

Measurement of the Stored Energy in X-Rayed Sodium Chloride*†

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The stored energy in sodium chloride crystals irradiated with x rays at room temperature was measured by dissolving the crystals in water and measuring the temperature changes. In the range of F -center densities between 2.5×10^{17} and 6.5×10^{17} per cm^3 , the curve of stored energy versus F -center density was a straight line, whose extrapolation did not intersect the origin. Quantitative interpretation of the slope of this line is difficult because of lack of knowledge about the chemical nature of a solution of irradiated NaCl. According to the interpretation favored in this article, the stored energy associated with one F center in this coloration range is 9.2 ± 0.3 eV. This value for the stored energy is in good agreement with a simple energy level scheme involving the F center, so that if there are any defects produced by x rays at room temperature which have not yet been discovered, they probably do not involve much stored energy. Crystals which have been irradiated and then thermally bleached no longer have any stored energy, from which we conclude that chlorine does not leave the crystals during irradiation or subsequent heating.

I. INTRODUCTION

THE production of F centers in alkali halide crystals by x rays is generally believed to occur in two stages: For small amounts of irradiation, halogen vacancies which are already present, or easy to produce, are filled by electrons freed by the radiation; for larger doses, the radiation must produce the vacancies as well as the free electrons. This second stage presents a major problem: How can x-ray photons produce vacancies? The mechanism must be more complicated than a simple collision, since although the photons have plenty of energy, they do not have nearly enough momentum to displace an atom. Several mechanisms have been proposed,¹⁻⁴ all of which involve the production of a local "hot spot," and then the ejection or diffusion of an atom or vacancy from this region. There might be different mechanisms at low temperature and room temperature.⁵ Another important problem is: What happens to the holes when electrons are trapped at room temperature? At low temperatures the V centers presumably account for them, but at room temperature most of the V centers disappear.

Many experiments on color centers have dealt primarily with the optical properties, from which one can learn, among other things, about the energy levels of electrons and holes. In attempting to find a mechanism to explain such data, there is often an implicit assumption that all of the defects produced by the radiation are observed optically. There is, of course, the possibility that other defects are produced, but not observed optically, either because their optical absorption is not in the wavelength range of the

instruments used, or because the oscillator strength of the absorption is very small.

The purpose of the work reported in this article is to examine the stored energy of an x-rayed crystal (that is, the energy involved in the rearrangement of atoms and electrons) by a means (solution calorimetry) which will insure that no large amounts of stored energy will be neglected. In the experiments to be described below, stored energy in NaCl was measured at 25°C as a function of F -center concentration for F -center densities between 2.5×10^{17} and 6.5×10^{17} per cm^3 , which is in the second stage of coloration. The graph of stored energy vs F -center density is a straight line. From the slope of this line we calculate a stored energy of 9.2 eV per F center, after making certain assumptions about M centers and about the chemical nature of a solution of irradiated NaCl in water. This result is in good agreement with the presently accepted model of the F center, so that, at least in so far as stored energy is concerned, the x rays do not produce many more defects than are detected optically. We also find that crystals which have been irradiated and then annealed do not have stored energy, which we regard as an indication that the mechanism for production of F centers does not involve loss of chlorine by the crystal.

II. EXPERIMENTAL

Details of the apparatus and method are described elsewhere,⁶ so only the most important parts will be described here.

A. General Method

The stored energy is measured by dissolving the crystals in water and noting the temperature change. Since the heat of solution of sodium chloride is very large compared to the stored energy to be measured,

⁶ F. T. Phelps, Ph.D. thesis, University of Nebraska, 1961 (unpublished). Some extra copies of this thesis are available. (Write to E. P.) Some of the numerical conclusions in the thesis are different from those of this article because of new information and thought regarding M centers.

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† Taken from a Ph.D. thesis submitted by F. T. Phelps to the University of Nebraska. See footnote 6.

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¹ F. Seitz, *Revs. Modern Phys.* **26**, 7 (1954).

² C. C. Klick, *Phys. Rev.* **120**, 760 (1960).

³ J. H. O. Varley, *Nature* **174**, 886 (1954).

⁴ P. V. Mitchell, D. Wiegand, and R. Smoluchowski, *Phys. Rev.* **121**, 484 (1961).

⁵ H. Rabin and C. C. Klick, *Phys. Rev.* **117**, 1005 (1960).

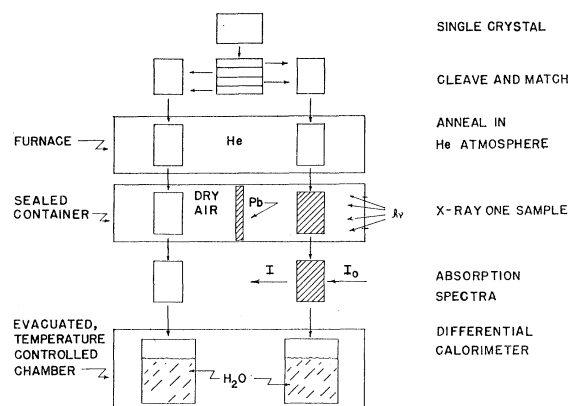


FIG. 1. Diagram of procedure.

it is necessary that means be provided to detect very small temperature differences. For the conditions of our experiments (10 g of NaCl dissolved in 100 g of water) there is a temperature drop of about 1.1°C upon dissolving, while for measuring the effect of the stored energy due to irradiation with x rays it is desirable to detect differences in temperature of 10^{-4} deg. In order to avoid the necessity for extreme repeatability and accuracy, a differential method was chosen. Two specimens, identical except that one had been irradiated, are dissolved in identical amounts of water in identical containers, and the temperature difference between containers is measured with a thermocouple and sensitive dc detector. (In order to test for unexpected asymmetries, the irradiated crystal was not always put in the same side of the calorimeter.) Using a standard chemical balance, the amounts of salt and water can be made equal to within a few parts in 10^5 . Figure 1 illustrates the method.

B. Crystals

The sodium chloride crystals were obtained from the Harshaw Chemical Company. Specimens were cut from three large pieces, obtained at two different times. We found no difference in these in the stored energy per F center, although there was a small difference in the M -center coloration.⁶

For each experimental run a "matched pair" of samples was needed—one to be irradiated and one to be the "dummy" in the differential calorimeter. Each such sample had a mass of 10 g and consisted of either four or five pieces with dimensions of about $3.4 \times 2.4 \times (0.06 \text{ to } 0.19)$ cm. The samples were "matched" in that: (1) Their masses were equal to better than one part in 10^4 , with the masses known to one part in 10^5 . (2) Their surface areas were the same within a few percent. (3) They had the same impurities and history, since they came from neighboring positions in the same large crystal.

Since the crystals were often deformed considerably in cleaving, they were annealed afterwards in order to

relieve mechanical stresses which might not be equal in the two samples. Annealing was in a helium atmosphere at temperatures of 600 to 640°C , for times of 1.5 to 42 h, with cooling rates of 22 to 110°C per h. Our data do not indicate whether the conditions are critical, or whether the annealing was even necessary.

As far as possible, the two parts of a sample were given identical handling and subjected to identical environments of temperature and humidity.

C. Irradiation

All irradiations were carried out in a dried atmosphere at room temperature, with a tungsten target x-ray tube having filtration approximately equivalent to 0.6 mm of aluminum, at a distance of about 11 cm. The crystals were turned over and exchanged in position with each other from time to time during irradiation, in order to improve uniformity. Behind the crystals was a sheet of lead, which, through backscattering, increased the irradiation dosage by about 10%. Because of apparatus difficulties, voltage and current conditions were not constant. They ranged from 100 to 140-kV peak and from 5 to 8 mA. Total times of irradiation ranged from 60 to 267 h.

D. Optical Measurements

Immediately after irradiation, measurements of optical density were made. The instrument used was a Cary Model 11-MS spectrophotometer. Its useful wavelength range is 210 to $800 \text{ m}\mu$, which covers the F and M bands of NaCl, and its direct reading optical density range is 0 to 3.4. Some crystals had optical densities greater than 3.4, so a special technique was used: Another crystal of smaller optical density was put in the "reference" beam of the instrument, and the difference in optical densities of the two crystals was measured. This method is good only if the instrument has sufficiently small stray light. The stray light was determined by comparing the measured optical densities of several colored crystals individually and in series, using both beams of the spectrophotometer. We found that for the F band of NaCl the stray light was 2 parts in 10^6 , and it was never necessary to make more than a small correction to our measurements.

In order to determine whether any bleaching occurred during the handling of crystals subsequent to their irradiation, a spare crystal always received identical treatment, except for the final dissolving in water. At the conclusion of an experimental run, optical measurements were again made on this spare crystal. No bleaching was detected.

E. The Calorimeter

1. General

The calorimeter is quasi-adiabatic. That is, it is well insulated, but not perfectly insulated, from the sur-

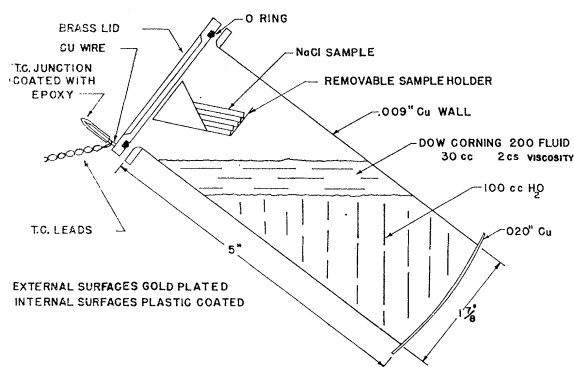


FIG. 2. One of the calorimeter containers with its contents.

roundings. The materials are placed inside metal containers, which are then sealed and put into a temperature-controlled vacuum chamber. When the proper temperature and vacuum equilibria have been established, a motor is turned on which rocks the containers back and forth, thus mixing the crystals and the water, until dissolving is complete. Temperatures of the containers and of the vacuum chamber are measured as a function of time before, during, and after the mixing.

2. Containers

Figure 2 is a drawing of one of the containers loaded with its contents. The crystals are mounted on a shelf above the water, and they are not immersed until the container is rocked. In order to prevent water vapor from attacking the crystals before rocking is begun, silicone oil of specific gravity 0.87 is floated upon the water.

The external surfaces of the containers are gold plated in order to reduce radiation loss. (The major source of heat exchange is radiation.) The internal surface of the lid is chromium plated, and the sample holder and the internal surface of the container are coated with "Tygon" (a plastic paint manufactured by the United States Stoneware Company), in order to prevent chemical action with the salt solution.

The two containers were made as nearly identical as possible. After each stage of their construction they were weighed, and appropriate amounts of material taken off or added. Each empty container had a heat capacity of about 17 cal/C°.

3. Vacuum Chamber

The vacuum system is of conventional metal design, with a liquid-nitrogen trap. The calorimetric measurements were made with the pressure at about 2×10^{-6} mm Hg.

The main chamber, which houses the containers and rocking mechanism, is a vertical brass cylinder 12 in. high and 12 in. in diameter. It has a removable top, for loading, and a small glass window in front through

which light can be shone on one or the other of the containers, in order to make their temperatures equal at the beginning of a run. The bottom of the chamber contains the vacuum pumping line, a vacuum-sealed rotating shaft for rocking the containers, and small copper tubes through which the thermocouple wires enter.

In order to minimize heat exchange between the containers and their surroundings, the walls of the vacuum chamber are temperature controlled. Water flows around it through copper tubes, the temperature of the water being controlled by a thermistor controller and an electric heater. With this apparatus, the temperature of the walls can be held equal to that of the containers to better than 0.2°C during most of a run. Immediately before dissolving, the temperature is very close to 25°C. During dissolving, the temperature of the containers decreases by about 1.1°C due to the heat of solution of NaCl, and the vacuum chamber temperature is made to follow this.

4. Temperature Measurements

Temperatures are measured with No. 36 copper-constantan thermocouples, made of wire specially chosen for nonresponse to temperature gradients.⁶ Thermocouples are placed to indicate directly the following temperature differences: (1) between the two containers, (2) between one of the containers and the walls of the vacuum chamber, and (3) between the walls of the vacuum chamber and an ice bath. The first of these gives the important calorimetric data; the second is used to set the temperature control for the chamber; the third is used merely to insure that all work is done at 25°C. The second two measurements can also be used to get the heat of solution of NaCl, and, as a check on the reliability of the method, this was done for every run; the results⁶ compared very well with published data.^{7,8}

Thermocouple emf's were measured on a Rubicon Microvolt Potentiometer. The null detector was a chopper dc amplifier, with usable sensitivity (limited by noise) of 0.01 μ V for a single measurement, and about one-third this for the average of a number of measurements. Such an average corresponds to a temperature difference of about 10^{-4} C° and an energy difference of about 0.01 cal for the heat capacity used in these experiments.

5. Techniques

After the containers are loaded with water and silicone oil, the crystals are placed on the shelves and the lids screwed onto the containers. The assembled

⁷ F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, *Selected Values of Chemical Thermodynamic Properties*, National Bureau of Standards Circular 500 (U. S. Government Printing Office, Washington, D. C., 1952).

⁸ S. G. Lipsett, F. M. G. Johnson, and O. Maass, *J. Am. Chem. Soc.* **49**, 1940 (1927).

containers and their carriage are carefully lowered into the vacuum chamber, which is then sealed and pumped down to forepump pressure. A small amount of dried air is admitted in order to provide heat transfer for establishing the desired initial temperature. (This establishment cannot be done adequately at atmospheric pressure because subsequent pumping will cool things in an erratic manner.) The temperature of the water circulating around the chamber is then varied until the containers reach a temperature within a few tenths of a degree of 25°C, after which the water temperature is set at 25°C. The chamber is then pumped down to ultimate vacuum of about 2×10^{-6} mm Hg.

At this point the containers still have slightly different temperatures. Heat is added to the colder one by focusing light on it from a 150-W lamp through the glass window in the chamber, until the two temperatures are sufficiently close.

To make sure of equilibrium, the apparatus now is left undisturbed overnight. After this overnight period, the container temperature, for various runs, ranged from 0.18°C below to 0.32°C above 25°C, and the magnitude of the temperature difference between containers ranged from 0.4×10^{-3} to 6.6×10^{-3} °C.

After the overnight period, all temperatures are measured every few minutes for 2 or 3 h, to establish any drifts, and to make minor adjustments, if necessary, of the vacuum chamber temperature. Then the crystals are mixed with the water by turning on a motor which rocks the containers back and forth about once every 10 sec. Two minutes before this the temperature control setting for the chamber is reduced, so that the chamber walls will have about the same temperature as the solutions. The motor is on for 50 min, which is more than twice as long as necessary to dissolve the NaCl. Temperatures are measured as often as possible during this time. Then the motor is turned off, and temperatures measured every few minutes for another 2 or 3 h. In order to test for any asymmetry in the mechanical energy given to the containers, the motor is now again turned on for 50 min and temperatures measured.

III. ANALYSIS OF DATA

A. Optical

F-center concentrations were calculated using

$$n_F = 1.5 \times 10^{16} \text{ OD}_F/d, \quad (1)$$

where n_F is the concentration of centers per cm³, OD_F is the peak optical density of the absorption band, and d is the thickness of the crystal in cm. Equation (1) corresponds to the Smakula equation (assuming a Lorentzian form of the absorption) with a width at half maximum of 0.50 eV and an oscillator strength of 0.79.⁹ *M*-center concentrations were estimated accord-

⁹ This value of the oscillator strength of the *F* band falls within

ing to

$$n_M \simeq 10^{16} \text{ OD}_M/d, \quad (2)$$

which corresponds to an *M*-band half-width of 0.18 eV and a ratio of the oscillator strength of the *M* band to that of the *F* band of 0.5.¹⁰ The baseline from which the height of the *F* band was measured was the straight line drawn between the two points of minimum optical density, at about 300 and 650 mμ. The minimum optical density occurring near 650 mμ was used as the zero of the *M* band. No attempt was made to correct the *F* absorption for any underlying *M* transitions.¹¹

B. Calorimetric

1. Derivations and Definitions

The heat, $Q(T)$, of a reaction occurring isothermally at the temperature T , is the heat which must be removed from the system, during the reaction, in order to keep the temperature at T . If the reaction occurs adiabatically, then the heat will be

$$Q(T_i) = \int_{T_i}^{T_f} h_f dT, \quad (3)$$

where T_i and T_f are the initial and final temperatures, and h_f is the heat capacity of the system in the final chemical state. Equation (3) follows from the first law of thermodynamics, assuming that no work is done. In the case where the process is not adiabatic, one can readily show⁶ that

$$Q(T_i) = \int_{T_i}^{T_f} h_f dT - \int_{t_i}^{t_f} c(T - T_0) dt - Q_M, \quad (4)$$

where t_i and t_f are times before and after the reaction takes place, T_0 is the temperature of the environment, and c is a constant describing the heat gain of the system due to conduction, convection, and radiation from the surroundings. (As here defined, c is a negative number.) Q_M represents energy added to the system by mechanical means.

In the experiment described in this paper, we are interested in the *difference* in the heats of reaction occurring in two systems: (a) normal NaCl dissolving in water and (b) irradiated NaCl dissolving in water. One can show,⁶ by subtracting equations such as (4)

about 10% of experimentally determined values. For a summary of these, see W. T. Doyle, Phys. Rev. **111**, 1072 (1958).

¹⁰ This value for the oscillator strength ratio does not disagree with the values found for KCl and KBr by B. J. Faraday, H. Rabin, and W. D. Compton, Phys. Rev. Letters **7**, 57, 433 (1961).

¹¹ F. Okamoto, Phys. Rev. **124**, 1090 (1961).

for the two systems:

$$Q_2(T_{i2}) - Q_1(T_{i1}) = \int_{T_{f1}}^{T_{f2}} h_{f1} dT - \int_{T_{i1}}^{T_{i2}} h_{f1} dT \\ + \int_{T_{i1}}^{T_{f2}} (h_{f2} - h_{f1}) dT - \int_{t_i}^{t_f} [(c_2 - c_1)(T_1 - T_0) \\ + (c_2 + 2c_{12})(T_2 - T_1)] dt - (Q_{M2} - Q_{M1}), \quad (5)$$

where the subscripts 1 and 2 refer to the two different systems, and c_{12} is a constant describing the direct heat exchange between the two systems. Since the heat capacity of our solution has a negligible dependence upon temperature, we can take h_f out of the integrals. Then, using the symbol Δ to represent the difference (number 2 minus number 1) of a quantity in the two systems, we find

$$\Delta Q = h_{f1}(\Delta T_f - \Delta T_i) + \Delta h_f(T_{f2} - T_{i2}) \\ - \int_{t_i}^{t_f} [\Delta c(T_1 - T_0) + (c_2 + 2c_{12})\Delta T] dt - \Delta Q_M. \quad (6)$$

In the above equation, ΔQ is the difference in the heat of reaction of the contents of the two calorimeter containers. We consider this to be made up of three parts:

$$\Delta Q = \Delta Q_{\text{sol}} + \Delta Q_{\text{chem}} + \Delta Q_x, \quad (7)$$

where ΔQ_{sol} is the difference in the heat of solution of the salt due to inequalities in mass and in the initial temperatures of the two systems, ΔQ_{chem} is the difference due to any actual chemical reaction (other than dissolving) which might occur between an irradiated crystal and water (discussed in Sec. IV below), and ΔQ_x is the energy necessary to rearrange the atoms and electrons in the irradiated crystal to form vacancies, trapped electrons, etc. ΔQ_x is what we call the "stored energy" due to the x-ray irradiation.

It turns out that ΔQ_{sol} is small, and for some of our data negligible. ΔQ_{chem} is probably large, and will be discussed in Sec. IV.

In Eq. (6), the first term on the right-hand side is the primary experimental term, and would be the only one if the calorimeter were perfectly adiabatic and perfectly balanced. The other terms may be considered as correction terms. It turns out that the second and fourth terms are small, while the third term is for some runs large and for some runs small.

2. Method

The data consist of direct measurement of thermocouple emf's corresponding to T_1 , T_0 , and ΔT as a function of time, as well as the amounts of salt, water, silicone oil, etc., in the containers. In order to perform the calculations indicated in Eq. (6), it is also necessary

to know the heat loss constants c_2 , Δc , and c_{12} . These can be obtained from the measurements of temperature as a function of time during periods when there is no mixing. It was found⁶ that c_{12} was negligible, that c_2 was consistent with an emissivity of the gold plating of 0.06, in reasonable agreement with a value reported in the literature,¹² and that $|\Delta c|$ was about 5% of c_2 . Heat flow by conduction through the thermocouple wires and the residual air was calculated to be negligible.

The difference in mechanical energy given to the two containers, ΔQ_M , was obtained at the close of each run by turning on the mix motor again for the same time that it was on while the crystals were dissolving. This quantity was always in the same direction (perhaps one container tipped through a larger angle than the other) but smaller than the errors assigned to other terms.

h_{f1} , Δh_f , and ΔQ_{sol} can be readily obtained from the known masses of the constituents and the temperatures.

IV. THE SOLUTION OBTAINED WHEN COLORED NaCl DISSOLVES

It is necessary to consider whether the chemical nature of a solution of colored NaCl is different from that of uncolored NaCl. If so, then there may be energy involved, which would have to be taken into account in the interpretation of our calorimetric data; i.e., there will be a ΔQ_{chem} .

The situation seems relatively clear for the case of additively colored salt, where there are excess alkali atoms. Then, upon dissolving, hydroxide and free hydrogen are formed.^{9,13,14} However, the case of irradiated salt dissolved in water is not nearly so clear. Irradiated crystals, like additively colored crystals, contain halogen vacancies occupied by electrons, which might behave chemically like free alkali. But they must also contain other defects, such as alkali vacancies or interstitial halogens occupied by holes, in order that the net result is stoichiometry. (Experimental indications that chlorine does not escape from irradiated NaCl are discussed below.) These latter defects might behave chemically like free halogen. The problem, then, is this: As water attacks the surface of irradiated NaCl, do the trapped electrons and holes find each other (i.e., do the F -center electrons find neutral chlorine atoms), thus yielding merely a solution of NaCl in water, or do they react with the water and form other things? The products of such reactions might include H_2 , OCI^- , and OH^- in various amounts.

There is experimental evidence that such reactions do occur. Hacskaylo, Otterson, and Schwed¹⁵ measured,

¹² J. T. Gier, R. V. Dunkle, and J. T. Bevans, *J. Opt. Soc. Am.* **44**, 558 (1954).

¹³ F. G. Kleinschrod, *Ann. Physik* **27**, 97 (1936).

¹⁴ A. B. Scott and M. E. Hills, *J. Chem. Phys.* **28**, 24 (1958).

¹⁵ M. Hacskaylo, D. Otterson, and P. Schwed, *J. Chem. Phys.* **21**, 1434 (1953). We are grateful to Dr. Otterson for correspondence regarding this work.

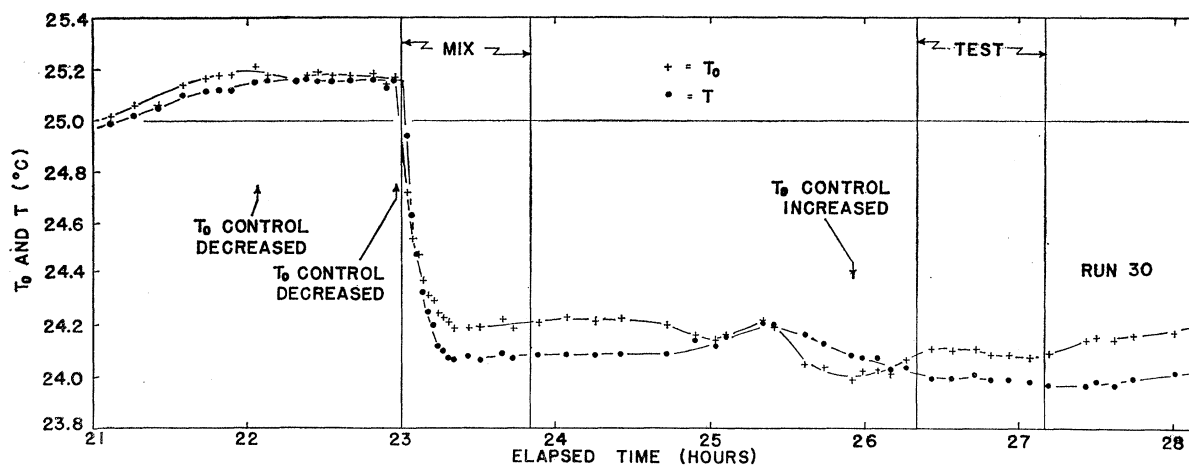
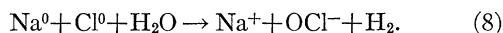


FIG. 3. The temperature of the walls of the vacuum chamber (T_0) and of one of the calorimeter containers (T) during a typical run. Time is measured from the time the containers are sealed. T was not measured directly, but was calculated from measurements of T_0 and $T - T_0$. "Test" means that the mix motor was turned on a second time in order to check for mechanical energy added to the system.

by a sensitive chemical indicator method, the free chlorine concentration in NaCl crystals which had been colored by x raying and by electrolysis. They compared this with the concentration of vacancy pairs as determined by flotation. The result, for x-rayed crystals, was 0.6 free chlorine atom per vacancy pair, at a concentration of 2.5×10^{18} pairs per cm^3 . Also, pH measurements on solutions of x-rayed NaCl yielded a figure of 0.12 free sodium atom per vacancy pair. The low value of this number is ascribed by these workers to the fact that the reaction of free chlorine with the water is such as to reduce the concentration of hydroxyl ions, thus affecting the pH measurements. These investigators also found that a crystal which had been irradiated and then annealed showed no free chlorine or sodium, which is an indication that over-all stoichiometry is not changed by the irradiation. (See below for an identical conclusion based on our work.)

Burns and Williams,¹⁶ working with NaCl irradiated by 1.25-MeV electrons, measured the hydrogen evolved when the crystals were dissolved, and also the free chlorine content. There was good agreement between these two quantities. Their results confirm the work of Hacskaylo *et al.*

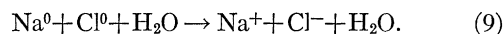
We must now decide upon the specific chemical reaction involved. We know from the experiments discussed above that hydrogen gas and free chlorine are produced when irradiated NaCl is dissolved, and that the solution is alkaline. Also, it is known¹⁷ that free chlorine reacts with water, especially when alkaline, to form hypochlorous acid, HOCl. It appears, then, that the reaction of interest is



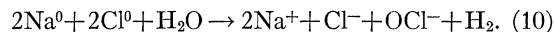
¹⁶ W. G. Burns and T. F. Williams, *Nature* **175**, 1043 (1955). We are grateful to Dr. Burns for correspondence regarding this work.

¹⁷ L. Pauling, *General Chemistry* (W. H. Freeman & Co., San Francisco, 1954), 2nd ed., p. 268.

(Note that we are dealing here with single atoms of chlorine, rather than chlorine molecules.) Reaction (8) is to be compared in energy with the case where NaCl solution is formed



We do not know in what form the free chlorine might exist in the crystal. We are here assuming that it exists as separated atoms, so that we assume that reaction (8) is the one of interest. However, if the free chlorine should exist as Cl_2 molecules, then the reaction might be



The right-hand side of Eq. (9) is a lower energy state than the right-hand side of Eq. (8) by 3.57 eV.⁷ Thus, if reaction (8) occurs for every F center, then the heat that we measure in our experiment is too low by 3.57 eV per F center; that is, ΔQ_{chem} is -3.57 eV per F center.

We now discuss the extent to which reaction (8), instead of (9), occurs for F centers produced by x rays. The work of Hacskaylo *et al.*¹⁵ indicates that this occurs for about 0.6 of the F centers, with accuracy such that a ratio of unity is not inconsistent. It is possible that the fraction would be closer to unity for our experiments than for those of Hacskaylo *et al.*, since those investigators dealt with defect densities a factor of four higher than the largest one we had, so that in their specimens there was a greater opportunity for an F -center electron to attach itself to a neutral chlorine atom before the chlorine could react with the water. On the other hand, our dissolving conditions might be considered relatively "dirty"—the water was only singly distilled and there was silicone oil and chromium in contact with the solution—so that there might have been a catalytic action which would affect things. This seems to us unlikely. For simplicity, we prefer to assume that the

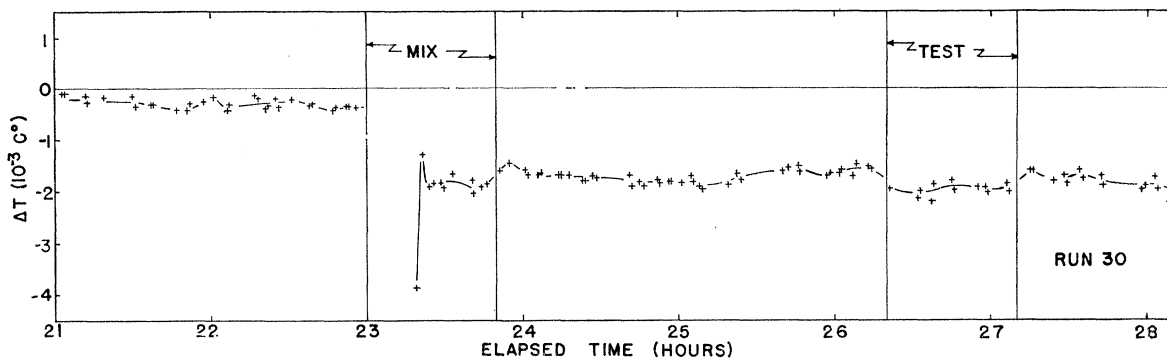


FIG. 4. The temperature difference between the two calorimeter containers during a typical run. For this run, the irradiated crystal was in container number 1, so ΔT decreases upon dissolving. See Fig. 5 for details during the dissolving period.

fraction is unity, and thus to add 3.57 eV per F center to our measured heats. Any new knowledge on this point might necessitate a correction.

We wish to emphasize here that we are not confident about this question. It is to us the weakest link in the quantitative interpretation of our data. Really settling the matter would appear to be a challenging problem in chemistry.

V. RESULTS

A. Presentation of Data

Data for a typical run are shown in Figs. 3, 4, and 5. Figure 3 shows the temperature of one of the containers (T) and of the vacuum chamber (T_0) before, during, and after mixing. Figure 4 shows the difference in temperature of the two containers (ΔT) during the same times. Figure 5 shows, on a different scale, ΔT during the mix period.

Table I gives the results of the measurements and calculations for all runs, and shows the importance of the various terms in Eqs. (6) and (7). The various experimental runs may be divided into three categories: (1) the "regular" runs, where the NaCl in one of the containers had been irradiated, (2) the "zero" runs (numbers 25, 27, and 37), where nonirradiated NaCl was used in both containers, and (3) the "thermally bleached" runs (numbers 33, 35, and 36) using crystals which had been irradiated and then annealed to where the F -center density was of the order of 10^{15} per cm^3 or less. Also, when irradiated crystals were used, they were sometimes placed in one container, and sometimes in the other.

Figure 6 is a graph of the total result given in Table I. Note that, in Table I, the heat loss terms (column I_3) are for some runs very large and for some runs small, but the total results, as shown in Fig. 6, are quite self-consistent. We consider this a good indication that the method and technique are adequate.

B. The Possibility of a Systematic Error

The data suggests that there is a small systematic error. If $+0.04$ cal is added to the results for all runs

(last column of Table I), more consistent points are obtained, in that the zero and thermally bleached data are closer to a null result, and there is better agreement in a comparison of data where the irradiated crystal was in container number 1 vs number 2. Such a systematic error might be caused by (1) the two containers of the calorimeter not "seeing" exactly the same surroundings temperature, T_0 , or (2) a small (but considerably larger than we thought) error in determining the mismatch in heat capacity of the containers from the masses of the materials of which they were constructed. If the above correction of 0.04 cal is made, then the "regular" run data shown in Fig. 6 would fit a straight line a little better than shown, with slope of 6.7 eV per F center and intercept of 8.5×10^{16} F centers per cm^3 . Since it is the slope which is important for this work, and it is essentially unchanged by whether we assume the correction, we need discuss it no further.

C. Corrections and Final Figure for the Stored Energy

It is desired to obtain, from the data, a value for the "stored energy" associated with an F center. The slope

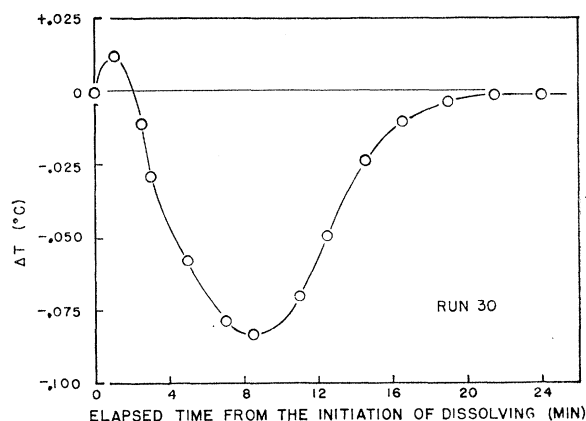


FIG. 5. Details of the temperature difference between the two containers during the dissolving period. This is the "mix" part of Fig. 4 plotted in more detail and on a different scale.

TABLE I. Results of measurements and calculations for all experimental runs. All energies (last six columns) are in units of 10^{-3} calorie. The chemical effect discussed in Sec. IV of the text, and the possible systematic error discussed in Sec. V are not included in this table. The final column is plotted in Fig. 6.

Run No.	F center ^a conc. ($10^{17}/\text{cm}^3$)	M center ^a conc. ($10^{16}/\text{cm}^3$)	Container which has irradiated crystal	I_1^b	I_2^b	I_3^b	$-Q_m^c$	$-Q_{\text{sol}}^d$	Total ^e
25	0	0	...	-82 ± 19	+17	-17 ± 9	-10	-3	-95 ± 21
27	0	0	...	$+8 \pm 19$	+14	-59 ± 9	-11	+3	-46 ± 22
37	0	0	...	$+41 \pm 21$	+13	-94 ± 19	-11	+12	-39 ± 29
31	2.47 ± 0.04	0.84 ± 0.08	2	$+139 \pm 13$	+7	$+78 \pm 10$	-10	-12	$+201 \pm 17$
34	2.70 ± 0.02	1.32 ± 0.08	1	-64 ± 14	-2	-195 ± 39	-11	+26	-245 ± 42
30	2.77 ± 0.02	1.10 ± 0.08	1	-126 ± 15	-11	-74 ± 17	-11	-23	-245 ± 23
32	3.26 ± 0.02	1.72 ± 0.08	1	-342 ± 18	-3	$+68 \pm 16$	-10	-20	-306 ± 24
26	4.37 ± 0.04	2.44 ± 0.07	1	-429 ± 22	+3	-31 ± 5	-10	0	-467 ± 23
28	6.34 ± 0.11	3.99 ± 0.09	2	$+688 \pm 25$	+8	-84 ± 11	-11	+17	$+618 \pm 28$
29	6.48 ± 0.17	4.40 ± 0.07	1	-655 ± 26	+2	-15 ± 8	-11	-29	-707 ± 27
35 ^f	2.46 ± 0.02	1.12 ± 0.08	2	$+6 \pm 12$	+4	-24 ± 9	-11	-1	-26 ± 16
33 ^f	3.48 ± 0.03	1.96 ± 0.08	2	$+177 \pm 22$	+5	-187 ± 24	-11	-11	-27 ± 33
36 ^f	4.28 ± 0.04	3.00 ± 0.08	1	-40 ± 12	-3	$+60 \pm 10$	-10	+8	$+14 \pm 16$

^a F - and M -center concentrations were calculated by the Smakula formula, using an oscillator strength of 0.79 for F centers and 0.40 for M centers. The errors assigned are from the determination of optical density and thickness.

^b These columns list the first three terms on the right-hand side of Eq. (6) of the text: $I_1 = hf_1(\Delta T_f - \Delta T_i)$ is the major experimental term, and would be the only term if the calorimeter were perfectly adiabatic and perfectly balanced. $I_2 = \Delta h_f(T_{f2} - T_{i2})$ is the correction necessary to take into account the slightly different heat capacities of the two containers with their contents. The experimental uncertainty is $\pm 1 \times 10^{-3}$ cal. $I_3 = -\int t_i^f [\Delta c(T_1 - T_0) + (c_2 + 2c_1)\Delta T] dt$ is the correction necessary to take into account the heat exchange between the two containers and their surroundings, and between the containers themselves.

^c ΔQ_M is the difference in the mechanical energy added to the two containers. The experimental uncertainty is $\pm 5 \times 10^{-3}$ cal.

^d ΔQ_{sol} is the difference in heat of solution in the two containers due to inequalities in masses and initial temperature of the constituents. The experimental uncertainty is $\pm 1 \times 10^{-3}$ cal.

^e This is the sum of the previous five columns. It is equal to $\Delta Q_z + \Delta Q_{\text{chem}}$ as defined in Eq. (7) of the text. Except for the chemical effect and a possible systematic error, this would be the "stored energy."

^f For runs 35, 33, and 36 the irradiated crystals were thermally bleached before being dissolved. Bleaching temperatures were approximately 360, 600, and 360°C, respectively. The color-center concentrations given in this table for these runs refer to the concentrations before the thermal bleaching.

of Fig. 6 will give this after two corrections are made. The first correction is that associated with the chemical constitution of the solution of irradiated NaCl. As discussed in Sec. IV, this means that we must add 3.6 eV per F center to the 6.7 eV per F center obtained from Fig. 6. The second correction is for M centers. Since, as shown in Table I, the concentration of M centers is, for our data, always less than about 7% that of F centers, this correction need be only approximate. At present, it appears¹⁰ that the best model for the M center is a two-electron one—the F_2 model. We therefore assume that the stored energy associated with an M center (and also its chemical behavior) is the same as that of two F centers.

When the data are corrected for the chemical effect and for the M centers, we get 9.2 ± 0.3 eV for the stored energy of an F center. The uncertainty given here is the standard deviation coming from the spread of the data, and does not include any uncertainty in the chemical effect, the M -center model, or the oscillator strengths.

We now state what the stored energy per F center would be if the data were analyzed according to some other assumptions. If the chemical effect were completely absent, this figure would be 5.6 eV. If the M center had a stored energy equal to that of only one F center (but still behaved chemically like two F centers), the figure would be 9.9 eV. If the oscillator strength of the M center were twice as high as we assumed, the figure would be 9.6 eV. If the oscillator strength of the

F center were different from 0.79, then the stored energy per F center would be $[5.6(f/0.79) + 3.6]$ eV.

VI. DISCUSSION

A. The Two-Region Character of the Stored Energy Curve

The general form of our results, as shown in Fig. 6, is what is to be expected on the basis of growth curve data^{4,18-20} on F centers, where it is observed that during irradiation the F band at first grows quite rapidly, and then slowly. The transition between these two stages generally occurs¹⁸⁻²⁰ at F -center densities between 10^{16} and 10^{17} per cm^3 for Harshaw NaCl. Unfortunately, our data do not extend into the low coloration region, but it is clear from Fig. 6 that the stored energy per F center at low coloration must be smaller than at high coloration.

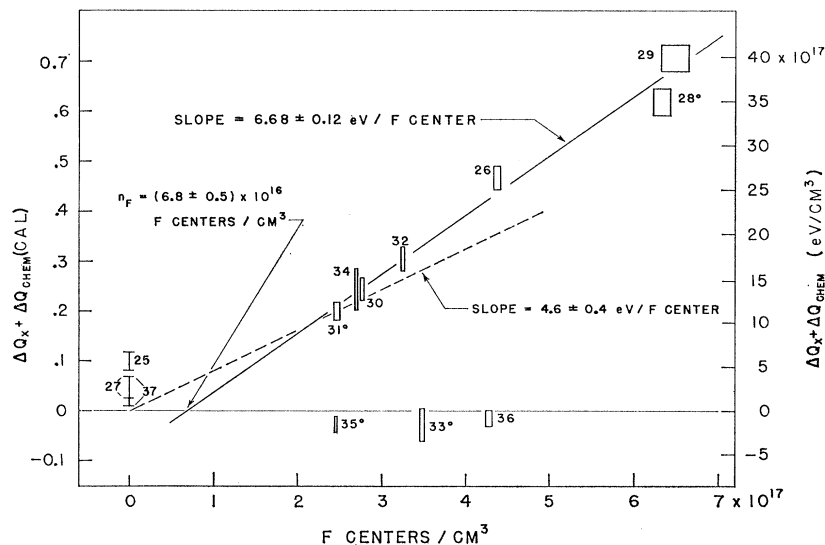
Our data behave, in agreement with the growth curve data, as if there are defects, perhaps chlorine vacancies, initially present in the crystals, such that it is relatively easy for the x rays to produce F centers until these initially present defects are used up. If the essential difference between the two regions of the growth curve is that in the initial region electrons are filling already-present vacancies, while in the later region vacancies must be produced by the x rays, then the difference in

¹⁸ R. B. Gordon and A. S. Nowick, Phys. Rev. **101**, 977 (1956).

¹⁹ H. Rabin, Phys. Rev. **116**, 1381 (1959).

²⁰ H. W. Etzel and J. G. Allard, Phys. Rev. Letters **2**, 452 (1959).

FIG. 6. The "stored energy," not corrected for the chemical effect discussed in Sec. IV, in x-rayed NaCl. The abscissa is the second column of Table I. The ordinate is the negative of the last column, except that, when the irradiated crystal was in container number 1 (points marked \circ), the last column itself is plotted. The number at each point is the number of the run (in chronological order). The solid straight line is obtained by a weighted least-squares fit of the "regular" runs, numbers 26, 28, 29, 30, 31, 32, and 34. The dashed line is discussed in Sec. VIA.



stored energy between the two regions would be the thermal energy for production of these vacancies. There does not seem to be evidence as to whether such vacancies, at room temperature, are of the nature of Frenkel defects, Schottky defects, or clusters of some sort. For purposes of further discussion, we will arbitrarily assume that the energy involved is 2.0 eV, which is the energy for Schottky defects.²¹

The dashed line of Fig. 6 indicates approximately the maximum slope to be expected in the low coloration region. Thus, the difference in slopes of the two regions would be 1.7 eV or greater. Then, assuming equal corrections for the chemical effect in the two regions, the difference in stored energies per F center would be 1.7 eV or greater. This is consistent with the ideas presented in the previous paragraph.

B. The Magnitude of the Stored Energy—Comparison with a Model

We now investigate what we might expect on the basis of theory to be the stored energy associated with an F center. Figure 7 shows the thermal energy levels for an electron in NaCl. According to Ferguson²² and Mott and Gurney,²³ the optical energy difference between the valence and conduction bands is 9.6 eV. If the band structures are simple (single valley), then this would also be the thermal energy difference.

The thermal activation energy to excite an F -center electron into the conduction band in NaCl is given by Mott and Gurney²⁴ as 1.89 eV. This figure includes the relaxation energy of the surrounding ions.

We must next consider the hole. Here we are on poor ground, since at room temperature there is not much optical absorption which can be attributed to trapped holes, except perhaps for the V_3 band at about $210 \mu\mu$, which in our specimens was small. Presumably there are holes trapped somewhere at room temperature, but, since they have not been detected, they must be in centers having very low oscillator strength, or very large width of absorption peak, or very low energy of absorption. The last two of these possibilities might occur if a number of holes were trapped at a cluster of atoms or vacancies. In any case, we have available some information which enables us to guess at the thermal dissociation energy of the holes. The work of Dutton and Maurer²⁵ on KCl and KBr indicates that, for hole centers stable at low temperature, the thermal dissociation energy is quite small—of the order of one-tenth the optical excitation energy. We will, therefore, assume for our case that the holes are trapped in a

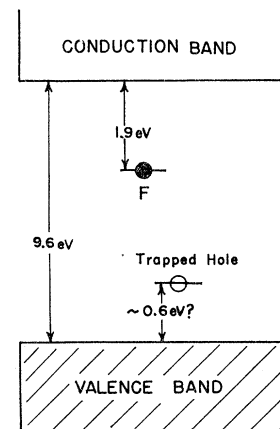


FIG. 7. Thermal energy level diagram for electrons in NaCl.

²¹ H. W. Etzel and R. J. Maurer, *J. Chem. Phys.* **18**, 1003 (1950).

²² J. N. Ferguson, *Phys. Rev.* **66**, 220 (1944).

²³ N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1948), 2nd ed., pp. 97, 268.

²⁴ Reference 23, p. 143.

²⁵ D. Dutton and R. J. Maurer, *Phys. Rev.* **90**, 126 (1953). See also reference 1, p. 73.

thermal depth of the order of 0.6 eV, which is one-tenth the optical depth of the V_3 center.²⁶

From Fig. 7, we then arrive at the conclusion that, when an F -center electron combines with a trapped hole, the energy release is about 7.1 eV. The total stored energy associated with the F center will be this plus the 2.0 eV (assuming Schottky defects) necessary to produce the vacancy pair: 9.1 eV. This is in excellent agreement with the value of 9.2 ± 0.3 eV derived from our data. But such good agreement is perhaps fortuitous, since we are not at all certain of the values of the energy to produce the vacancy (assumed to be 2.0 eV) and the stored energy of the trapped hole (assumed to be 0.6 eV). Moreover, the experimental figure of 9.2 eV includes the 3.6 eV associated with OCl production, which is not on firm ground.

Note added in proof. Two recent publications cast additional uncertainty upon the specific models we assumed for arriving at the thermal energy to produce the vacancy and the thermal energy of the trapped hole. D. A. Wiegand [Phys. Rev. Letters **9**, 201 (1962)] gives evidence for the existence of interstitial chlorine in NaCl irradiated with x rays at room temperature. F. Lüty [J. Phys. Chem. Solids **23**, 677 (1962)] gives evidence that the V_3 center is not a hole center.

If we take this agreement seriously, we can conclude two things: (a) X rays at room temperature do not produce appreciable numbers of defects other than those detected optically, unless such defects have a small stored energy; (b) trapped holes at room temperature are unlikely to be at a thermal depth greater than about one eV.

C. The Effect of Thermal Bleaching and the Possibility of Chlorine Escaping

The stored energy data on crystals which had been irradiated and then thermally bleached (run numbers 33, 35, and 36) indicates that the heat treatment returns the crystals to their initial condition. The same conclusion is obtained from the chemical work of Burns and Williams¹⁶ and of Hacskaylo *et al.*,¹⁵ although the accuracy of their work precludes setting very small limits on the amount of disarrangement still present. The work of Kobayashi²⁷ on the annealing of density changes produced by proton irradiation also supports this conclusion, as does the work of Pearlstein,²⁸ Kobayashi,²⁹ and Christy and Harte³⁰ on ionic conductivity changes produced by ionizing radiation.

When speculating about possible mechanisms for color center production by x rays, one sometimes wonders whether any chlorine escapes from the crystal in the process. Our result for the thermal bleaching enables us to set an upper limit to the amount of

chlorine that might escape. Assume that for each chlorine atom that escapes, an extra sodium atom is left in the crystal. When the crystal is subsequently dissolved in water, the excess sodium reacts with the water, releasing an energy of⁷ 1.9 eV per atom of sodium. This assumes that the binding energy of the excess Na (after annealing) in NaCl is the same as Na in the metal. A straightforward calculation,⁶ using this energy and the results of our thermally bleached runs, yields the result that no more than about 3×10^{16} chlorine atoms per cm^3 left the crystals during the irradiation and bleaching, for initial F -center densities in the vicinity of 3×10^{17} per cm^3 . Thus, a mechanism involving escape of chlorine cannot account for more than 10% of the F centers. This conclusion would not hold if sodium also escapes during our process, for then the figure given above would refer only to the excess of chlorine over sodium escaping.

D. Comparison with Other Work

The experiment which can be compared most directly with ours is that of Kobayashi.²⁹ He irradiated NaCl crystals with high-energy protons, and then measured the energy released as the crystals were heated from room temperature to 400°C, obtaining curves of energy release vs temperature. Some of the features of these curves were correlated with the behavior of optical absorption bands and electrical conductivity during annealing. Unfortunately, the crystals used in his stored energy experiment were so highly colored (about 3×10^{19} F centers per cm^3) that he could not measure the absorption spectra, but could only infer the color center densities by extrapolation from coloring data at smaller irradiations. The total measured stored energy divided by the inferred F -center density was 4.3 eV per F center, which is about one-half that of our work. This discrepancy is not surprising, since, as Kobayashi points out, his extrapolation of color center density is quite likely to overestimate the densities at such high irradiation. In addition, it is barely conceivable that 400°C was not a sufficiently high temperature to remove all of the stored energy.

A somewhat roundabout comparison can be made of our work with that of Etzel and Allard and of Feldtkeller. Etzel, and Allard²⁰ measured the coloration of NaCl crystals as a function of x-ray energy absorbed. They found that, in the early stage of coloration, 96 eV was absorbed for every F center produced, and this number increased considerably at the later stages. Feldtkeller³¹ measured the change in temperature of KBr crystals as they were irradiated, and found that in the early stage of coloration 90% of the absorbed energy became thermal energy, so that 10% was stored. If we assume this fraction for NaCl, and combine it with the datum of Etzel and Allard, we get 9.6 eV of

²⁶ W. H. Duerig and J. J. Markham, Phys. Rev. **88**, 1043 (1952).

²⁷ K. Kobayashi, Phys. Rev. **107**, 41 (1957).

²⁸ E. Pearlstein, Phys. Rev. **92**, 881 (1953).

²⁹ K. Kobayashi, Phys. Rev. **102**, 348 (1956).

³⁰ R. W. Christy and W. E. Harte, Phys. Rev. **109**, 710 (1958).

³¹ E. Feldtkeller, J. Phys. Chem. Solids **4**, 50 (1958).

stored energy per F center. (It is necessary to use the low coloration data of Etzel and Allard because, apparently, Feldtkeller's work was done at low coloration. Presumably, the high coloration value of stored energy would differ from the low coloration value by 2.0 eV, assuming Schottky defects.) In view of its uncertainties, this figure may be considered as consistent with our value.

VII. SUMMARY

The stored energy in NaCl irradiated with x rays at room temperature has been measured by solution calorimetry, for F -center densities between 2.5×10^{17} and 6.5×10^{17} per cm^3 . The stored energy per F center is the sum of three numbers: the measured excess heat of solution, a correction for the M centers in the crystals, and a correction for what we believe to be a difference in the chemical nature of a solution of colored NaCl and of uncolored NaCl. Our analysis yields a stored energy per F center of 9.2 ± 0.3 eV, based upon the following specific assumptions: (1) The oscillator strength for the F center is 0.79; (2) the oscillator strength for the M center is 0.4; (3) the stored energy associated with an M center is equal to that of two F centers; (4) when x-rayed NaCl is dissolved in water,

one hypochlorite ion (OCl^-) is formed for every F center that was in the crystal. We consider the first three of these assumptions to be sufficiently accurate so that any new information regarding them is unlikely to change our result by more than a few percent. The fourth point, however, involves 3.6 of the 9.2 eV, and is a major difficulty in the interpretation.

Our value of 9.2 eV is compared with a simple energy level scheme for the F center which yields a value of 9.1 eV. This scheme, however, involves two questionable assumptions: (1) holes at room temperature have a thermal binding energy of 0.6 eV, (2) the thermal energy for rearrangement of ions in order to produce the chlorine vacancy for the F center is 2.0 eV—as if Schottky defects are produced.

From the result that heat treatment removes all of the stored energy, we conclude that chlorine does not leave a crystal during x raying or subsequent heating.

ACKNOWLEDGMENTS

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