

Mechanism of Point-Defect Formation in Ionic Crystals*

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The energetics of point-defect formation in ionic crystals based on $V_K + e$ recombination has been investigated in detail. A sequence of [110] replacement collisions involving a neutral halogen atom is energetically possible and leads to the formation of well-separated F and H centers. Zero-point energy vibrational and librational amplitudes may lead to defocusing of the early collisions and to the creation of nearby F and H centers from which subsequently F^+ centers (vacancies) and I centers (interstitial ions) can be formed. Direct formation of these charged centers by a replacement sequence is not possible.

Ionizing radiation produces vacancies and displaces ions¹ in ionic crystals (alkali halides), even near 4°K as long as the photon energy is higher than the band gap. Several mechanisms for this effect have been proposed over the years, but none of them has been entirely satisfactory either because they do not provide sufficient kinetic energy or because they lead to difficulties in accounting for the efficiency of the process. The present model combines two ideas: The first, proposed by Pooley,² is that the source of energy is the recombination of a self-trapped hole (V_K center) with an electron, and the second, proposed by Howard *et al.*,³ is that the interhalogen repulsion may lead to a replacement sequence involving a neutral halogen atom (rather than an ion) in a [110] direction. Each such replacement sequence results in the formation of well-separated F and H centers, as observed. If, on the other hand, the replacement sequence is short, then nearby F and H centers are formed which can transform into F^+ centers (vacancies) and I centers (interstitial ions) as shown below. The electrical field of the ion prevents the vacancy from capturing an electron,⁴ thus assuring the required stability of these centers.

This paper outlines results which were obtained using the standard so-called point-ion model in which several computational improvements have been made. The details of the calculations will be published elsewhere. The Gilbert and Wahl

potential for the Cl_2^- molecule-ion⁵ and the resonating-hole corrections used earlier in the study of the H center⁶ were employed in estimating the energies of other molecular configurations in which the presence of interactions other than those between ions was expected to be dominant. Results obtained for KCl, which is probably the most studied ionic crystal, concern (1) the structure and dynamics of a V_K center (Cl_2^- molecule-ion replacing two adjoining Cl^- ions), (2) the distribution of kinetic energy between the two Cl^- ions upon $V_K + e$ recombination, (3) the likelihood that the momenta of the halogen ions are large enough and close enough to a [110] direction to initiate a replacement collision, (4) the probability that a moving Cl^- ion loses its electron to the vacancy and forms an F center, (5) the mechanism and the activation energy of the replacement collisions in a [110] direction involving neutral Cl atoms which result in the formation of an H center (substitutional Cl_2^- molecule-ion), and (6) the probability that the moving Cl^- ion does not lose its electron to the vacancy (an F^+ center) but becomes a nearby interstitial (I center).

(1) Apart from its internal vibration which changes its length in the [110] direction, the Cl_2^- molecule-ion of the V_K center vibrates as a whole around its ideal position in the lattice and librates in the (001) and (110) planes. The three motions with respect to the lattice were found to have

wave numbers 400, 150, and 300 cm^{-1} , respectively, and in the range of temperatures of interest, the displacements are determined primarily by the zero-point energy rather than by the thermal excitation. The maximum displacement of the molecule from its ideal position is 0.15 Å while the maximum angle it forms with the [110] direction is around 5 degrees. Thus, about one third of the time the molecule is at an angle of 4 to 5 degrees and is displaced by 0.12 to 0.15 Å. As shown below, these displacements combined with the mean amplitudes of the surrounding K^+ ions can affect considerably the probability of starting a replacement collision sequence in the [110] direction upon recombination of the V_K center with an electron.

(2) The energy available from the V_K -center-electron recombination is about 9 eV for KCl. This energy consists of two parts: 6.4 eV is available from the radiationless hole-electron recombination² and about 2.6 eV from the potential energy of the two Cl^- ions after the Cl_2^- bond is broken. As indicated in (1), the Cl_2^- molecule-ion is likely to be off its ideal position when the recombination occurs and therefore the kinetic energy may well be imparted asymmetrically to the two Cl^- ions. This asymmetric distribution of the kinetic energy is essential to the mechanism for two reasons: (a) 4.5 eV is not quite sufficient to form the F and H centers (as discussed below), and (b) there is no evidence for the formation of two adjacent F centers which would occur if the energy were shared equally.

(3) The possibility of initiating a Cl^- replacement sequence was investigated using a dynamic Torrens-Chadderton procedure⁷ modified to take into account the polarization effects in a consistent point-ion treatment. Calculations show that it would require 12–15 eV of kinetic energy imparted to a Cl^- ion in the KCl lattice in a [110] direction to initiate a Cl^- collision sequence leading to the formation of a stable interstitial

Cl^- ion (I center) and a negative-ion vacancy (F^+ center). Clearly there is not enough energy available for this process.

(4) An alternative mechanism is provided by the possibility that the Cl^- ion moving in a [110] direction loses its electron and becomes neutral, and an F center is formed at the origin.^{3,8} The energetics of this event was investigated using a simple model of the F center in which the charge is distributed among the nearest K^+ and Cl^- ions. From the ionization energy of an F center (2.2 eV), the self-energy of a vacancy with the same displacements⁹ as the F center (5.1 eV), and the energy of an electron in the conduction band (−0.6 eV), we estimate that the energy of the F center relative to the perfect lattice is about 2.3 eV. Considering the fraction of the F -center charge that rests on the K^+ ions as an adjustable parameter, it was possible to satisfy the above energy requirement in a point-ion model with about 50% of the charge on the six nearest K^+ ions, in reasonable agreement with electron-nuclear double-resonance results.¹⁰ Using this model two cases were investigated. In the first an F center at (0, 0, 0) and an interstitial Cl^0 at (0.5, 0.5, 0) are formed, requiring 8.2 eV which is very high since additional energy has to be expended to move the Cl^0 into the next cell. This process appears therefore to be very unlikely if not impossible. The second case is similar to the first, but the Cl^0 atom joins a nearby Cl^- ion at (1, 1, 0) and forms immediately an H center.

Table I shows the energy requirements obtained in this calculation for several choices of charge distribution and of the position of the H center. These results indicate that the simultaneous formation of F and H centers is energetically possible. Once the H center has been produced by this mechanism it continues, with kinetic energy provided by the original Cl^- , as a replacement sequence along the [110] direction eventually forming stable separated F and H centers. Since

TABLE I. Energy requirements for defect production.

Position of Cl^-	Fraction of F -center charge on positive ions	Energy to put Cl^- at position (eV)	Energy to convert to H and F (eV)	Energy to form $H+F$ from V_K (eV)
(0.5, 0.5, 0)	0.6	5.0	2.0	7.0
	0.5	5.0	1.0	6.0
	0.4	5.0	−0.1	4.9
(0.55, 0.55, 0)	0.5	6.0	−1.0	5.0

both the F and H centers are neutral defects relative to the perfect lattice, there should be little attraction present, and since each of them separately gives rise to an expansion of the lattice they should tend to repel each other. The energetics of the H -center motion is discussed briefly below.

(5) From annealing experiments¹¹ the activation energy for the motion of an H center appears to be about 0.15 eV (i.e., the center becomes mobile at about 56°K in KCl). A theoretical estimate of this activation energy is as follows: The likely saddle-point configuration for the replacement motion of an H center along $[110]$ is a Cl_3^{-2} molecule-ion with its center at a face-centered position and spread out over two nearest-neighbor halogen sites of the normal lattice. An approximate model for such a molecule turns out to be a hole shared by all three halogens, the outer ones having about half a hole each. By adjusting slightly the charge sharing and the fraction of the electrical and repulsive interactions operative between the halogens, it is possible to obtain an activation energy of about 0.2 eV in reasonable agreement with experiments.

(6) It is known that F^+ and I centers are also formed by ionizing radiation, especially at low temperatures.^{12,13} Experimental evidence¹⁴ suggests strongly that these charged centers are not of primary origin, but are formed from existing F and H centers by the incident ionizing radiation or by the strong radiation emitted during electron-hole recombination. If the F and H centers are very near to each other, the necessary electron transfer may also occur directly by electron tunneling from the F center (or, in particular, from its long-lived excited $2p$ state) to the H center. In any case the initial F and H centers have to be close to each other to assure the stability of the ensuing F^+ and I centers.⁴ It follows that the replacement collision sequence has to be short which in turn implies that the direction of separation of the initial two Cl^- ions has to be noncollinear with $[110]$. This noncollinearity can occur in at least two ways: First, the condition for the propagation of a focused collision sequence¹⁵ along a row of atoms is $D < 4R$, where D is the spacing and R is the energy-dependent hard-sphere atomic radius, a condition which is not satisfied for the initial collision between the Cl^- ion originating in the V_K center and the near-

est Cl^- ion in the $[110]$ direction. Second, as discussed in (1), the zero point librational displacement of the nearest Cl^- ion (as well as of other positive and negative ions near the $[110]$ direction) may shorten the replacement sequence. Static calculations indicate that the energy of formation of a vacancy at $(0, 0, 0)$ and an interstitial Cl^- at $(1.5, 0.5, 0.5)$ is about 3 eV and that this configuration is stable against small perturbations (i.e., is metastable). A dynamic calculation shows that the available kinetic energy is not sufficient to produce F and I centers directly even if noncollinearity and zero-point amplitudes are taken into account. A detailed analysis of this process, however, requires lengthy computational investigations which are not yet completed.

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