Volume Expansion and Color Center Behavior of NaCl X-Ray Irradiated at Low Temperature*

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Volume expansion of x-ray irradiated NaCl was measured in the range 15–90°K and its optical behavior was analyzed from 15 to 300°K. An improved photoelastic method showed that strain profiles agree with the shape predicted by the linear theory and that slow cooling (10°C per h) is essential to minimize background strain. Twenty-four hours of irradiation by 45 kV, 30 mA x rays at 15°K produces $\Delta V/V$ of the order of 10^{-5} which does not anneal below 80°K while, in contrast, the F band shows in this range one-stage annealing. Growth curves of the F band and of the 343-mμ band were made at 15°K. Annealing at 80°K followed by reirradiation at 15°K indicates that these bands recover quickly and a comparison with results on KCl and KBr suggests that the F centers are annihilated by hole capture. If follows also that in the range 15 to 80°K electronic changes in these centers do not lead to volume changes greater than the experimental error, $\Delta V/V \simeq 10^{-6}$. Heat-treated crystals presented a different behavior of thermal annealing of the F band with several annealing stages between 15 and 80°K.

I. INTRODUCTION

THE mechanism of defect formation in alkali halides at low temperatures presents many interesting problems. In particular, the F-center formation is still not understood satisfactorily in spite of the fact that the F center itself has been extensively studied. The Varley mechanism[1] as considered by several authors[2] is suggested by the evidence obtained for the existence of interstitials[3] as well as by experimental observations of Rabin and Klick[4] that F-center growth curves approached an "intrinsic" behavior near liquid-helium temperatures. Recently, Wiegand[5] has reported precision lattice parameter measurements in single crystals and Sharma and Smoluchowski[6] have analyzed F-center formation by very soft x rays near the chlorine K edge. Although the first experiment was done at room temperature and the latter at low temperature, both are taken by their authors as an indication of the interstitial mechanism of F-center formation.

Investigations with another class of techniques were initiated at low temperatures using photoelastic volume expansion measurements. Modifying the Primak et al.[7] technique, Wiegand and Smoluchowski[8] analyzed the LiF system at liquid-nitrogen temperature. In the present work the same technique is applied, with several experimental additions, to analyze the behavior of NaCl at liquid-helium temperature. NaCl behavior under x-ray irradiation at this temperature has been first studied by Duerig and Markham.[9] They identified several bands, including one at 330 mμ, probably related to the H center, which involves an interstitial configuration. They did not study, however, its detailed thermal behavior besides observing that at liquid-nitrogen temperature the 330-mμ band annealed out together with part of the F band and that some of the V centers also suffered modifications. Of special interest for this paper was a band at 345 mμ that was identified as the V_1 band, this band appearing after heating to liquid-nitrogen temperatures. This V_1 band had been previously observed by Casler, Pringsheim, and Yuster[10] in several alkali halides. Seitz, who first proposed a model for the center responsible for the V_1 optical absorption, has recently reanalyzed the situation[11] and proposed a new model based on a Cl$^-$ interstitial ion in a $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ position. We shall discuss our results in relation to this proposal in a later section of this paper.

In the present work, we observed (a) the growth and

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

[2] D. A. Wiegand and R. Smoluchowski, Phys. Rev. **110**, 991 (1958); C. C. Klick, Bull. Am. Phys. Soc. **5**, 185 (1960); R. E. Howard, S. Vosko, and R. Smoluchowski, Phys. Rev. **122**, 1406 (1961); appropriate also, are F. Seitz, Rev. Mod. Phys. **26**, 7 (1954); D. L. Dexter, Phys. Rev. **118**, 934 (1960); R. Smoluchowski and D. A. Wiegand, Discussions Faraday Soc. **31**, 151 (1961). A resume of the point defect formation problem by B. S. H. Royce, J. Sharma, R. Smoluchowski, and R. N. Euwema has also recently appeared in the Proceedings of the Kyoto Lattice Defect Conference, 1962 (unpublished).

[3] W. Kanzig and T. O. Woodruff, Phys. Rev. **109**, 220 (1958).

[4] H. Rabin and C. C. Klick, Phys. Rev. **117**, 1005 (1960).

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[7] W. Primak, C. J. Delbecq, and P. H. Yuster, Phys. Rev. **98**, 1708 (1955).

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

[10] R. Casler, P. Pringsheim, and P. H. Yuster, J. Chem. Phys. **18**, 887, 1564 (1950).

[11] F. Seitz, Phys. Rev. Letters **7**, 282 (1961).

regrowth curves of the F and 343-mμ bands, (b) the thermal bleaching of both bands up to liquid-nitrogen temperature, and (c) with the photoelastic technique we observed the volume expansion $\Delta V/V$ as a function of temperature, including the range in which optical thermal annealing takes place.

II. EXPERIMENTAL

The importance of the photoelastic technique in the study of defects lies in the fact that it can be used at low temperatures. In order to do so, however, important modifications had to be introduced in the method. First of all, slow cooling of the crystal proved to be an absolute necessity. In some cases the crystal was previously annealed in vacuum or in helium atmosphere at 650°C and cooled down to 15°K with a rate of cooling never exceeding 10°C/h. In all cases, unless otherwise indicated, a freshly cleaved crystal was used which was slowly cooled from room temperature down to 15°K. In this way, background strain could be reduced to a minimum as required by the method. Also a double-slit system, situated outside the Dewar, was used to scan both the irradiated and the nonirradiated sides of the crystal. In this way the birefringence could be measured at each point in the crystal by observing the rotation angle of the polarized beam. Visual observations were replaced by electronic detection with a photomultiplier which permitted reading of the rotation angle to ±0.01 deg. The Dewar used was a double metal container with two pairs of windows. One pair was made of Al, through which x-ray irradiation was made, and the other was transparent for optical measurements (photoelastic or photometric). After cooling the crystal successively with N_2, H_2, and He, a final temperature of 15°K was reached, and this was maintained throughout the irradiation, which could last as long as 30 h. 15°K was the lowest temperature that could be obtained in this series of measurements, presumably because of imperfect thermal contact between the liquid He and the sample. Wires used for temperature measurements were wound several times around a portion of the Dewar containing liquid He before going to parts of the Dewar at higher temperatures. Considerable care was taken in calibration of carbon resistors and in temperature measurements. It is the authors' opinion as a result of the experience with the Dewar used in this work and other similar Dewars that many experiments reported in the literature as having been carried out at "liquid-helium temperature" were actually performed at higher temperatures. All measurements and bombardments were made in the dark except, of course, for the measuring beam. A measurement of optical bleaching caused by the photoelastic or photometric measurements showed it to be negligible. For thermal bleaching the Dewar was allowed to heat under its natural heat-leakage so that data points could be taken continuously from 15 up to 300°K. The rate of heating in a 10^{-6} mm Hg vacuum (with N_2 in the radia-

tion shield) was not greater than 2°C/h up to 77°K. Some isothermal annealings were also taken for the photometric observations, and in this case all the optical measurements, after thermal annealing, were taken at 15°K.

Samples were obtained from the Harshaw Chemical Company and it was requested in ordering that the material be of high purity. The samples were thus presumably taken from pure sections of the boule. Radiation was from a Machlett tungsten tube operated at 45 kV and 30 mA or from a General Electric Maxitron 300 operated at 60 kV and 20 mA. Radiation was filtered through a 0.5 mm Al and the sample was placed about 5 cm from the tube window except where otherwise indicated. Optical density measurements were made either with a Beckman Spectracord or a Cary Spectrophotometer. Crystals were not more than 0.8 mm thick, the other dimensions being about 2 and 1.5 cm. The temperature was measured either with a carbon-resistor or with a special Au/Ag thermocouple previously calibrated. Below 20°K calibration was made against vapor-pressure curves of H_2.

Since the Dewar had to be taken off the spectrophotometer for x-ray irradiation of the sample, one had to insure its correct positioning in the beam. This was done by measuring absorption at a fixed wavelength; in our case this reference was 8000 Å.

III. RESULTS

In interpreting photoelastic measurements, one should be very careful about the accuracy of the method. As pointed out by Wiegand and Smoluchowski,[8] the method is very reliable for obtaining annealing behavior and relative volume expansion, but it should be stressed that one cannot put too much confidence in absolute measurements of $\Delta V/V$. The relation between $\Delta V/V$ and optical rotation for NaCl is

$$\Delta V/V = 1.3k(T)\Delta\theta,$$

where $k(T)$ is a temperature-dependent parameter which is related to elastic and photoelastic constants, $\Delta\theta$ is the optical rotation per unit thickness of crystal as measured with the quarter wave-plate photoelasticimeter. Merriam[12] gave the temperature dependence of $k(T)$ at high temperatures down to 0°C. In order to get an estimate for $\Delta V/V$ one can further consider Wiegand and Smoluchowski's results for NaCl in which there was no appreciable change in $\Delta\theta$ from 80°K up to 0°C and take the $k(T)$ value at 0°C as being a constant down to 15°K. Then one obtains $\Delta V/V$ of the order of 2×10^{-5} which is of the same order of magnitude as $\Delta V/V$ calculated assuming the volume dilation to be due to F centers vacancies present in the crystal.

A typical strain against position curve was obtained for NaCl, which showed that a definite volume expan-

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[12] M. Merriam, thesis, Carnegie Institute of Technology, 1960 (unpublished).

sion had occurred after 24-h irradiation at 15°K, corresponding to a rotation of about 0.6 deg.

Thermal annealing of this volume expansion was not observed below 77°K (Fig. 1). In this range of temperature the F and 343-mμ bands suffer rapid annealing. The possible meaning of this fact will be discussed later.

The optical absorption curves shown in Fig. 2 indicate pronounced F and V_1 (343 mμ) bands but not the 330-mμ band (supposedly the H band) observed by Duerig and Markham. Thus one may infer that in the temperature range 5 to 15°K the 330-mμ band anneals and the V_1 appears. This is in accord with the well-known H to V_1 transformation. What is different in our results is that our 343-mμ band anneals at about 65°K and little of it is left at 80°K. This might perhaps be explained by the slow rate of warming. Unfortunately, Duerig and Markham do not give any information about their rate of heating. They indicate, however, that the V_1 band as obtained and thermally treated at 80°K shows thermal instability at this temperature. Still
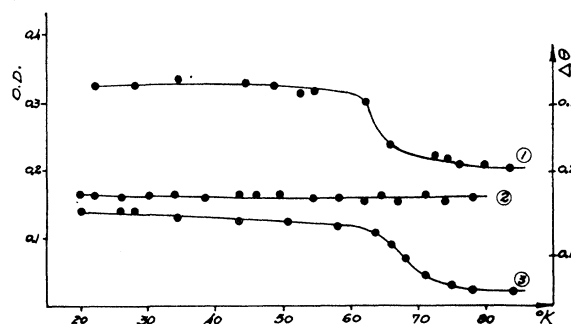

FIG. 1. Thermal annealing of NaCl crystals irradiated at 15°K: (1) F band, (2) $\Delta V/V$, and (3) 343-mμ band. Conditions: (a) for optical bands 12 h at 60 kV and 20 mA, 0.8-mm Al x-ray filtration, sample thickness 0.62 mm, samples "as cleaved." (b) For $\Delta V/V$ measurements 21 h at 45 kV at 30 mA, 0.5 mm Al filtration, sample thickness 0.80 mm and samples thermally annealed at 650°C. Similar annealings of the F and 343-mμ bands were observed for samples having the same irradiation conditions as $\Delta V/V$ above.

another point of divergence in our experimental results is the spectrum at 80°K. We find a prominent and very well defined band at 278 mμ which does not appear in their results. As a matter of fact this band is not reported in the literature concerning NaCl.

The broad absorption band to the long-wavelength side of the F band (Fig. 2, curve 1) is most probably due to the F' center. The absorption in the vicinity of 800 mμ is, however, unfortunately distorted because of the method of measurement. While this band is not identical to the F' band as given by Pick, it is similar in shape to the F' band for other alkali halides.[13] Because of this similarity in shape and because of the location of this band relative to the F band we will assume here that it is in fact the F' band.

The growth curve of the F and of the supposed

[13] H. Pick, Ann. Physik **31**, 365 (1938). However, see also R. Hilsch and R. W. Pohl, Z. Physik **68**, 721 (1931).
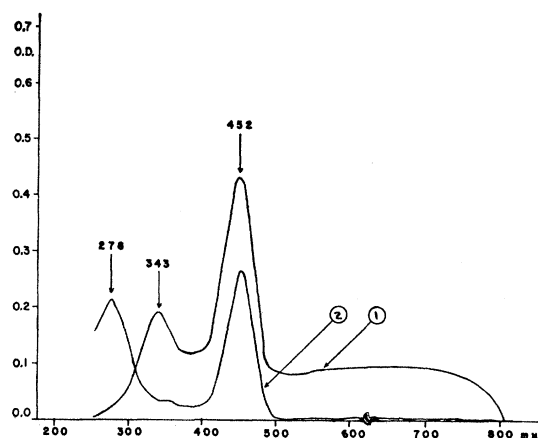

FIG. 2. Optical absorption curves: (1) after x raying at 15°K, (2) after annealing to 80°K. Irradiation at 60 kV and 20 mA for 12 h, 0.8-mm Al filtration. "As cleaved" samples.

(343 mμ) V_1 band was also analyzed. This is shown in Fig. 3. After thermal annealing of both bands at 80°K had occurred, a recool down to 15°K was made and a regrowth curve was taken. As can be seen from Fig. 3, the F band recovered very quickly back to its former value and rate of growth.

On regrowth the optical absorption in the vicinity of the 343-mμ band is more complex than before the annealing. Apparently, however, the 343-mμ band regrows more slowly than the F band (see Fig. 3).

As mentioned before, great care was exercised to avoid background strains. To do this, some crystals were thermally treated at 650°C to eliminate internal strains. This treatment proved to be extremely important for the annealing characteristics of NaCl. Crystals annealed in helium atmosphere for 12 h at 650°C and slowly cooled (cooling rate no greater than 10°C/h) showed many new annealing stages of the F band between 15 and 80°K as can be seen from Fig. 4.

This different behavior for the same grade of purity samples, which differ only in thermal treatment, seems to us to be a point which merits further consideration. First of all it points out the absolute necessity of knowing the previous history of materials before a comparison of results can be confidently made. It also points out another important point: Though the results by Rabin
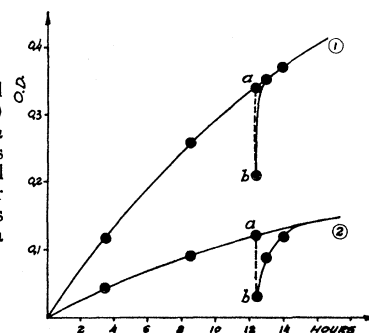

FIG. 3. Growth and regrowth curves of (1) F band and (2) 343-mμ band. Same crystal as Fig. 1. In a to b, thermal annealing occurred after which irradiation was continued to obtain a regrowth curve.
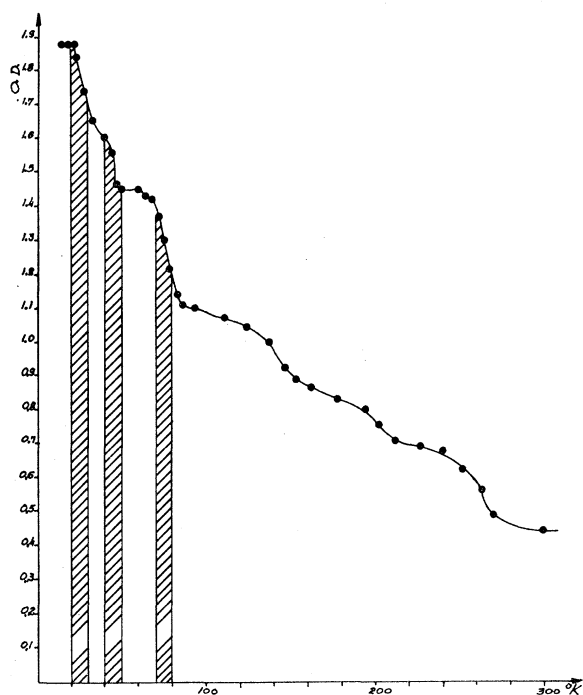
FIG. 4. Annealing behavior of F band in a crystal kept for 12 h at 650°C in a He atmosphere before irradiation. Irradiation at 45 kV and 30 mA for 21 h, 0.5-mm Al filter. Sample thickness 0.82 mm.

and Klick on the growth curves of the F band seem to indicate an intrinsic behavior at very low temperatures, this does not seem to be the case for our annealing curves. Thus the influence of a thermal treatment on the annealing of the F band reflects at least a partly nonintrinsic character of the growth curves of other centers in this low-temperature region.

CONCLUSIONS

Clearly, the basic factual conclusions from our results are:

(1) There is volume expansion due to x-ray bombardment of NaCl at 15°K of the order of 10^{-5} after 21 h of irradiation with 45 kV/30 mA x rays.

(2) The volume expansion does not anneal below 80°K although drastic changes in the optical spectra occur.

(3) The F and 343-mμ bands grow together, bleach together (though not to the same extent) and recover quickly after thermal annealing, upon reirradiation, to their former values and rates of growth.

(4) Thermal pretreatment of the crystals affects their annealing behavior.

The fact that volume expansion does not change measurably even after the 343-mμ band and the F band have partly annealed out indicates that changes in defect configuration, through electron and hole motion, do not affect much the lattice relaxation. The rapid

recovery of both F and 343-mμ bands indicates that their annealing was related to an electronic change. Should any point defect motion have occurred, during the thermal annealing, the regrowth curve could not have been so rapid. Presumably, the x-ray reirradiation only furnishes the necessary electrons and holes to refill the empty vacancies or traps. If *volume expansion* is brought about by the creation of vacancies or interstitials the addition or subtraction of electrons and holes to those does not seem to alter appreciably the lattice relaxation.

If the defect associated with the 343-mμ band is a "complementary" defect to the F center, the partial annealing of the F and the almost complete annealing of the 343-mμ band indicate that other centers are taking part or appearing during the various annealing stages. We propose to interpret those annealing, not as ionization of F center through electron motion, but rather as annihilation of the F-center electron by holes coming from hole centers, probably the 343 mμ. This interpretation is supported by the following observations:

(a) We have found a very pronounced F' band in our crystals. This suggests that their purity was high since otherwise divalent impurities would have quickly trapped most of the excess electrons. This F' band *did not increase* with F-center annealing, but rather decreased. Regrowth of F' band occurred with regrowth of F band.

(b) A band to the uv at 278 mμ which is probably a V band gradually appeared during annealing of 343 mμ. This would also explain why the 343 mμ bleaches almost completely and the F band only partially. Holes would not only be used up for F- and F'-band annihilation but also probably in the formation of the new V band. Another conclusion can be based on our results: the new band is not the 343-mμ center stripped of a hole, for not only does the 343 mμ recover, but the new band keeps growing during the regrowth curve.

(c) Electron-hole annihilation probably by motion of holes is also evidenced by other results, such as glow peaks, and luminescence peaks in similar systems such as KCl, found by Cape and Jacobs.[14]

In connection with the reported behavior of the V_1 band one can make other comments of a somewhat more speculative nature: (a) The structure of the defect associated with the 343-mμ band is extremely important for supporting a Seitz-Markham or a Varley mechanism for F-center formation. If this band is associated with an interstitial, then it would be expected that changes in the electronic configuration of the center would lead to changes in lattice relaxation, as was pointed out by Wiegand and Smoluchowski. Unfortunately, no magnetic studies have been made of this band in NaCl. On the other hand, the possibility exists that this band is associated with a positive ion vacancy, and that hole

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[14] J. Cape and G. Jacobs, Phys. Rev. 118, 946 (1960).

addition or subtraction to the vacancy does not change appreciably the relaxation, as seems to be the case of the F center. Of course, another possibility exists that the volume expansion is not associated at all with the optical centers. In any case, this type of analysis should be extended to KCl or KBr where the magnetic and optical centers have been more extensively studied. (b) If we suppose that the 343-mμ band is a V_1 band, then one must make some comments about the model recently proposed by Seitz[11] for this center. According to this model, the V_1 center consists of a chlorine ion in a $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ position which accounts for the absence of paramagnetism and dichroism of the center. The center would be formed from an H center by an electron capture and transfer of the Cl^0 into the body-centered position. Our H center should thus have annealed below 15°K and would probably be related to the 330-mμ band observed by Duerig and Markham at 5°K. The annihilation of the Cl^- interstitial with the F center would most likely give rise to an annealing of the volume expansion which was not observed. One might thus say that our band is not the V_1, but rather that it is associated with the V_k center. In this case holes from this center would annihilate the F and F' centers. In addition, the growth and regrowth curves for this band (see Fig. 2) indicate a center composed of a point defect plus an electronic component. Thus the energetically "expensive" point defect is left after the annealing and the copious electrons and holes provided during x-ray irradiation just fill them up during the regrowth. Of course, the possibility also exists that the growth of the 343-mμ band is controlled by an electron or hole capture at other traps. If, on the other hand, the Cl^- interstitial model is responsible for our band, then it is very difficult to understand its relatively rapid recovery upon reirradiation.

Recently, Yuster[15] reported dichroism of the V_1 band. This adds support for our interpertation of the results here reported.

ACKNOWLEDGMENTS

[15] P. H. Yuster, Color Center Conference, Stuttgart, 1962 (unpublished).

Low-Temperature Annealing of the X-Ray-Induced Volume Expansion and Coloration of LiF*

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It has been shown previously that both $\Delta V/V$ and the density of F centers produced by x irradiation of LiF at 80°K anneal out partially near 130°K. Upon reirradiation at 80°K the F band quickly recovers while $\Delta V/V$ does not recover. In the present study, an additional annealing stage of $\Delta V/V$ and the F band was found near 270°K. Upon reirradiation at 80°K after annealing at 270°K, neither $\Delta V/V$ or the F band recover in contrast to the recovery after annealing at 130°K. The irreversibility of the 270°K annealing of the F band indicates vacancy annihilation which apparently does not occur at 130°K. The formation of M centers at the higher temperature suggests vacancy motion. The fractional annealing at 130°K was found to be smaller than in previous work, presumably because of different sample perfection before irradiation.

I. INTRODUCTION

IN this paper, the annealing of defects induced by low-temperature x irradiation of LiF is described. The general problem was considered previously by Wiegand and Smoluchowski and the present work is a continuation of the earlier investigation.[1] In the present study, the irradiation-induced volume expansion has been studied by a more precise photoelastic technique.[2]

[1] D. A. Wiegand and R. Smoluchowski, Phys. Rev. 110, 991 (1958); 116, 1069 (1959).
[2] S. Mascarenhas, D. A. Wiegand, and R. Smoluchowski, Bull. Am. Phys. Soc. 5, 422 (1960).