

final numerical results for Sn have assumed the BCS value of  $E_g(0) = 3.53kT_c$ .

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## Varley Mechanism for Defect Formation in Alkali Halides\*

D. L. DEXTER

*University of Rochester, Rochester, New York*

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The Varley mechanism is examined, according to which Frenkel defects are produced in the halogen sublattice of alkali halides subsequent to multiple ionization of the halide ions. Arguments are presented to show that the lifetime of a positive halogen ion against recapture of electrons in orders of magnitude smaller than the ejection time of the halogen, and thus that the Varley mechanism is inoperative. The arguments may not be applicable for inner shells alone, but experimental evidence is adduced to eliminate this case.

THE so-called Varley mechanism<sup>1</sup> for the x-ray production of interstitial halogen, negative-ion vacancies, and *F* centers in alkali halide crystals has recently been receiving increasing attention. This proposed mechanism postulates the multiple ionization of a halide ion in its normal position surrounded by positive alkali ions, thus resulting in the presence of a *positive* halogen ion in a region of high-electrostatic (Madelung) potential, from which the halogen may be ejected under the influence of lattice vibration. This would give rise to the presence of interstitial halogen and negative-ion vacancies, which could easily trap electrons to become *F* centers. There are indications from experiments on multiple ionization in rare gases that if the Varley mechanism were the only one operative, a sizable fraction of multiple ionization events in alkali halides would have to result in the production of *F* centers, in order to be consistent with the efficiency of coloration at low temperatures.

Though no direct evidence has been adduced for this mechanism, it has increasingly been invoked because of its apparent consistency with low-temperature experiments for which most other mechanisms seem inappropriate.

Howard and Smoluchowski<sup>2</sup> have commented on some of the critical factors involved in this mechanism, one of which is the lifetime of the positive halogen ion against recapture of an electron from the conduction band, and they estimate this quantity in terms of the

concentration and mobility of free electrons. They conclude that if the electron concentration in the conduction band is  $\lesssim 10^{17} \text{ cm}^{-3}$ , the probability for recapture of one electron (sufficient, in the case of *double* ionization, to "turn off" the Varley mechanism) is less than  $10^{12} \text{ sec}^{-1}$ , the reciprocal of which, they suggest, is a reasonable characteristic time for the ejection of a positive halogen ion from its lattice site.

The above views are seen to be expressed in terms of a "hard billiard ball," or "very tight binding" approximation, as if the removed electrons can be localized on a particular lattice site. The purpose of this note is to point out that if this extreme point of view is relaxed, another and far more probable mechanism exists in many cases for rendering inoperative the Varley mechanism.

In the tight-binding approximation, when we allow for a nonzero overlap of neighboring halogen wave functions, so as to give a nonzero width to the valence band, we suspect that in a very short time an electron will be "sucked" by the strong Coulomb field to the postulated positive halogen ion from an adjacent halide ion, thus producing two adjacent halogen atoms. (This initial transition, which in itself is sufficient to render inoperative the Varley mechanism, could be followed by other jumps of electrons, further separating the neutral halogen atoms.) The initial jump time will of course depend on the extent of overlap, and if the latter is not zero, the former is not infinite. This point of view, while suggestive, does not easily allow a computation of the original jump time nor a description of what happens to the original large potential energy.

These questions are readily answered, at least in part, on going to an energy-band picture. In this description we would say that double ionization corre-

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<sup>1</sup> J. H. Varley, *Nature* **174**, 886 (1954); *J. Nuclear Energy* **1**, 130 (1954).

<sup>2</sup> R. E. Howard and R. Smoluchowski, *Phys. Rev.* **116**, 314 (1959).

sponds to the creation of two positive holes localized around the same halogen lattice site, perhaps in different filled bands. The Coulomb repulsion between the holes would be very large, and they would move off in opposite directions. At some later time, then, one could describe the crystal as containing two separated holes (or two separated neutral halogen atoms). The original large potential energy of interaction would be transformed to kinetic energy of the holes, eventually to be transformed into lattice vibrations or possibly additional electron-hole pairs.

If one takes this point of view, one can estimate the length of time for the holes to separate. The electric field felt by each hole is originally about  $10^8$  v/cm, if both charges are created in a region a few angstroms in linear extent. Thus if either hole has a mobility as large as  $1 \text{ cm}^2/\text{volt sec}$ , their relative velocity will become at least  $10^8$  cm/sec, and they will separate by an atomic spacing in a time less than  $10^{-15}$  sec. After they have separated, of course, there is no reason for an ion or atom to be ejected to an interstitial position; i.e., the Varley mechanism does not apply.

Actually, since the time we have computed by this method is less than the average electron scattering time, the use of a mobility is not correct. Accordingly, we give up this concept and compute the length of time required for free particles of the electronic mass to separate by an atomic spacing under their mutual repulsion. Again we find a separation time of  $10^{-15}$  sec.

In the event that one of the holes is in an inner shell where its effective mass might be very large, one would expect the "outer" hole to be repelled in a time of about the same magnitude, or perhaps a little greater because of the symmetry of the repulsive potential.

The case in which both holes exist in inner shells requires special attention. For example, consider a single ionization in the  $K$  shell of chlorine; following the event, the Auger transition probability is about  $8 \times 10^{14} \text{ sec}^{-1}$ , some seven times greater than the total radiative transition probability  $1.1 \times 10^{14} \text{ sec}^{-1}$ .<sup>3</sup> Thus there is a good likelihood that two holes will be produced in the same ion in higher bands. If at least one of them is in the valence band, it will move off in  $10^{-15}$  sec, and the Varley mechanism will not apply. On the other hand, in the evidently more likely event that both holes appear in the  $L$  levels, a strong polarization of the surroundings would occur, but a permanent neutralization of the doubly-ionized halogen ion would require the acquisition of an electron from a neighbor. This might be a process slow in comparison with  $10^{-12}$  sec, depending on radiative and Auger transition probabilities, and one might conclude that in this event ejection of the halogen could occur before its neutralization.

<sup>3</sup> D. L. Dexter and W. W. Beeman, Phys. Rev. **81**, 456 (1951).

Additional information on this point might be expected from the absolute low-temperature efficiency of coloration, but unfortunately most measurements have been made on the chlorides at x-ray energies large compared with the  $K$ -ionization limit. Thus any specificity on double, inner hole production has been obliterated.

Since the initial  $K$  ionization of a halogen atom (particularly a light one) represents the most efficient source of two inner holes, it appears that a low temperature measurement of the x-ray colorability of, say, LiCl at x-ray energies just below and just above the  $K$ -ionization limit for Cl, would give a definitive experimental answer about the applicability of the Varley mechanism for inner holes.

Less direct, but still convincing experimental evidence against the efficacy of this mechanism involving inner holes alone has recently been obtained.<sup>4,5</sup> Most pertinent to the present argument are (1) the observation of Rabin and Klick<sup>4</sup> that the x-ray coloration efficiency at He temperature is the same for KBr, KCl, and NaF, all with different halogen ions, suggesting that phenomena in inner shells are not important, (2) their observation in LiF that the energy required per  $F$  center is less than the  $K$ -ionization energy, which in F corresponds to the only original single event capable of creating double ionization in an inner shell (the  $2s$  band), and (3) the measurement of Wiegand and Smoluchowski<sup>5</sup> that the x-ray energy expended in LiF at  $N_2$  temperature is only 150 eV per  $F$  center. In terms of the Varley proposal, as discussed by the latter writers, this observation would be consistent with multiple ionization in the *outer shell alone*, if the probability for double ionization is indeed no less than one tenth that for single ionization. This high efficiency evidently precludes the possibility of *inner* ionizations contributing to the coloration mechanism in an important way.

In conclusion, we do not believe that the Varley mechanism as now understood can be applicable when outer holes are involved, because of their expected low masses, nor for inner holes alone, because of the high efficiency of coloration. The possibility that multiple ionization may be of importance is still an attractive one, particularly inasmuch as the experiments of Rabin and Klick demonstrate that x-ray coloration is indeed a bulk process at He temperatures.

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<sup>4</sup> H. Rabin and C. C. Klick, Phys. Rev. **117**, 1005 (1960).

<sup>5</sup> D. A. Wiegand and R. Smoluchowski, Phys. Rev. **116**, 1069 (1959).