

X-Ray Study of Interstitial Defects in Radiation-Damaged Alkali Halides and LiH†

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The effects of exposure to tritium β particles at 77°K on the lattice parameters of Si, LiH, LiF, NaCl, KCl, and KBr were examined by x-ray diffraction studies by employing a sample stage cooled by liquid nitrogen. The Si and LiH lattice parameters remained constant during β irradiation from an external source, but all of the alkali halides showed large increases in lattice parameter. Maximum unit cell volume expansions observed were 0.2% in LiF, 0.6% in NaCl and KCl, and 0.3% in KBr. Measurements of unit cell expansion and bulk crystal expansion of LiH crystals containing LiT were also continued to determine more accurately the expansion per interstitial He³ atom. The results are interpreted on the basis of the formation of Frenkel pairs (interstitial anion plus anion vacancy) in the alkali halides by a moderately efficient process. The process involves the transport of interstitial defects through 50 μ into materials for which the β range is about 2 μ . It is proposed that this may occur either directly, by an interstitialcy mechanism, or indirectly, by exciton interactions within the crystals. Comparisons between the results of low-temperature studies of lattice expansion and color centers in alkali halides are made, and possible interrelations between the various defects formed by radiation damage are proposed.

INTRODUCTION

THE x-ray lattice parameter studies reported previously¹ for NaCl and LiH containing LiT have been repeated and extended to include LiH, LiF, KCl, KBr, and Si as target materials. The target materials were irradiated by β particles in powder mixtures with LiH containing a higher fraction of LiT than was previously used. Although the dose rate used in this series of experiments was higher, other irradiation conditions were the same as those used previously. These include the use of low-energy β particles (18-keV maximum) with a maximum range that is small compared to the radii of the target grains, and the use of low temperatures during irradiations and measurements.

The lattice expansions of the β -irradiated alkali halides are interpreted in terms of the formation of anion interstitials and vacancies (Frenkel defects) caused by an indirect mechanism. Mechanisms for the production of F and H centers in KCl exposed to x rays at low temperatures have been proposed which assume the initial formation of a doubly ionized anion intermediate. These have been presented by Klick² and, in more detail, by Howard, Vosko, and Smoluchowski.³ The unit cell expansions associated with the postulated Frenkel defects in the alkali halides were calculated on a hard-sphere approximation, and these values were used to estimate the efficiency of the interstitial process. The more refined calculation developed by Hatcher and Dienes⁴ for a neutral interstitial should be particularly applicable to interstitial He in LiH containing LiT.

The x-ray lattice parameter increase in neutron-irradiated LiF was studied by Binder and Sturm,⁵

Smallman and Willis,⁶ and others.⁷ Energetic charged particles were produced by the $\text{Li}^6(n,\alpha)\text{T}^3$ reaction in these experiments, and the lattice changes were interpreted on the assumption that ions were displaced directly into interstitial sites.⁸ The equivalence of unit cell and bulk crystalline expansion was demonstrated by Binder and Sturm for LiF. This result and the observation of relatively sharp diffraction lines from the expanded crystals have been considered on the basis of two theoretical models,^{9,10} and both observations were found to be evidence for a relatively uniform distribution of interstitial defects.

An increase in the Si lattice parameters after exposure to fast neutrons has been observed,¹¹ but Vook¹² has attributed these changes in Ge and Si to the formation of clusters of interstitials. Little lattice dilatation is expected around an isolated interstitial defect in the diamond-type lattice. This covalent semiconductor was included in the investigation because it was not expected to respond to electronic excitation in the same way as insulating ionic materials.

EXPERIMENTAL

The apparatus and procedure used for the low-temperature x-ray lattice parameter measurements were essentially the same as those described previously.¹ More care was taken in selecting powders of known grain

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¹ F. E. Pretzel and R. L. Petty, Phys. Rev. **123**, 464 (1961).

² C. C. Klick, Phys. Rev. **120**, 760 (1960).

³ R. E. Howard, S. Vosko, and R. Smoluchowski, Phys. Rev. **122**, 1406 (1961).

⁴ R. D. Hatcher and G. J. Dienes, Phys. Rev. **124**, 726 (1961).

⁵ D. Binder and W. J. Sturm, Phys. Rev. **96**, 1519 (1954).

⁶ R. E. Smallman and B. T. M. Willis, Phil. Mag. **2**, 1018 (1957).

⁷ A recent review is contained in D. S. Billington and J. H. Crawford, Jr., *Radiation Damage in Solids* (Princeton University Press, Princeton, New Jersey, 1961), p. 290.

⁸ F. Seitz and J. S. Koehler, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 305.

⁹ J. D. Eshelby, J. Appl. Phys. **25**, 255 (1954); and *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 3, p. 79.

¹⁰ R. W. Balluffi and R. O. Simmons, J. Appl. Phys. **31**, 2284 (1960).

¹¹ M. C. Wittels, J. Appl. Phys. **28**, 921 (1957).

¹² F. L. Vook and R. W. Balluffi, Phys. Rev. **113**, 70 (1959); and F. L. Vook, Phys. Rev. **125**, 855 (1962).

size for the mixed samples, and a monitoring thermocouple and a pentane-graphite medium for thermal contact were used to assure reproducible measurement temperatures. The details of the experiments will be described separately.

All of the target powders were ground from optical quality single crystals except Si (supplied by A. D. Mackay and Company), which was regularly used as an x-ray standard. The alkali halide single crystals were prepared by E. W. Fullman of this Laboratory, and the LiH crystal was prepared by a method outlined previously.¹³ All were ground under dry conditions, and the fraction caught between 140-mesh and 250-mesh sieves was taken as the target material for most of the samples. To test the effect of going to smaller grain size, NaCl powder was taken from the fraction between 250-mesh and 325-mesh sieves.

The radioactive LiH salt was very old material that had been used for previous studies¹⁴; for the present experiments it was found by calorimetry to contain 24.5 mole % LiT. This LiH salt was ground in a dry box to pass a 140-mesh sieve, and equal volumes of the salt were carefully mixed with alkali halide and LiH "target" powders before the mixed powders were packed into aluminum sample holders for the diffractometer stage. The chemically reactive powders were protected by a 0.00025-in. Mylar film sealed with silicone grease and clamped at the edges. An extra aluminum cover plate was added to protect the samples from damage during handling and storage under liquid nitrogen. Single samples of powder mixtures containing 50 vol % LiH, LiF, NaCl, KCl, or KBr were prepared, except that replacement samples were made for those damaged and rendered unusable during the course of the experiments.

For studies of lattice expansion caused by the production of interstitial He³ atoms in LiH, the old radioactive salt was annealed at 450°C for 20 h in H₂ gas to remove the effects of previous radiation damage and to replace the hydrogen lost by tritium decay. The annealed radioactive LiH salt gave x-ray diffraction lines in the back reflection region that were sufficiently sharp for analysis of the initial lattice parameter and of subsequent changes, although the lines were only one tenth as intense as those found for unirradiated LiH. Previous to the anneal, these lines were also so broad and diffuse that they were not even apparent on diffraction patterns from a sample containing LiH as the target salt. Two samples of the annealed LiH salt containing 24.5% LiT were prepared in mixtures with 20 vol % Si for comparison.

The vacuum x-ray diffractometer stage was precooled to about 145°K to allow a suspension of graphite in pentane to be painted on it before the sample was

quickly removed from liquid nitrogen and transferred to the stage. This procedure supplied a reliable thermal contact medium that rigidly froze the sample in position on the diffractometer stage after the compartment was evacuated and liquid nitrogen was made to circulate through the stage. The maximum deviation in sample temperature during x-ray measurements was 6°K, according to a thermocouple located in the top of the sample stage next to the support. About 100°K was generally recorded while liquid nitrogen was circulating through the sample stage, but, because of the location of the thermocouple, this value probably is a maximum estimate of the true sample temperature. The stage was warmed to about 145°K to remove the sample, which was again stored at 77°K under liquid nitrogen until the next measurement.

The x-ray diffraction lines, which were generally read in the 100- to 160-deg back-reflection region, from materials exposed to x radiation from a Cu target were as follows: LiF (400), (331), (420), (422); NaCl (440), (600), (620), (622), (444), (640); KCl (620), (622), (640), (642); KBr (622), (640), (642), (644); and Si (440), (531), (620), (533), (444). Softer Cr x radiation was used to obtain the (220), (311), (222) lines from LiH. The maxima of the lines were read from the diffractometer traces, and the lattice parameter calculations were performed with an IBM 704 program based on Hess's modified least-squares extrapolation.¹⁵

Some hazard was associated with the experimental procedure because liquid nitrogen had a tendency to leak under the protective Mylar film during prolonged low-temperature storage. The liquid nitrogen boiled and occasionally caused the explosive disruption of a sample that was being mounted on the diffractometer stage. Other samples were rendered less useful because the powders became displaced during storage and handling and no longer provided a flat surface for diffraction studies. This caused loss of intensity and some splitting of x-ray lines from the disturbed samples, and it may have obscured significant changes in the lattice structures of the heavily irradiated salts. Most of the samples reported on previously¹ were also found to have disturbed surfaces after subsequent observations.

The combined influence of disturbed sample surface and of thermal annealing at room temperature was investigated during the final measurements on the mixed powder samples. These were made after the samples had been stored at 77°K for 200 to 300 days. The procedure involved repacking the powder samples in a drybox after the first measurements, and this required that the samples be warmed to 300°K for about one hour before the final x-ray diffraction measurements could be made. The examination revealed that most of the sample surfaces had been disturbed during storage. In most cases repacking affected an improvement in the resolution of the x-ray lines but did not change the lattice parameter.

¹³ F. E. Pretzel, G. N. Rupert, C. L. Mader, E. K. Storms, G. V. Gritton, and C. C. Rushing, *J. Phys. Chem. Solids* **16**, 10 (1960).

¹⁴ F. E. Pretzel, W. B. Lewis, E. G. Szklarz, and D. T. Vier, *J. Appl. Phys.* **33**, 510 (1962).

¹⁵ J. B. Hess, *Acta Cryst.* **4**, 209 (1951).

Low-angle x-ray scattering could not be determined in our experimental arrangement to measure the possible effects of defect aggregation in samples exposed to large β doses. However, since large reductions in x-ray line intensities were observed with old LiT-containing samples which were known to contain large concentrations of aggregates, intensity measurements were used to give an indication of defect aggregation in our samples.¹⁶

RESULTS

1. Effects of External β Irradiation

The effects of external β radiation from mixed LiT powders on the lattice dimensions of the five target salts are summarized in Fig. 1. The LiH lattice parameter was constant during 158 days exposure to β radiation at 77°K. The weighted lattice parameter obtained for LiH at the measurement temperature was 4.0655 ± 0.0001 Å, and this standard deviation was consistent with the maximum deviation in the measurement temperature. The results obtained with Si are not illustrated, but a weighted lattice parameter of 5.4294 ± 0.0003 Å was found at the measurement temperature with no indication of a dependence on β dose.

The LiF lattice undergoes a regular expansion with β dose from an initial lattice parameter $a_0 = 4.0076$ Å. The curve for LiF indicates saturation at a value slightly below 0.2% unit cell expansion. The maximum unit cell expansion observed by Smallman and Willis⁶ for neutron-irradiated LiF was similar, but, on an absorbed energy basis, the β -activated low-temperature process is about 20 times as efficient as the neutron-activated 55°C process. The original lattice parameter was observed after 182 days storage at 300°K under continuous β irradiation.

The maximum unit cell expansion of the NaCl lattice observed was 0.57% in volume, compared to the reference lattice parameter $a_0 = 5.6007$ Å. The first two measurements on this NaCl sample showed unexplained deviations from the curve, but the next three measurements showed more consistent behavior. A rise and subsequent drop in the NaCl unit cell volume was also observed in samples exposed at a lower β -dose rate for a longer period of time. A repacked NaCl sample, which had been exposed at the lower dose rate for 500 days, was found to have recovered its initial lattice parameter. The average lattice expansion obtained from NaCl samples previously reported¹ is shown as an open circle in Fig. 1. These results were corrected to approximately the same integrated dose as the newer NaCl sample before plotting, but it is not certain that the remaining

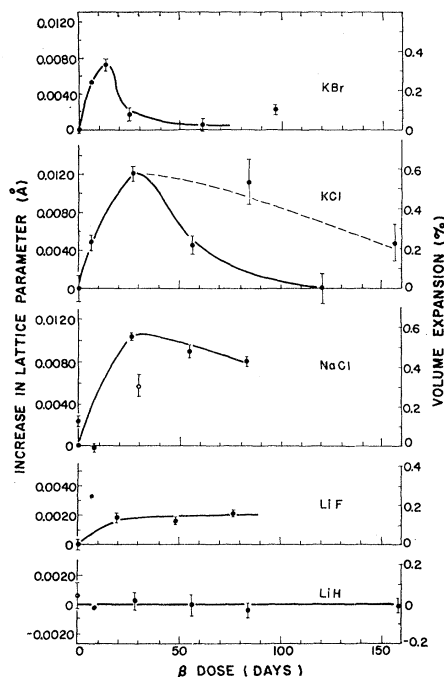


Fig. 1. Lattice changes in ionic crystals exposed to tritium β particles in mixed powder samples at 77°K.

difference indicates a higher than first-order dependence on dose rate or a possible grain size effect.

The KCl lattice expanded regularly to 0.58% unit cell expansion, compared to the initial lattice parameter of $a_0 = 6.2511$ Å. After 27 days of β exposure, the determination of the lattice parameter became less certain because of an apparent broadening and splitting of the x-ray diffraction lines. This effect was apparently due to a disturbed sample surface because it was removed by repacking the sample. It is not certain that the lattice recovery of KCl followed the solid curve of Fig. 1 more closely than the dashed one, but recovery was shown to be complete in the repacked sample.

The KBr rapidly grew to a maximum unit cell expansion of 0.33% by volume in 13 days, but the lattice recovered approximately to its original parameter, $a_0 = 6.5553$ Å, by about 60 days. The lattice parameter of the repacked KBr after 208 days exposure was 0.0035 Å lower than the original value.

The initial rise of the curves for KBr, KCl, and NaCl, illustrated in Fig. 1, can be superimposed within the limits of errors of the determinations of unit cell expansions. Lattice recovery apparently proceeds in the sequence KBr, KCl, NaCl, LiF, and this is consistent with comparative ease of lattice relaxation expected from relative lattice energy and strength measurements. Similar relative stabilities were found in the alkali halides by Känzig and Woodruff¹⁷ for an interstitial

¹⁶ At some stage during the aggregation of impurities and other defects in a crystal a maximum number of lattice sites may become effectively disordered so that x-ray diffraction from these regions is minimized, as it also is for amorphous deposits. For general reference see F. Schossberger, *Advances in X-Ray Analysis* (Plenum Press, Inc., New York, 1957), Vol. 1, p. 73.

¹⁷ W. Känzig and T. W. Woodruff, *J. Phys. Chem. Solids* **9**, 70 (1959).

defect with the crowdion configuration, the X_2^- molecule ion in an H center. The only salt for which the paramagnetic H centers showed comparative stability at 77°K is LiF.

2. Crystals Containing LiT

Lattice changes associated with tritium decay in LiH containing combined LiT are illustrated in Fig. 2. The solid circles in the figure indicate the present set of measurements made on annealed LiH powder containing 24.5% LiT in samples stored at 77°K. The open symbols in the figure show the data obtained previously with LiH samples containing 5.56% LiT.¹ On the basis of known tritium content and exposure times, both sets of data were plotted vs absorbed β dose (or He^3 atoms produced) per unit volume. The bars associated with the symbols indicate the standard deviation of the calculated lattice parameter, and, as elsewhere in this paper, the approximate inverse of the standard deviation was used to compute weight factors for a least-squares treatment of the data. Increased standard deviations observed in the later determinations were probably associated (at least in part) with disturbances of the sample surfaces.

The solid line in Fig. 2 was drawn so that its slope corresponds to the average value obtained from flotation measurements of the expansion of two LiH crystals containing 5.56% LiT. The average from these measurements was $13.06 \pm 0.85 \text{ \AA}^3/\beta \text{ decay}$.¹⁸ A least-squares analysis of the x-ray determinations of unit cell expansion for the same β -dose range gave $14.7 \pm 2.2 \text{ \AA}^3/\beta \text{ decay}$, which is in substantial agreement with but less

accurate than the flotation measurement values. Although the equivalence of the unit cell expansion and bulk crystal expansion has been demonstrated only to within 12%, the slope derived from the x-ray results has a standard deviation of 15%.

3. X-Ray Line Profile

In most of the observations made on samples exposed to β radiation at 77°K, the x-ray diffraction lines remained symmetrical and sharp, and retained their initial intensity, at least until the maximum lattice expansion was reached. This is consistent with observations on the (422) line in neutron-irradiated LiF.⁶ Subsequent uncertainties regarding possible changes in x-ray line profiles exist because of problems related to alignment and planarity of the surfaces of our samples. These effects tend to exaggerate line broadening and intensity losses.

LiH diffraction patterns were obtained with x rays from a Cr target to obtain symmetrical lines and avoid some distortion observed with the harder Cu x rays.¹ LiH powder derived from a single crystal containing 5.56% LiT gave a (311) line after exposure to $6.7 \times 10^{19} \beta/\text{cm}^3$, which was within 4% of the width for a reference LiH powder. Annealed LiH powder containing 24.5% LiT gave a (311) line that was approximately as broad as the reference line right after the anneal, but the pattern was about 0.1 times as intense as the reference. This indicates that considerable local disorder exists in the annealed material, which still contains a large concentration of He^3 impurity. Before annealing, the radiation-damaged LiH containing large amounts of separated Li metal, He^3 , and H_2 in voids¹⁴ had a (311) line that was 3 times as wide as the reference line, and the diffraction pattern was also of low intensity. The lattice parameter of the material containing 24.5% LiT was not significantly changed by annealing at 450°C, and it was consistent with the parameter calculated for LiH of this isotopic composition. This observation confirms the interpretation that no large concentration of interstitial atoms is retained in crystals stored at room temperature.¹⁴

For the β -irradiated alkali halides, the widths of selected high-angle lines obtained from the first few measurements were intercompared in order to minimize the complications that increase with storage. The LiF (422) line remained within 10% of its initial width during 0.13% volume expansion of the unit cell. The NaCl (622) linewidth remained constant within 6% during 0.57% unit cell expansion. The KCl (642) line remained within 20% of its initial width during 0.58% unit cell expansion. The KBr (644) linewidth remained constant within 15% during 0.33% unit cell expansion. In general, these results are representative of the changes in the over-all diffraction patterns, and the linewidths observed for the alkali halide crystals are 0.8 to 2 times

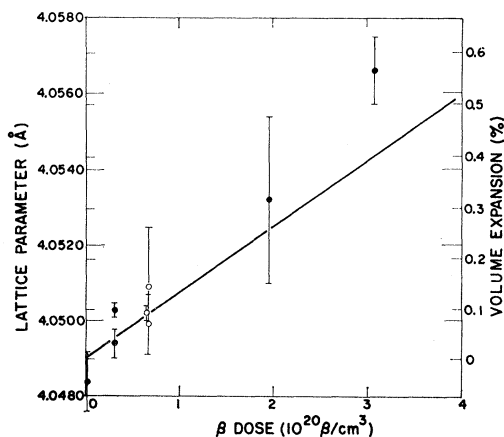


FIG. 2. Lattice expansion associated with He^3 formation in LiH crystals containing 24.5% LiT stored at 77°K. Previous data on crystals containing 5.56% LiT are plotted to scale in the open circles. The line fits bulk crystal expansion found by flotation measurements.

¹⁸ F. E. Pretzel, G. V. Gritton, C. C. Rushing, R. J. Friauf, W. B. Lewis, and P. Waldstein, *J. Phys. Chem. Solids* **23**, (1962). These values are more complete than similar ones contained in the preceding reference or in footnote 14.

as great as the normalized angular displacements caused by the observed maximum lattice expansions.

Loss of x-ray line intensity, as determined by comparing the initial low-temperature diffraction patterns to those obtained after repacking the samples, is subjected to large errors and losses under 20% are of doubtful significance. NaCl, Si, LiF, and KCl fit into the class for which no significant loss in intensity was found, but KCl is just at the arbitrary 20% limit. The average loss in intensity for all of the KBr lines was 50%, and a 70% loss in intensity was found for lines of the externally irradiated LiH. For all of the LiH samples (including those containing 5.56% or 24.5% LiT) a loss of about 50% of the average integrated line intensity was observed after repacking the samples at 300°K, despite an apparent sharpening of lines compared to the diffraction patterns obtained from some samples just before repacking them.

DISCUSSION

A possible mechanism, which may be derived from these lattice studies, for the production of interstitial defects in β -irradiated alkali halides may be of general significance for the interpretation of radiation damage to these materials. The experimental results supply information regarding the nature of the interstitial defects, the energy required to produce them, and their range or that of the energy carrier.

According to the experimental observations, similar radiation-damage processes either do not occur in Si or LiH under the conditions of these experiments, or the interstitial defects are unstable. The first statement is probably applicable to Si and the second to LiH. Color center studies have shown that F centers are formed by irradiating LiH crystals at liquid nitrogen temperature, and that most of these F centers are destroyed by recombination or form Li colloid if the crystals are warmed to room temperature.¹⁸ Presumably the vacancies required to form F centers are introduced into LiH by evaporation from dislocations¹⁹ and these subsequently form aggregates, which are responsible for the loss of x-ray line intensity observed with all repacked LiH samples. Previous measurements have demonstrated that vacancy mobility in LiH at room temperature is comparable to that in NaCl at 300°C,¹³ and that one hour at room temperature is adequate for extensive Li colloid formation in LiH irradiated at liquid nitrogen temperature.¹⁴

Lower defect mobility can be used to explain our observation that no comparable loss in x-ray line intensity was found associated with repacking the alkali halide samples. Extensive aggregation of F centers and vacancies evidently does not occur in them during a brief anneal at room temperature, and isolated lattice defects should not have much effect upon the shape or intensity of the x-ray diffraction lines.^{9,10} The production of inter-

stitial defects may supply anion vacancies required for F -center formation, but color center studies have not produced F -center growth curves comparable to those of Fig. 1. F -center growth curves show some saturation, at most, instead of a maximum. Presumably the alkali halide lattice parameters approximately recover their unirradiated values after prolonged exposure to β particles at 77°K because the interstitial defects are replaced by others which cause little lattice strain. Evaporation of vacancies from dislocations¹⁹ into the strained crystals could account for the annihilation of the interstitials. The resulting crystal would be relatively free from lattice strain, but it could still contain F centers, V_1 centers, higher V centers, and other defects found in crystals exposed to intensive irradiation at 77°K. Loss of intensity of x-ray lines from KBr indicates that some aggregation may have occurred in the "softest" alkali halide studied. A negative deviation in lattice parameter, such as was observed in the repacked KBr sample, has also been reported for annealed LiF crystals that had previously been damaged by neutron irradiation.⁷

1. Nature of Interstitials

The regular lattice expansion of LiH containing LiT serves as an excellent basis for comparison with the alkali halides, because the mechanism is more easily understood. Interstitial He³ atoms are produced at a predictable rate in homogeneous samples wherein the formation of the complementary defect, the F center, occurs at a parallel rate.¹⁸

An illustration of the simplified calculation for the unit cell expansion associated with an interstitial He atom in LiH is given in Fig. 3. The configuration is the same

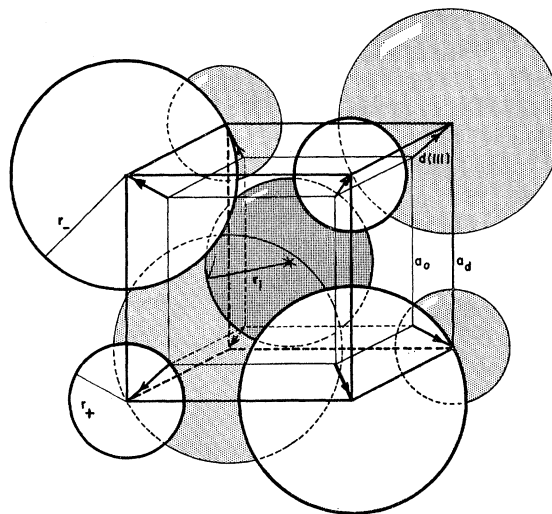


FIG. 3. Model for the hard-sphere calculation of lattice expansion associated with an interstitial He atom in LiH. (Approximately to scale.)

¹⁹ F. Seitz, Revs. Modern Phys. 26, 7 (1954).

as that used by Hatcher and Dienes,⁴ but the ions and the interstitial are all assumed to be hard spheres, and the expansion of the eight ion cube is assumed to be transmitted through the lattice by elastic displacements without further expansion. The last approximation is probably correct within 10 or 20%,⁹ and the success of the calculation is strongly dependent on the choice of a consistent set of ionic and atomic radii. A criterion of reasonableness that may be applied to all calculations based on this model is that Frenkel pair volumes should be comparable to ion pair volumes.^{7,8}

For LiH the radii used were 1.36 Å for the H⁻ ion and 0.68 Å for the Li⁺ ion. The effective radius of a He atom in the interstitial position is 1.01 Å, if the +0.08 Å correction for coordination number²⁰ 8 is added to the 0.93-Å crystal radius.²¹ The He interstitial and the nearest neighbors H⁻ and Li⁺ ions were drawn approximately to this scale in Fig. 3. The calculated diagonal (111) displacement of the H⁻ ions was 0.60 Å, and the Li⁺ ions were assumed to be displaced by an equal amount.⁴ The volume of the cube of Fig. 3 increased from 8.51 Å³ to 20.5 Å³ for a 12.0 Å³ volume increase. This result is within 10% of the 13.0 Å³ determined experimentally, and the simple model appears to give a satisfactory approximation of the crystal expansion associated with a neutral interstitial in a NaCl-type lattice.

Hatcher and Dienes's calculation⁴ for an interstitial Cl atom in a NaCl lattice gave a 26% increase in the edge dimensions of a cube like that in Fig. 3. They calculated the Cl atomic radius, since no Goldschmidt radii for halogen atoms were available. However, paramagnetic resonance studies indicate that Cl atoms are combined in a crowdion configuration as Cl₂⁻ molecule ions at an anion site (*H* center), and studies of the *H* center have shown that it too is unstable in most of the alkali halides at the temperatures used for our lattice parameter experiments.¹⁷ It does not seem probable that interstitial cations are formed by an ionization mechanism. For these reasons and those given previously,¹ we have assumed that the interstitial defect produced in β -irradiated alkali halides is an interstitial halide ion, and further discussion is based on this assumption.

A consistent set of radii²⁰ is available for calculating the crystal expansion caused by introducing an interstitial anion into an alkali halide crystal according to the method illustrated in Fig. 3, but complications arise because of polarization of the lattice by the negatively charged interstitial. Calculations of polarization and ionic displacements near vacancies and cation interstitials have been made for a few alkali halides.²² For

TABLE I. Expansion calculation for a Frenkel defect.

Quantity	Salt				
	LiH	LiF	NaCl	KCl	KBr
$\frac{1}{2}a_0$ (Å)	2.042	2.014	2.820	3.147	3.298
$V_0 = (\frac{1}{2}a_0)^3$ (Å ³)	8.51	8.17	22.43	31.17	35.87
$r_-(\text{coord no. 6})(\text{Å})$	1.36	1.33	1.81	1.81	1.96
$r_i(\text{coord no. 8})(\text{Å})$	1.44	1.41	1.89	1.89	2.04
$r(\text{void})(\text{Å})$	0.41	0.41	0.63	0.92	0.90
$d(111)(\text{Å})$	1.02	1.00	1.26	0.98	1.14
$\frac{1}{2}a_d(\text{Å})$	3.23	3.15	4.27	4.27	4.62
$V_d = (\frac{1}{2}a_d)^3$ (Å ³)	33.8	31.2	78.1	78.1	98.5
$V_d - V_0$ (Å ³)	25.3	23.0	55.7	46.9	62.6
$V_i = 1.10(V_d - V_0)$ (Å ³)	28	25	61	52	69
$V_{Fp} = V_i + 0.1V_0$ (Å ³)	29	26	63	55	73
$\alpha = V_{Fp}/2V_0$	1.7	1.6	1.4	0.9	1.0

simplicity, we have ignored the difference in the displacements of the neighboring anions and cations to the interstitial halide ion and as a first approximation, we have calculated the crystal expansion as in the case of a neutral He interstitial. The results of these calculations for LiH, LiF, NaCl, KCl, and KBr are given in Table I. The initial nearest-neighbor distances $\frac{1}{2}a_0$ and the halide ion radii r_- and r_i , for the respective coordination numbers 6 and 8, were used to calculate ionic displacements $d(111)$ and the expansion of the nearest-neighbor cube $(\frac{1}{2}a_d)^3 - (\frac{1}{2}a_0)^3$. Consistent with the case for the He interstitial atom in LiH, it was assumed that the calculated values are about 10% lower than the probable expansion associated with the interstitial anion V_i . To complete the estimate of the lattice expansion associated with a Frenkel pair V_{Fp} , the expansion of the anion lattice site containing the vacancy was assumed to be 10% of half of the ion pair volume V_0 .^{22,23} The calculated Frenkel pair volume is generally somewhat larger than the ion pair volume according to the ratio α given in the last row of Table I.^{7,8}

It is apparent that radiation effects on LiH are somewhat different from those on the alkali halides. In a previous paper¹⁸ it was observed that strong saturation of *F*-center formation by radiation damage to LiH occurred about 2×10^{18} *F* centers/cm³. The possibility that 10^{18} /cm³ interstitial H₂ molecules may have also been formed can be examined in light of the data of Fig. 1 and the previous calculation. For 10^{18} /cm³ H₂ interstitials with an effective radius of 1.36 Å, the corresponding unit cell expansion would be 0.003%, or a 0.0004-Å increase in a_0 . A statistical analysis of the data obtained from unirradiated and β -irradiated LiH (Fig. 1) shows that with 97% confidence a 0.0004-Å expansion in lattice parameter has not occurred. These results indicate that the maximum concentration of interstitial H⁻ ions or H₂ molecules in LiH is of the order of 10^{17} /cm³, compared to concentrations of about 10^{20} /cm³ in the alkali halides.

²⁰ W. H. Zachariasen quoted in C. Kittel, *Introduction to Solid-State Physics* (John Wiley & Sons, Inc., New York, 1953), p. 40.

²¹ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), p. 514.

²² N. F. Mott and M. J. Littleton, *Trans. Faraday Soc.* **34**, 485 (1938).

²³ C. R. Berry, *Phys. Rev.* **98**, 934 (1955).

In view of these experimental results, it is of interest to try to compare the relative stability of an interstitial H^- ion in LiH toward electronic dissociation to comparable processes for interstitial halide ions in the alkali halides. For this purpose we want to estimate the energy change for a process by which two electrons are raised to the conduction band from an interstitial H^- ion and one of its neighbors, which then combine to form a H_2 molecule at the lattice site. We compare this to a similar calculation for an interstitial F^- ion combining with a neighbor to form a F_2 molecule in LiF.²⁴ The calculation may be broken into the following steps: (1) The interstitial H^- ion and an adjacent H^- ion are removed from the lattice and the energy change is calculated. This requires a detailed calculation that involves polarization terms and has not been done; but, because of the comparable sizes of H^- and F^- ions, the change in lattice energies for LiH and LiF should be similar; (2) In vacuum, two electrons are removed from the ions and the atoms combine to form a molecule according to the net equations $2H^- = H_2 + 2e^-$, and $2F^- = F_2 + 2e^-$. From the known value of the electron affinities of the atoms²⁵ and the dissociation energies of the molecules,²⁶ the corresponding heats of reaction are found to be -3.06 eV for hydrogen and $+5.48$ eV for fluorine; and (3) Each molecule is placed in the corresponding vacant lattice site and the electrons in the conduction band. Since the H_2 and F_2 molecules are each about the size of individual H^- and F^- ions, and since the vacant lattice sites should have expanded slightly,²² the molecules should be accommodated in the ion sites with very small changes in repulsive energy. The energy differences between the vacuum levels and conduction bands for the electrons are assumed to be comparatively small.

From the preceding estimates, we expect the interstitial F^- ions in LiF to be more stable than the interstitial H^- ions in LiH by the order of 8 eV. Step (2) for the other halogens also shows large heats of reaction ($+4.92$ eV for Cl and $+4.90$ eV for Br), and the interstitial halide ions are expected to show similar stability toward electronic dissociation. More detailed calculations of energy changes associated with steps (1) and (3) are needed before the relative stabilities of a Frenkel pair and complementary color centers in a given salt can be determined.

2. Energy of Defect Formation

To estimate the efficiency with which interstitial defects are formed in alkali halides exposed to tritium

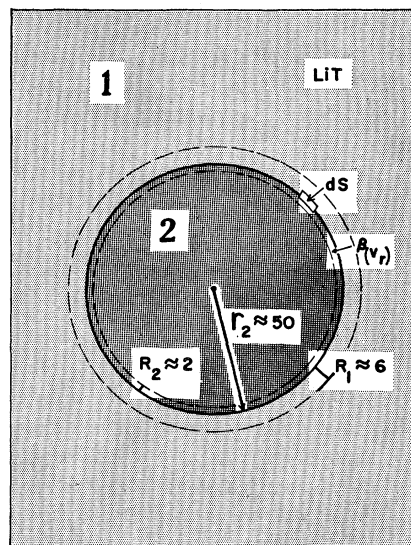


Fig. 4. Comparison between the tritium β -particle ranges and target grain size used to estimate the β -dose to the alkali halides and the distribution of the dose in the grains.

β particles at low temperatures, it is necessary to calculate the average β energy dissipated in the target powders of our mixed powder samples. We need to know the properties of the bombarding β particles²⁷ as well as the densities, dimensions, and distribution of the powder grains. Tritium β particles from a "thin" source have a maximum energy of 18 keV and a mean energy of 5.6 keV, and the shape of the energy distribution of β particles from a "thick" source is approximately the same.²⁸ The maximum range of tritium β particles is 0.6 mg/cm^2 ,²⁸ which is equivalent to about $6 \times 10^{-4} \text{ cm}$ in LiH containing LiT ($\rho = 0.8$ to 0.9), and 2×10^{-4} to $3 \times 10^{-4} \text{ cm}$ in the alkali halides ($1.98 \leq \rho \leq 2.75$). Mean grain sizes of all of the target powders were large compared to the β -particle ranges.

The β energy dissipated in a target grain 2 of radius r_2 imbedded in a LiT matrix 1 can be estimated by using the geometry illustrated in Fig. 4. In a spherical coordinate system the β flux crossing an element of surface dS at r_2 from matrix 1 from $r > r_2$ is approximately

$$dS[\frac{1}{2}N_1^0 \int_0^{R_1} e^{-\mu x} dx] = dS[\frac{1}{2}N_1^0(1/\mu)],$$

where $x = r - r_2$, and N_1^0 and R_1 are the β -particle production rate and range in the source material 1. The factor $\frac{1}{2}$ enters in because only β particles originating in matrix 1 with component $v_r < 0$ can cross the boundary at r_2 .²⁹ The source of the β -dose inside the "thick"

²⁴ This is equivalent to the formation of a possible V_1 center. Some differences in electronic and lattice strain energy occur if an H center is formed, but its thermal bleaching characteristics indicate that the H center is a shallow trap for electrons (reference 17).

²⁵ F. D. Rossini *et al.*, National Bureau of Standards Circular No. 500 (U. S. Government Printing Office, Washington, D. C., 1952).

²⁶ D. Cubicciotti, J. Chem. Phys. **31**, 1646 (1959).

²⁷ G. H. Jenks, F. H. Sweeton, and J. A. Ghormley, Phys. Rev. **80**, 990 (1950); W. M. Jones, *ibid.* **100**, 124 (1955).

²⁸ R. D. Evans, *The Atomic Nucleus* (McGraw-Hill Book Company, Inc., New York, 1955), pp. 624-628.

²⁹ An additional correction for losses due to the angular distribution of β particles originating in the "thick" source reduces this factor to 0.4. T. Rockwell, *Reactor Shielding Design Manual* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1956), pp. 346, 353, 373.

TABLE II. Interstitial defect formation by β radiation.

Quantity	LiH	LiF	Target salt NaCl	KCl	KBr
Grain radius (10^{-4} cm)	50	50	25	50	50
β range (10^{-4} cm)	6	2.0	2.4	2.6	1.9
Maximum expansion (%)	~ 0.001	0.2	0.57	0.58	0.33
Expansion rate (%/day)	~ 0	0.007	0.023	0.025	0.032
V_{FP} (10^{-24} cm ³)	29	26	63	55	73
Maximum Frenkel pair concentration (cm ⁻³)	$\sim 10^{17}$	0.8×10^{20}	0.9×10^{20}	1.1×10^{20}	0.5×10^{20}
Rate of Frenkel pair formation (cm ⁻³ day ⁻¹)	~ 0	2.7×10^{18}	3.6×10^{18}	4.5×10^{18}	4.1×10^{18}
Energy per Frenkel pair (eV)	...	370	280	220	240
Exciton band (eV)	4.9	12.7	8.0	7.9	6.9

matrix 1 has been approximated by an exponential function, and the integral of this function has been estimated by using $\mu = 0.15 \times 10^{-4}$ cm⁻¹ for tritium β particles in the source material.²⁸ Subsequent integration over the total surface of a spherical grain of radius $r_2 = 50 \times 10^{-4}$ cm, a "thick" target, yields the total absorbed dose rate, and the average volume dose rate for grain 2 is then found to be $(3/r_2)(0.4N_1^0/\mu) = 0.16N_1^0$.

The energy dissipated (and generated) deep inside grains of matrix 1 containing 24.5% LiT is 1.22×10^{22} eV/cm³ day.²⁷ If the same average β energy is assumed in source and target, and the expression is corrected because only one-half of the target sphere surface "sees" LiT surface in equal volume mixtures of source and target grains, the average absorbed dose rate for the target materials is 1×10^{21} eV/cm³ day.³⁰ These estimates are appropriate for most of our samples, which consisted of equal-volume mixtures of components with an average grain radius of 50 μ ; but the situation is less clear for the NaCl sample in which only the target grains had an average radius of 25 μ .

A summary of experimental and calculated results for interstitial defect formation at 77°K in equal-volume salt mixtures with 24.5% LiT powder is presented in Table II. The properties of the average target grains are given in the table, together with the maximum expansions and the average initial expansion rates derived from the data of Fig. 1. The expansion data were translated into interstitial defect concentrations by using the calculated Frenkel pair volumes from Table I. The energy required to produce a Frenkel pair in each salt was calculated from the average rate of defect formation and the mean β -dose rate. The energies of the first exciton absorption bands are given for comparison.³¹

The values given in Table II are generally correct within 20 to 50%, and the calculated average energies to create Frenkel pairs are probably within a factor 2 of the true values. Simplifying assumptions that were used to calculate the β -dose rate in the target powders

included the use of an average radius and a uniform random distribution of the grains of both components of the mixture. These assumptions received some practical justification from the observation of relatively sharp x-ray diffraction patterns from the expanded powders. Finer grains that were not discarded from the LiT-containing fraction could be expected to raise the average β dose to the target powders somewhat; but experience has shown that such fine grains have higher chemical reactivity and tend to lose tritium. The β -dose rate to the target powders could have been significantly reduced by the introduction of foreign materials into the mixtures, and liquid nitrogen is known to have leaked into some of the samples during storage.

The efficiency of Frenkel defect formation in alkali halides at 77°K is not as high as the maximum efficiencies reported for F -center formation near 300°K; but the "easy" stage of F -center formation generally saturates at about 10^{17} /cm³. The energy required for the production of F centers in most of the alkali halides at low temperatures is about 1 to 10 keV/center.^{8,32}

3. Distribution of Interstitials

The sharpness of the x-ray diffraction lines obtained from all of the expanded powders indicates that a relatively uniform random distribution of interstitial defects existed within the grains of each material.^{9,10} Additional evidence for the uniform distribution of interstitial He³ atoms in the LiT-containing grains is derived from the equivalence of the x-ray and bulk crystal expansions, and from the *a priori* knowledge of a uniform random distribution of tritide ions. Alkali halide lines were not comparatively more broadened than those of LiT-containing powders showing equivalent unit cell expansion. Extra line-broadening would have been expected if the alkali halide grains possessed a surface distribution of interstitials comparable to the β -dose distribution illustrated in Fig. 4. Such a surface distribution of defects would have distorted the lattice planes; and, since the x rays used did penetrate the grains, elastic continuum calculations indicate that the expansion determined by x-ray diffraction should have been less than the true expansion of the crystal grains.⁹

³⁰ This calculation gives about 8% of the source dose rate for the target grains. The value given for NaCl in reference 1 was only $\frac{1}{10}$ as large because of an incorrect estimate of the value of μ .

³¹ R. Kato, J. Phys. Soc. Japan **16**, 1476 (1961); J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. **116**, 1099 (1959); and reference 13.

³² H. Rabin and C. C. Klick, Phys. Rev. **117**, 1005 (1960).

This apparently uniform distribution raises the problem of how the interstitials got into the interior of the crystal grains, if the β particles were stopped within about 2×10^{-4} cm from the surface.

The samples were exposed to more penetrating radiations from two sources, and the possible effects of these should be considered first. Bremsstrahlung x-ray production by low-energy β particles in materials of low atomic number is an inefficient process,³³ and about 2×10^{17} eV/cm³ day was generated in each of our mixed powder samples. If all of the bremsstrahlung energy were absorbed by the target grains, this is still less than 0.02% of the energy derived from stopping β particles, and it can scarcely be sufficient to cause the large effects which we have observed. Another source of x radiation was the x-ray machine (Norelco, operated at 30 kV and 20 mA with a Cu target), but this was operated only during the measurements. Several successive measurements at low temperatures were made on mixed powder samples and on nonradioactive reference powders, mainly to test the effect of sample alignment. No effect of x rays from the machine on the lattice parameters was found, and certainly no changes in lattice parameter like those shown for successive measurements on the alkali halides in Fig. 1 were observed.

4. Summary

From the preceding discussion, three major requirements can be seen to exist for a mechanism to produce the postulated Frenkel defects in alkali halides exposed to β particles. (1) The mechanism must allow the interstitials to be produced by an indirect process, presumably involving electronic excitation, because tritium β particles with maximum energy are incapable of producing direct displacements in the alkali halides.^{1,8} (2) The mechanism must be efficient enough to produce interstitial defects with unit cell expansion comparable to the ion-pair volume at an energy requirement of less than 500 eV/defect. (3) The mechanism should include the transport of the defect, or of the energy required to produce it, over ranges that are much larger than the maximum range of the bombarding β particles.

The first requirement of an indirect mechanism for the production of Frenkel defects can be met by a modification¹ of the multiple-ionization mechanism proposed by Klick,² or by a similar modification of the mechanism proposed by Howard *et al.*³ The Auger process for producing multiple ionization, which may be considered as a first step for both of the preceding mechanisms, probably is less efficient³ than the process needed to fulfill the second requirement of efficiency. Perhaps this requirement could be met by assuming that sufficient extra excitation energy may be concentrated in the neighborhood of neutral halogen atoms produced

by a single ionization so that the appropriate intermediates to either mechanism are formed before the ionized electrons are retrapped. Such intermediates might be separated halogen molecules and vacancies in anion sites² or separated interstitial halogen atoms and vacancies.³

The third requirement forces one to seek a mechanism for the transportation of a defect, directly or indirectly, into a crystal. A direct mechanism might be pictured as an interstitialcy migration of the interstitial halide ion following closely packed planes, much like the focused collision processes that have been studied in metals.³⁴ In this case the distance traveled might depend on the rate of energy loss by the interstitialcy, on its mobility at low temperature, and on its possible encounter with a dislocation or some other defect. This process is hypothetical because interstitialcy motion and focuson collisions have not been observed in the alkali halides, but the indicated mechanism would remove interstitials from heavily strained surface regions toward the interior in such a manner as to relieve the stress caused by differential expansion.

The third requirement might also be met by an indirect process if excitons produced in the radiation-damaged surface region migrate into the interior of the crystal grains and there interact with other excitons, phonons, or different defects to produce interstitials. This process essentially transports the energy into the interior of the crystal grains where, through electronic excitation, interstitial defects are formed. Also, there is not much experimental evidence related to exciton processes in the alkali halides; but kinetic measurements related to *F*-center production by exciton processes indicate that the exciton range may be about 10^{-5} cm,³⁵ which is small compared to 5×10^{-3} cm found in the present experiments. The exciton mechanism might be used to explain the absence of any interstitial defects in LiH exposed to external β radiation, because, as Table II shows, most of the excitons would be comparatively low energy; but this point is of little value because of the inherent instability of interstitial H^- ions in LiH.

Some comments regarding the mechanism of color center formation in the alkali halides may be made after comparing observations on color centers to those on interstitial defects. Our results indicate that large concentrations of Frenkel pairs are rapidly formed in alkali halides exposed to β radiation, and observations on the growth of the α band at low temperatures^{1,19,36} indicate that one of the components of a Frenkel pair is formed by x irradiation. It may be possible to explain the linear *F*-center growth rates found in alkali halides irradiated at low temperatures by assuming that they

³⁴ R. H. Silsbee, J. Appl. Phys. **28**, 1246 (1957).

³³ E. Fermi, *Notes on Nuclear Physics* (University of Chicago Press, Chicago, Illinois, 1949), p. 47.

³⁵ M. Ueta, M. Hirai, and H. Watanabe, J. Phys. Soc. Japan **15**, 593 (1960); J. H. Parker, Jr., Phys. Rev. **124**, 703 (1961).

³⁶ R. Rüchardt, Phys. Rev. **115**, 67 (1959).

are formed by trapping electrons at anion vacancies produced previously as parts of Frenkel pairs. Companion hole centers include V_1 (halogen molecule) and V_k (self-trapped) centers according to this mechanism. The simultaneous formation of F and H centers would be a competing process¹ associated with less unit cell expansion for each defect pair. F -center production near room temperature may be complicated because of the thermal annealing of Frenkel defects and the introduction of vacancies from dislocations, as well as impurity effects.^{37,38}

The saturation of magnetic F centers³⁹ at $8 \times 10^{19}/\text{cm}^3$ in neutron-irradiated LiF agrees with that of Frenkel defects (Table II), and this is indicative of a possible connection between the production of the two types of defects. Spaepen⁴⁰ found that the fractional density recovery of neutron-irradiated LiF, during subsequent annealing, was reduced by increasing the neutron dose beyond the first saturation level found in the expansion curve, which he also compared with the maximum found in lattice parameter curves for samples exposed to about $2 \times 10^{17} \text{ nvt}$.⁶ This observation may also be taken as evidence for the introduction of vacancies into irradiated crystals by a second mechanism, presumably evaporation from dislocations,¹⁹ which becomes increasingly important as the total dose is increased.

³⁷ H. W. Etzel and D. A. Patterson, Phys. Rev. **112**, 1112 (1958).

³⁸ J. H. Crawford and C. M. Nelson, Phys. Rev. Letters **5**, 314 (1960).

³⁹ R. T. Bate and C. V. Heer, J. Phys. Chem. Solids **7**, 14 (1958).

⁴⁰ J. Spaepen, Phys. Rev. Letters **1**, 281 (1958).

It is possible that fresh dislocations formed in the preparation of our powder grains alter color-center stabilities and production rates compared to published results for single crystals. We hope to remove some uncertainties by making both x-ray diffraction and paramagnetic resonance measurements on compresses made from mixed powders. Such measurements should also allow greater precision in the examination of x-ray diffraction line profiles.

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