The Nature of Trapped Hole Color Centers in the Alkali Halides*

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THE ultraviolet bands (V-bands) formed in KCl by x-irradiation and in KBr and KI by additive coloration have been attributed by Seitz[1] to centers in which a hole is trapped at a positive ion vacancy. Alexander and Schneider[2] suggest further that bleaching the V-band in KCl, by irradiation in the band, frees the holes which are assumed to have a low mobility. The slow restoration of the band is then attributed to the slow diffusion of the positive ion vacancies to the free but relatively immobile holes which are then retrapped. The recent observation of other ultraviolet bands when KCl and KBr are x-irradiated at low temperatures[3] and the existence of more than one room temperature band indicate, however, that more than one type of trapped hole centers (hereafter called H-centers) are involved. Data obtained at this laboratory on color center formation in KCl, KBr, and KI under various conditions (Fig. 1) have revealed still other bands. It is the purpose of this note to present some suggestions concerning the nature of the centers responsible for the various ultraviolet bands which may account more adequately for the experimental data.

By analogy with the formation of trapped electron centers (hereafter called E-centers) one may in general expect various H-centers to be formed in which one or more holes are trapped at a single positive ion vacancy or at an aggregate of vacancies.[4] Such centers, if they exist, may be expected further to exhibit optical and photo-conductive properties similar to those of the corresponding E-centers.[5] Holes may also be "self-trapped." In addition, two holes may combine to form a halogen molecule (X_2-center) in which a pair of neutral halogen atoms are held together by a covalent bond. In forming an X_2-center the two holes effectively vanish and the optical properties of the center are determined rather by the two electrons which make up the covalent bond. The trapped electron analog of this center, a diatomic alkali molecule, probably also exists under appropriate conditions.

The analogy between E- and H-centers may break down in some cases. For example, the energy of formation of halogen molecules may be sufficiently large, even in the crystal, that the trapping of two holes at a positive ion vacancy will yield an X_2-center having a neighboring positive ion vacancy rather than an F' type of center. It is also possible that an X_2-center having two neighboring positive ion vacancies will be formed when two holes are trapped at a pair of positive ion vacancies. In both cases the vacancies play only an auxiliary role and, depending on the temperature, may or may not remain attached by Coulomb attraction to the X_2-center. X_2-centers which do not have neighboring positive ion vacancies will, at appropriate temperatures, tend to combine with them to form X_2-centers having one or two positive ion vacancies as neighbors.

The numerical distribution of the various H-centers at any given temperature will be considerably different from that of the corresponding E-centers as a result of the very large differences between the rates of thermal diffusion of positive and negative ion vacancies and between those of single holes trapped at single positive ion vacancies (hereafter called G-centers) and single electrons trapped at negative ion vacancies (F-centers). In general only the positive ion vacancies show appreciable thermal diffusion at room temperature. The G-centers, whose activation energy of diffusion will be roughly that of the positive ion vacancy, may also be expected to be mobile at room temperature, whereas F-centers are probably immobile. As a result of the migration of G-centers and positive ion vacancies at room temperature the G-centers will tend to combine with one another and with positive ion vacancies to form such centers as single holes trapped at a pair of positive ion vacancies, X_2-centers, and larger aggregates. The G-centers will also combine with various E-centers which may be present to produce permanent bleaching. This recombination of trapped holes and electrons is largely responsible for the low yields in KBr and still lower yields in KI obtained by room temperature x-irradiation, and also plays an important role in the thermal luminescence of x-irradiated alkali halides. The equilibrium distribution of the various E- and H-centers formed by x-irradiation will depend on a number of factors: the temperature, the number of holes and electrons that are formed, the number of positive and negative ion vacancies, the activation energies for diffusion of the various centers and of the positive

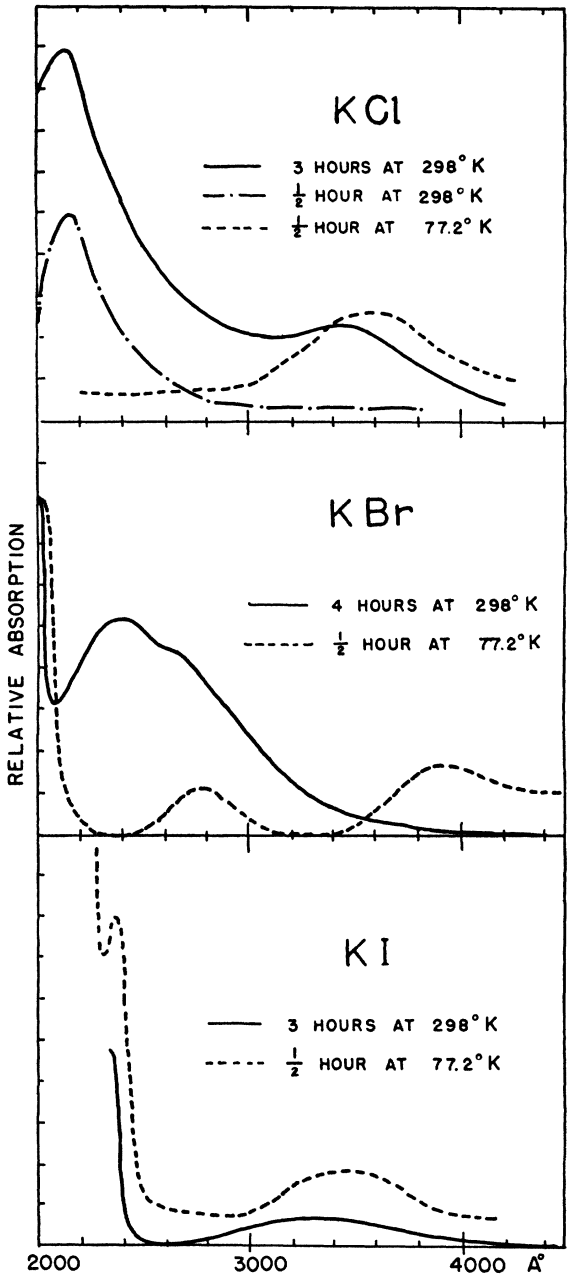

FIG. 1. Absorption bands formed in KCl, KBr, and KI by x-irradiation at room and liquid nitrogen temperatures. The bands at 2000A in KBr and at 2300A in KI have not been previously reported. A corresponding band is probably also formed at the absorption edge in KCl.

and negative ion vacancies, and the energy of formation of the various aggregates.

On the basis of these considerations, it seems probable that the room temperature V-bands reported by Alexander and Schneider[2] for KCl and KBr are due to halogen molecule centers and other aggregates of holes and vacancies rather than to single holes trapped at a single positive ion vacancy. In particular the 2200A band in KCl and the 2300A band in KBr which do not bleach when the F-center is irradiated are probably due to halogen molecule centers with two positive vacancies. Bleaching these centers by irradiation in the band probably involves either the thermal decomposition of the excited center into two G-centers or the splitting away of the positive ion vacancies from the halogen molecule. The slow restoration of the center is then due either to the slow migration of G-centers, or of positive ion vacancies and halogen molecules, and recombination.

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[3] Casler, Pringsheim- and Yuster, Quarterly Report of Argonne National Laboratory (1949).
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Multiple Scattering of the Particles Producing the "Positive Tracks" Appearing near Beta-Ray Emitters*

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A SERIES of investigators[1-5] have observed cloud-chamber tracks in the neighborhood of beta-ray emitters of curvatures corresponding to positively charged light particles moving away from the source. From energy considerations the particles producing these tracks cannot be positrons resulting from the decay of the beta-ray emitters. While most of the investigators are of the opinion that the cloud-chamber evidence favors the existence of these positive particles (they could not be observed in beta-ray spectrographs), in some recent investigations[6-8] the "positive" tracks have been attributed (1) to electrons emerging from the source, multiply scattered in such a way that their tracks have curvatures opposite to that which would be produced by the magnetic field alone, and (2) to electrons re-entering the source after being either reflected from the walls of the chamber or traversing an (unobserved) full circle.

We have compared the multiple scattering of 20 of these positive tracks emerging from various P^{32} source[9] arrangements with that of about 100 electrons in a mixture of 2 parts argon and 3 parts helium at one atmosphere total pressure in a magnetic field of approximately 340 gauss. The minimum track length was 7 cm and the average in both groups approximately 10 cm. Use was made of a method recently described[10] in which from deflections ω_i between subsequent chords of equal length connecting a series of points of a track an estimate for the momentum and a root-mean-square angle of scattering $[(\omega^2)_{Av}]^{\frac{1}{2}}$ (see Eq. (23) of reference 10) is derived. Due to the shorter minimum length of the tracks which had to be chosen in this investigation in order to include a larger number of positive tracks, a chord length of one centimeter only had to be used for the sake of improved statistics. In a section of such a short length the condition for multiple scattering is not fulfilled in our mixture of helium and argon for the higher momenta considered by us. For the sake of better statistics tracks in the momentum range between 1500 and 2000 gauss-cm were also included, although for such low momenta the

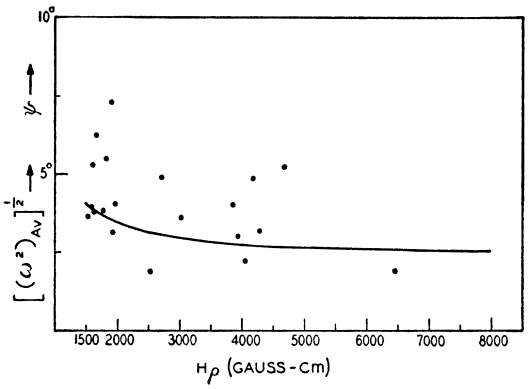

FIG. 1. Dots: root-mean-square scattering angles derived from 20 "positive tracks" as a function of H_ρ. Curve: least-squares curve derived from the root-mean-square scattering angles of 104 electrons.

method is not suitable for the determination of an absolute (experimental) scattering law. Both facts are however of minor importance for a comparison of the scattering of two groups of particles. Figure 1 shows the individual root-mean-square angles of scattering for the 20 positive tracks and a curve ψ_1 obtained by a least-squares fit of the data obtained for 104 electrons. In all individual cases corrections were made for errors in the optics, photography, and the measurements of the deflections, as previously described.[10] The difference between the scattering of the particles responsible for the positive tracks and the electrons, which follows from an inspection of Fig. 1, seems to be significant in view of the fact that all the tracks were obtained under the same conditions and treated in the same manner, and that furthermore it was ascertained in two different ways that the difference in the spectral distributions of the particles producing the "positive tracks" and the electrons from which the 104 cases were selected cannot be responsible for the higher scattering of the positives.

If one wishes to attribute the difference in the scattering to a difference in mass of both groups of particles, he can use the following approach. From the curve ψ_1 one can compute scattering curves corresponding to different masses, m, by the use of the approximate relation $\psi_m \propto 1/(pv)$ and compare the distribution of the individual scattering angles of the electrons about their least-squares curve ψ_1 with the distribution of the individual scattering angles of the positive tracks about the curves ψ_m corresponding to different masses. If a^2 is the ratio between an individual mean square angle $(\omega^2)_{Av}$ and a $\psi_m{}^2$ of the same momentum, then for $k^2 \geqslant 0$ we have plotted in Fig. 2 the number of particles (in percent) for which $a^2 \geqslant k^2$, as a function of k^2. The dashed curve A gives this cumulative distribution for the electrons about ψ_1 and the solid curves B, C, and D the distributions for the positive tracks about ψ_1, $\psi_{1.5}$, ψ_2, and $\psi_{2.5}$ corresponding to 1, 1.5, 2, and 2.5 electron masses. It can be seen that curve D agrees fairly well with curve A from which it follows that the individual root-mean-square scattering angles derived from the positive tracks are distributed about a scattering curve corresponding to mass two in a manner similar to that in which the root-mean-square scattering angles derived from electron tracks are distributed about a scattering curve corresponding to mass one. It should be mentioned in this connection that Smith and Groetzinger[3,11] have derived previously a mass of 1.5 to 2 electron masses for the particles producing the positive tracks from their momentum loss in a foil.

Two further results of some rather extensive investigations to be published later will be mentioned here briefly. It can be shown that it is extremely unlikely that any one of the observed positive tracks of a length exceeding 5 cm and an ionization smaller than five times the minimum ionization is, under the conditions used in our investigations, due to one of the decay electrons of P^{32}