Dynamics of Positive-Ion Vacancies in X-Irradiated NaCl by Positron Annihilation*

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A fraction of thermalized positrons in a NaCl crystal can be trapped in crystal defects to form annihilation or A centers. This fraction is found to increase after x irradiation of the crystal. The increase is measured through the coincidence count rate of the two 0.51-MeV positron-electron-annihilation γ quanta emerging from NaCl single crystals in exactly opposite directions. Isothermal annealing at various temperatures T between 55 and 185 °C always increases the count rate further, in time intervals ranging, respectively, from 10^2 to 10 min. When $T > 100$ °C, the count rate as a function of time passes through a pronounced maximum and diminishes slowly (in 10^3 to 10^2 min) toward the count rate of the annealed crystal. The activation energy for the rate of increase is 0.4 eV, and for the decrease 1.2 eV. Both values coincide with the activation energies for the rise and decline of the ionic conductivity in isothermal anneals at $T \geq 130$ °C. To the extent that the dominant A centers are positrons trapped in mobile or immobile positive-ion vacancies, and that the dominant charge carriers in ionic conductivity are the mobile positive-ion vacancies, our data support the long-held conjecture that x irradiation creates vacancies and that during incipient periods of annealing additional vacancies are released from radiation-induced vacancy aggregates. The positive-ion vacancy-diffusion constant is deduced to be 2×10^{-11} cm^2/sec, corresponding to a mobility $\sim 10^{-9}$ cm^2/V sec, by Einstein's relation. The ubiquitous initial rise in our count rates implies that the initial drop in conductivity for isothermal anneals at moderate temperatures, $T \lesssim 100$ °C, is caused not by the neutralization of positive-ion vacancies but by their immobilization through complex formation. The decline at long anneal times in both our count rates and the conductivities, with identical activation energies, signifies the slow formation of positive-ion-vacancy sinks leading to the complete annealing of the radiation-induced defects so observed.

I. INTRODUCTION

In recent years, substantial evidence has accrued that the positron-annihilation characteristics in metal and insulator crystals are sensitive to the crystal defect structure.[1] In particular, studies with ionic crystals on the effects of defect concentrations as introduced by plastic deformation,[2] by radiation with x rays,[2] protons[3] and γ rays,[3] by heat treatments,[4] and by impurity doping[5-8] support the following idealized picture. Almost all positrons annihilate after thermalization with an electron into two γ quanta, each of energy $m_0c^2 = 0.51$ MeV. Only a negligible fraction annihilates into three γ quanta. The annihilation rates are proportional to the overlap between the positron and electron wave functions in the crystal domains where the positrons dwell at the time of annihilation. Conservation of momentum requires that in the rest frame of the annihilating positron-electron pair the two γ quanta leave the site of annihilation in exactly opposite directions. In the laboratory frame of reference, the momentum distribution of the annihilating pairs manifests itself through the angular distribution $I(\vartheta)$ about 180° of the emerging γ's, where $\vartheta = P/m_0c$ is related to the momentum of the pair P in the direction normal to the plane of the two γ-coincidence-counter slits. Since the positrons are virtually at rest at the time of annihilation, $I(\vartheta)$ reflects the momentum distribution of the crystal electrons in the domain of the positron-electron wave-function overlap.

Positrons can be trapped by defects such as positive-ion vacancies to form annihilation or A centers.[9] Here they are localized in a region of lower electron density than in the crystal bulk and hence live longer. Moreover, the localization reduces the overlap with the atom-core electrons of high momenta. As a consequence the angular correlation function $I(\vartheta)$ of the two γ quanta issuing from such A centers is narrower than that of the perfect crystal. The annihilation rates and the two-γ angular correlation give complementary information on the nature and the concentration of defects that trap positrons to form A centers.[1] If $I(\vartheta)$ becomes narrower with A center formation, $I_0 \equiv I(\vartheta = 0)$ increases nearly linearly with the A center formation probability. Changes in the two-γ coincidence-counting rate at $\vartheta = 0$ are a direct measure of the change in the fraction of all positrons that annihilate in A centers.[1,10,11] This is the basis for the experiments described in the following.

The study of the dynamics of positive-ion vacancies after irradiation of ionic crystals has relied on measurements of the ionic conductivity. It is generally agreed that positive-ion vacancy migration is the dominant mechanism of ionic conductivity.[12] Then the conductivity σ of a crystal

of density ρ, in molecules per unit volume, is proportional to the product of the concentration C and the mobility χ of the mobile vacancies of effective charge q,

$$\sigma = qC\rho\chi.$$

Conductivity measurements alone cannot distinguish between changes in C and the total vacancy concentration $N = C + S$, which comprises also the concentration of immobile (trapped) vacancies S. By contrast, if A-center formation is indicative of the total N, but independent of whether a vacancy is pinned to a trap (such as a divalent impurity atom) or is mobile, positron-annihilation studies can contribute to the elucidation of the relative magnitude of C and S. Evidence has been given that A-center formation is unaffected by positive-ion vacancy trapping.[13] This opens a wide range of problems of the imperfect crystal to renewed scrutiny through combined studies of color centers, ionic conductivity, and positron A centers.[14]

As a case in point, this paper examines the dynamics of positive-ion vacancies in NaCl single crystals following x irradiation as revealed by the I_0 count rate. That such effects exist was reported earlier.[15] The results are compared with the changes of the ionic conductivities during isothermal anneal periods at different temperatures.[16,17] Section II summarizes the experimental details and gives the results. They are discussed in relation to conductivity data in Sec. III. Section IV develops a simple diffusion and reaction model, which affords an approximate parametrization of our data and gives a tentative quantitative description of microscopic aspects of positive-ion vacancy formation and disappearance in x-irradiated crystals during isothermal annealing.

II. EXPERIMENTAL

The use of the coincidence-counting rate at $\vartheta = 0$, I_0, presupposes that the angular correlation curve for annihilations in the crystal bulk and in A centers is well defined (if unknown), and time or temperature independent by comparison with the changes in the A-center concentrations under study. More detailed information can be obtained only through time-consuming angular-correlation measurements over a range of ϑ. This reduces drastically the resolution in following time-dependent events. In our experiments, a statistically accurate point at time t, $I_0(t)$ with 1% uncertainty, accumulated in approximately 3 min, permitting us to observe processes evolving in times longer than 10 min. Isothermal annealing phenomena in ionic crystals proceed sufficiently slowly to be resolved by this method.

A positron source of ~ 1-Ci ^{64}Cu was affixed 0.3 cm from a sample located at the pivot point of two collimators 180° apart.[18] The two 0.51-MeV annihilation γ quanta were registered in coincidence by two collinear NaI scintillator-phototube assemblies, each placed 2 m from the sample. One of the arms holding an assembly can swing about the pivot point through angles ϑ of order milliradians. We opened the slits to 2 mm, to ensure rapid data accumulation over a range of ~ 1 mrad of the angular-correlation curve centered about $\vartheta = 0$, corresponding to 16% of the full width at half-maximum. Before every run, the $\vartheta = 0$ position was determined with care by positioning the movable collimator at the maximum counting rate with 1-mm slits. Then the reference value at $t = 0$, $I_0(0)$ was measured at 22 °C with 2-mm slits and an error of < 0.3%.

All our data were obtained with samples cut from one single-crystal NaCl boule manufactured by Quartz et Silice, Paris, France. Slabs of dimensions 15×10×3 mm were irradiated for 2 h with x rays from a 40-kV W-cathode tube run at 25 mA, corresponding to a dose of ~ 6×10^8 rad. We found that further increase of the dose does not change our results noticeably, as illustrated in Fig. 1. The crystals were clamped to a holder containing an electric heater and placed in contact with a thermocouple. After each experimental run to be described, the crystal was placed in an oven and annealed for 3 h at 350 °C and cooled while in the oven.

The experiment proceeded as follows. The crystal, after x irradiation at room temperature, was placed in the apparatus, the angle of maximum count rate (corresponding to $\vartheta = 0$) determined and the reference value $I_0(0)$ measured. This value was typically ~ 10% higher than in the

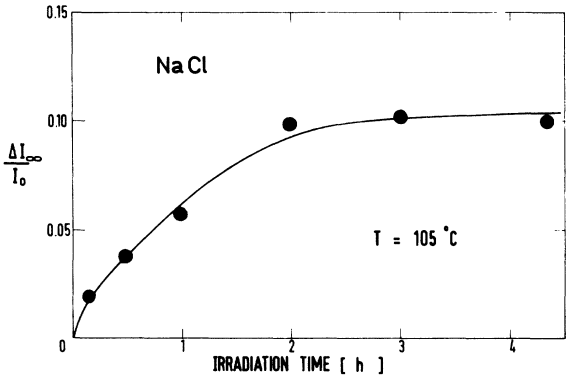

FIG. 1. Asymptotic plateau value of the count rate I_0 ($t \to \infty$) relative to I_0 ($t = 0$) in the form $\Delta I_\infty/I_0 \equiv [I_0(\infty) - I_0]/I_0$, at anneal temperature $T = 105$ °C, as a function of the x-ray dose in units of hours of exposure administered at room temperature before the anneal. The curve is empirical.

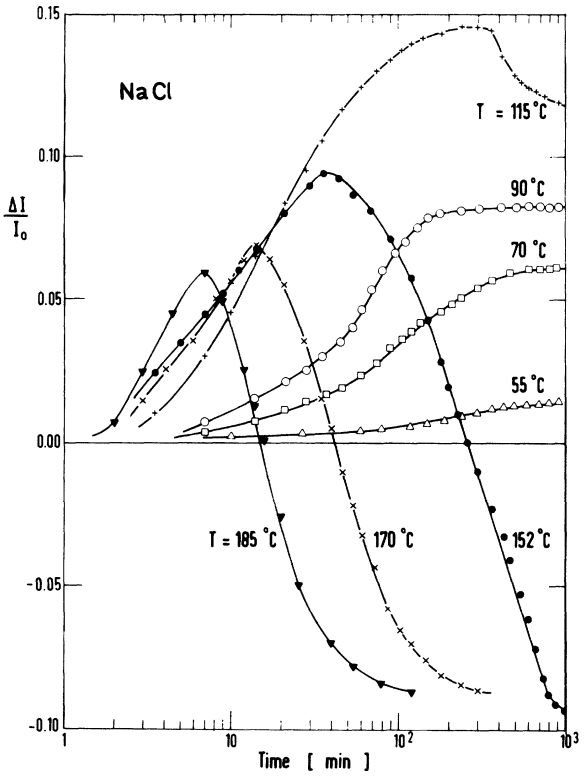

FIG. 2. Relative coincidence count rates between the two γ quanta emitted in positron annihilation from x-irradiated NaCl crystals in opposite directions, as a function of the isothermal anneal time at the temperatures indicated. I_0 refers to the count rate at room temperatures after x irradiation. It is $\sim 10\%$ larger than I_0 of the annealed crystal, corresponding to the value $\Delta I/I_0 = -0.1$ on this plot.

annealed crystal.[15] The sample heater was turned on at $t = 0$. The sample temperature stabilized at some preset value T in approximately 4 min. Also starting at $t = 0$, the count rate $I_0(t)$ was determined continuously. The data of $I_0(t)$ are the readouts of the number of coincidences counted until a separate counter, monitoring the source,[18] had accumulated 4×10^5 counts. This procedure made the data collection insensitive to variations in the source strength. Each point required 2–3 min of counting time. In this manner, $I_0(t)$ data were recorded as a function of the isothermal anneal time t for some 10^3 min $\simeq$ 17 h. The half-life of the ^{64}Cu source is only 12.8 h, so that the data accumulation time for each point increases throughout anneal period by a factor of 3. Since the phenomena under investigation are relaxation processes which proceed first in time intervals of order 1 h, and later of order 10 h, this change in data accumulation time throughout a day was unimportant for the time resolution of the events.

The results are shown in Fig. 2. Changes after x irradiation $\Delta I(t)/I_0 \equiv [I_0(t) - I_0(0)]/I_0(0)$ are plotted as a function of the anneal time t at the seven temperatures indicated. Only a small fraction of the total number of data points (one per ~ 3 min) is shown. Two distinct trends appear. At temperatures $T \lesssim 100$ °C, $\Delta I/I_0$ rises and approaches asymptotically a plateau $\Delta I_\infty/I_0$. The level of the plateau increases, and is reached in shorter times as T increases. As Fig. 3 demonstrates, the rise can be described on the average by a rise time $\tau_r(T)$ through

$$(\Delta I/I_0)_T = (\Delta I_\infty/I_0)_T \, (1 - e^{-t/\tau_r(T)}), \tag{1}$$

where $\tau_r(T)$ approximately depends on T as

$$\tau_r(T) = \tau_{0r} \, e^{E_r/kT}. \tag{2}$$

A fit in Fig. 4 through the solid points taken from the slopes in Fig. 3 yields the rise parameter $\tau_{0r} = 8.2 \times 10^{-3}$ sec and the activation energy $E_r = 0.40$ eV.

The asymptotic plateau values cover too limited a range to give more than a trend with T. It can roughly be summarized as $(\Delta I_\infty/I_0) \sim e^{-3700\,°\mathrm{K}/T}$ corresponding to an activation-type energy of 0.3 eV.

The second trend in Fig. 2 appears for $T > 100$ °C. The data rise rapidly to a maximum before declining slowly. For $T > 150$ °C, the points

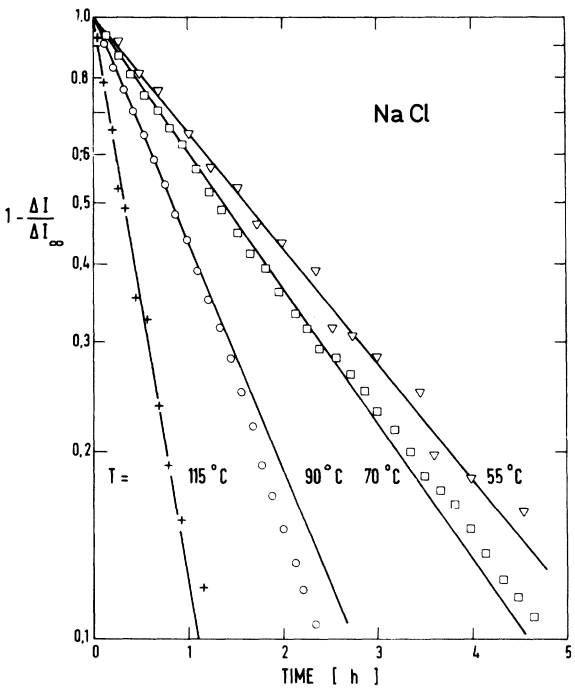

FIG. 3. Semi-log plot of rising data displayed in Fig. 2, in the form suggested by Eq. (1). The slopes yield the characteristic rise times $\tau_r(T)$ plotted in Fig. 4.

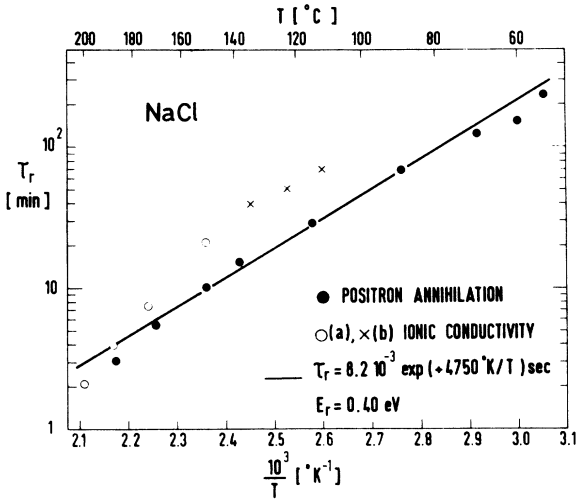

FIG. 4. Rise times, as extracted from Fig. 3 vs $1/T$ (solid points). The values for the highest temperature can only be estimated because a maximum develops, cf. Fig. 2, before a plateau is reached. The open and crossed symbols give the equivalent values reported by (a) Christy and Harte (Ref. 16) and (b) Ingham and Smoluchowski (Ref. 17) from isothermal conductivity measurements.

reach negative values during the time of observation and approach the relative count rates of the annealed NaCl crystals, $\sim(-0.1)$. The maxima are reached sooner and become smaller as T increases to the highest value investigated (185 °C). At even higher temperatures, the time interval over which $I_0(t)$ varies significantly approaches the data collection time. It precludes meaningful experiments at $T > 185$ °C. We have analyzed the decline in a manner analogous to the rise, and extracted characteristic decline times $\tau_d(T)$, which are plotted in Fig. 5. A fit to the form given in Eq. (2) yields the decline parameters $\tau_{0d} = 3.7 \times 10^{-11}$ sec and $E_d = 1.2$ eV.

For completeness we measured some positron lifetime spectra of these NaCl crystals. The data accumulation time for the lifetime spectra is of order 10^3 min, which precludes the study of dynamic anneal effects by this method. One can only compare crystals under conditions where I_0 has reached plateau values. An example is listed in Table I. In the virgin crystals we find two lifetime components in agreement with literature values. After x irradiation, a third component appears with lifetimes comparable to those found in crystals with positive-ion vacancies.[6,13] No detailed study was made of the dependence of the intensity of the third component on irradiation and anneal conditions.

We confirmed earlier findings[15] that protracted optical bleaching in white light from a fluorescence lamp decreases the plateau values slowly by some 10%, but we did not pursue optical bleaching further. Also, if the crystal after having reached the plateau at 90 °C (Fig. 2) is permitted to cool to room temperature, the plateau drops slowly and settles in at a new lower plateau value. The following discussion does not accommodate this behavior.

III. DISCUSSION

We approach our findings in two ways. In this section we compare them with ionic conductivity measurements that were performed under conditions very similar to ours. In Sec. IV, we construct an idealized model of positive-ion vacancy formation and migration which permits us, on the one hand, to understand the differences and similarities between our observations and the conductivity behavior in isothermal anneals and, on the other hand, to connect the observed quantities to microscopic processes.

First we summarize the results of measurements of ionic conductivities in x-irradiated NaCl as they are contained in the papers by Christy and Harte[16] and by Ingham and Smoluchowski.[17] When NaCl crystals are exposed to ionizing radiation (protons, x, or γ rays) the ionic conductivity σ is always lower by some 10–40% than the value σ_0 of the fully annealed crystal, i.e., $\sigma/\sigma_0 < 1$. Annealing at various fixed temperatures changes σ/σ_0 in three ways.

(i) At low anneal temperatures $\lesssim 100$ °C, σ/σ_0

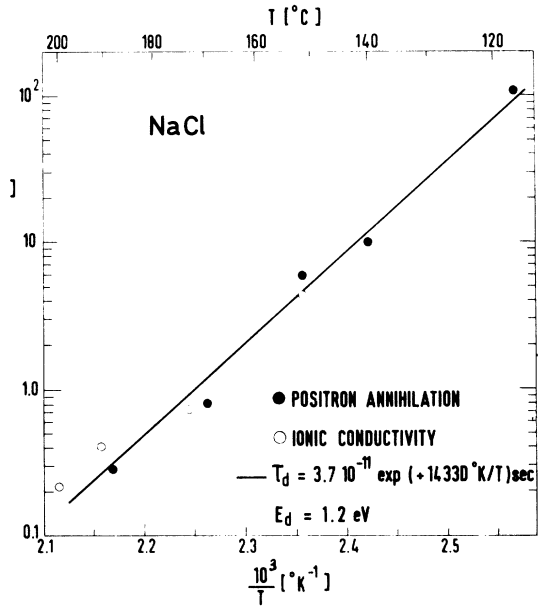

FIG. 5. Decline times as determined from the data shown in Fig. 2 (solid points). The open circles give the equivalent values reported by Christy and Harte (Ref. 16) from isothermal conductivity measurements.

TABLE I. Characteristics of three positron lifetime spectra in the NaCl crystals studied in this paper. The samples were exposed to x rays for 2 h. Lifetimes τ_i are given in nsec and intensities I_i in fractions of all annihilations such that $\sum_i I_i = 1$.

Crystal	T (°C)	τ_1	τ_2	I_2	τ_3	I_3
Virgin	22	~0.2	0.41 ± 0.02	0.43 ± 0.02	•••	•••
Irradiated	22	~0.2	0.43 ± 0.02	0.41 ± 0.02	8.1 ± 0.1	0.17 ± 0.01
Irradiated	90	~0.2	0.52 ± 0.02	0.52 ± 0.02	1.2 ± 0.1	0.04 ± 0.01

decreases further in ~ 100 min to a few percent and then stays constant.[17]

(ii) At intermediate temperatures > 100 °C, σ/σ_0 increases at first to reach a plateau or maximum after 100–10 min. The maximum, however, is always < 1 (Refs. 16 and 17) and leads into a slow decline which begins to level off after ~ 10^3 min.[16]

(iii) Only thermal treatments at temperatures exceeding ~ 0.6 of the melting temperature (1073 °K) restores the crystal to its preirradiation state in a few hours.

The interpretation of these trends can be paraphrased briefly as follows. The conductivity σ_0 of the annealed crystal is determined to a large extent by the concentration of positive-ion vacancies in the annealed crystal. At moderate temperatures, positive-ion vacancies are present at a concentration N_0, to maintain the charge neutrality of the crystal in the presence of doubly charged impurity ions (such as Ca^{++}) imbedded in the crystal with concentration N_0. By the mass-action law, the concentration of free vacancies C_0 is related to N_0 as

$$C_0 \simeq (N_0/Z)^{1/2} e^{-E_a/kT}, \tag{3}$$

where Z is the crystal cation coordination number ($Z = 12$ in NaCl) and E_a the free energy of activation for the separation of the vacancy and the impurity from a nearest-neighbor cation site to infinity. Theoretical and experimental evidence indicates that $E_a \simeq 0.4$ eV.[19] The concentration $S_0 = N_0 - C_0$ is immobilized by "complex formation." Ionizing radiation creates defect clusters or vacancy aggregates which release positive-ion vacancies during anneal.[20] This increases the vacancy concentration to $N > N_0$. However, radiation-induced vacancy traps immobilize vacancies and reduce C to such an extent that $\sigma/\sigma_0 = C/C_0 < 1$, which implies that $S > S_0$. At low anneal temperatures $T < 100$ °C, therefore, vacancies are released from aggregates and diffuse through the crystal bulk to approach a uniform distribution. In the process, most of them are immobilized in bimolecular reactions with traps. This decreases σ/σ_0 with time.[17] At temperatures $T > 100$ °C, the trapping is less efficient and σ/σ_0 increases with time until a maximum is reached.[16,17] The subsequent decline signifies either the creation of new vacancy traps owing to the long-term break-up of clusters, which decreases only C, or the disappearance of positive-ion vacancies in sinks amounting to vacancy neutralization or annihilation, which decreases S as well as C. Conductivity measurements alone cannot distinguish between these two alternatives. Several variants of this account exist, but the basic story is the same.

A comprehensive display of phases (i), (ii), and (iii) was given by Kobayashi[21] who measured the conductivity as a function of temperature for a fixed rate of temperature increase. His curves, one of which is displayed in Fig. 6, show the initial decline (i), the rise to a maximum at intermediate temperatures and the subsequent drop at higher temperatures (ii). The curve rises again at even higher temperatures (not included in Fig. 6) toward the value 1 as all defects anneal out (iii). It is interesting to compare this curve with the model calculations on an analog computer by Sosin[22] with constants appropriate for a metal. The free-vacancy concentration C (curve marked "mobile" in Fig. 6) clearly follows Kobayashi's experimental curve. The model calculation, however, furnishes also the concentration S for vacancy-trap complexes (curve marked "trapped") which the conductivity experiment cannot. After release, vacancies are trapped and C declines while S increases with $N = C + S \sim$ const. After a maximum in S is reached, both curves fall because the vacancies flow to sinks so that C and S decrease; that is, the total concentration of vacancies N declines as the crystal anneals.

Ionic conductivity follows the curve marked "mobile."[23] If it holds under our conditions that positive-ion vacancies are equally operable as A-center precursors whether they are mobile or immobilized by complex formation,[13] I_0 is proportional to $N = C + S$ and can only increase initially when vacancies are released from the aggregates during heating. As Fig. 2 shows, our data do so whether we observe at $T < 100$ °C, where σ/σ_0 drops,[17] or at $T > 100$ °C, where σ/σ_0 rises[16,17] with time. It is consistent with this interpretation that the time scales and the activation energies for the rise are the same (Fig. 4) and that E_r ~ 0.4 eV is comparable to the value of E_a in Eq. (3).

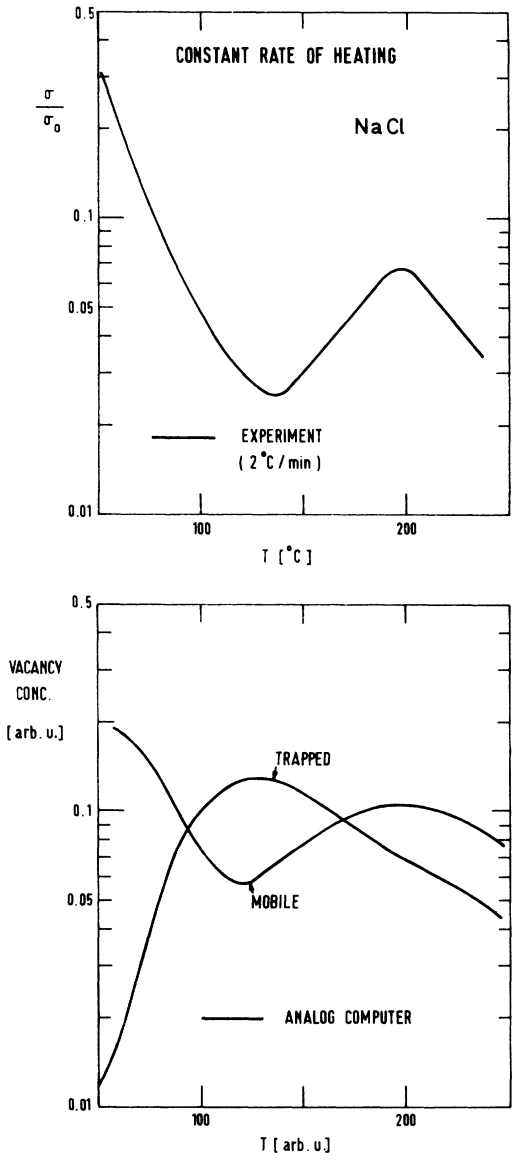

FIG. 6. Ionic conductivity after proton irradiation for constant rate of heating (upper figure modeled after Ref. 21). The lower figure gives analog computer curves for the free vacancies (mobile) and vacancy-trap complexes (trapped) at a constant rate of heating (modeled after Ref. 22).

While there are, then, countercurrent or concurrent trends in $\Delta I/I_0$ and σ/σ_0 at short times depending on the temperature, both quantities eventually stabilize to a constant value when $T < 100\,^{\circ}\mathrm{C}$, or both decline when $T > 100\,^{\circ}\mathrm{C}$. There can only be a common cause for the latter behavior, namely, the disappearance in sinks, i.e., the annealing of positive-ion vacancies.

In summary, the following over-all picture emerges from considerations of the positron-annihilation data $\Delta I(t, T)/I_0$ and the ionic conductivity data $\sigma(t, T)/\sigma_0$. Radiation-induced vacancies are clustered in aggregates distributed such that most positrons do not encounter positive-ion vacancies for A-center formation before annihilating in the crystal bulk. During the initial isothermal anneal stages at temperature T, vacancies are released from the aggregates. In time, the vacancy distribution gains in uniformity, with the result that more and more positrons can form A centers. Therefore, $\Delta I/I_0$ always increases at the beginning of an anneal period. As long as $T \lesssim 100\,^{\circ}\mathrm{C}$, most of the vacancies become trapped along their diffusion paths and form complexes by bimolecular reactions. Although they are removed from the conduction process by the loss of mobility, they retain their role as potential A-center precursors. At higher temperatures $T > 100\,^{\circ}\mathrm{C}$, both $\Delta I/I_0$ and σ/σ_0 increase at the same rate with the same activation energy, but still, vacancies are trapped copiously whence $\sigma/\sigma_0 < 1$, while $\Delta I/I_0 > 1$, always. On extended annealing, the vacancy distribution becomes uniform which gives the maximum number of positrons the possibility to form A centers, as evidenced by the plateaus of $\Delta I/I_0$. For $T > 100\,^{\circ}\mathrm{C}$, the vacancies disappear slowly and both $\Delta I/I_0$ and σ/σ_0 decline at the same rate. Asymptotically at very long times compared to the initial rise (Fig. 2), $\Delta I/I_0$ approaches the value of the completely annealed crystal. It is to be expected that then $\sigma/\sigma_0 \to 1$, although this has not as yet been observed in isothermal anneals.

IV. MODEL ANALYSIS

The physical conditions in a heavily x-irradiated NaCl crystal are complex, and a detailed account of the processes during anneals is out of the question. It appears nevertheless desirable to develop some quantitative feeling for the physical parameters. A stylized model serves for a first attempt in this direction. It can guide experiments to test some of its inferences.

Suppose x-irradiation-induced vacancy aggregates are distributed in the crystal interspersed by domains of only slightly imperfect bulk material. The results of our analysis turn out to be insensitive to the particular model chosen to describe the inhomogeneous initial distribution of vacancy aggregates. For definiteness we assume in the following that the bulk domains are spherical with mean radius a and volume $v = \frac{4}{3}\pi a^3$, surrounded by a shell of thickness d and volume $V \simeq 4\pi a^2 d \ll v$ that is populated with vacancy aggregates. The total volume of such a "cell" is then $V_c = v + V$. Before an isothermal anneal period begins, most positrons annihilate in v. When the temperature is raised, the aggregates in V release positive-

ion vacancies into the volume V_c. Initially, their distribution in v is highly anisotropic. At this stage, only a few positrons encounter vacancies close to the domain V where they can form A centers, but most positrons encounter none. As time passes, the vacancies distribute themselves by diffusion and by trapping and untrapping throughout V_c until a uniform distribution is reached. As a consequence, a growing fraction of the randomly distributed thermal positrons sees at least one vacancy before annihilation to form an A center. $I_0(t)$ increases monotonically and levels off toward a plateau as a uniform vacancy distribution is attained.

Let c be the radiation-induced increment of the concentration of freely moving vacancies emanating from the aggregates hence contributing to the ionic conductivity; and s be the concentration increment of vacancies trapped into complexes which do not contribute to the conductivity. The total radiation-induced concentration increment in V_c, $n = c + s$, can trap positrons to form A centers and thus contributes to I_0. The vacancy diffusion obeys the equation

$$\frac{\partial c}{\partial t} = D\nabla^2 c - \frac{\partial s}{\partial t}, \tag{4}$$

subject to the subsidiary condition

$$\frac{\partial s}{\partial t} = \lambda c - \mu s, \tag{5}$$

where D is the vacancy diffusion constant. Equation (5) assumes that the vacancies after release from V diffuse throughout V_c where they are immobilized in complexes at the rate λ and proportional to their concentration, c; and that they are detrapped from these complexes at the rate μ and proportional to the concentration of trapped vacancies, s, with the initial condition $s = c = 0$ in v at $t = 0$. The solution of Eqs. (4) and (5) for these conditions as a function of the radius r from the center of V_c can be written[24]

$$c(r,t) = \frac{c_0}{1+\alpha^{-1}} + \sum_{n=1}^{\infty} \frac{c_0 e^{p_n t}}{1+[1+\lambda\mu/(p_n+\mu)^2](2\pi a^3/V - p_n/2Dk_n^2 + Vp_n^2/8\pi aD^2k_n^2)} \frac{a}{r}\frac{\sin k_n r}{\sin k_n a}. \tag{6}$$

The concentration increment s of immobilized vacancies follows from c [Eq. (6)] by multiplying the nth term with the factor $\lambda/(p_n+\mu)$ including the first $p_n = 0$ term. The constants p_n and k_n are determined by

$$1 - V/4\pi Da = k_n a \cot k_n a, \tag{7}$$

$$k_n^2 = -(p_n/D)(p_n+\lambda+\mu)/(p_n+\mu). \tag{8}$$

We make use of the abbreviations

$$\alpha \equiv V/v(R+1), \quad c_0\rho \equiv \nu_T/V, \quad R \equiv \lambda/\mu, \tag{9}$$

where ν_T is the number of vacancies released into V_c by the aggregates in V during an isothermal anneal at temperature T. The increment of vacancies $M(t)$, both free to diffuse and immobilized in V_c at the time t, becomes

$$\frac{M(t)}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{(1+\alpha)e^{p_n t}}{1+[1+\lambda\mu/(p_n+\mu)^2(2\pi a^3/V - p_n/2Dk_n^2 + Vp_n^2/8\pi aD^2k_n^2)}, \tag{10}$$

where $M_\infty \equiv Vc_0\rho/(1+\alpha)$ denotes the total increment of vacancies, theoretically after infinite time. The mean time-dependent increment of the vacancy concentration in the crystal is

$$\bar{n}(t) = \frac{M(t)}{\rho V_c} = V_c^{-1}\int n(r,t)\,d^3r = V_c^{-1}\int [c(r,t)+s(r,t)]d^3r, \tag{11}$$

where the integration extends over V_c. For $t \to \infty$, Eq. (11) yields the uniform concentration of mobile vacancies

$$c_\infty = c_0/(1+\alpha^{-1}) \tag{12}$$

and of immobilized vacancies

$$s_\infty = Rc_\infty, \tag{13}$$

because we assume conservation of vacancies $\rho(c_\infty + s_\infty)V_c = M_\infty$.

Positrons are stopped in the substance with uniform probability density, $\rho_+ \simeq$ constant in V_c, such that $\int \rho_+ d^3r \simeq \rho_+ V_c = 1$. Since the positron diffuses with a diffusion constant D_+, and annihilates in times $\tau_s \equiv \gamma_s^{-1}$ vanishingly small compared to the times t over which the vacancy concentration n changes, the mean positron capture rate κ by the radiation-induced positive-ion vacancies into A centers of capture radius r_ν, becomes, with Eq. (11),

$$\kappa(t) = 4\pi\rho r_\nu D_+ \int \rho_+ n(r,t)d^3r = 4\pi\rho r_\nu D_+ \bar{n}(t). \tag{14}$$

The increment in the fraction of positrons annihilating in A centers, $F = \Delta I/\Delta I_\nu$, is related to κ such that[1]

$$\frac{\Delta I(t)}{I_0} = \frac{\kappa(t)\tau_s}{1+\kappa(t)\tau_s}\frac{\Delta I_\nu}{I_0}$$

$$\simeq 4\pi\rho r_\nu D_+ \bar{n}(t)\ \frac{\Delta I_\nu}{I_0}\ , \qquad (15)$$

where ΔI_ν is the saturation value of the change at $\vartheta = 0$ if all positrons were to be trapped in vacancies, corresponding to the limit $\kappa\tau_s \gg 1$. Equation (15) simplifies to the last expression because in the cases studied here, $\kappa\tau_s < 0.3$. In contrast to the $\bar{n}(t)$ dependence of $\Delta I(t)/I_0$ for positrons, the ionic conductivity depends on the mean concentration of mobile vacancies $\bar{C}(t) = V_c^{-1}\int C(r,\ t)d^3r$.

The evaluation of Eq. (10) presents a precarious eigenvalue problem. Fortunately, Crank[24] tabulated some solutions for a range of parameters. We have compared in detail our curve measured at 90 °C (cf. Fig. 2) with his tables, assuming that the experimental curve at the end of the observation time scale has reached the plateau corresponding to the theoretical $t \to \infty$ limit. Only a very restricted range of model parameter values is compatible with the measurements. The most decisive statement can be made with regard to $R \equiv \lambda/\mu$. It is certainly larger than 10 and presumably close to 100. Comparison of the tables for $R = 100$ with experiment yields the following set of parameters: $\lambda = 0.2\ \text{sec}^{-1}$; $\mu = 2\times10^{-3}\ \text{sec}^{-1}$; $D/a^2 = 0.2\ \text{sec}^{-1}$. They imply that, after the vacancy release from the aggregates, the characteristic time for vacancy trapping by diffusion a^2/D is very small compared to that for detrapping μ^{-1}. That is, the process of the redistribution of vacancies is not diffusion limited but is governed by the detrapping rate μ. $R = 100$ implies, by Eq. (12), that only 1% of all vacancies released from the aggregates remain mobile. This is qualitatively consistent with the observation that while $\Delta I/I_0$ always increases toward a plateau with time (Fig. 2), σ/σ_0 can decline toward a limiting value at low anneal temperatures.[25]

It is instructive to estimate the vacancy diffusion constant D from the model parameters. We invoke the fact that the density of NaCl crystals decreases by a fraction $\sim 3\times10^{-4}$,[26] during irradiation. If in the domain $V = 4\pi a^2 d$, a fraction g of all lattice sites is affected by the radiation damage in forming vacancy aggregates, then $gV/V_C = 10^{-4}$, and the radius of V_c becomes $a \sim 10^4 dg$. Let us assume that $g \sim 10^{-2}$ and $d \sim 10$ Å, then $a \sim 10^{-5}$ cm. An independent estimate of this quantity can be made by noting that $\Delta I/I_0$ always increases during isothermal anneals. That means, at $t = 0$, most positrons cannot diffuse far enough to reach a domain V during their lifetime to form radiation-induced A centers. Therefore, v must be so large that $a \gtrsim 10(2D_+\tau_s)^{1/2}$, where $(2D_+\tau_s)^{1/2}$ is the mean positron diffusion length until annihilation in the crystal bulk. The positron diffusion constant[13] is $D_+ \sim 5\times10^{-4}\ \text{cm}^2\text{sec}^{-1}$, and $\tau_s \sim 0.4$ nsec (Table I) so that one obtains by this route $a \gtrsim 0.6\times10^{-5}$ cm consistent with the former estimate. From the model parameter $D/a^2 = 0.2\ \text{sec}^{-1}$ it follows that $D \sim 2\times10^{-11}\ \text{cm}^2/\text{sec}$, corresponding to a vacancy mobility $\chi \sim 10^{-9}\ \text{cm}^2/\text{eVsec}$, by Einstein's relation $\chi = qD/kT$. This value compares well with an earlier estimate.[27]

We conclude from this model study that the increase of $\Delta I/I_0$ toward an asymptotic value during the isothermal anneal of x-irradiated NaCl at $T = 90$ °C is determined mainly by the detrapping rate of vacancies which leads to a uniform vacancy distribution by diffusion from trap to trap. Under these conditions, only the term $n = 1$ in Eq. (10) contributes significantly. All higher terms decay in times short compared to the experimental resolution (~ 3 min). As a consequence, the results of the analysis become insensitive to the initial conditions, i.e., whether one views the vacancy aggregates to be surrounded by slightly imperfect bulk material, or vice versa as we have done here: A uniform vacancy distribution is reached at the mean rate $[D/a^2(R+1)] \simeq \mu$ and Eq. (10) reduces to $M(t)/M_\infty = \bar{n}(t)/n_\infty = 1 - e^{-\mu t}$ in terms of the vacancy detrapping rate μ. Equation (15) then becomes

$$\frac{\Delta I(t)}{I_0} = \frac{\Delta I_\nu}{I_0}\ 4\pi\rho r_\nu D_+ \tau_s n_\infty (1 - e^{-\mu t}), \qquad (16)$$

which constitutes a derivation of the empirical *Ansatz* equation (1). From the temperature dependence of the annealing plateaus we estimate $\Delta I_\nu/I_0$ to be of order 0.3, or perhaps larger. It follows from the value measured at 90 °C for $t \to \infty$, $\Delta I_\infty/I_0 = 0.8$, that $n_\infty \simeq 300$ ppm. This is consistent with the concentration one obtains in distributing a fraction $g = 10^{-2}$ of vacant lattice sites, initially aggregated in V, uniformly over the entire volume V_c. The activation energy of $\mu = \tau_r^{-1}$, $E_r = 0.4$ eV, is comparable to E_a [Eq. (3)], the free energy of dissociation of a positive-ion vacancy from a doubly charged trap.

Starting from our assumption that vacancy A-center formation is at the root of our effect, the dynamic positron-annihilation study reported here bears out, on a microscopic scale, some of the conjectures advanced earlier about the dynamic processes underlying the isothermal anneal behavior of the macroscopic ionic conductivity in NaCl crystals. This encourages one to explore the positron method further. For example, the extraordinarily high positive-ion vacancy concentrations presumed to exist in LiF after neutron irradiation, where conductivities of some 300 times the conductivity of the virgin crystals have been observed,[28] should be corroborated by $I_0(t, T)$ measurements. The origins of the two components in the conductivity curve observed in NaCl

crystals which had been subjected to hydrostatic pressure before x irradiation[29] might be traced by a combination of the positron and traditional methods. It may be possible to study the dynamics of vacancies in metals with positrons, for example through hystereses in the annihilation characteristics during rapid sample heating and cooling cycles, if the time resolution of the positron method can be improved significantly. This should be perhaps possible not so much through improvements of the two-γ-coincidence technique as employed here but rather through rapid measurements of the Doppler broadening[30] of the energy distribution of the annihilation γ quanta owing to the momentum distribution of the annihilating positron-electron pairs.

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