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Formation of Interstitials in Alkali Halides by Ionizing Radiation*

R. E. Howard and R. Smoluchowski
Carnegie Institute of Technology, Pittsburgh, Pennsylvania

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Recent experimental evidence seems to indicate that interstitials in alkali halides are formed by ionizing radiation. The validity of the so-called Varley mechanism depends on several factors such as the lifetime of the positive halogen ion, lattice geometry, etc. These are evaluated and found favorable.

It is well known that ionizing radiation like x-rays or β rays produce lattice defects in alkali halide crystals,[1] but, so far, the processes whereby defects are formed are not well understood. Seitz[2] and Markham[3] have proposed that defects are produced by the interaction of radiation with dislocation jog sites. Recently, however, experimental evidence has been obtained for the presence of interstitial halogen ions in irradiated alkali halides.[4,5] This lends support to Varley's suggestion made five years ago that defects might be produced through the multiple ionization of halogen ions.[6] Multiply ionized halogen ions would find themselves in a labile equilibrium position with a large electrostatic energy of the order of 5–10 ev and hence would tend to be displaced into energetically more favorable neighboring interstitial sites. Thus a halogen ion vacancy and a halogen ion interstitial would be created, which, by a subsequent capture of electrons, could transform into an F center and an interstitial halogen atom.

From very limited evidence on the electron bombardment of rare gases, Varley estimated that the cross section for double ionization is about one-tenth the cross section for single ionization. If one assumes that most double ionizations lead to the formation of an F center, then this ratio of cross sections is of the right order of magnitude to account for experimental observations on the rate of growth of F-center concentrations.

Whether or not a large number of defects can be actually produced by such a mechanism depends also on (1) the average lifetime of a doubly ionized center against recapture of an electron, (2) the ease with which the positive halogen ion can reach an interstitial site, and (3) the stability of an interstitial halogen, once it is formed, against return to its initial site. Calculations of Hatcher and Dienes[7] provide a partial answer to the last problem. They find that the energy of activation for the motion of a Cl interstitial atom from one interstitial site to another is large, of the order of 2 ev. This means that if a halogen ion were ejected via the Varley mechanism from a normal position to a next nearest interstitial site it could not easily return to the vacancy once it captured an electron, at least by a direct interstitial jump. The possibility of an interstitialcy mechanism accompanied by a charge transfer has not as yet been investigated. Three important observations can be made about the second problem at this stage: first, as far as the electrostatic energy alone is concerned, a positive halogen ion in its original position is on top of a potential hill and thus a small vibration may start it on its way down away from the initial lattice site. Further, the potential has a downward slope in all of the $\langle 111\rangle$ directions, even beyond the nearest interstitial sites. Finally, the positive halogen ion is smaller[8] than the opening between the three metallic ions which are its neighbors and which would obstruct the passage of a normal negative halogen ion in the $\langle 111\rangle$ direction. It seems thus that none of the original high energy of the ion is used up in reaching the first interstitial site which is in a $\langle 111\rangle$ direction, though not necessarily in the cube center. Whether it could also reach a next nearest interstitial site is more difficult to estimate, although the smallness of the ion and the availability of high energy make the situation qualitatively favorable. In view of the large difference in size of the normal halogen and metal ions the path of least activation energy connecting two neighboring interstitial sites lies almost certainly not in a straight $\langle 100\rangle$ direction.

The first problem, i.e., the question of the lifetime of a doubly ionized halogen against electron recapture will be considered here. We would expect that unless this were at least comparable to the period of a lattice vibration ($\sim 10^{-12}$ sec) the ionized center would recapture an electron before it could move to an interstitial site. We shall derive by very simple kinetic arguments an expression relating a lower limit of the capture time of a center to the density of conduction electrons present in the crystal during irradiation. From this we can show that below a critical density of conduction electrons the lifetime of a center is sufficiently long for the formation of an interstitial.

Suppose an initially uniform distribution of N doubly

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ionized halogen ions and n conduction electrons per unit volume. We assume that the density of the centers is sufficiently small for interactions between them to be neglected, and that the mobility of an electron is much larger than that of an ionized center. Since a doubly ionized halogen ion has an effective charge $+2e$, it exerts a Coulomb attraction on the surrounding electrons. The lifetime of a center is (a) the time that an electron takes to reach the center, plus (b) the time that an electron takes, once in the immediate neighborhood of a center, to be captured. A lower limit is obtained if we neglect the latter. The average time for an electron to reach a center may be estimated very simply. At the time $t=0$, the closest electron to a given center is about $[(4\pi/3)n]^{-3}$ cm away. This electron will be attracted toward the center with a force $2e^2/Kr^2$ and move toward it with a velocity $\mu E=2\mu e/Kr^2$. Here K is a dielectric constant and μ is the mobility of an electron. The time for the electron to reach the center is

$$\tau=\int_0^{\bar{r}}\frac{Kr^2}{2\mu e}dr=\frac{K}{8\pi e\mu n},$$

where $\bar{r}=[(4\pi/3)n]^{-3}$.

For NaCl at 200°K, the high-frequency dielectric constant $K\sim 2$, and $\mu=40$ cm^2/v-sec,[9] which gives $\tau\simeq 10^5/n$ sec. If $n\lesssim 10^{17}/\text{cm}^3$, then $\tau>10^{-12}$ sec, and it is thus very likely that a doubly ionized halogen has time to escape into an interstitial position. It should be possible to estimate n by measuring the electrical conductivity of a crystal during irradiation. Such measurements are now in progress.

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Spatial Diffusion of Spin Energy

A. G. Redfield
International Business Machines, Watson Laboratory at Columbia University, New York, New York

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A procedure is outlined for evaluating the spatial diffusion coefficient of magnetization of spins on a rigid lattice. The temporal recession of a spatially sinusoidally varying magnetization is analyzed, and is reduced to the problem of finding a function whose moments are known. An unambiguous value of diffusion coefficient can be obtained but the possibility of a complete lack of diffusion cannot be ruled out.

SOME years ago Bloembergen[1] pointed out that certain spin relaxation phenomena could be explained if it was assumed that energy can be spatially transported in the spin system of a rigid lattice via mutual spin flips of near neighbors, brought about by the dipole-dipole interaction. He was able to make a rough estimate of the diffusion coefficient, but efforts to improve on his theory have failed because of the inapplicability of perturbation theory to this problem.

In many cases it is difficult, if not impossible, to prove theoretically whether or not such spin diffusion actually occurs,[2] but if we assume that it does, then it is possible in principle to find a unique value for the diffusion coefficient D. We consider for simplicity the high-field case, for which total M_z is conserved, and for which the Hamiltonian can be suitably truncated.[3] It suffices to consider a single spatial Fourier component of the spin magnetization. At time $t=0$, we assume $M_z=M_0+C(0)\sin kx$. Such a nonuniform magnetization could be produced by adding a nonuniform field to the uniform high field for $t<0$ and switching this added field off at $t=0$. According to the usual diffusion equation, $C(t)$ will decay exponentially for $t>0$ with time constant $\tau^{-1}=Dk^2$. We *assume* that this is the case, and find that the consequences of this assumption are consistent with a certain rigorous quantum calculation provided k^{-1} is large compared to the interspin distance. The resulting diffusion coefficient D can be regarded as an upper limit and is probably the true one for those cases in which spin diffusion actually does occur.

We consider the time derivatives of $C(t)$ at $t=0$; these can be calculated assuming that the system is described for $t=0$ by the density matrix

$$\rho\simeq A(1-\mathcal{H}/kT+BU), \tag{1}$$

where

$$U=\textstyle\sum_j \sin kx_j S_{zj}. \tag{2}$$

Here A and B are suitable constants, $\mathcal{H}$ is the Hamiltonian[3] of the spin system for $t>0$, S_{zj} is the z component of spin angular momentum operator for the jth spin, and x_j is its x coordinate. The fact that (1) is written as a series rather than an exponential form implies that we are considering the high-temperature limit only.

The expectation value of U, $\text{Tr}U\rho(t)$, is proportional to $C(t)$; thus the derivatives of C at $t=0$ can be calcu-

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