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Point Defect Formation in Alkali Halides*

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The essential features of defect formation in a perfect lattice by ionizing radiation are the multiple ionization and the mechanism of displacement of a halogen to an interstitial position far from the vacancy. In this connection the role of the Auger process, the possibility of *M*-center formation and the tunnelling process which affects the probability of an electron capture by a vacancy are discussed.

1. The Auger Process

The interaction of x-ray photons with alkali halides to produce radiation damage detectable as color centers necessarily involves an initial ionization process since the photon itself is unable to produce the direct displacement of lattice ions. For the *F*-center it is a negative ion that has to be displaced from its lattice site, the negative ion vacancy appearing in the absorption spectrum of the material either as the α-band or as the *F*-band, depending on whether or not it is occupied by an electron.

There is evidence that at least two mechanisms have to be considered for the formation of the negative ion vacancies. One, suggested by Seitz[1)] involves the formation of these vacancies at dislocations and another due to Varley,[2)] suggests a mechanism whereby point defects may be formed in the perfect lattice by a process involving multiple ionization of a negative ion.

Experimental data seem to be available to support both mechanisms: Bauer and Gordon,[3)] investigating the pinning of dislocations during x-irradiation by ultrasonic attenuation techniques, found that the pinning rate was independent of temperature (in contradistinction to their data on copper) and concluded that no diffusion is necessary in the pinning process. This tends to support the Seitz concept of defect formation at the dislocations by the irradiation. Perhaps the most compelling evidence for a Varley type mechanism is the unambiguous identification of interstitial chlorines as *H*-centers by Känzig[4)] and the observation by Rabin and Klick[5)] that the rate of *F*-center formation at liquid helium temperatures is independent of the defect history or purity of the material.

Once the need for a Varley type mechanism is established it is necessary to provide a method whereby double ionization may take place and to show how this leads to the displacement of the doubly ionized ion at low temperatures into an interstitial position sufficiently distant from the vacancy. Howard, Vosko and Smoluchowski[6)] have suggested that in KCl the double ionization occurs by means of an Auger type process, the x-ray photon removing an electron from the *K* shell of chlorine, giving rise to a high energy photoelectron. A transition of an electron from the *L* to the *K* shell then takes place, followed by the ejection of an additional photoelectron from the *L* shell by an internal conversion process. By considering the nature of the interaction between the Cl^+ so formed and one of the neighboring Cl^- ions, these authors have shown that a displacement of a Cl° in a preferred [110] direction may take place. A series of replacement type collisions may result in a considerable separation between the vacancy and the interstitial atom, *i.e.* the *H*-center, as required by experiment. The subsequent capture of an electron by the vacancy yields an *F*-center.

Since this argument depends upon an initial ionization process in the *K* shell of the Cl^-, or at least in the *L* shell, it was decided[7)] to test the mechanism by observing the radiation damage produced by x-ray photons having energies in the vicinity of the *K* absorption edge of chlorine (2.825 kv). Following a *K*-ionization, an Auger process rearrangement in chlorine is about nine times more probable

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than a radiative one. At the short wave length vicinity of the *K* limit, about 80% of the incident photons are expected to give at least double ionization. Initial experiments were conducted using white radiation from a copper target x-ray tube, the peak voltage on the tube being adjusted to give rise to x-ray photons having energies below (2.70 kev) or energies greater (3.3 kev) than the K ionization energy.

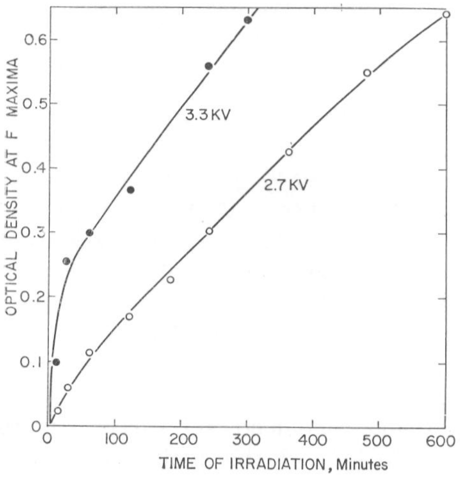

Fig. 1. *F*-band coloration in KCl produced by 2.7 kv and 3.3 kv x-rays (*K*-ionization potential of chlorine 2.825 kv).

Curves (Fig. 1) showing the rate at which *F*-centers were formed at liquid nitrogen temperature were taken for both energies of incident x-ray photons. The curve for the 2.70 kv photons was first followed, the crystal was then thermally bleached, cooled to nitrogen temperature again and the growth curve for 3.3 kv photons taken. It is apparent that the rate of color center formation is higher using photons of the higher energy. Measurements with a Bendix photon detector indicate that the difference cannot be attributed to an enhanced photon flux at the higher energy, with the proviso that the intensity dependence of the rate of formation of centers is not completely understood and the change in the absorption coefficient by an order of magnitude may alter the above conclusion if some highly nonlinear intensity dependence were present. Since the thermal history of the crystal, especially after the initial irradiation, might be expected to influence the rate of color center formation, another series of runs was made at liquid nitrogen temperature using alternate periods of irradiation with photons of 2.7 and 3.3 kv on the same crystal. The form of the data so obtained is shown in Fig. 2. Again the rate of *F*-center formation is higher using the high energy photons than when the low energy photons are employed. In the early part of the growth curves the 'zig-zags' are not apparent, this being attributed to the usual filling of initial vacancies in the crystal at this stage of the irradiation, rather than the production of new vacancies. There are many free electrons available at both irradiation voltages.

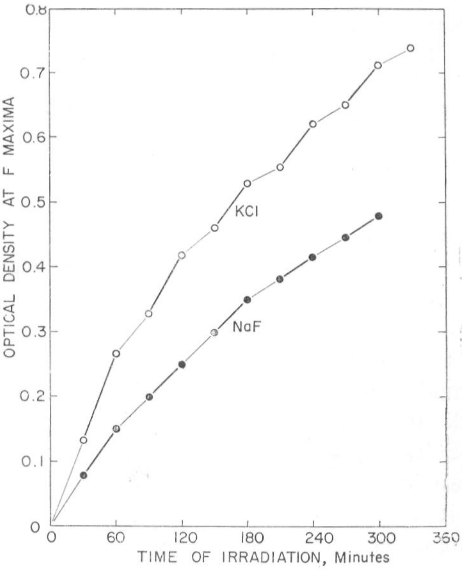

Fig. 2. *F*-band coloration in KCl and NaF produced by alternate irradiations of 30 minutes with 2.8 kv (thin line) and 3.3 kv (thick line) x-rays.

Due to the broad spectral distribution of the white radiation obtained from the x-ray tube for both 2.7 and 3.3 kv excitation potentials, a quantitative interpretation of the above data is difficult. However, assuming that the generation mechanism depends linearly on x-ray intensity and combining these results with photon counts made with the Bendix detector it follows that some 50% of the *F*-centers produced during the high energy irradiation could have resulted from a process of the type indicated by Howard, Vosko and Smoluchowski. The same effect appears even more strongly in recent measurements obtained using a curved crystal monochromator: On the short wavelength side of the spectrum the *F*-coloration is much stronger than on the other side of the chlorine absorption edge.

An important consequence of this mechanism is that it would predict large differences in the behavior of various alkali halides. For instance, in fluorides the *L* shell of the halogen forms partly the broad valence band thus the probability of an Auger transition will be reduced as compared to chlorides although on the other hand the probability of a direct multiple ionization may be higher. Similarly in bromides and iodides many additional Auger transitions are possible although the probability of a particular transition decreases with increasing atomic number. Another effect which may influence the colorability is the range of the photoelectrons as affected by the atomic numbers of metal and halogen ions. In the heavier alkali halides there would be a tendency to produce defects in small clusters while in the lighter ones a greater dispersion would be noted. This may have important consequences as pointed out below in section 3.

2. *M*-Center Formation

Another essential feature of the mechanism here discussed is that the energy of ionization and of attraction between a positive and negative halogen ion is transformed into repulsion between two adjoining halogen atoms. For KCl this energy is about 9 ev. If the energy required to displace both of these atoms were less than the energy available, then in principle two adjoining halogen vacancies might be created simultaneously. One might expect then that all these events would lead directly to the formation of *M*-centers by a capture of two electrons at low temperatures, *i.e.* without diffusion. Events in which the kinetic energy was acquired mostly by one atom would lead to single vacancies and to individual *F*-centers. A random distribution of such *F*-centers would in turn yield *M*-centers in the usual manner. The essential difference between the two mechanisms of *M*-center formation is that in the first the *M*-center concentration would be proportional to the concentration of *F*-centers while in the second it would be proportional to its square.

So far all observations indicate that the latter is the case. At low temperatures the *M*-centers are formed as a result of a random probability that an *F*-center is created next to an already existing *F*-center. It is thus interesting to inquire why the linear part does not appear. The first and most obvious possibility is that double vacancies do not form either because the available energy is not sufficient to displace two halogen atoms simultaneously or because the energy is so unequally divided that only one of the atoms can be displaced. At present there are no data to evaluate the minimum energy for such a displacement. On the other hand, a simple geometrical consideration of the atomic and ionic radii and of the available space shows that the originally multiply ionized halogen will probably carry away more energy than its partner.

Another and probably deciding factor why the double vacancies, if at all formed, do not become *M*-centers is the known instability of the *2p*-state of an *F*-center in an electric field discussed further below. The electric field of one of the two vacancies will prevent the other one from capturing an electron. Clearly this difficulty does not arise when a vacancy is formed next to an already existing *F*-center. It appears thus that the formation of double vacancies could show up only as an additional change of crystal density or of lattice parameter above and beyond that which can be accounted for by alpha and *F*-centers. This may not be measurable with sufficient precision at the present time.

3. The Effect of Internal Fields

Lüty[8] has stressed that the formation and stability of an α-band may be related to the instability of the *2p*-state of an *F*-center if it is in a sufficiently high electric field. In order to see whether the fields are of the right magnitude a calculation has been made of the rate of tunnelling out of the *2p*-state in a uniform external field ε. It appears that the logarithm of the rate of escape of electrons from the center is a linear function of $F(k)d^{-1}E^{-1/2}$ where d is the dielectric constant, E is the positive binding energy of the electron, k is the ratio of the classical turning points for an electron in the combined coulomb and external fields (in parabolic coordinates) and $F(x)$ is a rather complicated numerical function. For a given decay time τ and given d and E one calculates F and thus k. The latter then gives the required applied field from the relation

$$\varepsilon=\frac{2kE^2d}{(1+k)^2}\,.$$

The results, calculated for $d=1$, are shown in Fig. 3 for $\tau=10^{-3}$ and 10^{-8} sec. It is easily seen that for a given applied field the decay rate is a rapidly varying function of the binding energy E. This poses some difficulty in assessing the quantitative validity of the theory because the value of E is only poorly known. Nevertheless the order of magnitude of ε is that used by Lüty in his experiments.

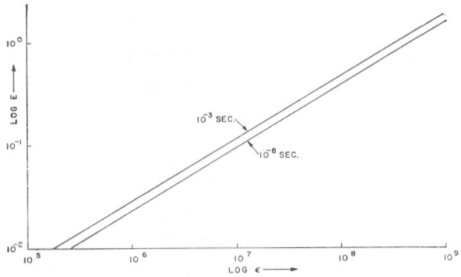

Fig. 3. Relation between the lifetime of an electron in the excited state of an F-center, its binding energy (in atomic units) and the applied field (in volts per cm). Dielectric constant taken as unity.

The binding energy E which appears in this calculation is the difference between the *2p*-state of the F-center, with lattice adjusted to this state, and the conduction band also adjusted to the *2p*-state. The available experimental thermal dissociation energies actually correspond to the same lower state but with the conduction band adjusted to an electron missing from the center. The difference between these two energies is difficult to estimate. For illustration some specific results are as follows: KCl, $d=2.13$, $E=0.1$ ev, $\varepsilon=5.3\times10^4$V/cm, $\tau=10^{-5}$ sec; NaCl, $d=2.25$, $E=0.15$ ev, $\varepsilon=9.4\times10^4$V/cm, $\tau=10^{-5}$sec. The sensitivity of the value of ε on E would make it reasonable to reverse the procedure and to try to estimate the binding energy from the experimental values of the required field.

We have also considered the internal electric field which can be provided either by interstitial ions such as V_1-centers, according to Seitz' model,⁹⁾ or by nearby empty vacancies (positive or negative) or, finally, by a charged dislocation. The proximity of other vacancies will be particularly important when the defects are formed in clusters as mentioned above. The charge at dislocations will obviously play a significant role if the point defects are generated at dislocations. In this case a freshly formed negative ion vacancy would remain empty (*i.e.* an α-center) until it either diffused away from the dislocation or until the dislocation climbed away through subsequent defect generation. This would lead to a delay in the onset of F-center formation upon irradiation and to a temperature dependence. An analysis of the data¹⁰⁾ shows that the available growth curves are not sufficiently accurate to make a positive identification of this effect.

The authors are indebted to Professor S. Mascarenhas for interesting comments on various problems discussed in this paper.

References

1 F. Seitz: Phys. Rev. **80** (1950) 239.
2 J. H. O. Varley: Nature (London) **174** (1954) 886; J. Nucl. Energy **1** (1954) 130.
3 C. Bauer and R. Gordon: J. Appl. Phys. **33** (1962) 672.
4 M. H. Cohen, W. Känzig and T. O. Woodruff: Phys. Rev. **108** (1957) 1096; J. Phys. Chem. Solids **9** (1958) 70.
5 H. Rabin and C. Klick: Phys. Rev. **117** (1960) 1005.
6 R. E. Howard, S. Vosko and R. Smoluchowski: Phys. Rev. **122** (1961) 1406.
7 J. Sharma and R. Smoluchowski: Bull. Amer. Phys. Soc. **7** (1962) 178.
8 H. Bauser and F. Lüty: Phys. Status Solidi **1** (1961) 608; F. Lüty: Z. Physik **160** (1960) 1.
9 F. Seitz: Phys. Rev. Letters **7** (1961) 282.
10 P. V. Mitchell, D. A. Wiegand and R. Smoluchowski: Phys. Rev. **121** (1961) 484.

DISCUSSION

Bragg, R. H.: I think your use of monochromatic x-rays is a significant step forward in studying the defect formation mechanisms. Did you say that the softer x-rays penetrate farther into the crystals?

Smoluchowski, R.: The longer wave length x-rays are not absorbed by *K*-shell, thus penetrate deeper.

Klick, C. C.: In the normal case of x-raying with tubes with window, x-rays below 4 kev are absorbed by the windows. In this case Auger processes would arise from energetic electrons rather than from x-rays as in the experiments you have been describing. Is it possible to go from the x-ray case to the electron case in a simple way so as to be able to assess the x-ray effects in the more usual experiments?

Smoluchowski, R.: This is a very important point and some estimates were made in our paper (Howard, Vosko and Smoluchowski). I do feel, however, that a careful study of the voltage dependence should be made.

Klick, C. C.: The depth of the *2p*-level of the *F*-center below the conduction band for optical transitions may possibly be estimated from the low temperature photoconductivity experiments. Both the *F* and *K* transitions are not photoconductive, while *L* transitions are. Since the *K* band is separated from the *F*-band by about 0.5 ev, the *2p*-level should be at least far below the conduction band.

Smoluchowski, R.: I am afraid this will not do since in these transitions the electrons are not always in the *2p*-state and thus the lattice changes its relaxation. What we need is the *2p*-conduction band distance while the electrons are in the *2p*-state.

Pick, H.: What do you think of the number of color centers produced by one x-ray quantum?

Smoluchowski, R.: Unfortunately I do not have experimental numbers at hand. Theoretically I could expect that in chlorides in which the Auger process has very high probability, near the *K*-edge (short wave length) the number of vacancies per quantum will be close to unity. At higher voltages this is entirely overshadowed by ionization due to photoelectrons and there the number should be much higher.

Howard, R.: I wonder if you might comment on Professor Lazarus' results on the pressure dependence of *F*-center formation, particularly the difference between the behavior of KC1 and KBr.

Smoluchowski, R.: I feel that there should be a separable Klick-Rabin curve for bromides, chlorides, etc. The Varley mechanism is very sensitive to the nature of the halogens. Perhaps the bromide curve intersects the chloride curve near the experimental point for KBr.

Young, F.W.: Would you comment on the conditions for which you would expect the Seitz mechanism for the formation of *F*-centers to be possible?

Smoluchowski, R.: I feel that the main role of dislocations is to produce sites on which ionization may produce vacancies with less expenditure of energy than in a perfect lattice. At higher temperatures when certain degree of mobility of negative ion vacancies is present the ionization process at or near dislocations may be particularly efficient. This has been discussed in some detail in a paper by Mitchell, Wiegand and myself.