

Accumulation, spatial correlation, and electron-hole reactions of radiation-induced paramagnetic defects in KClO_4 crystals

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The accumulation of paramagnetic defects in KClO_4 crystals during x irradiation at 26 K has been studied by ESR. The dose dependence of the yields is described in terms of processes involving already formed radiation-induced defects. A kinetic analysis of a post-irradiation reaction between ClO_4^{2-} and $(\text{ClO}_4)_2^-$ defects reveals a marked spatial correlation between the defects, which stems from the initial pattern of energy deposition. Our results indicate that recombination of holes and electrons occurring during the irradiation proceeds *via* unstable configurations of $(\text{ClO}_4)_2^-$ and ClO_4^{2-} in a process analogous to the observed post-irradiation reaction.

I. INTRODUCTION

The formation of defects in crystals exposed to x rays is initiated by emission of fast electrons in photoionization and Auger processes, giving rise to tracks of primary excitations in which electrons are transferred to conduction bands. With 50-kV x rays most of these excitations occur in dense clusters.¹ Studies of luminescence and transient optical absorption in alkali halides have revealed that the primary excitations in this class of solids are followed by recombination of electrons and holes *via* "self-trapped excitons", which are the precursors of defects of the Frenkel-type.²

Unlike the alkali halides, solids with polyatomic anions can effectively stabilize both electrons and holes by self-trapping, thus forming electron-excess and hole defects such as CO_3^{3-} and CO_3^- in CaCO_3 ,³ and NO_3^{2-} and NO_3^- in KNO_3 .^{4,5} Accordingly, electron-hole reactions occurring during irradiation may follow different paths in the two classes of solids. At present little experimental information is available about the radiation-induced processes in solids with polyatomic ions, which presumably are too fast for direct study with pulse methods. However, information about these processes may be obtained from collective properties of the stable radiation-induced defects.

In the present ESR study of radiation damage in KClO_4 crystals, a description in terms of a nonuniform spatial distribution of primary excitations and a set of radiation-induced processes is derived from the observed accumulation of paramagnetic defects combined with the kinetics of a post-irradiation electron-hole reaction. KClO_4 appeared particularly suited for a quantitative ESR study, since only four types of abundant paramagnetic defects arise from x irradiation of this compound at low temperature, all of which exhibit distinct ESR spectra without the com-

plication of resolved superhyperfine structure. Moreover, the identity of these defects now seems well established.^{6,7}

II. EXPERIMENTAL

Single crystals of KClO_4 (Merck p.a.) were grown by slowly cooling an aqueous solution. The ESR spectrometer, the cryogenic equipment, and the method of irradiation in the microwave cavity are described elsewhere.⁸ The Machlett OEG 60 x-ray tube with tungsten target was operated at 50 kV, 30 mA in all experiments reported here.

The mean dose rate was obtained from the decomposition of KClO_4 as indicated by the amount of Fe^{3+} produced by dissolving an irradiated crystal in H_2SO_4 containing Fe^{2+} .⁹ Assuming that the yields of the various radiolytic products of KClO_4 measured after γ irradiation at 77 K (Ref. 10) apply also to the decomposition by x rays at 26 K, the mean dose rate is $1.0 \times 10^{18} \text{ eV g}^{-1} \text{ min}^{-1}$, corresponding to a total decomposition of 0.05% per hour. To estimate the variation of the dose rate through the crystal due to the absorption of x rays, thin layers of powdered KClO_4 were irradiated at 77 K through Al filters of varying thickness, and subsequently analyzed.⁹ Using the x-ray absorption coefficients for Al, KClO_4 , and quartz,¹¹ the absorption in the quartz wall of the cryogenic system and in the KClO_4 crystal was derived. For a typical path length in KClO_4 of 2 mm, the radiation is attenuated by 85%.

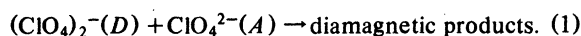
The relative yields of paramagnetic defects were obtained from the ESR spectra. The spectrometer was so calibrated that the intensity of spectra recorded with different settings of microwave power, receiver gain, and modulation amplitude could be compared. Linear combinations of Gaussian and Lorentzian functions fitting a selected line in each

spectrum were integrated analytically to yield the area under the absorption curve. This method of integration is relatively insensitive to overlapping signals, and for a given line shape the area is reproducible within a few percent. However, since the unobservable tails of an ESR line may contribute materially to its area, significant systematic errors may occur when lines of different shape are compared. The absolute yields of defects were determined by comparing the ESR spectrum from an irradiated KClO_4 crystal recorded at 26 K with that recorded at 10 K from a phosphorus-doped silicon crystal mounted similarly in the microwave cavity, taking the Boltzmann factors into account. The silicon crystal obtained from Wacker-Chemitronic, Burghausen, W. Germany, was of *n*-type Waso-quality material having a specific resistivity of $5 \pm 1 \Omega\text{cm}$. Assuming that the conductivity arises from the phosphorus impurities alone, the corresponding concentration is $(1.0 \pm 0.2) \times 10^{15}$ atoms cm^{-3} .¹² At such low concentrations effects from exchange coupling between neighboring pairs of phosphorus impurities are negligible.¹³ Since the binding energy of the unpaired electron is 0.045 eV or 520 K,¹³ practically all phosphorus impurities are in the electronic ground state at 10 K.

III. RESULTS AND DISCUSSION

A. Yields of paramagnetic defects

The electron-excess defect ClO_4^{2-} and the hole defects ClO_4 and $(\text{ClO}_4)_2^-$ have been detected by ESR in KClO_4 crystals after irradiation with x rays at 10 or 26 K.^{6,7} The ESR signals from these defects account for more than 95% of the total intensity in the spectral region at $g \approx 2$. The O_2 molecules appearing also as defects during irradiation¹⁴ are ignored in the present investigation. The ClO_4^{2-} defects appear in three modifications, A' , A'' , and A''' , having slightly different spin Hamiltonians. A' and A''' are transformed into A'' at 50 and at 100 K, respectively. We denote by A all ClO_4^{2-} defects when the distinction between modifications is immaterial. Analogously, the ClO_4 defects, denoted collectively by B , are formed in four modifications, the three of which become transformed into the stable modification between 30 and 45 K. The defects A'' , A''' , and B were in Ref. 6 labeled A , B , and C , respectively. The $(\text{ClO}_4)_2^-$ defects, which we label D , disappear at 32 K in the electron-hole reaction⁶



A' , A'' , and A''' may be regarded as chemically equivalent in spite of their spectroscopic individuality. The diamagnetic products of reaction (1) probably include ClO_3^- ions, which are the main products of the radiolysis.

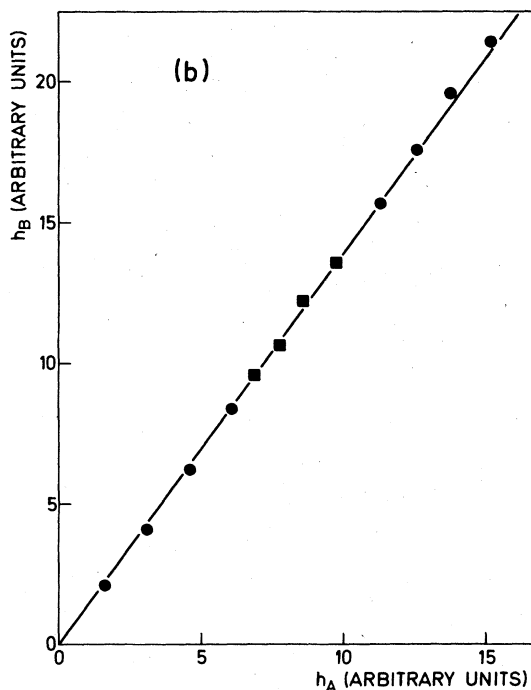
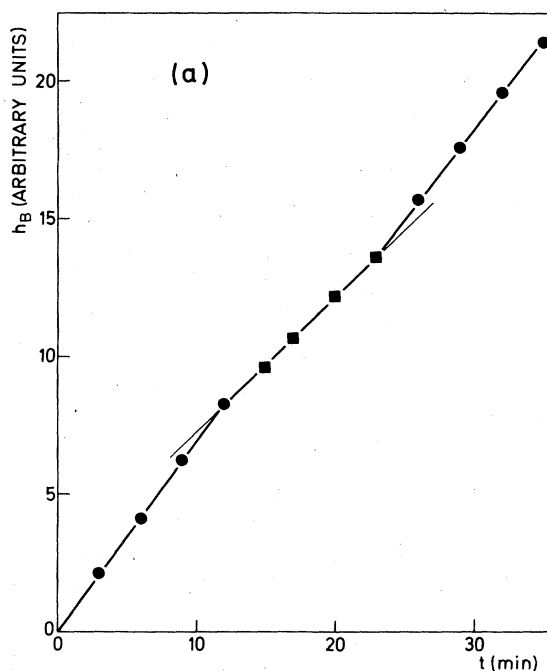


FIG. 1. Heights, h_B and h_A , of $\text{ClO}_4(B)$ and $\text{ClO}_4^{2-}(A)$ ESR signals measured after the decay of $(\text{ClO}_4)_2^-(D)$. (a): h_B vs irradiation time, t . (b): h_B vs h_A . Circles \bullet represent heights measured at 26 K after irradiation at 26 K and annealing at 60 K until D , A' , and the metastable modifications of B have disappeared. Squares \blacksquare represent heights measured at 26 K after irradiation at 60 K.

The ratios $h_A:h_A':h_A''$ as well as those of the heights of the signals from the four modifications of B depend little on the x-ray dose at 10 and 26 K in the dose range investigated (0–3 Mrad), whereas h_D decreases markedly relative to h_A or h_B with increasing dose. The initial yield of D relative to that of A is 0.4. In Fig. 1 is shown the growth of the A and B signals during irradiation at 26 and at 60 K measured after completion of reaction (1). As apparent from Fig. 1 (a), the growth rate of the B signal decreases with increasing temperature during irradiation, whereas Fig. 1 (b) shows that the growth rates of the A and B signals depend on the temperature in exactly the same way, suggesting that B is the only type of hole defects present after the decay of the D signal. This implies that the amount of A defects present after completion of reaction (1) should equal the amount of B defects. However, the intensities of the ESR signals determined by integration show an apparent deficit of holes approximately equal to the amount of B . We attribute this apparent deficit to magnetic-dipolar broadening of a part of the B signal arising from defects situated in clusters.

The determination of the absolute amounts of paramagnetic defects and the dose rate leads to an initial yield at 26 K of 1.1 A defects, or, a total of 2.2 defects (electrons and holes) per 100 eV absorbed. The estimated uncertainty of these yields is 40%. Since 4.0 ClO_4^- ions are decomposed per 100 eV absorbed,¹⁰ A , B , and D account for a significant portion of the radiation damage in KClO_4 at low temperatures, although other defects are also formed.

B. Post-irradiation electron-hole reaction

Reaction (1) requires that D and A defects somehow approach each other. The considerable distortion of A with respect to the normal configuration of the ClO_4^- ion, as indicated by the spin Hamiltonians,⁶ makes migration in the lattice of the self-trapped electron unlikely at low temperature. The absence of electron-hole reactions involving B is in line with this observation. On the other hand, D consists of 2 almost undistorted ClO_4^- ions,⁶ suggesting a low barrier to migration for this type of self-trapped hole. We propose, therefore, that reaction (1) occurs when D defects performing thermally activated migration encounter stationary A defects. This mechanism is consistent with the chemical equivalence of A' , A'' , and A''' .

Employing irradiations and ESR measurements at 10 K, changes in h_A and h_D during successive annealings at increasing temperatures in the range 10–32 K were examined. In Fig. 2 is shown a plot of h_A vs h_D measured between the annealings. h_A decreases throughout the range, while h_D increases slightly from 10 to 16 K. However, the linewidth of signal D decreases simultaneously, and it appears that the

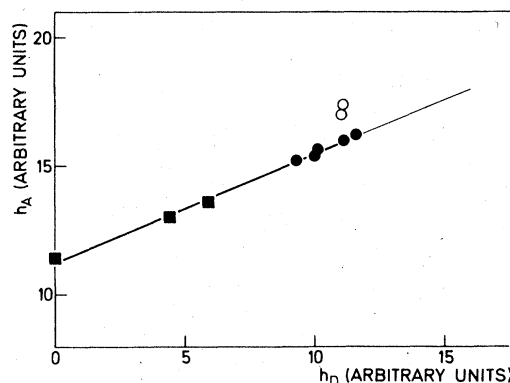


FIG. 2. Heights, h_A and h_D , of ClO_4^{2-} (A) and $(\text{ClO}_4)_2^-$ (D) signals measured at 10 K between successive annealings at increasing temperatures in the range 10–32 K. Open circles \circ represent heights measured immediately after irradiation and after annealing in the range 10–16 K, solid circles \bullet represent heights measured after annealing in the range 16–26 K, and solid squares \blacksquare represent heights measured after annealing above 30 K.

amount of D actually decreases. In the range 16–26 K, h_D decreases without observable changes of the linewidth. As apparent from Fig. 2, h_D and h_A decrease in the same proportion in the range 16–26 K as at 32 K, suggesting that reaction (1) accounts for the decreasing amounts of D and A throughout the temperature range investigated.

During the first 15 minutes after termination of the x irradiation at 10 K, h_A decreases by a few percent, suggesting that reaction (1) proceeds slowly, whereas no further changes are observed during the next 30 minutes. By annealing at any fixed temperature between 10 and 23 K, h_A decreases rapidly for the first few minutes and then very slowly, whereas raising the temperature by a few degrees causes a new rapid decrease. This observation indicates that D has varying barriers to migration, the Coulomb interaction enabling closely spaced D and A defects to react at temperatures at which defect configurations with larger separations are virtually stable. Since the proportion of D defects formed close to an A defect is expected to increase with increasing dose, so should the fraction of D defects decaying below 23 K. In fact, the values 0.3 and 0.5 for this fraction were found after irradiation for 3 and 60 minutes, respectively.

C. Kinetics of the electron-hole reaction

Reaction (1) comprises the reaction between defects formed simultaneously along the same track, as well as the reaction between defects belonging to different tracks, which may arise at different times. As shown below, the two parts may be distinguished because the participating A defects can be labeled ac-

ording to their time of formation by means of the chemical equivalence of A' , A'' , and A''' combined with the thermally induced transformations of A' and A''' into A'' .

A KClO_4 crystal was seven times (i) irradiated at 26 K, (ii) heated briefly to ~ 32 K and recooled to 26 K a number of times until completion of reaction (1), and (iii) heated to 110 K until A' and A''' were transformed into A'' . The A'' defects present at the end of each treatment we label "old", while D , A' , A'' , and A''' defects formed during the subsequent irradiation at 26 K are labeled "new". A' , A'' , and A''' are formed in the proportion 1:2:3 in the first irradiation and consumed in this proportion during the first annealing at 32 K. A' and A''' are formed and consumed in the proportion 1:3 also in each of the subsequent irradiations and annealings. From these observations we assume that the new A' , A'' , and A''' defects are each time formed and consumed in the same proportion, 1:2:3.

Figure 3 displays $h_{A'} + h_{A''}$ vs $h_{A''}$ during the first three annealings at 32 K. If the correlation of the new D and A defects belonging to the same tracks were of no consequence for the electron-hole reaction, the points in the figure should define a set of lines passing through the origin because of the chemical equivalence of A' , A'' , and A''' . If, on the other hand, only defects belonging to the same track reacted, the new A defects alone would be consumed and the points should follow the broken lines drawn parallel to line No. 1. Since neither of these extremes are observed, reaction within the tracks competes with reaction between defects from different tracks.

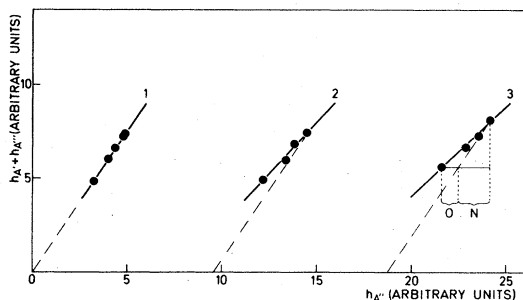


FIG. 3. Sum of the heights, $h_{A'} + h_{A''}$, of the $\text{ClO}_4^{2-}(A')$ and (A''') signals vs the height, $h_{A''}$, of the $\text{ClO}_4^{2-}(A'')$ signal measured at 26 K between brief heatings of the irradiated crystal to 32 K. After each annealing sequence at 32 K causing completion of reaction (1), the crystal was annealed at 110 K until the transformations of A' and A''' into A'' were complete. Then the crystal was reirradiated at 26 K. Each series of points, labeled by the number, n , of irradiations preceding the annealing sequence, represents the consumption of $\text{ClO}_4^{2-}(A)$ through reaction with $(\text{ClO}_4)_2^-(D)$. Broken lines are drawn parallel to line No. 1. O and N indicate the amounts of "old" and "new" A consumed.

The amounts, O and N , of old and new A'' defects consumed during a given annealing sequence at ~ 32 K may be determined as indicated in Fig. 3.

Representing the n th series of points in the figure by a straight line of slope a_n , the probability that a D defect reacts with an old A defect is

$$P_{\text{old}} = O/(O + 3N) = (1 - a_n/a_1)/(1 + 2a_n/a_1), \quad (2)$$

since all the old and one-third of the new A defects are present as modification A'' . Assuming that the probability, P_{dif} , of reaction between defects belonging to different tracks is the same for old and new A , we obtain

$$P_{\text{dif}} = P_{\text{old}} C_A / C_{A0}, \quad (3)$$

where C_A is the total macroscopic concentration of A and C_{A0} is the concentration of old A . By introducing concentrations, we ignore effects arising from the variation in the dose rate through the crystal. The ratio C_A/C_{A0} changes little during the course of the reaction. We calculate, therefore, P_{dif} from Eqs. (2) and (3) with the values C_A^0 and C_{A0}^0 of C_A and C_{A0} determined immediately after irradiation using the proportion 1:2:3 of the new A defects. The experimental values of P_{dif} vs C_A^0 in units of C_1 , the concentration of A after the first minute of irradiation, are shown in Fig. 4.

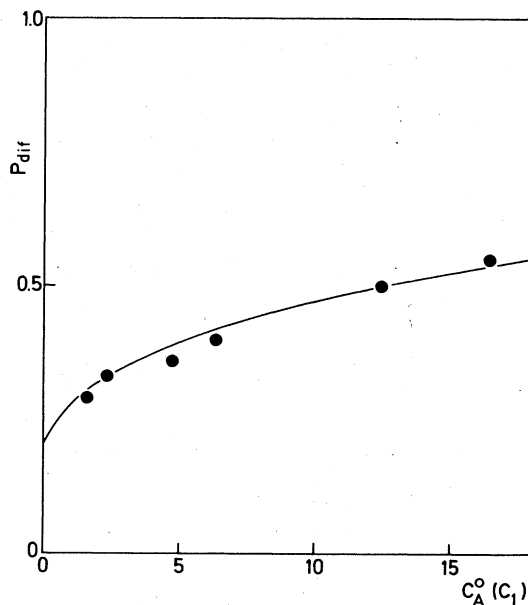


FIG. 4. Probability, P_{dif} , of reaction between $(\text{ClO}_4)_2^-(D)$ and $\text{ClO}_4^{2-}(A)$ defects belonging to different tracks versus the concentration, C_A^0 , of A before annealing in units of C_1 , the concentration of A after the first minute of irradiation. Circles \bullet represent probabilities obtained from experiment, the solid curve is calculated from the model described in Sec. III D with $\lambda = 0.8$, $\frac{4}{3} \pi r_0^3 C_1 = 0.026$, and $C_B^0/C_A^0 = 0.2$.

D. Model for the electron-hole reaction

The model for the reaction between D and A described in this section is based on Waite's treatment of diffusion-limited bimolecular reactions.¹⁵ As noted above, the reaction presumably takes place when D defects migrating in the KClO_4 lattice encounter stationary A defects. We consider the migration of D as a diffusion in an isotropic, continuous medium. The diffusion is assumed to be unaffected by the presence of other defects when the distance, r , to the nearest A exceeds a critical value, r_0 , whereas the reaction occurs spontaneously at $r \leq r_0$. The complex spatial distribution of defects along the tracks is represented by assuming that D and A are

formed in pairs. The probability, that the defects belonging to the same pair have initially the distance r , is taken to be

$$\rho(r) = \begin{cases} 4\pi r^2 M \exp[-(r/\lambda r_0)^2], & r > r_0 \\ 0, & r \leq r_0, \end{cases} \quad (4)$$

where M is a normalization constant, and λ is a parameter determining the spatial extent of the distribution. Except for the correlation between defects belonging to the same pair, the defects are assumed to be randomly distributed.

Waite¹⁵ discussed this model with the constraint of equal concentrations of the reactants. Adapting his result to the present problem we obtain

$$\begin{aligned} \frac{d\phi}{dz} = & 2\pi C_A^0 r_0^3 (1-\phi) \left[1 - \frac{\phi C_D^0}{C_A^0} \right] \left[z + \frac{2}{\sqrt{\pi}} \right] \\ & + 2\pi M r_0^3 \exp \left[- \int_0^z 2\pi C_A^0 r_0^3 \left(1 + \frac{(1-2\phi) C_D^0}{C_A^0} \right) \left(x + \frac{2}{\sqrt{\pi}} \right) dx \right] \\ & \times \left[\left[\frac{2}{\sqrt{\pi}} \right] \exp \left[- \frac{1}{\lambda^2} \right] \left[\frac{\lambda^2}{\xi} \right]^2 + \left[\frac{z}{\lambda} \right] \exp \left[- \frac{1}{\xi} \right] \xi^{-1/2} \operatorname{erf} \left[\frac{z}{\lambda \xi^{1/2}} \right] 2\lambda^4 (\xi^{-1} - 2\xi^{-2}) \right]; \quad \xi \equiv \lambda^2 + z^2, \end{aligned} \quad (5)$$

where ϕ is the fraction of D defects consumed, C_A^0 and C_D^0 are the initial concentrations of A and D , respectively, and z is a parameter proportional to the square root of the time. The function erf is here defined by

$$\operatorname{erf}(x) = \int_x^\infty \exp(-y^2)/\sqrt{\pi} dy, \quad (6)$$

The observed variation in the barriers to migration of D is not taken into account in the model. Therefore, the time dependence of the reaction rate is ignored, and we discuss only the probabilities for reaction of D with its A partner and with any other A . The first term in Eq. (5) accounts for the reaction between defects which do not belong to the same pair. Thus the probability for this type of reaction is the contribution, α , from the first term to the integral $\int_0^\infty (d\phi/dz) dz$. α is taken to represent the probability, P_{dif} , of reaction between defects belonging to different tracks. For comparison with the experimental values of P_{dif} , α was calculated as a function of C_A^0 with different values of λ and r_0 . The experimental points correspond to different values of C_D^0/C_A^0 in the range 0.13–0.23. Accordingly, α should be determined for the actual value in each case. However, since α is insensitive to C_D^0/C_A^0 , the function $\alpha(C_A^0)$ shown in Fig. 4 was calculated with the fixed value $C_D^0/C_A^0 = 0.2$. Agreement between α

and the experimental value of P_{dif} is obtained with $\lambda = 0.8$ and $\frac{4}{3}\pi r_0^3 C_1 = 0.026$ (Fig. 4). Using the initial yield for A and the dose rate we obtain $r_0 = 62 \text{ \AA}$. The pair distribution function (4) is depicted in Fig. 5.

E. Accumulation of paramagnetic defects

The observation that the relative yields of D and A depend markedly on the x-ray dose suggests that some kind of electron-hole reaction involving defects already present occurs during the irradiation. In or-

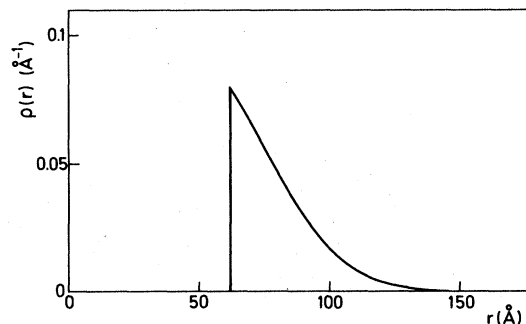


FIG. 5. Pair-distribution function, $\rho(r)$, Eq. (4) with $\lambda = 0.8$ and $r_0 = 62 \text{ \AA}$.

der to investigate how the defects accumulating in the crystal interfere with the radiation-induced processes characteristic of the undamaged lattice, the yields of the various types of paramagnetic defects were determined as functions of the dose. A KClO_4 crystal was irradiated for 135 minutes at 26 K, annealed at 32 and 110 K until the electron-hole reaction (1) and the transformations of the metastable A and B modifications were complete, and reirradiated for 45 minutes at 26 K.

The yields of paramagnetic defects were monitored by ESR. The intensities of the A and B signals were taken proportional to h_A and h_B , since changes in the linewidths of these signals were at most barely observable. The intensity of the D signal was inferred from computer simulations of the actual line shape of each spectrum. The intensities determined in this way were converted into yields expressed as concentrations in units of C_1 using the decrement of the A signal observed by annealing after irradiation for 135 minutes. The relative yield of B was chosen by setting equal the amounts of A and B present after irradiation for 135 minutes and annealing at 110 K. By this procedure an electron-hole balance with an accuracy of $\pm 1.5 C_1$ is maintained throughout the entire dose range investigated. In Fig. 6 the yields of paramagnetic defects are shown as functions of the irradiation time.

The differential yields, Y_i (\equiv yields of defect i per unit dose) of all the paramagnetic defects decrease

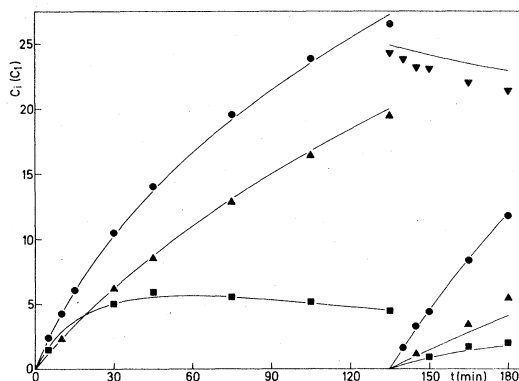


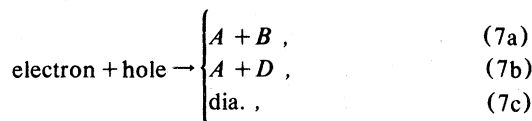
FIG. 6. Concentrations, C_i , of paramagnetic defects in KClO_4 at 26 K vs irradiation time, t . After irradiation for 135 minutes, the crystal was annealed at 110 K until reaction (1) and the transformations of the metastable modifications of ClO_4^{2-} (A) and ClO_4 (B) were complete. Then the crystal was reirradiated. The concentrations are given in units of C_1 , the concentration of A after the first minute of irradiation. Circles \bullet represent $C_{A''}$, triangles \blacktriangledown represent $\frac{1}{2}C_{A''}$, squares \blacksquare represent $2C_D$, triangles \blacktriangle represent $4C_B$. A denotes ClO_4^{2-} , B' denotes a metastable modification of ClO_4 , and D denotes $(\text{ClO}_4)_2^-$. Curves are calculated from the model described in Sec. III F with $C_1\nu_c = 0.016$ and $C_1\nu_g = 0.032$.

with increasing dose. Y_D even becomes negative after about 45 minutes. During the reirradiation after annealing all Y_i are smaller than during the first irradiation, and $Y_{A''}$ is even negative. The yield of A' decreases by 15% relative to that of A'' during the first 135 minutes of irradiation, whereas the yield of $A' + A''$ relative to that of A''' is constant within the experimental accuracy. Spectral overlaps preclude the observation of possible minor changes in the relative yields of the modifications of B .

F. Model for the accumulation of paramagnetic defects

The observed accumulation of paramagnetic defects in KClO_4 may be interpreted in various ways. The decreasing differential yields would seem to indicate that a limited supply of inherent defects or impurities involved in the formation of the irradiation-induced defects becomes depleted during the irradiation. However, the reproducibility of yields in nominally pure crystals from different batches suggests that inherent defects are in general of minor importance. Moreover, the fact that some differential yields become negative after prolonged irradiation indicates an interplay between radiation-induced defects and radiation-induced processes. Accordingly, we shall describe the dose dependence of the yields in terms of processes involving only the perfect KClO_4 lattice and the radiation-induced defects, which may influence both the formation and the stability of subsequently formed defects. This influence is exerted during the later stages of the formation process, since the cross sections for the primary excitations are insensitive to the presence of defects in small concentrations, whereas trapping of electrons and holes at defects may well compete with recombination and self trapping. Hence we shall assume that electrons and holes are the only primary species throughout the dose range investigated.

The relaxation of electrons and holes into defects and the reactions between unstable defects may be represented by the scheme



where "dia." denotes diamagnetic products. Letting processes (7a)–(7c) represent the fate of electrons and holes belonging to the same track, we represent

by (7d)–(7g) the processes occurring when radiation-induced species are formed in the vicinity of already existing defects. Process (7g) is analogous to the post-irradiation electron-hole reaction (1); it occurs when an A defect is formed within the critical distance r_0 from an already existing D defect or *vice versa*.

The yields of processes (7d)–(7g) as functions of the concentrations of defects may be described in terms of a simple model for the probability of reaction between a species, j , generated by the radiation, and defects already present in the crystal at the moment when j is generated. Supposing that j is formed with equal probability per unit volume independently of the defects, we define a reaction volume, v_{ij} , so that the probability of reaction between j and the defect in a crystal of volume V containing just one defect of type i is v_{ij}/V for $V \gg v_{ij}$. Then the probability, $P_{i'j}$, of reaction between j and a defect of type i' in a crystal containing several types of noninteracting, randomly distributed defects is

$$P_{i'j} = \left[\frac{n_{i'} v_{i'j}}{\sum_i n_i v_{ij}} \right] \left[1 - \prod_i \left(1 - \frac{v_{ij}}{V} \right)^{n_i} \right], \quad (8)$$

where n_i is the number of defects of type i . The term $\prod_i (1 - v_{ij}/V)^{n_i}$ is the probability that j does not react with any defect. Introducing the concentrations $C_i \equiv n_i/V$ and observing that n_i are very large numbers, we obtain

$$P_{i'j} = \left[\frac{C_{i'} v_{i'j}}{\sum_i C_i v_{ij}} \right] \left[1 - \exp \left(- \sum_i C_i v_{ij} \right) \right]. \quad (9)$$

For each process we define a reaction radius, r_{ij} , as the radius of a sphere of volume v_{ij} . We note that the reaction radius, $r_{AD} = r_{DA}$, for process (7g) equals the critical distance, r_0 , for the analogous post-irradiation reaction (1).

The experimental yields do not allow the determination of v_{ij} for all processes in Eq. (7). The electron-hole reactions occurring before self-trapping, (7e) and (7f), cannot be distinguished experimentally from those occurring after self-trapping, (7g). We include, therefore, the processes (7e) and (7f) in (7g). The reaction radius r_g for the compound process will considerably exceed r_0 if (7e) and (7f) occur with high probability. Furthermore, there is no indication that already existing B defects are consumed during irradiation. Hence we ignore process (7d) and account for the observed decrease in Y_B by making the presence of B defects inhibit process (7a) while enhancing process (7c) correspondingly. The reaction radius for this process is denoted r_c . The small change in the relative yields of A' , A'' , and A''' is ignored. Using Eq. (9) we derive the following cou-

pled differential equations describing the accumulation of paramagnetic defects in KClO_4 :

$$Y_{A''} = (Y_{A''}^0 / Y_A^0) [Y_B^0 \exp(-C_B v_c) + Y_B^0] \times \exp(-C_D v_g) - (Y_B^0 C_{A''} / C_A) [1 - \exp(-C_A v_g)], \quad (10)$$

$$Y_B = Y_B^0 \exp(-C_B v_c), \quad (11)$$

$$Y_D = Y_D^0 \exp(-C_A v_g) - [Y_B^0 \exp(-C_B v_c) + Y_B^0] \times [1 - \exp(-C_D v_g)]. \quad (12)$$

Here Y_i^0 denotes the value of Y_i extrapolated to zero dose. The accumulation of A' and A''' is described by equations similar to Eq. (10), since the relative yields A' , A'' , and A''' are assumed to be independent of dose. If the concentration of A'' is made abnormally high by annealings which transform A' and A''' into A'' , and the irradiation is subsequently continued at 26 K, the destruction of already existing A'' defects represented by the second term in Eq. (10) may outweigh the formation of new A'' [first term in Eq. (10)]. This was in fact observed in the experiment shown in Fig. 6, where $h_{A''}$ decreases during reirradiation after annealing at 110 K. Similarly, the differential yield for D may become negative at high concentrations of A and D .

The differential equations (10)–(12) were solved numerically, taking into account the attenuation of the x rays through the KClO_4 crystal by adding ten solutions calculated for the dose rates appropriate at the depths 0.1, 0.3, ..., 1.9 mm. The parameters v_c and v_d were varied until overall agreement with the observed yields of defects was obtained (Fig. 6). A significant systematic deviation of the calculated from the observed yields, arising from the neglect of the dose dependence of the relative yields of A' , A'' , and A''' , is exhibited by A'' after annealing.

The gradual suppression of process (7a) and enhancement of process (7c), attributed above to accumulating B defects, might be simulated equally well on the assumption that all radiation-induced defects (diamagnetic as well as paramagnetic) influence the processes. Since the differential yield of B decreases with increasing temperature as well as with increasing concentration of defects, we propose that disorder in the crystal enhances the self-trapping of holes in form of D at the expense of self-trapping as B .

The value of r_g is 67 \AA , which is very close to the critical distance $r_0 = 62 \text{ \AA}$ for the post-irradiation reaction between D and A . The ratio $r_g:r_0$ is presumably fairly accurate, whereas errors in the dose rate and in the absolute yield of A may offset the values of r_g and r_0 by a substantial common factor. Accordingly, the result $r_j \approx r_0$ indicates that the dominant

part of process (7g) is the collapse of unstable configurations of A and D , consisting of one new and one old defect, whereas free electrons and holes have only a low reactivity toward defects of opposite effective charge. This observation in turn suggests that the probability of recombination of electrons and holes prior to self-trapping is also low, so that process (7c) may be expected to proceed *via* unstable configurations of new A and D , formed within the same track.

IV. SUMMARY

The present results show that the accumulation of paramagnetic defects in a solid during irradiation and the kinetics of post-irradiation reactions, when interpreted in terms of simplified models, convey information about the spatial distribution of defects as well as about the processes governing the formation of defects. The relaxation processes following the primary excitations depend to some extent on the condition of the crystal lattice, since the fraction of

holes which becomes self-trapped as ClO_4 defects decreases with increasing temperature and with increasing concentration of defects. However, the probability that electrons and holes become trapped at defects or react directly with oppositely charged radiation-induced defects is low even after prolonged irradiation.

After the trapping of electrons and holes has taken place, $(\text{ClO}_4)_2^-$ and ClO_4^{2-} react spontaneously when brought within some critical distance ($\sim 65 \text{ \AA}$ at 26 K). This tends to produce voids in the distribution of the defects. However, $(\text{ClO}_4)_2^-$ and ClO_4^{2-} exhibit at low dose a marked spatial correlation which is attributed to the pairwise formation of these defects combined with the nonuniform distribution of primary excitations.

The finding that self-trapping in KClO_4 precedes the electron-hole reactions during irradiation, which we believe applies also to other solids with polyatomic ions, is in contrast to the observation that electron-hole recombination in alkali halides precedes the formation of defects.

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