Back reactions in color-center production: A study of a di-interstitial center in Li-doped KBr

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The production of $V(306)$ centers, constituted by two interstitial halogen atoms trapped at a lithium impurity, is studied in doped KBr in the 190–300°K temperature range. Above 210°K the $V(306)$-center production saturates and the saturation concentration decreases with increasing temperature. The saturation of the $V(306)$-center production is correlated to a first stage in the F center growth curve. Some evidence for a mechanism of saturation of the $V(306)$-center production based on the mobility of anion vacancies is given.

I. INTRODUCTION

It is well known that back reactions due to mobile interstitial halogens play an important role in color-center production in alkali halides.[1] Recombinations between vacancies and interstitials due to the motion of anion vacancies have also been considered, but no clear evidence has up to now been obtained for such processes.

It has been found[2] that in Li-doped KBr near room temperature the production of $V(306)$ centers—constituted by two interstitial halogen atoms at a lithium impurity and responsible for an absorption band peaking at 306 nm—saturates at concentrations much lower than that of the impurities and is correlated with a first stage in the F-center production. It has been suggested[2] that the saturation of the $V(306)$-center production could be the result of interstitial-vacancy recombination at lithium impurities due to the motion of anion vacancies.

The aim of the present work is to find experimental evidence for this suggestion, i.e., for a back reaction due to mobile anion vacancies.

II. EXPERIMENTAL

The experimental apparatus and conditions were the same as those described earlier.[2] In the present work the temperature of the sample during x irradiations and optical absorption measurements was maintained within ±0.1 °K of the reported temperature.

The thermal destruction of α centers produced by optical ionization of F centers in x-irradiated samples has been studied by a step annealing method following a procedure already used by Giuliani.[3] In the present experiment, however, the sample after x irradiation at 80 °K was warmed in the dark and kept at 300 °K for 30 min; then it was recooled and optical bleaching of F centers was performed at 170 °K; after that the crystal was warmed to various annealing temperatures and held in the dark for 5 min. Finally, from the annealing temperatures the sample was cooled to 80 °K for the optical-absorption measurements.

The samples used have been grown in nitrogen atmosphere by the Kyropoulos method. The molar concentration of lithium impurities was 1% (in the melt). The starting KBr powder was Merck Suprapur.

III. RESULTS

Figures 1 and 2 show the growth curves for the $V(306)$ and the F band in the 190–300 °K temperature range. The increasing of the temperature of irradiation from 190 to 220 °K makes the growth curve of the $V(306)$ band to saturate (Fig. 1). Correspondingly, the F-center growth curve shows a distinct first stage whose saturation value decreases—as that of the $V(306)$ band—with increasing temperature (Figs. 1 and 2).

In the temperature range considered another band due to hole centers is produced along with the $V(306)$ band: its peak is at 265 nm (at 80 °K) and its overlapping with the $V(306)$ band cannot be ignored in our temperature interval.

However, we have found that there is no correlation between the growth of this band with the saturation of the $V(306)$ band and the first stage of the F-center production. On the other hand the overlapping of the 265-nm band with the $V(306)$ band

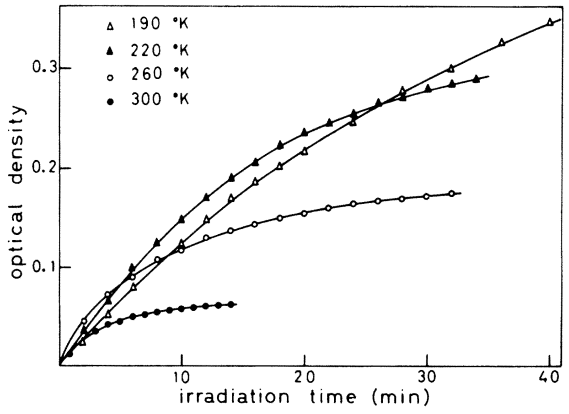

FIG. 1. Growth curves for the $V(306)$ band. Absorption measurements taken at the irradiation temperatures.

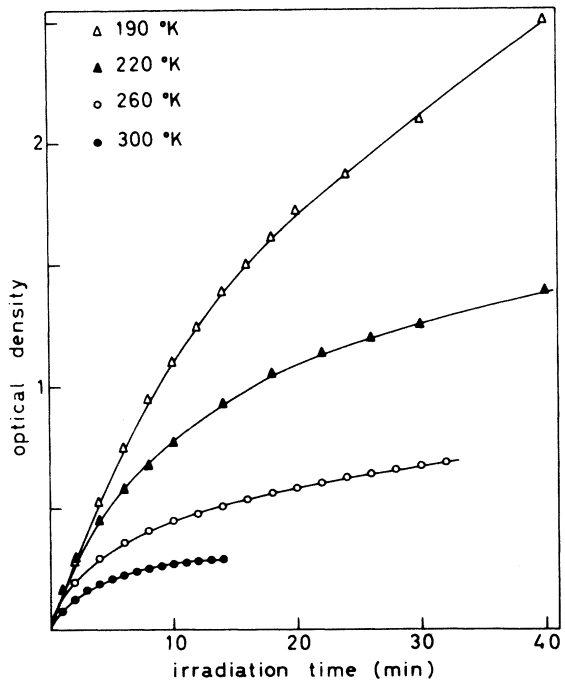

FIG. 2. Growth curves for the F band. Absorption measurements taken at the irradiation temperatures.

can reasonably account for the apparent growth of the last one after saturation.

One can try to describe the saturation behavior of the $V(306)$-center production by the equation

$$\frac{dn}{dt} = A - Bn, \tag{1}$$

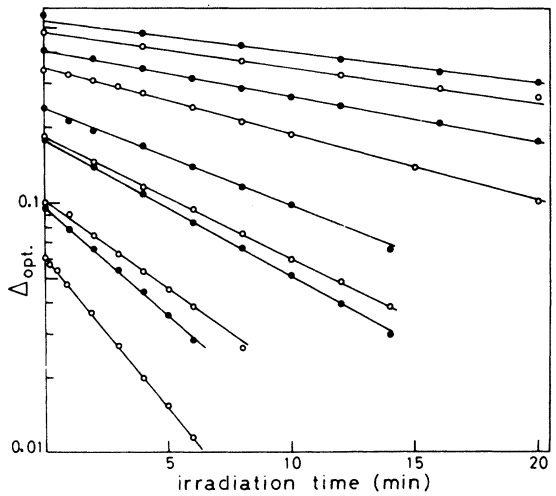

FIG. 3. Semilog plot of the quantity $\Delta_{opt.}$ for the $V(306)$ band as a function of irradiation time. $\Delta_{opt.}$ is the difference between the saturation value of the optical density and the value measured after a time t of irradiation. The temperatures of irradiation are, starting from the top (in °K): 200, 205, 210, 215, 220, 230, 240, 280, 290, 300.

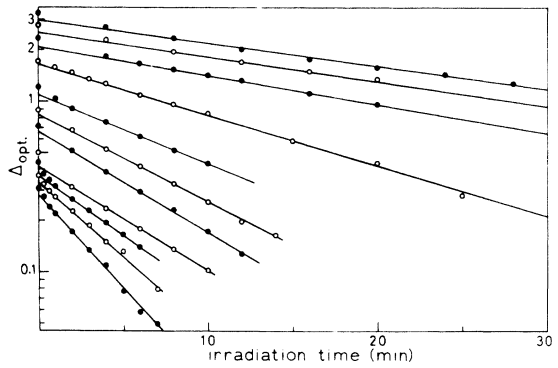

FIG. 4. Semilog plot of the quantity $\Delta_{opt.}$ for the first stage of the F-band growth as a function of irradiation time. $\Delta_{opt.}$ is the difference between the saturation value of the optical density and the value measured after a time t of irradiation. The temperatures of irradiation are, starting from the top (in °K): 200, 205, 210, 215, 220, 230, 240, 270, 280, 290, 300.

where n is the $V(306)$-center concentration and A and B are temperature-dependent parameters. The solution of this equation is given by

$$n = n_s[1 - \exp(-Bt)],$$

where $n_s = A/B$ is the saturation value of the $V(306)$-center concentration.

If Eq. (1) describes the production of $V(306)$ centers, a semilog plot of the difference between the optical densities corresponding to n_s and $n(t)$ as a function of irradiation time would yield a straight line whose slope is given by the parameter B. Figure 3 shows that this is indeed the case.

At this point one is tempted to try to describe the F-center production in the first stage also by use of Eq. (1). The results are shown in Fig. 4. As one should have expected the F-center production is more complicated than that of the $V(306)$ centers. In particular, the first stage of the F-center production seems to be composed of two processes a fast and a slow one. If we focus our attention on the slow process—which is also the main component of the first stage of the F-band growth—we find that it can be described by Eq. (1) and that the temperature dependence of the destruction coefficient B_F is the same as that of the coefficient B_V which governs the destruction process of $V(306)$ centers (Fig. 5).

IV. DISCUSSION AND OTHER RESULTS

The main feature of the results of Sec. III that must be explained is the temperature-dependent saturation behavior of the $V(306)$-center production and the associated first stage of the F-band growth. [From now on in relating to the first stage of the F-band growth we will refer to its main component described by Eq. (1) and char-

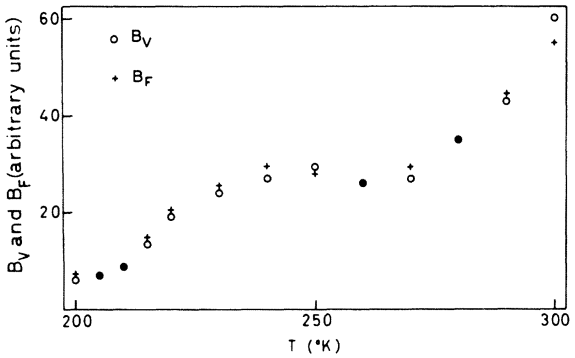

FIG. 5. Plot, as a function of temperature, of the destruction coefficient B_v responsible for the saturation of the $V(306)$ band and of the coefficient B_F responsible for the saturation of the main component of the first stage of the F-band growth.

acterized by the destruction parameter B_F of Fig. 5.]

Several mechanisms could be responsible for the destruction parameter B_V.

A. Thermal decomposition of $V(306)$ centers

We have measured the thermal destruction parameter of $V(306)$ centers by following in the dark at a constant temperature the decrease in absorption of the $V(306)$ band after x irradiation. The time elapsed from the switchoff of the x rays and the start of the absorption measurement was of the order of 10 sec. It turns out that the thermal destruction parameter is negligible at all temperatures except the higher ones. For instance, at 270 °K its value is about 1.5 which must be compared with the value of about 30 of Fig. 5. At 300 °K its value is about 10: the thermal destruction process becomes appreciable though it remains less efficient than the one operative under x irradiation.

B. Destruction process due to x rays

The destruction process due to x rays is expected to be temperature independent. In any case it cannot explain the temperature dependence of B_V reported in Fig. 5.

C. Aggregation of interstitials around $V(306)$ centers

It has been shown that the thermal decay of H_A(Li) centers takes place around 200 °K.[4,5] However, the thermal destruction of H_A(Li) centers due to the migration of the trapped interstitial hologen atoms ends up in an increase of the $V(306)$-center concentration.[4,5] Accordingly, we have found that the production parameter A_V of Eq. (1) increases in the same temperature range in which the thermal decay of H_A(Li) centers takes place. Therefore, we can conclude that the release of interstitial halogen atoms by lithium impurities mainly affects the production process of $V(306)$ centers and not their destruction.

D. Interstitial-vacancy recombination at lithium impurities due to the motion of anion vacancies

Figure 6 shows the thermal decay of isolated anion vacancies produced either directly by x irradiation at 80 °K (data taken from Ref. 4) or by optical bleaching of F centers in x-irradiated Li-doped samples. The difference between the two curves is due to the fact that the migration of interstitial halogen ions trapped at lithium impurities (I_A centers) and their recombination with anion vacancies play an important role in the thermal destruction of α centers produced by x rays. On the other hand, isolated interstitial negative ions are not present before the thermal destruction of anion vacancies produced by optical bleaching of F centers as described in Sec. II. In this case the disappearence of anion vacancies should be due to their own migration.[3]

Let us now focus our attention on Fig. 5, which gives the dependence of B_V on temperature. B_V begins to increase just around 210 °K, i.e., around the same temperature at which anion vacancies begin to migrate. Furthermore, the increase of B_V in the 210–240 °K range bears a qualitative relation with the thermal decay curve of α centers produced by x rays. This can be understood on the basis of the fact that, if B_V is due to the motion of anion vacancies, then it will depend on the concentration of α centers under x irradiation and this concentration will depend in turn, besides other factors, not only on the mobility of anion

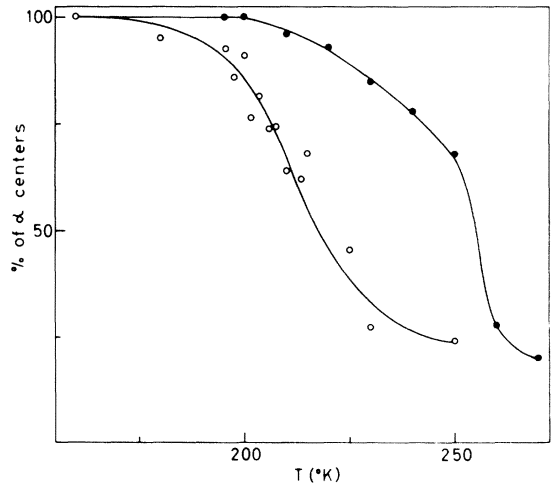

FIG. 6. Thermal decay of isolated anion vacancies produced either by x irradiation at 80 °K (open circles) or by optical bleaching of F centers (full circles) in x-irradiated samples. The data for α centers produced by x rays have been taken from Ref. 4.

vacancies but also on the concentration and mobility of interstitial halogen ions.

Finally, we must add that during the thermal decay of anion vacancies obtained by optical bleaching of F centers no decrease of the $V(306)$ band has been detected. This would imply that the migration of anion vacancies could be a necessary but not a sufficient condition for the destruction of $V(306)$ centers. Some other condition not verified during the thermal decay of anion vacancies but easily met under x irradiation must be fullfilled. This condition could be the presence of free electrons.

We are now in a position to suggest a possible mechanism for the destruction of $V(306)$ centers which will also explain the correlation between the saturation behavior of the $V(306)$ band and the main component of the first stage of the F-center production and, in particular, the data of Fig. 5 concerning the temperature dependence of B_V and B_F:

x rays → free electron plus free hole,

$V(306)$ plus electron → $(I_{Br^0} I_{Br^-})$ trapped at a Li impurity,

$(I_{Br^0} I_{Br^-})$ trapped at a Li impurity plus anion vacancy → $H_A(\mathrm{Li})$ (thermally unstable),

$H_A(\mathrm{Li})$ plus F center → perfect crystal,

hole plus F-center → anion vacancy.

It is worth stressing that this mechanism is based on the assumption of the existence, as an intermediate product, of a defect composed by an *interstitial* halogen Br_2^- molecule trapped at a lithium impurity.

Coming back to Fig. 5 some word must be said about the temperature dependence of B_V and B_F above 240 °K. In particular, their increase above 270 °K is not clearly understood. Besides the thermal decomposition of the $V(306)$ center to which we have referred to above, the thermal instability of α_A centers may play a role as suggested by the decrease of the production efficiency of F_A centers which we have observed to occur above 260 °K.

Finally, it is worth stressing that another possible mechanism for the destruction of $V(306)$ centers based on the mobility of the F center in its excited relaxed state (F^*) must be kept under consideration. It is known that F^* centers can jump around a cation impurity of size smaller than that of the substituted ion with an activation energy of the order of 0.1 eV.[6] Reasonably, the motion of F^* centers in a perfect lattice could occur with an activation energy of some tenths of eV. This is just of the right order of magnitude for a process—as the destruction of $V(306)$ centers—which occurs above 210 °K. However, it must be observed that, apart from these considerations, no other evidence for the role played by mobile F^* centers in the saturation of the $V(306)$ band is now available.

V. CONCLUSIONS

The results reported in this paper give new support to the existence of back reactions in color-center production based on the mobility of anion vacancies. However, no conclusive evidence has been obtained and further investigations are needed in order to settle this rather central problem.

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[1]See, for instance, E. Sonder and W. A. Sibley, *Point Defect in Solids* (Plenum, New York, 1972), Vol. 1, Chap. 4.

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[3]G. Giuliani, J. Phys. Chem. Solids 30, 217 (1969).

[4]G. Giuliani, Phys. Rev. B 2, 464 (1970).

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[6]See, for instance, F. Lüty, *Physics of Color Centers* (Academic, New York, 1968), Chap. 3.