Long-term kinetics of the activation spectra of postirradiation relaxation of glasses

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Experimental investigations have been made of isothermal partial annealing of radiation defects in glasses over periods on the order of 10^4 h. It was found for the first time that postirradiation relaxation of inorganic glasses can be described by a universal fractional exponential dependence. The Kohlrausch relaxation function was found to satisfy the principle of temperature–time scaling. However, all the moments except the zeroth were missing from the corresponding spectrum of the relaxation probabilities. This difficulty was avoided by proposing a model relaxation function characterized by fractional-exponential behavior in a limited time interval and satisfying all the criteria of the hierarchically limited dynamics of relaxation in glasses. The parameters of the model function were determined from the experimental results. This yielded the spectra of the relaxation probabilities as well as the activation spectra describing postirradiation relaxation of glasses. The experimental behavior of the nonexponential relaxation parameters of the radiation defects was interpreted quantitatively in terms of the long-term kinetics of the activation spectra representing the contributions of parallel correlated relaxation channels in radiation damage regions in a glass. Such relaxation makes charge exchange, followed by stabilization, possible for each defect.

1. INTRODUCTION

Irradiation of solids and particularly of insulating glasses creates local defects and disordered microregions whose number densities can be determined by optical or ESR spectroscopy as a function of the radiation dose.[1,2] Such electrically and magnetically active radiation structure damage is unstable. It is followed by long-term (very slow) nonexponential relaxation manifested, for example, by ESR signals of paramagnetic centers[3] which can be explained in a natural manner by thermally stimulated changes in the atomic configuration of the glass network.

It is assumed in some treatments[3,4] that a theoretical description of the kinetics of such isothermal annealing of radiation centers in noncrystalline materials can be based on the universal Kohlrausch law for relaxation in glasses (see, for example, Refs. 5 and 6):

$$q(t)=\exp\left(-(t/\tau_0)^{\alpha}\right),\quad 0<\alpha<1, \tag{1}$$

where τ_0 is the characteristic relaxation time and α is the index of the fractional-exponential function. However, experimental data to support this law is available only for organic solids and for relatively short observation times (for the bibliography of the subject, see Refs. 3 and 4).

The mechanisms of the cooperative processes that occur in disordered systems with a strong interaction, giving rise to the fractional-exponental function of Eq. (1), can vary greatly, but they can be divided nominally into two main groups. The mechanisms belonging to the first group represent different variants of the model of diffusion-controlled reactions[3,4,7–9] based on the concept of dispersive transport in disordered structures. The second group is based on the model of hierarchically limited dynamics of the relaxation in glasses[8–12] which postulates that the relaxation processes are correlated: in contrast to parallel relaxation of independent degrees of freedom, the nonexponential nature of the relaxation kinetics is attributed in this model more to dynamic constraints than to the random distribution in each of the degrees of freedom.

The difficulties encountered in the interpretation of the experimental data on glass relaxation on the basis of Eq. (1) arise because all the moments of the relaxation rate

$$\langle k^n\rangle=(-1)^n d^n q(0)/dt^n \tag{2}$$

diverge for $n = 1, 2, \ldots$. This is due to the nonphysical behavior of the function (1) for short times. If we consider the nonexponential relaxation function $q(t)$ to be a superposition of the contributions made by elementary exponential relaxation processes

$$q(t)=\int_0^{\infty} dt\, e^{-kt}\varphi(k), \tag{3}$$

we find that the weighting function $\varphi(k)$, representing a normalized distribution function of the relaxation rates, is characterized by a power-function asymptotic form which applies in the limit $k\to\infty$: $\varphi(k)\propto k^{-(1+\alpha)}$, which is the reason for the divergence of the moments. This nonphysical feature is avoided in the present treatment by introducing a model relaxation function characterized by the fractional-exponential behavior of Eq. (1) in a wide range of observation times and also by finite values of all the moments described by Eq. (2).

Our aim was to investigate experimentally the nonexponential kinetics of postirradiation relaxation of glasses and to obtain on this basis the activation spectra of such relaxation. The methods and results of an experimental study of the kinetics of thermal annealing of radiation centers (as a function of the radiation dose and annealing conditions) are reported in Sec. 2. An analysis of the results obtained is used to show for the first time that the kinetics of postirradiation relaxation of inorganic glasses follows a fractional exponential form. A modification of the model of hier-

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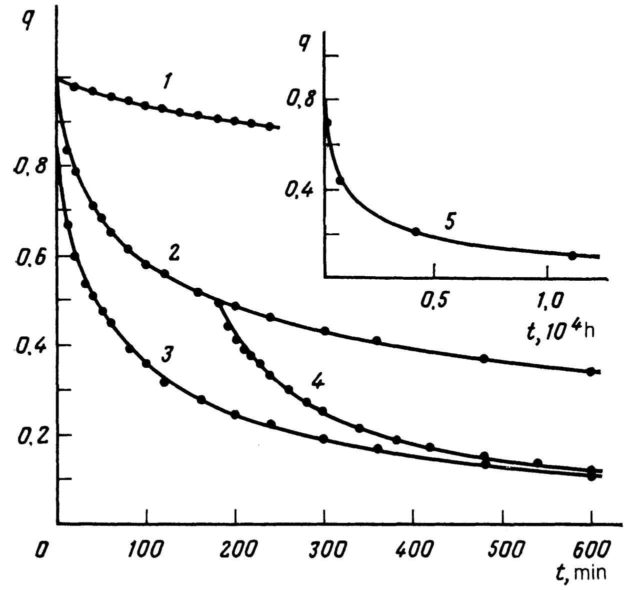

FIG. 1. Kinetics of thermal annealing represented by the relaxation function $q(t) = N(t)/N_0$ (N is the number of radiation centers) of glassy $NaPO_3$ irradiated with a dose of 3×10^5 rad and subjected to annealing at temperatures (1) $T = 293$ K, (2) 343 K, (3) 363 K, and also (4) the results of step annealing characterized by an abrupt temperature jump $\Delta T = 20$ K. The inset (5) shows the kinetics at $T = 293$ K throughout the range of observation times investigated.

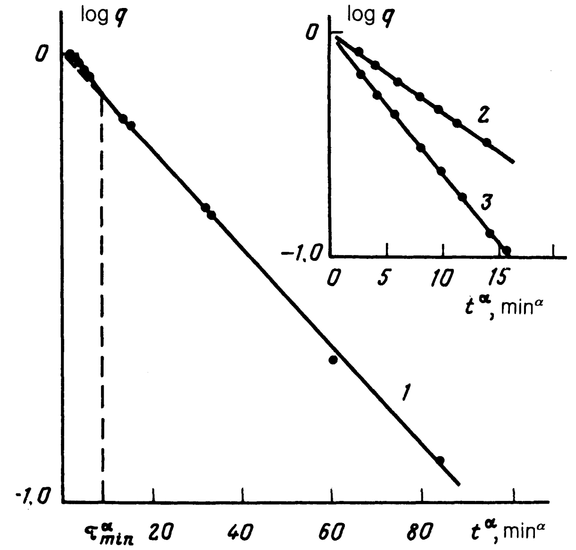

FIG. 2. Fractional-exponential [$\alpha \sim 0.4$ cm, see Eq. (6.2)] irradiation relaxation of glassy $NaPO_3$ at annealing temperatures (1) $T = 293$ K ($\tau_0 = 6.5 \times 10^4$ min), (2) 343 K ($\tau_0 = 464$ min), (3) 363 K ($\tau_0 = 93$ min). The results given in the inset are on a different time scale. Radiation dose 3×10^5 rad.

archically limited dynamics of glass relaxation, suitable for the description of three time regimes of postirradiation relaxation in a quasiergodic system, is given in Sec. 3. It is shown in Sec. 4 that the corresponding spectra of the rates of postirradiation relaxation have finite moments in every order and are in agreement with the familiar results of Pollard. Moreover, it is found that the function $\varphi(k)$ behaves asymptotically at low and high relaxation rates and in the former case there is a delta-function singularity in the spectrum. The long-term kinetics of postirradiation relaxation can be interpreted by reactions of defects in glasses (Sec. 5) and described quantitatively by the activation spectra of relaxation deduced from the experimental data (Sec. 6).

2. CHARACTERISTICS OF NONEXPONENTIAL KINETICS OF SYSTEMS OF RADIATION CENTERS: EXPERIMENTAL RESULTS

We investigated pure phosphate glasses of the compositions $NaPO_3$ and $Ca(PO_3)$ irradiated with gamma rays from the ^{60}Co isotope at room temperature at a dose rate of 100 rad/s. Irradiation of initially nonparamagnetic samples created metastable (at room temperature) radiation color centers with an ESR spectrum which was recorded using an SE/X-2544 rf spectrometer (operating at a frequency $f = 9.0$ GHz) with automatic data storage and processing by a MERA-CAMAC 125/SM4A system. Irrespective of the radiation dose and of the temperature of the subsequent heat treatment, the ESR spectrum representing the phosphorus–oxygen PO_4^{2-} centers of the dangling bond type[1,13] showed no changes in the profile and was characterized by the g-tensor components $g_\parallel = 2.012$ and $g_\perp = 2.0$, and by the hyperfine splitting constants $A_\parallel = A_\perp = 3.8$ mT. The concentration $N(t)$ of the radiation centers, deduced from the ESR signal intensity, depended on the isothermal annealing conditions and on the radiation dose (Figs. 1 and 2).

Annealing at temperatures between 273 and 343 K (curves 1 and 2 in Fig. 1) involved heating samples directly in the rf-spectrometer resonator cavity using a special 650H attachment with a temperature controller designed for the SE/X-2544 spectrometer; this attachment made it possible to maintain the required temperature to within 0.1 K. At higher temperatures we used the method of fractional annealing which made it possible to eliminate the effects of the detuning of the spectrometer resonator and of the temperature dependence of the ESR signal. The method involved repetition of the following cycle: a) fast heating of a sample to a given temperature (heating time $t_h = 1$ min); b) isothermal exposure to the selected temperature; c) rapid cooling to room temperature (cooling time $t_c = 1$ min) during which the ESR spectrum was recorded. The metastability of the radiation centers at room temperature (curve 1 in Fig. 1) made it possible to carry out annealing outside the resonator. Control experiments carried out at $T = 343$ K showed that the results of heat treatments were the same under fractional and isothermal annealing conditions. The observation time was varied from 10 min to 10^4 h (Figs. 1 and 2).

The use of a method involving detection of paramagnetic centers of one type in a glass of simple composition led us to the conclusion that the nonexponential kinetics of postirradiation relaxation (Fig. 1) was typical of retarded reactions in disordered systems and was specific to the glassy state and not a consequence of superposition of the contributions of centers of different nature, as could happen in multicomponent glasses as a result of chemical differentiation. The strong reduction in the reaction rate in the solid phase after a long observation time ($t > 10$ h) was not due to a reduction in the induced radiation centers, but due to the existence of a broad spread in the relaxation rates or times.[14] Consequently, the results of nonexponential postirradiation relaxation (Fig. 1) could be interpreted in terms of long-term kinetics of the activation spectra.

A nontrivial feature of the retarded kinetics was a temperature–time hysteresis (curve 4 in Fig. 1), representing a memory effect typical of relaxation processes in glasses.[8,9]

It follows from the above that the kinetics of postirradiation relaxation (Fig. 1) is described by Eq. (3) and the relaxation function $q(t) = N(t)/N_0$ [N_0 is the concentration of the PO_4^{2-} centers observed 1 h after irradiation at room temperature (see curves 1 and 2 in Fig. 3)] on condition that an elementary recombination event is a first-order reaction. This hypothesis was checked by investigating the dependence of $dN(t)/dt$ on the radiation dose at the initial times during measurements (curves 3 and 4 in Fig. 3). Accurate numerical differentiation was ensured by smoothing out the kinetic curves during the initial period ($t<1$ h). The constancy of the derivative in the region of the linear dose dependence of the concentration of the centers (Fig. 3) provided the experimental proof that the reaction was of the first order. However, in the case of the $Ca(PO_3)_2$ glass this statement was only approximately true (curve 4 in Fig. 3).

An analytic approximation for the kinetic curves (Fig. 1) was based on a least-squares analysis carried out for exponential, logarithmic, and fractional-exponential test functions $q(t)$. The best approximation was provided by the function (1) shown in Fig. 2, where the range of variation of the Kohlrausch relaxation function (from 0.99 to 0.01) agreed with the theoretical estimates of Refs. 8, 11, and 12. It is important to note that the fractional-exponential behavior of the function $q(t)$ was retained even in the case of very long observation times ($t > 10^4$ h) with a characteristic value of $\alpha \approx 0.4$ (Fig. 2). The use of the approximation (1) in the range $t < \tau_{\min}$ (Fig. 2) increased the exponent α (for example, $\alpha = 0.68$ was found for curve 1 in Fig. 1).

The Kohlrausch function of Eq. (1) satisfies the principle of temperature–time scaling,[8,15] provided the fractional exponent α in the argument and the characteristic time τ_0 are both independent of the observation time and α is independent also of temperature.[8,9] An investigation of this dependence showed that glass with the composition $NaPO_3$ satisfied these requirements (Fig. 4). The observed Arrhenius-type temperature dependence of τ_0 (Fig. 4b) made it possible to use the concept of the activation spectra of postirradiation relaxation. In the case of glass of composition $Ca(PO_3)_2$ the temperature dependence of α was weak, which caused breakdown of the temperature–time scaling relationships and was clearly associated with the competition between the tunnel and activation mechanisms in the recombination of radiation centers.

3. MODEL OF HIERARCHICALLY LIMITED DYNAMICS OF POSTIRRADIATION RELAXATION

We interpret the experimental data of Sec. 2 by a modification of a model of hierarchically limited dynamics of relaxation in glasses.[8,12] The approach developed by Palmer *et al.*[10] is based on the following representation of the relaxation function of a quasiergodic system:

$$q(t)=\sum_{n=0}^{\infty} w_n \exp(-k_n t), \qquad w_n=w_0/\lambda^n,$$
$$k_n=k_0\exp\left(-\mu\sum_{j=1}^{n} j^{-p}\right), \qquad n\geqslant 1, \tag{4}$$

where w_n is the statistical weight of a correlated relaxation process consisting of n successive steps; k_n is the total probability of this process; μ is a parameter describing the dynamic limitations on the atomic motion ($1<\mu<10$); w_0 and k_0 are, respectively, the statistical weight and the rate of relaxation of the fast recombination process; and $\lambda, p \gg 1$ are dimensionless parameters. The value of p is close to unity. Physically, Eqs. (4) mean that the relaxation function is represented as a superposition of the contributions of correlated relaxation processes with an arbitrary number of steps n (Ref. 8).

In contrast to the treatment of Palmer *et al.*,[10] in the

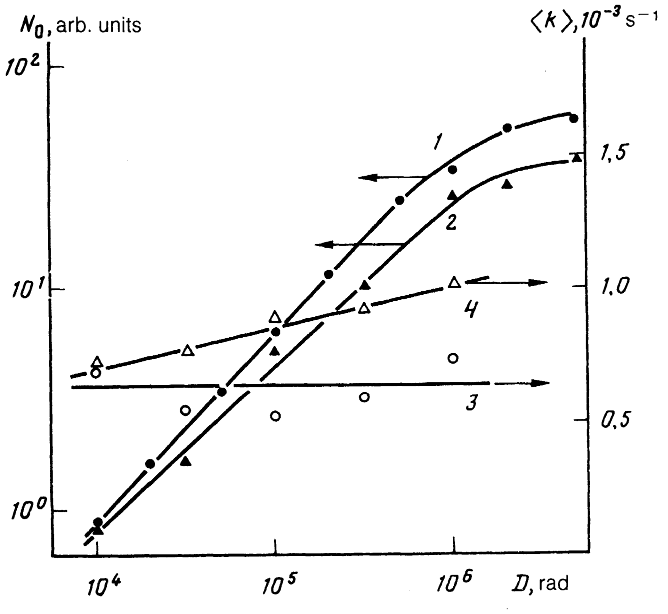

FIG. 3. Dependence of the initial concentration N_0 of radiation centers (1,2) and of the first moment of the relaxation function $\langle k \rangle = dq(0)/dt$ (3,4) for glassy $NaPO_3$ (curves 1 and 3; $T = 363$ K) and $Ca(PO_3)_2$ (curves 2 and 4; $T = 413$ K) on the radiation dose D.

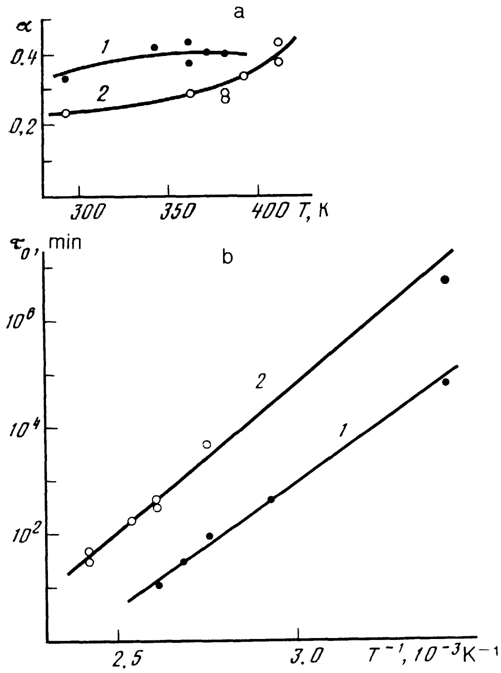

FIG. 4. Temperature dependence of the exponent α (a) and of the relaxation (b) of (1) $NaPO_3$ and (2) $Ca(PO_3)_2$ glasses.

case of postirradiation relaxation the slow degrees of freedom of a glass block relaxation of the faster degrees of freedom in disordered regions created by irradiation. In a given disordered region the process of postirradiation relaxation terminates with the recombination of a radiation defect characterized by a probability k_0, which occurs when the relaxation of the local environment is complete. We shall show below (Sec. 5) that such a recombination reaction is the fastest relaxation process in the system because it consists of atomic modification which effectively occurs along one generalized lattice coordinate. On the other hand, relaxation of the local environment involves atomic modifications which affect simultaneously a large number of generalized coordinates and, consequently, are characterized by fairly large potential barriers. The presence of such barriers in a system of radiation defects makes each atomic modification an allowed process, provided all the preceding levels of the hierarchy are already relaxed and have liberated the necessary free volume. A one-electron energy level of radiation defects needed for detection of relaxation on the basis of the ESR signal (Sec. 2) is located in the band gap. On the other hand, the level of a second (correlated) electron at the same defect is located in the conduction band of the glass immediately after irradiation, so that an electron transition to this level is not favored by energy considerations (Sec. 5). Therefore, the physical reason for this sequence of relaxation processes is the lowering and stabilization of a level of a nonparamagnetic two-electron state of a defect in the bandgap of the glass.

The Kohlrausch function (1) with an exponent $\alpha = 1(1+\mu)$ is the asymptotic form of the sum of Eq. (4) obtained on going over from a discrete to a continuous distribution of the degrees of freedom in a glass.[8-12] However, according to Eq. (4), the behavior of the relaxation function at short times is nearly exponential, which is fundamentally different from Eq. (1). In fact, if the time t is short, the sum contains only the first exponential function with the highest relaxation rate k_0 and the remaining exponential functions in Eq. (4) are equal to unity. This is due to an exponential decrease of k_n and w_n with increasing n: the numerical data used in the present study (Secs. 2, 5, and 6) indicate that k_1 is approximately 4.5 times less than k_0. Inclusion of higher exponential terms in Eq. (4) cannot alter the qualitative picture of the process of relaxation in the case of short times t, i.e., it cannot account for the absence of infinite rates of relaxation in Eq. (4), in contrast to Eq. (1). Moreover, as shown in Ref. 10, quasiergodic systems are characterized by the maximum characteristic time $\tau_{\max}$ of atomic modifications when a transition takes place from the Kohlrausch relaxation mechanism of Eq. (1) to the slower Debye relaxation. These three regimes of the relaxation behavior can be described over the full range of times in a unified manner using the following modified relaxation function:

$$q(t) = \exp\left[-z\left(\nu_1 \frac{1+\nu_2 z}{1+\nu_1 z}\right)^{1-\alpha}\right], \quad z = \frac{t}{\tau_0}, \tag{5}$$

where z is the dimensionless time; $\nu_1 = \tau_0/\tau_{\min}$, $\nu_2 = \tau_0/\tau_{\max}$; $\tau_{\min}^{-1}$ and $\tau_{\max}^{-1}$ are the upper and lower limits of the spectrum of the relaxation rates $\varphi(k)$ $(\nu_1 > 1 \gg \nu_2)$. The simplest interpolation function of Eq. (5) is our main assumption, which will be used later to interpret the experimental data on relaxation in glasses (Sec. 2). It satisfies the criteria of hierarchically limited dynamics of relaxation in glasses[10] and makes it possible to find the distribution $\varphi(k)$ including all the moments. The function (5) exhibits three main types of behavior (Fig. 5) and the Kohlrausch law is obtained only for intermediate times. Elsewhere the exponent α in the fractional argument of the exponential function varies slowly with time, approaching unity:

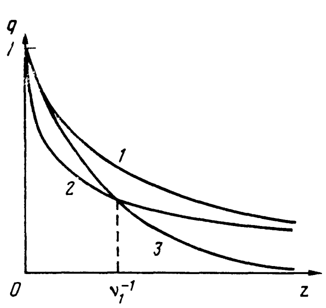

FIG. 5. Dependence of the relative concentration of the radiation centers on the duration of annealing: modified postirradiation function (1), Kohlrausch function (2), and Debye function (3) for $\alpha = 0.4$.

$$q(t) = \begin{cases} \exp(-\nu_1^{1-\alpha} z), \quad t \ll \tau_{min}, & \text{(6a)} \\ \exp(-z^\alpha), \quad \tau_{min} < t < \tau_{max}, & \text{(6b)} \\ \exp(-\nu_2^{1-\alpha} z), \quad t \gg \tau_{max}. & \text{(6c)} \end{cases}$$

The value of $\tau_{\min}$ can be found from the experimental data as the lower limit of the transition region where deviations from the fractional-exponential behavior disappear (Figs. 2 and 5). The values of $\tau_{\min}$ used in the calculations were obtained by analytic approximation of the kinetic curves (Fig. 1) by the method of least squares using the test function (5). It was found that the value of $\tau_{\min}$ is of the same order of magnitude as $\nu_1^{1-\alpha}/\tau_0$, which is the first moment of the spectrum of Eq. (2) corresponding to the function (5). Bearing in mind the comment about the behavior of the function (4) at short times, we readily find from Eq. (6a) that the use of the interpolation (5) is justified in this range.

We can expect the characteristic times $\tau_{\min}$ and $\tau_{\max}$ in Eqs. (5) and (6) to depend on the temperature in an activated manner. It follows from the results of Sec. 2 on the reaction order that the spectrum of the relaxation rates is governed by the inverse Laplace transformation of the function (5):

$$\varphi(k) = \int_{-i\infty}^{i\infty} \frac{dt}{2\pi i} e^{kt} q(t), \tag{7}$$

where the integration contour lies to the right of all the singularities of the function $q(t)$.

4. SPECTRA OF POSTIRRADIATION RELAXATION RATES

The problem of inversion of the relaxation function (7) in the specific case of the Kohlrausch law (1) has been considered before.[16-18] In the case described by Eq. (5) this problem has nontrivial features; the results of an investigation of these features are presented below and used in Sec. 5 in an analysis of the experimental data given in Sec. 2.

The relaxation function of Eq. (5) is analytic throughout the complex plane of the variable z with a cut along the negative part of the real axis from $-\nu_2^{-1}$ to $-\nu_1^{-1}$. Substituting Eq. (5) into Eq. (7), we find that simple transformations yield the following expression

$$\varphi(k)=\tau_0\int_0^\infty \frac{dz}{\pi}\exp\{-zh(z)\sin[(1-\alpha)\chi(z)]\}$$

$$\times\cos\{z[x-h(z)\cos[(1-\alpha)\chi(z)]]\},\qquad(8)$$

where $x = k\tau_0$,

$$h(z)=\nu_1^{1-\alpha}[(1+\nu_2^2z^2)/(1+\nu_1^2z^2)]^{(1-\alpha)/2},\qquad(9)$$

$$\chi(z)=\mathrm{arctg}[z(\nu_1-\nu_2)/(1+\nu_1\nu_2z^2)].\qquad(10)$$

In the limit with $\nu_1\to\infty$ and $\nu_2\to 0$ the relationships (8)–(10) reduce to the familiar Pollard representation[16]

$$\varphi(k)=\tau_0\int_0^\infty \frac{dz}{\pi}\exp[-xz-z^\alpha\cos(\pi\alpha)]\sin[z^\alpha\sin(\pi\alpha)],\qquad(11)$$

which corresponds to the fractional-exponential relaxation process of Eq. (1). In the case with $\alpha = 1/2$ and $\alpha = 1/3$, it is possible to express Eq. (11) explicitly in terms of special functions.[16,17] We can easily show that in the limit $k\to\infty$ the asymptotic form of Eq. (11) has the form [$\Gamma(x)$ is the gamma function]

$$\varphi(k)=\frac{\tau_0\sin(\pi\alpha)}{\pi x^{1+\alpha}}\Gamma(1+\alpha),\qquad(12)$$

which gives rise to the divergence of all the moments in the spectrum of the relaxation rates in the case described by Eq. (1). It should be mentioned that the spectrum of the relaxation rates corresponding to the original model (4) proposed by Palmer *et al.*[10] is a superposition of the delta functions

$$\varphi(k)=\sum_{n=0}^\infty w_n\delta(k-k_n).\qquad(13)$$

The envelope of the spectrum (13) can be represented by a series of discrete maxima of amplitude w_n [see Eq. (4)] at the points k_n (Fig. 6) or as a histogram of the function $\varphi(k)$ which is obtained by dividing the quantity w_n by the length of the corresponding segment along the abscissa $(k_{n+1} - k_{n-1})/2$ (Fig. 6). We shall show that smoothing out of the histogram (dashed curve in Fig. 6) gives results which are close to the exact calculation of the integral of Eq. (8) given in Fig. 7.

In the case of the spectrum described by Eq. (8) we can check that all the moments of the relaxation rate of Eq. (2) are finite by considering the asymptotic behavior in the limit $k\to\infty$ $(x > \nu_1^{1-\alpha})$. It follows from the general properties of the Laplace transformation that in this case the integral of Eq. (8) is governed by the range of low values of z $(\nu_1 z < 1)$. Since according to Eqs. (9) and (10) we obtain in this limit

$$h(z)=\nu_1^{1-\alpha},\qquad \chi(z)=z(\nu_1-\nu_2),\qquad(14)$$

we find that $\varphi(k)$ is now described by

$$\varphi(k)=\tau_0\int_0^\infty \frac{dz}{\pi}\exp(-az^2)\cos(bz)=\frac{\tau_0}{(4\pi a)^{1/2}}\exp\left(-\frac{b^2}{4a}\right),$$

$$a=(1-\alpha)\nu_1^{1-\alpha}(\nu_1-\nu_2),\qquad b=x-\nu_1^{1-\alpha}.\qquad(15)$$

The advantage of this approach to interpreting the experimental data (Sec. 2) on the basis of the relaxation function of Eq. (5) is the exponential smallness of the "tail" of the distribution given by Eq. (15) at high relaxation rates. In the limit $\alpha\to 1$ the spectrum (15), which in this case corresponds to the exponential relaxation process, degenerates into the delta function $\delta(k - \nu_2^{1-\alpha}/\tau_0)$. Therefore, in function (5), unlike Eq. (1), relaxation times shorter than $\tau_0\nu_1^{\alpha-1}$ are excluded.

An analysis of Eq. (7) shows that the result of integration depends on the selection of the contour in the complex plane of the dimensionless time z: the integrals along the axis in Eq. (8) along the imaginary axis and along the cut mentioned above differ by an amount equal to the integral along an infinite semicircle in the left half-plane, which in this case does not vanish. We can show that the contribution of this integral is proportional to the delta function $\delta(x - \delta_2^{1-\alpha})$. In the opposite limit of low relaxation rates the asymptotic form of the relationship (8) should reflect this. The main contribution to Eq. (8) comes from the range of large values of z $(\delta_2 z > 1)$, where [see Eqs. (9) and (10)]

$$h(z)=\nu_2^{1-\alpha}\left[1+\frac{1-\alpha}{2}\left(\frac{1}{\nu_2^2}-\frac{1}{\nu_1^2}\right)\frac{1}{z^2}+\dots\right],$$

$$\chi(z)=\frac{\nu_1-\nu_2}{\nu_1\nu_2z}\left[1-\frac{1}{3}\left(\frac{\nu_1-\nu_2}{\nu_1\nu_2z}\right)^2+\dots\right].\qquad(16)$$

To within terms of order z^{-1} in the integrand, we find that Eq. (8) becomes

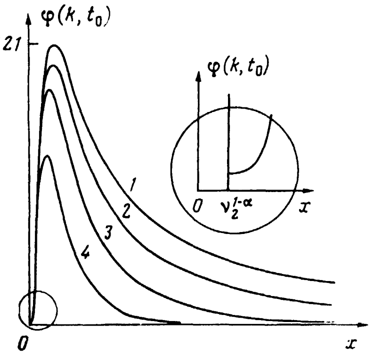

FIG. 7. Kinetics of the spectrum of postirradiation relaxation rates of Eq. (8) ($x = k\tau_0$) plotted for (1) $t_0 = 0$, (2) τ_0, (3) $3\tau_0$, and (4) $10\tau_0$. The inset shows schematically the delta-like singularity in the spectrum of $\varphi(k,t_0)$ at low values of k.

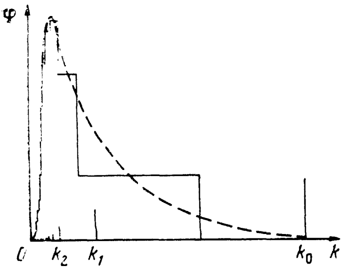

FIG. 6. Envelope of the spectrum of the relaxation rates obtained in the model of hierarchically limited dynamics proposed in Ref. 10; $\mu = 1.5$, $\lambda = 2$, $p = 1.01$.

$$\varphi(k)=\tau_0\exp\left[-(1-\alpha)\frac{\nu_1-\nu_2}{\nu_1\nu_2^{\alpha}}\right]\int_0^{\infty}\frac{dz}{\pi}\cos\left[z(x-\nu_2^{1-\alpha})-\frac{C}{z}\right], \tag{17}$$

$$C=\nu_2^{1-\alpha}(1-\alpha)[\alpha\nu_1^2-(2+\alpha)\nu_2^2+2(1-\alpha)\nu_1\nu_2]/2(\nu_1\nu_2)^2.$$

The final result for low values of k can be represented conveniently in the following form:

$$\varphi(k)=\tau_0\exp[-(1-\alpha)(\nu_1-\nu_2)/\nu_1\nu_2^{\alpha}]$$
$$\times[\delta(x-\nu_2^{1-\alpha})+C\theta(x-\nu_2^{1-\alpha})], \tag{18}$$

where $\theta(x)$ is the Heaviside step function. It is important to note that Eq. (18) is identically equal to zero if $k<\nu_2^{1-\alpha}/\tau_0$. If the system has a finite time $\tau_{\max}$, i.e., if the system of radiation centers is quasiergodic (see Refs. 8 and 10), it follows from Eq. (18) that the distribution $\varphi(k)$ becomes a constant at low values of k and is "terminated" by a delta function (inset in Fig. 7). If ν_2 falls, the quantity C in Eq. (18) tends to approach $\alpha(1-\alpha)/2\nu_2^{1+\alpha}$. However, the exponential factor in Eq. (18) drops rapidly and balances out the effects of the rise of C, so that both the normalized delta-like peak and the height of a "step" at the point $k\approx\nu_2^{1-\alpha}/\tau_0$ [see Eq. (18) and the inset in Fig. 7] become small quantities and can be detected experimentally if the observation time is $t>\tau_{\max}$ (10^5 h) when the Kohlrausch law is no longer obeyed [see Eq. (6c)]. Basically, the presence of these singularities in the relaxation rate spectrum of Eq. (8) corresponding to the function (5) indicates that the analysis given in Ref. 10 is incomplete [compare with Eq. (13) and Fig. 6]. The existence of the delta function in the spectrum (18) is a common property of quasiergodic systems. The result given by Eq. (18) in the limit $\nu_2\to 0$ is in full agreement with the asymptote found in Eq. (18) by the steepest-descent (saddle-point) method in the Kohlrausch relaxation case (see Ref. 17).

We evaluated the integral of Eq. (8) numerically for the experimentally obtained (using the data in Sec. 2) values of the parameters $\alpha=0.4$, $\nu_1=21.2$, and $\nu_2=10^{-4}$. The results are presented in Fig. 7 (curve 1). The calculated spectrum of the relaxation rates $\varphi(k)$ has the properties established above [Eqs. (15) and (18)], and in the range of intermediate values of k it is in good agreement with the predictions of the model of hierarchically limited dynamics of relaxation in glasses (Fig. 6).

5. PROBABILITY OF A RECOMBINATION REACTION OF A RADIATION CENTER

The experimentally observed activated dependence of the characteristic relaxation time (Fig. 4b) is in agreement with the model of hierarchically limited dynamics of postirradiation relaxation (Sec. 3), provided that the constants k_n [see Eq. (4)] have the Arrhenius dependence for all values of n. This is sufficient to make this dependence typical of the fastest process in a correlated relaxation chain, specifically, recombination of a radiation defect. Disappearance of the signal due to the ESR centers in the course of postirradiation relaxation (Sec. 2) indicates that the recombination completing the modification processes represents the reaction of charge transfer of a defect accompanied by pairing of spins and atomic modification of the lattice.[19-21]

In a calculation of the probability of this reaction we can use the standard methods of the theory of nonradiative multiphonon transitions in deep centers.[19-21] The charge transfer rate τ^{-1} can be related to the first moment of the spectrum $\varphi(k)$; according to Refs. 20 and 21, it is described by the expression ($\hbar=1$)

$$\frac{1}{\tau}=\frac{\nu_1^{1-\alpha}}{\tau_0}=2\pi\left(\frac{a_0}{a_D}\right)^3\Lambda N(E). \tag{19}$$

Here, a_0 is the localization radius of an electron captured by a center; a_D is the Bohr radius of a shallow impurity which releases an electron in stabilizing a radiation center;

$$\Lambda=\exp\left(-\frac{2r}{a_D}\right)\int\frac{d^3\mathbf{q}}{(2\pi)^3}|C_q|^2(2N_q+1) \tag{20}$$

is the average value (obtained using the phonon occupation numbers N_q) of the square of the total matrix element of a transition; $\mathbf{q}$ and $\omega_1=v_q$ are the quasimomentum and frequency of acoustic phonons in glass, which in this case play the role of a promoting mode; v is the velocity of sound; $|C_q|^2=\Xi^2q/2\rho v$ is the square of the matrix element; Ξ is the deformation potential; ρ is the density of the investigated glass; r is the average distance in a donor–acceptor pair[1)];

$$N(E)=(2\pi\Delta^2)^{-1/2}\exp[-(E+I)^2/2\Delta^2] \tag{21}$$

is the effective density of the final states participating in the charge transfer reaction; I is the thermal ionization potential of a stabilized radiation defect; $E<0$ is the energy level of a shallow trap; and Δ is the half-width of the line profile of a multiphonon transition (see Ref. 19). It should be pointed out that, according to Eq. (21), stabilization of a radiation defect accompanies nonoptimal quantization of the multiphonon process (see Ref. 21).

In the semiclassical approximation for multiphonon transitions ($T>\omega_0$, ω_q) the quantities Δ^2 and N_q are proportional to the temperature of a sample[19] and the probability (19) is characterized by the Arrhenius dependence:

$$1/\tau=f_0\exp(-E_0/T). \tag{22}$$

Here, ω_0 is the frequency of a local accepting mode of a defect; the following notation is used in Eq. (22) for the activation energy and the preexponential factor:

$$E_0=\frac{(E+I)^2}{4W},\quad f_0=\frac{1}{6\pi^{1/2}}\left(\frac{a_0}{a_D}\right)^3\left(\frac{T}{W}\right)^{1/2}\frac{\Xi^2\omega_D^3}{\rho v^5}\exp\left(-\frac{2r}{a_D}\right), \tag{23}$$

where $W=S\omega_0$ is the polaron shift; S is the Huang–Rhys factor; and ω_D is the Debye frequency.

The first moment of the spectrum $\varphi(k)$ deduced from the experimental data (Sec. 2) agrees with the results of calculations carried out using Eqs. (22) and (23) and the following values of the parameters of the irradiated material: $a_0=1$ Å, $a_D=5$ Å, $\Xi=3$ eV, $\omega_D=5$ meV, $\rho=2.5$ g/cm^3, $T=343$ K, $v=5\times10^5$ cm/s, $\tau_0=7.2\times10^3$ s, $r=21$ Å; the concentrations of radiation defects and shallow traps are assumed to be 10^{17} and 10^{20} cm^{-3}, respectively. The other parameters are $E_0=0.67$ eV, $f_0=5\times10^6$ s^{-1}, $I=0.64$ eV, and $W=0.16$ eV. The dependence of the Debye frequency of the material on the radiation dose affects E_0 only logarithmically. The photon energy $h\nu=I+W$ corresponds to the wavelength of light 520 nm at the maximum of the observed optical absorption by stabilized PO_4^{2-} centers in irradiated and annealed phosphate glasses.[22]

It therefore follows that the proposed approach allows us to relate the average statistical characteristics of postirradiation relaxation with a microscopic quantum theory of atomic modifications in glasses.

6. ACTIVATION SPECTRA OF POSTIRRADIATION RELAXATION

An analysis of the experimental data of postirradiation relaxation in glasses (Sec. 2) in terms of the activation spectra was made using the Arrhenius dependence of the relaxation rate (Sec. 5)

$$k=k^* \exp(-G/T), \tag{24}$$

where k^* is the maximum rate of postirradiation relaxation in the system and the activation energy G assumes positive values. The normalized distribution function $P(G)$ of the activation spectrum is related to the spectrum $\varphi(k)$ as follows:

$$P(G)=\int_0^\infty dk\,\delta\left(G+T\ln\frac{k}{k^*}\right)\varphi(k)$$

$$=\frac{k^*}{T}\exp\left(-\frac{G}{T}\right)\varphi\left(k^*\exp\left(-\frac{G}{T}\right)\right). \tag{25}$$

We can easily see [cf. Eq. (8)] that the characteristic rate k^* occurs in Eq. (25) in the dimensionless combination $x^* = k^*\tau_0$ the values of which depend strongly on the behavior of the relaxation function $q(t)$ at short times. In the case of the Kohlrausch law (1) the unbounded nature of the spectrum at high relaxation rates [see Eqs. (11) and (12)] makes it impossible to determine uniquely the value of k^*. In fact, using Eq. (1) in the calculation of the activation spectrum of Eq. (25), we find that for $\alpha = 1/2$ and for any finite value of k^* we can use the following analytic representation:

$$P(G)=\frac{1}{2T(\pi x^*)^{1/2}}\exp\left(\frac{G}{2T}\right)\exp\left(-\frac{1}{4x^*}\exp\frac{G}{T}\right). \tag{26}$$

Since the function (26) differs from zero for $G = 0$ [at this point its characteristic value is close to $(2T)^{-1}(\pi x^*)^{-1/2}$)], the interpretation of postirradiation relaxation on the basis of Eqs. (1) and (26) becomes inconsistent because it is then necessary to postulate the existence of nonphysical negative values of the activation energy.

It follows from the above discussion that if we use the modified relaxation function (5), these difficulties do not appear: the spectrum of Eq. (8) is bounded at large values of k, in agreement with Eq. (15) [but in contrast to Eq. (12)]. This makes it possible to determine the upper limit to k^* for the spectrum of Eq. (8) with logarithmic precision. Obviously, the value of k^* should exceed the rate of the fastest relaxation process (Sec. 5). We therefore obtain the following estimate:

$$x^*=\nu_1^{1-\alpha}+n_0(2a)^{1/2}, \tag{27}$$

where $2a$ is the variance which occurs in the asymptotic form of Eq. (15), and $n_0 \sim 10$. Clearly, the second term dominates Eq. (27). Moreover, we must allow for the fact that the measurements began 1 h after irradiation (Sec. 2) and during this time the degrees of freedom with activation energies of the order of T were annealed. This should increase the estimate given by Eq. (27) by almost another factor often: for example, for typical values of $\alpha = 0.4$ and $\nu_1 = 21$, we now obtain $x^* = 800$.

The changes in the distribution of $\varphi(k)$ in the course of isothermal annealing are governed by the fact that the first to be annealed are the "fast" radiation centers, which correspond to high probabilities k. Depending on the annealing duration t_0, these changes become

$$\varphi(k,\, t_0)=\exp(-kt_0)\varphi(k). \tag{28}$$

The zeroth moment of the "annealed" spectrum of Eq. (28) is identical with $q(t_0)$, i.e., it is identical with the fraction of the radiation centers remaining in the glass. The dependence of the activation spectrum $P(G,t_0)$ on the duration of annealing is expressed in terms of the function $\varphi(k,t_0)$ by a relationship analogous to Eq. (25). We used Eqs. (8), (24), (25), and (28) to investigate the long-term kinetics of the activation spectrum of postirradiation relaxation $P(G,t_0)$. The results of the calculations (Fig. 8) confirmed that the experimental data can be interpreted on the basis of Eq. (5): curves 1–5 in Fig. 8 correspond to consecutive stages of the kinetics of isothermal annealing of the activation spectra of the experimental postirradiation relaxation parameters (Sec. 2) and at low values of G the function $P(G,t_0)$ is close to zero for any value of t_0. This long-term kinetics of the activation spectra is a clear manifestation of isothermal annealing of radiation defects with different activation energies for the processes of correlated relaxation with an arbitrary number of steps (stages).

The characteristic features of the behavior of $P(G)$ are consequences of the three regimes described by Eqs. (6a)–(6c) [see also Eqs. (15) and (18)]: the asymptotic form of Eq. (15) is related to the existence of a low-temperature "wing" of the function $P(G)$ shown in Fig. 8. It follows from

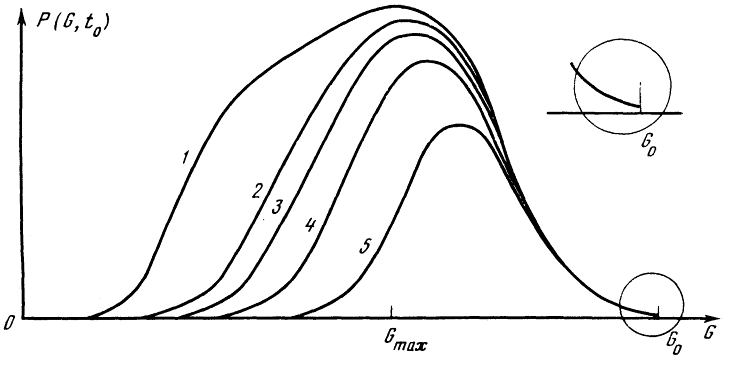

FIG. 8. Kinetics of the activation spectrum of postirradiation relaxation in glassy NaPO$_3$ plotted for different annealing durations: (1) $t_0 = 0$, (2) $0.2\tau_0$, (3) $0.5\tau_0$, (4) τ_0, and (5) $2\tau_0$. The inset shows the behavior of the function $P(G,t_0)$ at the upper limit of the spectrum ($G \lesssim G_0$).

these results that the long-term kinetics of the activation spectra of postirradiation relaxation $P(G,t_0)$ is insensitive to the profile of this wing, firstly because of the exponential dependence of the annealing time in Eq. (28) and, secondly, because of the logarithmic dependence of G on k. However, if instead of Eqs. (8) and (25) we describe the spectrum $P(G)$ using Eq. (26), we find that a considerable error is made in the normalization procedure. It should be stressed that the selection of the value of k^* on the basis of the experimental data affects the calculated results logarithmically. In fact, the position of the maximum of the function $P(G)$ depends logarithmically on x^*: $G_{\max} = T\ln(x^*/x_{\max}) = 7.2T$ eV, where $x_{\max} = 0.6$ is the position of the maximum of the function $k\tau_0\varphi(k)$; $G_{\max} = 0.23$ eV at $T = 380$ K, which is supported by the numerical data in Fig. 8. The maximum activation energy G_0 governing the asymptotic relaxation described by Eq. (6c) (see the insets in Figs. 7 and 8) can also be described in terms of the fundamental parameters of a quasiergodic system of radiation defects: $G_0 = T\ln(x^*/\nu_2^{1-\alpha}) = (1-\alpha)T\ln(\tau_{\max}/\tau_{\min}) = 12.3T$ eV, where $\alpha = 0.4$, $\nu_2 = 10^{-4}$, $G = 0.4$ eV at $T = 380$ K (Fig. 8). Here, $\nu_2^{1-\alpha}$ is the lower limit of the relaxation rate spectrum of Eq. (18). Therefore, we can conclude that the characteristics of the activation spectra (modulo T) are universal and, in particular, the values of $G_{\max}$ and G_0 are the same for the investigated model of postirradiation relaxation.

It should be pointed out that the delta-like singularity in the spectrum of the relaxation rates occurring at low values of k has an important consequence: in the case of asymptotically long times t_0 of isothermal annealing, the activation spectrum of $P(G)$ degenerates to the delta function. This corresponds to the presence of a residual concentration of slowly relaxing radiation damage zones. This feature is associated with the use of the relaxation function (5) and is missing from the theory of Palmer *et al.*[10]

From this it follows that in estimating the characteristic activation energy E_0 on the basis of the relationships (19), (22), and (23) it is more natural not to use the first moment of the spectrum $\varphi(k)$, but the value of k^*. The latter describes on the average the very fastest correlation relaxation processes in a glass characterized by a small number of steps n (Sec. 3). However, this improvement does not alter significantly the estimates given in Sec. 5, because the activation energy depends logarithmically on the probability. Nevertheless, we may conclude that the inequalities $E_0 > G_0$ and $f_0 > k^*$ apply. This is due to the fact that, by definition the quantities f_0 and E_0 apply to a problem with one degree of freedom, whereas k^* and G_0 are the statistical characteristics of a cooperative relaxation process as a whole, i.e., they describe on the average the contribution of an infinite number of the degrees of freedom.

Subject to the comments made above, it is clear that the results in Secs. 4–6 provide a complete description of the kinetics of nonexponential relaxation in glasses (Sec. 2) throughout the investigated range of observation times.

7. CONCLUSIONS

We have discussed here postirradiation relaxation in inorganic glasses. We have demonstrated for the first time that the relaxation kinetics is described by the universal Kohlrausch law. An investigation of the dose dependences indicated that annealing of radiation defects is a first-order reaction and the temperature dependence of the characteristic relaxation time is governed by the Arrhenius exponential function. A method was developed for an analysis of the experimental data on such nonexponential relaxation in glasses, which satisfied all the criteria of the model of hierarchically limited dynamics of relaxation in glasses[10] and can be used to calculate the normalized spectra of the relaxation rates and activation energy as a function of the observation time, to investigate their asymptotic behavior in the range of low and high relaxation rates, and to determine the parameters of the theoretical model from the experimental data. It is shown that, from the point of view of postirradiation relaxation a glass is a quasiergodic system in which cooperative atomic processes occur, and these can be described by the long-term kinetics of the activation spectra. In fact, the problem of quasiergodicity of a system is the problem of the validity of the inequality $\tau_{\max} < \infty$. On the other hand, experimental investigations and theoretical ideas lead to the Arrhenius dependence of all the characteristic times of atomic modifications in a glass, so that at high temperatures $\tau_{\max}$ should be an observable quantity. Our experiments showed that high-temperature annealing of defects was terminated very rapidly, but the residual concentration of the defects could not be detected by ESR spectroscopy methods. Our results demonstrated the existence of an exact upper limit to the activation spectrum of quasiergodic systems of this kind. It should be stressed however that the analysis of relaxation in glasses given above applies also to nonergodic systems, since all the moments of the spectra of the relaxation rates and of the activation spectra remain finite, although the spectra themselves are unbounded.

The new experimental and theoretical results obtained in the present study can be used as the basis for the investigation of nonexponential relaxation in glasses under complex thermal annealing conditions.

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[1)] The distance inside a donor–acceptor pair is a random quantity and there is no experimental information on the distribution function of this quantity. Therefore, we replaced a real disordered system of donor–acceptor pairs with an effective disordered system characterized by an average internal distance in a pair.

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