Figure 4 shows a typical desorption run. At time $t=0$ the Pt sample, which had previously been flashed and bombarded as specified above, was suddenly heated from room temperature to 870°K. It can be seen that the K^+ peak decayed exponentially with time in accordance with the relation

$$i=i_0e^{-t/\tau}.$$

The characteristic time constant τ is obtained from the slope of the straight line in Fig. 5, the same data replotted on a semilog scale.

The activation energy for desorption Q_d is related to τ by the expression

$$\tau=\tau_0e^{Q_d/kT}.$$

Thus, by measuring τ for several different temperatures and plotting $\log\tau$ vs $1/kT$, one obtains Q_d directly from the slope of the resulting straight line. Figure 6 is such a plot and the desorption energies for K and Na are recorded in Table II. Reliable values for Ca were not obtained.

It is interesting to note that although the volume diffusion energies were appreciably different for the two samples, the desorption energies were very nearly the same.

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Ionic Conductivity of Gamma Irradiated Sodium Chloride*

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Single crystals of NaCl were subjected to about 5×10^5 roentgens of Co^{60} gamma irradiation at 5°C, and then rapidly heated and maintained at a fixed temperature in the range 65°C to 135°C. The dc ionic conductivity at this temperature was measured by means of a vibrating reed electrometer as a function of time. It decreased in the temperature range 65°C to 80°C during a period of several hours to a value that was less than the preirradiation conductivity by a factor which was typically about 30. The conductivity is presumed to be a direct measure of the number of positive ion vacancies. The data fit a rate equation describing the bimolecular process $A+B\rightarrow AB$, with an activation energy approximately equal to that of the mobility of the positive ion vacancies. This confirms the supposition that the change of conductivity reflects the clustering of the positive ion vacancies with other imperfections at a rate controlled by the diffusion of these vacancies. Above 100°C, many of the clusters appear to break up again with an accompanying increase of conductivity. The conducting vacancies appear to be localized in a rather small fraction of the total volume of the crystal.

I. INTRODUCTION

SEVERAL studies have been made of the ionic conductivity of NaCl and KCl which were irradiated with ionizing radiations.[1–5] In such crystals, whether irradiated or not, it has been accepted that the current is ordinarily due to the motion of free positive ion vacancies, each having an apparent negative charge. The presence of positive divalent impurities and the requirement of charge neutrality necessitates that there are many more positive than negative ion vacancies below temperatures (about 500°C in ordinary so-called "pure" crystals) at which the number of vacancies is primarily intrinsic. In addition, positive ion vacancies are considerably more mobile and thus conductivity can be taken as a direct measure of their number.

Measurements of density changes and of coloration[6] which occur when crystals are irradiated with x rays indicate creation of new vacancies. In an apparent contradiction with this increase of vacancy concentration there have been observed decreases in diffusion[7] and in ionic conductivity resulting from irradiation. Of particular interest here are studies[2–4] in which NaCl and KCl crystals were exposed to either 350-Mev protons or 2-Mev gamma rays and then their conductivity measured while the temperature increased at a constant rate (1–2°C/min) from room temperature to about 400°C. Typical results[4] are illustrated in Fig. 1, which shows the ratio of the conductivity σ of irradiated crystals to the conductivity, σ_0, of unirradiated crystals at the same temperature. It is important to remark that,

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[†] Now at the International Business Machines Corporation Research Laboratories, Poughkeepsie, New York. Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology, June, 1959.

[1] Nelson, Sproull, and Caswell, Phys. Rev. **90**, 364 (1953).

[2] E. A. Pearlstein, Phys. Rev. **92**, 881 (1953); *ibid.* **94**, 1409(A) (1953).

[3] R. Smoluchowski, *Report of Bristol Conference on Defects in Crystalline Solids, July, 1954* (The Physical Society, London, 1955), p. 252.

[4] K. Kobayashi, Phys. Rev. **102**, 348 (1956).

[5] R. W. Christy and W. E. Harte, Phys. Rev. **109**, 710 (1958).

[6] Estermann, Leivo, and Stern, Phys. Rev. **75**, 627 (1949).

[7] D. E. Mapother, Phys. Rev. **89**, 1231 (1953).

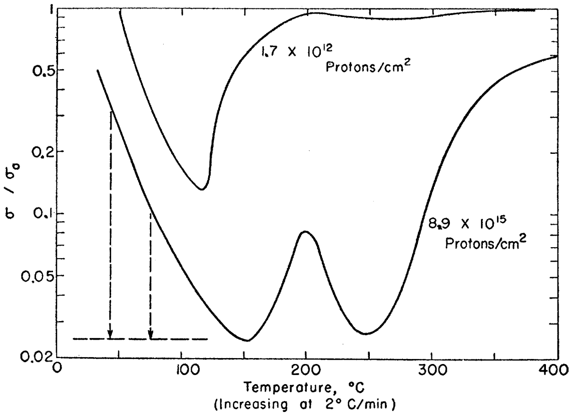

FIG. 1. σ/σ_0 vs temperature of proton irradiated NaCl with temperature increasing at 2°C/min [from Kobayashi[4]]. Gamma irradiation causes essentially the same effect. Horizontal line at 0.025 indicates the approximate value of σ_∞/σ_0 and the arrows visualize the progress of isothermal anneals.

qualitatively, the results for gamma and for proton irradiations were the same. The primary characteristic of these results is that, with the exception of the vicinity of room temperature, the conductivity was below that of unirradiated crystals, signifying that there were fewer free positive ion vacancies after irradiation. The existence of two minima suggests that there is more than one process for immobilizing or removing vacancies. All the effects of irradiation anneal out upon heating to about 300°C–400°C. The nearly normal conductivity of the irradiated crystals near room temperature rules out the neutralization of vacancies by trapping of holes during irradiation. It appears instead that these changes of conductivity have to be accounted for in terms of immobilizing existing vacancies rather than in terms of annealing out of defects. This is based upon the important observations by Kobayashi[8] that the density decrease, thus the total number of point defects, introduced by irradiation near room temperature does not anneal out until a temperature of about 200°C is reached. Smoluchowski[3,9] proposed that the decrease in conductivity was the result of the formation of clusters at elevated temperatures, whereas Seitz[10] suggested that the positive vacancies may trap holes and thus become neutralized at the higher temperatures. The first mechanism would be a slow ionic diffusion mechanism while the latter would be a more rapid electronic process.

The logical extension of the conductivity measurements described above is the study of conductivity changes during isothermal annealing. Christy and Harte[5] have recently reported such investigations between 150°C and 200°C: They observed first an increase and then a decrease in conductivity, which is all the while still less than its pre-irradiation value. These results are consistent with those shown in Fig. 1. The work here reported is concerned with the measurement and interpretation of the conductivity changes in gamma irradiated NaCl crystals held at constant temperatures in the range between 65°C and 135°C.

II. THEORY

A. Bimolecular Trapping Process

This section is a discussion of the nature of the conductivity changes that should result if positive ion vacancies were to combine with other imperfections, "traps," during an isothermal anneal. It is assumed that the vacancies are able to diffuse randomly, and that when one accidentally comes within some distance r_0 of an immobile trap then Coulomb, or electron exchange forces or lattice relaxation cause the vacancy and trap to become bound to each other. Initially it will be required that a trap be incapable of trapping more than one vacancy, and that only one kind of trap exists. Neither of these two requirements may be actually attained but, as it will be brought out later, they do not alter strongly the conclusions of the discussion.

A simple way of treating the process is to consider it as a "bimolecular" reaction $A+B\rightarrow AB$, where "A" is a free positive ion vacancy; "B" is a trap; and "AB" is a combined vacancy-trap cluster. The rate dn/dt at which this process takes place is[11]

$$\begin{aligned} dn/dt &= -Knn_B \\ &= -Kn[n_{Bi}-(n_i-n)], \end{aligned} \tag{1}$$

where n is the concentration of positive ion vacancies; n_B is the concentration of traps; K is a rate constant; n_i is the initial concentration of positive ion vacancies; n_{Bi} is the initial concentration of traps; and t is the annealing time.

The rate constant is expected to depend on absolute temperature T in the usual way: $K=K_0\exp(-\epsilon/kT)$, in which ϵ is an activation energy. If the process is diffusion controlled, K includes D_A, the diffusion coefficient of A (so that ϵ is ϵ_μ, the mobility activation energy), and some measure of the size of the traps. Equation (1) has well known applications in chemistry, and its solution for the required initial concentration is

$$n=\frac{n_i-n_{Bi}}{1-(n_{Bi}/n_i)\exp[-(n_i-n_{Bi})K(t-t_0)]} \tag{2}$$

in which $n=n_i$ when $t=t_0$.

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[8] K. Kobayashi, Phys. Rev. **107**, 41 (1957).

[9] R. Smoluchowski, Phys. Rev. **94**, 1409(A) (1953).

[10] F. Seitz, Rev. Modern Phys. **26**, 7 (1954).

[11] The term "bimolecular" will be used throughout this report to refer to the type of reaction stated above. It should be distinguished from the so-called "second order" reaction in which A is identical with B. (This would be the case in which the positive ion vacancies were to cluster with each other.) The latter reaction would occur at a rate which is proportional only to the square of the concentration. In the actual process being considered here, the rate is proportional to both square and linear terms of the concentration.

Waite[12] has analyzed the diffusion controlled reaction rigorously and has obtained a result which approaches Eq. (2) after the anneal has progressed beyond a time $t'=4r_0^2/\pi D_A$, where r_0 is the radius of the trap. This time decreases with increasing temperature and is estimated to be about 10 sec for NaCl at room temperature. Therefore, for the conditions of this experiment, Waite's solution is effectively the same as the bimolecular solution. His analysis is, however, of particular interest here because it yields an explicit expression for the rate constant

$$K=4\pi r_0 D_A, \tag{3}$$

which is valid whenever trapping is complete for A and B, separated by not more than r_0. Equation (3), with an appropriate "effective" size of the trap r_0, can be applied to more complicated trapping models such as a trap surrounded by a zone in which there is partial trapping with some probability for the vacancy to escape. Equation (2) can be put into the form

$$1-(n_\infty/n)=C_0\exp(-K_e t),$$

with $n_\infty=n_i-n_{Bi}$, $K_e=n_\infty K$, and $C_0=(n_{Bi}/n_i)\exp(K_e t_0)$ in which a positive n_∞ represents the number of positive ion vacancies after a long time of anneal and a negative n_∞ represents the remaining traps after the anneal. Since n is not directly measured, it is necessary to introduce the quantity actually measured, i.e., the conductivity. It is possible that vacancies and traps are not uniformly distributed throughout the crystal but exist mainly in localized regions. These higher densities, rather than the average densities, would then govern the rate of trapping. The conductivity, in terms of the local density of positive ion vacancies, n, is then $\sigma=Ne\mu=fne\mu_0T^{-1}\exp(-\epsilon_\mu/kT)$ where N is the average density of vacancies; f is the effective fraction of total volume in which the vacancies and traps exist in the higher densities; e is the electronic charge; and μ is the vacancy mobility. Thus

$$1-(\sigma_\infty/\sigma)=C_0\exp(-K_e t), \tag{4}$$

where

$$\sigma_\infty=fn_\infty e\mu, \tag{5}$$

and the three parameters σ_∞, K_e, and C_0 can be experimentally determined. Irradiation and subsequent complete isothermal anneal reduce the number of free positive ion vacancies by

$$R_n=\sigma_0/\sigma_\infty=n_0/n_\infty, \tag{6}$$

where σ_0 is the ionic conductivity before irradiation, at the temperature of the anneal and n_0 is the number of free positive ion vacancies before irradiation at the temperature of the anneal. Assuming now that the initial concentrations of positive ion vacancies and of traps depend on the irradiation time $n_i=n_0+\eta(\tau)$ and $n_{Bi}=n_{Bi}(\tau)$, where τ is the irradiation time, and using the definition of n_∞ and Eq. (6), one obtains

$$n_0^{-1}[n_{Bi}(\tau)-\eta(\tau)]=1-R_n^{-1}. \tag{7}$$

Thus the experimentally observable dependence of R_n on τ gives information about the difference in the rates of creation of traps and vacancies.

It is convenient to introduce the parameter K' defined by

$$\begin{aligned}K'&=K_e/T\sigma_\infty=K/f\mu Te\\&=(f\mu_0e)^{-1}K_0\exp[(\epsilon_\mu-\epsilon)/kT].\end{aligned} \tag{8}$$

It will be shown later that experimentally both K' and R_n are approximately proportional to the irradiation time and that R_n is independent of temperature. It is therefore useful to "normalize" K' to the same quantity and efficiency of irradiation for all the crystals by using the ratio

$$K'/R_n\propto\exp[(\epsilon_\mu-\epsilon)kT], \tag{9}$$

which should be independent of τ. A study of the temperature dependence of K'/R_n gives a comparison of the activation energy for the rate constant with that for the mobility. In particular, if K'/R_n is independent of T then one can conclude that the observed conductivity changes are controlled by the mechanism of positive ion vacancy diffusion. In this case Eq. (3) is a reasonable expression for K. If so, K' can be calculated from Eqs. (3), (8) and the Einstein relation $\mu/D_A=e/kT$:

$$\begin{aligned}K'&=4\pi r_0D_A/f\mu Te\\&=(4\pi k/e^2)(r_0/f).\end{aligned}$$

Putting $r_0=\lambda a$, where "a" is the lattice constant (2.8 A for NaCl) and λ is a number greater than one and probably less than about five, we have

$$\begin{aligned}K'&=(4\pi ka/e^2)(\lambda/f)\\&\cong1.9\times10^8\lambda/f(\Omega\text{ cm}/^\circ\text{K sec}).\end{aligned} \tag{10}$$

It should be noted here that since λ is a measure of the size of the traps it may take on different values for different conditions of irradiation.

The parameter C_0, mentioned earlier, does not turn out to be useful because t_0 cannot be determined experimentally with sufficient accuracy.

B. Deviations from the Bimolecular Process

If positive ion vacancies are rapidly released, for instance from clusters, in significant numbers during an anneal the effect should be to decrease the apparent rate at which vacancies become trapped. It will be brought out in the results that such an effect probably occurs during the initial part of each anneal. Therefore, there will be some effective time t_1 after which the bimolecular theory is applicable, but before which it is not.

Another deviation from the ideal process may occur towards the end of an anneal where the number of vacancies and traps in a crystal may be determined by approach to an equilibrium situation (in which the rate

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[12] T. R. Waite, Phys. Rev. **107**, 463 (1957).

of release of vacancies equals the rate at which they are trapped), rather than by the bimolecular trapping process alone. Therefore, it is not expected that the actual limit of the conductivity as t approaches infinity necessarily corresponds to the parameter σ_∞ if $\sigma_\infty < 0$, or approaches zero if $\sigma_\infty \geqslant 0$. It is expected thus that the bimolecular process will dominate the reaction up to a certain time t_2, greater than t_1, before the reverse process becomes significant. It follows that Eq. (4) will apply only during the portion of an anneal between times t_1 and t_2.

Other factors which may cause a deviation from a rigorous bimolecular behavior are (a) the presence of various sizes of traps, (b) consecutive trapping, and (c) change of spacial distribution (geometry) of traps and vacancies during the progress of the reaction. A more detailed analysis[13] shows that in most of these instances the simple bimolecular formalism outlined above is still a good approximation if average, effective parameters are used.

Since the effective parameters for an anneal depend on t_1 and t_2, it is necessary to choose these times in such a manner as to allow a rigorous comparison of anneals carried out at different temperatures. This can be done by noting that for all the crystals here compared $(K_e t)$ represents the same stage of anneal. Knowing that the temperature dependence of K_e, or K, is $\exp(-\epsilon_\mu/kT)$, t_1 can be chosen for each crystal such that $(K_e t_1)$ is the same for all crystals. A similar choice can be made for t_2. Although $\epsilon_\mu(\sim 0.9 \text{ ev})$ is only known at present to within about 15%, the experimental results show that an exact choice of ϵ_μ and thus of t_1 and t_2 is unimportant compared to other sources of error. For instance, an error of 20% in ϵ_μ leads to an error of only 2% in σ_∞.

III. EXPERIMENT

A. Samples and Conductivity Measurements

Sodium chloride single crystals, approximately 2 cm $\times 2\frac{1}{2}$ cm$\times 1\frac{1}{2}$ mm, were cleaved from blocks of "pure" optical quality Harshaw Chemical Company crystals. The samples were annealed in vacuum at 425°C for about 5 hours, and the temperature was then lowered at 2°C/minute. Electrodes were provided by painting the two large surfaces of each crystal with alcohol "Dag."

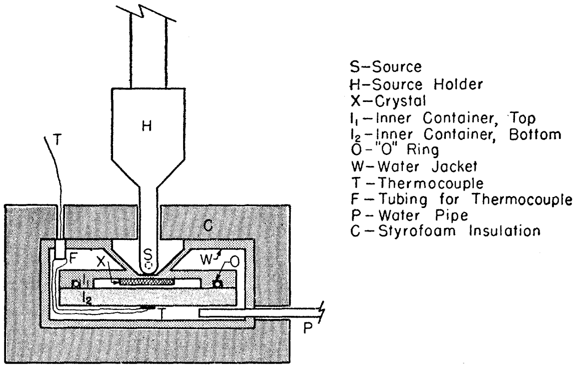

FIG. 2. Crystal container for gamma irradiation.

The crystals were irradiated with Co^{60} gamma rays from a 1.2 Curie source. During irradiation the crystals were mounted in a brass container, shown in Fig. 2, designed to maintain a fairly constant, repeatable temperature below room temperature by means of circulating cold water. One reason for this was to prevent as much annealing during irradiation as conveniently possible. The other reason was the possibility that the radiation effects themselves may depend upon the temperature of irradiation, and, therefore, elimination of this variable was desirable. The crystal was held in a water-tight inner container in helium atmosphere which was introduced before irradiation. It was found that 5±2°C was a convenient temperature to maintain. With the source about 1 cm above the crystal, the intensity of radiation was about 50% greater near the center of the crystal than near its edges. The average intensity was estimated to be 1.45×10^4 roentgens/hour or 2.3×10^{13} photons/cm^2 hour. Irradiation times were from 3 to 35 hours.

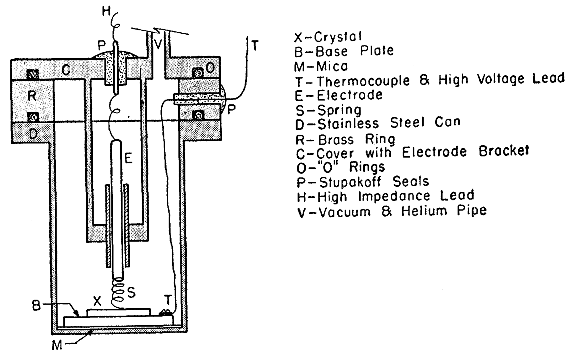

FIG. 3. Crystal container for conductivity meausrements.

For the conductivity measurements, the crystals were held in helium or low vacuum in a container, shown in Fig. 3, which was placed in an electric furnace. The crystal rested on a base plate which provided electrical and thermal contacts and its temperature, repeatable to about 0.1°C, was determined with a thermocouple attached to the base plate in the crystal container. A thermocouple fused into a crystal showed that for the first 10 minutes of the anneals the temperature of the base plate was not a good measure of the crystal temperature, but that thereafter they were within 0.1°C of each other. Thus only data taken after 10 minutes were considered meaningful. This, as shown later, was not a serious limitation. During the anneals the temperature fluctuated as much as 1°C, but an average temperature

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[13] H. S. Ingham, Jr., thesis, Carnegie Institute of Technology, 1958 (unpublished).

for each anneal was determined and then a correction was introduced to each conductivity measurement on the basis of the known temperature dependence of the conductivity of unirradiated crystals.

The basic circuit for measuring the conductivity is similar to that used by Pearlstein.[2] In essence, the unknown crystal resistance is compared to a known resistance R_s, ranging up to $10^{10}\Omega$ in series with the crystal. A potential of 50 volts was applied to the crystal by way of the thermocouple leads to the base plate in the crystal container, and the voltage across R_s measured by means of a vibrating reed electrometer (VRE). During each isothermal anneal a continuous record was kept of this voltage (typically about 5 mv) with a recording meter attached to the output of the VRE.

B. Polarization

A major problem in conductivity measurements was the decrease in the apparent conductivity over a period of several minutes after the application of voltage. In order to reduce and control such effects, the input voltage to the crystal was periodically reversed, each reversal separated by a 1.5 min period of recovery of zero voltage. This is illustrated in Fig. 4, which shows the recorded indications of the VRE. Such effects[2,14] can be due either to the usual "polarization," i.e., reduction of the effective voltage by accumulation of free charges near the electrodes, or due to a decrease in the total number of carriers by the sweeping action of the field. In order to obtain meaningful conductivity measurements for our purposes, the effect was investigated in some detail and the results can be summarized as follows:

(a) Freshly cleaved crystals, or those which were not exposed to air for more than about a half hour, did not exhibit any noticeable changes if the conductivity measurements were made with the crystal in vacuum. On the other hand, crystals exposed to air for several days showed changes in conductivity comparable in magnitude to the conductivity itself. It was also found that the effect was decreased by a factor of two or more when a crystal was placed in low vacuum (10^{-2} mm), although this did not completely eliminate it. Helium atmosphere did not cause conductivity changes except with prolonged exposure, presumably because of contamination of the gas. Water adsorbed on the surfaces did not seem to produce any changes if the crystals were not otherwise exposed excessively to air.

(b) If a constant prolonged voltage was applied to a crystal which exhibited conductivity changes of not more than about the same magnitude as the conductivity, the VRE output seemed to come to a final constant value in about 5 min. This time showed no temperature dependence. Furthermore, this "final value" was independent of the initial current indication and, in particular, it was the same as that for crystals which did not show any polarization. (The experimental accuracy of these comparisons was about 10% of the conductivity.) This led to the conclusion that the "final value" of the VRE output was a reasonable, repeatable measure of the dc conductivity. This is especially true for a relative comparison of conductivities.

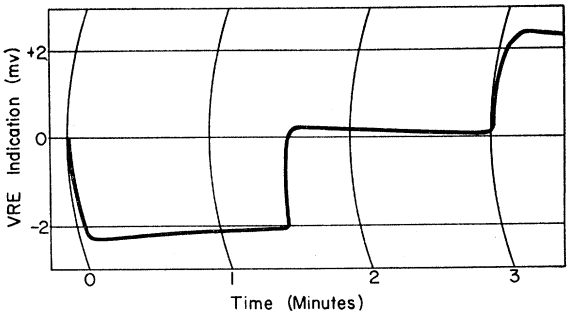

FIG. 4. Trace of VRE output vs time, illustrating polarization.

(c) There did not seem to be any direct correspondence between the magnitude of the changes in conductivity and the conductivity itself. Furthermore, the magnitude of these changes remained constant for at least 2 or 3 hours at the temperatures required for isothermal anneals.

(d) There does not appear to be any evidence that the gamma irradiation had a direct influence on the observed changes.

(e) The magnitude of the conductivity change relative to the conductivity was temperature dependent: it was essentially absent below about 50°C and near 75°C and it had a maximum at about 65°C. Above 75°C the effect increased again and then disappeared above 100°C.

In view of the above behavior of the conductivity changes, crystals were exposed to air as little as possible, although it was difficult to completely eliminate it. The following procedure was finally adopted for obtaining meaningful data from the VRE output: It was assumed that all of the changes were essentially gone after 6 min of constant applied voltage, $V_a=50$ volts, and that the VRE output at this time was a "true" measure of the conductivity. Since it was not very practical to wait this long after each voltage reversal, the VRE output was determined one minute after each voltage application, that is, every three minutes. At some convenient time during or immediately after each anneal, V_a was held constant for more than 6 min and the change determined. This change was then applied as a correction to all the VRE output measurements.

The results make it reasonable to conclude that the observed changes were not due to the motion of vacancies but to extra charge carriers, possibly electrons, introduced into the crystal when nitrogen or oxygen is absorbed at the surface. These added carriers "collect" at some crystalline boundaries in a few minutes, leaving

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[14] D. B. Fischbach and A. S. Nowick, J. Phys. Chem. Solids 2, 226 (1957).

only the vacancies to contribute to the conductivity. It might be expected that a polarization would affect the electric field in the crystal so as to decrease the flow of positive ion vacancies. If this situation exists, the effect is small compared to the magnitude of the current from the added carriers.

C. Summary of the Experimental Procedure

After a crystal was prepared, its conductivity was measured at several temperatures in order to determine the pre-irradiation conductivity at the temperature of the isothermal anneal of the irradiated crystal. The crystal was next irradiated. Immediately after irradiation the inner crystal container (of the irradiating apparatus) was immersed in ice-water where it remained until the beginning of an isothermal anneal, usually a period of about a half hour. Several hours in advance of the anneal, the furnace assembly, including the holder for the crystal, was heated to approximately the desired annealing temperature. When this was ready, the crystal irradiating container was warmed for about 10 minutes to room temperature (to prevent condensation of water on the crystal); then it was opened and the crystal was inserted into the furnace assembly. The air in the crystal holder was then removed and helium introduced. Helium was kept in the holder for about 10 min, then it was replaced with vacuum. (The helium aided in bringing the crystal to annealing temperature more rapidly.) Measurements of conductivity and temperature were then commenced.

IV. RESULTS AND DISCUSSION

The conductivity of unirradiated crystals was found to be independent of time and to obey the expected temperature dependence:

$$\sigma_0 \sim T^{-1} \exp(-\epsilon'/kT),$$

with an activation energy $\epsilon' = 1.15$ ev as measured between room temperature and 100°C. For most of the crystals, group "*a*," the pre-irradiation conductivities at a given temperature were within 10% of each other and at 75°C were approximately 1.0×10^{-14} $(\Omega\ \text{cm})^{-1}$. Another group of crystals presumably less pure, group "*b*," had conductivities about 2.2 times higher. Measurements made at room temperature immediately after irradiation indicate that, prior to the anneals, the ionic conductivity was not changed by more than a factor of two by the irradiation which is small compared to the changes introduced by subsequent annealing.

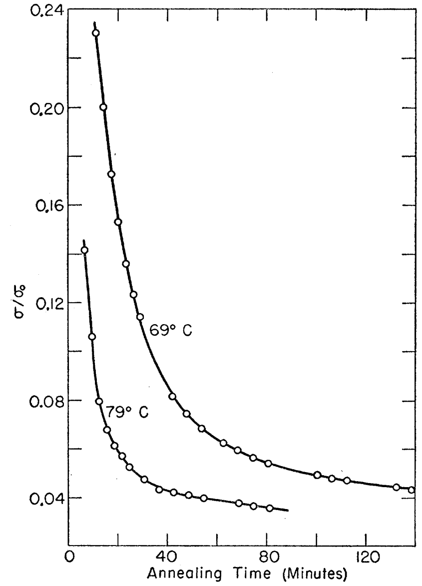

FIG. 5. σ/σ_0 for irradiated crystal vs t. Isothermal anneals are shown for two different temperatures.

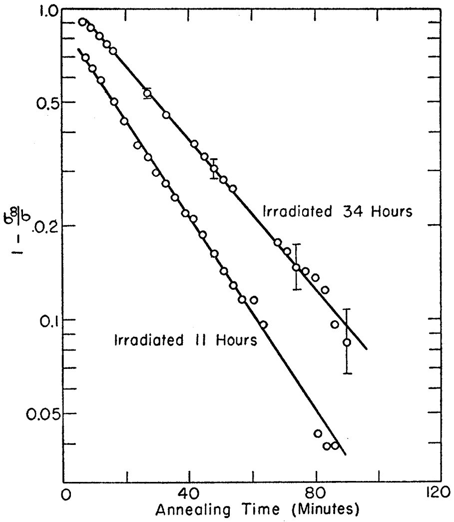

FIG. 6. $\log(1-\sigma_\infty/\sigma)$ vs t. Both anneals were at about 75°C.

Typical σ/σ_0 vs t curves for irradiated crystals annealed at 69°C and 79°C are plotted in Fig. 5. The parameters σ_∞, C_0, K_e were determined by fitting Eq. (4) to such data. If one uses the thus determined values for σ_∞, typical plots of $\log(1-\sigma_\infty/\sigma)$ vs t are shown in Fig. 6. These illustrate the fact that in each anneal there is a significant part which follows, with a very good approximation, a bimolecular process mechanism. Some of the early points in one of the anneals shown in Fig. 6 are slightly below the straight line, a result which is typical of most of the anneals and suggests that at this stage, as discussed above, vacancies may be released for a short time. Similarly at a late stage of the anneals the points again fall somewhat below the line, suggesting the existence of one of the previously discussed possible deviations from a simple bimolecular process.

By far the most significant source of error in the values of the parameters was caused by a temperature drift of about 0.1°C. If other experimental fluctuations are also taken into account, there is about 10% uncertainty in σ_∞, K_e, and R_n. The uncertainty in the repeatability of the quantity of irradiation, and therefore effectively in τ, was about 20%. Optical bleaching of the crystals during transfer to the holder for annealing was too small to affect the results.

Figure 7, a plot of R_n and K' vs τ, shows the effect of irradiating crystals for various times τ and annealing them at very nearly the same temperature. For a given irradiation time, R_n was independent of the annealing temperature in the range 69°C to 80°C. It is evident from Fig. 7 that both R_n and K' for crystals of group "*a*" depend linearly upon irradiation time τ. An exception is a crystal of the "impure" group "*b*," No. 30, which had an anomalously high initial conductivity σ_0 but even in this case both R_n and K' deviate in the same direction and by roughly the same amount. It appears that if there is a difference in the efficiency of the irradiation for different samples it is apparently applicable to both R_n and to K'. This shows that K'/R_n [given by Eq. (10)] is indeed "normalized" to a constant quantity and efficiency of irradiation, as mentioned earlier. This ratio is plotted as a function of annealing temperature in Fig. 8. Most of the crystals investigated were in group "*a*" for which K'/R_n appears to be independent of T, within the accuracy of the experiment, and, therefore, according to Eq. (9), $\epsilon=\epsilon_\mu$ to within 0.15 ev. This indicates that the trapping mechanism is indeed controlled by the diffusion of the positive ion vacancies to the traps. One cannot make an equally strong statement for the three points for the less pure crystals of group "*b*," although even there the quantity K'/R_n is within 20% temperature independent.

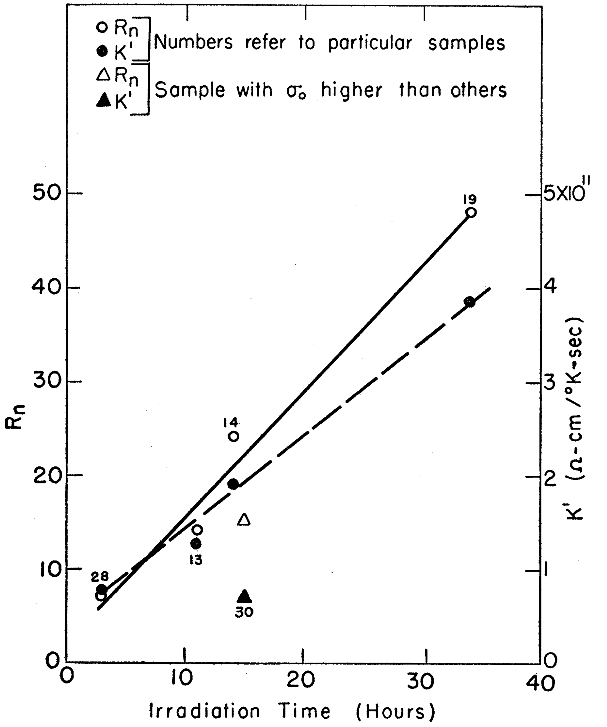

FIG. 7. $R_n=\sigma_0/\sigma_\infty$ vs τ is represented by the open circles and solid line, and K' vs t is represented by the closed circles and dashed line. The triangles are for a crystal with a preirradiation conductivity 2.2 times higher than that of the other crystals.

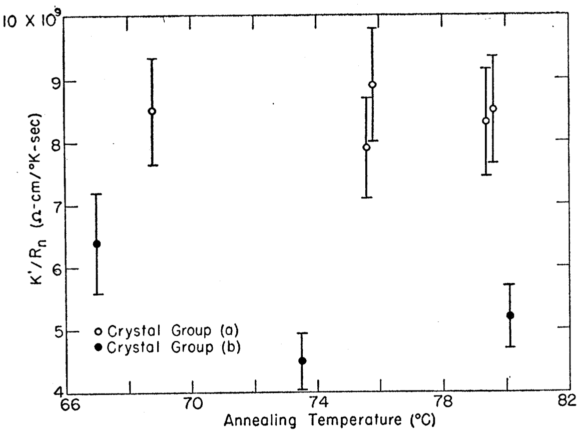

FIG. 8. K'/R_n vs temperature. The crystals in group (*b*) have pre-irradiation conductivities 2.2 times higher than those in group (*a*).

Of interest also are the results of annealing of a crystal which was optically bleached after irradiation but before the anneal. The bleaching caused R_n to be increased by a factor of 10, but left K' nearly the same. This gives further support to the bimolecular theory because it indicates that the effective rate constant is indeed proportional to n_∞.

It is suggested that the strong dependence of the parameter K' on irradiation time τ is the result of one or more of the following mechanisms: (1) there are several types of traps and their average size increases in proportion to the amount of irradiation; (2) some of the traps are capable of trapping two vacancies, and increasing amounts of irradiation increase the proportion of this kind of trap; and finally, (3) large spacial inhomogeneities of concentration of vacancies and traps may cause different rates of increase in the number of traps in these different regions, resulting in an apparent dependence of K_e on τ. An investigation of the influence of the temperature of irradiation on K' may make it possible to distinguish between these possibilities.

The magnitude of K' is useful for obtaining an upper limit to the fraction f of the total crystal volume in which vacancies and traps occur in significant numbers: Extrapolating to zero irradiation time [see Fig. 7] one obtains the minimum possible value of $K'\approx 5\times 10^{10}\Omega$ cm/°K sec, or $\lambda/f=260$. Putting $f=1$ one obtains the quite unreasonable result that the trap size is of the order of several hundred Angstroms. It appears much more sensible to assume that λ is of the order of unity and that f is of the order 10^{-2} to 10^{-3}. Thus one concludes that only a small fraction of the total crystal volume contains significant concentrations of the conducting vacancies.

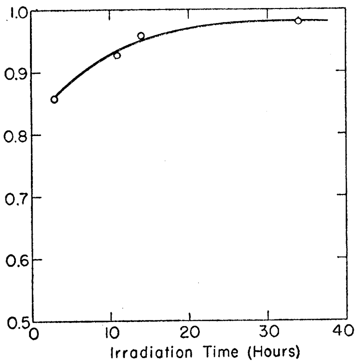

FIG. 9. The quantity $(1-R_n^{-1})=n_0^{-1}\times(n_{Bi}-\eta)$ vs τ.

The growth curve of $(n_{Bi}-\eta)$ vs τ,[15] shown in Fig. 9, does not permit a drawing of definite conclusions concerning η or n_{Bi} alone, although probably (see reference 13) it represents the initial rapid growth and later saturation of the number of traps n_{Bi} as a function of τ.

Measurements of the conductivity σ' vs temperature in the range 45°C to 100°C were made on several crystals *after* each was annealed isothermally for a long time in the same temperature range. Although $R_n=\sigma_0/\sigma_\infty$ was independent of temperature, it was found that σ_0/σ' was somewhat temperature dependent and was greater than the σ_0/σ_∞ calculated from the results of the isothermal anneal. The temperature dependence of σ_0/σ' leads to an activation energy of about 1.28 ev for the conductivity after the anneal which is somewhat higher than the activation energy before irradiation. This may indicate the existence of an association energy of 0.1 to 0.2 ev between the conducting vacancies and those defect clusters which do not anneal out at these times and temperatures. Between 85°C and 100°C, no isothermal changes in conductivity were observed for periods of over an hour, presumably because the reaction was completed by the time temperatures of the measurement were reached.

Figure 10 shows σ/σ_0 vs t for crystals irradiated for about 17 hours and then annealed at 113°C, 125°C, and 135°C. At each temperature the conductivity shows an increase over a period of about three hours to a value which is still approximately a factor of three less than the preirradiation conductivity. Assuming a simple monomolecular process for the release of vacancies from traps, calculation of the rate constant was made for each anneal between the times 20 min and 100 min. The results for the three temperatures are 0.015, 0.020, and 0.022 min^{-1}, respectively. These increases of conductivity show that vacancies are being released from their traps. The fact that the rate constants do not vary much over this wide temperature range may indicate the existence of several types of traps and several activation energies. Continued annealing at 135°C resulted in the conductivity reaching a maximum [not shown in Fig. 10] and then at the end of 17 hours decreasing again to about a factor of five less than the preirradiation value. This decrease in conductivity after a long time of anneal at 135°C was expected because of the original observations by Kobayashi[4] and Pearlstein[2] and because this effect was prominent in the results obtained by Christy and Harte[5] on x-rayed crystals annealed isothermally between 150°C and 200°C. This decrease is presumably the result of an increase in the number of small traps at these temperatures caused by a gradual dissociation and breaking up of larger clusters of defects.

The crystal which was annealed at 115°C was cooled after five hours to 75°C and its conductivity remeasured, giving $\sigma_0/\sigma=13$, as compared to $\sigma_0/\sigma=18\pm3$ for similar crystals annealed in the lower temperature range. This suggests that some of the traps may have become inactive at the higher temperature.

For comparison, some qualitative measurements were made on the optical absorption of irradiated crystals. After irradiation the optical absorption was measured; then the crystal was annealed at about 75°C for about 1½ hours, cooled and the absorption measured again at room temperature. The crystals were very lightly colored, and only two bands were observed—the *F* band and the *M* band. The anneal decreased the *F* band by about 25%, while the *M* band seemed to disappear completely.

As far as the various possible models of the traps are concerned, it seems most reasonable to assume that the traps consist of negative ion vacancies or clusters of vacancies. If this is correct, the irradiation either transforms existing vacancies and clusters into traps, or creates vacancies and clusters, or possibly does both of these things. We shall consider here clusters composed of up to five vacancies and will make the following assumptions: The original clusters are either "neutral" (such as an *F* center or a pair of positive and negative ion vacancies) or may have one effective charge, either positive or negative. Those clusters which act as traps must be either neutral, or, preferably, charged positively —for example, a free negative ion vacancy is considered a good trap. Since there is no trapping observed in an unirradiated crystal one concludes that the positively charged traps (including the free negative ion vacancy) can exist only in equilibrium concentration with positive ion vacancies before irradiation. Conversely, if a particular type of neutral cluster exists in regions where there are positive ion vacancies in an unirradiated crystals, it must be concluded that it cannot trap.

Three distinct processes for creating traps appear to be possible:

(a) The simplest case is that in which a trap is created by ionization of an existing cluster—for example, a neutral cluster is made positive. A trap consisting of a positive ion vacancy with one or two trapped holes can be eliminated because the conductivity at

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[15] See the discussion leading to Eq. (7).

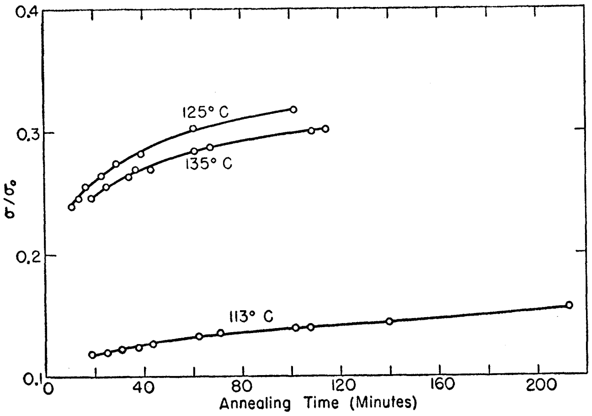

FIG. 10. σ/σ_0 for irradiated crystals vs time for three different anealing temperatures.

room temperature is changed so little by the irradiation. There are thus essentially four possibilities: a cluster of two positive-one negative ion vacancies with either one or two holes, a cluster of three positive-two negative ion vacancies with one hole, and two positive-two negative ion vacancies with one hole. It is to be noted that this last cluster may be capable of trapping two vacancies.

(b) It is possible that in addition to the previous mechanism positive-negative ion vacancy pairs are created at dislocation jogs during irradiation.[16] These pairs may migrate during irradiation[17] to each other or to existing clusters, and could thereby cause the growth in the size of clusters. Of the smaller clusters (five vacancies or less), those predicted in (a) are still allowed but, in addition, there is now the possibility that the cluster of two positive-two negative ion vacancies exists as a trap.

(c) Large clusters either already existing or formed by the growth mechanism of (b) may be caused to break up under the influence of the ionizing irradiation. This mechanism adds four more types of possible traps to the list: Negative ion vacancies and F centers can apparently be created, as can the cluster of one positive-two negative ion vacancy with one electron (the M center) or without one. The possibility that F centers and M centers are traps is supported by the observed decreases in these color bands that result from annealing. Also, the growth curve for the number of traps [see discussion of Fig. (9)] seems similar to a growth curve for the F band as observed by Kobayashi[18] and Nowick.[19] In conclusion, there is the particularly interesting possibility that there exists a mechanism whereby the irradiation causes positive-negative ion vacancy pairs to be created at internal surfaces or dislocations; these pairs cluster with each other, trap an electron or hole, then break up to form F centers, M centers, and traps.

V. SUMMARY

The main conclusions of the research described above are as follows:

(1) The observed changes in the conductivity of NaCl upon annealing in the range 65° to 80°C after gamma irradiation obey very well a bimolecular process which is assumed to be the trapping of mobile positive ion vacancies by immobile traps created during irradiation.

(2) The rate parameters are independent of the annealing temperature.

(3) The activation energy of the annealing process is equal within 0.15 ev to the mobility activation energy of positive ion vacancies.

(4) It appears that the conducting vacancies are localized in a rather small fraction of the total volume of the crystal.

(5) The irradiation dose affects the rate of the annealing in a manner which indicates the existence of several kinds of traps. Possible trap models are discussed.

(6) There is a release of conducting vacancies from traps near 125°C.

Note added in proof.—An alternate interpretation of the results here reported is perhaps possible on the basis of thermoluminescence observations by Halperin, Kristianpoller, and Ben-Zvi (Phys. Rev., to be published). It appears that in x-ray irradiated crystals there are several peaks in the glow curve. This suggests that x-ray irradiation suppresses ionic conductivity by a factor of the order of 50 by trapping positive ion vacancies and that these do not become free until a temperature of perhaps 200°C is reached. The almost normal conductivity of an irradiated crystal near room temperature would be thus caused by an accidental presence of a current glow peak in this neighborhood. Further studies are necessary to distinguish between the two interpretations.

VI. ACKNOWLEDGMENT

The authors are grateful to Dr. D. A. Wiegand for performing optical measurements and for his many helpful discussions.

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[17] G. J. Dienes, J. Chem. Phys. **16**, 620 (1948).
[18] K. Kobayashi (private communication).
[19] A. S. Nowick, Phys. Rev. **111**, 16 (1958).

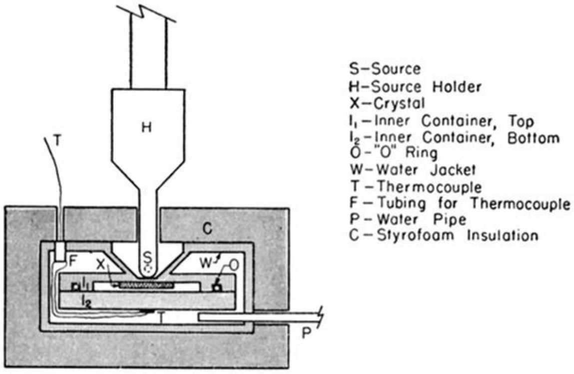

FIG. 2. Crystal container for gamma irradiation.

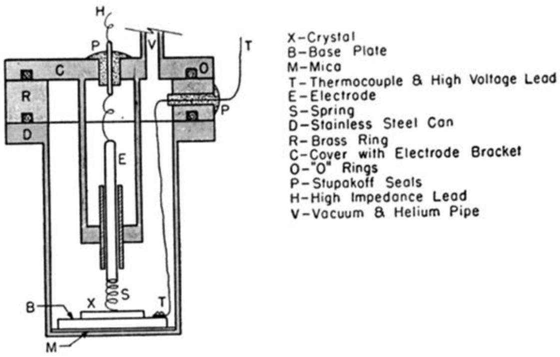

FIG. 3. Crystal container for conductivity meausrements.