

## Evidence for Electron-Hole Recombination Mechanism of Defect Production in KCl and NaCl at 20°K \*

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Measurements of the x-ray-induced expansion of KCl and NaCl have been carried out with a capacitive dilatometer at temperatures near 20°K. The expansion of KCl was found to be more than an order of magnitude greater than that of NaCl. Greater probability of nonradiative electron-hole recombination in KCl is suggested as the principal cause of the disparity.

### I. INTRODUCTION

RECENTLY, Crawford<sup>1</sup> has pointed out that the nonradiative recombination mechanism of Hersh<sup>2</sup> and Pooley<sup>3,4</sup> is a "front runner" in explaining radiation damage caused by low-energy x rays in alkali halides. According to this model, the energy necessary to create a vacancy and an interstitial in the close-packed direction is obtained from the energy released during exciton recombination via a nonradiative mode. Numerical estimates of the energy available and necessary indicate that this mechanism should be effective in all alkali halides except LiBr, LiI, and NaI, and has had particular success in explaining the results of several radiation-damage experiments, particularly with KI.

This paper reports measurements of the strain resulting from x-ray irradiation of KCl and NaCl at 20°K. From an experimental point of view, measurements at low temperatures have an advantage, since the contribution to the observed strain that arises from the heating of the sample is an order of magnitude less than it is at room temperature because of the large reduction of the thermal-expansion coefficient and the great increase in the thermal conductivity that take place on cooling the salts to 20°K. Likewise, at low temperatures intrinsic damage mechanisms are believed to predominate.<sup>5</sup> Impurity effects certainly contribute: Sonder and Sibley<sup>6</sup> indicate that small amounts of lead impurity may increase the defect production rate in KCl at temperatures as low as 80°K, Etzel and Allard<sup>7</sup> have found that the presence of H<sup>-</sup> and OH<sup>-</sup> can increase the F-center production rate in NaCl at room temperature; and Hall *et al.*<sup>8</sup> have found that the F-center production rate depends somewhat on the sample even at helium temperatures. Nevertheless, Rabin and Klick's results<sup>5</sup> suggest that the impurity contribution is likely to be

smaller at low temperatures than at high, particularly if the samples are nominally pure Harshaw crystals as were those used in this work. Thus the strains experimentally observed in KCl and NaCl were felt to be comparable with the prediction of Pooley's model; they were found to be reasonably consistent with this model, thus giving it further experimental support.

### II. EXPERIMENTAL

Rectangular (5.08×1.5×0.7 cm) single crystals of "pure" NaCl and KCl (obtained from Harshaw Chemical Company, Cleveland, Ohio) were mounted in the aluminium dilatometer, shown schematically in Fig. 1, with the long dimension vertical so as to form the central support for the lower plate (of 3.5 cm diam) of a two-terminal capacitor. The crystals were bound to the capacitor plate and dilatometer base with epoxy adhesive, and were irradiated *in vacuo* in a helium cryostat by a collimated beam of 68-kv-peak x rays confined to one of their two 1.5- × 0.7-cm surfaces. A tungsten-target Picker Px-2A x-ray tube was operated with a filament current of 10 mA, and the resultant beam was filtered with 0.8 mm of aluminum and 0.1 mm of Mylar. The fact that the irradiated face of the crystal expands more than the rear parallel face causes a slight tilting of the lower capacitor plate by an amount that depends on the geometrical configuration of the crystal, its elastic constants, and x-ray absorption properties. The effect of tilting of the lower plate on the measured capacitance change was investigated both by a simple mathematical analysis applicable to the apparatus used and by simulating the actual experimental situation in a separate experiment. For this experiment, the single-crystal sample was replaced by two thin rods, one of Invar and one of NaCl, separated by a short distance and symmetrically placed with respect to the axis of the capacitor. The temperature of the system was raised above room temperature a measured amount and the change in capacitance was observed. From the known dissimilar values of the thermal expansion coefficients of the two posts and the dimensions of the system, the amount of tilt and the change in the center-to-center separation of the plates could be calculated. The results of this experiment confirmed the mathematical analysis and the conclusion that the measured capacitance change was

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<sup>1</sup> J. H. Crawford, Jr., *Advan. Phys.* **17**, 93 (1968).

<sup>2</sup> H. N. Hersh, *Phys. Rev.* **148**, 928 (1966).

<sup>3</sup> D. Pooley, *Proc. Phys. Soc. (London)* **87**, 245 (1966).

<sup>4</sup> D. Pooley, *Proc. Phys. Soc. (London)* **87**, 257 (1966).

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

<sup>6</sup> E. Sonder and W. A. Sibley, *Phys. Rev.* **140**, A539 (1965).

<sup>7</sup> H. W. Etzel and J. G. Allard, *Phys. Rev. Letters* **2**, 452 (1959).

<sup>8</sup> T. P. P. Hall, D. Pooley, and P. T. Wedepohl, *Proc. Phys. Soc. (London)* **83**, 635 (1964).

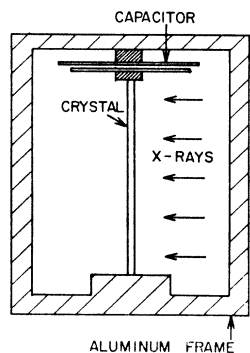


FIG. 1. Schematic drawing of the dilatometer. The dilatometer was cooled by a thermal contact made between the frame and a liquid-helium bath.

directly proportional to the change in center-to-center separation of the plates within the whole range of the strains encountered in all the experiments reported here. The constant of proportionality depends primarily on three factors: the elastic constants, geometrical configuration, and x-ray absorption properties of the crystal. Provided these factors are sufficiently similar in all the salts studied, as in fact they were,<sup>9</sup> this constant of proportionality would be very closely the same for all salts studied. Therefore, although the absolute values of the strain are in some doubt, the relative values are accurate enough to indicate clearly differences between the different salts studied.

The temperature of the crystals and of the dilatometer frame was 20.0°K at the beginning of irradiation and increased nonlinearly to a new steady-state value of no more than 20.3°K as irradiation progressed. This temperature change was measured during a control experiment with a KCl crystal, using calibrated thermocouples of Au+2.10% Co versus Ag+0.37% Au. One arm of the thermocouple was attached to the outer dilatometer frame, and the other was soldered to an indium peg snugly inserted a short distance into a drilled hole in the back of the specimen. For NaCl, thermal effects were calculated using accepted values of the thermal properties<sup>9</sup> of this salt. They were found to be much smaller than those for KCl and thus no temperature measurements were made during the NaCl runs.

### III. RESULTS

Two crystals of KCl and three of NaCl were irradiated and all the results were found to be reproducible to  $\pm 15\%$ . The results of a typical run are shown in Fig. 2 where the ordinate was calculated from center-to-center changes in plate separation deduced from the measured capacity changes. The maximum strain attributable to thermal expansion is represented by the lower curve, and can be seen to be particularly important only at the beginning of the irradiation period. The rate of increase of strain, as given by the slope of the linear portion of the upper curve corrected for

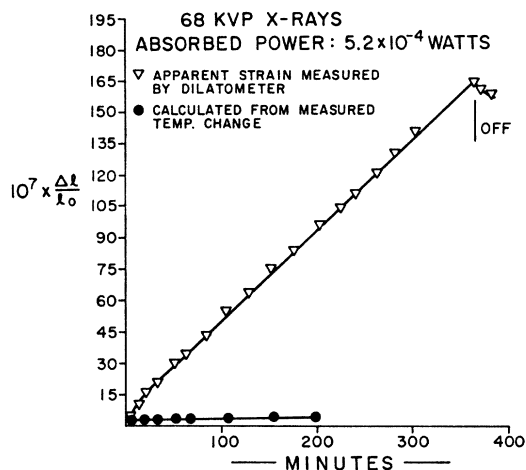


Fig. 2. x-ray-induced strain in KCl at 20°K as a function of the time of irradiation.

thermal expansion effects, reflects the rate of production of Frenkel defects. This rate of increase of strain was found to be 37 times larger for KCl than for NaCl. It may therefore be concluded that the ratio of the steady-state rates of creation of Frenkel defects in KCl and NaCl is approximately 37 also, since the same interstitial anion species is present in both salts, and the Poisson ratios of these, and indeed of most fcc alkali halides,<sup>9</sup> are similar with the consequence that the macroscopic volume changes per Frenkel defect expected on Eshelby's theory<sup>10</sup> should be similar.

The total absorbed x-ray power in both salts was measured *in situ* by a calorimetric method of the type carried out by Skarsgard and Johns.<sup>11</sup> A slug of lead was mounted in place of the specimen in such a way that it was thermally isolated and its change in temperature was monitored upon irradiation. The typical spectrum of a tungsten-target x-ray tube<sup>12</sup> operating at 68 kv peak was assumed and the mass absorption coefficients<sup>13</sup> of both salts were used to calculate total absorbed power. For the 68-kv-peak, 10-mA irradiation employed, this was found to be  $5.2 \times 10^{-4}$  and  $4.6 \times 10^{-4}$  W, respectively, in the KCl and NaCl specimens used. The profiles of absorption through the specimens were also calculated and found to be roughly similar: at a depth of 1 mm from the irradiated surface, 38% of the beam is absorbed in NaCl versus 50% in KCl. At 3 mm the fractions are 60 and 70%, and at 5 mm, 70 and 79%, respectively. Thus, the ratio of the strain rates for KCl and NaCl normalized to the same power actually absorbed, will be about 13% smaller than the factor of 37 quoted earlier.

<sup>10</sup> J. D. Eshelby, *J. Appl. Phys.* **75**, 255 (1954).

<sup>11</sup> L. Skarsgard and H. E. Johns, *Radiation Res.* **7**, 217 (1957).

<sup>12</sup> J. H. Aitken and W. R. Dixon, National Research Council (Canada) Report No 4864, 1958 (unpublished).

<sup>13</sup> H. E. Johns, *The Physics of Radiology* (Charles C Thomas, Springfield, Ill., 1961), 2nd ed.

<sup>9</sup> C. P. Martel, Ph.D. thesis, University of Toronto, 1966 (unpublished).

#### IV. DISCUSSION

Pooley<sup>3</sup> has carried out detailed calculations using the continuum approximation of the relative probability of nonradiative recombination of electrons with  $V_k$  centers. These exciton decay events initiate focused collisions in the [110] direction and lead to Frenkel defect production in the lattice. Thus the rate of production of such defects at a temperature  $T$  is

$$dF(T)/dt \propto R(T)/[1+R(T)], \quad (1)$$

where  $R(T)$  is the ratio of the nonradiative to radiative transition probabilities. Following Pooley, evaluation of  $R(T)$  for KCl and NaCl at 20°K yields 0.75 and 0.16, respectively, for the right-hand side of (1). Therefore, considering this effect alone, one would expect the rate of expansion of KCl to be 4.7 times that of NaCl.

Another contributing factor arises from the relative ease of initiation of [110] replacement sequences<sup>4</sup> in these two salts. As shown by Balarin,<sup>14</sup> this direction is the only one in the NaCl type of structure which satisfies the requirements for a simple but effective replacement sequence. According to Pooley's<sup>4</sup> semiquantitative calculations the values of the critical threshold energy  $E_c$  for initiating such a replacement sequence are of the order of 8 and 4 eV in NaCl and KCl, respectively. The effect of this factor of 2 between these energies on the ratio of the rates of defect production is very difficult to assess, but when this is combined with the factor of 4.7 mentioned above, it seems quite likely that at least the possibility of an order-of-magnitude difference in defect production rates in these two salts would be indicated. Thus, Pooley's model seems to form a basis for explanation of these experimental results.

<sup>14</sup> M. Balarin, *Kernenergie* 7, 434 (1964).

We have also measured, using the same apparatus, the rate of expansion of one sample of KF, and found that this was 8.7 times that for NaCl. This is much smaller than the factor of 37 found for KCl, partly because the ratio of the ionic volumes of chlorine and fluorine is<sup>15</sup>  $(1.65/1.19)^3 = 2.7$ , so that the effective strain resulting from each defect is much smaller for KF than for KCl by a factor of about 2.7 from this consideration alone. Thus, allowing for this volume difference, the rate of defect production in KF would be about  $2.7 \times 8.7 \sim 23$  times that of NaCl. Since the x-ray energy-absorption properties of KF are almost identical to those of NaCl, this result indicates that the rate of defect production in NaCl at low temperatures is indeed very small, and that this small value is characteristic of NaCl and not a result of some peculiarity of the experimental apparatus. Unfortunately, there is insufficient optical data to permit calculation of  $R(T)$ , and thus of  $dF(T)/dt$  for KF, in order to make a direct comparison between the results for KF and KCl in terms of Pooley's model. But since  $E_c$  for KF was calculated by Pooley<sup>4</sup> to be very similar in magnitude to that for KCl, it seems quite reasonable that the rate of defect production in KF would be more similar to that in KCl than to that in NaCl, and that the Pooley mechanism would be successful in explaining this result also.

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<sup>15</sup> F. G. Fumi and M. P. Tosi, *J. Phys. Chem. Solids* 25, 31 (1964).