TRAPPING OF MOBILE INTERSTITIALS DURING IRRADIATION OF ALKALI HALIDES*

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The goal of our group at ORNL for a number of years has been to understand the processes that occur when an alkali halide is subjected to ionizing radiation. I shall describe today one small part of this effort. A number of groups have been working in this field, and it has been the large variety of experiments performed by these various groups that has made progress possible. Thus, the present state of understanding should be credited as much to other workers¹ as to us at Oak Ridge. In particular, there are two major conclusions drawn from previous work which I take as a starting point:

1. Ionizing radiation in alkali halide crystals produces primarily Frenkel defects in the anion sublattice. This fact was first suspected as a result of the analysis of the spin resonance of the H center² and was later confirmed by mechanical measurements³ and by precise x-ray lattice constant measurements.⁴

2. Interstitials are much more mobile than are vacancies. This information came chiefly from a variety of annealing experiments.⁵ Figure 1 is a summary of the temperatures at which interstitial and vacancy centers become mobile. This figure illustrates that there is a large range of temperatures for which only one member of the Frenkel pair, the interstitial, is mobile. Let us limit ourselves to that temperature range.

*A more detailed description of some of this work is published in Phys. Rev. B 5, 3259 (1972).

[†]Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corporation.

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Consider what happens when an alkali halide is irradiated: Energy is absorbed from the electron or photon beam at the rate $\dot{E}$. This energy, causing primarily electronic excitation, results in the formation of ionic displacement by a mechanism such as that proposed by Pooley⁶ and by Hersch.⁷ Let us define the efficiency of this series of steps as the primary production efficiency, α , that is

$$(dN_F/dt)_p = \alpha \dot{E} . \quad (1)$$

If either member of the defect pair is mobile, there will be recombination, and only those pairs for which recombination does not take place will be observed when a measurement is made at a later time. Above we limited this treatment to the case in which interstitials are mobile but vacancies are not. A newly produced, mobile interstitial may do one of two things: It may recombine with an F center, or it may be trapped by some species of trapping center. The probability that it NOT recombine is simply the ratio of trapping probability at all trapping sites to the sum of trapping and recombination probabilities, or

$$\sum_i p_i N_i / [\sum_i p_i N_i + p_F N_F] .$$

In this expression p_i is the trapping probability at a site of type i which exists in concentration N_i . The subscript F refers to F centers. It is now possible to write an equation for the F center concentration in terms of the energy absorbed, the primary production efficiency of Frenkel pairs, and the concentrations and trapping probabilities of interstitials traps and F centers:

$$dN_F/dt = \dot{E} \alpha \sum_i p_i N_i / [\sum_i p_i N_i + p_F N_F] . \quad (2)$$

The difficulty in applying this rate equation to experimental data of F-center concentration as a function of absorbed dose is that one doesn't know the various species of interstitial traps or how their concentrations and trapping probabilities vary with irradiation-dose. Those symbols under the sum have been the source of much of the difficulty in trying to understand quantitatively radiation defect production.

There is a method of solving this problem. Consider one particular type of interstitial trap: Let its concentration be N_A and let us assume that every time one of these centers traps an interstitial, it ceases to exist. The same reasoning, which was used above for F-center production, can be used to formulate a rate equation for the destruction of these traps:

$$-dN_A/dt = \dot{E} \alpha p_A N_A / [\sum_i p_i N_i + p_F N_F] . \quad (3)$$

Note that there is no sum term in the numerator. If, moreover, the F-center concentration and recombination probability is much greater than that of the traps, then the equation for the destruction rate of these traps can be approximated and integrated as follows:

$$\frac{-dN_A}{dt} \approx \dot{E} \alpha \frac{p_A}{p_F} \frac{N_A}{N_F} , \quad (4a)$$

$$N_A = N_{A(t=0)} \exp - [\alpha \frac{p_A}{p_F} \frac{\dot{E} t}{N_F}] . \quad (4b)$$

In order to apply Eq. 4b to experimental data, it is necessary to find a trap center whose concentration is easily measured--one which can be introduced prior to the experiment in which the parameters of Eq. 4 are to be measured. Moreover, throughout that experiment $p_F N_F$ must be greater than

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$\sum_i p_i N_i$. A number of investigators have observed that the F_2 center (two adjacent negative ion vacancies containing two electrons) can be produced only in the vicinity of room temperature and disappears upon low temperature irradiation. This defect is an excellent candidate for our trap center, A. It absorbs light in an easily measured absorption band so that N_A is easily determined. It has the same charge state with respect to the lattice as the F center and therefore, it should have a recombination probability of the same order of magnitude as that of the F center. Moreover, in a KCl sample irradiated so that $\sim 10^{18}$ F centers are produced, there will be approximately 10^{17} F_2 centers; thus on the one hand, the F_2 centers are a significant, if not the most significant interstitial traps and, on the other hand, their concentration is less than that of the F center, thereby establishing the validity of the approximation of Equations 4.

The experiments we have performed consisted of first pre-irradiating samples of KCl (pure or lead-doped) near room temperature until they contained a few times 10^{18} F centers/cm³ and a few times 10^{17} F_2 centers/cm³. The samples were then cooled and irradiated at various temperatures between 80°K and 250°K. These irradiations were interrupted repeatedly to measure the F- and F_2 -center concentrations.

Figure 2 shows how N_A decays with dose. It is clear from the data in the figure that the decay rate depends upon the initial F center concentration and that the curves deviate slightly from a pure exponential dose dependence. If, however, $\log N_A$ is plotted vs. $(\dot{E}t/N_F)$, then, as shown in the inset, the slopes are constant and independent of F-center concentration. Equation 4b shows that this is what one should expect from the model proposed and the assumptions made. The slope gives a value for $\alpha(p_A/p_F)$; all other symbols appearing in the equation are measured quantities.

Figure 3 shows decay curves for three samples doped with differing amounts of Pb^{++} . There is no great difference in the slope for the three samples. Compare this with F-center production curves shown in Figure 4. For these, lead doping causes a 5-fold increase in the F-center production rate. According to our model, the data illustrated in Figures 3 and 4 can be represented by Equations 4 and 3, respectively. If these equations are compared, it is clear that the only difference between dN_F/dt and $-dN_A/dt$ is in the numerator of the recombination probability expression. The obvious interpretation is that one of the terms under the sum of Equation 3 is $p_{\text{Pb}} N_{\text{Pb}}$. The fact that there is no effect of impurity on $-dN_A/dt$ shows not only that the numerator of the recombination probability ($p_A N_A$) in Equation 4 is unrelated to the lead concentration, but more important, that the primary production efficiency, α , is independent of impurity.

Figure 5 shows how the slopes of curves such as those of Figure 3 vary with temperature. Also shown is the temperature dependence of the F-center production rate. The most obvious conclusion to be drawn from the almost identical curve shapes is that the temperature dependence illustrated is related to the same factor in both Equations 2 and 3. Thus, recalling the assumption leading from Equation 3 to Equations 4, the temperature dependence of the data illustrated in this figure cannot be attributed to the recombination probability expression. Rather, it must be due to the factor αE which appears in both Equations 2 and 3.

It would be very difficult indeed to account for more than an order of magnitude change in the ratio p_A/p_F (Equations 4). However, the production efficiency, α , could very well increase with temperature, if, as one would expect, most of the Frenkel pairs are initially produced close enough to attract each other. Consider the potential energy of a Frenkel

pair as a function of separation distance. Such a curve has a shape similar to that shown in Figure 6. An interstitial in a well, as illustrated, can recombine thermally with the vacancy if it surmounts the energy barrier, E_r ; it can wander further from the vacancy if it surmounts the larger barrier, E_s . The ratio of probabilities of separation to recombination is $(\omega_s/\omega_r)\exp(E_r-E_s)/kT$, where ω_s and ω_r are entropy factors for which the chief contribution comes from the number of possible ways an interstitial can move away from (or towards) the vacancy. At relatively low temperatures the difference E_r-E_s is large enough to cause recombination to predominate. At high temperatures, however, $(E_r-E_s)/kT$ is smaller and the entropy factor predominates and hence separation is favored. Since there are a number of metastable energy wells and a variety of paths, and since, moreover, we do not know the distribution of separation distances with which the Frenkel pairs are produced, it is not possible to arrive at a relation between E_s-E_r and the activation energy deduced from the data of Figure 5. However, the slope of/more or less linear portion of the curve of Figure 5 corresponds to .07 eV, which is of the order of magnitude to be expected for the interaction energy between the members of a Frenkel pair.

Finally, let us extract some numbers from these data. As mentioned previously, the slopes of curves such as those of Figure 2 yield values for $\alpha(p_A/p_F)$. The ratio of p's can be approximated by the ratio of the geometric cross sections of F_2 and F centers, which is between 3/2 and 2. This means that the value for α (see Figure 5) rises to above 0.01 Frenkel pair per eV of absorbed energy near 250°K. In other experiments, performed with purer samples, the reversal at $1000/T = 4.5$, evident in the curves of Figure 5, did not occur until higher temperatures were reached, and the efficiency

climbed to 0.02 defects per eV. That is, it was possible to form a defect in the primary process with as little as 50 eV of absorbed energy.

A number of calculations¹⁰ have been made of the efficiency of defect production due to multiple ionization of a halide ion, either directly from the ionizing radiation or by an Auger process. The probability of such multiple ionization is of necessity lower than that for single ionization. Such a defect production mechanism requires a minimum of a few hundred eV of absorbed energy to produce a defect. Thus, the very high production efficiency deduced from these experiments is contrary to that expected, if double ionization is the principal mechanism for producing defects in alkali halides.

In summary we have been able to draw three conclusions from measurement of interstitial trapping by F-aggregate centers:

1. The impurity dependence of F-center production at liquid nitrogen temperature is due to trapping of interstitials by these impurities.
2. The rapid rise of the defect production efficiency with temperature is not related to interstitial trapping, but appears to be due to the variation of interaction potential with separation distance for interstitials and vacancies.
3. The defect production efficiency is sufficiently high to be inconsistent with multiple ionization mechanisms for defect production.

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FIGURE CAPTIONS

Figure 1. Temperature at which defects in alkali halides become mobile.

The lines connecting the point symbols have no significance aside from connecting all the points, respectively, for interstitial ions (far left), interstitial atoms or H centers (left border of shaded region), and negative ion vacancies or F^+ centers (right border of shaded region). The different point symbols are indicative of the different halide compounds. The shaded region indicates the large temperature range within which interstitial ions and atoms are mobile but vacancies are not.

Figure 2. Radiation-induced decrease of F-aggregate centers plotted vs. dose for two initial F-center concentrations. The same data are plotted vs. the ratio of (dose/F-center concentration) in the inset.

Figure 3. Aggregate-center-decay curves for KCl samples containing different amounts of impurity. The numbers on the curves refer to lead impurity in ppm. The data were obtained by irradiating the samples with 2 MeV electrons at 80°K.

Figure 4. F-center production curves for KCl samples containing different amounts of lead impurity. The data were obtained by irradiating at 80°K.

Figure 5. Rates of F-aggregate-center decay and F-center growth in KCl containing 100 ppm Pb^{++} plotted vs reciprocal temperature.

Figure 6. Proposed form of the potential between a vacancy and an interstitial in an alkali halide crystal.

ORNL-DWG 71-6530R

ORNL - DWG 73 - 5992