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Low-Temperature Annealing of Irradiation-Induced Defects in LiF†

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The expansion of alkali halides due to x-ray irradiation has been observed at 90° and 300°K. Simultaneous measurements of the *F* band indicate that the expansion can be roughly explained on the basis of the generation of negative ion vacancies. However, partial annealing of the expansion of LiF at approximately 130°K after irradiation at 90°K is not accompanied by a decrease in the density of negative ion vacancies associated with *F* centers, therefore indicating that the expansion cannot be completely due to the increase in the density of *F* centers. The low-temperature annealing of the expansion can be associated with either vacancy pair diffusion or interstitial motion. While experiments with plastic deformation and *M* band formation in LiF argue against vacancy pair diffusion, the spin resonance experiments of Känzig and Woodruff support the interstitial interpretation. It is therefore tentatively concluded that halogen vacancy interstitial pairs are generated by x-ray irradiation in LiF at 90°K and that the low-temperature annealing is due to a change in interstitial configuration.

I. INTRODUCTION

It is well established that large numbers of lattice defects can be introduced into alkali halide crystals by ionizing radiation.[1,2] However the mechanism by which energy, given to the lattice in the form of electronic excitation and ionization, is converted into lattice defects has not as yet been determined. This mechanism is of rather general importance for this class of crystals since independent of whether the radiation is in the form of high-energy charged particles, gamma rays, or x-rays the vast majority of the damage is caused by ionization. The silver halides are also very sensitive to ionizing radiation. However, in this case the mechanism of defect generation has been fairly well established, and diffusion appears to be necessary for large numbers of defects to be introduced. This limits the photodestruction of the silver halide lattice during irradiation to a particular temperature range. In contrast, in the alkali halides large numbers of defects can be generated even at 4°K, indicating that appreciable ionic diffusion is not necessary.

Intimately associated with the question of defect generation is the question of the types of defects which are introduced. While the latter question has also been answered for the silver halides, it has only been partially answered in the case of the alkali halides. Although it is well established that large numbers of negative ion vacancies are generated by irradiation because of the observed *F* optical absorption band, very little is known about the presence of other defects such as positive ion vacancies or interstitials. Probably the most convincing arguments for associating the *F* band with electrons trapped at negative ion vacancies come from spin resonance experiments.[3] While Seitz[1] has suggested that the *V* bands are associated with holes trapped at positive ion vacancies, spin resonance experiments have failed as yet to verify this postulate.[4] Therefore it is not possible to detect the presence of positive ion vacancies in an equally convincing way. However, since the ionic conductivity is due to the motion of positive ion vacancies, a change in the conductivity can indicate a change in the number of free positive ion vacancies. No such changes have been observed by several workers at room temperature in either NaCl or KCl after irradiation with high-energy protons or Co^{60} gammas.[5,2] It must therefore be concluded that either the density of positive ion vacancies is not increased as a result of irradiation, or that all additional vacancies are rendered immobile by trapping or clustering processes which take place during the irradiation. Indirect evidence for the presence of positive ion vacancies may be taken from measurements of the change in lattice parameter by Berry.[6] While a fractional increase in lattice parameter of the order of 10^{-5} was observed, Berry concluded from a comparison of his results with measurements by others of the expansion of the crystal[7] that a much larger fractional change in lattice parameter should have been observed if Frenkel defects had been generated. He therefore concluded that Schottky disorder predominated, thus implying the presence of positive ion vacancies. However, because the lattice parameter measurements were made on powders it was not possible to measure also the *F*-center density and, in particular, to determine if the observed coloration was due to negative ion vacancies already present in the lattice or to newly generated vacancies. In view of the large range

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† Research supported by U. S. Atomic Energy Commission and an Office of Naval Research contract.

[1] F. Seitz, Revs. Modern Phys. **26**, 7 (1954).

[2] K. Kobayashi, Phys. Rev. **102**, 348 (1956).

[3] See, for example, C. A. Hutchison, Phys. Rev. **75**, 1769 (1949); M. Tinkham and A. F. Kip, Phys. Rev. **83**, 657 (1951); C. A. Hutchison and G. A. Noble, Phys. Rev. **87**, 1125 (1952).

[4] T. G. Castner and W. Känzig, J. Phys. Chem. Solids **3**, 178 (1957); T. O. Woodruff and W. Känzig, J. Phys. Chem. Solids **5**, 268 (1958); Cohen, Känzig, and Woodruff, Phys. Rev. **108**, 1096 (1957); W. Känzig and T. O. Woodruff, Phys. Rev. **109**, 220 (1958).

[5] E. A. Pearlstein, Phys. Rev. **92**, 881 (1953); H. S. Ingham, Jr., thesis, Carnegie Institute of Technology, 1958 (unpublished); H. S. Ingham, Jr., and R. Smoluchowski, Bull. Am. Phys. Soc. **3**, 143 (1958).

[6] C. R. Berry, Phys. Rev. **98**, 934 (1955).

[7] Estermann, Leivo, and Stern, Phys. Rev. **75**, 623 (1949); K. Sakaguchi and T. Suita, Technol. Repts. Osaka Univ. **2**, 177 (1952).

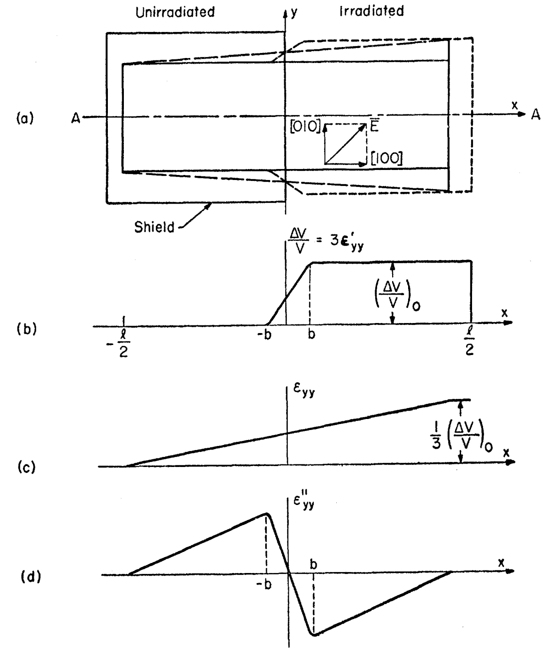

FIG. 1. (a) Crystal and shield orientation during irradiation. The irradiation direction is normal to the plane of the figure. The solid lines give the boundaries of the crystal before irradiation, while after irradiation the smaller dashed lines give the boundaries for a free expansion and the larger dashed lines give the boundaries with elastic constraints taken into account. (b) Free fractional volume expansion *vs* position. (c) Actual strain in the [010] direction *vs* position. (d) Irradiation-induced strain in the [010] direction *vs* position (see discussion).

of sensitivity of alkali halide crystals from different sources to irradiation it would seem desirable to repeat this experiment using single crystals and making simultaneously measurements of expansion and coloration.[8]

An increase in the densities of both positive and negative ion vacancies with irradiation would imply the dislocation-jog mechanism of generation[9] in which vacancies are evaporated from dislocation-jogs by dislocation climb, the evaporation being caused by thermal spikes due to exciton decay or electron-hole recombination in the vicinity of the jogs. Details of the process require that equal numbers of positive and negative ion vacancies be generated. Recent evidence, however, indicates the presence of vacancy-interstitial pairs in x-ray irradiated LiF[10] and thus throws some doubt on the dislocation-jog mechanism of defect generation. The present paper is a more complete report and extension of this work.

Defect generation has been observed as a change in the optical absorption and by the expansion of the crystal as a result of ionizing irradiation. These parameters have been studied as a function of temperature to determine thermal stability and as a function of plastic deformation.

While it is well established that alkali halide crystals expand upon irradiation,[7,11] measurements have been made only in the vicinity of room temperature largely because of the limitations of the conventional methods. Diffusion and annealing processes during the irradiation at room temperature, however, make the analysis of the results very complex and thus in general irradiations should be carried out at low temperatures whenever possible. For this reason, in the present investigation, a modification of a photoelastic method first used by Primak, Delbecq, and Yuster[12] has been used. It has the advantage that it can be easily used over a wide temperature range.

II. METHOD OF VOLUME EXPANSION MEASUREMENTS

Crystals are irradiated in a nonuniform manner so as to produce a nonuniform expansion. Because of elastic constraints, strain is introduced into the crystal and from an analysis of the strain pattern with polarized light it is possible to obtain a measure of the free volume expansion. The essential features of the method can be illustrated in a qualitative fashion with the aid of Fig. 1. The samples have generally been in the form of thin plates. The boundaries of such a plate before irradiation are given in Fig. 1(a) by the solid lines, the plane of the plate lying in the plane of the figure. The irradiation is in the direction of the reader's line of sight normal to the plane of the page and one-half of the sample is shielded from the irradiation as indicated. After irradiation the boundaries of the sample for a free expansion, i.e., with no elastic constraints, might be as indicated by the smaller dashed lines. The free fractional volume expansion, $\Delta V/V$, is shown in a schematic fashion in Fig. 1(b) as a function of position along the line AA, Fig. 1(a). The gradient at the boundary between the irradiated and unirradiated halves of the crystal indicates, in an exaggerated manner, the fact that the x-irradiation cannot be cut off infinitely sharp.

The elastic constraints placed upon the irradiated portion of the crystal by the unirradiated portion will prevent a free expansion and the actual boundaries will be as given by the larger dashed lines of Fig. 1(a). The strain, ϵ_{yy}, for the solution of the elastic problem, as given in the Appendix, is indicated in Fig. 1(c). In the irradiated portion, the crystal is then in compression in the [010] direction because the expansion has been limited by the constraints of the unirradiated half of the crystal. In addition, the crystal is in tension in the unirradiated portion. The irradiation-induced strain is then defined as the difference between the actual strain,

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[8] H. Rabin and C. C. Klick, Bull. Am. Phys. Soc. Ser. II, **4**, 147 (1959).

[9] F. Seitz, Phys. Rev. **80**, 239 (1950); and **89**, 1299 (1953). J. J. Markham, Phys. Rev. **88**, 500 (1952).

[10] D. A. Wiegand and R. Smoluchowski, Phys. Rev. **110**, 991 (1958).

[11] H. Witt, Nachr. Akad. Wiss. Göttingen Math.-physik. Kl. IIa No. 4, 17 (1952); Lang-Ying Lin, Phys. Rev. **102**, 968 (1956); K. Kobayashi, Phys. Rev. **107**, 41 (1957); H. Rabin, Bull. Am. Phys. Rev. Soc. Ser. II, 3, 126 (1958).

[12] Primak, Delbecq, and Yuster, Phys. Rev. **98**, 1708 (1955).

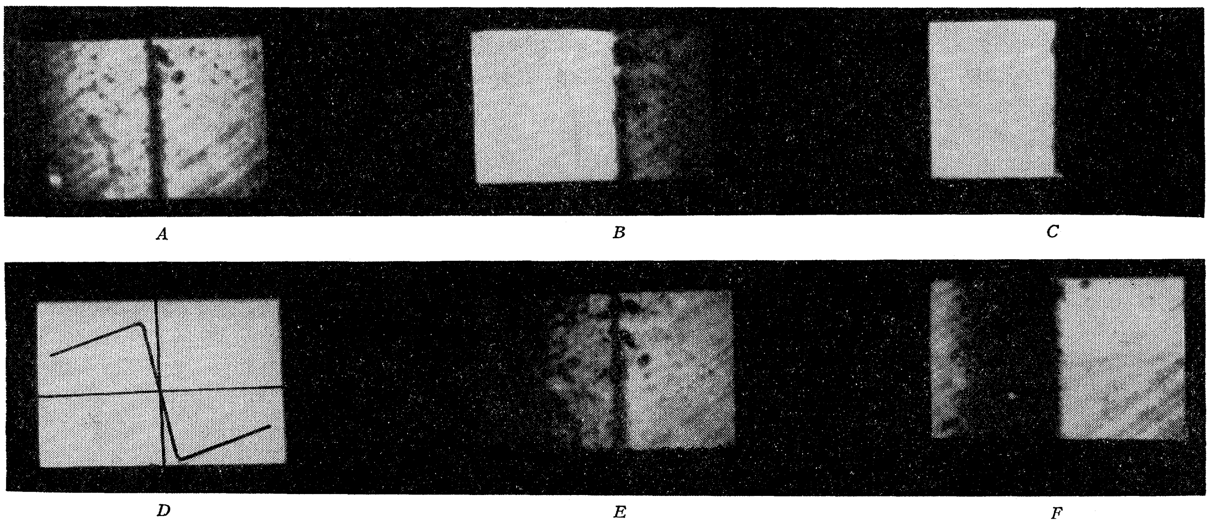

FIG. 2. Photographs of an irradiated crystal in the vicinity of the boundary between the irradiated and unirradiated halves are given in *A*, *B*, *C*, *E*, and *F* as viewed through nicols and a quarter wave plate. The nicols are crossed in *A* and are set for the conditions of maximum strain in compression and tension, respectively, in *C* and *F*. Intermediate settings are shown in *B* and *E*. A sketch of the irradiation-induced strain *vs* position in the vicinity of the boundary is given in *D*.

ϵ_{yy}, and the strain ϵ_{yy}' [Fig. 1(b)] for a free expansion. This strain should be distinguished from ϵ_{yy} which is the desired quantity. If the irradiation-induced strain, $\epsilon_{yy}''=\epsilon_{yy}-\epsilon_{yy}'$ is plotted as a function of position, a curve similar to Fig. 1(d) is obtained. Note that the strain is zero at three positions, at either end of the crystal and at the boundary between the two halves. Since, as shown in the Appendix, the free volume expansion is directly proportional to the irradiation-induced strain it is possible to obtain the free expansion from a measurement of the strain as indicated in Fig. 1(d).

Because the index of refraction is a function of strain, it will be modulated by a curve such as Fig. 1(d) for light polarized in the [010] direction. Therefore, from a measurement of the index of refraction as a function of position it is possible to obtain the strain as a function of position. In practice, light polarized at 45° with respect to the boundary between the irradiated and unirradiated portions of the crystal and in the direction of the irradiation is used as shown in Fig. 1(a). This beam can be considered to be composed of two equal components polarized in the [010] and [100] directions. After passing through the crystal the light beam will in general be elliptically polarized because the two waves travel with different velocities. The beam can then be converted back into plane polarized light by the use of a quarter wave plate, but the direction of polarization will be rotated with respect to the incident beam. The angle of rotation is directly proportional to the difference in indices of refraction for the [010] and [100] waves and so directly proportional to the strain and to the free expansion.[13] [The relationships between the strain, the volume expansion, the difference in the indices of refraction of the two waves and the angular rotation are given in the Appendix in Eqs. (9), (10), and (11).] It is to be noted that since the method is a measure only of the differences in indices of refraction of the two waves, it is not sensitive to other changes in the index due to irradiation unless these changes differ for the two cubic directions. The angular rotation and so the strain at any point in the crystal is determined by the angular position of the analyzer for "null," i.e., for minimum light transmission. The optical system for measuring the strain then consists of a light source, monochromator, polarizer, quarter wave plate, and analyzer, the sample being placed between the polarizer and the quarter wave plate.

In Fig. 2(*D*) the strain *vs* position curve of Fig. 1(d) is given for the region near the boundary between the irradiated and unirradiated portions of the crystal. Figure 2(*A*), directly above this diagram, is a photograph of the central section of an irradiated crystal taken through crossed nicols and a quarter wave plate as outlined above. Since the field would be completely dark if there were no strain, the dark areas indicate regions of zero strain, while the light areas indicate strained regions. The vertical bar indicates the region of zero strain between the irradiated and unirradiated halves of the crystal while the light areas on either side indicate the regions of the crystal in compression and tension, respectively. The shaded areas at either end of Fig. 2(*A*) indicate the approach to the regions of zero strain at the ends of the crystal as shown in Fig. 1(d).

Since the angular rotation of the analyzer is directly proportional to the strain, it is possible to move the null along the curve of Fig. 2(*D*) by adjusting the analyzer. For a rotation in the direction of compression the central

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[13] R. W. Goranson and L. H. Adams, J. Franklin Inst. **216**, 475 (1933).

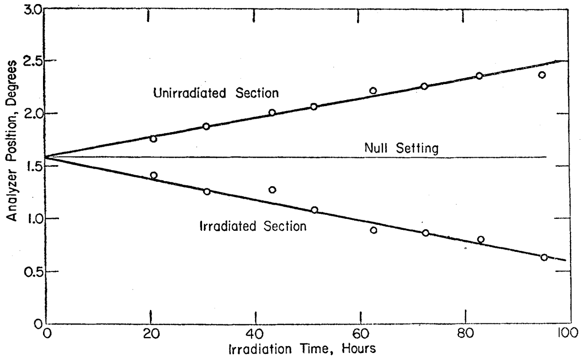

FIG. 3. Analyzer setting for the null condition at the position of maximum strain in the unirradiated and irradiated halves of the crystals *vs* irradiation time.

dark line of Fig. 2(*A*) will move to the right while the shaded area at the compressive (right) end of the crystal will move to the left. This is shown in Fig. 2(*B*). A further rotation of the analyzer causes the two dark areas to merge at the position of maximum compressive strain as shown in Fig. 2(*C*). Similar effects are observed in the unirradiated half of the crystal for a rotation of the analyzer in the direction of tension and the corresponding photographs are given in Figs. 2(*E*) and 2(*F*). By noting the angular rotation for null at any portion of the crystal the strain can be obtained. It has been found, however, that the strain can be measured in the most reproducible manner at the position of maximum strain, i.e., at the position where the two dark areas merge, Figs. 2(*C*), 2(*F*).

In Fig. 3 the analyzer position is shown, for the condition of maximum strain, in the unirradiated and irradiated halves of the crystal, *vs* time of x-ray irradiation. The data are for LiF irradiated and measured at 90°K, and the center line is for the condition of null without a crystal in the light beam. The straight lines drawn through the points in the two halves of the crystal have the same absolute slope within experimental error, indicating that the maximum strain in the two halves of the crystal is the same and that the strain pattern is symmetrical about the boundary between the irradiated and unirradiated halves as indicated in Fig. 1(d).

To obtain the free volume expansion from the angular rotation data, it is necessary to know the photoelastic constants which relate strain to rotation and to solve an elastic problem which relates the strain to the expansion. The values of the elastic constants are obtainable from the literature but the stress-rotation constants were measured, in compression, for several of the alkali halides. Since there were indications that slip may be important from some of the alkali halides, even for the low strains observed in this work, the appropriate strain rotation constant was measured in compression for LiF using a Baldwin Strain Gauge Type *C*-11.[14] It appeared that appreciable slip is not present in the range of strains used here and that the slope of the stress-strain curve is as predicted by the elastic approximation. In solving the elastic problem, which is treated in the Appendix, the following assumptions have been made: (1) Slip is not important and linear elasticity is applicable, (2) The variation of the expansion with position near the boundary between the irradiated and unirradiated protions of the crystal can be represented by a linear function of position, (3) Strains are only a function of x, Fig. 1; a one-dimensional problem has then been solved. Assumption one is justified by the results of the compression experiment mentioned above. Assumption two is less justifiable since the x-ray dose and so the expansion is certainly not a linear function of position as assumed. However, the results are probably not very sensitive to the functional dependence as long as it is monotonic and symmetrical about the boundary between the two halves of the crystal. The data of Fig. 3 indicate that the strain is indeed symmetrical about the boundary. Probably assumption three is the least justifiable since observations of the strain pattern show that the strains are not functions of x alone and appreciable relaxation of the strain is observed in the regions near the boundaries of the crystal. Fortunately the dimensions of the crystals have been of sufficient size in the y direction to contain a region in which the strain is independent of y, but it has not been possible to do the same in the z direction because the dimension in this direction is limited by the penetration of the x-rays and so by the condition of uniform damage. Since the violation of assumptions one and three will make the calculated expansion less than the actual one, the calculation gives a lower limit. For this reason, in this work emphasis should be placed on the relative values of expansion rather than on absolute values. As pointed out later, for NaCl it was possible to measure the volume changes both by the photoelastic method described here and by the standard flotation method. The results agreed to within 16%, indicating the degree of justification of the assumptions discussed here. The free expansions have been calculated on the basis of Eq. (16) of the Appendix using the rotations at the position of maximum strain.

III. EXPERIMENTAL

Both irradiation and measurements at low temperatures were performed with the sample mounted in a vacuum cryostat in direct contact with a copper block connected to the reservoir of liquid nitrogen. A copper-constantan thermocouple was glued to the sample for temperature measurements. Since it is desirable to view both the irradiated and unirradiated halves of the crystal during the strain measurements, and since the irradiation and observation directions are the same, the shield used to protect one-half of the crystal from irradiation is made of soft iron and mounted in rails so

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[14] T. Okada (private communication).

that it can be moved by an external magnet. The vacuum jacket is six-sided in the vicinity of the sample and has six windows, one pair of opposite windows being of quartz to enable optical absorption measurements to be made in the ultraviolet. A second pair of windows is of strain-free glass for the optical rotation measurements. Irradiations are carried out through a fifth window made of thin aluminum and the sixth window is generally an absorber. The portion of the vacuum jacket on which the windows were mounted is connected to the main jacket by a rotating seal, therefore making it possible to rotate any pair of windows into alignment with the sample.

Whenever data obtained by irradiation and measurements at room temperature were compared directly with the corresponding low-temperature data, all the operations were carried out with the sample mounted in the cryostat. In other cases the sample was irradiated and measured in air. Most of the irradiations were made with a 45-kv constant potential machine operating at 35 ma, although a 140-kvp machine operating at 5 ma was also used. In both cases the focal spot to sample distance ranged between one and three inches and the targets were of tungsten.[15]

Samples were generally in the form of thin plates cleaved from larger pieces obtained from the Harshaw Chemical Company. The irradiation was normal to the plane of the plate and filters were used to take out the soft components of the x-ray beam so that fairly uniform damage was obtained in the sample in the direction of the x-ray beam. Data obtained by using stacks of thinner plates or by cleaving indicate that the maximum variation of damage in the direction of irradiation is 20% for all data presented in this paper. A Beckman Model DU Spectracord was used to obtain the optical absorption data.

IV. MEASUREMENTS

In Fig. 4 the irradiation-induced fractional volume change, $\Delta V/V$, as determined by the optical rotation method outlined above, is plotted *vs* irradiation time for a NaCl crystal at room temperature. In this case 140-kvp x-rays were used to give uniform damage within 20% throughout a crystal 0.3 cm thick. The results indicate a saturation type of curve typical of irradiations at room temperature. The minimum detectable expansion is determined by the threshold strain necessary to make the pattern detectable visibly. This "threshold" for observation, indicated in Fig. 4 by the third point, is rather large compared to the probable error associated with each point. Changes of volume much smaller than the threshold can be detected by irradiating the unirradiated half of a previously irradiated crystal, the expansion of the previously unirradiated portion being detected as a decrease in strain. In this case the threshold does not exist because the crystal already contains a detectable strain pattern. The first two points of the curve of Fig. 4 and the first six points of the room temperature curve of Fig. 5 were obtained in this manner. It should be possible to decrease this threshold by the use of a photoelectric device in place of visual observations.

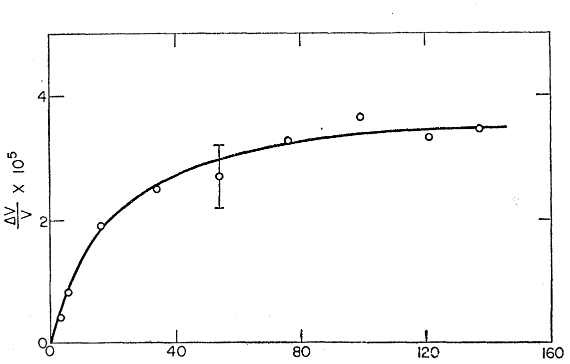

FIG. 4. Fractional volume expansion of NaCl *vs* irradiation time at room temperature.

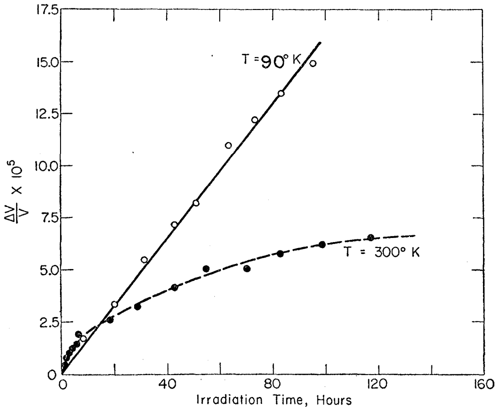

FIG. 5. Fractional volume expansion of LiF *vs* irradiation time.

After irradiation the crystal of Fig. 4 was cleaved into several sections and pieces from the two halves were placed in the flotation apparatus and the mass densities measured.[16] The fractional density difference between the two halves was found to be greater than but within 16% of the value of the fractional volume change. Assuming no loss of mass the fractional density and volume changes should be the same. That they are within 16% suggests that there is little or no mass loss and that the method of obtaining the fractional volume change as used here gives reasonable results. Portions of the NaCl crystal were also cleaved into thin plates and the F-center densities measured. It is possible to associate an expansion with a given F-center density by

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[15] The authors are indebted to Professor W. H. Robinson for making available the 140-kvp x-ray machine.

[16] The density determing apparatus is similar to that described by Kobayashi.[11] The apparatus has been modified by Marshal F. Merriam so as to give greater sensitivity and the authors are indebted to Mr. Merriam for performing the density measurements given above.

assuming that per F center the crystal has expanded by a volume equal to the volume occupied by a negative ion in a perfect section of the lattice. While this may be somewhat too naive an assumption, it allows comparison with earlier work.[17] The fractional expansion calculated in this way is 2.2×10^{-5} which is less than but of the same order of magnitude as that obtained by the other methods and in agreement with the work of others.[7,11] The difference may be due to incomplete filling of negative ion vacancies by electrons and relaxation effects in the vicinity of vacancies.[18] It appears thus that it is possible to explain the expansion of the crystal on the basis of the generation of negative ion vacancies, most of which capture electrons to become F centers.

The majority of the remaining data pertains to LiF. Samples of this crystal have been in the form of thin plates, 0.03 to 0.05 cm in thickness, and were irradiated with 45-kv x-rays. In Fig. 5 the fractional volume change is given *vs* time of irradiation for LiF at 90° and at 300°K. While at the low temperature the crystal expands linearly between roughly 10^{-5} and 10^{-4} with irradiation dose, a typical saturation curve is obtained at room temperature. It is interesting to note, however, that the initial expansion at room temperature is greater than that at the low temperature. Since there seems to be a correlation between the expansion of the crystal and the introduction of F centers, it is instructive to observe the growth of the F band for the same conditions as those of Fig. 5. The results are shown in Fig. 6. While the F-band growth curves are given for a more limited range of dose than the volume expansion, the F band also increases linearly with time of irradiation at 90°K and a saturation curve is observed at 300°K. In addition, the F band increases at a faster rate at 300°K than at 90°K initially but the curves cross as do the expansion curves of Fig. 5. Therefore, qualitatively, the agreement between the growth of the F band and the expansion of the crystal is good. The rate of expansion as calculated from the curve of n_f *vs* t at 90°K is twice that obtained from the curve of $\Delta V/V$ *vs* t, although the data were taken on the same sample and over approximately the same range of damage. The expansion as calculated from the F band after irradiation at room temperature was found to vary between one-half and four times the expansion obtained by the optical rotation technique. Differences in the ratio of expansions are found not only for different samples but also for different doses for a given sample. These differences could be due to M or other more complex center formations. Slight differences in temperature may account for the variation from one sample to another, while a complex center formation which does not proceed at the same rate as F-center formation could account for the variation with dose for a given sample. Therefore, quantitatively, while there are variations at room temperature which are not observed at low temperature, the expansion of the crystal calculated from the observed density of F centers is in rough agreement with the observed expansion and indicates that the expansion can be attributed to the introduction of negative ion vacancies, the majority of which become F centers.

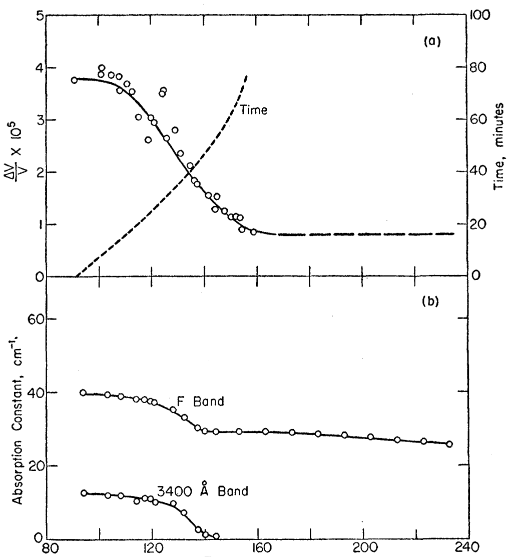

FIG. 7. (a) Annealing of the fractional volume change in LiF after irradiation at 90°K for 44 hours. (b) Annealing of the optical absorption of LiF at the maximum of the F band and at 3400 A after irradiation at 90°K for 3 hours.

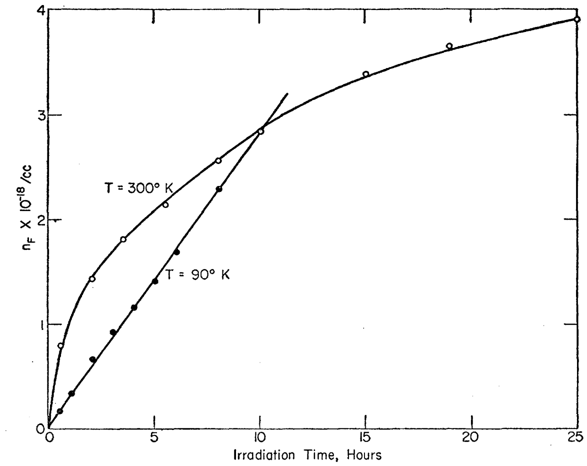

FIG. 6. Density of F centers in LiF *vs* irradiation time.

Figure 7(a) shows the annealing of the expansion of of LiF after irradiation at 90°K. Between roughly 110° and 150°K approximately 75% of the irradiation-induced expansion anneals out. While detailed data will not be presented, it should be mentioned that NaCl has

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[17] While others have assumed that for each F center a vacancy pair is introduced it is important to note that for NaCl the volume of a positive ion vacancy is only roughly $\frac{1}{6}$ that of a negative ion vacancy if relaxations are neglected.

[18] M. P. Tosi and F. G. Fumi, Nuovo cimento 7, 95 (1958).

also been found to expand on x-ray irradiation at 90°K. In contrast, however, annealing has not been observed between 90° and 300°K. Because of the similarities between the expansion of LiF and the growth of its *F* band it is interesting to consider the annealing of the *F* band in the same temperature range. However, first it is desirable to consider the change in optical absorption due to irradiation at 90°K, as illustrated in Fig. 8. In addition to the prominent band at about 2425 A, which is generally considered to be due to the *F* center, several other bands are found on its long-wavelength side. One band in particular is centered at approximately 3400 A. In Fig. 9 the increase due to irradiation of the optical absorption constant of the *F* band and the band at 3400 A are given for comparison purposes. While the *F* band increases linearly with time of irradiation, the band at 3400 A quickly saturates at a rather low level. All the other bands on the long-wavelength side of the *F* band saturate in a similar manner. Therefore, since the crystal is found to expand linearly with irradiation, as shown in Fig. 5, it is quite clear that the bands on the long-wavelength side of the *F* band and, in particular, the band at 3400 A cannot be associated with the defect which is causing the expansion.

In Fig. 7 (b) the annealing of the absorption constant at the maximum of the *F* band and at 3400 A are given after irradiation at 90°K. The time-temperature relationship is as given in Fig. 7 (a). Similar observations of annealing have been made by Delbecq, Pringsheim, and Yuster.[19] While the *F* band is found to decrease in the vicinity of 130°K and so in the same temperature range as the expansion, the decrease is only by roughly 25% compared to a 75% annealing of the volume expansion. The partial annealing of the *F* band cannot be thus associated directly with the mechanisms of expansion or annealing. While the volume expansion can be attributed to the generation of negative ion vacancies, the majority of which become *F* centers, the annealing of this expansion can only at best be partially attributed to an annihilation of negative ion vacancies which had been *F* centers.

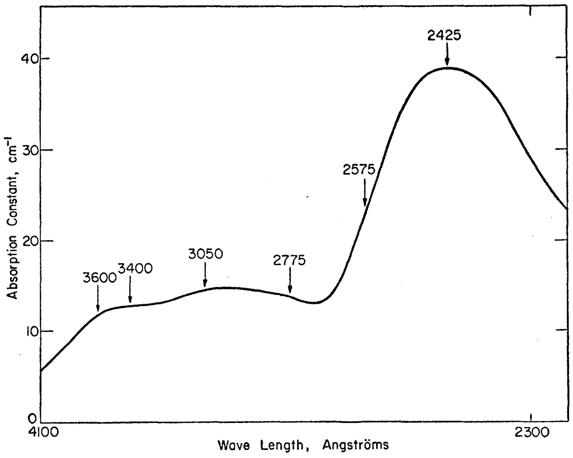

FIG. 8. Optical absorption change *vs* wavelength for LiF irradiated at 90°K for 3 hours.

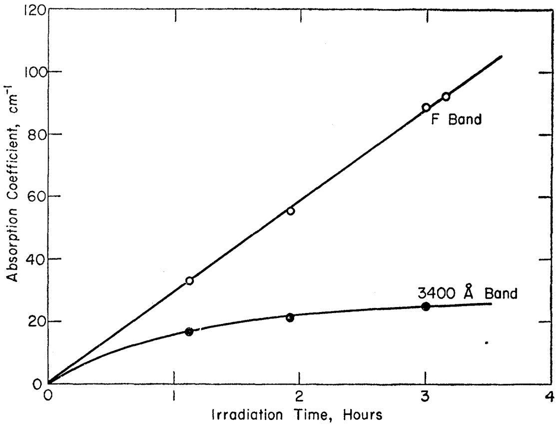

FIG. 9. Optical absorption constant for LiF at the maximum of the *F* band and at 3400 A *vs* irradiation time at 90°K.

In a comparison of the data of Figs. 7 (a) and 7 (b) it should be noted that the crystal of Fig. 7 (a) has been irradiated for a considerably longer time than the crystal of Fig. 7 (b). Since the damage increases linearly with irradiation dose, the damage is an order of magnitude greater in the crystal of Fig. 7 (a). This difference is due to the fact that the methods of measuring the optical rotation and the optical absorption are most accurate for different degrees of damage. While thin crystals must be used to measure the optical absorption of heavily irradiated crystals, the total optical rotation is directly proportional to the thickness of the crystal so that, within limits, the sensitivity of the method is increased by increasing the crystal thickness. Therefore, with available equipment and for crystals of roughly the same thickness as used here, the optical rotation cannot be measured very accurately over the same range of damage as the optical absorption. It has been found, however, by using thicker crystals to increase the sensitivity of the optical rotation measurements, that the annealing of the expansion is similar to that of Fig. 7 (a) for total amounts of damage roughly equivalent to that of Fig. 7 (b).

As shown in Fig. 7 (b) the band at 3400 A anneals completely in the same temperature range as the partial annealing of the *F* band. If the two annealing curves of Fig. 7 (b) are superimposed it becomes apparent that the two annealing processes may be associated.[10,19] In fact, it has been suggested that the 3400 A band is due to trapped holes which become mobile at 130°K. The mobile holes are then captured by *F* centers by annihilation of *F*-center electrons, thereby accounting for the simultaneous decrease of the band at 3400 A and the *F* band.[19] Thermoluminescence and electrical conductivity have also been observed in this tempera-

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[19] Delbecq, Pringsheim, and Yuster, Z. Physik **138**, 266 (1954).

ture range after irradiation in the vicinity of 90°K.[19,20]

Part of the gradual decrease in the optical absorption at the maximum of the *F* band with increasing temperature between 150°K and 240°K as shown in Fig. 7(b) is due to the broadening of the *F* band. The remainder is apparently due to a gradual decrease in the density of *F* centers. Between 240°K and 300°K there is a further annealing of the *F* band by roughly 30% which is accompanied by an annealing of the bands between 3400 A and the long-wavelength tail of the *F* band. The optical absorption in the short-wavelength tail of the *F* band increases on warming to 240°K and then abruptly decreases between 240°K and 300°K presumably due to the growth and annealing of a band in the vacuum ultraviolet.

In Fig. 10 the fractional volume change is given for an irradiation annealing, and re-irradiation cycle. After exposing the crystal to x-rays for 20.5 hours the irradiation was interrupted and the crystal warmed through the annealing range to 160°K and recooled. The vertical dashed line indicates the amount of the annealing. The crystal was then re-irradiated and, as shown in Fig. 10, the fractional volume expansion continued to increase along a straight line which is parallel to the initial growth curve but displaced from it by the amount of the annealing. In Fig. 11 the density of *F* centers is given for a similar cycle of irradiation, annealing, and re-irradiation. The vertical dashed line again gives the annealing of the *F* band. However, on re-irradiation the density of *F* centers increases quickly to a point which lies on an extrapolation of the initial growth curve and then continues to grow at the same rate as before annealing. The initial increase in the density of *F* centers after annealing is much faster than at any other time during the irradiation. It is to be noted that the annealing data of Figs. 10 and 11 had to be obtained for quite different amounts of damage because of the usual difficulty of measuring both quantities for the same amount of damage.

The data of Fig. 11 can be interpreted in the following manner: The linear increase in the density of *F* centers with irradiation time is determined by the rate at which negative ion vacancies are produced by the irradiation. On warming to 160°K a fraction of these lose electrons, possibly to holes associated with the band at 3400 A. However, the negative ion vacancies are not destroyed. On re-irradiation then the rapid rise of the *F* band is due to the refilling of these negative ion vacancies with electrons. When this process has been completed the *F* band continues to grow as before annealing, i.e., limited by the rate at which new negative ion vacancies are generated by the irradiation.

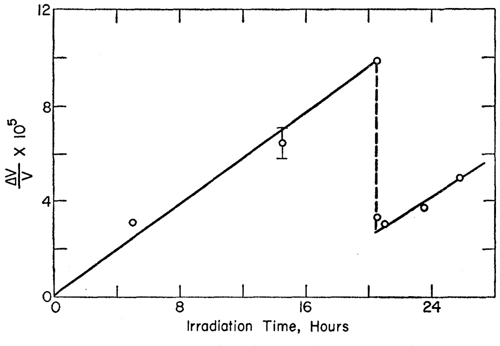

FIG. 10. Fractional volume change of LiF *vs* irradiation time at 90°K.

If this interpretation is correct it is necessary to conclude from Figs 10 and 11 that an annealing of 75% of the irradiation-induced volume expansion takes place without a decrease in the density of negative ion vacancies associated with the *F* band. This conclusion then suggests that the expansion of the crystal cannot be associated with the introduction of *F* centers alone.

V. DISCUSSION

In order to interpret the data presented it is desirable to consider possible mechanisms by which defects may be introduced by ionizing radiation and the possible mechanisms of annealing of these defects. Vacancies may be introduced into the alkali halides by ionizing radiation by the so-called dislocation-jog mechanism considered briefly in the introduction. As noted, a mark of this mechanism would be the introduction of both positive and negative ion vacancies. While there is insufficient experimental evidence to reach a conclusion concerning the presence of positive ion vacancies, it is heuristic to consider possible mechanisms of annealing if vacancy pairs are generated by the dislocation-jog mechanism. While the activation energies for random diffusion of single positive or negative ion vacancies are much too large to account for the annealing of the expansion at 130°K on this basis, the annealing could be due to the diffusion of neutral vacancy pairs. From a consideration of the calculations of Dienes[21] and the recent analysis of diffusion data by Lidiard[22] it seems reasonable to assume the activation energy for pair diffusion to be approximately a few tenths of an electron volt. For example, a pair will make of the order of 10^4 jumps per hour at 130°K if the activation energy is taken to be 0.3 ev. Since the defect density is of the order of 10^{-4} it is possible that a clustering of defects may take place at this temperature. The annealing of the expansion may then be due to the collapse of platelets formed in this manner into dislocation loops. Alternately, pairs may diffuse back to dislocations. In this case, the annealing process is the reverse of the generation process. It is important to note that if the generation and annealing occurs by the above processes it is necessary to conclude from the annealing data that as a result of irradiation at 90°K both single vacancies

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[20] J. A. Ghormley and H. A. Levy, J. Phys. Chem. **56**, 548 (1952).

[21] G. J. Dienes, J. Chem. Phys. **16**, 620 (1948).

[22] A. B. Lidiard, J. Phys. Chem. Solids **6**, 298 (1958).

and pairs are generated. Neglecting relaxation, the data of Fig. 7(a) indicate that only roughly one-quarter of the total number of negative ion vacancies are not in the form of pairs. *Note added in proof.*—Recent results of Barr, Hoodless, Morrison, and Rudham (to be published) indicate that the low temperature diffusion of chlorine which might have been associated with vacancy pair diffusion appears to be related to dislocation density and so presumably to diffusion along dislocations or internal boundaries.

It may then be reasonable to conclude that vacancies are generated by the dislocation-jog mechanism and that the low-temperature annealing in LiF occurs by vacancy pair diffusion. However, there are at least two additional experimental observations which seem to argue against this interpretation. First, the rate of *F*-center formation in LiF has been found to be insensitive to plastic deformation which increases the dislocation density by roughly a factor of twenty.[23] The number of jogs should be increased both because of the intersection of dislocations during the deformation process and because of the increase in dislocation density. This increase in the density of jogs, and thus in the number of sites at which vacancies can be evaporated, should increase the rate of vacancy production unless there are no other major means of recombination of electron-hole pairs or exciton decay. While the question of the importance of other forms of recombination cannot be answered quantitatively at this time, Delbecq *et al.* have observed a strong fluorescence during irradiation at 83°K and thermoluminescence has been observed after irradiation at the low temperature.[19,20] Both of these observations suggest that there are other important forms of recombination. It follows thus that the insensitivity of the rate of *F*-center formation to plastic deformation indicates that dislocations play little or no role in the mechanism of vacancy generation in LiF. An increase in the rate of generation of *F* centers at room temperature in NaCl has been observed by Nowick[24] as a result of plastic deformation. Since the mode of deformation, the range of *F*-center densities, and material are all different for this work, the results cannot be directly compared with those cited here. It is of course very possible that different mechanisms of defect generation are important in the various alkali halides.

The second argument against the above interpretation is that the *M* band is not formed during annealing at 130°K. The *M* center is thought to be composed of an *F* center plus an adjoining vacancy pair. Because of the high concentration of *F* centers and vacancy pairs left in the wake of dislocation climb by this mechanism of defect generation, it might be expected that there should be substantial *M*-center formation at the expense of *F* centers at the temperature at which vacancy pairs become mobile. However, measurements on a very heavily irradiated crystal failed to show any increase in the *M* band between 90° and 165°K, while between 165° and 300°K the *M* band increased by at least a factor of 45. Thus the lack of *M*-band formation argues against the interpretation of the low-temperature annealing as being due to vacancy pair diffusion provided that the assumed structure of the *M* center is correct.[25,26]

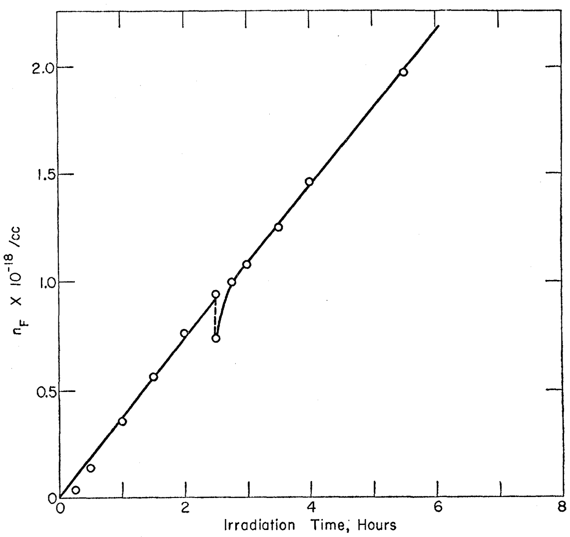

FIG. 11. Density of *F* centers in LiF *vs* irradiation time at 90°K.

It is also possible that the expansion of the lattice is associated with purely electronic defects, i.e., due to the relaxation of the lattice in the vicinity of electronic imperfections. The expansion is most probably not associated with electronic trapping at defects existing before irradiation because such effects should saturate due to either a limited number of traps or to a kinetic equilibrium between capture and escape from the traps. The saturation of the band at 3400 A is apparently an example of such a saturation. It is important to note, however, that for each *F*-center electron there must be a hole somewhere in the lattice. The annealing might then be due to a change in configuration of the hole with a resulting contraction of the lattice. The holes could be trapped at positive ion vacancies (*V* centers), or they could exist in the form of halogen atoms. A simple argument shows, however, that if holes escape from positive ion vacancies an expansion of the lattice is to be expected rather than the observed contraction.

It is therefore interesting to consider the possibility that as a result of irradiation *F* centers and interstitial halogen atoms are introduced. If for example, by an unspecified mechanism, a halogen vacancy-interstitial pair is generated during irradiation, the vacancy might capture an electron to become an *F* center while the interstitial halogen ion could capture a hole to become

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[23] D. A. Wiegand and R. Smoluchowski, Bull. Am. Phys. Soc. Ser. II, 4, 148 (1959).

[24] A. S. Nowick, Phys. Rev. **111**, 16 (1958).

[25] A. W. Overhauser and H. Ruchardt, Phys. Rev. **112**, 722 (1958).

[26] R. S. Knox, Phys. Rev. Letters **2**, 87 (1959).

neutral, thus preserving charge balance. The expansion in this case will be primarily due to the interstitial since very little relaxation is expected in the vicinity of a negative ion vacancy containing an electron. However, since the interstitials are produced at the same rate as the vacancies, the expansion and the growth of the F band should proceed at the same rate as observed. It is necessary to conclude in this case, however, that the low-temperature annealing is not due to vacancy-interstitial recombination since a decrease in the density of negative ion vacancies associated with F centers is not observed during the annealing. The contraction of the lattice must then be due to a change in configuration of the interstitials.

A mechanism by which halogen vacancy-interstitial pairs might be generated by ionizing irradiation has been suggested by Varley.[27] If a halogen ion loses at least two electrons by ionization, i.e., if it becomes positively charged, it might be easily removed from its normal lattice position into an interstitial position by the lattice potential. If then both the interstitial and the vacancy capture electrons, the net result is an F center and an interstitial atom. The capturing process may also stabilize the pair against recombination. While a complete quantitative estimate of the feasibility of this mechanism is not possible at the present time, Howard and Smoluchowski[28] have discussed its various aspects and, in particular, have found the lifetime of the positive halogen ion to be several orders of magnitude longer than the vibrational period of the lattice. Here we should like to comment only upon the probability of double ionization which has been estimated by Varley to be one-tenth that of a single ionization for high-energy electron irradiation. This estimate seems quite reasonable considering the reported energies absorbed per F center formed.[1,29] For example, Kobayashi *et al.* have found that roughly 2000 ev is absorbed per F center formed in NaCl at room temperature as a result of high-energy proton irradiation. It is, however, important to note that the quantity of interest here is the energy absorbed per negative ion vacancy formed. Therefore, the much lower estimates of energy absorbed per F center formed, taken from the initial parts of the growth curves, are not applicable because they presumably are a measure of the energy absorbed per F center formed from vacancies existing in the crystal prior to irradiation. The measurements of Kobayashi *et al.* are for very high densities of F centers and are certainly in the range of newly created negative ion vacancies. It is also important to note that the typical saturation curve observed at room temperature suggests that annealing occurs during irradiation. In this case the measured energies will tend to be high.

These objections to some of the previous measurements of energy per F center, however, may not be applicable to LiF x-ray irradiated at 90°K. Simultaneous measurements of coloration and expansion indicate that in these experiments the measurements are made in the range of F-center formation from newly generated negative ion vacancies. In addition, the growth curve is linear, suggesting that thermal annealing is not important. Approximately 140 ev is absorbed per F center formed by x-ray irradiation of LiF at 90°K. This result is in agreement with the estimates of Varley if it is assumed that the energy per ionization is the band gap energy or roughly 15 ev, and that almost all of the absorbed energy is converted into single ionizations. Then roughly one F center is produced for each 10 single ionizations. This result also suggests that the probability of forming an F center from a doubly ionized state is close to unity.

It is of course possible that interstitials and/or vacancies are generated by other mechanisms than those considered above. For example, interstitials could be evaporated from dislocations in much the same fashion as vacancies, or interstitial-vacancy pairs may result from thermal spikes due to electron-hole recombination or exciton decay at other lattice positions than dislocations. In addition, vacancy-interstitial pairs may be generated by single ionization if it is possible for the halogen atom to diffuse away from the vacancy before the hole.

Evidence for the presence of interstitials in low-temperature x-ray irradiated alkali halides is also obtained from the investigations of spin resonance by Känzig and Woodruff.[4] These investigators have suggested that the H center as detected by magnetic resonance is associated with an extra halogen atom in a crowdion configuration along a [110] direction. However, the hole is not localized on the extra halogen but is shared by four halogen ions. This magnetic resonance center anneals completely at 130°K in LiF or at roughly the same temperature as the volume expansion. The volume expansion may then be due to the relaxation of the lattice in the vicinity of the H center. The annealing of the H center may take place by the formation of halogen molecules as suggested by Känzig and Woodruff or by the expulsion of the extra halogen atom into a body-centered interstitial position. In either case there should be a contraction of the lattice. As pointed out by Känzig and Woodruff the halogen molecule should fit into the negative ion vacancy which was occupied by the lattice halogen component of the molecule or, on a naive basis, the body-centered position may be large enough to accommodate the extra halogen atom without considerable relaxation. It is important to note that in either case vacancy-interstitial recombination does not occur, so that the F-center vacancy is not disturbed as observed. This recombination then must take place

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[27] J. H. O. Varley, Nature **174**, 886 (1954); and J. Nuclear Energy **1**, 130 (1954).

[28] R. E. Howard and R. Smoluchowski, Phys. Rev. **116**, 314 (1959).

[29] Kobayashi, Mozer, and Pearlstein, Color Center Symposium, Argonne National Laboratory, November, 1956 (unpublished); and Bull. Am. Phys. Soc. Ser. II, **2**, 150 (1957).

above room temperature. It is also interesting to note that the H center as detected by optical absorption in NaCl anneals between 5° and 78°K.[30] The annealing of the low-temperature volume expansion in NaCl might then be expected to occur in this temperature range if the optical H center can be identified with that detected by magnetic resonance. The lack of annealing of $\Delta V/V$ in NaCl between 90°K and 300°K is consistent with this interpretation and the measurements are now being extended to the low-temperature range.

In summary then, the low-temperature annealing of the volume expansion can be explained either on the basis of vacancy-pair diffusion or by interstitial motion. Vacancy pairs imply the dislocation-jog mechanism of defect generation, while interstitials suggest something like the multiple ionization mechanism. The experiments with plastic deformation seem to argue against the dislocation-jog mechanism of generation, while the lack of M-band formation argues against pair diffusion as the annealing mechanism. In contrast, the magnetic resonance experiments support the interstitial interpretation, and the evaluation of the Varley proposal lends support to the multiple ionization mechanism. Therefore, it is tentatively concluded that halogen vacancy-interstitial pairs are generated by ionizing radiation in LiF at low temperatures. Further experiments are necessary to support the conclusion.

ACKNOWLEDGMENTS

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VI. APPENDIX

Consider that the dilation, $\Delta V/V$, is only a function of x and is as given in Fig. 1(b) where the zero of coordinates is taken at the boundary between the irradiated and the unirradiated portions of the crystal. For the purpose of calculations the variation of $\Delta V/V$ with x is simplified to the following form

$$\frac{\Delta V}{V}=0, \qquad x\leqslant -b \tag{1a}$$

$$=\left(\frac{\Delta V}{V}\right)_0\left[\frac{x+b}{2b}\right], \qquad -b\leqslant x\leqslant b \tag{1b}$$

$$=\left(\frac{\Delta V}{V}\right)_0, \qquad x\geqslant b. \tag{1c}$$

It is then desirable to solve for $\Delta V/V$ in terms of the strains which can be determined by the optical rotation method. As a further simplification, following Primak *et al.* assume that the crystal is infinite in the y and z directions so that all quantities become functions of x only.[12]

The strains are then given by the following relationships

$$\epsilon_{xx}=\frac{k_2+\beta(\Delta V/V)-2c_{12}(k_3x+k_4)}{c_{11}}, \tag{2a}$$

$$\epsilon_{yy}=k_3x+k_4, \tag{2b}$$

$$\epsilon_{xy}=k_1, \tag{2c}$$

where

$$\beta=\tfrac{1}{3}(c_{11}+2c_{12}). \tag{3}$$

The constants in the above equations which are obtained by considering the surface conditions, i.e.,

$$X_x=Y_y=Z_z=X_y=X_z=Y_z=0, \tag{4}$$

are as follows:

$$k_1=0, \tag{5a}$$

$$k_2=0, \tag{5b}$$

$$k_3=\left(\frac{\Delta V}{V}\right)_0\bigg/3l, \tag{5c}$$

$$k_4=\frac{1}{6}\left(\frac{\Delta V}{V}\right)_0. \tag{5d}$$

Therefore we have

$$\epsilon_{xx}=\frac{\beta}{c_{11}}\left(\frac{\Delta V}{V}\right)-\frac{c_{12}}{3c_{11}}\left(\frac{\Delta V}{V}\right)_0\left(\frac{2x}{l}+1\right), \tag{6a}$$

$$\epsilon_{yy}=\frac{1}{6}\left(\frac{\Delta V}{V}\right)_0\left(\frac{2x}{l}+1\right), \tag{6b}$$

$$\epsilon_{xy}=0. \tag{6c}$$

Here, ϵ_{yy}, which is a measure of the actual change in dimensions of the crystal in the y direction, is then as shown in Fig. 1(c). However, for a free expansion

$$\epsilon_{yy}'=\frac{1}{3}\frac{\Delta V}{V}, \tag{7}$$

where $\Delta V/V$ is given in Fig. 1(b) and Eq. (1). As pointed out above, the strain due to irradiation as defined here is the difference between the actual strain, ϵ_{yy}, and the strain that would be associated with a free expansion and so is given by

$$\epsilon_{yy}''=\epsilon_{yy}-\epsilon_{yy}' \tag{8a}$$

$$=\frac{1}{6}\left(\frac{\Delta V}{V}\right)_0\left(\frac{2x}{l}+1\right)-\frac{1}{3}\frac{\Delta V}{V}, \tag{8b}$$

which is indicated in Fig. 1(d). In Figs. 1(b) and 1(d) the corners have been rounded so as to conform more to

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

physical realizability than the conditions of Eq. (1) allow. However, by the method which is used, a measure of

$$K=\epsilon_{yy}''-\epsilon_{xx}''=\epsilon_{yy}-\epsilon_{xx} \tag{9a}$$

$$=\left(\beta\frac{\Delta V}{V}\Big/c_{11}\right)-\frac{1}{6}\left(\frac{\Delta V}{V}\right)_0\left(\frac{2c_{12}}{c_{11}}+1\right)\left(\frac{2x}{l}+1\right) \tag{9b}$$

is obtained.

It is only necessary now to relate the measured quantity, i.e., the angular rotation of the direction of polarization of plane polarized light to the strain and to the free volume expansion $(\Delta V/V)_0$. The difference in the indices of refraction for light polarized in the x and y directions, n_y and n_x, can be written as

$$n_y-n_x=r(\epsilon_{yy}''-\epsilon_{xx}'')=r(\epsilon_{yy}-\epsilon_{xx})=rK, \tag{10}$$

where r is the constant relating the index to strain.[31] Since the direction of polarization of the light beam makes an angle of 45° with the boundary, the light beam can be considered to be composed of equal components in the direction of the boundary and normal to it [see Fig. 1(a)]. Because of the difference in the strain in the two directions, a phase angle time-wise will be introduced between the two components on passing through the crystal. It is easy to show that this phase angle results in a rotation of the direction of polarization of the emergent beam relative to the incident beam by a space angle

$$\alpha=\frac{\pi d}{\lambda}(n_y-n_x)=\frac{\pi dr}{\lambda}(\epsilon_{yy}''-\epsilon_{xx}'') \tag{11}$$

after the beam has passed through a quarter wave plate. d is the path length in the crystal. Therefore, by measuring the angle α at any given position, x, it is possible to calculate $(\Delta V/V)_0$.

As indicated in the discussion of the method the rotation can be measured most precisely at the positions $x=-b$; b. We then have

$$K_1(x=-b)=-\left(\frac{\Delta V}{V}\right)_0\left(\frac{2c_{12}+c_{11}}{6c_{11}}\right)\left(1-\frac{2b}{l}\right), \tag{12a}$$

$$K_2(x=b)=\left(\frac{\Delta V}{V}\right)_0\left(\frac{2c_{12}+c_{11}}{6c_{11}}\right)\left(1-\frac{2b}{l}\right). \tag{12b}$$

Therefore

$$\Delta K=K_2-K_1=\left(\frac{\Delta V}{V}\right)_0\left(\frac{2c_{12}+c_{11}}{3c_{11}}\right)\left(1-\frac{2b}{l}\right) \tag{13a}$$

$$=(\lambda/\pi dr)(\alpha_2-\alpha_1), \tag{13b}$$

where α_1, α_2 are the angular rotations at the positions $x=-b$, $x=b$, respectively. Then

$$\left(\frac{\Delta V}{V}\right)_0=\frac{\lambda}{\pi dr}(\alpha_2-\alpha_1)\left(\frac{3c_{11}}{2c_{12}+c_{11}}\right)\left(\frac{1}{1-2b/l}\right). \tag{14}$$

Therefore by measuring the angular rotation at $x=-b$; b and knowing the r and c's it is possible to obtain $(\Delta V/V)_0$.

From experiment it is found that

$$b\ll\tfrac{1}{2}l, \tag{15}$$

and therefore the final expression is

$$\left(\frac{\Delta V}{V}\right)_0\approx\frac{\lambda}{180dr}(\alpha_2-\alpha_1)\left(\frac{3c_{11}}{2c_{12}+c_{11}}\right), \tag{16}$$

where the α's are now in degrees.

The temperature dependence of (16) was determined by measuring the angular rotation as a function of temperature on cooling after irradiation at 300°K. By assuming that $(\Delta V/V)_0$ is independent of temperature for these conditions, the temperature dependence of r and the c's can be compensated for.

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[31] E. G. Coker and L. N. G. Filon, *A Treatise on Photoelasticity* (Cambridge University Press, London, 1957), second edition.

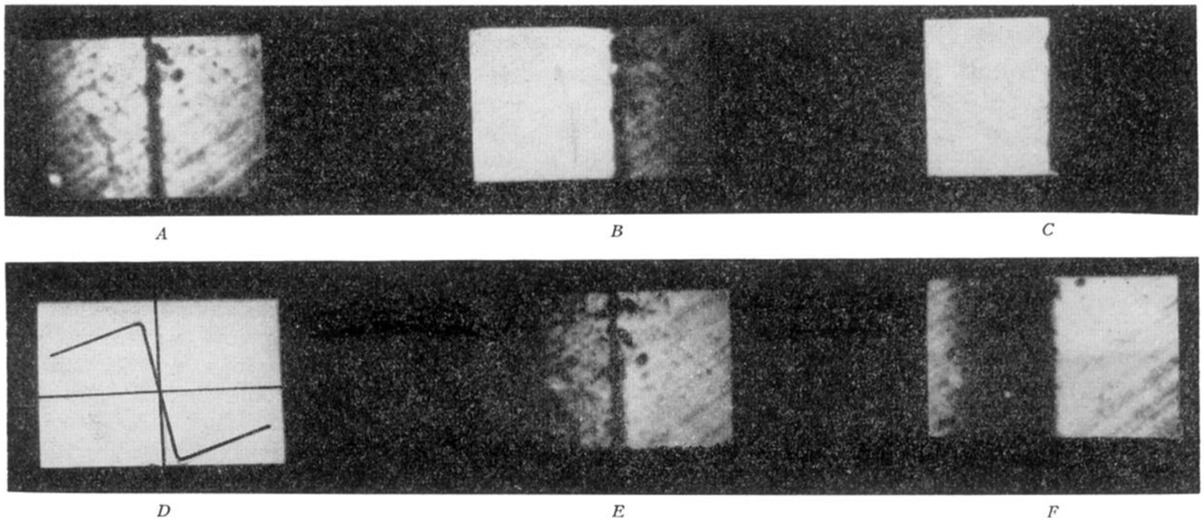

FIG. 2. Photographs of an irradiated crystal in the vicinity of the boundary between the irradiated and unirradiated halves are given in *A*, *B*, *C*, *E*, and *F* as viewed through nicols and a quarter wave plate. The nicols are crossed in *A* and are set for the conditions of maximum strain in compression and tension, respectively, in *C* and *F*. Intermediate settings are shown in *B* and *E*. A sketch of the irradiation-induced strain *vs* position in the vicinity of the boundary is given in *D*.