

addition or subtraction to the vacancy does not change appreciably the relaxation, as seems to be the case of the F center. Of course, another possibility exists that the volume expansion is not associated at all with the optical centers. In any case, this type of analysis should be extended to KCl or KBr where the magnetic and optical centers have been more extensively studied. (b) If we suppose that the 343-m μ band is a V_1 band, then one must make some comments about the model recently proposed by Seitz¹¹ for this center. According to this model, the V_1 center consists of a chlorine ion in a $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ position which accounts for the absence of paramagnetism and dichroism of the center. The center would be formed from an H center by an electron capture and transfer of the Cl^0 into the body-centered position. Our H center should thus have annealed below 15°K and would probably be related to the 330-m μ band observed by Duerig and Markham at 5°K. The annihilation of the Cl^- interstitial with the F center would most likely give rise to an annealing of the volume expansion which was not observed. One might thus say that our band is not the V_1 , but rather that it is associated with the V_k center. In this case holes from this center would annihilate the F and F' centers. In addition, the growth and regrowth curves

for this band (see Fig. 2) indicate a center composed of a point defect plus an electronic component. Thus the energetically "expensive" point defect is left after the annealing and the copious electrons and holes provided during x-ray irradiation just fill them up during the regrowth. Of course, the possibility also exists that the growth of the 343-m μ band is controlled by an electron or hole capture at other traps. If, on the other hand, the Cl^- interstitial model is responsible for our band, then it is very difficult to understand its relatively rapid recovery upon reirradiation.

Recently, Yuster¹⁵ reported dichroism of the V_1 band. This adds support for our interpretation of the results here reported.

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¹⁵ P. H. Yuster, Color Center Conference, Stuttgart, 1962 (unpublished).

Low-Temperature Annealing of the X-Ray-Induced Volume Expansion and Coloration of LiF*

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It has been shown previously that both $\Delta V/V$ and the density of F centers produced by x irradiation of LiF at 80°K anneal out partially near 130°K. Upon reirradiation at 80°K the F band quickly recovers while $\Delta V/V$ does not recover. In the present study, an additional annealing stage of $\Delta V/V$ and the F band was found near 270°K. Upon reirradiation at 80°K after annealing at 270°K, neither $\Delta V/V$ or the F band recover in contrast to the recovery after annealing at 130°K. The irreversibility of the 270°K annealing of the F band indicates vacancy annihilation which apparently does not occur at 130°K. The formation of M centers at the higher temperature suggests vacancy motion. The fractional annealing at 130°K was found to be smaller than in previous work, presumably because of different sample perfection before irradiation.

I. INTRODUCTION

IN this paper, the annealing of defects induced by low-temperature x irradiation of LiF is described. The general problem was considered previously by Wiegand and Smoluchowski and the present work is a

continuation of the earlier investigation.¹ In the present study, the irradiation-induced volume expansion has been studied by a more precise photoelastic technique.²

¹ D. A. Wiegand and R. Smoluchowski, Phys. Rev. **110**, 991 (1958); **116**, 1069 (1959).

² S. Mascarenhas, D. A. Wiegand, and R. Smoluchowski, Bull. Am. Phys. Soc. **5**, 422 (1960).

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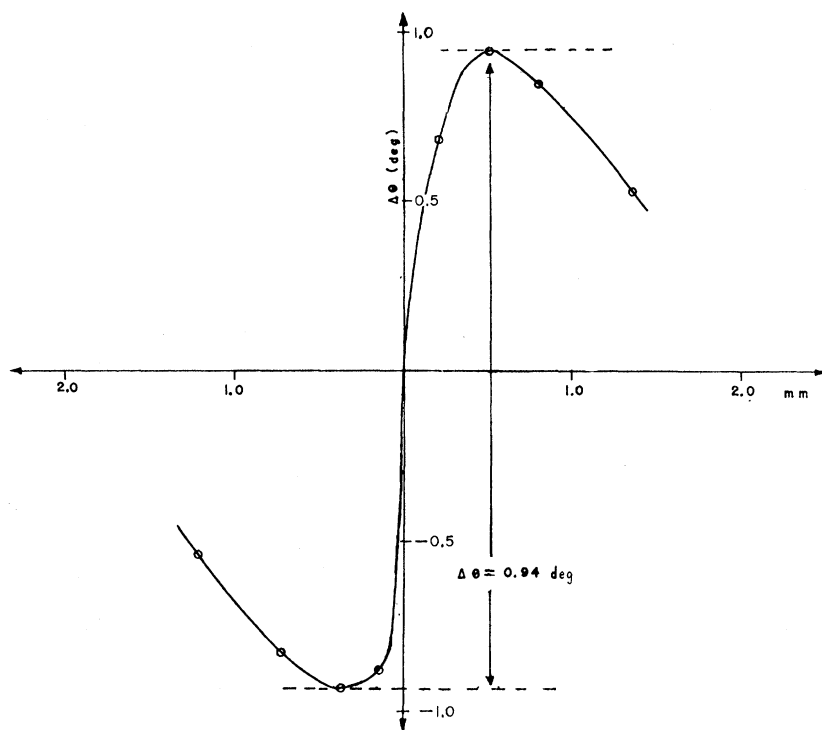


FIG. 1. A typical curve of optical rotation θ versus position for LiF x irradiation at 80°K. Half of the specimen in the form of a thin plate has been exposed to irradiation. The measurements were taken along a line perpendicular to the interface between the irradiated and unirradiated portions and lying in one of the large surfaces of the plate. The irradiation direction was perpendicular to this surface. Further details are given in Ref. 1.

In addition to an annealing in the vicinity of 130°K, an additional annealing has been observed at a higher temperature. This new annealing region can be explained in terms of vacancy diffusion.

II. EXPERIMENTAL

The general characteristics of the photoelastic technique used to determine the irradiation-induced expansion were discussed previously.¹ The following modifications and details should be noted: Radiation was obtained from a tungsten Machlett tube, operated at 45 kV and 30 mA, but was filtered by 0.5 mm of aluminum. Samples of Harshaw special purity crystals were not more than 0.5 mm thick and optical measurements were made with either a Beckman Spectracord or a Cary instrument. Special care was exercised in the application of the photoelastic method to increase the precision and reproducibility of the technique. Residual strain was kept at a minimum by specimen selection and it was found that the rate of cooling should not exceed 10°C per h. In order to obtain this cooling rate a special system was built to inject controlled bursts of liquid nitrogen into the Dewar.³

The precision of the actual photoelastic measurements was improved by the use of a photoelectric device to determine optical rotations rather than by visual observation as had been done previously.¹ The optical rotation was measured as a function of position along

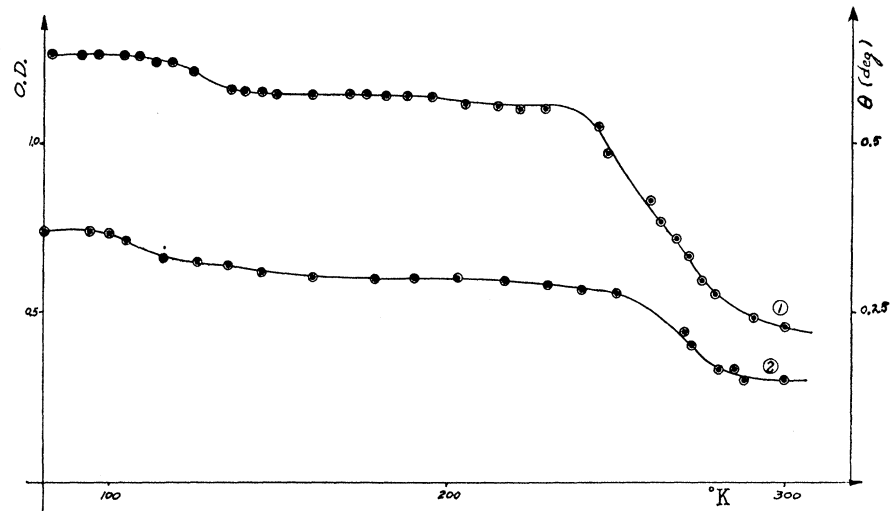
the crystal in both the irradiated and unirradiated portions. This permitted a comparison with the strain profiles expected from the one-dimensional analysis of the strain problem.¹ At each measurement position the rotation observed before irradiation was subtracted from that observed after irradiation. This difference was then used to calculate $\Delta V/V$ using Eq. (14), Ref. 1. Room-temperature values for the elastic and photoelastic constants were used in calculating $\Delta V/V$ at all temperatures and corrections were not made for different thermal expansion coefficients of the irradiated and unirradiated portions of the samples.⁴

A double-slit system was used to make photoelastic measurements as a function of position. This was necessary in order to obtain a narrow light beam at the crystal which was placed about 3 cm from the front slit. The beam width at the crystal was of the order of 0.1 mm. The rotation of the plane of polarization of the beam θ after passing through the crystal and a quarter wave plate was determined by the use of a photomultiplier and an amplifier system. An analyzer was used but an absolute minimum in intensity was not sought. Instead symmetrical readings were taken for analyzer angles on either side of the minimum and from this the minimum was calculated. In this way rotations could be measured to ± 0.01 deg. The double-slit system was held by a micrometer and birefringence could be measured at positions separated by steps of 0.05 mm.

³ A detailed description of the slow cooling system, which is useful for general applications, will be given elsewhere.

⁴ M. F. Merriam, D. A. Wiegand, and R. Smoluchowski, *Phys. Rev.* **125**, 52 (1962); (to be published).

FIG. 2. Thermal annealing of the F band (curve 1) and $\Delta V/V$ (curve 2) for LiF x irradiated at 80°K.



A typical curve of optical rotation versus position for a partially irradiated LiF sample is shown in Fig. 1. These data should be compared with the predicted curve of Fig. 1(d), Ref. 1. Reasonable agreement is apparent. It is seen that the curve of Fig. 1 is very well defined and that the two extrema are almost symmetrical in relation to the interface position as expected from theoretical and intuitive considerations. The method here described increases the precision considerably over that previously reported.¹

Sometimes it has been observed that the whole curve of Fig. 1 tends to be displaced up or down. While this fluctuation is not understood it does not affect the precision of the measurements reported here since $\Delta V/V$ is proportional to the differential rotation indicated by the arrow in Fig. 1. This displacement may, however, introduce errors when the rotation is measured only in the unirradiated part of the sample because the angle reference ($\Delta\theta=0$) is then difficult to determine.

It is, of course, necessary that the sample be mounted in such a way as to minimize thermal strains produced by temperature gradients. In the present case the sample, in the form of a thin plate, was mounted so as to lie in an axial plane of a copper cylinder, half of which was removable to permit access for positioning the crystal. For optical measurements an opening was cut through the cylinder perpendicular to the plane of the sample. In addition, the crystal was covered with aluminum foil except for a small circular region where the optical rotation measurements were made. This type of mounting appears to minimize successfully end effects and thermal gradients. Thermocouples and temperature measuring resistors were attached to the crystal holder rather than to the crystal.

III. RESULTS

Figure 2 shows the annealing of the F band and $\Delta V/V$ for LiF x irradiated at 80°K. While both the F band

and $\Delta V/V$ anneal somewhat in the vicinity of 130°K, this annealing is much less pronounced than that recorded earlier by Wiegand and Smoluchowski.¹ In addition to the F band, a band was observed at approximately 3450 Å after irradiation at 80°K which is presumably due to the self-trapped hole. The saturation level of this band as a function of irradiation time was lower in the samples used in this work than that reported previously,¹ but the annealing in the vicinity of 130°K was the same. The LiF used for the measurements discussed here was obtained at a later time from Harshaw Company than that used for the earlier measurements and may be purer. Also shown in Fig. 2 are pronounced annealings of the F band and $\Delta V/V$ in the

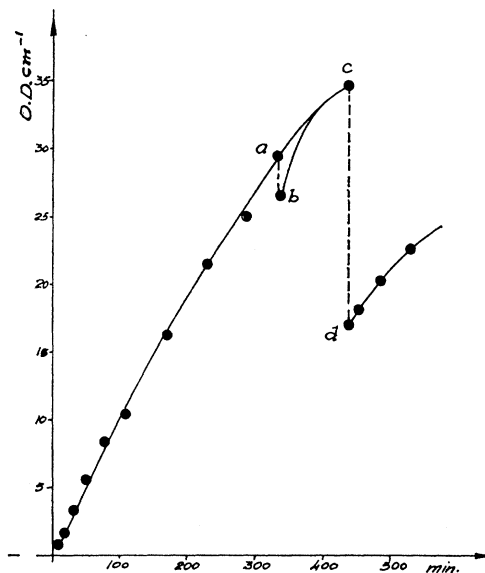


FIG. 3. Growth and regrowth data for the optical densities at the F -band maximum for LiF x irradiated at 80°K. The dashed lines represent thermal annealings as described in the text.

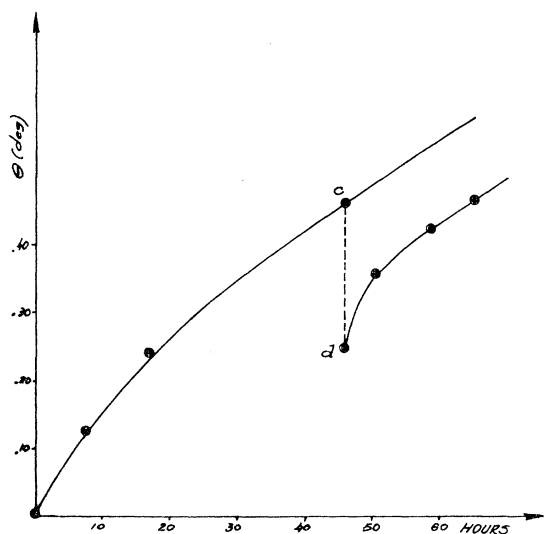


FIG. 4. $\Delta V/V$ of LiF versus x irradiation time at 80°K. The dashed line indicates annealing on warming to 300°K (see text).

vicinity of 270°K. These annealings were also observed with the older and presumably less pure LiF.

In Fig. 3 growth and regrowth curves for the optical densities at the maximum of the F band are given after irradiation at 80°K. For a short time the irradiation was interrupted, the sample was warmed to approximately 150°K, and then recooled to 80°K. The first decrease in optical density as indicated by the dashed line in Fig. 3, is due to the annealing at approximately 130°K. Upon reirradiation, the optical density at the F and 3450-Å bands rose very quickly and then continued to grow along an extrapolation of the initial growth curve as reported previously.¹ After a short additional irradiation period the same sequence of operations was carried out with the exception that the sample was warmed to approximately 300°K. The dashed line at the longer time represents the annealing during this warming and recooling. Upon reirradiation the F band did not recover as it did after the lower temperature annealing, thus suggesting a loss of negative ion vacancies due to the annealing at 270°K. In Fig. 4 $\Delta V/V$ is given versus time of irradiation with the dashed line representing annealing upon warming to 300°K. These data indicate that $\Delta V/V$ does not recover upon reirradiation after warming to 300°K. Similar results are obtained when a sample is warmed to only 150°K.¹ It should be noted that the F -band data of Fig. 3 are given for only 8 h of irradiation while the $\Delta V/V$ data of Fig. 4 correspond to about 50 h of irradiation. The same difference exists for the F band and $\Delta V/V$ data of Fig. 2. In general, it has been difficult to obtain measurements of the F band and $\Delta V/V$ for the same irradiation dose because conventional apparatus for measuring optical absorption will not measure the high optical densities found in the heavily irradiated samples necessary for the $\Delta V/V$ measurements.

Optical absorption measurements at room temperature of a sample which had been heavily irradiated at 80°K for the $\Delta V/V$ studies revealed a rather prominent M band. A LiF sample was then x irradiated at liquid-nitrogen temperature for 28 h and the optical absorption measurements made during warming. In Fig. 5(a) the optical density at the maximum of the M band is given versus temperature during warming. The observed absorption band is termed the M band because the wavelength for the band maximum and the half-width at room temperature are approximately the same as those for the M band produced by x irradiation at room temperature. A very weak band was observed at 80°K after irradiation but before warming which is presumably due to the M center. It was, however, impossible to determine the magnitude of this band at all temperatures during warming because of overlap with other bands which grew, decayed, and shifted during the warming process. In particular, reliable data for the M band were not obtained between 213 and 275°K. The vertical dashed line indicates an increase in the M band at room temperature over night. Unresolved R bands were observed to grow in the same temperature range as the M -band growth. The M -band data shown

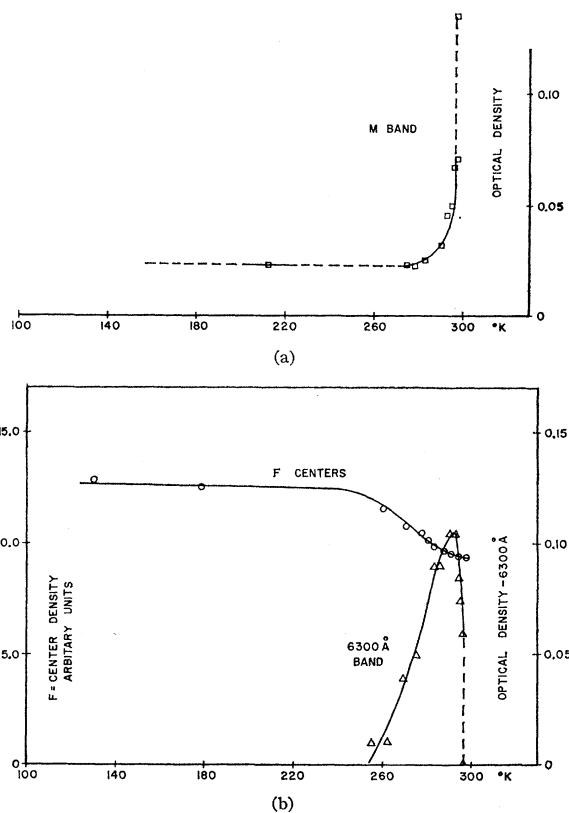


FIG. 5. (a) Optical density at the maximum of the M band as a function of temperature during warming after x irradiation at 80°K. (b) Estimated F -center densities and optical density of the 6300-Å band as a function of temperature during warming after x irradiation at 80°K.

in Fig. 5 have been corrected for overlap with other bands.

Because of the large optical density at the F -band maximum it was not possible to observe the F band over the whole wavelength range. The densities of F centers for this same sample were, however, estimated from the absorption at 2660 Å and the data are given in Fig. 5(b). The annealing of the F band was determined by comparing the optical density at 2660 Å with the optical density of a sample which had a constant and known density of F centers as a function of temperature.

A comparison of the data of Figs. 2 and 5 indicates that the F -band annealings in these two samples occur in similar temperature ranges, although the rates of warming are somewhat different. The growth of the M band apparently occurs at a somewhat higher temperature than the annealing of the F band and $\Delta V/V$. It can be estimated from the data that the number of vacancies necessary to account for the growth of the M band is only a few percent of the number of F centers annealed in the vicinity of 270°K.⁵

Also shown in Fig. 5(b) is the optical density at the maximum of a band at 6300 Å as a function of temperature during warming. This band has a width at half-maximum of approximately 1100 Å and a correction has been made for the overlap of this band with other absorption bands. An examination of Figs. 2 and 5 reveals that the 6300-Å band begins to grow at the same temperature as the initiation of the annealing of the F band and $\Delta V/V$. The 6300-Å band reaches a maximum shortly after the start of the growth of the M band and then anneals while the M band grows. Rabin has found a similar relationship between the M band and a band at 13500 Å in KCl.⁶ The ratios of the wavelengths for the maxima of the two bands are also approximately the same in LiF and KCl.

IV. DISCUSSION

Annealings of $\Delta V/V$ and the F band have been observed at approximately 130 and 280°K. These two temperature ranges are discussed separately.

A. Annealing in the Vicinity of 130°K

It was suggested previously that the annealing of $\Delta V/V$ at 130°K is due to a change in configuration of the halogen interstitials.¹ It was concluded that vacancy interstitial recombination does not take place in this temperature range because of the ease with which the F centers could be regenerated by irradiation as shown in Fig. 3. The annealing of the F band was thought to be due to the annihilation of F -center electrons with F_2^- center holes. The new data indicate that the

amounts of annealing of both $\Delta V/V$ and the F band are variable from sample to sample and thus are presumably dependent on the quality of the sample. A comparison of Fig. 2 with Fig. 7 of Ref. 1 also reveals that the $\Delta V/V$ annealing at 130°K is apparently much more variable from sample to sample than the F -band annealing. If the above explanation for the annealing of $\Delta V/V$ is to be correct it is necessary to conclude that the interstitial configuration is influenced by other imperfections. While Känzig and Woodruff⁷ have reported that the H center as detected by paramagnetic resonance is not associated with other defects, they have also reported a variable ratio of H to F_2^- centers for different samples. It may be, however, that an interstitial other than the H center is sensitive to sample perfection. It is possible that other configurations of the halogen interstitial, in addition to the H center, are stable.⁸

The smaller annealing of the F band can be attributed to the smaller number of self-trapped holes before annealing. The smaller number of the latter is most probably due to a lower number of electron traps in the lattice before irradiation and thus suggest samples of higher purity. Johnson⁹ has in fact reported that Harshaw LiF has become progressively purer over the past few years. Since the LiF used in this work was purchased approximately two years after the LiF used previously it is quite possible that a difference in purity exists. The LiF used in this work cleaved very well and therefore was not of the extremely soft variety.

Känzig¹⁰ has suggested that the kind of volume expansion discussed here is associated with the F_2^- center and not the halogen interstitial. There are a number of reasons why this appears not to be the case. An examination of Fig. 2 reveals that the F band^{10a} anneals at a slightly higher temperature than $\Delta V/V$ in the vicinity of 130°K. Känzig has also found that the H center anneals at a slightly lower temperature than the F_2^- center. Unfortunately, the temperatures cannot be compared directly because Känzig has used pulse annealing whereas the present study is based on a continuous warming technique. Strains induced by sudden changes in temperature in a pulse-annealing technique preclude the use of the photoelastic technique. Känzig's main argument regarding the relationship of $\Delta V/V$ to the F_2^- center seems, however, to be based primarily on his observation that the density of self-trapped holes is an order of magnitude greater than the density of H centers for his conditions of irradiation. It appears that this cannot be the case for our irradiated samples used for $\Delta V/V$ studies. The intensity of x

⁷ W. Känzig and T. O. Woodruff, *Phys. Chem. Solids* **9**, 70 (1958).

⁸ D. A. Wiegand and R. Smoluchowski, *The Chemical and Biological Actions of Radiation*, edited by M. Haissinsky (Academic Press Inc., New York, to be published).

⁹ W. Johnson, *Bull. Am. Phys. Soc.* **7**, 210 (1962).

¹⁰ W. Känzig, *Phys. Chem. Solids* **17**, 88 (1960).

^{10a} The F and 3450 Å (F_2^-) bands anneal at the same temperature.

⁵ B. J. Faraday, H. Rabin, and W. D. Compton, *Phys. Rev. Letters* **7**, 57 (1961); H. Rabin, Conference on Defect Production by Irradiation, Gattlinburg, Tennessee, 1963 (unpublished).

⁶ H. Rabin, *Phys. Rev.* **129**, 129 (1963).

irradiation used in the present work have been as much as two orders of magnitude greater than those used by Känzig. Since the density of F centers and $\Delta V/V$ increase linearly with time¹ and intensity¹¹ of x irradiation, while the F_2^- optical absorption band saturates after a very short time (see Figs. 5 and 9, Ref. 1), it is quite reasonable to conclude that the densities of F and presumably H centers were significantly larger than the density of F_2^- centers for the conditions under which the annealing of $\Delta V/V$ was observed. There may also be other types of interstitial centers. It is clear that the expansion of the lattice during irradiation is not associated with the generation of F_2^- centers because of the saturation of the F_2^- optical absorption band as a function of time of irradiation.

It is also necessary to consider the possibility that an annealing of the strain detected photoelastically is due to the occurrence of slip and is therefore not a true annealing of $\Delta V/V$. Slip may take place in either the irradiated or unirradiated parts of the sample and it is expedient to consider the two parts separately. Nadeau has observed an increase in the flow stress of "soft" LiF as a result of irradiation at 78°K.¹² In addition, part of the increase in flow stress anneals in the same temperature range as $\Delta V/V$ and the F band in the vicinity of 130°K. If the yield stress were also to increase with irradiation, and this increase were to anneal in the vicinity of 130°K, it would be indeed possible for slip to occur at this temperature. This would relax the strain detected photoelastically and would indicate an apparent rather than a true annealing of $\Delta V/V$. There are, however, experimental data which suggests that yield phenomena do not depend on irradiation and annealing in the same manner as the flow stress. It is well known from internal friction measurements that dislocation pinning occurs in a very short time of irradiation compared to the growth of the F band.¹³ In contrast, the increase in flow stress varies as the square root of the F -center densities.¹² Since yield is probably determined at least in part by the stress necessary to pull dislocations away from pinning points whereas the flow stress is apparently determined by the obstacles to dislocation motion, it is reasonable to conclude that these two stresses may depend differently on irradiation. In addition, dislocation pinning by irradiation at low temperatures has been reported not to anneal on warming to room temperature.¹³ While the above discussion has dealt only with slip occurring in the irradiated portion of the sample, it is also necessary to consider slip in the unirradiated portion of the sample. Wolfe and Bauer have, in fact, found evidence for dislocation multiplication in the unirradiated half of partially irradiated alkali-halide samples.¹⁴ This multi-

plication is apparently due to slip which in turn is caused by strain resulting from partial irradiation and nonuniform volume expansion. Although the strain is symmetrical about the boundary interface (see Fig. 1), the same process of dislocation multiplication apparently does not occur in the irradiated portion because of radiation-induced dislocation pinning. To demonstrate this Wolfe and Bauer have given the whole sample a very short dose of radiation (5 min), and have then irradiated half of the sample for extended periods up to 48 h. The short period of irradiation of the whole sample is sufficient to prevent dislocation multiplication in the unirradiated portion during the extended periods of irradiation of the other half of the sample. In contrast, in samples which did not have the short period of preirradiation (of the "so-called" unirradiated part) the increase in dislocation density in the unirradiated portion was found to be proportional to the F -center density in the irradiated portion. This proportionality between the increase in dislocation density and the density of F centers is presumably due to a proportionality between $\Delta V/V$ (and strain) and n_F . These experiments clearly demonstrate that dislocation multiplication and slip for strain due to the expansion of the partially irradiated alkali halides are dependent on irradiation in quite a different manner than the increase in flow stress. It is thus possible to conclude that a decrease in the flow stress due to annealing is not necessarily accompanied by a decrease in the stress necessary for slip. It is also important to note that Wolfe and Bauer have observed these effects only at very low F -center densities ($\sim 10^{16}/\text{cc}$) compared to the densities measured in this work. Their results also suggest that the dislocation multiplication saturates at very low F -center densities.

It should be also pointed out that if the apparent annealing of $\Delta V/V$ is due to slip then it is necessary to conclude that the amount of the slip is dependent on sample perfection before irradiation. There are several observations, however, which argue against this interpretation of the annealing of the strain. Following irradiation of LiF at room temperature, the annealing of $\Delta V/V$ above room temperature as detected by the photoelastic technique¹¹ is very similar to the annealing of the density change produced by neutron irradiation.¹⁵ Nadeau has observed an annealing of the flow stress in the same temperature range. It seems most reasonable to attribute the annealing of both $\Delta V/V$ and the change in flow stress to an annealing of lattice defects. The annealing of $\Delta V/V$ detected by the photoelastic technique and the change in mass density in the high-temperature range are also very similar for NaCl^{4,16,17} and can be attributed to lattice defect recombinations. Nadeau has observed in LiF an additional annealing of

¹¹ D. A. Wiegand (to be published).

¹² J. Nadeau, J. Appl. Phys. **33**, 3480 (1962).

¹³ See for example, C. L. Bauer and R. B. Gordon, J. Appl. Phys. **33**, 672 (1962).

¹⁴ R. L. Wolfe and C. L. Bauer (to be published).

¹⁵ J. Spaepen, Phys. Rev. Letters **1**, 281 (1958).

¹⁶ M. F. Merriam, D. A. Wiegand, and R. Smoluchowski (to be published).

¹⁷ K. Kobayashi, Phys. Rev. **107**, 41 (1957).

the flow stress in the vicinity of 320°K following irradiation at 78°K.¹² In contrast $\Delta V/V$ detected by the photoelastic technique is found to anneal at 280°K (Fig. 2) and an additional annealing has been observed at 370°K.¹¹ Thus it is possible to conclude that these two higher temperature annealings are not caused by a decrease in the yield stress but are due to contractions of the lattice. A direct comparison between the work of Nadeau and the work reported here is difficult because of differences in the annealing procedure and also differences in the intensity and total irradiation dose. It is estimated from the F -band data of Nadeau that the total dose of irradiation for samples in which $\Delta V/V$ has been studied is at least an order of magnitude greater than the total dose used by Nadeau. Finally, it should be pointed out that the ratio of $\Delta V/V$ detected by the photoelastic technique to the F center densities has always been observed to be rather close to values obtained by measuring the crystal expansion in other ways.^{8,18}

In summary the following points are of significance: (a) The flow stress and the stress necessary for slip do not depend on irradiation in the same manner and are apparently not related to the same phenomenon; (b) slip which does occur in the unirradiated portions saturates at very low irradiation dose presumably because of work hardening; (c) the annealing of $\Delta V/V$ detected by the photoelastic method is similar to the annealing of the expansion detected by other techniques in all cases where measurements have been made. It thus seems possible to conclude that any slip which takes place due to partial irradiation of a sample does not produce important strain relaxation and thus does not influence the $\Delta V/V$ as calculated from photoelastic data by a significant amount for the conditions of these experiments.

B. Annealing in the Vicinity of 280°K

The formation of the M band during the annealing in the vicinity of 280°K suggests that this annealing is due to the motion of negative ion vacancies. The annealing of $\Delta V/V$ can be attributed to any one of the

following processes: (a) vacancy clustering, (b) vacancy-interstitial annihilation, (c) vacancy migration to sinks. It is difficult to choose between these possibilities on the basis of the information now available. The regrowth data after warming to room temperature and recooling indicate a net reduction in the number of negative ion vacancies which can easily trap electrons to become F centers. Not all of the defects have annealed, however, and additional annealing stages have been observed above room temperature.¹¹

The growth of the 6300-Å band upon the decrease of the F band at about 260°K (Fig. 5) and the rapid growth of the M band following the decrease of the 6300-Å band above 290°K suggest the possibility that the 6300-Å band is due to an intermediate configuration between the F center and the M center. Others also observed the formation of a band at 6200 Å at room temperature after low-temperature irradiation and have further noted a decay of this band and the growth of the M band with time at room temperature.^{19,20} Pringsheim and Yuster have reported that this band at 6200 Å is stable at -195°C after formation at room temperature. The thermal time histories in these cases are not given with sufficient precision to allow comparisons with the work reported in this paper. Delbecq, Pringsheim, and Yuster have also observed bursts of luminescence and conductivity at approximately -20°C on warming after irradiation at low temperature.²¹

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¹⁹ P. Pringsheim and Philip Yuster, Phys. Rev. **78**, 293 (1950).

²⁰ K. Kubo and K. Ozawa, International Conference on Crystal Lattice Defects, Kyoto, Japan, 1962 (unpublished).

²¹ C. J. Delbecq, P. Pringsheim, and P. H. Yuster, Z. Physik **138**, 266 (1954).

¹⁸ D. A. Wiegand, Phys. Rev. Letters **9**, 201 (1962).