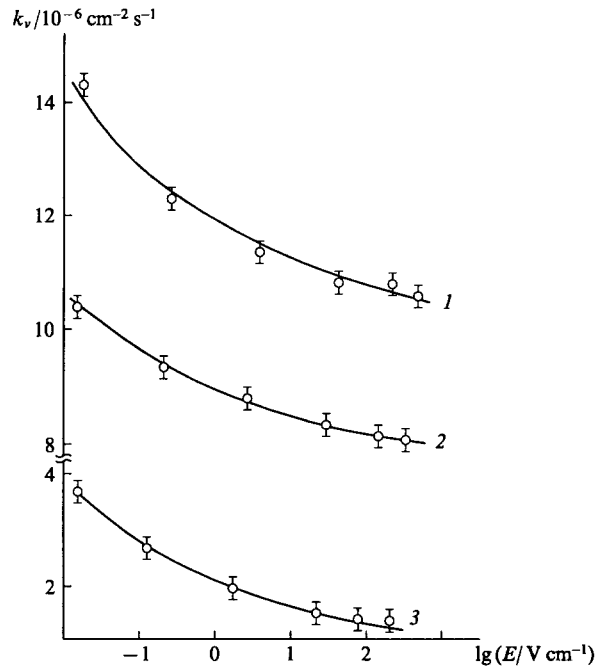


Figure 11. Changes in the rate constant for the dissolution in water for different values of the electric field strength (crystal polarisation). (*1*) NaF; (*2*) LiF; (*3*) $SrSO_4$.

In experiments on the action of fast electrons on LiF crystals[38] the thickness of the plates was chosen so that almost all the electrons with an energy of ~3.5 MeV were absorbed by the sample. After the irradiation the plates darkened, and a visual inspection showed that all the electrons had been absorbed near the irradiated surface. According to the experimental results the excess space charge was negative. Some of the irradiated crystals were placed in an electric field in a direction which increased the radiational polarisation, others were placed in a depolarising field (see Table 1). The lowest value of the dissolution rate constant was observed for the crystals in which the radiational polarisation was increased by the electric field. Decreasing the polarisation in the stimulated discharge of the irradiated LiF increases the rate of dissolution.

Table 1. Changes in the dissolution rate constant of LiF crystals irradiated with electrons and polarised in an external electric field[38] with a strength of 1500 V cm^{-1}.

Application conditions of electric field	$k_v/10^{-6}$ cm^{-2} s^{-1}	Notes
No field, crystal not irradiated	12.4	–
No field, crystal irradiated	11.2	Dose absorbed during irradiation 5×10^2 Gy
Field depolarisation used	10.4	Polarisation (depolarisation) time 48 h
Field polarisation used	9.4	–

The radiation-induced charging is often masked, and even counteracted, by the action of the radiation-induced defects. Obviously, opposing factors are developed simultaneously in the irradiated compounds: the dissolution is retarded by the radiational polarisation and the transfer of ions from the solid into the solution is accelerated by the formation of radiation defects. Similar effects are also seen in the dissolution of radioactive crystalline compounds, in which a stationary electric charge is permanently maintained during the disintegration of the radionuclides.[5, 38, 39]

A relationship between the charge in the crystals and their rate of dissolution was first established in studies of the dissolution of radioactive $SrSO_4$ crystals in water. It was then shown that NaCl, $SrSO_4$, and other salts dissolve more slowly than the nonpolarised compounds. The polarisation of the solvents also has an effect, and therefore the change in k_v is strongly dependent on the ratio of the dielectric constants of the solid and the liquid phase.[38, 39] Furthermore, the solubilities of the components of the system also play an important part.

Thus, according to the data in Fig. 11, the dependence of the change in the dissolution rate constant (in water) on the intensity of the electric field shows that as the field E is increased the k_v value decreases most markedly in $SrSO_4$, which has the lowest solubility. The decrease in k_v in a series of salts of the same type (NaCl, LiF, NaF) is strongest in the least soluble compound (LiF), which has the highest dielectric permittivity. The slower dissolution of ionic crystals after irradiation may to some extent be associated with their radiation-induced charging.

Let us examine the relationship between k_v and the strength of the field in the crystal. We shall express k_v in terms of two factors, one dependent and one independent of the polarisation of the crystal, and we shall discuss the elementary act of the dissolution of the crystal from the standpoint of the change in energy of the molecule during its transfer to the liquid phase. It will be assumed that the dissolution process obeys the Brønsted relation

$$\Delta Q_a = b\Delta Q_h , \tag{33}$$

where ΔQ_a is the activation energy of the dissolution; ΔQ_h is the heat of dissolution; b is an empirical constant ($0 \leqslant b \leqslant 1$). We can then write the following expression for the dissolution rate constant;

$$k_v = k_v^0 \exp\left(-\frac{b\Delta Q_h}{kT}\right), \tag{34}$$

where k_v^0 is a temperature-independent quantity. Formula (34) can be rewritten

$$k_v = k_v^* \exp\left(-\frac{b\Delta F_{el}}{kT}\right), \tag{35}$$

where ΔF_{el} is the change in the 'electric' component of the free energy (the Helmholtz free energy) of the molecules of the ionic crystal during the dissolution, and k_v^* includes both the entropy term and a term which characterises the free energy in terms of the strength of the electric field applied to the crystal. The parameter ΔF_{el} is $U_2 - U_1$ (the difference between the 'electric' free energies of the dissolution of the molecule in the solution and in the crystal respectively).

The dependence of the rate constant for the dissolution on the external electric field can be influenced only by that part of the free energy of the molecule in the crystal which is contributed to by the polarisability of the molecule. Therefore we can write the following expression for U_1:

$$U_1 = -\alpha|E|^2 , \tag{36}$$

where α is the total polarisation of one molecule; E is the strength of the electric field within the crystal. In the case of crystals with a uniform charge of anions and cations the energy U_2 (in the Gouy–Chapman approximation) is given as

$$U_2 = -16C_0K_D\pi r_0^2kT\sinh^2\frac{ez\phi}{4kT}, \tag{37}$$

where C_0 is the average equilibrium concentration of ions in the bulk of the solution; $K_D = (8\pi e^2z^2C_0/\varepsilon_2kT)^{1/2}$ is the reciprocal Debye length; z is the charge of the ions in the crystal; r_0 is the corresponding radius of the ion in solution; ϕ is the average potential of the outer Helmholtz plane (in which the centres of the ions in solution nearest to the crystal surface are localised); ε_2 is the average dielectric permittivity of the solution.

The total polarisability of the molecule in the solid phase α can be calculated by the Clausius–Mosotti relation

$$\alpha = 3M\frac{\varepsilon_1 - 1}{4\pi dN_A(\varepsilon_1 + 2)}, \tag{38}$$

where ε_1 is the static dielectric permittivity of the crystal; M is the molecular mass; d is the density; N_A is the Avogadro number.

In order to calculate E and ϕ we need to solve the problem of the distribution of potential in a system consisting of a polarised crystal with Helmholtz layers at its boundaries with the solution, and surrounded by the diffuse parts of the electrical double layer. If we adopt the Gouy–Chapman model to describe the distribution of charge in the diffuse part of the double layer the problem of the distribution of the ϕ potential (even only in the plane separating the crystal from the solution) reduces to the simultaneous solution of a system of two Poisson–Boltzmann equations (for the diffuse parts of the double layer) and three one-dimensional Laplace equations (for the Helmholtz part of the double layers and for the polarised crystal). The boundary conditions should ensure the continuity of the potential and of the electric induction at the interface between the crystal and the solution. After some algebra we arrive at the expressions

$$|E| = -\frac{4\pi}{\varepsilon_1}\left[|P| - \frac{4ezC_0}{K_D}\sinh\left(\frac{ez\phi}{2kT}\right)\right], \tag{39}$$

$$\phi = \frac{4\pi e}{\varepsilon_1}\left[|P| - \frac{4ezC_0}{K_D}\sinh\left(\frac{ez\phi}{2kT}\right)\right], \tag{40}$$

where $|P|$ is the polarisation of the crystal.

By combining the well known relationship between $|P|$ and the strength of the field applied to the crystal with Eqns (35)–(40) we obtain the dependence of the rate constant for the dissolution of the crystals upon their polarisation:

$$\ln\frac{k_v^*}{k_v} = 16b\left\{\sinh^2\left(\frac{ez\phi}{4kT}\right) - \frac{\alpha\pi^2}{\varepsilon_1^2kT}\left[|P| - \frac{4ezC_0}{K_D}\sinh\left(\frac{ez\phi}{2kT}\right)\right]^2\right\}. \tag{41}$$

The parameter P is related to the intensity E_1 of the electric field applied to the crystal by the expression

$$P = \frac{(\varepsilon_1 - 1)E_1}{4\pi\varepsilon_1}. \quad (42)$$

We may conclude from (39)–(42) that for sufficiently large values of α and not too small bulk concentrations of the solution k_v decreases with increase in E_1 (or P). However, it should not be forgotten that in strong fields ($ez|\phi| \gg kT$) the polarisability α is itself dependent on the field strength, decreasing as $|\phi|$ increases. Therefore an increase in the potential difference applied to the crystal should suppress the dependence of the rate constant of the dissolution on E_1, as is found in practice.

The theoretical prediction of an increase in the rate of dissolution of polarised crystals has been confirmed by observations of the dissolution of crystals of tartaric acid in solvents having different dielectric permittivities (Fig. 12).

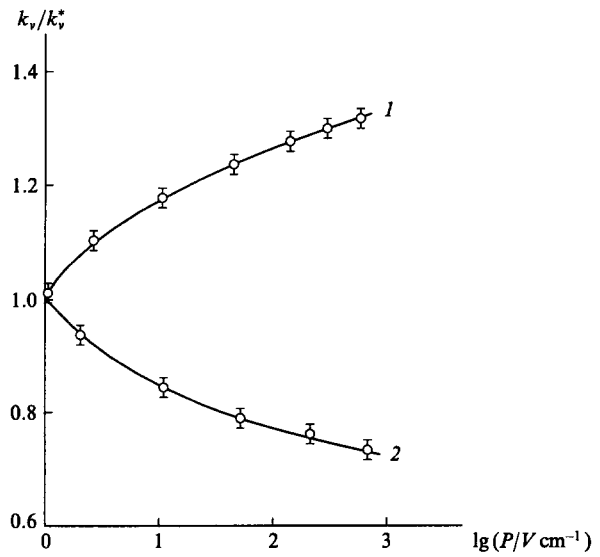


Figure 12. Changes in the rate of dissolution in water of crystals of tartaric acid as a function of the polarisation of the solid phase P ($\varepsilon_1 = 35.9$) in ethanol ($\varepsilon_2 = 20$) (*1*) and in water ($\varepsilon_2 = 80$) (*2*).

The physical significance of the slower dissolution of charged crystals is that the polarised dipole–molecule being transferred to the liquid phase must perform additional work against the force of the electric field. However, if the solvent also is polarised, it becomes more difficult for the dipole–molecule to return to the solid surface for $\varepsilon_{sol} \gg \varepsilon_{liq}$, i.e. the rate of dissolution increases and the molecule is 'pulled' into the liquid phase by the electric forces.

Similar effects have been observed[40] in a study of the rate of growth of etch pits at the emergence of dislocations on the surface of polarised LiF crystals.

Brief mention should be made of another possible way of suppressing the dissolution of crystalline dielectrics, in which the liquid phase is subjected to the orienting effect of an electric field. Thus, the polarisation of the solvent molecules in the boundary layer at the interface can stabilise the layer of liquid adjacent to the surface of the dissolving crystal.[41] In the present model the calculated strengths of the electric field produced by polarisation can vary between wide limits (from 0 to 10^3 V cm^{-1} or more). In actual systems the polarisation can strongly influence the viscosity and the perviousness of the surface layers. This is consistent with the views of a dependence of the viscosity of polar liquids on electric field effects. The dissolution of polarised crystals can also be retarded by the condensation (accumulation) of reaction products and other dissolved substances in the boundary layer under the influence of an electric field, and by the formation of crystal nuclei or polymer chains (for example, in P_2O_5 or SiO_2) able to interact with each other and with the molecules of the liquid medium. The new formations 'armour' the system and can induce the formation of a gel-like metastable state at the interface between the solid and the liquid phase. Therefore in some cases the polarisation of molecules on the surface of dissolving compounds can lead to the formation of protective gel-like films.

IX. Conclusions

The experimental work shows that the accumulation of electric charge in irradiated and in radioactive solid dielectrics is one of the most fundamental phenomena accompanying the action of ionising radiation on high-resistance materials. The developments in this field of study have been stimulated not only by their purely scientific interest but also by specific practical needs. Thus, the prediction of the service life of various electrical insulators and articles in fields of ionising radiation is impossible without a knowledge of the special features of the growth and relaxation processes which control the 'radiational' electric charging. This may ultimately determine the reliability of the operation of nuclear energy converters and apparatus used in cosmic flights when continuously exposed to ionising radiation, and other similar problems. Therefore further progress in this area is impossible without studies in depth of the mechanism of reversible and of irreversible processes initiated by ionising radiation in dielectrics.

At present the following promising fields of study in this area can be identified:

1. The development of a theory of the distribution of electric field in dielectric materials (or articles) in various configurations exposed to ionising radiation.

2. Improvements in the theory and methods of calculating the distribution of electric space charge (and its corresponding electric field) in heterogeneous structures (mixtures of solid substances, solid systems containing inclusions of various solid phases).

3. The acquisition of experimental information on the effect of external factors on the formation of an electric charge and on the 'freeing' of this charge from the given material (for example, in the form of electric discharges).

4. The study of the mechanism of radiation-chemical and radiation-physical processes in charged dielectrics: this should lead to the development of new methods of controlling the properties of these materials and of the physicochemical processes carried out by using them.

5. The modelling of actual operating conditions encountered by various materials in a field of ionising radiation, i.e. allowing for the combined effects on the dielectric of the charging, defect formation, temperature fields, mechanical interactions, and other factors.

The importance of this type of study arises because in many cases the formation of charge and the subsequent electric breakdown (which can even lead to the mechanical fracture of the dielectric) are the precursors of irreversible (and even, on occasions, reversible) radiation-chemical or radiation-physical changes in the material. For example, it has been shown[42] that at low temperatures (~77 K) the effectiveness of the charge accumulation in glasses irradiated by accelerated electrons increases, so that conditions conducive to electric discharges are produced even in a flow of 10^{12} electrons cm^{-2} (electron energy ~2 MeV). Heat treatment after irradiation merely accelerated this process. Similar effects are found in composite materials and polymers.

The solution of these problems should stimulate the development of reliable methods of increasing the radiation stability of various dielectric materials.

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