

experimental determination of the structure, our attention was drawn to the work of Hirone and Adachi⁶ who considered the magnetic properties of the NiAs structures in the molecular-field approximation. They showed that triangular spin configurations were stable over certain regions of the molecular-field coefficients of first, second, and third nearest neighbors. Indeed, the ordering in CrSe corresponds to a generalized form of their ordering of the third kind if the spins are tilted out of the basal plane, and corresponds exactly with it if μ_{11} is zero.

The noncollinear spin arrangement would also be expected to influence the susceptibility below the Néel temperature and may conceivably account for the anomalous behavior.

It is perhaps interesting to examine the possible mag-

⁶ T. Hirone and K. Adachi, J. Phys. Soc. Japan **12**, 156 (1957).

netic space groups which allow the proposed model; these include both ordinary as well as Shubnikov groups.⁷ $P\bar{6}2m$ and $P\bar{6}2'm'$, where the primes indicate antielements, restrict the Cr moment to the basal plane perpendicular and parallel to the unit-cell edges, respectively. $P321$ and $P31m'$ correspond to the more general cases in which the Cr moment has both a perpendicular and parallel component with respect to the c axis. The last group $P3$ permits the moments to have an arbitrary direction, simply maintaining threefold symmetry. It is seen that an independent determination of the space group below the transition could enable one to restrict the possible structures.

⁷ N. V. Belov, N. N. Neronova, and T. S. Smirnova, Kristallografiya **2**, 315 (1957); G. Donnay, L. M. Corliss, J. D. H. Donnay, N. Elliott, and J. M. Hastings, Phys. Rev. **112**, 1917 (1958).

Mechanism for Production of Interstitials in KCl by X Rays at Low Temperatures

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Experimental evidence indicates that halogen vacancies and interstitials may be formed by x irradiation of KCl at low temperatures. The validity of a mechanism based on multiple ionization depends upon several factors; among them efficiency of ionization and the availability of sufficient kinetic energy to remove the interstitial from the immediate vicinity of the vacancy. These two conditions are considered in some detail and found to be satisfied.

1. INTRODUCTION

OF the several mechanisms that have been suggested for the production of defects in alkali halides by ionizing radiation, the Varley mechanism¹ (and its modifications) is the only one that (1) accounts for the production of interstitial halogen ions and (2) describes the defect production in terms of bulk properties of the crystal rather than in terms of dislocations or impurities.²⁻⁴ It is consistent therefore with evidence for the ex-

istence of interstitials^{5,6} and also with recent experiments that strongly suggest that production of F centers at liquid He temperature depends only on bulk properties.⁷ According to Varley, a certain number of halogen ions become multiply ionized by the absorbed radiation. These ions are positively charged with respect to the lattice. Hence, a small perturbation, either by lattice vibrations or by other means, may be sufficient to eject a multiply ionized halogen from a normal lattice site to an electrostatically more favorable interstitial position. The vacancy left behind would capture an electron to become an F center. One of the objections to this process is that the ejected ion is very close to the vacancy and prompt recombination is likely. Also, the

* A large part of the work here reported was done when the authors were at the Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

¹ J. H. O. Varley, Nature **174**, 886 (1954) and J. Nuclear Energy **1**, 130 (1954).

² F. Seitz, Revs. Modern Phys. **26**, 7 (1954).

³ J. H. Crawford, Jr. and C. M. Nelson, Phys. Rev. Letters **5**, 314 (1960).

⁴ P. V. Mitchell, D. A. Wiegand, and R. Smoluchowski, Phys. Rev. **121**, 484 (1961) and P. V. Mitchell, Ph.D. Thesis, Carnegie Institute of Technology (1960).

⁵ W. Kaenzig and T. O. Woodruff, Phys. Rev. **109**, 220 (1958), and private communication.

⁶ D. A. Wiegand and R. Smoluchowski, Phys. Rev. **110**, 991 (1958).

⁷ H. Rabin and C. C. Klick, Phys. Rev. **117**, 1005 (1960).

recent optical measurements on KCl by Konitzer and Markham⁸ and the spin resonance measurements by Känzig and Woodruff⁵ indicate that F centers and interstitials produced at liquid He temperature are at least several lattice spacings apart. One of the purposes of this paper is to suggest a modification of the Varley mechanism which avoids this difficulty. The point here emphasized is that the doubly ionized halogen is in a highly excited state in the crystal. The suggested mechanism shows how, through a de-excitation collision, this internal energy can be converted into kinetic energy of the ions, and thus result in a well-separated interstitial and vacancy pair.

In order for a Varley-type mechanism to operate, the following requirements must also be satisfied; (1) the efficiency of multiple ionization must be sufficiently large, (2) the multiply ionized halogen must exist for a sufficiently long time. The stability of a doubly ionized halogen against capture of a conduction electron has already been considered⁹ and it was shown that under reasonable circumstances the capture time is longer than 10^{-12} sec. In a recent article, however, Dexter¹⁰ has discussed the possibility of a multiply ionized halogen capturing an electron from neighboring ions. If the holes on the multiply ionized halogen are treated on a band model and if they are assigned an effective mass equal to the free electron mass, Dexter finds that the holes would separate a distance of 1 Å in a time of the order of 10^{-15} sec. Whether a band description is appropriate in treating the two localized missing electrons is, however, not completely obvious.¹¹ In the present paper, requirement (1) with particular reference to KCl at low temperatures, is considered first. On the basis of the Bohr-Bethe theory of the penetration of radiation through matter it is shown that the efficiency for the production of the multiple ionization of halogen ions is about twice as large as the efficiency of F -center production in KCl at liquid He temperature. Further, the process whereby the internal excitation produced by x rays is converted into kinetic energy of individual atoms which then produce the defects is described in some detail.

II. EFFICIENCY FOR PRODUCTION OF DOUBLY IONIZED HALOGENS

It is the purpose of this section to estimate the number of multiple ionizations that occur on Cl^- ions when a KCl crystal absorbs monochromatic x rays. The estimate is based on the assumption that each inner shell (K or L) ionization is followed by the ejection of at least one

additional electron. Such an Auger process¹² is known to be more probable than competing radiative processes when the ionized inner shell level is less than about 15 kev.^{13,14} For argon, in which the K electron has roughly the same binding energy as in Cl^- (~ 3 kev), the calculations of Dexter and Beeman¹⁵ together with the measurements of Parratt¹⁶ show that, following a K ionization, an Auger process rearrangement is an order of magnitude more probable than a radiative transition. The relative probability of the ejection of an M electron after an L ionization would be even more likely. Let us assume that photons, having an energy E much greater than the binding energy of the inner shell electrons, are absorbed by the KCl crystal. Direct ionizations are produced by these photons, but most of the total number of ionizations come about through collisions of the ejected electrons. Almost all (about 90%)¹⁷ of the direct ionizations occur in the K shell. Since the binding energies of K electrons in both Cl^- and K^+ are about 3 kev, the absorption of each photon produces approximately one electron with an energy of about $(E-3)$ kev. Each of these ionizations is in turn followed by an Auger ejection of one or more electrons of energy of the order of 1 kev. The additional ionizations produced by the fast electrons are considered below.

According to the Bohr-Bethe^{17,18} theory, the probability of the ionization of a particular bound electron (by interaction with a fast electron traversing the material) is roughly proportional to the reciprocal of its binding energy. The binding energies of K , L , and M electrons in Cl^- are approximately 3000, 200, and 20 ev, respectively. Thus the relative number of K , L , and M ionizations occurring on Cl^- ions (due to interaction with the fast secondary electrons) are p_K , p_L , and p_M , respectively, where

$$p_\alpha = (n_\alpha/I_\alpha)/(\sum n_\alpha/I_\alpha).$$

Here n_α is the number of electrons in the α shell ($\alpha = K, L, M$) and I_α its ionization potential. We find that $p_K \approx 0.1\%$, $p_L \approx 10\%$, and $p_M \approx 90\%$. Having estimated the relative number of ionizations occurring in each shell, the efficiencies of these ionizations (in units of electron volts absorbed per ionization) may be found from an estimate of the over-all efficiency of ionization. This may be obtained from data on so-called "fast-stage" coloration in KCl, whereby a vacancy already present in the crystal captures an electron produced

⁸ J. D. Konitzer and J. J. Markham, J. Chem. Phys. **32**, 843 (1960).

⁹ R. E. Howard and R. Smoluchowski, Phys. Rev. **116**, 314 (1959).

¹⁰ D. L. Dexter, Phys. Rev. **118**, 934 (1960).

¹¹ H. Froehlich, Proc. Phys. Soc. (London) **A74**, 643 (1959), and private communication.

¹² The possible importance of an Auger process was pointed out early by R. L. Platzman, in *Symposium on Radiobiology*, edited by J. Nickson (John Wiley & Sons, Inc., New York, 1952).

¹³ E. H. S. Burhop, *The Auger Effect* (Cambridge University Press, New York, 1952).

¹⁴ C. D. Broyles, D. A. Thomas, and S. K. Haynes, Phys. Rev. **89**, 715 (1953).

¹⁵ D. L. Dexter and W. W. Beeman, Phys. Rev. **81**, 456 (1951).

¹⁶ L. G. Parratt, Phys. Rev. **56**, 295 (1939).

¹⁷ H. A. Bethe and J. Ashkin, *Experimental Nuclear Physics*, edited by E. Segrè (John Wiley & Sons, Inc., New York, 1953), Vol. 1, p. 166.

¹⁸ N. Bohr, Kgl. Danske Videnskab. Selskab, Mat-fys. Medd. **18**, 8 (1948).

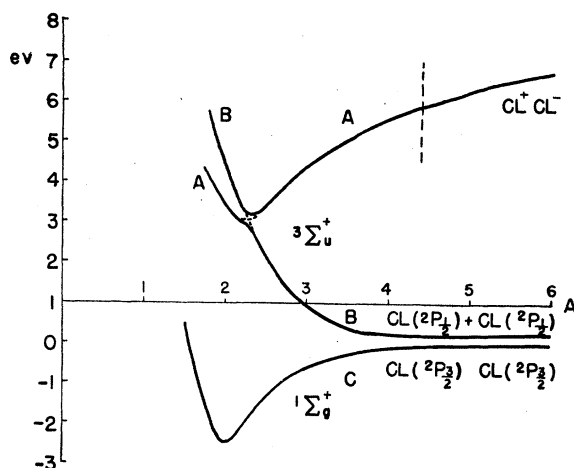


FIG. 1. Adiabatic potential curves for Cl_2 and for a Cl^+Cl^- configuration.

by the ionizing radiation. At this stage of coloration, about 30 eV are absorbed for each F center formed.^{4,7} This provides a lower limit on the efficiency of the production of an electron-hole pair. (An upper limit is, of course, the band-gap energy which is about 10 eV in KCl.) If one supposes that roughly half of the ionizations on a given shell occur on Cl^- ions, one obtains the following efficiencies for ionizations in the K , L , and M shells of Cl^- ions, respectively: $\eta_K = (1/2E + 10^{-3}/60)^{-1}$ eV per ionization, $\eta_L = 600$ eV per ionization and $\eta_M = 65$ eV per ionization. In our description, η_L and η_M are independent of the energy of the x rays while η_K decreases with increasing E . In particular, for $E = 20$ keV, it has the value $\eta_K = 25\,000$ eV per ionization. Thus at this energy, most of the multiple ionizations originate from ionization in the L shell with an efficiency of 1 multiple ionization per 600 eV. This is about twice as large as the efficiency of one F center per 1300 eV absorbed energy observed by Rabin and Klick⁷ in the production of F centers in KCl at 4°K.

III. EXCHANGE DE-EXCITATION

The electron affinity of Cl is 3.75 eV, while the ionization potential of Cl is 13.01 eV. Thus, if an electron is captured from a Cl^- into the ground state of Cl by the Cl^+ , approximately 9 eV of energy becomes available. During its formation, the Cl^+ ion receives recoil kinetic energy of the order of a few hundredths of an electron volt, and so is immediately displaced from its equilibrium position. Since the Cl^- and K^+ subtend approximately equal solid angles at the site of the Cl^+ , it is as likely that the Cl^+ will initially move towards a Cl^- as towards a K^+ .

In Fig. 1, we show the adiabatic potential curves for the interaction of two Cl atoms in various states. Curve

A represents the initial approach of the Cl^- and Cl^+ ions starting at the interionic distance indicated by the dashed vertical line. The distance at which the Cl^- and Cl^+ begin to repel one another can be estimated using the fact that the equilibrium distance of a KCl molecule is 2.8 Å, and noting that the ionic radius of Cl^+ is approximately 0.5 Å smaller than K^+ . The minimum would thus occur at about 2.2 Å which is just where curve A crosses the repulsive curve¹⁹ of $\text{Cl}+\text{Cl}$, i.e., the $3\Sigma_u^+$ state shown on curve B. Invoking the "no-crossing principle" gives the full curves of Fig. 1. The probability for a transition between curves of this type (i.e., the probability of "mutual neutralization") has been considered by various authors.²⁰⁻²³ It is very difficult to calculate this quantity accurately. It is possible to say, however, that since the separation of the two full curves at the crossover is small, the transition will be highly probable. (This condition may not, of course, be satisfied for other halides.) After making the transition to curve B, the two neutral chlorine atoms will move apart with at least 3 eV of kinetic energy. Recently Klick²⁴ has suggested that the system $\text{Cl}^- + \text{Cl}^+$ makes a transition to a bonding state shown in Fig. 1 as curve C. Such a transition is, however, extremely improbable due to the large separation between curves A and C.

The production of an interstitial chlorine sufficiently separated from a chlorine vacancy can now be envisaged as follows: the two chlorine atoms move apart along a [110] direction in a series of focussed collisions in analogy to the "dynamic crowdion" discussed by Vineyard.²⁵ Because of the large amount of energy available, it is probable that an electron will be transferred from the Cl^- to the Cl in such collisions, with the energy being carried off by the Cl. This results in the formation of an interstitial chlorine atom or H center, several lattice constants away from the vacancy. The vacancy and the other chlorine atom recapture electrons leading to a normal F center. This is the required final configuration.

ACKNOWLEDGMENTS

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¹⁹ R. K. Asundi and P. Venkateswarlu, *Indian J. Phys.* **21**, 101 (1947).

²⁰ L. D. Landau, *Physik Z. Sowjetunion*, **2**, 46 (1932).

²¹ C. Zener, *Proc. Roy. Soc. (London)* **A137**, 696 (1932).

²² D. R. Bates and H. S. W. Massey, *Phil. Trans. Roy. Soc. (London)* **A239**, 269 (1943).

²³ H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, New York, 1952).

²⁴ C. C. Klick, *Bull. Am. Phys. Soc.* **5**, 185 (1960).

²⁵ J. B. Gibson, A. N. Goland, M. Milgram, and G. H. Vineyard, *Phys. Rev.* **120**, 1229 (1960).