

Theory of Defect Formation in Alkali Halides by Ionizing Radiation

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(Received October 25, 1961)

Assuming the creation at low temperatures by ionizing radiation of two halogen atoms at adjacent halide ion sites, we have estimated in a tight-binding approximation the time constants for the electronic and atomic relaxation processes. It is concluded that an appreciable fraction of the atoms may move before the positive holes further separate. The atomic motion is most probably to form two negative halogen molecule ions rather than a neutral halogen molecule. Each halogen molecule ion acquires momentum in the $[110]$ direction from interaction with the asymmetric crystalline field; and by "billiard ball" collisions concurrent with tunnelling of the positive hole, separation of the halide vacancy and the molecule ion may be achieved. A related mechanism of defect formation, but requiring only a single ionization, is considered.

I. INTRODUCTION

EVEN at low temperatures, ionizing radiation such as x rays or β rays produces lattice defects in alkali halide crystals. Both the well-known F center and the H center or halogen molecule ion at a halide site¹ are formed. The x-ray production of F centers at liquid helium temperatures is primarily dependent on the type of alkali halide rather than on the defect structure of a particular crystal.² An analysis³ of the paramagnetic resonance spectra of the F and H centers so formed reveals that they are separated from each other by at least several interatomic distances. The efficiency of defect formation is found to depend on the space available in the $[110]$ direction and in the most efficient cases corresponds to 1300 eV per F center formed.²

Possible mechanisms of formation of defects in alkali halide crystals under these conditions have been considered theoretically. The number of defects formed is in excess of those accountable by the momentum transferred directly to the atoms from the energetic electrons. Varley⁴ suggested that defects are formed electronically by multiple ionization of the halide ions. The halogen thereby becomes positively charged and is repelled by the electrostatic potential into an interstitial site. The lifetime of a doubly ionized halide ion limited by capture of a conduction electron has been shown to be adequate⁵; however, the lifetime limited by capture of an electron from an adjacent halogen has become somewhat controversial. Dexter⁶ treated the multiply ionized system on the basis of the band model and assumed that each of the two positive holes has the free electron mass. The time for separation of the holes by an interatomic distance was found to be 10^{-15} sec, which obviates the Varley mechanism. The application of the band model and the use of the free electron mass for the holes for

alkali halides have, however, been questioned by other investigators.⁷

More recently, Klick⁸ has suggested that the double ionization of a halide ion or single ionization of two adjacent halide ions leads to the formation of a neutral halogen molecule which might become localized at one halide site, thereby forming a vacancy and an interstitial. This mechanism was recognized to yield F and H centers close to each other, in conflict with experiment. Also, quite recently, Howard, Vosko, and Smoluchowski⁷ have proposed that because the bound state formed from a doubly ionized halide ion and a normal halide ion interacts with the repulsive $^3\Sigma_u^+$ state of the nonpolar halogen molecule at a suitable interatomic distance, two neutral halogen atoms with at least 3 eV of kinetic energy may be formed. The criticism of Dexter, if valid, applies to these mechanisms as well as to the original proposal of Varley.

It is, therefore, of interest to determine theoretically, in other than the band approximation, the time constant for separation of positive holes at the same site or adjacent halide sites; and, if there is time for atomic motion, to estimate which molecules or molecule ions form.

II. TIGHT-BINDING CALCULATIONS

We assume the creation at low temperatures by ionizing radiation of two halogen atoms at adjacent halide ion sites. These may be formed directly by the ionizing radiation or indirectly from a doubly ionized halide ion capturing an electron from an adjacent halide. We shall be concerned primarily with the time constant for each positive hole to move an additional interatomic distance in the $[110]$ direction compared to the time constants for the formation of stable molecules or molecular ions.

The time constant for the positive holes to move can be estimated in the tight binding approximation by considering each halogen atom and an adjacent halide ion as a negative molecule ion X_2^- and then calculating from the time-dependent wave functions for the sym-

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¹ W. Kanzig and T. O. Woodruff, *J. Phys. Chem. Solids* **9**, 70 (1958).

² H. Rabin and C. C. Klick, *Phys. Rev.* **117**, 1008 (1960).

³ W. Kanzig (private communication).

⁴ J. H. O. Varley, *J. Nuclear Energy* **1**, 130 (1954).

⁵ R. E. Howard and R. Smoluchowski, *Phys. Rev.* **116**, 314 (1959).

⁶ D. L. Dexter, *Phys. Rev.* **118**, 934 (1960).

⁷ R. E. Howard, S. Vosko, and R. Smoluchowski, *Phys. Rev.* **122**, 1406 (1961).

⁸ C. C. Klick, *Phys. Rev.* **120**, 760 (1960).

metric and antisymmetric states the time elapsed from when the electron is on one ion core to when it is on the other.⁹ Since the cores at the halide sites are relatively weakly interacting, the states of the X_2^- can be described in terms of $3p_0$ hole wave functions of X^0 in the same way that states of H_2^+ are described in terms of $1s$ electron wave functions of H^0 . Hartree-Fock functions for Cl^0 were determined using the program of Piper,¹⁰ and these were approximated by Slater atomic orbitals. The exponential coefficients and the weights for these orbitals are given in Table I. The overlap, Coulomb, and exchange integrals necessary for determining the energies of the states of Cl_2^- and Cl_2 were evaluated by means of the program of Corbato and Switendick.¹¹ These integrals are tabulated in Table II for both the interatomic distance in the KCl crystal and in the Cl_2 molecule. From these integrals for the Cl-Cl crystal lattice distance, the energy difference between antisymmetric and symmetric states, $W_A - W_S$, can be calculated in the Heitler-London approximation and is found to be 0.07 ev. A time constant for hole motion without lattice polarization, τ_h , equal to 3×10^{-14} sec is obtained from this energy.

The time constant for formation of a Cl_2 imperfection can be estimated from the Morse function for the free molecule.¹² Taking account of the variable acceleration from the interatomic distance of the crystal to that of the free molecule, we compute a time constant $\tau(Cl_2) = 3.5 \times 10^{-13}$ sec. A similar calculation was not possible for Cl_2^- since the Morse function for this molecule ion is not available. However, by theoretical methods using the integrals of Table II and calculating the van der Waals' and ion-induced dipole energies, the relative magnitudes of $\tau(Cl_2^-)$ and $\tau(Cl_2)$ were estimated. For the nuclei at the lattice sites, the interaction energy and its gradient are greater for the Cl_2^- than for the Cl_2 , and since during the atomic relaxation processes the nuclei spend the most time while near the lattice sites, we find that $\tau(Cl_2^-) < \tau(Cl_2)$. This inequality is enhanced by

TABLE I. Parameters used in approximating $3p$ Cl^0 Hartree-Fock wave function in the form, $R(r) = \sum_i b_i r^{n_i} e^{-\kappa_i r}$.

| Component, i | Power of r , n_i | Exponential coefficient, κ_i | Weight, b_i |
|-------------------|-------------------------|--|------------------|
| 1 | 2 | 4.2435 | 0.22845 |
| 2 | 2 | 8.4758 | 0.11869 |
| 3 | 2 | 22.314 | 0.000991933 |
| 4 | 3 | 3.0000 | -0.45236 |
| 5 | 3 | 1.7800 | -0.52566 |
| 6 | 3 | 1.2200 | -0.19978 |

⁹ H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1944).

¹⁰ W. W. Piper, Trans. Am. Inst. Elec. Engrs. **75**, 152 (1956).

¹¹ F. J. Corbato and A. C. Switendick, Quarterly Progress Report, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Oct. 15, 1959, pp. 70-85; Share Code MI DIAT (unpublished).

¹² G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, New York, 1950), p. 392.

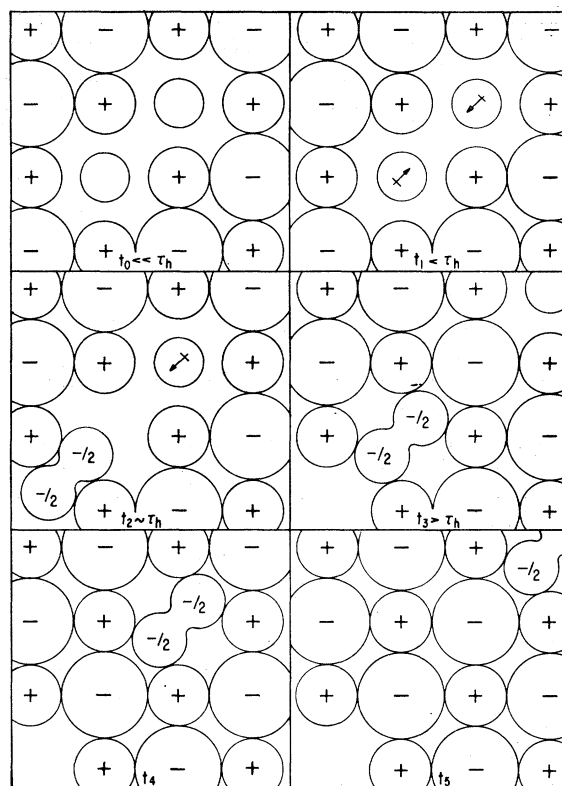


FIG. 1. Sequence of events illustrating dynamics of vacancy-interstitial formation and their separation.

the effect of the crystal forces as discussed in the next section. We conclude, therefore, that an appreciable fraction of the Cl atoms move before the positive holes further separate and the atomic motion is such as to most probably form Cl_2^- .

In addition to the net forces on the Cl atoms at adjacent Cl sites being such as to form two Cl_2^- rather than one Cl_2 , the thermodynamic stability is almost certainly in the same direction. The problem is similar to the problem of the relative stability of a given number of hydrogen atoms in a sea of protons. Because the binding energy $W(H_2^+) > W(H_2)/2$, the molecule ion rather than the neutral molecule is the more stable under these conditions.

III. DYNAMICS OF THE SEPARATION OF VACANCY AND INTERSTITIAL

In Fig. 1 the dynamics of the electronic and atomic relaxation processes following ionization of adjacent

TABLE II. Diatomic molecular integrals for Cl_2 internuclear separation and for Cl-Cl distance in KCl, from $3p_0$ Cl^0 wave functions of Table I.

| Separation, $R(\text{au})$ | Overlap, Δ | Resonance, K | Nuclear, J | Coulomb, J' | Exchange, K' |
|-------------------------------|----------------------|-------------------|-----------------|------------------|-------------------|
| 3.76 | 0.29817 | 0.14709 | 0.2944 | 0.3082 | 0.06872 |
| 8.39 | 0.01786 | 0.004591 | 0.1129 | 0.1159 | 0.0001229 |

halide ions are illustrated for KCl. The sizes of the ions and atoms are to scale. At time t_0 the Cl^0 occur in pairs occupying adjacent Cl^- sites. We shall consider two relaxation processes: separation of the two Cl^0 by positive hole migration according to the rate constant τ_h^{-1} , and relaxation of the atomic coordinates for each Cl^0 to form Cl_2^- with a nearest neighbor Cl^- according to the rate constant $\tau^{-1}(\text{Cl}_2^-)$. We shall neglect the less probable atomic process of forming Cl_2 . The Cl^0 will, therefore, be depleted according to the rate constant $[\tau_h^{-1} + \tau^{-1}(\text{Cl}_2^-)]$. The formation of Cl_2^- which does occur before pair separation, will take place, therefore, in a time of the order of $[\tau_h^{-1} + \tau^{-1}(\text{Cl}_2^-)]^{-1}$. Since $\tau(\text{Cl}_2^-) \gg \tau_h$, this time is of the order of magnitude but slightly shorter than τ_h .

At a time $t_1 < \tau_h$, only the high-frequency intra-atomic electronic modes will have relaxed and a dipole will have been induced on each Cl^0 by the noncentral Coulombic field arising from the other Cl^0 at the adjacent Cl^- site. Each Cl^0 is therefore attracted to its nearest Cl^- neighbor in the $[110]$ direction by an ion-induced dipole force. This force tends to separate the two Cl^0 and has been calculated to impart 0.04 eV of kinetic energy to each. The initial motion is nonadiabatic with respect to the lower frequency interatomic electronic modes.

By the time $t_2 \sim \tau_h$, the resonance and Coulomb interactions for the formation of Cl_2^- will have taken over and the two ion cores will approach each other adiabatically to form the stable molecule ion. The center of negative charge thus moves nearer the sites of the original two Cl^0 , thereby lowering the Coulombic energy. The additional displacement shown at time t_3 further lowers the Coulombic energy and creates a vacancy. This displacement in the field of the other Cl^0 imparts momentum to the Cl_2^- corresponding to 1.1 eV of kinetic energy. Concurrently, it is probable that the other Cl^0 will be displaced by positive hole migration as shown at time t_3 .

The kinetic energy acquired by the Cl_2^- in the field of the other Cl^0 combined with the energy of formation of the Cl_2^- is expected to lead to a series of "billiard ball" collisions of the ion cores concurrent with quantum-mechanical tunnelling of the positive hole, thereby separating the Cl_2^- interstitial from the Cl^- vacancy. Intermediate configurations are shown at t_4 and t_5 . It should be emphasized that only one in approximately ten of the original Cl^0 form Cl_2^- in the field of another Cl^0 . This field is necessary for the Cl_2^- to acquire the momentum required for its separation from the vacancy.

We shall now consider whether separated defects can be formed by a single ionization mechanism. A mechanism for defect formation dependent on a single ionization can be an order of magnitude less efficient than double ionization mechanisms because single ionizations by ionizing radiation are at least a factor of 10 more frequent. In the case of single ionization, the initial system involves only one Cl^0 at a Cl^- site. The Cl^0 is at a center of symmetry so that no net dipole is induced on it by the crystalline field. The formation of Cl_2^- proceeds adiabatically, and no momentum is acquired by the mechanism described for the double ionization mechanism. However, if we construct states of the system from linear combinations of one-hole wave functions on each Cl^- in the $[110]$ direction, we find antisymmetric states which tend to form atomic configurations which impart momentum to the Cl_2^- corresponding to kinetic energy of the order of $W(\text{Cl}_2^-)$. In addition, because the Cl^0 at the Cl^- site has orbital degeneracy, the Jahn-Teller effect can lower the symmetry and momentum is imparted to the Cl_2^- during its formation. Following either mechanism of imparting momentum to the Cl_2^- , the "billiard ball" collisions concurrent with hole tunnelling can then proceed as described for the double-ionization mechanism. There is some experimental evidence for a single-ionization mechanism for the production of H centers.¹³

IV. CONCLUSIONS

It is shown in the tight-binding approximation that the lifetime of positive holes on adjacent Cl^- sites in KCl is adequate for appreciable Cl^0 to undergo atomic displacements. These displacements are initiated by the field arising from the adjacent Cl^0 . This field imparts momentum to the Cl_2^- formed. It is proposed that this momentum leads to the separation of the Cl_2^- and the vacancy by means of "billiard ball" collisions concurrent with positive-hole tunnelling. In addition to this mechanism of defect formation, a single-ionization mechanism is considered.

ACKNOWLEDGMENTS

The author is indebted to D. S. Story for mathematical analyses and to J. D. Kingsley for many helpful discussions.

¹³ J. D. Kingsley, Ph.D. thesis, University of Illinois, 1960 (unpublished); J. A. Cape, Phys. Rev. **122**, 18 (1961).