On the Nature of V-Centers in the Alkali Halides

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ALEXANDER and Schneider[1] and Casler, Pringsheim and Yuster[2] have examined the production and bleaching of V-centers in alkali halide crystals darkened by x-rays and electron bombardment. The first investigators, studying NaCl, KCl and KBr, have found the following properties. (1) The number of V-centers is equal to the number of F-centers. (2) Irradiation with light in the F-band decreases the intensity of this band and also decreases the intensity of the V-band. (3) Irradiation in the V-band bleaches this band, but does not lead to any permanent removal, as is true at least in part for irradiation in the F-band, for the V-band returns to its original form in several days. (4) Light absorbed in the F-band is strongly effective in producing permanent bleaching if the crystal is irradiated either simultaneously or previously with light in the V-band, the total number of F-centers destroyed permanently in this efficient manner being equal to the number of V-centers which have been altered by irradiation in the V-band. (5) The F-band can be bleached with a strong electrostatic field during irradiation with light in the F-band, the centers wandering out of the crystal; however the V-centers cannot be removed in the same way.

The results of Casler, Pringsheim and Yuster on KCl and KBr differ from that of the previous work in the following important respects. (1) The V-band is somewhat weaker than the F-band; (2) when formed at room temperature, it is composed of two component bands (termed V_2 and V_3) which differ in relative intensity under different conditions of irradiation; (3) observations at liquid nitrogen temperature show that a new band (termed V_1) appears, having a peak at 3550A and 4100A in KCl and KBr, respectively. This may be bleached, along with part of the F-band, by irradiating with light in the V_1 band, or by warming. The V_2 band, which lies between V_1 and V_3, bleaches relatively slowly when the crystal is irradiated with light in the F-band, whereas V_3 is very difficult to bleach.

Alexander and Schneider have proposed an explanation of their results on the basis of a model suggested by the writer,[3] according to which the V-center formed at room temperature is represented by a hole trapped at an isolated positive-ion vacancy, which is the inverse of an F-center. They suggest that irradiation in the V-band frees a hole, and propose further that the hole possesses an exceedingly low mobility.

The writer would like to suggest an alternative explanation of the state of affairs, namely that the V-band as normally observed at room temperature arises from two centers which are composed of two positive ion vacancies to which one or two holes are attached respectively. Tentatively, these will be associated with the V_2 and V_3 bands of the Argonne group. Thus, the V-centers are the analog of the R-centers which are produced when F-centers are irradiated in such a way as to stimulate coagulation. This viewpoint is in accordance with the following facts.

(1) Mollwo[4] has found that the total number of V-centers formed in KBr and KI by additive means is proportional to the *first power* of the pressure of *diatomic* halogen molecules in the vapor.

(2) The positive ion vacancies are very mobile having a jump frequency of the order of unity or greater in KCl and NaCl at room temperature. As a result they may be expected to form the analog of the R-centers with ease at room temperature. In fact such centers will be the rule rather than the exception.

(3) It is reasonable to expect the first excited electronic level of a "diatomic" center either to join or cross the lowest electronic level for appropriate values of the configurational coordinates so that a hole is not automatically freed when the V-centers are excited. We may anticipate metastable states in which the excited hole is attached to the center. If we postulate that such states are formed when the V-band is bleached by irradiation in the V-band, it is unnecessary to assume that the hole has a very low mobility when free. In fact the experimental results of Mollwo on the electronic conductivity of KBr and KI containing excess halogen at elevated temperatures, which give experimental values of the product of the fraction of V-centers ionized and the mobility of holes (Figs. 10 and 11, reference 4), show, when extrapolated to infinite temperature where the fraction of ionized centers should be unity, that the mobility of holes is probably of the order of 1.0 cm^2/volt-sec. This is a respectable value and about what one would anticipate from the theoretical calculations of the width of the filled band in the alkali halides.

(4) We might expect an activation energy to be required for capture of a free electron by the V-centers when in the ground state, particularly in the case of V_3 which is analogous to a halogen molecule, because the nuclear coordinates will have values different from those for an ionic state. As a result bleaching by irradiation in the F-band, which produces free electrons, is difficult.

According to this model, V-centers cannot be removed by a combination of irradiation with light in the V-band and a strong electrostatic field because V-centers do not become ionized when irradiated with light in the V-band. There do not appear to be experiments available concerning the presence or absence of photo-conductivity when a crystal containing V-centers is irradiated in the V-band. The picture presented here suggests that such photo-conductivity should be absent because the holes are not made free.

The observations on the bleaching of V- and F-bands can be explained in terms of this model in the following way.

(1) Irradiation in at least one of the V-bands (such as V_2) produces a metastable state in which the electronic configuration is associated with the first excited electronic level, which has crossed the ground state, much like the case which the writer[5] has proposed to explain the absence of luminenscence when the alkali halides are irradiated in the fundamental absorption band. The metastable state decays to the ground state in the course of several days.

(2) The configurational coordinates of the nuclei associated with at least one of the V-centers in its normol state (such as the V_3 center) are such that the holes cannot be annihilated by free electrons. On the other hand, the configurational coordinates associated with the metastable V-center, obtained by exciting the latter with light in the V-band, are such that the holes can be annihilated with free electrons.

(3) It is likely that the original V-center proposed by the writer occurs during irradiation at low temperatures and is responsible for the band observed at 3550A in KCl by the Argonne group. This center may be sufficiently mobile at room temperature that it vanishes by migration and combination.

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A Note on the Vapor Pressure of He^3, He^4 Solutions

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RECENTLY Gorter[1] has applied the concept of minimum free energy at equilibrium to the Tisza two fluid model of He^4. De Boer[2] and Gorter and De Boer[3] have extended this treatment to cover solutions of He^4 and He^3. The above authors have treated He^4, He^3 solutions on two bases, (1) that the equilibrium fraction of the He^4 in the normal state (y_e) is an internal property of He^4 and is independent of the mole fraction of He^3 (X), and (2) that