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Investigations of Color Centers in Alkali Halides at Oak Ridge National Laboratory: Structure Sensitivity of Color Center Production in γ-Irradiated KCl*

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Investigations of the structure sensitivity of color center formation in γ-irradiated KCl at ORNL are reviewed. Both Stage I and Stage II coloration ranges are sensitive to the origin of the crystals studied. The presence of divalent cation (M^{++}) markedly enhances Stage I and suppresses Stage II relative to nominally pure crystals. The enhancement in Stage I can be explained by a model involving the conversion of an isolated cation vacancy into an *F*-center and a [Cl_3^-] ion by a radiolytic reaction. Mechanisms by which M^{++} might suppress Stage II coloration are explored. These are: (a) Suppression of the concentration of electrons and holes produced by the radiation field by acting as electron-hole recombination centers, (b) poisoning dislocations as a source of lattice defects, and (c) alteration of the nature of quenched-in defects. None of these possibilities is wholly satisfactory to explain experimental observations.

Introduction

A primary obstacle to understanding the mode of color center formation in irradiated alkali halides near room temperature is the highly varied response of specimens obtained from different sources. It is well known[1] that imperfections initially present markedly affect the early stages of *F*-center production and are to some extent responsible for other centers. For example, the presence of divalent impurities and OH^- are known to enhance the initial rate of *F*-center production (Stage I) by ionizing radiation[2]. Presumably, these impurities either increase the concentration of anion vacancies or introduce sites at which anion vacancies may be readily created by a radiolytic process. The course of color center production is also affected by impurities at much higher exposures (Stage II). Even for *F*-center concentrations comparable to or in excess of the impurity content, the coloration curves of specimens from different sources are different. Therefore, structure-sensitivity of the coloration process extends even into what is usually considered to be the intrinsic range.

In contrast to room temperature behavior, crystals irradiated at, or below, 78°K show little, if any, structure sensitivity[3]. Klick[4] has proposed a model based on the Varley mechanism[5] which accounts for this behavior. However, there is no assurance that the same intrinsic process is responsible for Stage II coloration at room temperature and recent studies[6] suggest that several processes may be operating in Stage II. Indeed, before the dominant process can be identified, it is necessary first to understand and to account for the structure sensitive reactions and products.

Experimental Results

The work described in this paper concerns the structure-sensitivity of room temperature coloration of KCl by Co^{60} γ-rays. A wide variety of both nominally pure and doped crystals were studied. The "pure" specimens include crystals from commercial suppliers (Harshaw, Isomet, and Optovac) and crystals produced in several laboratories, both by pulling from the melt and by zone-growth***. Impure specimens*** include crys-

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tals doped with Mg^{++}, Ca^{++}, and Sr^{++}. Dislocation densities of the crystals were determined by etch pit counting and each was analysed for divalent impurity by means of flame photometry.

The specimens were irradiated at 35°C in a Co^{60} γ-ray source at an intensity of 4.5×10^6r/hr. Their absorption spectra were measured after successive exposures in a Cary Model 14 spectrophotometer. Total exposures extended up to 70 hours in some cases. The investigations involved measurement of absorption in the *F*-, *M*-, and V_3-bands as a function of exposure. The relation between *F*-band and *M*-band absorption and between *F*-band and the V_3-region absorption was determined for the various specimens. The studies of the *M*-band are described in a recent paper[7)] and will not be considered further here.

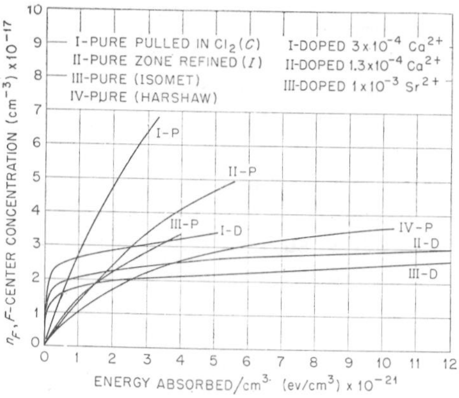

Fig. 1. *F*-center growth curves *vs* γ-ray exposure for a number of KCl specimens. The exposure is expressed as energy absorbed per cm³. (4.73×10^{20} ev cm^{-3} hr^{-1}.) $N_F=4.42\times 10^{15}\alpha_F$.

Typical curves of *F*-center concentrations *versus* γ-ray dose (expressed in energy absorbed per cm^3) are shown in Fig. 1. The following points should be noted: The doped crystals, which color much more rapidly initially, show the lowest *F*-band absorption at higher doses. In addition, there is a wide variation in the rate of coloration of the nominally pure crystals even though the dislocation density and divalent cation content were found to be comparable.

Absorption at 2150 Å (the region of the V_3-band), α_V, is plotted against *F*-band absorption, α_F, in Fig. 2 for typical specimens.

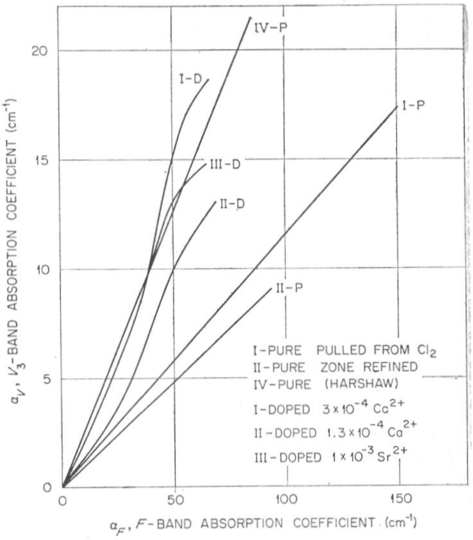

Fig. 2. *F*-band absorption *vs* V_3-band absorption for a number of KCl specimens.

Here it is noted that the curves for "pure" specimens are essentially linear whereas divalent cation doped crystals show an early sigmoid behavior, *i.e.*, the slope first increasing and then decreasing with increasing α_F. Also, the slopes for the "pure" specimens, with the exception of Harshaw material, are lower by as much as a factor of two than those of the doped crystals after prolonged exposure.

Discussion

The early stage of coloration in the doped crystals can be understood on the basis of the model of the V_3-center proposed by Crawford and Nelson[8)]. In this model cation vacancies are converted into anion vacancies (*F*-centers) by the radiolytic reaction:

$$V_c+h\rightarrow(Cl_3^-)_{[100]}+F \qquad (1)$$

where V_c is a cation vacancy, h is a hole, $(Cl_3^-)_{[100]}$ a molecular-ion complex oriented in the [100] direction and F the *F*-center. According to the model $(Cl_3^-)_{[100]}$ is the V_3-center. It was further suggested that only isolated cation vacancies could be readily converted into *F*-centers and molecular complexes. Therefore, the rapid initial rise and knee is attributed to the conversion of isolated cation vacancies according to Eq. (1). The concentration of *F*-centers $(n_F)_I$ produced in Stage I, obtained by extrapo-

Table I. Stage I coloration in doped KCl

Specimen	$(n_F)_I$ cm$^{-3}\times10^{-17}$	$N_M{}^0$ cm$^{-3}\times10^{-18}$	$N_V{}^+$ cm$^{-3}\times10^{-17}$
KCl:Ca^{++}	2.3	5.4	1.5
KCl:Ca^{++}	1.7	2.1	0.9
KCl:Sr^{++}	1.3	3.8	1.2
KCl:Sr^{++}	1.1	0.91	0.62
KCl:Mg^{++}	0.81	5.8	1.6
Harshaw$^{(a)}$	0.22	0.16	0.26

(*a*) 1.6×10^{17}cm^{-3} is the limit of detection of Ca^{++} and Sr^{++} by flame photometry.

lating the linear portion of the n_F *versus* exposure curves to zero exposure, are listed in Column 2 of Table I. In Column 3 are the total concentrations of divalent cation $N_M{}^0$ determined by analysis. In Column 4 are the concentrations of isolated cation vacancies $N_V{}^+$ calculated for 35°C from the relation$^{9)}$

$$\frac{N_V{}^+\cdot N_M}{N_{MV}}=\frac{N_L}{\omega}e^{-E_B/kT} \tag{2}$$

where N_{MV}, N_M, and N_L are the concentrations of associated divalent cation-cation vacancy complexes, isolated M^{++} ions and cation lattice-sites, respectively; ω the effective number of orientations possible for the complex; and E_B its binding energy; ω and E_B are taken to be 8 and 0.35 ev$^{10)}$ respectively; and $N_{MV}=N_M{}^0$. For all doped crystals $(n_F)_I$ is within a factor of two of $N_V{}^+$. In view of the errors of analysis, the assumption that all impurity is in solution, and the approximate nature of the calculation, this agreement is consistent with the proposed mechanism of cation vacancy conversion. Also shown in Table I are the values for a Harshaw specimen. The value of $(n_F)_I$ suggests an $N_M{}^0$ content of $\sim7\times10^{-6}$ atom fraction which is less than the detection limit of 10^{-5}. However, it is probable that the presence of OH$^-$ also contributes to $(n_F)_I$ in this crystal.

Although the influence of M^{++} impurity on the initial behavior of KCl during irradiation may be explained in this way, Stage II behavior requires some means by which this impurity can inhibit color center formation. Three possible mechanisms come to mind: (a) the M^{++} acts as an electron-hole recombination center, thereby decreasing the electron-hole lifetime, (b) the M^{++} "poisons" dislocations as a source of defects and (c) the presence of M^{++} alters the concentration of frozen-in defects.

(**a**) Isolated M^{++} ions are known to act as electron traps with an electron capture cross-section comparable to that of anion vacancies$^{11)}$. Therefore, one might expect M^{++} to act as an electron-hole recombination center with subsequent hole capture being the slow step. The M^{++} could thereby reduce the free carrier lifetime τ_c and hence the steady state concentration of electrons and holes, since the latter is given by the product of τ_c and the rate of carrier production by the radiation field. In order for this effect to have an important influence on the growth of *F*-centers, their mechanism of formation should involve a process of order higher than unity in either electron or hole concentration; for example, a process wherein a single ionization either in the bulk or at a special site (*e.g.*, a dislocation jog) is followed by a second ionization through either electron or hole capture during the lifetime of the singly ionized species. Observation$^{6)}$ that the production rate of *F*-centers per unit absorbed energy, increases with ionization intensity supports this mechanism.

However, for this interpretation to be realistic, recombination of free carriers must be dominated by M^{++}. The lifetime of a given type charge carrier is given by

$$\tau_c{}^{-1}=v_c\sum_i N_i\sigma_i \tag{3}$$

where v_c is the carrier velocity, N_i the concentration of centers of the i-th type and σ_i their carrier capture cross section. Anion vacancies (or *F*-centers) are also expected to be efficient recombination centers since capture of hole by an *F*-center leads to annihilation. Again hole capture would be the slow step in the over-all process. There appears to be no good reason why the hole capture cross section of M^{++} should be very much greater than that of an *F*-center. Therefore, because of the much higher *F*-center concentration in heavily irradiated "pure" specimens, τ_c in these should be even less than in doped specimens; yet the rate of *F*-center production in the former is the greater in Stage II. For this reason it appears doubtful that this mechanism can account for the observations.

(**b**) A widely used model[12)] for the production of F-centers in alkali halides by radiolysis involves the evaporation of Schottky pairs from jogs on dislocations by the energy released by recombining electrons and holes or excitons. Hence, production of defects by this mechanism would cause dislocation climb. Let us see how the presence of M^{++} impurity might alter the ease of radiogeneration of defects at jogs. It has been shown[13)] that the presence of M^{++} can alter the sign of the charge cloud surrounding dislocations and that borne by the dislocation itself. However, since the jog mechanism requires the generation of equal concentrations of both types of vacancies, it is difficult to see how either the presence or the sign of the space-charge region, which is required by the thermal equilibrium of Schottky defects, can influence the rate of defect generation by the ionizing field.

Alternatively, it is conceivable that the dislocations could be "poisoned" by the incorporation of M^{++} into the dislocation jog itself. The charge symmetry of the defect-generation process would thereby be distorted and the excess positive charge in the immediate vicinity of the jog would make it energetically difficult to generate cation vacancies at that site. The major difficulty with this argument is that there is sufficient M^{++} impurity in "pure" crystals to saturate jogs if its binding energy at these sites is large enough to make this means of "poisoning" feasible. The dislocation densities of the specimens employed here are $\sim 10^6\,\mathrm{cm}^{-2}$. For one jog every 10 lattice spacings, the upper limit of jog concentration is $\sim 10^{13}\,\mathrm{cm}^{-3}$, whereas the M^{++} concentration of the purest crystals is at least $10^{16}\,\mathrm{cm}^{-3}$. There is another objection to this mechanism: etching studies of γ-irradiated NaCl crystals reveal no evidence of climb[14)]. Therefore, "dislocation poisoning" by M^{++} seems to be incapable of explaining the observations.

(**c**) The final explanation requires the presence of M^{++} to alter the concentration of frozen-in defects. Upon cooling crystals from the melting point, thermal equilibrium of defects is maintained by migration of isolated vacancies and vacancy pairs to sinks (jogs, internal boundaries, and surfaces). Because of the requirement of electrical neutrality, annihilation of isolated vacancies is controlled by the slowest moving species, namely the anion vacancy. Annihilation of vacancy pairs, however, is subject to no such restriction, but recent studies[15)] indicate that their activation energy of motion is even greater than for anion vacancies. Thermal equilibrium is maintained as long as the cooling rate β is smaller than the reciprocal of $d\tau_i/dT$, where τ_i is the lifetime of the defect in question. The condition $\beta \simeq (d\tau_a/dT)^{-1}$ defines the effective quench temperature T_Q for anion vacancies, and with further decrease in temperature, the highly mobile cation vacancies combine with them to form vacancy-pairs for which $\tau_p > \tau_a$. Hence, the concentration of frozen-in defects (essentially all pairs) is determined by the Schottky defect concentration at T_Q. In crystals containing M^{++} the concentration of anion vacancies at T_Q is much suppressed by common ion effect. Hence, the concentration of quenched-in pairs is expected to be much lower in such crystals. This interpretation assumes that the dominant coloration process for the low ionization intensity employed in our experiments is structure sensitive, *i.e.*, results from two radiolytic reactions which involve defects initially present in the crystals. These are:

$$V_P + e \rightarrow F + V_c \qquad (4)$$

and the reaction of Eq. (1).

Let's now consider the consequences of mechanism (c) for coloration in the V_3-region. Some caution should be exercised here since the shape of the composite uv-band together with the observation that the maximum shifted by as much as 100 Å during coloration indicates the presence of bands other than V_3 and no doubt includes absorption due to V_2-, U-, and possible another band at 1990 Å. Nevertheless, because of the linear relation between absorption in this region (2150 Å) and the F-band in pure crystals which contain virtually no OH-band, we conclude that the V_3-band results from the presence of the Cl_3^- center and is the dominant component of the observed absorption band. This is contrary to the view expressed by Lüty[16)] that this band is due entirely to the U-center. From Eq. (1), one expects one V_3-center for each F-center produced, whereas radiolysis of vacancy pairs should produce two F-centers for each V_3-center. It is significant that the high purity specimens produced either by pulling from the melt or by zone growth (those with the most rapid cooling rate) show a smaller ratio of V_3- to F-band absorption than the doped crystals, whereas crucible grown commerical crystals, in particular Harshaw KCl, which is cooled much more slowly, exhibit a lower F-center production rate. (The high apparent V_3- to F-band ratio of Harshaw KCl may in part be associated with U-centers produced by radiolysis of OH^-.)

There are two objections to mechanism (c). First, Rabin[17] observed that, after Stage I, x-ray coloration was accompanied by a lattice expansion which was the expected magnitude if one Schottky pair was introduced for each F-center formed. It is difficult to see how transformation of an existing vacancy-pair into an F-center and a (Cl_3^-) ion could cause an expansion of this magnitude. Second, the magnitude of coloration observed in pure crystals would require a quench temperature of ~600°C: for $\beta=10^{-2}$ deg sec^{-1}, this corresponds to $\sim 10^{11}$ jumps for a vacancy before annihilation at 600°C, or the inordinately low sink concentration of $<10^{12}$ cm^{-3}. Although this mechanism is able to account for many of the observations reported here, the two difficulties just discussed must be dealt with before it can be taken seriously.

In summary, it is not possible to choose between the three mechanisms considered above to account for the structure sensitivity of Stage II coloration in both doped and "pure" KCl crystals. The difficulties inherent in each need more careful examination and study before it can be denfinitely accepted or rejected. For example, more intensive studies of the influence of radiation intensity on F-center formation, carrier lifetime in doped specimens, the influence of cooling rate after crystal growth, etc. are required. Alternative mechanisms should also be sought. Finally, it should be recognized that the origin of structure sensitivity in "pure" specimens may be quite different from that in doped crystals.

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