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Annealing of Irradiation Effects in Sodium Chloride Irradiated with High-Energy Protons*

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Single crystals of sodium chloride were subjected to irradiation at room temperature by 350-Mev protons with a total flux of 10^{12} to 10^{16} protons per cm^2, and changes in their electrical conductivity, stored energy, and optical absorption were studied. The relative resistivity changes due to irradiation were measured during warmup at a rate of 2°C/min, showing maxima at around 150°C and 250°C and annealing out at about 400°C. The stored energies released during annealing were measured in the same temperature range. The results indicate the presence of three stages of annealing, the first lies between room temperature and 150°C, the second between 150°C and 250°C and the third is above 250°C. The stored energy curve has maxima at 100°C, 200°C, and 310°C. The probable mechanisms of the various annealing processes are discussed. In particular specific mechanisms are proposed for the second stage of the annealing in which significant changes of the optical absorption bands take place. Efficiency of the production of defects was estimated to be the order of 10^3 per proton per centimeter path and this is compared briefly with the theories of Seitz and Smoluchowski.

I. INTRODUCTION

THE electrical conductivity of alkali halide crystals, in particular KCl and NaCl, which were irradiated by 350 Mev protons has been first measured by Pearlstein.[1] His results showed that on annealing there is a pronounced increase of resistivity above the values for normal crystals. His measurements on sodium chloride covered the range of proton flux from 2×10^{14} to 3×10^{15} protons per cm^2 and the resulting resistivity curves relative to the normal showed two definite peaks at about 150°C and 250°C.

It is rather well established that, at not too high temperatures, the carriers of an electric current in sodium chloride are positive ion vacancies. Thus Seitz[2] has suggested that the decrease of conductivity measured by Pearlstein might be caused by the tying down of the carriers responsible for conductivity by a capture of electrons or of holes. On the other hand, Smoluchowski[3] has suggested that this increase of resistivity may be caused by the formation of neutral clusters of positive and negative vacancies.

Since the measurement of electrical conductivity alone does not seem to provide sufficient information on which to base an understanding of the mechanism of these phenomena, it was decided to extend Pearlstein's observations by measuring other quantities. In particular, the purpose of this paper is to present the results of measurements of stored energy and of optical absorption together with additional conductivity data. While stored energy reflects the behavior of all defects, optical absorption is particularly suitable for the study of lattice defects associated with electrons and holes.

II. EXPERIMENTAL

A. Irradiation

All the specimens used in this study were pieces of sodium chloride crystals, about $10\times15\times4$ mm, which were cleaved from one big single crystal obtained from the Harshaw Chemical Company. They were annealed at 650°C for four hours in helium, the temperature being raised and lowered at a rate of 4°C/min.

Most of the irradiations with 350-Mev protons were made inside of the vacuum chamber of the Carnegie Institute of Technology synchrocyclotron in the direct path of the circulating proton beam. Particular care was exercised to avoid bleaching of the crystal by light or by heat during irradiation. The latter was assured by using a reduced intensity of the proton beam and cooling the crystal holder with water. The temperature of the crystal during irradiation was estimated to be near room temperature. The total flux of protons was determined[1] using aluminum foils which were mounted next to the crystal and measuring the activity of Na^{24} produced by the reaction Al$^{27}(p,3pn)$Na^{24}.[4] Since the range of protons of this high energy in sodium chloride is several inches, the observed changes are real volume effects.

B. Electrical Conductivity

The electrical conductivity was measured in vacuum by means of a one-tube balanced circuit,[5] using an FP-54 valve and a slightly modified circuit. The potential applied between the two electrodes of the specimen was 93 volts and the maximum resistance detectable with this circuit was about 1×10^{14} ohm which is the resistivity of most of our specimens at about 50°C. The irradiated crystal was placed in a small furnace in a vacuum together with a dummy, i.e.,

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[1] E. A. Pearlstein, Phys. Rev. **92**, 881 (1953); **94**, 1409 (1954); "Conference on Effects of Radiation on Dielectric Materials," ONR Symposium Report ACR-2, 31 (1954).

[2] F. Seitz, Revs. Modern Phys. **26**, 7 (1954).

[3] R. Smoluchowski, "Defects in Crystalline Solids," Report of the 1954 Bristol Conference, 1954, p. 252.

[4] L. Marquez, Phys. Rev. **86**, 405 (1952).

[5] W. Soller, Rev. Sci. Instr. **3**, 416 (1932); L. A. Dubridge, Phys. Rev. **37**, 392 (1931).

not bombarded, specimen of an equal size. The electrodes were made of silver conducting paint DuPont 4817.

The measurements were made while the crystals were heated at a constant rate of 2°C/min from room temperature to 400°C, and the resistivity of the irradiated crystal was directly compared with that of the dummy.

a. Normal Crystal

The absolute values of the conductivity of the dummy crystal varied slightly from crystal to crystal if they were cut from different parts of the original crystal. The maximum difference was about 20%.

Since the conductivity, σ is expressed approximately as $\sigma = ne\mu = (A/T)\cdot\exp(-U/kT)$, where n is the number of carriers, μ is their mobility and A is a constant, one might expect that the relation between $\log(\sigma T)$ and $1/T$ is linear if there is a unique activation energy for migration. Figure 1(a) shows a typical curve of $\log(\sigma T)$ *vs* $1/T$ of the dummy specimen. This curve indicates three regions, AB, BC, and CD, each of which has a somewhat different slope. The temperature at B and C are about 250°C and 175°C, respectively. Activation energy was estimated as 0.83 ev for AB, 1.17 ev for BC, and 0.93 ev for CD. Etzel and Maurer[6] have found that the number of positive-ion vacancies does not change in the temperature range of 250–400°C and that their activation energy for migration is 0.857 ev which is in good agreement with 0.83 ev here obtained in the temperature range of 250–400°C. They have also determined that the energy of dissociation of a positive-ion vacancy from a divalent Cd ion in NaCl is about 0.3 ev, while Lidiard[7] by a careful examination of the same data obtained 0.35 ev. Reitz and Gammel[8] have calculated this energy to be 0.44±0.1 ev. Since a difference between AB and BC is found to be 0.37 ev in Fig. 1(a), it will be safe to assume that, in the temperature range of 175–250°C, positive-ion vacancies are ejected from the impurity ions into the crystal. Below 175°C, some conductivity may be contributed by positive-ion vacancies which were frozen in by cooling from higher temperatures during the annealing process. The activation energy in this region, 0.93 ev is very near to 0.98 ev which was obtained by Bean[9] in the range of 160–250°C. From these considerations, the number of free positive-ion vacancies, n, in our normal crystal can be estimated from measured conductivity data using for mobility,

$$\mu = 19600/T\cdot\exp(-\epsilon_{+}/kT)\ \text{cm}^2/\text{volt sec}$$

as derived by Etzel and Maurer.[6] Figure 1(b) shows the value of n calculated using $\epsilon_{+} = 0.83$ ev. Near room temperature, n is about 3×10^{15} per cc, and it is 1.7×10^{16} per cc above 250°C.

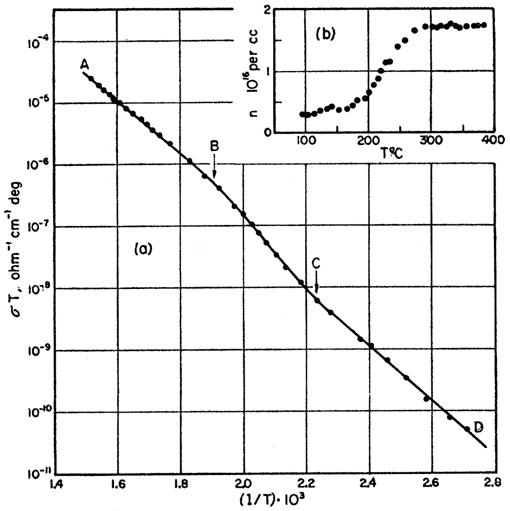

FIG. 1. (a) σT *vs* $1/T$ curve for nonirradiated NaCl crystal; (b) the change of the number of positive-ion vacancies in a nonirradiated NaCl crystal with temperature.

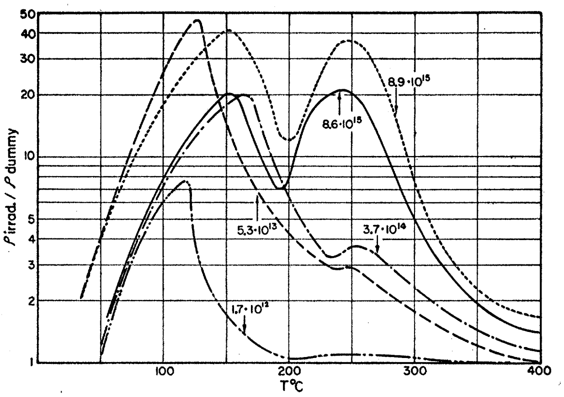

FIG. 2. Relative resistivity changes *vs* temperature for NaCl irradiated by protons. The rate of temperature rise 2°C per min. Resistivity is expressed as the ratio of the resistivity of the irradiated crystal (ρ_{irrad}) to that of a normal crystal (ρ_{dummy}). The numbers indicate the total flux of protons per cm^2.

b. Irradiated Crystal

The measurements of the resistivity of each irradiated crystal were made about 60 hours after irradiation. The total flux of 350-Mev protons was in the range from 1.7×10^{12} to 9×10^{15} per cm^2. Figure 2 shows the results, expressed as a ratio of the resistivity of irradiated crystal, ρ_{irrad}, to that of a dummy, ρ_{dummy}, *versus* temperature. The results are in a generally good agreement with those of Pearlstein.[1] For the irradiation by 1.7×10^{12} protons per cm^2, an external beam of the synchrocyclotron had to be used because of a difficulty in obtaining a sufficiently low intensity in an internal beam.

The curves in Fig. 2 show two distinct peaks at

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[6] H. W. Etzel and R. J. Maurer, J. Chem. Phys. **18**, 1003 (1950).

[7] A. B. Lidiard, Phys. Rev. **94**, 29 (1954).

[8] I. R. Reitz and J. L. Gammel, J. Chem. Phys. **19**, 894 (1951).

[9] C. Bean, thesis of University of Illinois, 1952 (unpublished).

about 150°C and 250°C. Except for the case of the irradiation by 1.7×10^{12} protons per cm^2, the height of the first peak does not seem to depend much upon the total flux. The temperature corresponding to the maximum shifts from 120°C to 160°C when the flux increases. The second maximum is strongly dependent upon the total flux. At about 9×10^{15} protons per cm^2, its height is about the same as the first peak. When the total flux decreases, the height decreases and at 1.7×10^{12} protons per cm^2, the peak almost disappears.

C. Stored Energy

a. Calorimeter

Since the energy which is released from an irradiated crystal during warmup was expected to be small, a calorimeter assembly was designed using the differential thermocouple method, as designed and used by Overhauser[10] at low temperature. The calorimeter itself was very similar to Overhauser's, except that in our assembly, there were no windows and it was made of aluminum instead of copper. The heating system was an electric furnace which was heated at a well-controlled rate of temperature.

Two specimens, both of which had equal weights and dimensions, i.e., 15×10×4 mm, were heated gradually to about 500°C. Then, by means of a small torch flame, a very small part of the surface of each crystal was melted and a copper-constantan thermocouple inserted. After gradually cooling down to room temperature, both crystals with the thermocouples were annealed in helium atmosphere at 650°C in the same manner as described above. One of the two specimens thus prepared was irradiated with protons inside the synchrocyclotron, and then together with a nonirradiated specimen it was suspended in the calorimeter and the measurement was made.

The stored energy released per degree per specimen, dU/dT, was calculated using Overhauser's formula.[10] The error in measurement itself was found to be negligibly small compared to the differences between the specimens themselves.

The systematic error associated with heat conduction between the calorimeter wall and the two crystals through the thermocouple is estimated to be less than 2%. Errors arising from the energy transfer between the two crystals through the thermocouple are about 0.06%. An error associated with the different thermal contact between both specimens and the calorimeter wall due to heat radiation is estimated as 0.5% at 600°K and 0.1% at 300°K. This assumes that the fraction of imperfection in the irradiated crystal is of the order 10^{-3}. The same kind of error arising from the energy exchange between the irradiated and the dummy crystal by heat radiation during measurement is about 1% at 300°K and 7% at 700°K. The error arising from the change of specific heat of NaCl due to the presence of imperfection in high concentration in the irradiated crystals is estimated using the theory of Overhauser.[10] The resulting maximum error is about 10%, assuming a magnitude of atomic fraction of the interstitial-vacancy pairs to be 10^{-3}. Therefore, it will be safe to estimate that the systematic error of the stored energy measurements here reported is less than 15%.

b. Results

Figure 3(a) shows the results of the stored energy measurements for NaCl irradiated by 350-Mev protons with a total flux of 9.3×10^{15} per cm^2. The total flux for Fig. 3(b) is 9.1×10^{15} per cm^2. In each case one can see a distinct peak in the temperature range from 150°C to 250°C with a maximum at 202°C. Below 150°C, a broad hump appears with a maximum at about 100°C, while above 250°C, another small hump seems to exist, with a maximum at about 310°C.

Figure 3(c) shows a stored energy curve for a bleached crystal which was irradiated by a total flux of 1.4×10^{16} protons per cm^2. Since bleaching of this heavily darkened crystal by sunlight or a usual tungsten lamp at room temperature was extremely slow, the bleaching

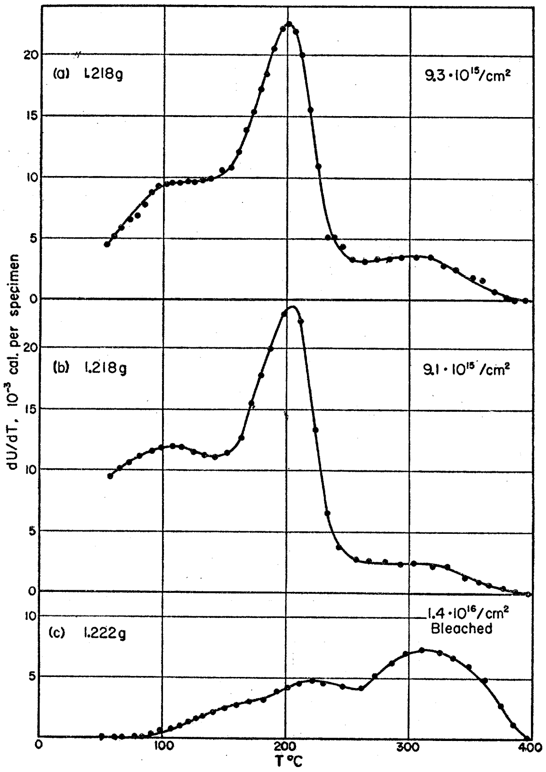

FIG. 3. Stored energy released from NaCl crystal irradiated with protons during annealing at a rate of 2°C per min. (a) total flux of 9.3×10^{15} protons per cm^2; (b) total flux of 9.1×10^{15} protons per cm^2; (c) crystal bleached at 90°C for six days after irradiation with 1.4×10^{16} protons per cm^2.

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[10] A. W. Overhauser, Phys. Rev. 94, 1551 (1954).

was finally done using a tungsten lamp at about 90°C for six days. Even in these conditions, it was impossible to make the color centers bleach out completely and the crystal showed a slightly reddish brown residual color. The heat curve in Fig. 3(c) shows that the second large peak centered at 202°C has almost disappeared and its decreasing small maximum seemed to have slightly shifted to higher temperatures. The third hump becomes distinct and its maximum at 310°C is in good agreement with that of the nonbleached crystal.

The integral heats released are listed in Table I in the range, from room temperature to 150°C, from 150°C to 250°C and from 250°C to 400°C. The magnitudes of the integral heats in the range of 150–250°C and 250–400°C for both measurements are in good agreement. In the range below 150°C, however, the agreement is not so good, and presumably the process in this region may be strongly influenced by variation in the room-temperature annealing.

D. Absorption Spectra

Absorption spectra for the irradiated crystals were measured at room temperature using a Beckman Model DU Spectrophotometer. The specimens used for this study were the same as used for electrical conductivity, the measurements were taken before conductivity measurements. Inasmuch as at high flux irradiations the crystals were heavily colored in their entire volume, measurements were restricted to low flux irradiations.

TABLE I. Integral heats released from 1 g of irradiated NaCl (in calories).

Total proton flux per cm^2	Room temp.–150°C	150°C–250°C	250°C–400°C	Total
9.3×10^{15}	0.72	1.18	0.28	2.18
9.1×10^{15}	1.02	1.21	0.22	2.45

a. Relation to the Total Flux

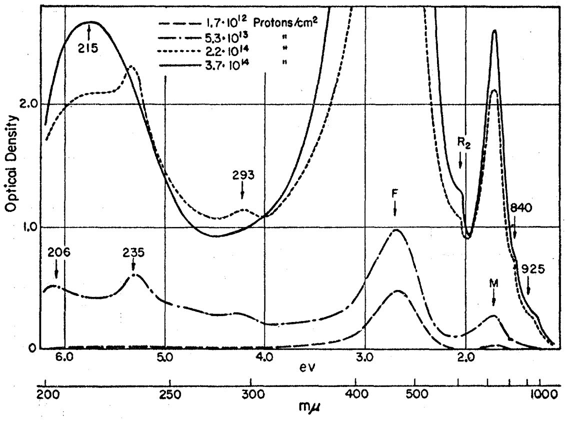

FIG. 4. Absorption spectra of NaCl crystals irradiated by protons for various values of total flux, measured at room temperature.

Figure 4 shows optical densities of crystals 4 mm thick irradiated with a total flux ranging from 3.7×10^{14} to 1.7×10^{12} protons per cm^2. Curve *a* in Fig. 5 shows the result for a crystal 0.325 mm thick irradiated with 8.0×10^{14} protons per cm^2. These curves show that the optical densities of F, M, R_2, 840-mμ, and 925-mμ bands increase with the increase of the total flux. In the ultraviolet region, however, shapes of the bands gradually change with increasing total flux. The spectrum of a crystal irradiated with 5.3×10^{13} protons per cm^2 shows the presence of three absorption bands with maxima at 206, 235, and 293 mμ. The 235-mμ and 293-mμ bands increase to some extent in the crystal irradiated with 2.2×10^{14} protons per cm^2 with no detectable peak at 206 mμ, presumably because of a superposition of the strongly increased 235-mμ band. For the crystal irradiated with 3.7×10^{14} protons per cm^2, 235-mμ and 293-mμ bands seem to disappear; this is accompanied by an appearance of a simple band with a maximum centered at about 215 mμ. The spectrum of the crystal irradiated with 8.0×10^{14} protons per cm^2 shows a band with a maximum at 210 mμ as shown in Fig. 5, which is in good agreement with the maximum of the V_3 band.[11] The nature of the 206-mμ, 215-mμ and 235-mμ bands which appear only at low intensity irradiation, however, are still in doubt. Presumably, they are in intimate relation to the growth of the V_3 band.

In Table II, are shown the numbers, n, of V_3, F, and M centers per cc of NaCl, which were calculated using Smakula's formula and assuming that the oscillator strength is 0.7 for the F center and unity in other cases. As the maximum optical densities of the F band for crystals irradiated with 3.7×10^{14} and 2.2×10^{14} protons per cm^2 were very much higher than the limit of our instrument, their magnitudes were only roughly estimated by an extrapolation of the curves. The maximum optical density for the F band of the crystal irradiated by 8.0×10^{14} protons per cm^2 was estimated as twice the density at 422 mμ,[11] which is the shorter wavelength corresponding to the half-maximum of the F band in NaCl.

The magnitudes of n for V_3 centers for crystals irradiated with 5.3×10^{13} and 2.2×10^{14} protons per cm^2

TABLE II. Concentration of color centers and efficiency for producing color centers by proton at room temperature.

Total proton flux per cm^2	V_3		F		M	
	n	α	n	α	n	α
1.7×10^{12}	$<2\times10^{15}$	$<1.2\times10^{3}$	1.7×10^{16}	1.0×10^{4}	4.6×10^{14}	2.7×10^{2}
5.3×10^{13}	3.6×10^{16}	6.8×10^{2}	5.1×10^{16}	9.6×10^{2}	6.0×10^{15}	1.1×10^{2}
2.2×10^{14}	1.5×10^{17}	6.8×10^{2}	6.1×10^{17}	2.8×10^{3}	3.9×10^{16}	1.8×10^{2}
3.7×10^{14}	1.9×10^{17}	5.2×10^{2}	1.1×10^{18}	3.0×10^{3}	4.4×10^{16}	1.2×10^{2}
8.0×10^{14}	4.8×10^{17}	6.0×10^{2}	2.2×10^{18}	2.7×10^{3}	1.0×10^{17}	1.3×10^{2}

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[11] See W. H. Duerig and J. J. Markham, Phys. Rev. **88**, 1043 (1952).

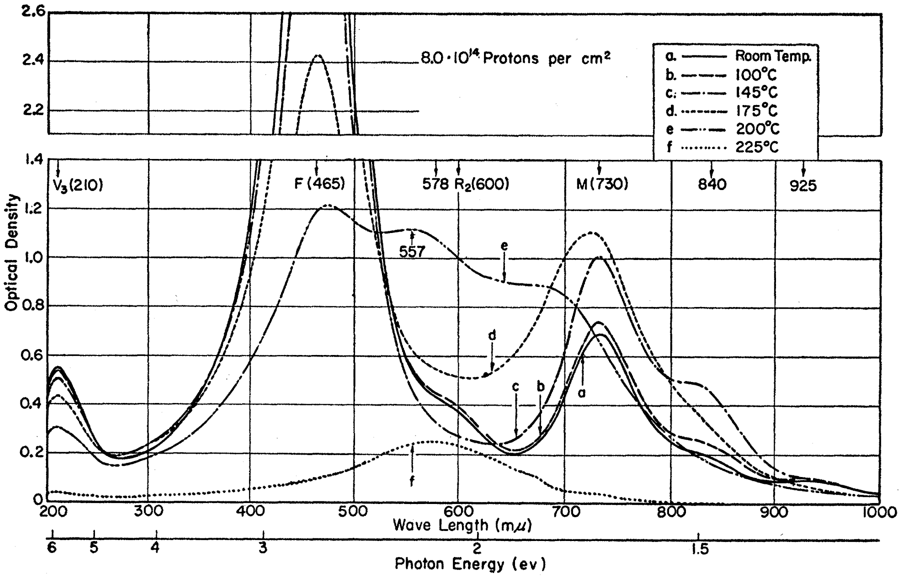

FIG. 5. Change of the absorption spectrum of an NaCl crystal irradiated with a total flux of 8.0×10^{14} protons per cm² during annealing at several temperatures. Measurements made at room temperature.

were estimated from the sum of 206-mμ and 235-mμ bands. α in Table II is the number of color centers which are produced by one proton per one centimeter path inside the crystal. These values appear to be almost constant for each center and the mean values are estimated to be about 6.2×10^2, 2.9×10^3, and 1.3×10^2 for V_3, F, and M centers, respectively, using data in Table II except those for the total flux of 1.7×10^{12} per cm².

It is interesting to note that the ratio of the number of F centers to V_3 is about 4.5 and the ratio of the number of F centers to M is about 21 assuming that the oscillator strength has a magnitude as mentioned previously. This leads to the conclusion that the number of negative ion vacancies is 2.3 times greater than that of positive ion vacancies. This assumes Seitz's model of the V_3, F, and M centers.

The magnitudes of α for the crystal irradiated with 1.7×10^{12} protons per cm² are found to be much greater than those for the crystal irradiated with a higher flux. This higher concentration is probably caused by initially present vacancies, since the number of color centers created by irradiation is of the same order of magnitude as the number of vacancies initially present. This can be estimated from the conductivity measurement of an unirradiated crystal.

b. *Thermal Bleaching*

Studies of the change of the color centers with temperature raising at a rate of 2°C/min were made using a crystal with a thickness of 0.325 mm which was irradiated with a flux of 8.0×10^{14} protons per cm². The specimen was heated to a given temperature in a helium atmosphere, quenched immediately to room temperature and then the absorption spectrum was measured at room temperature.

The temperatures chosen were 100, 145, 175, 200, 225, 250, 320, and 400°C. The results of the absorption spectrum measurements are shown in Fig. 5. In this figure, the results for 250, 320, and 400°C annealing are not shown, since no significant absorption in these three cases was measurable.

At room temperature, the absorption curve shows the presence of distinct V_3, F, and M bands and small R_2 and 840-mμ bands. At 100°C, V_3 and F are slightly decreased while R_2, M, and 840 mμ are slightly enhanced. An annealing at this temperature seems to produce only minor changes of the concentration of color centers. At 145°C, V_3 and F are decreased, R_2 has mostly disappeared, while the M and 840-mμ bands are considerably increased. At 175°C, the V_3, F, and 840-mμ bands are greatly decreased and the absorption in a region between F and M starts to increase. The M band seems not to change significantly, even though the curve is enhanced, because of a partial superposition of M and of the new band on the short wavelength side. At 200°C, the V_3 and F bands continue to decrease considerably, while a broad band between F and M, which appeared at the 175°C annealing, is greatly enhanced with its maximum at around 560 mμ. M is considerably decreased and the 840-mμ bands cannot be detected any more. At the 225°C annealing, the absorption curve is remarkably changed: The V_3, F, and M have practically disappeared and only a broad band is left between F and M with a maximum at 578 mμ. Above 250°C, there are no detectable bands and all color centers have disappeared.

Figure 6 shows the change of the concentration of color centers on annealing as estimated from the results shown in Fig. 5. For V_3, F, and M, the ordinates indicate numbers of these centers per cc, while for the R_2, 840-mμ and 578-mμ bands, the ordinates show maximum optical densities which were estimated by subtracting densities of other bands from the measured curve. The 578-mμ band in this figure is a broad band which appears between *F* and *M* in the temperature range from 150°C and 225°C as mentioned above.

Mollwo[12] has observed a colloidal sodium band in additively colored NaCl in a temperature range between 250°C and 500°C. Its maximum shifted from 570 mμ to 620 mμ when the colloid grew during heating from 300°C to 500°C. At 700°C, the colloidal band vanished and was replaced by an *F* band. Scott and Smith[13] and also Scott and Bupp[14] have found, with additively colored KCl, that, on heating, a broad band, which they termed *R′* band, grew between *F* and *M* accompanied by a decrease of the *F* band. Since the 578-mμ band of the present study grows with a large decrease of the *F* band and the wavelength of its maximum agrees with that of the colloidal band and also it shifts from 560 mμ to 578 mμ with increasing temperature, this band is expected to be similar in nature to a colloidal band. The broadness of the 578-mμ band indicates that it may also be a close relative to the *R′* band which is an absorption by an early stage of the colloidal sodium center as suggested by Seitz.[2] It appears thus plausible to assume that this band is some kind of a coagulate of *F* centers or of sodium atoms.

When the 578-mμ center dissociates, no *F* center seems to appear contrary to the dissociation of colloidal centers in additively colored crystals. This can be understood in the following way: In the case of additively colored crystals, the *F* centers are hard to bleach because of a lack of trapping centers for electron, and therefore, the *F* centers may reappear after the dissociation of the colloidal centers. In the case of the crystal irradiated by protons, electrons are produced leaving holes behind as trapping centers while the irradiation proceeds. Therefore, when the 578-mμ center dissociates, *F* centers will not be formed.

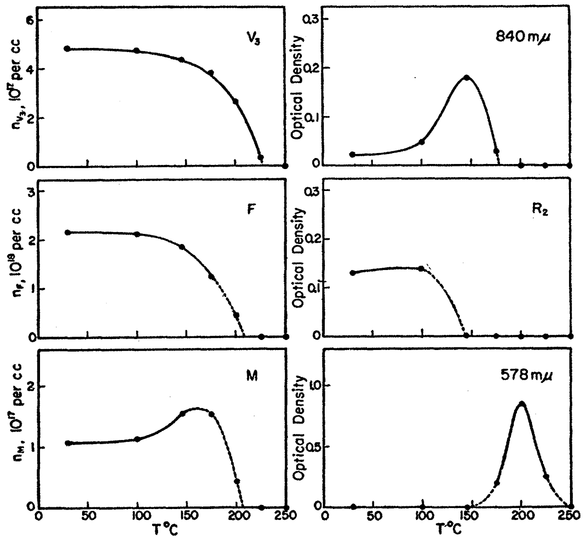

FIG. 6. Changes of concentrations of color centers in NaCl crystal irradiated with 8.0×10^{14} protons per cm² during annealing at a rate of 2°C per min. Dotted lines indicate rough estimates.

III. DISCUSSION

In view of the results of the present measurements, one can divide an annealing process of sodium chloride crystals irradiated with 350-Mev protons, into three stages: The first stage occurs in the temperature range between room temperature and about 150°C, where the electrical conductivity decreases considerably, the curve for the evolution of heat has its first hump and the number of color centers changes only by a relatively small amount. The second stage is in the range of 150°C–250°C, where the resistivity, particularly at high-flux irradiation, goes through a minimum, the heat curve has a large peak, and the concentration and nature of the various color centers are changed strongly, ending in the total disappearance of the color centers at the upper end of this range. In the third stage, i.e., above 250°C, the conductivity returns monotonically to its normal value, the heat curve shows a small hump, and the crystal does not show any presence of color centers.

a. The First Stage

We will discuss now the processes which presumably occur during the first stage. On annealing from room temperature to 100°C, the decrease of the number of V_3 and *F* centers in the crystal irradiated with a total flux of 8.0×10^{14} protons per cm² is about 1×10^{16} and 3×10^{16} per cc, respectively, while the increase of *M* centers is about 1×10^{16} per cc. If we now apply Seitz's model[2] of these centers, then about a half of the positive ion vacancies from V_3 center dissociation and most of the negative ion vacancies from the *F* centers seem to be converted to *M* centers. If the rest of the positive ion vacancies remains in free form in the crystal, then the electrical conductivity should increase with rising temperature in contrast to the observed rapid decrease. It must be, therefore, concluded that the positive-ion vacancies which do not contribute to the formation of *M* centers are absorbed in other centers. In the range of 100°C to 145°C, the amounts of change of V_3, *F*, and *M* centers are -3×10^{16}, -2.6×10^{17}, and $+4\times10^{16}$, respectively, which indicates that at slightly higher temperatures most of the positive-ion vacancies from the V_3 centers are presumably converted to the *M* centers.

The 840-mμ and the R_2 bands undergo relatively drastic changes and these may be significant for the concentration of free vacancies. In fact, the rapid

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[12] E. Mollwo, Nachr. Akad. Wiss. Göttingen, Math.-physik. Kl. **1932**, 254 (1932).

[13] A. B. Scott and W. A. Smith, Phys. Rev. **83**, 982 (1951).

[14] A. B. Scott and L. P. Bupp, Phys. Rev. **79**, 341 (1950).

increase of resistivity in the first stage of annealing may be mostly due to the formation of clusters of several positive- and negative-ion vacancies. These clusters may trap electrons (or holes) and produce color centers such as the 840-mμ centers, or they may have absorption bands nearer to the α and β bands of free vacancies.

Interesting conclusions can be drawn from the stored-energy curve. If we assume that a few ev of heat is evolved during the formation of a coagulation center on dissociation of V_3 and F centers, the total energy evolved would be expected to be less than 0.1 cal per gram of the crystal irradiated with 9×10^{15} protons per cm^2, in this first stage. This is about one tenth of the measured value. It seems, therefore, safe to conclude that a substantial part of the heat evolved in this stage of annealing is associated with interstitial-vacancy recombination and the formation of vacancy clusters rather than with any changes of the concentration of V_3, F, or M centers.

b. The Second Stage

Between 150°C and 200°C in the second stage of the annealing process, large decreases of V_3, F, M, R_2, and 840-mμ bands are accompanied by the appearance of the 578-mμ band, or some sort of coagulation of the F centers. This shows that the positive ion vacancies which originate in the dissociation of coagulation centers do not form new color centers but some of them may remain in the crystal in free state. Most of the F centers seem to be converted directly to 578-mμ centers with little chance to form vacancy pairs or other coagulates. If this interpretation is correct, one would expect an increase in electrical conductivity. This is confirmed by experiment.

Between 200°C and 250°C, the V_3, F, and M bands continue to decrease without forming any other color centers, while the 578-mμ band starts to dissociate at 200°C. This means that positive-ion vacancies which have been present and also new ones may form neutral clusters with negative-ion vacancies which are created by the dissociation of the 578-mμ and F centers, since a number of negative-ion vacancies created in this manner may be considerably higher than its saturation value in this temperature range, particularly for the crystal irradiated with high proton flux. Thus, the number of positive-ion vacancies will be decreased with a resulting increase of resistivity. Measurements show indeed an increase of resistivity in this temperature range.

If we accept this process for the second stage, then we can interpret the decrease of the height of the 250°C maximum in the resistivity curve with decreasing flux of irradiation. Scott and Smith[13] have demonstrated the presence of an equilibrium concentration of F centers and colloids in an additively colored KCl. One can assume thus that a similar equilibrium condition exists between F centers and the 587-mμ centers. When the concentration of F centers is much higher than its equilibrium, the 587-mμ center will be formed at a certain temperature at which the migration of F centers becomes effective. When the concentration of F centers is much smaller than this value, the 578-mμ centers will not be formed in sufficient amount to change the electrical conductivity. Therefore, the influence of the 578-mμ centers upon the electrical conductivity and thus the 250°C peak in the resistivity curve are expected to decrease when the total flux of irradiation is decreased.

In this second stage of annealing the most dominant change is the disappearance of F centers, since the number of F centers is much larger than the number of any other centers. Electrons, which are initially in the F centers, will be finally trapped by holes which at this stage form mostly neutral chlorine atoms. Therefore, the energy released by disappearance of F centers should be accounted for by the difference of energy levels of an electron in an F center and in a trapping center. The thermal dissociation energy of the F center has estimated to be 1.89 ev.[15] The thermal dissociation energy of an electron from the chlorine ion in NaCl was approximated roughly as 6.4 ev by assuming that the thermal dissociation energy is about two thirds of 9.5 ev,[16,17] that is, the optical excitation energy of an electron from the chlorine ion to the conduction band in NaCl. These values lead to 4.5 ev for the energy difference between the two states. If we assume that the magnitude of α still has a value of 3×10^3 for F centers in heavily colored crystals irradiated with 9.2×10^{15} protons per cm^2, then one can obtain the amount of energy released by the disappearance of F centers as 2.2 cal per gram of NaCl irradiated by 9.2×10^{15} protons per cm^2. This energy will be spent in radiation and in excitation of lattice vibrations. The latter is measurable by calorimetric means and should be smaller than 2.2 cal. The magnitude of α will be very likely smaller than the value 3×10^3 which was used in this calculation, since the concentration of F centers will reach a saturation value at high-flux irradiation. Thus the energy released by the dissociation of F centers will also be smaller than 2.2 cal and, therefore, the value 1.2 cal in Table I may be quite reasonable for this process.

The energy associated with the paring of vacancies which are formed by the dissociation of color centers is estimated to be less than 0.15 cal per gram of NaCl irradiated by 9.2×10^{15} protons per cm^2, using 0.9 ev as an energy for this process. This is a minor contribution to the evolution of heat compared to that due to the dissociation of F centers. Therefore, the peak in the heat curve in the second stage can be interpreted as due mostly to the bleaching out of F-centers. This

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[15] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), p. 143.

[16] Reference 15, p. 97.

[17] J. N. Ferguson, Phys. Rev. **66**, 220 (1944).

picture is also supported by the fact that a crystal optically bleached at around 90°C does not show in its heat curve any large peak near 200°C.

c. The Third Stage

The absence of color centers in this stage, 250–400°C, indicates that the recovery of resistivity and the small amount of heat evolved are not related to the behavior of color centers. If we accept a simple picture that the conductivity is increased as a result of a production of positive-ion vacancies by a dissociation of clusters, then, one might expect an absorption of heat during this process. The experimental results, however, indicate an evolution of heat. Therefore, this process is probably more complicated and, presumably, a number of rather unstable aggregates is changed to more stable ones or they are absorbed at dislocations, with an attendant evolution of heat and formation of free positive-ion vacancies.

d. Efficiency of Irradiation

It is interesting to inquire into the efficiency of the production of defects during irradiation.

Since the number of isolated vacancies initially existing in a normal crystal, as estimated from electrical conductivity measurement, is very much smaller than the number of color centers produced by irradiation with a high flux, it will be safe to assume that most of the vacancies associated with color centers are produced by irradiation. We can estimate thus that about 3.2×10^3 negative-ion vacancies and about 1.3×10^3 positive-ion vacancies are created by one proton per one centimeter path, in the form of V_3, F, and M centers, during room-temperature irradiation.

In order to compare this result with theory, let us first consider only the elastic collisions. A theory due to Seitz[18] allows an estimate of the number of ions which are displaced from their lattice positions into interstitial positions by elastic collisions. The value is about 5 for both kinds of ions for one 350-Mev proton per one centimeter path through a NaCl crystal. This may be an underestimate, since as pointed out recently by Smoluchowski, Pearlstein, and Ingham[19] in connection with their study of irradiation effects in tungsten for a high-energy proton irradiation, it is important to consider also the effect of the secondary particles which are created in inelastic collisions between protons and the component atoms of crystal. Assuming that a cross section for inelastic collisions is expressed as $\pi r_0^2 A^{\frac{2}{3}}$, where r_0 is 1.2×10^{-13} cm, the number of protons which are captured per centimeter path in NaCl can be estimated to be about 0.02. If four to five secondary nucleons with an energy of 20 Mev are emitted in this disintegration and if they are completely stopped inside of the crystal, a rough calculation shows that 4 to 6 displacements of each kind of ions are produced per incoming proton per centimeter path.

Both these calculations are evidently off by several orders of magnitude and it appears that one has to take into account also electronic excitation. Using a mean excitation energy of the electron of Na and Cl, Seitz's theory[18] indicates that the number of ionizations is at least about 4×10^4 for both ions per proton per centimeter path. This includes the effect of the secondary nucleons.[19] Therefore, there is a good possibility[20] of producing positively charged chlorine ions, and then, subsequently, the right order of magnitude of negative-ion vacancies and interstitial chlorine atoms by a mechanism first suggested by Varley[21] for F-center formation in x-rayed crystals. Furthermore, the vacancies produced in this manner are negative-ion vacancies and thus their total number in the crystal will be expected to be much greater than that of positive-ion vacancies. This is just the condition necessary to account for the rapid increase of resistivity in the first stage as discussed in the foregoing.

The fact that hard gamma radiation[1] produces quite similar effects to those produced by proton irradiation lends further support to the point of view that electronic excitations and not elastic collisions are here of primary importance.

It should be pointed out that there is also the possibility of formation of vacancies by collisions of electrons, holes, and excitons, and dislocation jogs and vacancy clusters, since the former may exist in very high concentrations during the irradiation. No quantitative estimates of the efficiency of these two processes have been made nor has any evidence for the presence of interstitials been obtained.

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[18] F. Seitz, Discussions Faraday Soc. No. 5, 271 (1949).

[19] Smoluchowski, Pearlstein, and Ingham, Phys. Rev. **98**, 1530 (1955).

[20] R. Smoluchowski, Proceedings of the International Conference on Peaceful Uses of Atomic Energy, Geneva, 1955 (to be published).

[21] J. H. O. Varley, Nature **174**, 886 (1954).