Interstitial Stabilization and Color-Center Production in KBr

G. Giuliani*

Istituto di Fisica dell' Università, 27100 *Pavia, Italy*

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This paper deals with the color-center production in KBr containing alkali impurities (Li, Na, and Rb). It turns out that alkali impurities enhance the color-center production at 80 °K only if their size is smaller than that of the substituted ion. Typically, in sodium- or lithium-doped samples (1% in the melt) the average α- and F-center production efficiencies are increased by more than an order of magnitude and by a factor of 2–3, respectively. In KBr:Na, the enhancement of the α- and F-center production is related to the growth of the well-known V_1 and I (interstitial negative ion) bands (not observed at 80 °K in sufficiently pure samples). Similarly, in KBr:Li, the increase of the α- and F-center production is related to the growth of an I-type band (peaking at 223 mμ) and of two V_1-type bands (peaking at 390 and 438 mμ). The analysis of the growth- and thermal-decay properties of the I- and V_1-type bands, with respect to those of the α and F bands, leads to the conclusion that the enhancement of the α- and F-center production is due to the trapping and the stabilization of interstitial halogens by sodium or lithium impurities. Finally, the fact that lithium-trapped interstitials are more stable than those trapped by sodium, along with the fact that rubidium impurities (1% in the melt) do not affect the color-center production, supports an interstitial-stabilization mechanism based on the reduction of the repulsive forces acting on the interstitials when they are trapped near suitable impurities.

I. INTRODUCTION

It has been shown that two types of Frenkel pairs are created in alkali halide crystals exposed to ionizing radiations near liquid-helium temperature: one consisting of an F center and an H center (interstitial halogen atom) and the other consisting of an anion-vacancy (α center) and an interstitial halogen.[1] Provided that the temperature of irradiation is low enough (very close to that of liquid helium), the production of these pairs is an intrinsic process, i. e., it does not depend on the degree of perfection of the sample.[2,3] However, when the temperature of irradiation is raised, the production of both the α and F centers is enhanced by positive divalent impurities.[3,4] It has been suggested[4] that the enhancement of the F-center production at 80 °K is due to the stabilization by divalent impurities of interstitials which would otherwise recombine with the corresponding anion vacancies. More recently, it has been shown that the α-center production in the 11–196 °K range (in KCl) can be accounted for in terms of an intrinsic production and of a structure-sensitive recombination of anion-vacancy–interstitial-halogen ion pairs. The structure dependence of the recombination process is easily understood in terms of interstitial stabilization by divalent impurities or other defects.[3] However, it must be stressed that though the hypothesis of interstitial stabilization explains several facts on the color-center production and stability, further data are needed for considering this hypothesis confirmed

by experiment and for finding out the mechanism by which interstitial stabilization occurs. As already suggested,[3] an interstitial may be stabilized by an impurity (or by other defects), if the repulsive forces acting on the interstitial are smaller near the impurity than in a perfect region of the crystal. This condition is expected to be verified in the dilated regions which surround impurities smaller than the substituted ion. For instance, if one chooses KBr as the host crystal, then sodium and lithium will be appropriate impurities. In fact, not only are lithium and sodium ions smaller than the potassium ion, but since they are monovalent, their possible influence on the interstitial stability will be uniquely due to their smaller size.[5] In particular, there cannot be any effect associated with extra charges or charge-compensating cation vacancies, which may be true in the case of positive divalent impurities. Furthermore, since the lithium ions are considerably smaller than the sodium ions, lithium-trapped interstitials are expected to be more stable than those trapped by sodium. Finally, on the basis of the above speculations, rubidium impurities (in KBr) cannot act as interstitial traps.

In this paper, we report the results of research suggested by the above considerations.

II. EXPERIMENTAL

The production efficiency and the thermal stability of interstitial halogens in KBr have been studied by looking at the optical-absorption bands

associated with interstitial halogens or with the complementary defects of interstitial halogens (α and F centers). All the optical-absorption measurements have been carried out at 80 °K using a Hitachi EPS-3T double-beam spectrophotometer. The irradiations have been performed at 80 °K, using an OEG-50T Machlett x-ray tube operated at 45-kV peak and 30 mA. The thermal destruction of the defects produced at 80 °K has been studied by a pulse-annealing method already described in a previous paper.[3] (In the present work, however, the samples were kept only for 5 min at the annealing temperature.) The samples used have been grown in nitrogen atmosphere by the Kyropoulos method. The reported impurity contents refer always to the amounts added to the KBr powder (Merck Suprapur).

III. RESULTS AND DISCUSSION

A. Sodium-Doped Samples

1. *Mainly F and V_1 Centers*

The first results obtained on KBr:Na have already been published in a previous paper from now on referred to as Paper I.[6] In Paper I the following was shown: (i) Sodium impurities enhance the production of both the α and F centers at 80 °K. (ii) The higher production efficiency of α centers is due to the stabilization of interstitial-bromine ions by sodium impurities. (iii) The enhancement of the F-center production is related to the growth of the V_1 band. In this section we report some additional data obtained with sodium-doped samples.[7]

Provided that the sodium content is high enough, the composite V_1 band is proportional to the F band for low radiation doses (Fig. 1). During the warming of the sample the decrease of both V_1-band com-
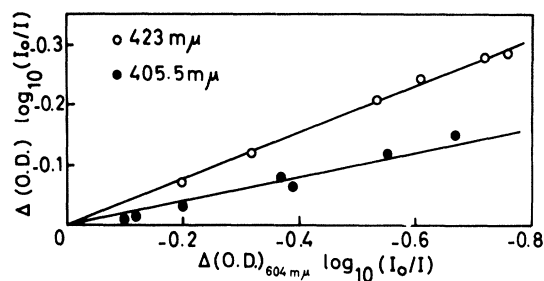
FIG. 2. Relations between the decreases of the two V_1-band components and the decrease of the F band during the warming of a sodium-doped (1%) KBr sample x rayed at 80 °K.

ponents is proportional to the decrease of the F band (Fig. 2). However, the percent decrease of the composite V_1 band is higher than the corresponding decrease of the F band (Fig. 3).

The decrease of the 423-mμ component of the V_1 band is accompanied by a proportional increase of the V_4 band (Fig. 4). The decay of the other component of the V_1 band is accompanied by an increase of the long-wavelength component (306 mμ) of the V_4-band envelope. (In dealing with the V_4-band envelope, we shall use the nomenclature suggested by Comins.[8])

A discussion of these results involves the structure of the V_1 center. According to recent EPR measurements, the V_1 center in KCl consists of an interstitial-halogen atom (H center) trapped at an alkali impurity.[9] Results supporting the same model for KBr have been obtained by the author.[10] Therefore, in the following discussion we shall assume that the V_1 center in KBr(Na) consists of an H center trapped at a sodium impurity. The fact that the assumed model explains all the experimental data (which we will discuss next) is a further argument in favor of its correctness.

The existence of stabilized H centers (V_1 centers) at 80 °K shows that F-center–H-center pairs are produced at 80 °K, as they are near liquid-helium temperature. In a pure sample, the produced H centers will recombine with the corresponding F centers or will give rise to some complex centers responsible for the V_4-band envelope.[8,11] However, in sodium-doped samples a fraction of the produced H centers will be trapped and stabilized by sodium impurities and will therefore be observable as V_1 centers. As a consequence, the V_1 band will grow at a rate proportional to that of the F band, provided that the effective concentration of impurities is high enough (Fig. 1).[12] On warming the sample the stabilized interstitial-halogen atoms become mobile and either recombine with F centers (Fig. 2), or form the defects responsible for the V_4 band (Fig. 4) or the 306-mμ com-
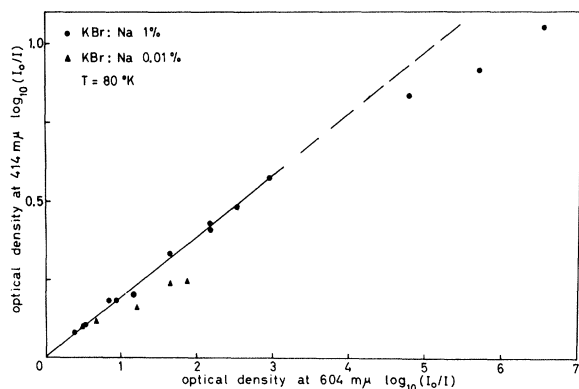

FIG. 1. Relation between the composite V_1 band (414 mμ) and the F band (604 mμ) during the x irradiation at 80 °K of KBr samples containing different amounts of sodium impurities.
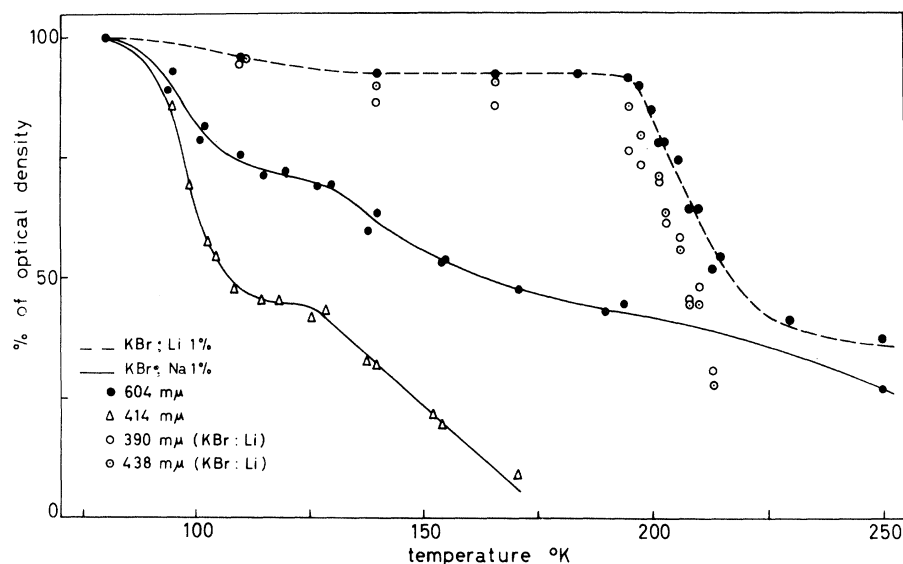
FIG. 3. Thermal decay
of the absorption at 414 and
604 mμ in a sodium-doped
(1%) KBr sample x rayed
at 80 °K, and thermal decay
of the absorption at 390,
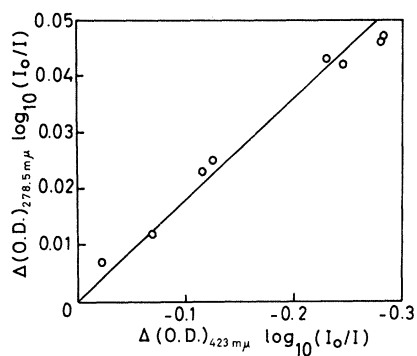438, and 604 mμ in a lithi-
um-doped (1%) KBr sample
x rayed at 80 °K.

FIG. 4. Relation between the decrease of the 423-mμ
component of the V_1 band and the increase of the V_4 band
during the warming of a sodium-doped (1%) KBr sample
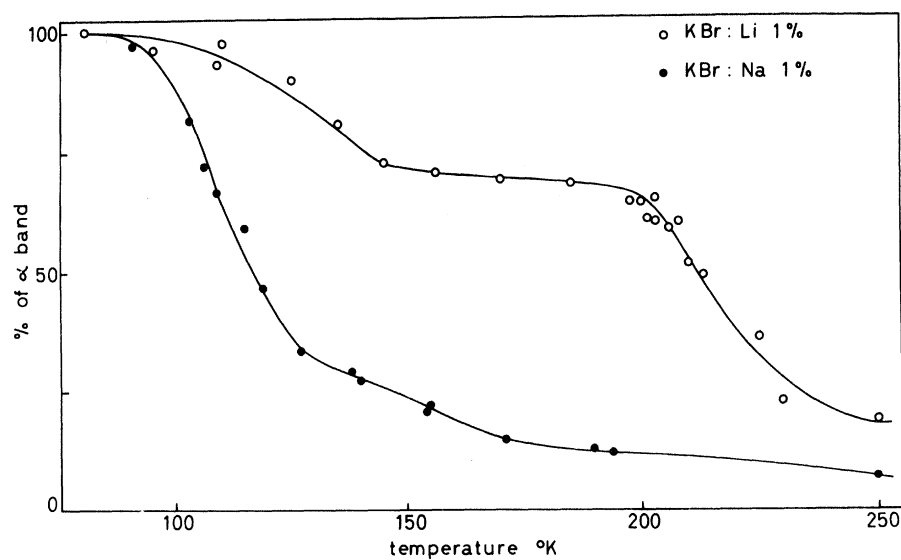x rayed at 80 °K.

FIG. 5. Thermal decay
curves of the α band in sodi-
um-doped (1%) and lithium-
doped (1%) KBr samples
x rayed at 80 °K.

ponent of the V_4-band envelope. This behavior of
the mobile intertitial-halogen atoms, along with
the fact that the V_1 centers are not the only com-
plementary defects of the F centers produced at
80 °K,[6] is responsible for the larger decrease of
the composite V_1 band as compared to that of the
F band (Fig. 3).

2. α-Center–Interstitial-Halogen Ion Pairs

The α centers produced at 80 °K in KBr:Na
disappear almost completely in two distinct stages
as the sample is warmed at 190 °K (Fig. 5, lower
curve). As shown in Paper I, the thermal destruc-
tion of α centers is due (at least in the 80–140 °K
range) to their recombination with interstitial-
halogen ions. In principle, the mobile entity re-
sponsible for the recombination process may be
either anion vacancy or interstitial. However,
in the former case one expects a fraction of the
mobile-anion vacancies to be trapped by sodium
impurities, i.e., one expects to observe the
growth of the α_A band.[13] This $\alpha \to \alpha_A$ conversion
is very likely responsible for the apparent shift
of the α-band peak, which is observed after the
sample has been warmed at 250 °K (Fig. 6). On
the other hand, since no shift is observed below
190 °K, we are led to the conclusion that no de-
tectable migration of anion vacancies occurs be-
low 190 °K and that the mobile entity below this
temperature is the interstitial. Finally, owing
to the overlapping of the α and the α_A band (Fig.
6), the point corresponding to 250 °K in Fig. 5
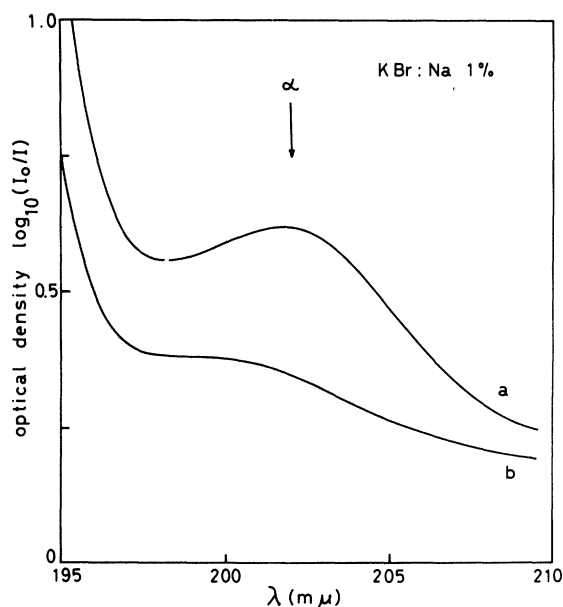(lower curve) overestimates the remaining α-
center concentration.

FIG. 6. (a) Absorption spectrum (measured at 80 °K)
in the α-band region of a sodium-doped (1%) KBr sample
x rayed for 210 min at 80 °K and warmed for 5 min at
190 °K; (b) absorption spectrum of the same sample of
(a) after it has been warmed for 5 min at 250 °K. Both
curves of this figure have been obtained by subtracting
the absorption curve obtained prior to the x irradiation
at 80 °K from the measured absorption curves.

B. Lithium-Doped Samples

1. α- and F-Center Production Efficiency at 80 °K

Figure 7 shows that lithium impurities enhance
the average α-center production efficiency at 80 °K

FIG. 7. α- and F-
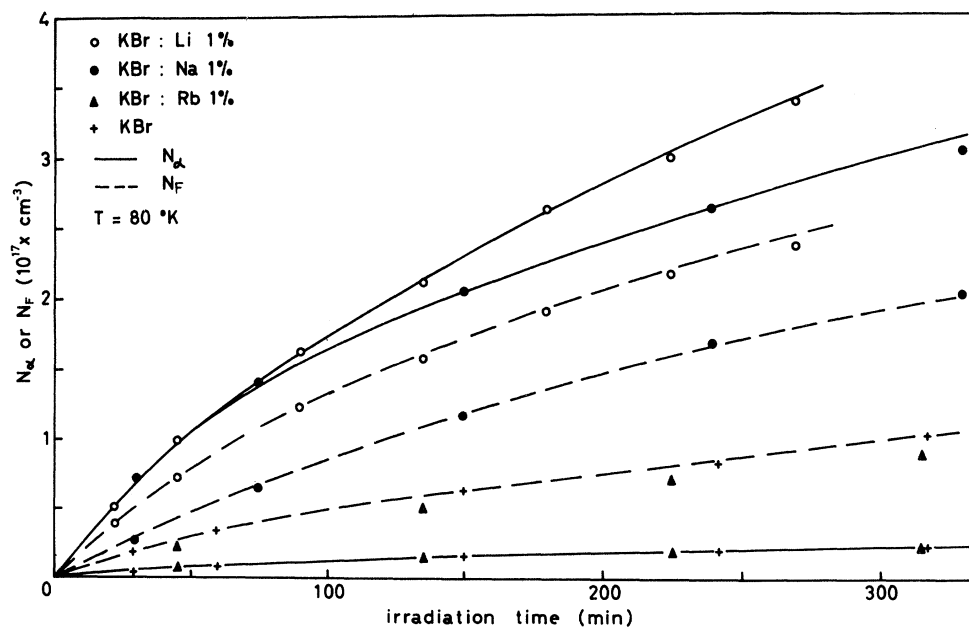center growth curves
for samples of pure
or doped KBr. The
defect concentrations
have been calculated
as indicated in Paper
I. Owing to the soft
x rays used and to the
thickness of the sam-
ples (0.76–0.80 mm)
the coloration was
strongly nonuniform.
Therefore, the values
reported here for the
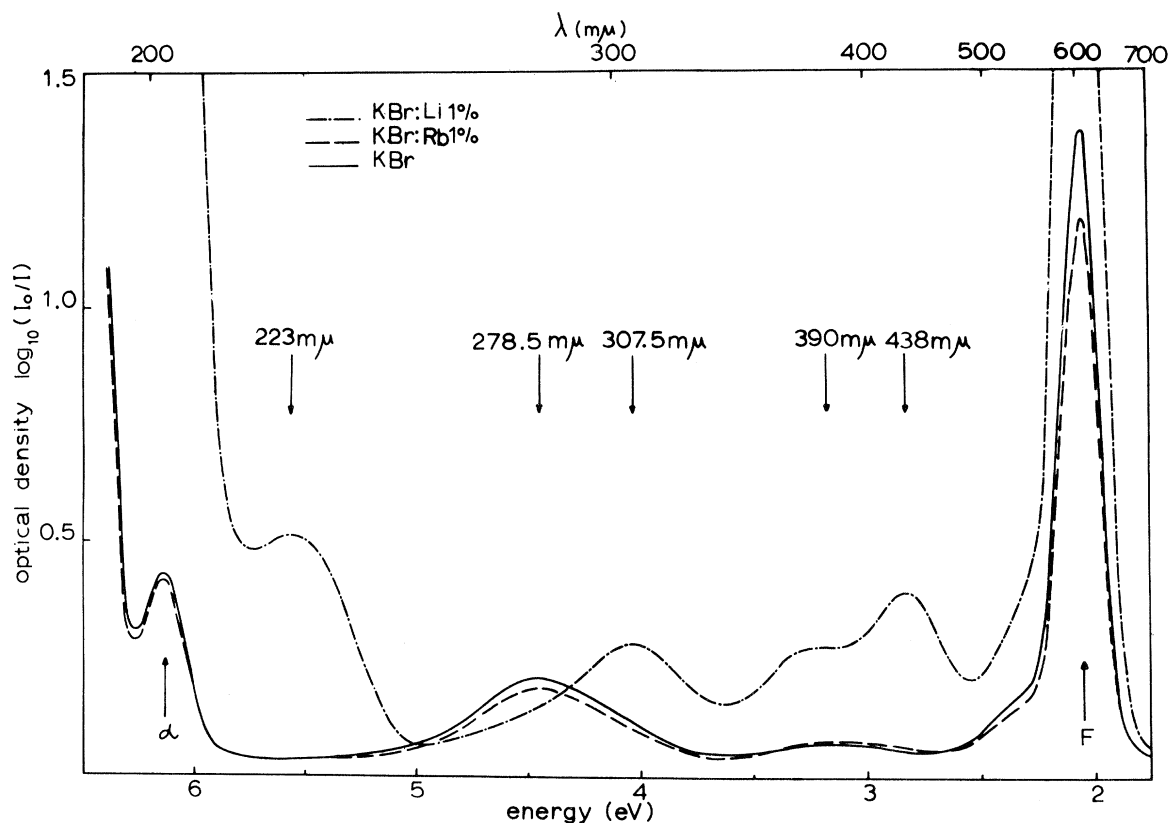defect concentrations
are average values.

FIG. 8. Absorption curves of three of the four samples of Fig. 7 after the x irradiation at 80 °K. The pure sample has been x rayed for 317 min, the rudidium doped for 315 min, and the lithium doped for 270 min. All the curves of this figure have been obtained by subtracting from the measured absorption curves the absorption curves measured prior to the x irradiation.
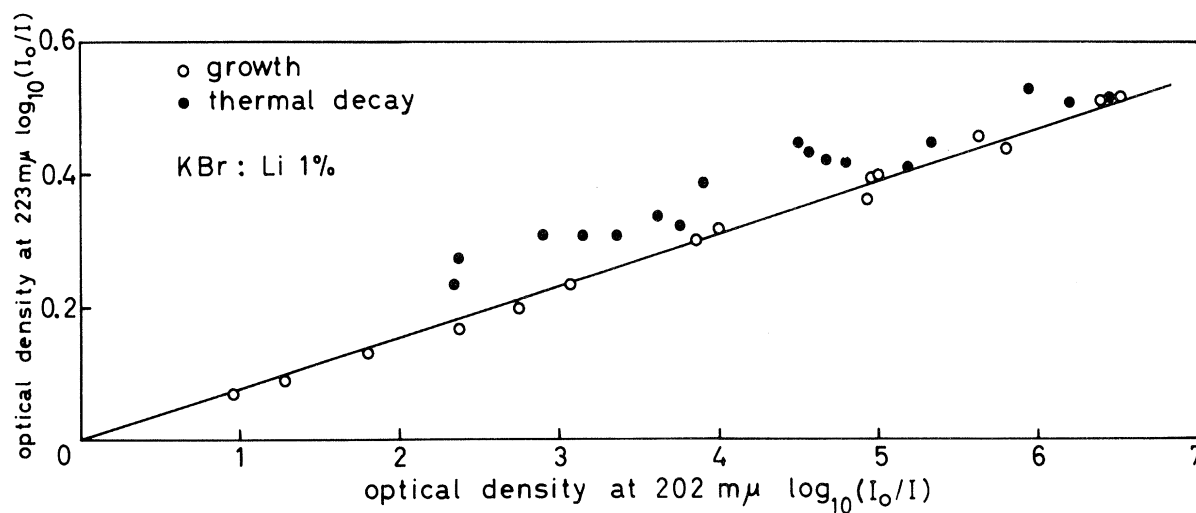

FIG. 9. Relation between the α and the 223-mμ band in a lithium-doped (1%) KBr sample during the x irradiation at 80 °K (open circles) and the subsequent thermal decay (full circles).
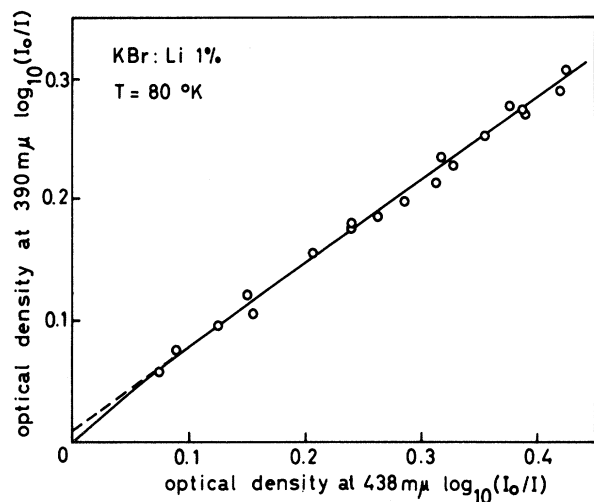
FIG. 10. Relation between the 390- and 438-mμ band in a lithium-doped (1%) KBr sample during the x irradiation at 80 °K.
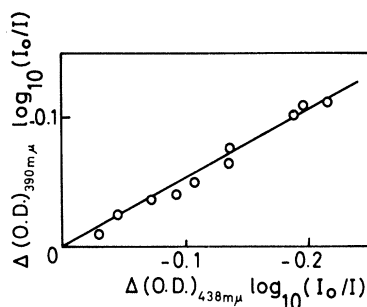

FIG. 12. Relation between the decreases of the 390- and 438-mμ bands during the thermal decay occurring above 195 °K in a lithium-doped (1%) KBr sample x rayed at 80 °K.

by a factor of about 17 and enhance the average F-center production efficiency by a factor of about 2.7.[14] The enhancement of the anion-vacancies production is accompanied by the growth of three absorption bands (at 223, 390, and 438 mμ) not observed in pure samples (Fig. 8). Moreover, while the pure samples exhibit the V_4-band envelope with a peak at 278.5 mμ, the lithium-doped samples show a (composite) band peaking at 307.5 mμ (Fig. 8).

2. α-Center–Interstitial-Halogen Ion Pairs

The proportionality between the α and the 223-mμ band observed during the x irradiation (Fig. 9) suggests that the 223-mμ band might be due to interstitial-bromine ions created in pairs with

α centers and stabilized by lithium impurities. This assignment seems reasonable in spite of the shift of the 223-mμ band with respect to the I band in pure KBr,[15] and in spite of the fact that the proportionality between the α and the 223-mμ band does not seem to be maintained during the warming of the sample (Fig. 9). Generally speaking, the shift of the I (Li) band can be understood on the basis that the environment of the lithium-trapped interstitial is highly perturbed by the presence of the small Li$^+$ ion. On the other hand, the breakdown of the linear relation between the α and the I (Li) band during the warming of the sample (Fig. 9) may be due to the growth of some other band overlapping the I (Li) band. (A similar result occurs also in KBr: Na above 140 °K; see Paper I.)

The thermal decay of α centers in KBr: Li is shown in Fig. 5 (upper curve). It takes place in two main stages. The first one occurs in the same temperature range in which interstitial-halogen ions are released by sodium impurities
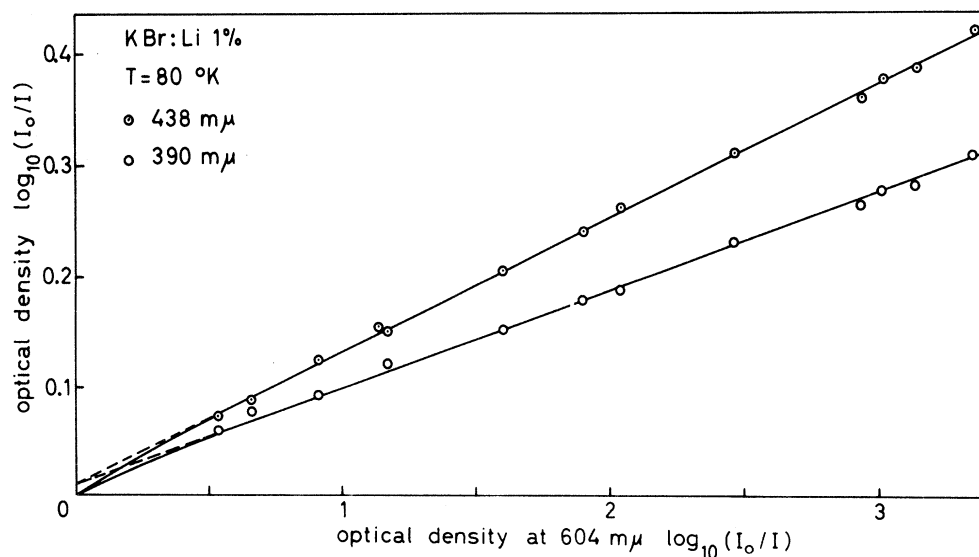

FIG. 11. Relation between the 390- and 438-mμ bands and the F band in a lithium-doped (1%) KBr sample during the x irradiation at 80 °K.

(Fig. 5, lower curve and Sec. III A 2). This co-incidence, however, is accidental. In fact, though some sodium impurities may be present in lithium-doped samples, their concentration cannot be so high as to be responsible for as much as $\frac{1}{3}$ of the stabilized interstitials. [Otherwise, the α-center production efficiency of the pure sample should be about $\frac{1}{3}$ that of the lithium-doped sample; but this is not observed (Fig. 7).] Therefore, we are led to suggest that the first stage of the upper curve of Fig. 5 is due mainly to the migration of interstitial-halogen ions loosely stabilized by lithium impurities. The second stage occurs above 195 °K (Fig. 5, upper curve). It has been shown in Sec. III A 2 that though the anion vacancies are not mobile below 190 °K, they migrate at temperatures as high as 250 °K. Unfortunately, we do not know at what temperature the migration of anion vacancies becomes appreciable. Thus, we cannot say what is the contribution of the anion-vacancies migration to the second stage of the upper curve of Fig. 5. As for the contribution of the interstitials migration, since interstitial-halogen atoms trapped at lithium impurities become mobile above 195 °K (see below) interstitial-halogen ions also will be very likely mobile above this temperature. Finally, it should be stressed that, as in the case of the KBr: Na sample (Sec. III A 2), the α-center concentration corresponding to 250 °K in Fig. 5 (upper curve) is overestimated, owing to the $\alpha \rightarrow \alpha_A$ conversion and to the overlapping of the corresponding absorption bands.

3. F and V_1 Centers

Figures 10 and 11 show that during the x irradiation at 80 °K (apart from an initial small curvature[16]) the 390- and 438-mμ bands (Sec. III B 1) are proportional to each other and both of them are proportional to the F band. During the warming of the sample above 195 °K, the decreases of the 390- and 438-mμ bands are proportional to each other (Fig. 12), and both of them are proportional to the decrease of the F band (Fig. 13). However, the percent decrease of the 390- and 438-mμ bands is higher than the corresponding

decrease of the F band (Fig. 3). Finally, the concomitant thermal bleaching of the 390- and 438-mμ bands (Fig. 12) is accompanied by an increase of the 307. 5-mμ band.

The above results show that the behavior of the 390- and 438-mμ bands in KBr: Li is the same (with some differences to be discussed below) as that of the V_1 bands in KBr: Na (Sec. III A 1). Therefore, we are led to the reasonable conclusion that the 390- and 438-mμ bands in KBr: Li are due to interstitial-bromine atoms (H centers) trapped and stabilized by lithium impurities and may, therefore, be referred to as V_1 (Li) bands. This statement deserves some discussion. In fact, as already stressed previously in this paper, there are some differences between the properties of the V_1 (Na) bands and the properties of the V_1 (Li) bands. In particular, in contrast to the behavior of the two components of the composite V_1 band in KBr: Na, the two V_1 bands in KBr: Li seem to have the same thermal stability (Fig. 12). This result, along with the other one which indicates that the two V_1 (Li) bands are proportional to each other during their growth (Fig. 10), introduces the possibility that the two V_1 (Li) bands are due to two different optical transitions of the same center Very recently, this hypothesis has been confirmed by means of dichroic-bleaching measurements.[17] Finally, it is worth stressing that the decrease of the V_1 (Li) bands is accompanied by an increase of the 307. 5-mμ band. This result agrees with the fact that the role played in sodium-doped KBr by the 278. 5-mμ band seems to be transferred in KBr: Li to the 307. 5-mμ band [at least for the x-ray doses used in our measurements (see Fig. 8)].

C. Rubidium-Doped Samples

As shown in Fig. 7, rubidium impurities do not affect the production efficiency of anion vacancies (with or without a trapped electron) at 80 °K. Furthermore, as shown in Fig. 8, x-irradiated samples of KBr: Rb exhibit the same absorption bands shown by samples of pure KBr. In particular, rubidium-doped samples do not show any V_1-type or I-type band.
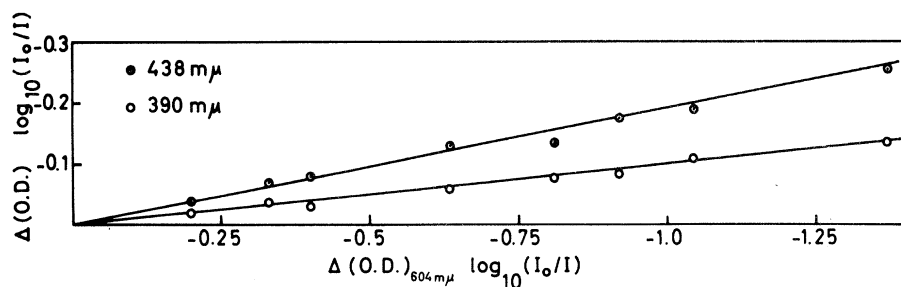

FIG. 13. Relation between the decreases of the 390- and 438-mμ bands and that of the F band during the thermal decay occurring above 195 °K in a lithium-doped (1%) KBr sample x rayed at 80 °K.

IV. CONCLUSION

The data reported in Paper I and in the present paper show that alkali impurities in KBr enhance the anion-vacancies production at 80 °K only if their size is smaller than that of the potassium ion (Secs. III A 1, III B 1, and III C; see, in particular, Fig. 7). This enhancement is very likely due to the trapping and the stabilization by alkali impurities of interstitial-halogen ions and atoms, which in a perfect lattice would recombine with α and F centers, respectively (Secs. III A 1, III

A 2, III B 2, and III B 3). The thermal stability of the trapped interstitials (ions or atoms) depends on the size of the impurity and increases as the size of the impurity decreases.[18] Therefore, we can conclude that the above results not only give further strong support to the hypothesis of interstitial stabilization (Sec. I), but the results are also consistent with a stabilization mechanism based on a reduction of the repulsive forces acting on the interstitial (Sec. I).

*Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche.

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[5]This is true only if lithium ions in KBr, like the sodium ions, are on center. Though theoretical calculations predict lithium to be off center, the available experimental data seem to exclude this possibility. See, for example, G. J. Dienes, Commun. Solid State Phys. 1, 81 (1968), and references therein.

[6]G. Giuliani, Solid State Commun. 7, 79 (1969).

[7]The analysis of these data involves the composite structure of the V_1 band in KBr(Na); see Ref. 10.

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[10]G. Giuliani, Nuovo Cimento 58B, 366 (1968).

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[12]In other words, the V_1-F linear relation breaks down for lightly-doped samples or for strongly doped samples exposed to high radiation doses, which is exactly the same as far as we are concerned with the number of impurities effective in trapping.

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

[14]For the reader's convenience, we have reported in Fig. 7 also the growth curves of a sodium-doped sample. For this sample the average α-center production efficiency is increased by a factor of about 14 and the average F-center production efficiency is increased by a factor of about 2.

[15]G. Kurz and W. Gebhardt, Phys. Status Solidi 7, 351 (1964).

[16]The curvatures in Figs. 10 and 11 are very likely due to the growth and saturation of the V_K and V_1(Na) bands.

[17]M. Saidoh and N. Itoh, Phys. Letters 31A, 68 (1970); M. Saidoh and N. Itoh (private communication) have also found that the V_1(Li) centers can be converted into I(Li) centers by electron capture. This result supports the models proposed above for the two centers.

[18]In fact, from Fig. 3 we can see that V_1(Li) centers are more stable than V_1(Na) centers, i.e., that lithium-trapped interstitial-halogen atoms are more stable than those trapped by sodium. A similar conclusion concerning interstitial-halogen ions can be drawn from the thermal-decay curves for the α band reported in Fig. 5, taking into account the fact that the thermal destruction of α centers is due mainly to the migration of the interstitials (Secs. III A 2 and III B 2).