electronic into electronic energy (Hg′+Na) and of electronic energy into a small amount of vibration (Hg′+various molecules). Possibly resonance is important in the transfer of vibration into vibration, but is certainly not important in the transfer of vibration into rotation. The energy of recombination of a colliding pair like N+N is not readily transferred by resonance

to electronic excitation of a third body but more probably is distributed over the various degrees of freedom of the collision complex. Furthermore, in exchange reactions resonance is not effective.

In general, resonance is ineffective in collision processes in which nuclei change positions by appreciable amounts.

Generation of Color Center Precursors in Alkali Halides by Electrolysis

MICHAEL HACSKAYLO AND GERHART GROETZINGER
Lewis Laboratory, National Advisory Committee for Aeronautics, Cleveland, Ohio
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Two types of imperfections (designated as color center precursors) are created in NaCl crystals when they are subjected to electrolysis. Both of these types are present in a crystal not colored by the electrolysis and lead upon irradiation by x-rays to the development of temporary color centers in much larger numbers than are ordinarily produced and to permanent centers in about the same numbers as result when a crystal is directly colored by electrolysis. In crystals colored directly by electrolysis, only the former type of precursor is present. The properties of crystals containing precursors and of those containing color centers derived from precursors have been studied and compared with those of crystals in the other previously known states. A proposal regarding the nature of the second type of precursor is presented.

I. INTRODUCTION

THE fact that it is possible to produce color centers in ionic crystals is of special interest in the field of solid state physics for essentially two reasons. First, they represent themselves a type of imperfection that is relatively easy to study. Second, it is possible to draw conclusions regarding other types of imperfections through their influence on the tendency of color centers to be formed under the proper circumstances.

Essentially three ways of producing color centers in alkali halides have been reported: irradiation of the crystal with x-rays; exposure of the heated crystal to alkali metal vapors; and electrolysis of the heated crystal (by the use of a pointed cathode and a flat anode). While irradiation with x-rays leads to color centers that are bleached out upon application of light of wavelengths corresponding to one of their absorption bands, the other two methods of coloring lead to permanent color centers which cannot be destroyed by irradiation with light.[1] The formation of color centers is accompanied by changes in other physical properties; for example, it has been reported that the density of CaF$_2$ decreases upon coloration by electrolysis[2] and the density of KCl decreases upon coloration by irradiation with x-rays.[3] An excess of alkali metal after additive coloring has been observed in NaCl[4] and in KCl.[5]

On the other hand, the extent to which nonpermanent color centers are produced is affected if a crystal undergoes plastic flow before irradiation.[6] Moderate amounts of plastic flow increase the extent to which the crystal is colored by such treatment while large amounts lead to a diminution of the colorability.

We have found that when a crystal is subjected to electrolysis in such a fashion that no coloration is produced, the nature of the color center formation resulting from irradiation by x-rays is altered in the following way. First, the number of nonpermanent color centers is appreciably increased compared to that occurring in a normal crystal irradiated under the same conditions. Second, in addition, permanent color centers are formed, an effect which does not occur when a normal crystal is exposed to x-rays.

It seems reasonable to suppose that this change in the susceptibility for the formation of the two types of color centers is indicative of the presence of new imperfections in the crystal. Reserving for the time being any attempt to specify the nature of these imperfections, we will designate them as color center precursors.[7] There are evidently two types of such precursors, the first kind leading to nonpermanent, the second kind to permanent color centers. The precursors leading to the permanent color centers are metastable in the sense that they persist when the crystal is subjected to heat

[1] See, e.g., P. W. Pohl, Physik. Z. **39**, 36 (1938); N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940); F. Seitz, Revs. Modern Phys. **18**, 384 (1946).
[2] E. Mollwo, Gött. Nach. No. **6**, 79 (1934).
[3] Estermann, Leivo, and Stern, Phys. Rev. **75**, 627 (1949).
[4] A. L. Hughes, Revs. Modern Phys. **8**, 294 (1936).
[5] A. B. Scott and L. P. Bupp, Phys. Rev. **79**, 34 (1950).

[6] K. Przibram, Z. Physik **41**, 833 (1927); Burstein, Smith, and Davisson, Phys. Rev. **86**, 615 (1952); for a complete account of the older work see, e.g., F. Seitz, Phys. Rev. **80**, 241 (1950).
[7] Strictly speaking, the vacancy pairs associated with the production of color centers in ordinary crystals are also precursors. We prefer to reserve this term in the present paper, however, for the precursors generated by electrolysis.

or light in the visible region but are irreversibly converted to color centers when the crystal is exposed to irradiation of sufficiently short wavelengths. Consequently, a crystal containing such precursors can be considered to be in a metastable state.

The object of this investigation was to study the properties of crystals containing precursors and crystals containing color centers derived from precursors. In order to carry out this program, measurements of the absorption spectrum, the density, and chemical composition were performed on such crystals. For the purposes of comparison, similar measurements were performed on crystals colored by irradiation with x-rays in the normal state and by the pointed cathode method, in which cases some results reported in previous investigations were checked and supplemented.
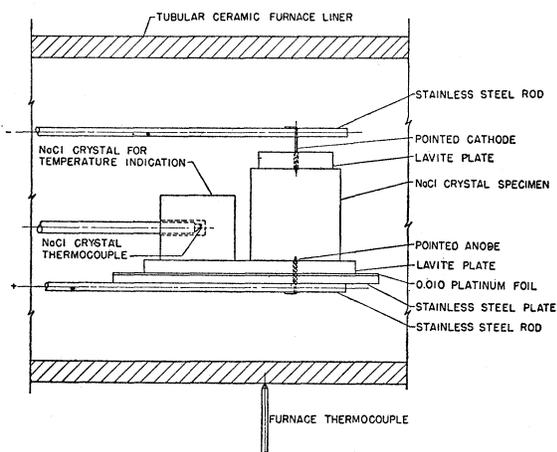

FIG. 1. Arrangement for subjecting crystals to electrolysis at elevated temperatures. In case a flat anode is desired, the lower lavite plate and the pointed anode are removed so that the crystal rests on the platinum foil.

II. EXPERIMENTAL PROCEDURE

The NaCl crystals used in these experiments were obtained from the Harshaw Chemical Company. In order to subject the crystals to electrolysis they were mounted in a Globar furnace in the way shown in Fig. 1. Two stainless steel rods served as the support for the crystal assembly and as part of the electrical circuit supplying the current for the electrolysis. The two electrodes making contact with the crystal were of nichrome wire filed to sharp points at the ends. In case a flat anode was preferred, the lower pointed electrode and lavite plate were removed so that the crystal made contact with the platinum foil. Current was supplied by a 360-volt battery with a 13,000-ohm resistor and a recording ammeter in series with the crystal. In all cases the furnace was brought up to a steady temperature before the crystals were inserted, the exterior of the ceramic tube being kept at 875°C. In order to determine the temperature of the electrolyzed crystal inside the furnace, a second crystal containing a thermocouple

connected to a Brown recording potentiometer was mounted close to the first crystal.

For the irradiations with x-rays, a Machlett A.E.G. 50 beryllium window tube was used which was operated at a voltage of 50 kv and a current of 30 ma. During the irradiation the crystals were kept in a dried helium atmosphere, the beryllium window being a part of the container in which the helium gas was kept at a slight positive pressure.

As a general rule, the crystals used were freshly cleaved on all sides at the last possible moment before the start of an experiment.

The absorption spectra of the NaCl crystals were obtained with a Beckman spectrophotometer model DU which permitted measurements in the spectral range of 210–1000 mμ. To provide the sensitivity necessary for the determination of the absorption of very densely colored crystals, the phototube of the spectrophotometer was replaced with a dry ice cooled type 5819 photomultiplier tube used in conjunction with a scale of 4096 counter. Since it was impossible to measure with this system both the intensity of the light incident upon the crystal and that transmitted by it, the following indirect procedure was used. First, the light intensity of the source was adjusted so that with the colored crystal in place the counting rate was about three times background. Next, the crystal was replaced by a gray filter (exposed and developed photographic film) of sufficient density that the resulting counting rate of the detector was still below saturation. The ratio of the two counting rates equaled the ratio of the transmission coefficients of the crystal and the filter. Finally, the transmission coefficient of the filter was measured in the usual fashion with a diminished source intensity. The transmission coefficient of the crystal is, of course, the product of the ratio of the coefficients and the coefficient of the filter.

Density measurements were made by the suspension method.[8] Twelve or so pieces of crystal were measured together, half of which were specimens which had been subjected to the particular treatment under investigation and the other half, control specimens that had not been treated but came from adjacent parts of the same crystal. The pieces, which were of different size in order to distinguish the two groups, were introduced into a 200-ml graduated cylinder filled with about 30 ml of the suspension liquid. This cylinder was kept almost completely immersed in a 60-gallon water bath. To make the measurement, the temperature of the bath was slowly raised until all the crystals in the suspension liquid were at the bottom of the graduated cylinder. Heating of the bath was then discontinued, and it was cooled at a rate of approximately 0.01°C per minute by means of manually controlled cooling coils. The

[8] D. A. Hutchison and H. L. Johnston, J. Am. Chem. Soc. 62, 3169 (1940); Phys. Rev. 62, 32 (1942); D. A. Hutchison, Phys. Rev. 66, 144 (1944); J. Chem. Phys. 10, 383 (1945); H. L. Johnston and D. A. Hutchison, J. Chem. Phys. 8, 869 (1940).

temperature at which each of the crystals first cleared a brass wire mesh placed near the bottom of the cylinder was recorded. It was found that introducing this mesh improved the reproducibility of the results.

The suspension liquid used for the density determination of NaCl was ethylene bromide.[9] The density of the ethylene bromide used in this experiment was determined in this laboratory to be 2.17820 g/cm³ at 20°C[10] which is close to the value of 2.17955 g/cm³ at 20°C obtained by Anderson.[11] In view of the fact that it would have been rather cumbersome to determine its density at another temperature with the equipment at hand, use was made of the volume thermal expansion coefficient of the liquid following from the measurement of Anderson. These measurements show that the density is a linear function of the temperature between 18° and 20°C, the thermal coefficient of expansion α being equal to $9.41 \times 10^{-4}/°C$. The thermal expansion coefficient β of NaCl can hardly depend to a great extent on the treatment to which the crystals were subjected, and therefore, the usual value[12] of $1.21 \times 10^{-4}/°C$ was used in our computations. The difference in the density $\Delta \rho$ between two specimens is then given by the relation

$$\Delta \rho = -\rho_0(\alpha - \beta)\Delta T,$$

where ρ_0 is the density of the normal crystal at the suspension temperature and ΔT the difference between the suspension temperatures. The crystals used had approximate dimensions of $0.3 \times 0.3 \times 0.08$ cm and $0.2 \times 0.4 \times 0.08$ cm. Before they were immersed in the suspension liquid they were out-gassed at a temperature of 100°C for twenty minutes.

To determine the amount of free sodium, samples of crystals were dissolved in water and the hydrogen ion concentration was measured using a Beckman pH meter model 50. Before dissolving the crystals in the triply distilled water, the surface layers were cleaved off to remove any contaminants and, in the case of the crystals that had been subject to electrolysis, the portions that had not carried any of the current were cleaved off. Any excess alkali present formed the corresponding hydroxide upon solution, with a resulting increase in pH which measured the departure from the stoichiometric ratio. A similar quantitative estimate of any excess halogen present could not be made.

III. RESULTS

A. Production of the Metastable State

There are essentially two ways of producing crystals in the metastable state. In the first place, the color cloud in an electrolytically colored crystal can be
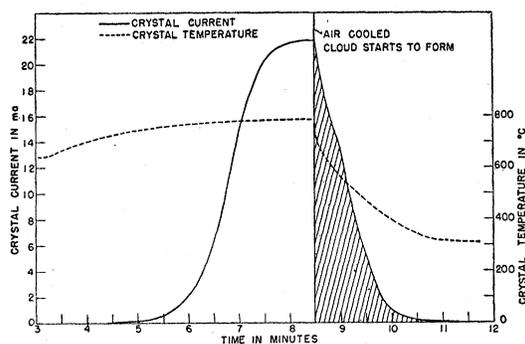

FIG. 2. Crystal temperature and electrolytical current as a function of the time at which the crystal was introduced and removed from a furnace at a temperature of 875°C.

removed either by reversing the polarity of the current before the cloud has spread from the cathode all the way to the anode or by continuing the flow of current in the same direction after the cloud has reached the anode.[13] Crystals treated in this manner were found to be in the metastable state. The second method consists of subjecting the crystals to electrolysis in such a fashion that no coloration is produced. The exact circumstances leading to this condition are not completely understood, but if the crystal is treated in essentially the normal fashion, such a result is often obtained with the pointed cathode and flat anode and, still more frequently, with two pointed electrodes. Since the second method is the more convenient one, it was used in most of our work.

Figure 2 shows the typical behavior of the electrolytic current through a crystal heated in the furnace. Two pointed electrodes were used in the way described above. The dashed curve in connection with the right-hand scale shows the temperature of the crystal as a function of the time after it was inserted into the
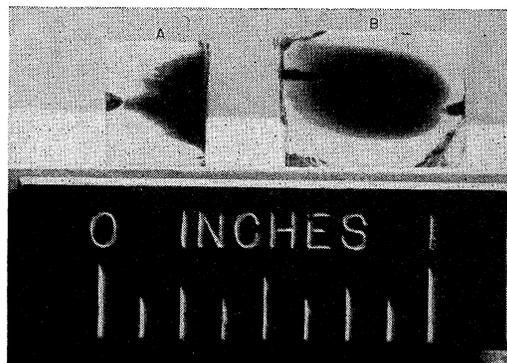

FIG. 3. NaCl crystals containing a region originally in the metastable state by electrolysis after coloration of x-rays and subsequent bleaching of nonpermanent centers. Left crystal: metastable state was obtained by a pointed cathode and a flat anode. Crystal to the right: by a pointed cathode and a pointed anode.

[9] Obtained from Ethyl Corporation of America.
[10] We are indebted to Dr. P. Wise for making these measurements.
[11] B. W. Anderson, Gemmologist 9, 141 (1940).
[12] Handbook of Chemistry and Physics (Chemical Rubber Publishing Company, Cleveland, 1949), p. 516.
[13] O. Stasiv, Gött. Nach. 50, 387 (1933).

TABLE I. Relative differences $\Delta\rho/\bar{\rho}_0$ of the densities with respect to the average density of the untreated NaCl crystals $\bar{\rho}_0$ at approximately 26°C.

Column	1	2	3		4		5	6	7
Color	Uncolored		Nonpermanently colored		Permanently and nonpermanently colored			Permanently colored	
State	Normal	Metastable state	Irradiation in normal state		Irradiated in metastable state		Irradiated after colored by electrolysis	Electrolytically colored	Bleached after irradiation in metastable state
			(a)	(b)	(a)	(b)			
Radiation time on each side of crystal			21 hours 21 hours	28 hours 66 hours	20 hours 22 hours	24 hours 65 hours	48 hours 68 hours		
$-\Delta\rho/\bar{\rho}_0\times10^5$	3.70	5.55	4.56	9.98	22.5	46.9	32.3	6.15	4.53
	2.94	3.91	3.74	9.12	20.8	46.9	31.5	6.15	3.65
	0.36	1.42	3.74	8.30	19.2	41.7	24.1	5.33	2.94
	−2.90	4.99	3.74	7.48	15.1	35.3	23.3	4.47	2.18
	−2.90	1.68	3.74	7.48	13.5	27.5	21.7	7.78	1.26
	0.40	0.00	2.92			45.2		7.78	
	−0.40	4.99	7.05			44.3		5.30	
	−0.40	2.49	6.24			41.7		1.16	
	−0.40	0.80	6.24			39.6		1.16	
	−0.40		5.42			39.1		0.34	
$[-\Delta\rho/\bar{\rho}_0\times10^5]_{Av}$	0.00	2.9	4.7	8.4	18	41	27	4.6	2.9
Corrected $[-\Delta\rho/\bar{\rho}_0\times10^5]_{Av}$	0.00	4.4	4.7	8.4	27	61	27	4.6	4.4

furnace. The current reaches a constant value after the temperature of the crystal becomes steady and drops rapidly after the assembly holding the two crystals is removed from the furnace. If a flat anode is used in connection with a pointed cathode the time dependence of the current and temperature is similar. The coloration started in most cases only at the time at which the crystal was removed from the furnace. In some crystals, coloration did not occur at all; in others it started at times at which the temperature was still increasing or already constant.

Figure 3 shows two crystals that had been colored by irradiation after having been brought into the metastable state and then heated to remove the temporary centers. The outside region is completely clear, but the part of the crystal in which the electrolysis occurred is colored. In case of crystal A, a pointed cathode and a flat anode, and in the case of crystal B, two pointed electrodes were used. Owing to the pressure, the pointed electrodes somewhat penetrated the crystals while they were at the elevated temperatures. The indentation marks can be seen in the figure.

B. Density of the Crystals

Crystals, which had undergone electrolysis without showing any coloration, were subjected to density measurements. In order to get more uniform results, parts of the region of each crystal that was believed to contain no precursors were cleaved off. It was possible to estimate the extent of this region since the color clouds that result after irradiation all have approximately the same shape (see Fig. 3).

The average density $\bar{\rho}_0$ of normal NaCl crystals was found to be 2.16472 at 20°C compared to the accepted value of 2.163 g/cm³.[14] The first column of Table I

[14] *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1929).

contains the deviations $\Delta\rho_0$ of the densities of the individual control pieces from their average density $\bar{\rho}_0$. Column 2 shows the deviations $\Delta\rho=\rho-\bar{\rho}_0$ of the densities ρ of crystals that had been subjected to electrolysis but were uncolored. The densities of these crystals were measured simultaneously with those of the crystals referred to in column 1. The values listed in the other columns are based on comparisons between the crystals in question and a group of control crystals measured simultaneously. The spread of the densities of these latter is not included, but it was in every case of the same order as the spread listed in column 1. Columns 3(a) and 3(b) refer to crystals, originally in the normal state, which were nonpermanently colored with x-rays. Columns 4(a), 4(b), and 5 refer to crystals in which permanent and nonpermanent color centers were present simultaneously. These crystals had either been irradiated with x-rays in the metastable state or else irradiated with x-rays after permanent color centers had been produced by the pointed cathode method. Columns 6 and 7 refer to permanently colored crystals which in the one case were colored by the pointed cathode method and in the other irradiated by x-rays while in the metastable state and then heated to bleach out the nonpermanent color centers. It is evident that the spread in the values $\Delta\rho/\bar{\rho}_0$ for the crystals subjected to electrolysis exceeds the spread due to errors of the density measurements (column 1). This is at least partly due to the fact that the volume affected by the electrolysis varies among samples.

Corrections to the results obtained had to be made in the case of crystals containing precursors because of the fact that these were not distributed uniformly throughout the sample. In the case where the density measurement was made before the sample was irradiated, the correction was achieved by dividing the measured value by a number equal to the proportion

of the crystal containing such precursors. This in turn was found by irradiating the sample with x-rays after the density measurement and then bleaching out the temporary centers. The appropriately corrected value is recorded in the last line of Table I.

Even though these measurements may not have too great an accuracy, the following results are quite obvious: (1) As has been observed by other investigators, crystals irradiated with x-rays show a decrease in the density. (2) Crystals in the colorless metastable state show a lower density than normal crystals. (3) Crystals with permanent color centers obtained either directly by electrolysis or indirectly by bleaching out the nonpermanent color centers after irradiation in the metastable state have approximately the same density as crystals in the colorless metastable state. (4) Crystals that have been subjected to electrolysis and then irradiated by x-rays show a decrease of density which exceeds that produced by irradiation in the normal state by a factor of 5 or 6 regardless of whether they are colored before being irradiated.

C. Deviation from Stoichiometric Ratio

Table II shows the results of the pH measurements.[15] These measurements were made within two days after the treatment of the crystal. Crystals having the weight given in column 2 were dissolved in 10 cc of triply distilled water. The slight change of the pH resulting was found to be approximately the same for untreated crystals, crystals in the metastable state, and crystals that had been colored by x-rays either in the normal or in the metastable state. Some of the crystals that had been colored by electrolysis did, however, display a significant increase of the pH. It was found that these crystals always exhibited minute dendritic patterns

TABLE II. Hydrogen ion concentration of NaCl crystals in different states dissolved in triply distilled water

State of crystal		Weight of crystal in grams	pH Triply distilled water	pH Crystal dissolved in 10 ml of water
Normal		0.1095	6.01	6.15
		0.1109	5.91	5.98
Metastable state		0.1282	6.15	6.20
		0.1690	6.19	6.25
Irradiated in normal state		0.1128	5.97	6.10
		0.1081	5.95	6.09
Irradiated in metastable state		0.0640	5.88	6.42
		0.1010	5.95	6.50
	(dendritic patterns)	0.1305	6.11	8.50
Electrolytically colored		0.1047	6.18	9.01
		0.0290	6.08	8.72
	(no dendritic patterns)	0.1590	6.05	6.20
		0.1110	6.01	6.40
		0.0265	6.15	6.20
Irradiated in metastable state, then bleached		0.1220	6.04	6.25
		0.0640	5.95	6.30

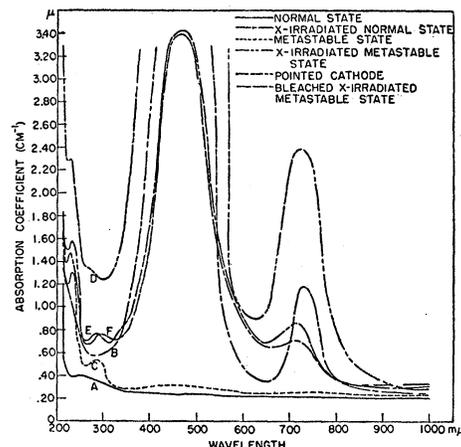[15] We are grateful to Mr. Dumas A. Otterson for performing the pH measurements.

FIG. 4. Apparent optical absorption of NaCl crystals: (A) normal state; (B) x-irradiated normal state; (C) metastable state; (D) x-irradiated metastable state; (E) pointed cathode coloration; and (F) bleached x-irradiated metastable state.

having a general direction from the cathode to the anode. This pattern might have been due to an electrical breakdown which led to a deposition of sodium inside the crystal. Except for such cases, there is probably no significant excess of negative vacancies over the positive ones.

D. Optical Absorption of the Crystals

Figure 4 shows the optical absorption spectra of crystals in all the states considered here (except for the irradiated electrolytically colored ones), arranged as follows: curves A and B refer to the normal and irradiated normal state, respectively; curves C and D, to the metastable and irradiated metastable states; and curves E and F, to the electrolytically colored and the bleached irradiated metastable. It may be noted that all the crystals that were subjected at some point to electrolysis (see curves C through F) show a pair of bands at 226 mμ and 285 mμ in the ultraviolet.[16]

In order to obtain curves E and F two crystals were selected which showed a relatively light coloration.[17] Unfortunately, the optical densities of crystals irradiated in the normal and metastable states to saturation were too high (curves B and D) to permit measurements over the whole range of the F band. However, some idea of their relative densities may be obtained from

[16] These two bands in the ultraviolet are not apparent in the absorption spectra obtained by J. P. Molnar [Ph.D. thesis, M.I.T. (1940)] for NaCl crystals colored by the pointed cathode method. Molnar was using a somewhat different condition during the electrolysis (". . . temperature from 550° to 650°C, a potential of up to 900 volts . . ."). He reports the appearance of a "yellow surface stain" which has been observed in this laboratory on only two occasions. Burstein et al. (see reference 6) report, however, the appearance of absorption bands at 240 mμ and 340 mμ in KCl crystals, which have been subjected to plastic deformation before irradiation with x-rays.

[17] On the other hand, crystals in which density measurements were performed were not selected in any way. The conditions during electrolysis that influence the resulting optical density are unknown.
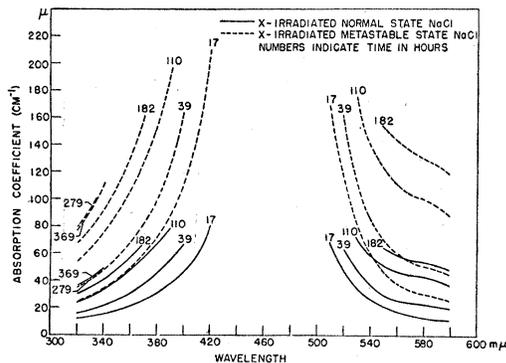
FIG. 5. Optical absorption of NaCl crystals x-irradiated in the normal state (solid curves) and metastable state (dashed curves). The curves were corrected for background.

Fig. 5, which shows the optical absorption spectra of two crystals in the normal and metastable state, respectively, at different times of irradiation. The greater sensitivity to radiation of the latter crystal is quite evident from the figure. Figure 6, which is based on the same experiment, shows the optical absorption at several different wavelengths as a function of time and clearly demonstrates the trend toward saturation.

E. Discussion

The fact that no significant change of the hydrogen ion concentration associated with the various treatments of the NaCl crystal can be detected proves that the number of negative vacancies per cm³, N^-, in no case exceeds the number of positive vacancies per cm³, N^+. If one assumes that N^+ and N^- are actually equal, the observed change in the density $\Delta\rho$, compared to that of the normal state, can be related to the number of missing atoms of either sign of electric charge irrespective of their arrangement in the form of single vacancies, pairs of vacancies, etc., by the equation

$$N^+ = N^- = (N/M)\Delta\rho,$$

where N is the Loschmidt number, M the molecular weight, and $\Delta\rho$ the change of density given in the last line of Table I. Table III gives the values of $N^-(=N^+)$ thus found.
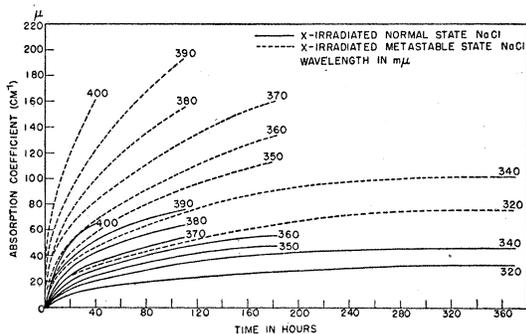

FIG. 6. Saturation of optical absorption of the x-irradiated normal state (solid curves) and metastable state (dashed curves) as a function of time. The curves were corrected for background.

It should be noted here that the values listed in column 2 refer to a crystal containing both the permanent and the nonpermanent color centers.

In the course of our experiments, we encountered essentially seven different states of the NaCl crystal as given in Table I. It seems apparent that the permanent centers associated with the states given in columns 6 and 7 are identical.

We have no explanation for the unusually high concentration of the nonpermanent centers resulting upon irradiating a crystal in the metastable state and shall, therefore, exclude them from consideration in the following. The discussion will be based on the usual concept that the basic entities connected with color centers are electrons trapped in negative vacancies and holes in the filled electron band trapped in positive vacancies.

In the normal state there are no isolated vacancies, but rather the equilibrium number of pairs of positive and negative vacancies; all the electrons are situated in filled bands. When such a crystal is irradiated, there is created temporarily a situation in which some of the electrons have been raised into one of the previously empty conduction bands leaving an equal number of holes. Color centers are formed when one of the electrons

TABLE III. Concentration of negative vacancies for various states.

Metastable state	Saturation x-irradiation of metastable state	Pointed cathode coloration	Saturation x-irradiation normal state
9.6×10^{17} cm⁻³	12.3×10^{18} cm⁻³	1×10^{18} cm⁻³	1.8×10^{18} cm⁻³

is trapped in a negative vacancy; and consequently, a hole, in a positive vacancy. This diminishes the number of free vacancy pairs, and therefore, new pairs enter from the surface in order to preserve equilibrium. This accounts for the decrease in density. A vacancy that has trapped an electron or a hole is no longer as tightly bound to the other member of its pair. The distance between such a vacancy and its mate therefore increases, but the two vacancies in question do not separate entirely. Consequently, if the electron or hole is removed from the vacancy owing to excitation by light or heat, the two vacancies may recombine to form a normal pair. Correspondingly, the electron recombines with a hole, thus returning to the filled band. This accounts for the process of bleaching. A crystal in the metastable state contains, in addition to vacancy pairs, also isolated positive and negative vacancies in approximately equal numbers. This accounts for the fact that such a crystal has a low density but the normal stoichiometric ratio. Because of the electrostatic forces involved, these vacancies are almost immobile, and therefore, the metastable state persists at high temperatures. When a crystal in the metastable state is irradiated, on the one hand, the same process occurs as in the case of a normal crystal. In addition, a certain number of the electrons or holes produced are

trapped by the isolated vacancies. Since the bleaching process described above, which is based on the recombination of vacancy pairs, is not available for the case of isolated vacancies, color centers involving such vacancies are permanent.

In terms of the above scheme, the following mechanism for the phenomena associated with electrolysis may be advanced. Under the influence of an electric field at elevated temperatures, the negative ions start to move toward the anode producing an excess of negative vacancies near the cathode, and conversely, the positive ions move toward the cathode producing positive vacancies near the anode. In order that the crystal be locally neutral, it is necessary that there be introduced at the cathode electrons equal in number to the excess negative vacancies and similarly holes in the electron band equal to the number of positive vacancies introduced at the anode. In general, the electrons and holes will be trapped in the vacancies, thus leading to color centers which spread from the cathode toward the anode. It is quite clear that the spreading reverses itself

if the polarity of the field is reversed at any stage. If the direction of the field remains unchanged, the nature of the process changes when the positive vacancies in which holes have been trapped arrive at the cathode. When this happens, the condition of the electric neutrality is satisfied if electrons entering from the cathode combine with the holes trapped in the positive vacancies. This allows the newly created negative vacancies to be formed free of electrons, i.e., as color center precursors. As the negative vacancies containing the electrons diffuse toward the anode they are replaced by these precursors and in this fashion the color cloud is swept out toward the anode. The above discussion does not take into account the inhomogeneity of the electric field produced by the pointed cathode and also fails to explain the direct production of precursors and the increased susceptibility of a crystal in the metastable state for the production of nonpermanent centers.

We are greatly indebted to Dr. Philip Schwed for valuable discussions and suggestions.

Motion of Gaseous Ions in a Strong Electric Field. II

GREGORY H. WANNIER
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received May 8, 1952)

This paper continues an earlier one on the same subject. Its object is to elucidate the nature of the random motion of an ion about its drift. In Sec. F it is shown that this motion can be described as a diffusion with a diffusion tensor axially symmetric about the field. If the mean free time between the collisions of an ion with molecules is independent of speed, then explicit expressions may be deprived for the two diffusion coefficients; these expressions are written down without proof in Sec. G; they are connected with the mobility by a natural extension of the Einstein relation. In Sec. H, the longitudinal diffusion coefficient is computed numerically for the hard sphere model, high field, and mass ratio 1; the method of computation is the same as in Sec. D. Finally, it is shown in Sec. I how approximate formulas of wider validity can be inferred from the ones obtained.

IN the first paper of this series[11] the problem of the motion of ions through a gas was formulated under the assumption that the electric field was too large to be treated as a perturbation, as is often done. This problem was solved in the sense that the values of some simple velocity averages were worked out precisely while no attempt was made to write down the entire velocity distribution function. I believe that this type of approach will yield most answers of experimental interest. The actual formulation was restricted, however, to uniform ion densities. In this paper the problem of nonuniform densities will be tackled in the same spirit.

F. CHARACTER OF THE RANDOM MOTION OF IONS

It is intuitively reasonable to suppose that the drift velocity of ions is their most important property from

the point of view of observation and that the random motion about this mean value is essentially a diffusion process. It will now be shown that this view is correct, provided the medium is thought of as anisotropic with the field direction as symmetry axis.

In order to prove this we modify Eq. (6) by assuming f to be a density in phase space, depending on space and time as well as velocity. If we adopt the notations

$$\partial/\partial \mathbf{r} \quad \text{and} \quad \partial/\partial \mathbf{c}$$

for the gradients in ordinary and velocity space, this formula reads

$$\partial f(\mathbf{c}, \mathbf{r}, t)/\partial t + \mathbf{a} \cdot \partial f(\mathbf{c}, \mathbf{r}, t)/\partial \mathbf{c} + \mathbf{c} \cdot \partial f(\mathbf{c}, \mathbf{r}, t)/\partial \mathbf{r}$$
$$= \int \int \{M(\mathbf{C}')f(\mathbf{c}', \mathbf{r}, t) - M(\mathbf{C})f(\mathbf{c}, \mathbf{r}, t)\}$$
$$\times \frac{1}{\tau(\gamma)} d\mathbf{\Pi}_c d\mathbf{C}. \quad (64)$$

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[11] Gregory H. Wannier, Phys. Rev. **83**, 281 (1951). The two papers will be treated as forming together a single unit.
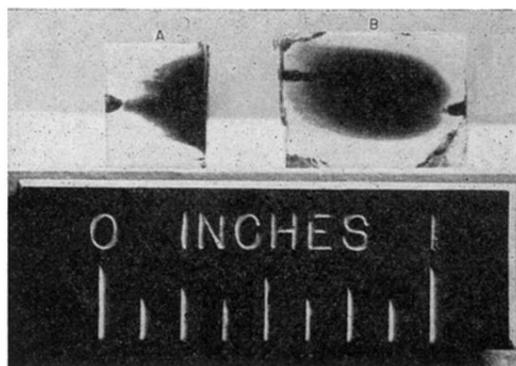
Fig. 3. NaCl crystals containing a region originally in the metastable state by electrolysis after coloration of x-rays and subsequent bleaching of nonpermanent centers. Left crystal: metastable state was obtained by a pointed cathode and a flat anode. Crystal to the right: by a pointed cathode and a pointed anode.