Irreversible changes occur when Rochelle salt measurements are taken above and below the transition point of 24°C. These changes are not understood.

The data can be analyzed and fitted closely by use of a generalized stress-strain relationship in which the stress is a function of the strain and its first and second time derivatives. Inclusion of the third derivative leads to an antidissipative term which can be used to account for the negative absorption found in sodium chloride. The resonances are tentatively explained by assuming that they correspond to exchange frequencies for energy passing back and forth among only a few of the available modes of vibration of the crystal lattice as previously described.[4]

The results presented here together with those previously reported for metals, polymers, and quartz, indicate that the phenomena of low-frequency resonance dispersion in the mechanical properties of crystalline solids are of general occurrence.

VI. ACKNOWLEDGMENTS

This work was supported in part by a grant from the National Science Foundation and in part by a grant from Research Corporation. Mrs. Charles L. Reiser and Mrs. Ronald C. Althouse assisted in calculations and in some of the measurements.

The advice and assistance of R. Pepinsky and K. Vedam were invaluable during these investigations.

PHYSICAL REVIEW VOLUME 112, NUMBER 4 NOVEMBER 15, 1958

Radiation-Induced Changes of Dimensions, Index of Refraction, and Dispersion of Lithium Fluoride*

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(Received April 28, 1958)

Deuteron, electron, gamma ray, and x-ray irradiated specimens were examined by a photoelastic method and by interferometric methods. In addition to the increase in physical dimensions, there were found an increase in refractive index and an increase in dispersion, and these were measured. The results agree with the classical dispersion formulas if it is assumed that the effects are caused by a change in the refractivity of the base material due to the introduction of vacancies and holes and a change in the refractivity due to the F centers and the 450 centers, the size of the vacancies being about that of the absent ions and the oscillator strength of the F centers being near unity.

INTRODUCTION

BIREFRINGENCE observed by Primak, Delbecq, and Yuster[1] in nonuniformly irradiated alkali halides was interpreted by them as due to strain, and from it they calculated the radiation-induced expansion which they inferred had taken place. The calculation involved the assumption of plane stress and strain. This was certainly only an approximation because of the small sizes of the specimens and, in some cases, because of the unsymmetrical geometry. The effects were explained as related to the color centers but the results deviated from proportionality to the color-center concentrations reported by them. The present investigation stemmed from an attempt to resolve these difficulties and has led to new results.

EXPERIMENTAL

All of the specimens used for interferometric observation were cleaved from a single block of lithium fluoride originally supplied by the Optovac Corporation. It was ground and polished approximately flat and parallel on two opposite faces which were then 1.20 cm apart. The cleaved blocks possessed an area of these polished surfaces about 1 cm by several millimeters. The fringes formed by normally incident light (546 mμ) reflected from the front and back surfaces (Fizeau interferometer) will be termed F fringes in this paper. The better specimens showed less than one such fringe, some of the poorer ones used in the later work, 2 or 3. Attempts to grind and polish several other specimens to this degree of perfection have thus far proven unsuccessful, and it is believed the original specimen possessed an unusually perfect crystallization. Some strain was introduced into the crystal by grinding and polishing and was evidenced by a narrow zone of birefringence parallel to this face which could be observed when viewed parallel to the polished surfaces with polarized light. Although no birefringence could be seen with light incident perpendicularly to the polished surfaces in the usual mode of examination, the strain present in the unseen perpendicular planes would cause some modification of the results through the introduction of shears. Some random cleavage scraps (unground and unpolished) of lithium fluoride from the Optovac Corporation and the Harshaw Chemical Company were employed for absorption measurements and observation of birefringence.

Three specimens were irradiated with deuterons, about 21 Mev, perpendicularly incident on a cleavage

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* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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

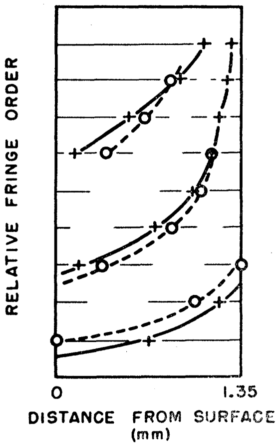

FIG. 1. Relative fringe orders seen along a central plane parallel to the line of sight and the deuteron direction in the irradiated region of three specimens bombarded for dosages in the ratios 1:2:4; crosses: Twyman-Green interferometer fringes (in transmission), circles: Fizeau fringes. The vertical displacements of the curves have no significance even for the members of a set.

face perpendicular to the polished faces for dosages in the ratios 1:2:4. The beam was swept over the crystal to achieve uniformity of irradiation, and hence the bombardment data did not give the dosage; but by comparison with other irradiated specimens, it was determined that the dosage of the most strongly irradiated specimen was $2\frac{1}{2}$ μa sec cm^{-2}. The fringes formed when the specimen is inserted into one leg of a Twyman-Green interferometer whose mirrors are equally perpendicular to the incident parallel light will be termed flat-field transmission Twyman-Green fringes and will be abbreviated TG-f fringes. The relative orders of the F and the TG-f fringes seen across a chosen nearly-central plane parallel to the deuteron path are plotted against distance across the specimens in Fig. 1. As pointed out by Twyman and Perry[2] (the relative orders Δn_f and Δn_t of the F and TG fringes, respectively; medium of refractive index N and thickness D), since Δn_f depends on $\Delta(ND)$ while Δn_t depends on $\Delta[(N-1)D]$, it is possible to solve for ΔN and ΔD independently; thus,

$$\Delta N = N\lambda[\Delta n_t - N^{-1}(N-1)\Delta n_f]/2D,$$

$$\Delta D = \lambda(\Delta n_f - \Delta n_t)/2.$$

There is no reference point in these samples where N and D are known, and, further, the fringes are packed too closely at the end of the range to connect them across the boundary of the irradiated region. It is evident, however, that ΔD is of about the magnitude of variations in D before irradiation. In the unirradiated region the values of ΔD were not inconsistent with the absence of appreciable change in refractive index. In the irradiated region, the large changes in relative order, which are the same for the F and TG-f fringes can only be interpreted as being due to a change in the refractive index accompanied by relatively negligible dimensional change. While the relative change in refractive index along the range is readily computed from the above curves, the absolute change cannot be. An increase in the length d of the Twyman-Green interferometer leg in which the specimen was inserted caused the fringes in the irradiated zone to move toward the beginning of the range, hence the refractive index was greatest at the end of the range.

The fringes formed with the specimen inserted in one leg of a Twyman-Green interferometer, one of whose mirrors is inclined to form fringes which are parallel to the direction of the deuterons in the field surrounding the specimen, will be designated TG-i fringes. Their appearance is sketched in Fig. 2. As shown in the figure, a fractional order displacement of the fringes was seen near the end of the range when rotating the plane of polarization and is in accord with the existence of birefringence. It is thus evident that the index of refraction changes here are an order of magnitude greater than the birefringence. The locations of the central white-light fringes seen at the beginning of the ranges when a white-light source replaced the filtered mercury arc source and an unirradiated specimen was used as a compensator in the other leg, are also shown in Fig. 2. The central white-light fringe could not be used to identify the zero-order fringe because the shift of this fringe was out of all proportion to the known ratio of effects along the range; and also, although this could not be determined with certainty because the fringes were so closely packed there, the fringe so identified seemed to alter its color value along the range. A change in dispersion thus seemed likely. To allay any questions concerning the possibility of a spurious result from confusion of the incident and reflected wave fronts in the Twyman-Green interferometer, a set of

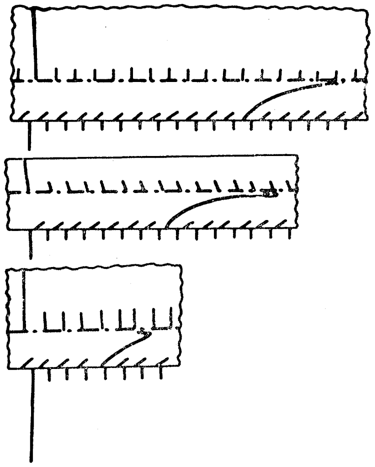

FIG. 2. Sketches of the Twyman-Green fringes seen with inclined mirror with the three respective deuteron-irradiated specimens alternately in one arm and a compensator crystal (unirradiated) in the other arm. Only the achromatic (or nearly-achromatic) fringes are drawn full, the location of the others being shown along one surface. In each case, the curved fringe is in the irradiated zone. For the intermediate dosage, the displacement seen on rotating the plane of polarization is easily indicated on this scale and is shown. The fringes near the end of the range of the most highly irradiated crystal were too closely packed to distinguish detail reliably.

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[2] F. Twyman and J. W. Perry, Proc. Phys. Soc. (London) 34 151 (1922).

observations were made with a Mach-Zehnder interferometer. Within the precision of measurement, the fringe displacements were just half those seen for TG-i fringes, hence further observation with the Mach-Zehnder instrument was abandoned in favor of the more easily manipulated Twyman-Green instrument.

To relate the fringe orders in the irradiated and unirradiated regions, specimens were required that possessed a less abrupt boundary for the irradiated zone. Specimens of this kind were prepared by moving a wedge between the deuteron beam and the crystal. However, it was found that more satisfactory gradients yet were obtained on bombardment with 1.1-Mev electrons. The TG-i fringes observed on three successive irradiations of the same specimen are shown in Fig. 3. The location of the central white-light fringe is also shown, and it is seen that its order shifts with respect to the fringe order in the same direction as the fringe order. The fringe order n, observed in a compensated Twyman-Green interferometer of physical path difference Δd (taken positive when the leg containing the irradiated specimen is longer), when the specimen is compensated by an unirradiated specimen of the same thickness and refractive index as the irradiated specimen possessed before irradiation, is

$$n=2\lambda^{-1}[(N-1)\Delta D+D\Delta N+\Delta d].$$

The position of the zero-order fringe occurs at

$$\Delta d_0=-[(N-1)\Delta D+D\Delta N],$$

displaced Δd_0 from the position where the zero-order fringe and the achromatic white light fringe would have been located had the specimen not been irradiated. Since the interferometer is no longer compensated, a truly-achromatic fringe no longer exists. However, a nearly-achromatic fringe is seen where

$$\frac{dn}{d\lambda}=0=-\frac{2}{\lambda^2}[(N-1)\Delta D+D\Delta N+\Delta d]+\frac{2}{\lambda}\left(\Delta D\frac{dN}{d\lambda}+D\frac{d\Delta N}{d\lambda}\right),$$

and hence when

$$-\Delta d_a=(N-1)\Delta D+D\Delta N-\lambda\Delta D(dN/d\lambda)+\lambda D(d\Delta N/d\lambda),$$

and at the fringe order

$$n_a=2[\Delta D(dN/d\lambda)+D(d\Delta N/d\lambda)].$$

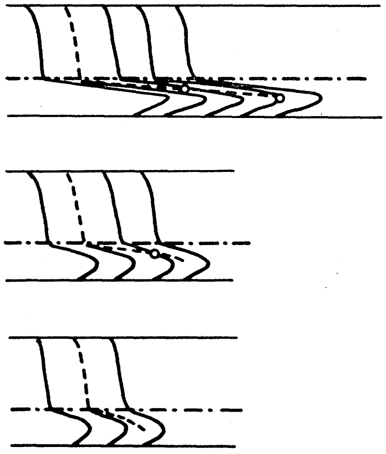

FIG. 3. Sketches of fringes seen with the arrangement described for Fig. 2, but for the three respective successive electron irradiations of a crystal. The achromatic (or nearly-achromatic) zone is dashed, having been located by the nearly-achromatic portions (shown circled) of the fringes. Only the achromatic (or nearly-achromatic) fringes and their neighbors are shown.

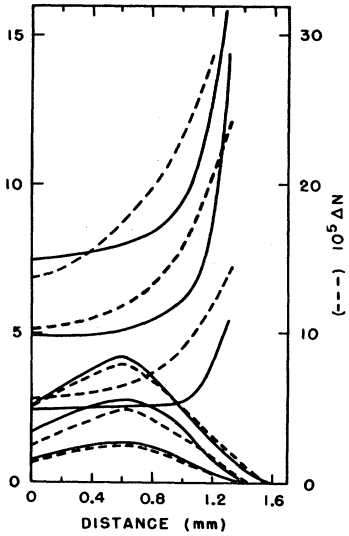

FIG. 4. The refractive index changes (dashed) and the dilatations computed from the birefringences (solid) for electron-irradiated specimens (lower 3) and for the deuteron-irradiated specimens (upper 3), shown as a function of distance from the irradiated face along a central plane parallel to the irradiation beams and the line of sight.

Over the restricted range (mainly from green through near red for visual observation) it is permissible to take

$$N=A+B/\lambda^2 \quad\text{and}\quad \Delta N=\Delta A+\Delta B/\lambda^2;$$

hence

$$n_a=-4\lambda_a^{-3}(B\Delta D+D\Delta B). \tag{1}$$

The value calculated for the dispersion constant B using the above formula is very sensitive to λ_a. Unfortunately the intensity of an incandescent source falls rapidly at the wavelengths of greatest perception, and absorption in the optical system is apt to cause a further change in λ_a. The correct value to use was therefore determined. The value of N for unirradiated lithium fluoride was taken as

$$N=1.3857+2.15\times10^{-11}/\lambda^2, \tag{2}$$

obtained by fitting the data given in the *American Institute of Physics Handbook*.[3] An unirradiated lithium fluoride specimen was placed in the leg of the Twyman-Green interferometer and rotated slowly from the normal position, the meanwhile moving the mirror inward decreasing d to retain the nearly-achromatic fringe in view. As this was done, the nearly-achromatic fringe was gradually displaced to lower order and the change Δd recorded when the displacement seemed an integral order; this amounted to about 0.001 cm. Here ΔB is zero, $n_a=-1=-4B\Delta D/\lambda^3$ where $\Delta D=-\Delta d/(N-1)$, hence λ was about 600 mμ. This is a rather high result, but the lamp filament was at about 1400 to 1700°C and the silver coating on the

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[3] *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957), pp. 6–24.

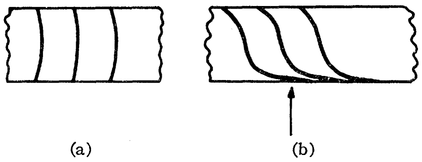

FIG. 5. Sketches of several fringes seen with the arrangement described for Fig. 2, but (a) before irradiating, (b) after irradiating with soft x-rays incident as shown by the arrow.

dividing plate was, at this time, partially changed to sulfide, which renders it brownish. From Fig. 3 it is seen that the fringe shift of the nearly-achromatic fringe in the irradiated region is about 5/3 of the displacement of the zero-order fringe from its position in the unirradiated portion. It was shown that the increase in refractive index caused the zero-order fringe to shift to lower order according to the convention employed here. The change in dispersion has caused the white light fringe to shift further in the same direction which from Eq. (1) is seen to denote a positive value for ΔB, since $B\Delta D$ is negligible in this case. Thus the dispersion defined as B or as $-dN/d\lambda$ has increased as a result of irradiation. The refractive index changes, calculated on the assumption that upon irradiation the zero-order fringe is displaced 0.6 of the displacement of the nearly achromatic fringe, are plotted in Fig. 4. The changes in dispersion are obtained from Eq. (1) by assuming that n_a is 0.4 of the displacement of the nearly-achromatic fringe from its original coincidence with the zero-order fringe in the unirradiated material, the term involving ΔD being negligible as pointed out above. The order of magnitude of ΔB then proves to be 10^{-13}, two orders of magnitude smaller than B, and this may be compared to ΔD, four to five orders of magnitude smaller than D.

That the effects described above were not related to bombardment by particles was demonstrated by securing similar results by means of x-ray irradiation. An interferometric specimen was irradiated with soft x-rays incident on one face perpendicular to the polished faces. The appearance of the TG-i fringes before and after irradiation is shown in the sketch, Fig. 5. Further work with x-ray irradiated specimens was abandoned because the specimen was partially colored throughout (i.e., there was no unirradiated zone), and because the large gradients near the specimen edge were not convenient for measurement.

The birefringence of the deuteron- and electron-irradiated specimens was determined along a central plane by the method described previously[1] and the results are plotted in Fig. 6. The strain-birefringence was redetermined as 0.15 by using dead weight loading and a calibrated quartz wedge, the elastic constants employed previously being assumed correct. The dilatation calculated from the theory given previously, plane stress and strain being assumed, is plotted in Fig. 4. The polished faces of the deuteron-irradiated specimens were examined interferometrically by making them the mirror of a Twyman-Green interferometer, an unsilvered flat being used as the mirror in the perpendicular leg, and poorly coherent light being used to avoid confusion from the other specimen face. The appearance of fringes formed with the mirrors inclined to produce fringes parallel to the deuteron direction is shown in Fig. 7. The thickness variations across the specimen faces are seen to be very small, in accord with the large F and TG-f fringe displacements being due to variations in refractive index. It is evident that the dilatation, at least in the direction examined, i.e., perpendicular to the polished face, has been largely confined by the unirradiated region. The dilatation of interest (and the one to be compared with the dilatation

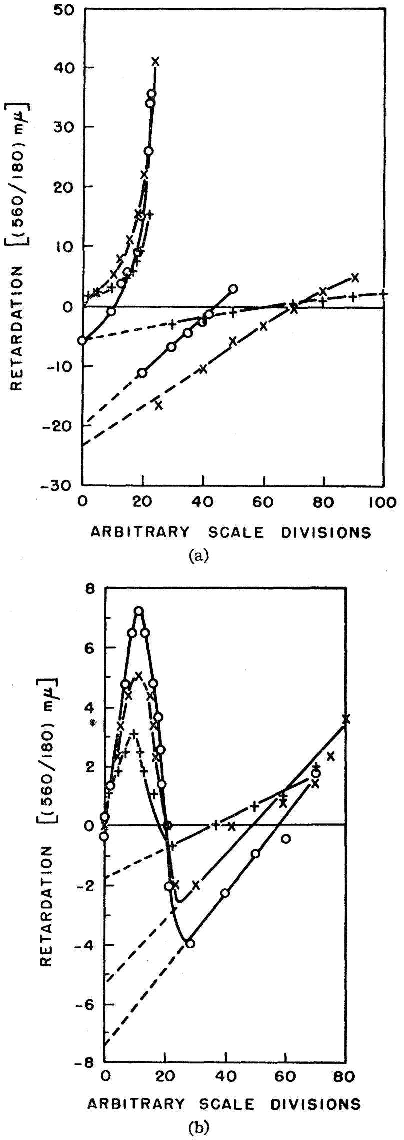

FIG. 6. Retardations along a central plane parallel to the line of sight and the irradiation beams as a functions of distance from the irradiated face; (a) the three deuteron-irradiated specimens, (b) the three successive electron irradiations of a specimen.

calculated from the birefringence) is the dilatation observed in the absence of elastic confinement. This was determined by using two adjacent cleaved specimens as end standards whose lengths were compared interferometrically. One mirror holder of the Twyman-Green interferometer was replaced with a special fixture which permitted adjustment of the inclination of the one specimen and the lateral motion of the other as well as inclination of both simultaneously. Thus, one end of each specimen was adjusted to be in the same plane as determined with the achromatic white-light fringe. The fixture was then reversed, and the relative displacement of the opposite ends was determined. One of the specimens was irradiated with gamma rays by placing it near an intense cobalt source for several intervals and a progressive increase in length was noted which was 0.38 fringe at the end of the second irradiation and 0.62 fringe at the end of the third irradiation. The refractive indices could not be compared because the specimens were not connected. However, the displacements of the nearly-achromatic white-light TG-i fringes were 3 fringes after the second irradiation and 6 fringes after the third irradiation, and the same displacements were seen with a yellow filter, proving that the result was not a spurious one due to absorption by the yellow-irradiated specimen. Thus the radiation-induced expansion of the alkali halides is easily observed by interferometric methods. However, because of the elastic deformation, a localized physical expansion is not observed at the boundary of an irradiated zone, and hence it would be difficult to observe the expansion in a magnified small area of an irregular face in the manner attempted by Smith, Leivo, and Smoluchowski.[4]

The major absorption of the crystals consists of a band with a maximum at about 248 mμ, the *F* band, and one with a maximum at 447 mμ, termed here the 450 band and considered by some to be an *M* band. These absorption bands were determined with a Cary-Model-11 recording spectrophotometer. The peak optical density was taken as the optical density at the maximum less the background optical density found at about 350 mμ. For nearly all the specimens, the full 450 band could be traced by the instrument which read to optical densities about 3.5. This was not possible for many of the *F* bands whose short-wavelength shoulders in some cases extended beyond the wavelength scale of the instrument, 200 mμ. For the *F* bands, the width from center (assumed unshifted) to the long-wavelength shoulder, where it appeared at the highest optical densities which could be read by the instrument, was taken. The ratio of peak optical density to this optical density above background was obtained from a graph in which the width of the long-wavelength shoulder from band center (taken in wave numbers) was plotted against this ratio for an *F* band which was completely within the instrument scale bounds. The method was tested by comparing a thick specimen with a thin plate cleaved from it and reasonable agreement was obtained. However, although graphs of peak widths (in wave numbers) to the ratio were about the same for deuteron and short electron irradiations, they were noticeably different for gamma-ray and long electron irradiations. Thus the peak shapes (which were close to Gaussian when plotted in wave numbers but which deviated sufficiently to make a calculation of peak height on this basis incorrect by 20–50% in particular cases) may alter somewhat with irradiation and the conditions of irradiation. The calculation of peak optical densities by this method is probably reliable to 20%. The peak optical densities of the specimens described above are given in Table I. For the deuteron- and electron-irradiated specimens they were measured in the direction of the beam, and thus represent the total absorption through the nonuniformly colored section. Several deuteron-irradiated specimens were measured in this same manner and then cleaved into sections (lettered *A*, *B*, *C*, etc.) perpendicular to this direction, and each section measured to learn something about the variation along the range. It is evident that the ratio of the *F* peak to the 450 peak is not constant. It decreases with dosage and is different, in addition, for the different irradiations. There is no consistent relationship of this variation to the kind of irradiation or to the rate of coloration. Rather, it seems related to the temperature of the lithium fluoride. The magnitude of the effect is shown by the fact that the gamma-ray-irradiated sample was most affected, and its temperature could not have been more than 40–50°C.

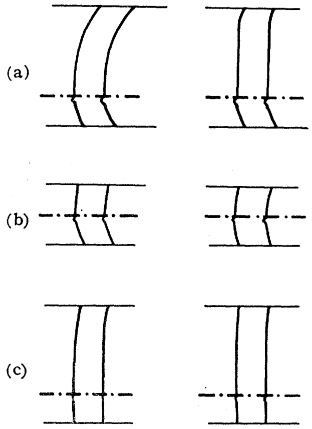

FIG. 7. Sketch of two adjacent fringes formed by making the respective faces of the deuteron-irradiated crystals the mirror (inclined) of a Twyman-Green interferometer. Deuterons were incident perpendicular to the bottom edge, and the uppermost specimen was most highly irradiated. The fringe disturbance at the internal irradiated zone boundary was, for the respective crystals, (a) 1/10 to 1/20 fringe, (b) 1/10 to 1/15 fringe, and (c) 1/40 fringe.

The widths of the bands of several specimens were measured at half-maximum optical density above background. For the *F* band, results from 6100–6500 cm^{-1} (0.75 to 0.80 ev) were obtained, a somewhat lower value than the 0.82 ev used previously,[1] and for the 450 band 1700–1900 cm^{-1} (0.21–0.234 ev) was obtained, about the same as the 0.22 ev used previously.[1] The ratios of *F* band to 450 band half-widths obtained here was thus 3.2 to 3.8 to be compared to the previous 3.7. In the calculations to be given in this paper, the half-

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[4] Smith, Leivo, and Smoluchowski, Phys. Rev. **101**, 37 (1956).

TABLE I. Absorption data for deuteron-, electron-, and gamma-ray-irradiated specimens.

Specimen No.	F peak $\ln(I_0/I)$[b]	450 peak $\ln(I_0/I)$[b]	Thickness (cm)	F absorption $\text{cm}^{-1}\ln(I_0/I)$	450 absorption $\text{cm}^{-1}\ln(I_0/I)$	Ratio[a] F/450
			Deuteron-irradiated			
898[c]	28	1.2				23
899[c]	58	4.5				13
896[c]	64	7.0				9.2
895	39	2.3				17
895*A*	22	1.3	0.19	250	14	17
895*B*	14	1.1	0.041	370	30	13
892	54	4.2				13
892*A*	13	0.69	0.037	350	18	18
892*B*	13	0.74	0.031	410	25	18
892*C*	12	0.88	0.029	410	30	14
892*D*	20	1.9	0.035	550	53	10
894	33	2.1				15
894*A*	8.1	0.32	0.038	210	8.5	25
894*B*	6.4	0.35	0.031	210	11	19
894*C*	8.8	0.51	0.031	280	16	17
894*D*	11	0.90	0.034	320	25	12
			Electron-irradiated			
949 II[c,d]	17	0.53				32
949 III[c,d]	23	1.75				13
946	3.7	0.46				8.1
947	6.8	0.92				7.4
948	13	1.95				6.7
920	55	4.7				12
			Gamma-ray-irradiated			
907[c]	100	12	0.466	220	29	7.6
900	6.4	0.23				28
901	8.6	0.99				8.7
902	110	22	0.580	190	38	5.0
902*A*	11.2	2.6	0.066	170	40	4.3

[a] Ratios were calculated from the original data before rounding off, and hence may not accord exactly with the data in the table.
[b] The value of $\ln(I_0/I)$ is 2.3 times the optical density.
[c] These specimens were used for interferometric observation.
[d] Irradiated with lower beam intensity for a longer time.

width of the F band will be taken as 6300 cm^{-1} and of the 450 band as 1800 cm^{-1}, giving the ratio 3.5.

DISCUSSION

The absorption and index of refraction are related to each other through the classical dispersion theory.[5–7] They are also related to the number of centers, which should be related to the dilatation. The relation of the absorption to the number of oscillating centers can also be derived quantum mechanically. The latter calculation gives the same proportionality constant as the classical calculation,[8,9] but since a set of energy levels and transition probabilities are employed, the theory can accommodate any kind of absorption band shape, while the classical theory starting with a particular kind of oscillator leads to a particular absorption peak shape, the Lorentz one. The actual peak shapes are not simple, but they do not differ greatly from the Lorentz shape. The classical form will be used here in accord with other work in this field.[10]

The application of dispersion theory to this subject is due to Smakula[5] and was made at a time when the F center was believed to be formed through the capture of an electron by a vacancy already existing within the crystal. He therefore assumed that the formation of the F center left the refractivity of the base crystal essentially unchanged and that there was an increase in refractivity due to the oscillators which had been added, i.e., the F centers. It has been shown[1] that the dilatation has a sharp boundary at a sharp boundary in color center concentration, that it is nearly proportional (this is confirmed here and more completely demonstrated below) to the color center concentration, and that it largely vanishes on optical bleaching. These facts have been interpreted[1] to mean that the vacancies in which the color centers are formed are not present in the crystal to begin with and that they do not diffuse into the crystal from the boundaries, but that they are largely generated in the crystal during irradiation, and that they are stabilized (at least at these temperatures) by trapping electrons to form color centers. More recently it has been shown[11] that initially there is a period of "rapid coloration" during which the dilatation may be much smaller, but that at about 10^{16} centers/cm^3 the coloration rate declines and the dilatation increases to the rates found here. This has been

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[5] A. Smakula, Z. Physik, **59**, 603 (1930).

[6] J. C. Slater and N. H. Frank, *Introduction to Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1933), p. 278.

[7] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 662.

[8] M. Lax, J. Chem. Phys. **20**, 1752 (1952).

[9] C. J. Rausch and C. V. Heer, Phys. Rev. **105**, 914 (1957).

[10] A. B. Scott and M. E. Hills, J. Chem. Phys. **28**, 24 (1958).

[11] H. Rabin, Bull. Am. Phys. Soc. Ser. II, **3**, 126 (1958).

interpreted to indicate that, in the initial period, centers are formed by trapping electrons in vacancies already present in the crystal. However, since for most of the irradiations for which quantitative results are given here the color center concentrations are two orders of magnitude greater than for the initial period, it will be disregarded in the present discussion.

Since the vacancies which form the color centers are now assumed to be generated during coloration, it is necessary to modify Smakula's theory starting from the equations obtained when the complex refractivity is resolved into its real and imaginary components:

$$R=R_b+\sum\frac{n_if_i}{3\pi}\frac{e^2}{m}\frac{\nu_{0i}^2-\nu_i^2}{(\nu_{0i}^2-\nu_i^2)^2+p_i^2\nu_i^2},\qquad(3)$$

$$\frac{6N}{(N^2+2)^2}k_i=\frac{n_if_i}{3\pi}\frac{e^2}{m}\left[\frac{p_i\nu_i}{(\nu_{0i}^2-\nu_i^2)^2+p_i^2\nu_i^2}\right],\qquad(4)$$

where $R=(N^2-1)/(N^2+2)$, the refractivity per unit volume; R_b is the refractivity of the base material including vacancies and holes but not including the oscillators in the following terms; n_i is the number of oscillators of class i having oscillator strength f_i, peak frequency ν_{0i}, and damping constant p_i; e is the electronic charge (esu); m is the electronic mass; N is the refractive index; and $k_i=\alpha_ic/4\pi\nu_i$, the extinction coefficient above background, where α_i is the optical density per cm above background (absorption coefficient), and c is the velocity of light. Equation (4) is the same as that derived by Smakula because the absorption which is measured is generally that above background, so that changes in the base material and effects due to the tails of nearby bands, even if they are significant, are neglected. Equation (3) differs from Smakula's in that changes in R_b will not be neglected. Since $\Delta R=[6N/(N^2+2)^2]\Delta N$, then

$$\Delta N=\Delta N_b+\frac{(N^2+2)^2}{6N}\sum\frac{n_if_i}{3\pi}\frac{e^2}{m}\left[\frac{\nu_{0i}^2-\nu_i^2}{(\nu_{0i}^2-\nu_i^2)^2+p_i^2\nu_i^2}\right].\qquad(5)$$

The change in refractive index of the base material due to the introduction of vacancies ΔN_{bv} is easily computed in the irradiation case since the positive and negative ion vacancies must be introduced in equal numbers. The resulting fractional change in refractivity $\Delta R/R$ must therefore be, closely, the negative of the dilatation $\delta=\Delta V/V$ where V is the volume, and hence

$$\Delta N_{bv}=\frac{(N^2-1)(N^2+2)}{6N}\frac{\Delta R_v}{R_v}=-0.439\delta.$$

The fluoride ion contributes about 90% of the refractivity of the crystal, as can be seen by consulting a table of molar refractivities, and the hole, which is an F^0, would possess a refractivity about 10% less than that of the fluoride ion. Thus ΔN_b is about 10% larger (in the negative direction) than ΔN_{bv}.

It is readily shown that p_i is the peak width at half-maximum. Equation (4) is greatly simplified when $\nu_i=\nu_0$ and can then be solved to give

$$\frac{n_if_i}{3\pi}\frac{e^2}{m}\frac{(N^2+2)^2}{6N}=\frac{\alpha_{0i}cp_i}{4\pi},\qquad(6)$$

the constants required in Eq. (5). Thus ΔN can be calculated from the measured dilatation and the measured absorption bands without making any assumptions regarding the number of centers or their oscillator strengths. Further, Eq. (6) can be solved for n_if_i which gives the result known as "Smakula's formula." The dispersion can be obtained by differentiating Eq. (5). For each term of the sum there is obtained a term

$$\left(\frac{d\Delta N}{d\lambda}\right)_i=-\nu_i^3\frac{\alpha_{0i}p_i}{2\pi}\frac{(\nu_{0i}^2-\nu_i^2)-p_i^2\nu_{0i}^2}{[(\nu_{0i}^2-\nu_i^2)^2+p_i^2\nu_i^2]^2}.$$

For the term describing the base material it was assumed that

$$\left(\frac{d\Delta N}{d\lambda}\right)_b=\left(\frac{dN}{d\lambda}\right)_b\frac{\Delta N_b}{N}=\frac{200\times0.44\delta}{1.39},$$

the value of $(dN/d\lambda)_b$ being taken from Eq. (2) using $\lambda=600$ mμ and the value of ΔN_b calculated above. The change in dispersion thus calculated for the base material was more than two orders of magnitude smaller than the changes due to color centers and was therefore neglected.

It is convenient to express the results in terms of the F-peak absorption coefficient α and the ratio θ of the 450- to F-peak absorption coefficients. Then, if it is assumed that besides those effects taken into account in considering the changes in the base material, only the 450 and F bands contribute significantly, the number of centers and the changes calculated from the above equations are

$$\sum n_if_i=0.90\times10^{16}\alpha(1+0.29\theta),\qquad(7)$$

$$\Delta N=3.85\times10^{-7}\alpha(1+2.3\theta)-0.48\delta,\qquad(8)$$

$$\Delta\mathfrak{D}=2.44\times10^{-3}\alpha(1+10.7\theta).\qquad(9)$$

It has been thought that the 450 band represents about half an oscillator strength, additional absorption from this oscillator being hidden by the F band. Further, it has been believed that there are two negative-ion vacancies associated with this center. Then, the number of vacancy pairs v introduced into the crystal to make these centers should very closely be

$$v=0.90\times10^{16}\alpha(1+1.15\theta)f^{-1},$$

since the contribution of the 450 band is quite small. In the previous paper,[1] it was assumed that the volume of the crystal pre-empted by these vacant lattice sites was the same as if they were normally occupied; i.e., that the dilatation was given by an expression of the following kind (the numerical values may differ slightly here):

$$\delta = 1.5\times 10^{-7}\alpha(1+1.15\theta)f^{-1}, \qquad (10)$$

since there are 6×10^{22} lattice sites/cm^3. In this previous work α_{450} was measured, θ^{-1} was assumed to be 10, and f unity; and good agreement of the dilatation (determined from the birefringence assuming plane stress and strain) with that calculated was obtained at the end of the deuteron range, but not at the beginning where the observed dilatation was considerably, perhaps twice, as great as that calculated. From the present work it is evident that θ is not constant along the range and can indeed vary by the factor needed to make agreement along the whole range equally satisfactory. The approximate values of the local absorption coefficients could be estimated for some of the specimens described here from the data which are given; and the calculated dilatation agreed with the birefringence-measured dilatation, being apparently randomly greater or smaller within about 20%. The results of the direct measurement of the expansion are in similar agreement with that obtained from the birefringence. The accumulated errors of the various determinations are at least this great.

Some of the experimental ratios which were determined afford, in addition to the kind of comparison with theoretical estimates made above, a comparison of the relative effects of the F band and the 450 band. The displacement of the zero-order fringe as a result of the irradiation is $(2/\lambda)D\Delta N$ orders and the nearly-achromatic fringe is displaced a further $2D(d\Delta N/d\lambda) = 2D\Delta\mathfrak{D}$ orders. The ratio of the displacements is then

$$\frac{n_0}{n_0+n_a} = \frac{\Delta N}{\Delta N+\lambda\Delta\mathfrak{D}},$$

where λ is the wavelength at which the index of refraction is measured, 546 mμ. Then from Eqs. (8)–(10) there is obtained, if f is taken as unity,

$$\frac{n_0}{n_0+n_a} = \frac{3.85(1+2.3\theta)-0.72(1+1.15\theta)}{3.85(1+2.3\theta)-0.72(1+1.15\theta)+1.33(1+10.7\theta)},$$

which is quite insensitive to reasonable values for f. The function varies from 0.36 to 0.70 over the range θ^{-1} varying from 0 to ∞, and for the values of θ^{-1} of interest here, 7.5 to 25, it is in the range 0.57 to 0.65, thus justifying the use of 0.6 for all the specimens as determined above for specimen 949-III. For this specimen θ^{-1} had the value 13 and the function is thus 0.605. Thus the agreement seems to be excellent. Unfortunately, in the highly irradiated specimens there enters an experimental error in determining the nearly-achromatic fringe, and this is discussed below.

The other ratio determined experimentally was that of the dilatation to the birefringence as shown in Fig. 4. From Eqs. (8) and (10),

$$\frac{\delta}{\Delta N} = \frac{1.5(1+1.15\theta)f^{-1}}{3.85(1+2.3\theta)-0.72(1+1.15\theta)f^{-1}}.$$

If f is assumed unity, this function is 0.21 for $\theta^{-1}=0$ and increases as θ^{-1} increases, approaching 0.48 asymptotically as $\theta^{-1}\rightarrow\infty$; over the range of interest of θ it varies from 0.4 to 0.46. The experimental ratios for the electron-irradiated specimens shown in Fig. 4(b) are a little greater than $\frac{1}{2}$. This could be explained by an oscillator strength a little less than unity, but the experimental data cannot be considered precise enough to reach such a conclusion. No corrections have been made for variations in thickness for the ΔN data (about 2% in ΔN) nor for original birefringence in the specimen. The latter is especially important here because of the small effect measured. The appearance of the experimental ratio for each of the deuteron-irradiated specimens [Fig. 4(a)] shows the correct behavior qualitatively for the changing ratio θ, but the progressive change along the range is quantitatively greater than predicted. It is not to be explained by the bending of the specimens because correcting for bending would increase the birefringence at the beginning of the range relative to that at the end, i.e., in the wrong direction. The large birefringence measured for the deuteron-irradiated specimens probably made the original birefringence of little importance. However, the asymmetric shape of the extinction band would have introduced some error in locating it. More serious are the interferometric observations by which ΔN was determined. The large index of refraction gradients, especially toward the end of the range, distorted the wave fronts noticeably and altered the fringe pattern shapes somewhat. Further, it is to be noted that the experimental ratio $\delta/\Delta N$ at the beginning of the range increases for the successively longer irradiations in opposition to that predicted, the value of ΔN becoming too low in comparison to δ. For these specimens, the values of ΔN at the beginning of the range were obtained from the displacement of the nearly-achromatic fringe, in the use of which three difficulties appear. First, it is usually very difficult to estimate fractional order displacements of the nearly-achromatic fringe, and thus an error of half an order can always be present. Second, as the displacement of the nearly-achromatic fringe from the zero-order fringe increases, the nearly-achromatic fringe becomes successively less achromatic and more difficult to identify. Third, the fringe which is judged to be nearly achromatic is quite strongly dependent on the color value of the light employed, for it depends inversely on the third power of the appropriate mean wavelength, and thus the displacement observed becomes increasingly less than the calculated one as the irradiation is extended and absorption is introduced at the blue end of the spectrum. It is this effect which accounts for the low value of the refractive index change and of the dispersion change found experimentally for the gamma-ray-irradiated specimen 907, 30% smaller than that calculated from Eqs. (8) and (9).

It is apparent that the results are in good agreement with the modified dispersion theory introduced here, which assumes that the vacancies are generated during irradiation and are stabilized by the trapping of electrons to form color centers. The assumptions that the vacancies pre-empt a volume of the crystal about that of an equivalent number of occupied lattice sites and that the oscillator strength of the *F* centers is nearly unity, appear to be correct within the estimated precision of the work, about 20%. The results lend additional confirmation to the dispersion theory first introduced into the subject by Smakula[5] and modified somewhat here, and about which some question has recently been raised.[10] The advantage of also measuring the real part of the complex refractivity which was done here, is that it is sensitive to the whole spectrum of effects which take place in the crystal, whereas the imaginary part of the refractivity which has been used exclusively in the past investigations is sensitive only to particular oscillators under investigation. Although the relative precision obtained here was low, it is quite evident that there are no important contributions to the effects from oscillators outside of the range of the instruments used other than those that are summed by considering the refractivity changes in the "base material," nor from very broad bands of small absorption coefficient within the wavelength range of the instruments. Since unknown effects were being investigated, the experiments were not designed to obtain specific information, but rather to elucidate the phenomena. It should now be possible to design experiments which would give specific information about the relationship of the number of centers to the dilatation and the absorption, and to the refractivity changes in the rest of the crystal, the "base material."

ACKNOWLEDGMENTS

I am indebted to Charles J. Delbecq and Philip H. Yuster for assistance in these studies: for supplying lithium fluoride of selected quality, for assisting in the absorption measurements, and for advice and criticism in the interpretation of the results. The deuteron and electron irradiations were performed by Warren J. Ramler and his staff.

PHYSICAL REVIEW VOLUME 112, NUMBER 4 NOVEMBER 15, 1958

Specific Heat of Gallium and Zinc in the Normal and Superconducting States*†

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(Received June 19, 1958)

By using a He^3 cryostat the specific heat of gallium has been measured between 0.35°K and 4.3°K, and that of zinc between 0.42°K and 4.2°K. Measurements on Ga in the normal state indicate that the coefficient of the electronic specific heat, γ, is 0.601 millijoule/mole (°K)^2 while the Debye characteristic temperature θ at 0°K is 317°K. For Zn, $\gamma=0.640$ millijoule/mole (°K)^2; $\theta=309$°K. The electronic specific heat in the superconducting state, C_{es}, for both metals for T well below the transition temperature, T_c can be represented by the expression $C_{es}=a\gamma T_c e^{-bT_c/T}$. For Ga, $T_c=1.087$°K, $a=7.0$, and $b=1.35$. The zinc sample measured has a broad transition, T_c taken as 0.852°K. Also for Zn, $a=6.4$ and $b=1.27$. The magnetic threshold field curves are calculated from these specific heat results. The critical field at 0°K for Ga is 59.4 gauss and for Zn, 53.4 gauss.

In comparing these measurements with the calorimetric results of other superconductors a definite variation is noted in the parameters a, b, $(C_{es}-C_{en})/\gamma T_c$ at T_c, and $\gamma T_c^2/V_m H_0^2$. There appears to be a correlation between the magnitudes of these quantities and the transition temperature.

INTRODUCTION

In the past few years a great deal of evidence has been presented in support of the idea that in the superconducting state there exists an energy gap in the single electron energy spectrum. One of the first experiments of this kind was the measurement by Corak *et al.*[1] of the specific heat of vanadium. They found that in the temperature region $T<0.7T_c$ (T_c being the transition temperature), the electronic specific heat in the superconducting state could be represented by an equation of the form

$$C_{es}=a\gamma T_c e^{-bT_c/T}, \tag{1}$$

where γ is the coefficient of the electronic specific heat in the normal state. They also suggested that there may, indeed, be a law of corresponding states for superconductors in which case the constants a and b would be the same for all superconductors. For vanadium and

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* This work was supported in part by a Signal Corps contract.

† This paper is based partly on a thesis submitted by George M. Seidel to the Faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[1] Corak, Goodman, Satterthwaite, and Wexler, Phys. Rev. **96**, 1442 (1954); **102**, 656 (1956).