# SCHOTTKY DISORDER AND LATTICE RELAXATION IN SINGLE CRYSTALS OF NaCl DUE TO X IRRADIATION AT ROOM TEMPERATURE*

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Samples of single-crystal NaCl obtained from the Harshaw Chemical Company have been x irradiated at room temperature at 250 to 300 kV peak and 20 mA for varying periods of time. Irradiation from both sides of the samples plus filtration of the beam assured uniformity of damage for all samples except one. The uniformity was checked by optical-absorption measurements. Sample $D$-1 was irradiated without filtration and consequently had a gradient of damage. Appropriate corrections were made, however, so that the various measurements could be compared. Standard procedures were used to measure the fractional lattice-parameter change, $\Delta d/d$,[1] the fractional mass-density change, $\Delta\rho/\rho$,[2] and the fractional concentration of negative-ion vacancies $n/N$.[3] An oscillator strength of 0.7 was used in the calculation of $n/N$. Integrated absorption curve areas from $E=1.0$ eV to $E=4.5$ eV were used in an effort to obtain a measure of all negative-ion vacancies associated with $F$-type centers.[4,5] The results are given in Fig. 1. The macroscopic fractional volume expansion, $\Delta V/V$, is given by

$$\frac{\Delta V}{V}=3\frac{\Delta d}{d}+\left(\frac{\Delta V}{V}\right)_S=-\frac{\Delta\rho}{\rho}. \qquad (1)$$

It is assumed that there is no loss of mass.[6] $(\Delta V/V)_S$ is defined as the unrelaxed fractional expansion due to the production of internal voids which may always be interpreted in terms of Schottky disorder, while $3\Delta d/d$ is the fractional expansion due to lattice relaxation. This lattice relaxation may be associated with several kinds of defects, e.g., interstitials, impurities, and also Schottky vacancies. If the expansion is due solely to relaxation processes, e.g., Frenkel disorder, then Eq. (1) becomes $3\Delta d/d=-\Delta\rho/\rho$.[7-11] However, whenever $3\Delta d/d$ is less than $-\Delta\rho/\rho$, void volume and thus Schottky disorder must be present. The results in Fig. 1(a) clearly indicate that for the four samples $P$-4, $D$-3, $P$-3, and $P$-2, $(\Delta V/V)_S$ is not zero. The ratio

$$\frac{3\Delta d/d}{-\Delta\rho/\rho}$$

for these samples is, respectively, $0.6\pm0.2$, $0.67\pm0.14$, $0.55\pm0.22$, and $0.52\pm0.16$. Hence it can be concluded that Schottky disorder was produced in these samples by the irradiation.

These results raise anew the question as to the mechanism or mechanisms by which Schottky disorder is produced by ionizing radiation. The theoretical aspects of such mechanisms have received little attention in recent years[12,13] and many recent experimental results have been interpreted in terms of Fren-

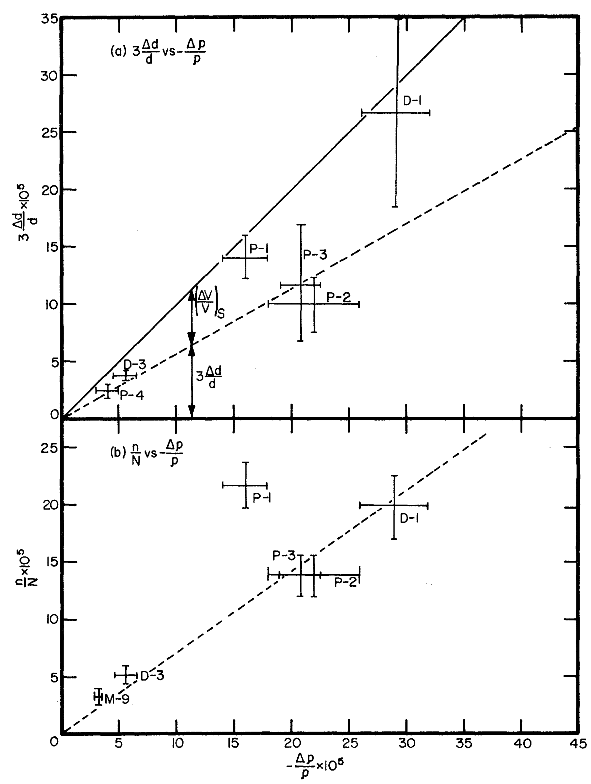


FIG. 1. Fractional density of negative-ion vacancies, $n/N$, and fractional volume change due to lattice relaxation, $3\Delta d/d$, versus fractional mass-density change $-\Delta\rho/\rho$. The solid line in (a) represents the relationship between $3\Delta d/d$ and $-\Delta\rho/\rho$ for pure relaxation effects, e.g., Frenkel disorder. The dashed lines are smooth curves drawn through the observed points (with the exception of the data for samples $P$-1 and $D$-1). The vertical lines show the relationship of $3\Delta d/d$ and $(\Delta V/V)_S$ to $-\Delta\rho/\rho$ for a hypothetical point on the dashed line. [See Eq. (1).] Error bars indicate standard errors.

kel disorder.[14-16] In addition, the presence of Schottky disorder raises anew the question of why positive-ion vacancies have not in general been detected as components of color centers by such standard techniques as optical absorption and magnetic resonance.[12,13] The data of Fig. 1(b) indicate that the negative-ion vacancies are detected as $F$ or $F$-aggregate centers.[1,17,18]

The data of Fig. 1(a) indicate that $(\Delta V/V)_S$, which is equal numerically to $(n/N)_S$, the fractional concentration of Schottky pairs, increases approximately in proportion to $3\Delta d/d$. While $3\Delta d/d$ cannot from the data presented be separated into components associated with various kinds of disorder, this proportional increase of $3\Delta d/d$ with $(\Delta V/V)_S$ strongly suggests that a significant portion of the $3\Delta d/d$ is due to relaxation in the vicinity of Schottky vacancies.[14,19]

Two samples, $D$-1 and especially $P$-1, have small most probable values of $(\Delta V/V)_S$ compared to the $3\Delta d/d$. [See Fig. 1(a).] Thus the expansion of these samples is due primarily to lattice relaxation [Eq. (1)] and there is comparatively little Schottky disorder. While it is not possible from these results to deduce the type of disorder which causes the relaxation, the large expansions and the large fractional concentrations of negative-ion vacancies in these two samples suggest that the disorder is of the Frenkel type in the halogen sublattice. Although other types of disorder are possible causes of the expansion,[12,20] this tentative conclusion is in agreement with the interpretation of other experimenters.[10,11,15,16] The differences between the results for samples $D$-1 and $P$-1 and the results for the other samples are not understood.

In summary, the most important conclusion from this work is that Schottky disorder is produced by ionizing radiation. The results also indicate that there is a mechanism by which another type of disorder, e.g., Frenkel disorder, is produced which causes expansion solely by lattice relaxation.

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