



FIG. 6. Comparison of calculated and observed relative modulus defect for crystal No. 6. Curve, calculated. Points, experimental.

may be roughly approximated over a substantial range of depths by an exponential. Hence we write

$$f(x) \cong Ae^{-\gamma x} \quad (13)$$

where  $\gamma$  is the effective absorption coefficient of X-rays in the crystal. Making this substitution in equation (10), the integration may be carried out to obtain

$$\frac{\Phi(t)}{\Phi_0} = \frac{1}{\gamma b} \left\{ \frac{1}{1 + Kt} - \frac{1}{1 + Kte^{-\gamma b}} + \ln \frac{1 + Kte^{-\gamma b}}{(1 + Kt)e^{-\gamma b}} \right\} \quad (14)$$

where  $K = A/Nn_0$ . The expression on the right-hand side of equation (14) has the property that, in a plot of  $\Phi(t)/\Phi_0$  vs.  $\log$  (irradiation time), the factor  $\gamma$  determines the shape of the curve while  $K$  only determines its position along the log-time axis. The best fit of equation (14) to the data of Fig. 5 is obtained with  $\gamma = 9.5 \text{ cm}^{-1}$ . Fig. 6 shows the theoretical expression fitted to data for crystal No. 6, using this value of  $\gamma$  and  $K = 1.76 \text{ min}^{-1}$ . Values of  $K$  for the other crystals are proportional to the values of  $C$  given in Table 4.

The value of  $\gamma$  obtained by means of this analysis agrees, within experimental error, with a rough value obtained from optical measurements on similarly irradiated crystals. It is also equal to the absorption coefficient of NaCl for X-rays of wavelength  $0.55 \text{ \AA}$ . This wavelength falls close to that for maximum intensity in the continuous spectrum of the X-rays used.

Assumption I may be expressed by the statement that  $\beta F$  centers are formed for each pinning point created by irradiation. Then, according to the assumptions of equations (9) and (13), the number of  $F$  centers generated per unit volume per unit time at

depth  $x$  is  $Be^{-\gamma x}$ , where  $B = \beta A$ . The quantity  $B$  may be obtained from optical data on the rate of formation of  $F$  centers at a given depth in a rock-salt crystal irradiated in the same way as the modulus specimens. From such data<sup>(6)</sup>  $B$  is found to be  $1.5 \times 10^{15} \text{ cm}^{-3} \text{ sec}^{-1}$ . The definition of  $K$  and equation (8a) provide two equations in  $N$  and  $n_0$ , which when solved for these quantities give

$$\left. \begin{aligned} N &= (B^2 \xi \Phi_0 / \beta^2 K^2)^{1/3} \\ l_0 &= n_0^{-1} = (B \xi K \Phi_0 / B)^{1/3} \end{aligned} \right\} \quad (15)$$

Since all the quantities on the right-hand sides of the above equations are known, except  $\beta$ , the quantities  $N\beta^{2/3}$  and  $l_0\beta^{-1/3}$  may be determined from the experimental results. Values for these quantities are displayed in the final columns of Table 4, calculated with  $\xi = 2.5$  (see Appendix).

Comparison of the values of  $N\beta^{2/3}$  and  $l_0\beta^{-1/3}$  presented in Table 4 for crystals Nos. 5 and 9 suggests that the annealing out of the modulus defect produced by cold-working results from a decrease in  $N$ , and that  $l_0$  remains about constant. This result is in contrast to the suggestion previously advanced,<sup>(17)</sup> according to which this recovery effect is the result of rearrangement of the dislocation network generated by deformation into a more stable configuration, i.e. that recovery results from a decrease in  $l$  rather than a decrease in  $N$ . Further experiments along these lines would be most desirable.

Values for  $\beta$ , the number of  $F$  centers per pinning point, which fall in the range from 1 to 100, would appear to be reasonable. For crystal No. 6 (deformed 4%)  $N$  values of  $3 \times 10^9$  and  $1 \times 10^8 \text{ cm}^{-2}$  and  $l_0$  values of 100 and 500 atomic distances correspond to  $\beta = 1$  and 100 respectively. A comparison of these results with Harper's estimates of dislocation densities

in lightly cold-worked iron,<sup>(19)</sup> favors values of  $\beta$  near unity; on the other hand, to obtain a reasonable value for  $N$  for the as-received crystal (No. 4, Table 4) would require a relatively high value for  $\beta$ .

Since Assumption II above has been ruled out, the results of the preceding analysis support the hypothesis already developed on the basis of optical data,<sup>(6)</sup> viz. that vacancies are not generated at dislocations during short-time X-irradiation, except in a layer of the specimen less than 0.01 cm thick adjacent to the irradiated surface (the region of "slow-type" coloring). This thin layer near the surface does not appreciably influence the observed modulus defect which derives from the entire volume of the crystal, as demonstrated in these experiments.

If vacancies which produce the pinning of dislocations during irradiation are not generated at dislocations, what then is their source? According to Frankl and to Seitz,<sup>(1)</sup> positive-ion vacancies, liberated from vacancy pairs (or larger aggregates) when the negative-ion vacancy of a pair becomes an  $F$  center, may migrate to the dislocation lines, where they may act as pinning points either individually or after condensation into clusters. It appears that the jump-frequency of positive-ion vacancies in NaCl at room temperature is great enough to allow vacancies liberated in this way to reach dislocations.\*

Since the above mechanism of dislocation pinning involves vacancy diffusion, no modulus change is to be expected when irradiation and modulus measurement are *both* conducted at low temperatures. If, as in the present experiments, a crystal is irradiated at low temperature and warmed up without first bleaching out the color centers, the usual modulus change may still be observed at room temperature. This is due to the fact that dissociation of vacancy pairs will have occurred during irradiation at the low temperature, leaving the positive-ion vacancies free to migrate to dislocations during the warm-up period. This explanation accounts for the results of the low-temperature experiments on crystals Nos. 19 and 21 (Table 3). Since there is no appreciable bleaching of  $F$  centers formed at 78°K or 180°K during illumination at the temperature of irradiation, it is no surprise that the same modulus change is obtained even when the specimens are illuminated before warm-up (crystals Nos. 20 and 22). Only in the case of illumination *during* slow warm-up (crystal No. 23) is the room-temperature modulus change substantially reduced. This result may be explained

if it is assumed that during warm-up the bleaching process takes place before the positive-ion vacancies become mobile. When an electron is released from a negative-ion vacancy by the action of light quanta, this vacancy regains its net charge and is then electrostatically attracted to the positive-ion vacancy with which it was originally associated. Thus, as soon as the specimen reaches the temperature range in which vacancy mobility begins, recombination will take place. The fact that there is a small change in modulus in crystal No. 23 shows that recombination is not complete, i.e. some vacancies escape and produce pinning. On the other hand, when warm-up is in the dark, there is no electrostatic attraction, so that positive-ion vacancies are free to migrate when the temperature becomes sufficiently high.

The decrease in damping due to irradiation seems to be due to the same cause as the increase in elastic modulus, i.e. to dislocation pinning. In view of the fact that substantial bleaching does not take place at liquid-nitrogen temperature, it is difficult to see why the damping was not suppressed in Frankl's experiment in which a specimen was first irradiated and illuminated at 78°K, then warmed to room temperature. Since Frankl illuminated his crystal with an ordinary incandescent lamp placed close to the specimen,<sup>(20)</sup> it is suggested that the light-source employed by Frankl warmed the crystal up to the range of temperatures where a substantial amount of bleaching could take place.

## 5. CONCLUSIONS

1. Pinning points on dislocations are created during X-irradiation of an alkali halide crystal at room temperature through the release of vacancies within the volume of the crystal and the migration of these vacancies to dislocations.

2. Relatively few pinning points are produced in a crystal irradiated at 78°K and slowly warmed up under strong bleaching illumination. Under these conditions vacancies of opposite sign, which were originally dissociated through the action of the radiation, may recombine.

3. The dislocation density calculated from curves of modulus vs. irradiation time is of the order of  $10^8$ – $10^9$  cm<sup>-2</sup> for a crystal deformed 4%; the corresponding mean length of free dislocation segment is of the order of 100 atom distances. Upon recovery at room temperature, there appears to be a substantial decrease in dislocation density.

4. The pinning of dislocations by vacancies is by no means restricted to ionic crystals. Recent experiments show that excess vacancies produced in metals by

\* Positive-ion vacancies have a significantly lower activation energy for migration than negative-ion vacancies in most alkali halides.<sup>(1)</sup>