

Interstitial Defects in LiH and NaCl Irradiated at Low Temperatures*

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Expansions of the lattice parameters of both LiH and NaCl exposed to β radiation at 77° and 245°K have been observed using a vacuum x-ray diffractometer stage operated at 77°K. The source of the β radiation was 5.56% LiT contained in a LiH crystal which was ground and mixed with NaCl in the samples. The LiH lattice parameter increased 0.0020 ± 0.0007 Å in three samples. This result is consistent with density measurements and with the formation of interstitial He³ atoms in the LiH lattice. The NaCl lattice parameter increased 0.0061 ± 0.0009 Å even though the average β does for the NaCl was less than 1% of that in the Li(H,T) and tritium β particles with maximum energy cannot produce direct displacements in NaCl. A mechanism is proposed for the production of Cl⁻ interstitials and vacancies (Frenkel defects) in NaCl which is similar to one proposed by Klick for the production of *F* and *H* centers. This mechanism is related to observations of the production of α centers in alkali halides irradiated at low temperatures.

THE purpose of this paper is to report the observation of lattice expansion in NaCl and LiH irradiated by tritium β particles at 77° and 245°K. This work was done as part of a study of radiation effects on LiH crystals and is correlated with optical absorption, electron spin resonance, and expansion measurements made on samples from the same LiH single crystal containing LiT.¹ This work and additional comparisons between LiH and other alkali halides will be published in more detail elsewhere.

Previous work has been done at room temperature on the x-ray determination of changes in lattice parameters induced by irradiation. Berry² found small lattice changes consistent with the introduction of vacancy pairs into KCl exposed to x rays. Binder and Sturm's³ report of interstitial formation in LiF exposed to neutrons was found to be consistent with a displacement mechanism according to calculations of Seitz and Koehler.⁴ The present work demonstrates that interstitials are formed in NaCl by electrons of 18-kev maximum energy which can only transmit 1.7 ev to a Na⁺ ion by direct collision. Since approximately 25 ev is required to produce a displacement,⁴ it is evident that some indirect process for the production of interstitials must be considered. It is possible to explain these observations by using a mechanism for the production of *F* and *H* centers proposed by Klick⁵ which is essentially a refinement of one first given by Varley.⁶

The x-ray measurements of the lattice parameters were carried out in a vacuum attachment for the x-ray diffractometer which held the samples at approximately 77°K on a stage cooled by circulating liquid nitrogen. Transfers of samples stored under liquid nitrogen to

the diffractometer stage were made without significant warming. Mixtures containing 20 vol. % NaCl with LiH (+5.56% LiT) powder ground to approx 200 mesh from portions of single crystals were stored in protected sample containers. X radiation from a Cu target was used to determine the diffraction pattern from the samples and NaCl reference powder. Better results were obtained by using softer Cr x radiation for the LiH reference powders. All results were analyzed with an IBM-704 program utilizing Hess's⁷ modified least-squares extrapolation.

The results of the measurements on NaCl and LiH samples used for reference are given in Table I.

The samples marked "crystal" were ground from single crystals and packed into the holders, as were the mixed active samples; the LiH compress was glued into the sample holder and polished but contained some Li₂O. The room temperature value for LiH crystal is in excellent agreement with the value reported by Staritzky and Walker.⁸ The change of LiH lattice parameter in going to liquid nitrogen temperature is in good agreement with the 0.45% length change calculated from the dilatometric measurements of Laquer and Head.⁹ The NaCl values are in similar agreement with published values.¹⁰

The results of the low-temperature measurements on three samples containing mixed salts after storage at low temperature are contained in Table II. A correction

TABLE I. Reference lattice parameters, a_0 (Å).

Sample	296°K results	77°K results	$\Delta a_0/a_0$ (296°K)
			296 to 77°K
NaCl (crystal)	5.6506 ± 0.0003	5.6007 ± 0.0004	0.883%
LiH (crystal)	4.0837 ± 0.0002	4.0656 ± 0.0005	0.443%
LiH (compress)	4.0842 ± 0.0004	4.0660 ± 0.0002	0.446%

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¹ F. E. Pretzel, G. V. Gritton, C. C. Rushing, R. J. Friauf, W. B. Lewis, and P. J. Waldstein, *Bull. Am. Phys. Soc.* **6**, 114 (1961).

² C. R. Berry, *Phys. Rev.* **98**, 934 (1955).

³ D. Binder and W. J. Sturm, *Phys. Rev.* **96**, 1519 (1954).

⁴ F. Seitz and J. S. Koehler, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 307.

⁵ C. C. Klick, *Phys. Rev.* **120**, 760 (1960).

⁶ J. H. O. Varley, *Nature* **174**, 886 (1954).

⁷ J. B. Hess, *Acta Cryst.* **4**, 209 (1951).

⁸ E. Staritzky and D. J. Walker, *J. Anal. Chem.* **28**, 1055 (1956).

⁹ H. Laquer and E. Head, Los Alamos Scientific Laboratory Report, AECD-3706, December 9, 1952 (unpublished).

¹⁰ Swanson and Fuyat, *NBS Circ.* **539** 2, 41 (1953).

of -0.0014 ± 0.0001 Å was applied to the LiH reference measurements to allow for the presence of 5.56% LiT from the values of Vier.¹¹

The average lattice parameter increase of the three LiH(+LiT) crystals is 0.0020 ± 0.0007 Å, which corresponds to $(0.147 \pm 0.06)\%$ lattice expansion. Flotation density measurements on crystals from the same single crystal gave a bulk expansion of $(0.101 \pm 0.01)\%$ for the same exposure of 6.7×10^{19} β/cc. These results agree within the errors of the determinations, and they are consistent with the interpretation that interstitial He³ atoms are formed by tritium decay at 77°–245°K. According to the more accurate flotation measurements, the expansion associated with the formation of an interstitial He³ atom is about 15 Å³, which is in approximate agreement with the calculated expansion of the cube of 8 nearest neighbors to the interstitial.

The NaCl increased 0.0061 ± 0.0009 Å in lattice parameter from the average of the 3 samples which is taken as a strong indication for the production of interstitial defects under these conditions. The corresponding expansion is $(0.33 \pm 0.05)\%$. This result is too large to explain on the basis of the formation of *F* and *H* centers at the usual energy requirement of 1000–2000 eV/*F* center at low temperatures, since the calculated average β exposure is only about 4×10^{17} β/cc for 0.01-cm NaCl particles homogeneously irradiated but inhomogeneously colored.

The expansion associated with an interstitial Cl[−] ion in NaCl is nearly 60 Å³ according to the same calculation used for interstitial He in LiH. This value can be used to account for the magnitude of the observed lattice expansion if a large fraction of *F* centers produced at an energy requirement of about 50 eV/*F* center recombine to produce interstitial Cl[−] ions or if a competing process exists. Such a mechanism is illustrated in Fig. 1. With Klick⁵ we assume that the double ionization of a Cl[−] ion quickly produces an intermediate complex with a Cl₂ molecule in one of a pair of anion vacancies, from which the anion vacancy can dissociate because of electrostatic repulsion. At higher temperatures it is more probable that the vacancy will migrate some distance from the Cl₂ molecule before both sites

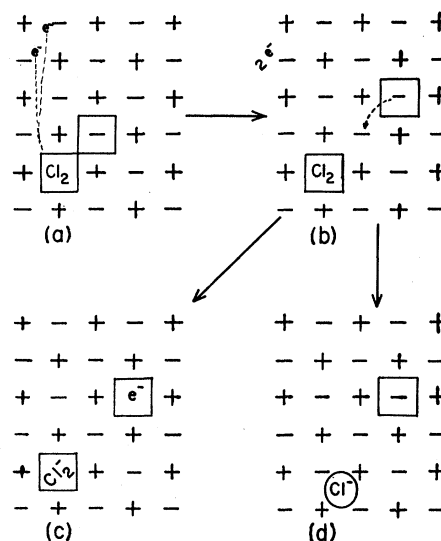


FIG. 1. Mechanism for low temperature radiation damage. (a) Loss of a pair of electrons from a pair of adjacent Cl[−] ions to produce the Cl₂–vacancy complex. (b) Dissociation of anion vacancy from the complex. (c) Trapping of electrons to form *F* and *H* centers. (d) Trapping of both electrons by Cl₂ to form Frenkel defect.

have the chance to trap electrons. If they each trap one electron, the net result is the formation of *F* and *H* centers as proposed by Klick. However, if the Cl₂ molecule traps both electrons, the net result is the formation of a Cl[−] vacancy and a Cl[−] interstitial. The yield of these Frenkel defects may be increased relative to that of *F* and *H* centers at very low temperatures because *F* and *H* centers tend to be produced close together under these conditions, and the probability that the *H* center can capture the *F* center electron by a tunneling process is increased.

The production of Frenkel defects in the anion lattice of alkali halides irradiated at low temperatures according to the preceding model is consistent with the observations of α-center formation in these crystals.¹² Rüchardt's¹³ observations on the yield of α centers in KBr irradiated at temperatures down to 4°K and of their subsequent annealing behavior can also be explained on the basis of this model. The annealing curves for α centers in KBr are similar to those obtained for the stage I annealing of Frenkel defects in Cu.¹⁴ We obtained no evidence for interstitial H[−] ions in LiH, in accord with calculations which indicate that they should be unstable.

TABLE II. Lattice parameters a_0 (Å) at 77°K.

Sample No.	Age (days)	Storage temperature	NaCl	Li(H,T)
2	133	77°K	5.6069 ± 0.0015	4.0669 ± 0.0016
3	133	77°K	5.6048 ± 0.0033	4.0659 ± 0.0008
5	129	245°K	5.6064 ± 0.0005	4.0662 ± 0.0002

¹¹ D. T. Vier (private communication).

¹² F. Seitz, Revs. Modern Phys. **26**, 7 (1954).

¹³ R. Rüchardt, Phys. Rev. **103**, 873 (1956).

¹⁴ J. W. Corbett and R. M. Walker, Phys. Rev. **115**, 67 (1959).