

creased by about 20% at room temperature to give a value of 9.2×10^{10} dynes/cm². Nash and Smith⁹ by ultrasonic techniques determined the single-crystal stiffnesses of natural lithium at 78°K. From their values the elastic modulus for a polycrystalline aggregate can be calculated to be 18×10^{10} dynes/cm² by Voigt's analysis, and 7×10^{10} dynes/cm² by Reuss's analysis (see Hearmon¹⁰ or Huntington¹¹ for a description of

these analyses). At room temperature these two values would decrease to perhaps 15×10^{10} and 5.5×10^{10} dynes/cm², respectively, to bracket the values cited above for the present work (8.0×10^{10}) and for Bender's work (9.2×10^{10}).

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⁹ H. C. Nash and C. S. Smith, *Bull. Am. Phys. Soc.* **3**, 123 (1958).

¹⁰ R. F. S. Hearmon, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1956), Vol. 5, p. 323.

¹¹ H. B. Huntington, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, p. 213.

F-Center Growth Curves*

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It is shown that the increase in the density of *F* centers in KCl due to x-ray irradiation can be described kinetically by considering two independent groups of negative ion vacancies. One group is composed of vacancies in the lattice before irradiation, while the other is composed of vacancies generated during the irradiation. It is concluded from the difference in the electron capture cross sections for the two groups of vacancies and the intensity dependence of the rate of generation of new vacancies that the vacancies are generated at dislocations by a multiple ionization process.

AN investigation has been made of the growth curves of *F* centers in KCl at room temperature. It appears that the experimental data can be very well fitted by a theoretical curve based on the assumption that the vacancies involved in the rapid growth (initial portion) and those involved in the slow growth (later portion) may be treated independently and have different rate constants for the capture of electrons. The vacancies associated with the rapid growth are assumed to be in the lattice before irradiation, while the vacancies associated with the slow growth are assumed to be generated during the irradiation. In general we have

$$\begin{aligned} df_i/dt &= b(n - f_i), & df_o/dt &= c(at - f_o), \\ f_i &= f_o = 0 \text{ at } t=0, \end{aligned} \quad (1)$$

where f_i and f_o are the densities of *F* centers produced from initially present and from freshly generated vacancies, respectively; b and c are the corresponding rate parameters for the capture of electrons; n is the initial density of vacancies; and a is the rate constant for the generation of new vacancies. This leads to

$$f = f_i + f_o = n(1 - e^{-bt}) + at - (a/c)(1 - e^{-ct}). \quad (2)$$

The form of f is not changed if a bleaching term $-af$, which is important only at low intensities, is included in each of Eqs. (1).

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A set of KCl Harshaw crystals was irradiated simultaneously with 140 kev, 5 ma x-rays through not less than $\frac{1}{16}$ in. of Al to insure body coloration. The radiation flux was controlled within the limits of 1 to 100 by focal spot to sample distance. All growth curves showed a tendency to saturation for very high irradiations but only the portions given in Fig. 1 were taken into account. Using an IBM 650 computer the data were then fitted to Eq. (2) by the least squares method and the fit of the calculated curve to experimental points is very good as shown in Fig. 1 and is within 2%. The parameters a , b , c , and n were thus obtained as a function of x-ray intensity. The most notable result is an apparently quadratic dependence of the parameter a on the x-ray intensity, which suggests a two-step process for the generation of new vacancies. The value of n is essentially constant with intensity and of the order of 10^{16} per cc as expected. The parameter b is of the order of 2–3 hr⁻¹, increases with irradiation intensity, and is 10 to 20 times greater than c .

The striking difference between the two rate parameters b and c indicates that the two groups of negative ion vacancies differ considerably in their physical environments. If new vacancies are found in the vicinity of dislocations and the old vacancies are randomly distributed, several qualitative reasons can be proposed to account for the fact that b is much bigger than c . The basic assumption that the two groups

of vacancies can be treated independently is thus justified by their physical separation.

The probability of multiple ionization by a two-step process is very small unless the energy absorbed is delivered to a preferred volume of the crystal. We propose therefore that the new vacancies are created by multiple ionization of Cl ions, similarly to the Varley^{1,2} mechanism, but that the process takes place in the immediate vicinity of an edge dislocation. A rough estimate indicates that this assumption raises the value of a by a factor of about 10^{10} above the value for a random process and makes it comparable to the observed parameter. The high electrostatic potential surrounding a positive halogen ion, perhaps assisted by the strain field about the dislocation, makes it favorable for the ion to leave the lattice and join the incomplete plane at the dislocation. This is followed by a recapture of electrons and by a jump of metal ions, thus preserving the electrostatic neutrality of the dislocation. In this manner only vacancies and, in contrast to the normal Varley mechanism, no interstitials are formed. Also, in contrast to the usual Seitz³-Markham⁴ mechanism, the initially present jogs would play only a secondary role.

The process predicts high local concentrations of F centers in the wake of dislocations. This is compatible with the results of Ingham's⁵ studies of the annealing of conductivity changes in irradiated crystals. The different environments of the two groups of F centers, one localized and one distributed through the crystal, may explain the existence of the well-known fast and slow bleaching rates.

In considering various other explanations of growth curves like those in Fig. 1, it is important to note that the linear range at longer times predicted by Eq. (2) does not extrapolate to zero and, in fact, in some cases has a negative intercept for $t=0$. While a detailed analysis has not been made, similar types of growth curves have been observed in NaCl. Growth curves of

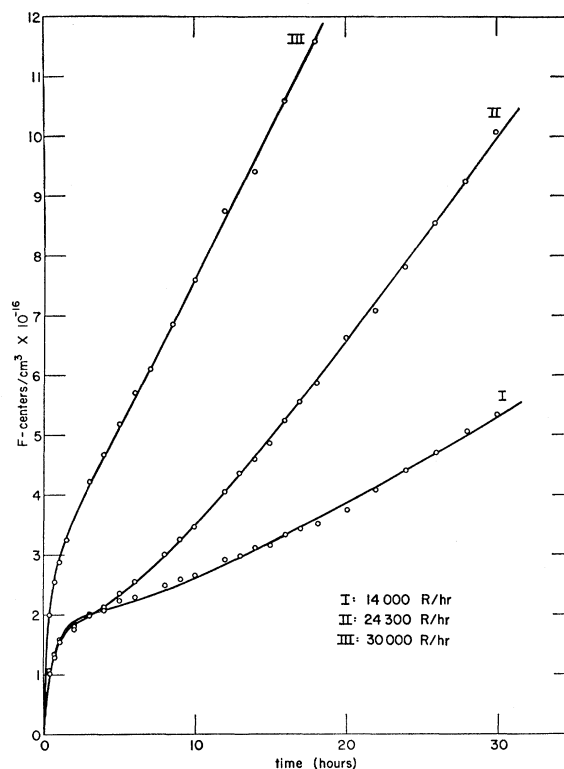


FIG. 1. F -center growth curves in KCl. The lines indicate the best fit of Eq. (2) to the data (circles).

the general sort shown in Fig. 1, i.e., containing an inflection point, were to our knowledge first observed by Mozer and Levy⁶ and more recently by Etzel and Allard.⁷

Experiments are now in progress to measure the parameters in Eq. (2) as a function of plastic deformation and heat treatment.

Note added in proof.—The quadratic dependence of the rate of vacancy formation on intensity of irradiation is analogous to similar dependence of the rate of photolytic decomposition of potassium azide [see J. G. N. Thomas and F. C. Tompkins, Proc. Roy. Soc. (London) **A209**, 550 (1951), and F. C. Tompkins and D. A. Young, Proc. Roy. Soc. (London) **A236**, 10 (1956)].

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