PHYSICAL REVIEW B VOLUME 12, NUMBER 4 15 AUGUST 1975

Temperature dependence of Frenkel-pair production from *F*-aggregate center destruction*

Edward Sonder
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830
(Received 29 August 1974)

Measurements of the radiation destruction of *F*-aggregate centers between 70 and 250 K have yielded values for the primary-Frenkel-pair production efficiencies in NaCl, RbCl, KBr, and KI as a function of temperature. The so far unexplained increase in production efficiency with temperature originally demonstrated for KCl has also been observed in these materials, and has been found to be only a slight function of the species of cation, but a strong function of anion species making up the alkali halides. The apparent agreement between the activation energy obtained for KBr in these measurements and pulsed radiolysis measurements is discussed, and a problem concerning previously proposed explanations is indicated. In addition, the very strong temperature dependence previously observed in KI and attributed to the disappearance of luminescence has been observed and correlated with the thermal quenching of the 3.31-eV component of the fundamental luminescence.

I. INTRODUCTION

Although there now is general agreement concerning the basic mechanism of defect production by radiolysis in alkali halides,[1,2] some aspects of the processes involved are still not understood. In particular, the temperature dependence of defect production includes an increase of production efficiency with temperature,[3–5] which for[5] KCl has been shown to be more than a factor of 20 over the temperature range 100–250 K. Explanations in terms of dissappearance of luminescence[6] or onset of defect mobility do not satisfactorily account for these results, and it has been suggested by one investigator[5] that the attractive potential between vacancy-interstitial pairs gives rise to this temperature dependence, and by others[7] that it is due to motion of *H* centers in the excited state, immediately after the production event.

An increase of stable *F*-center production with temperature has been observed in a number of alkali halides between liquid-nitrogen (LNT) and dry-ice temperature.[3–5] However, it has been difficult to separate behavior due to the primary-Frenkel-defect production mechanism from that due to secondary reactions involving mobile defects. Two techniques, used only recently, permit the observation of the primary-Frenkel-pair production efficiency. In one, short pulses of electrons or γ rays make possible the measurement of the *F*-center concentration soon enough after defect production to preclude some secondary reactions. This technique has been applied to KBr.[7] In the other, *F*-aggregate center destruction by radiation-produced interstitials is observed, and from the destruction rates, Frenkel-pair production efficiencies can be computed. This latter technique has previously been applied to KCl.[5] It also has been used in this work to measure the Frenkel-pair production efficiencies as a function of temperature in NaCl, RbCl, KBr, and KI. These results, along with earlier ones for KCl, make it possible to see how the increase of production efficiency with temperature depends upon cation and anion species.

II. EXPERIMENTAL TECHNIQUES AND TREATMENT OF DATA

A detailed description of the experiment has been given previously.[5] *F* and *F*-aggregate centers are first introduced into the alkali halide at room temperature by irradiating thin samples (~ 0.05 cm) with 2-MeV electrons. This ensures a fairly uniform deposition of energy and results in a defect distribution that is uniform to better than 90%. Then the *F*-aggregate centers are annihilated by irradiating at a variety of temperatures between 70 and 250 K. Within that temperature range only interstitials are mobile,[8] so that no new *F*-aggregate centers are formed by vacancy motion, and the *F*-aggregate center destruction rate dN_A/dt can be described by the rate equation

$$\frac{dN_A}{dt} = -\alpha\dot{\epsilon}\,p_A N_A \bigg/ \left(\sum p_i N_i + p_A N_A + p_F N_F\right), \quad (1)$$

where the subscripts A, i, and F refer to *F*-aggregate centers (chiefly F_2 and a few F_3 centers), interstitial traps (impurities, interstitial cluster, etc.), and *F* centers, respectively; and where $\dot{\epsilon}$ is the rate of energy introduced by the radiation in eV/sec; α is the Frenkel-pair production efficiency in defects/eV; p is the trapping (or recombination) probability of interstitials with species A, i, or F; and N is the number of centers per unit volume. In all of these experiments the most numerous defects present are *F* centers, so that the sum and aggregate center terms in the denominator can be considered small in relation to $p_F N_F$. This makes it possible to write the approximate expression

$$-\ln\left(\frac{N_A}{N_A(t=0)}\right) \approx \alpha\frac{p_A}{p_F}\int_0^t \frac{\dot{\epsilon}dt'}{N_F}\,, \qquad (2)$$

in which only the term $\alpha p_A/p_F$ is not a measured quantity. The trapping and recombination probabilities p_A and p_F contain the diffusion coefficient for interstitials and the interaction radius for interstitials with aggregate and F centers, respectively.[9] The former cancels in the ratio and the latter may be estimated from the relative size of aggregate and F centers. We have assumed $p_A/p_F = 2$ in previous work[5] and will do likewise here, even though a smaller value (between 1 and 2) may be more reasonable.

For most of the samples N_F varied less than 10% during experimental runs, so that plotts of $\ln N_A$ vs $\dot{\epsilon}t/N_F$ could be used to yield values of $\alpha p_A/p_F$ from the slope. However, for RbCl and KBr the F-center concentrations grew significantly during the aggregate center decay experiments, so that plots of $\ln N_A$ vs $\sum_j \dot{\epsilon}t_j/(\bar{N}_F)_j$, had to be used.[10] In using this expression the sum was taken over the approximately seven separate irradiations that made up an experimental run and $(\bar{N}_F)_j$ was the average of the measured values before and after the jth irradiation. More accurate graphical integrations indicated that errors due to these procedures were only (2–3)% and were negligible compared to the imprecision of determining absorption band heights. This imprecision was as much as 25% at times, particularly during the last few measurements of some of the runs, for which the optical density at the peak of the F-aggregate bands had decreased to values less than 0.03.

Uncertainty in temperature also contributed to the scatter of data. Even though a platinum resistance thermometer made it easy to measure the temperature of the sample holder to better than $\frac{1}{2}$ K, impinging radiation caused the sample to become warmer than the sample block, and moreover caused a slow saturating temperature rise which varied from run to run. On the basis of these observations it would appear that the temperatures were uncertain to ± 3 K.

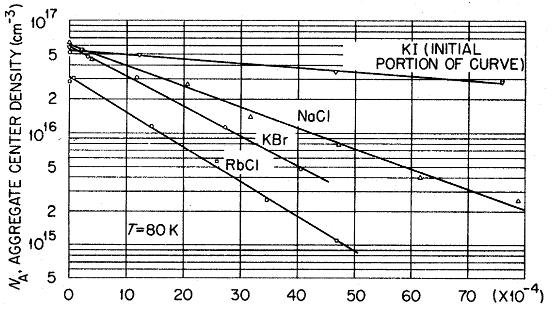

FIG. 1. Radiation destruction of aggregate centers at 80 K in a number of alkali halides. N_A is a measure of aggregate-center density, and is plotted vs the sum of the dose of each irradiation divided by the average F-center concentration during that irradiation. For KI and NaCl for which the F-center concentration varied only slightly, N_A is plotted vs $\dot{\epsilon}t/N_F$ (see text).

Figure 1 is a plot of typical data. It depicts the radiation caused F-aggregate center decrease in four alkali halides at 80 K. The abcissa scale is $\sum_j \dot{\epsilon}t_j/(\bar{N}_F)_j$ for RbCl and KBr, as discussed above, and simply $\dot{\epsilon}t/N_F$ for NaCl and KI. It may be noted that the F-center concentration appears in this expression, and that therefore the constant used to compute N_F from the measured optical densities can contribute to a systematic error. Table I gives oscillator strengths, halfwidths, and refractive indices used in the Smakula equation to relate N_F to absorption coefficient $\alpha = 2.303A/\delta$ (where A is the absorbance at the F-band peak and δ is the sample thickness). Oscillator strengths are difficult to measure and may be accurate to no better than 25%. This is particularly true for KI, for which the only measured value[11] appears to be anomalously low.

In Table I are also shown the constants used to estimate N_2 and N_3 from the heights of the M and R_2 bands of the F_2 and F_3 centers, respectively. Since aggregate band oscillator strengths have in general not been determined, these constants were estimated as described in the appendix of Ref. 5. Fortunately the value of these constants is of only small importance, since in plots similar to those shown in Fig. 1 it is the $\log_{10}$ of N_A that is plotted on the ordinate; and errors in the constants used to calculate N_2 and N_3 will partially cancel when the slope of such a curve is determined. Although, as shown earlier,[5] it makes only a small difference in the values of the slopes whether N_2 or $(N_2 + 3N_3)$ is taken as a measure of the aggregate center density, we have chosen the latter for consistency with the earlier work[5] and because, as discussed in that work, it appeared to be somewhat more justified.

III. RESULTS

The slopes of curves such as those depicted in Fig. 1 (with the assumption that $p_A/p_F = 2$) have been used to calculate values of α^{-1} (energy necessary to produce a Frenkel pair). These are shown as $\log_{10}\alpha^{-1}$ vs T^{-1} in Figs. 2 and 3. Figure 2 is a comparison of chlorides having different cations; data for KCl have previously been published[5]; the curves are included for comparison; KCl data points have been omitted for clarity. Figure 3 is a comparison of potassium salts of different halides. The KCl curves are also included there. The most noteworthy result demonstrated by these data is that the cation appears to have little effect on the magnitude of the temperature dependence (activa-

TABLE I: Constants used to calculate defect densities from absorption spectra.

	F band					F_2-center band		F_3-center band	
Compound	Oscillator strength(f_g) (assuming Gaussian band)	Ref.	Half-width[a–c]	Refractive index (n)	N/α[d] (cm^{-2})	Half-width[b,c]	N/α (cm^{-2})	Half-width[b,c]	N/α (cm^{-2})
NaCl	0.54	e, f	0.27	1.56	3.5×10^{15}	0.085	1.6×10^{15}	0.10	2.1×10^{15}
RbCl	0.54	assumed	0.19	1.49	2.5×10^{15}	0.065	1.3×10^{15}	0.065	1.4×10^{15}
KCl	0.56	g, h	0.198	1.494	2.5×10^{15}	0.07	2.0×10^{15}	0.06	1.4×10^{15}
KBr	0.54	i	0.21	1.56	2.7×10^{15}	0.065	1.2×10^{15}	0.09	1.9×10^{15}
KI	0.43	j	0.21	1.68	3.3×10^{15}	0.08	2.0×10^{15}	0.08	2.2×10^{15}

[a] Reported values for NaCl vary between 0.28 and 0.41; for KBr between 0.19 and 0.30; for KI between 0.19 and 0.26; see W. D. Compton and H. Rabin, in *Solid State Physics* edited by F. Seitz and D. Turbull (Academic, New York, 1964), Vol. 16, p. 126.

[b] Estimated from spectra.

[c] Halfwidths ($W_{1/2}$) measured at liquid-nitrogen temperature.

[d] Calculated from formula: $N = 0.87\times10^{17}\,[n/(n^2+2)^2]\,(W_{1/2}\alpha/f_g)$. See, for example, D. L. Dexter, *Solid State Physics* edited by F. Seitz and D. Turnbull (Academic: New York, 1958), Vol. 6, pp. 355–395.

[e] H. Pick, Ann. Phys. (Leipz.) 31, 365 (1935).

[f] R. H. Silsbee, Phys. Rev. 103, 1675 (1956).

[g] E. Sonder, Phys. Rev. 125, 1203 (1962).

[h] F. G. Kleinschrod, Ann. Phys. (Leipz.) 27, 97 (1936).

[i] W. T. Doyle, Phys. Rev. 111, 1072 (1958).

[j] The only measured value for the F-band oscillator strength in KI appears to be anomalously low: $f_g(\mathrm{KI}) = 0.31$ (Ref. 10) as compared to $f_g \sim 0.5$ for other halides. Consequently, a value of 0.43 ± 0.12 was chosen.

tion energy), whereas the temperature dependence becomes progressively smaller as one goes from smaller to larger anions. Table II is a summary of the slopes of the linear portions of the curves of Figs. 2 and 3, given as activation energies.

The data for KI in Fig. 3 are limited to temperatures above 110 K in order to prevent confusion. The whole curve for KI is given in Fig. 4, where it is evident that another, very steep, decrease in production efficiency occurs as the temperature is lowered from 100 to 70 K. This latter decrease, which goes over almost three orders of magnitude, as compared to the approximately 1½ orders or less indicated in Figs. 2 and 3, has a slope that corresponds to an activation energy of 0.15 eV. Pooley and Konitzer *et al.*[6] have suggested that the large temperature dependence of color-center production efficiency observed in iodides is related to a thermal quenching of the fundamental luminescence. The present data make it possible to confirm this. In the inset of Fig. 4 the ratio of Frenkel-pair production as obtained from the solid curve of Fig. 4 to that predicted by extrapolating to lower temperatures along the straight dashed line of Fig. 4 is drawn, as is the ratio of the luminescence intensity emitted at 3.31 eV to that emitted in the 3.31 eV band at low temperature. The latter data were obtained from the work of Ikezawa and Kojima.[12] There is some uncertainty in the exact shape of the curve of Fig. 4 between the data points at $1000/T = 9$ and 11½ (and therefore in the "defect production" curve of the inset). Also there is some uncertainty in the "luminescence" curve of the inset due to difficulty in reading intensity values from the published figure.[12] Nevertheless, it is clear that the two curves drawn in the inset are complementary. As drawn, their sum varies between 1.1 and 1.2. It is also possible to compare the activation energy derived from the slope of Fig. 4 with the published activation energy for thermal quenching of luminescence. The former is 0.15_5 eV; the latter is 0.132 eV.[12] Agreement between these two values is better than it first appears when it is realized that the value derived from the low-temperature portion of Fig. 4 should be interpreted as the sum of the activation energies of two processes. These are the thermal quenching of luminescence with an activation energy of 0.132 eV, and the unknown process that is the main subject of this

TABLE II: Activation energies for temperature dependence of Frenkel-pair-production process.

Material	Activation energy[a] (eV)	Temperature range (K)
NaCl	0.07_9	130–220
RbCl	0.06_5	150–220
KCl	0.07_5	140–250
KBr	0.03_2	80–200
KI	0.01_5	110–170
	0.15_5	80–100

[a] Slope of $\log_{10}$ production rate vs $1/T$ multiplied by 1.98×10^{-4} eV K^{-1}.

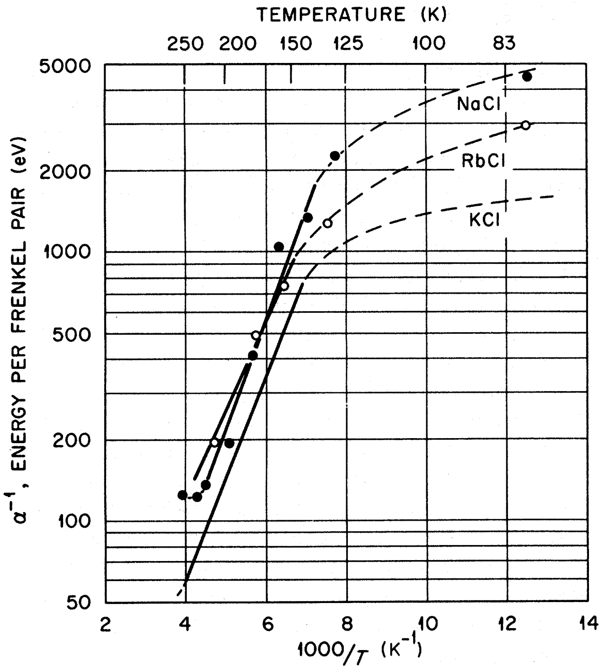

FIG. 2. Reciprocal of Frenkel-pair-production efficiency for chlorides with different cations vs reciprocal temperature. The best estimates for straight lines through the linear portion of the experimental points are shown as heavy solid lines and are compared with a curve for KCl, published previously (Ref. 5).

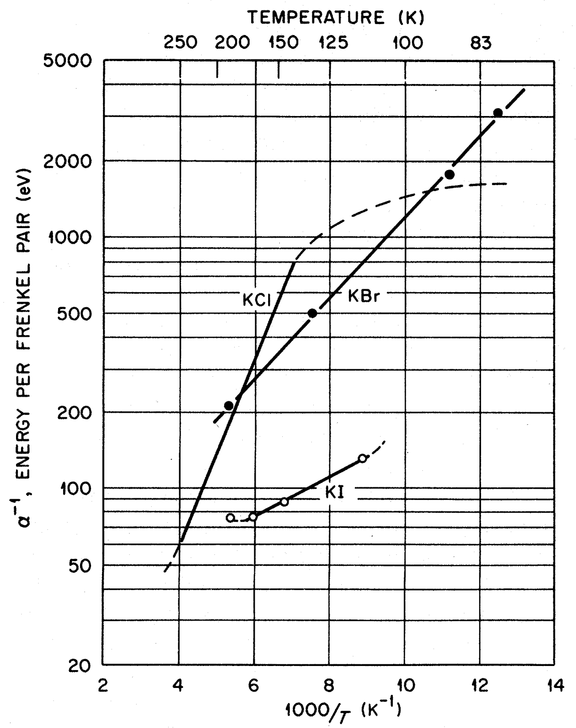

FIG. 3. Reciprocal of Frenkel-pair-production efficiency for potassium halides vs reciprocal temperature. Heavy solid lines are drawn for linear portions of curves. A curve for KCl is included for comparison.

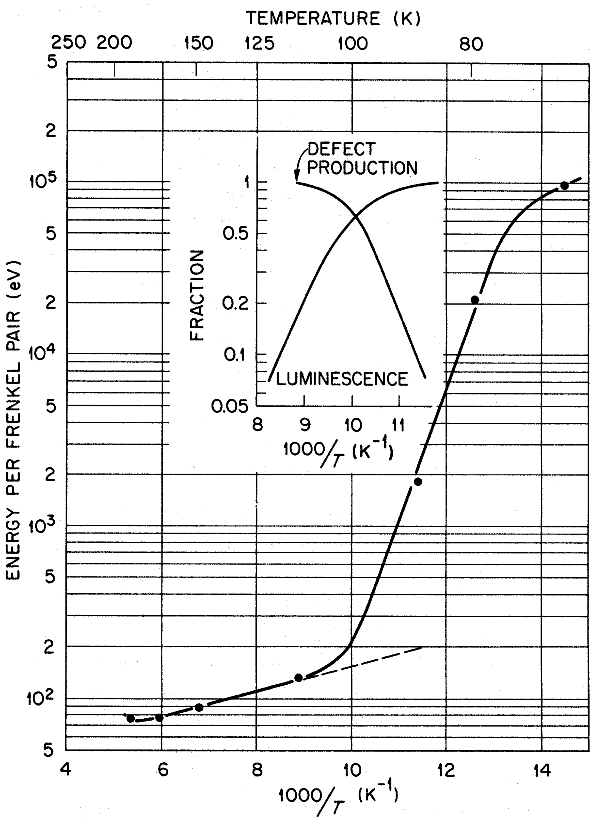

FIG. 4. Temperature dependence of reciprocal Frenkel-pair-production efficiency for KI, showing both the slow increase in production efficiency between 110 and 170 K and the rapid rise between 80 and 100 K. In the inset, labeled fraction and plotted on the same reciprocal-temperature scale, are the fraction of the maximum luminescence intensity, observable at a given temperature, (labeled luminescence) and the ratio of the production efficiency (so labeled) depicted by the solid curve below it to that of the dashed straight-line extrapolation of the higher-temperature linear portion of the solid curve.

work, for which the high-temperature-portion of Fig. 4 has yielded an activation energy of 0.01_5 eV.

IV. DISCUSSION

The experiments described here show that the increase in defect production efficiency with temperature, originally discussed for KCl is not unique to that material. Moreover, the analysis used, both here and earlier,[5] suggests that the effect is not related to secondary processes involving diffusion and recombination of defects. Thus, this temperature dependence must be due to a step in the following chain of events that make up the primary production mechanism: (a) initial excitation or ionization of the halide; (b) transfer of excitation energy to a collision sequence (first part of the Pooley-Hersch mechanism); (c) separation of defects via a collision sequence and stabilization (second part of the Pooley-Hersch mechanism). It appears unlikely that (a) is temperature dependent. It will be shown in Sec. IV A that the temperature dependence that is due to (b) appears to be limited to a narrow temperature range in iodides and is not the effect we are chiefly concerned with here. Thus it appears probable that the temperature dependence documented here is connected with the interstitial-vacancy separation process (c). In Secs. IV B and IV C, two suggestions made previously are described, and in Sec. IV D one reason is given for not taking the details of these suggestions too seriously.

A. Correlation of temperature dependence of fundamental luminescence and defect production

As discussed in connection with Fig. 4 the correlation existing between the temperature dependence of defect production and thermal quenching of luminescence in KI can be demonstrated. Ikezawa and Kojima[12] have also published data on the temperature dependence of luminescence intensity for all of the other materials discussed here and it can be clearly stated that for these no correlation exists between the luminescence data and the temperature dependence of defect production. A similar result has recently been obtained for NaCl by Karasawa and Hirai.[13] It thus appears that these more recent data are not in complete agreement with the conclusions of Hughes *et al.*[14] These authors found, on the basis of a survey that included data only for a few temperatures (including the liquid-nitrogen and dry-ice points but no temperature inbetween), that an increase in defect production efficiency and a decrease in luminescence intensity occurred in many alkali halides as the temperature was raised. From that they concluded that the increased production efficiency with temperature was in general due to the thermal quenching of luminescence. It is now clear that more detailed data, as for example those reproduced here in Fig. 4, are necessary to demonstrate correlation, and that the conclusion reached by Hughes *et al.* may apply only to iodides, and that even for these an additional temperature dependent process may be observed.

B. Excited-state diffusion model

Saidoh *et al.*[7] have measured the temperature dependence of the relative production of free and impurity trapped interstitials by measuring the ultraviolet light absorption in the H-band region 200 nsec after an irradiation pulse in KBr. They have interpreted their results in terms of a temperature-dependent interaction volume v between the impurity ions, and the replacement collision chain that is a part of the defect production process

$$v=s(l_0+l_1 e^{-E/kT}), \tag{3}$$

where s is the cross-sectional area of interaction of a collision sequence and l_0 and $l_1 e^{-E/kT}$ are, respectively, temperature-independent and -dependent path lengths of the collision sequence. For KBr they found the temperature dependence to be described by an activation energy, $E = 0.025$ eV over the temperature range 78–200 K. Since this activation energy is far smaller than that of thermal H-center annihilation (0.09 eV) they suggested that the length of the collision sequence depends upon diffusion of an H center in an excited state.

It should be pointed out that the primary production process defined by this experiment includes everything taking place in less than 200 nsec, whereas anything happening thereafter is considered a secondary reaction. This 200-nsec time is as valid a way of defining primary and secondary processes as any other. However, some care is necessary in comparing different experiments where the definitions may be different, as we shall see below.

C. Vacancy-interstitial interaction model

An attractive potential between an interstitial and vacancy has been suggested as the cause of the increasing defect production efficiency with increasing temperature in KCl.[5,15] On the basis of this model it is thought that a distribution of vacancy-interstitial separation distances results from the production process, and that those pairs that are close together and tightly bound will recombine whereas those farther apart will have a higher probability of separation by diffusion of the interstitial. The temperature dependence then stems from the fact that the ratio of probability of separation to recombination, P_s/P_r depends upon the difference in heights of the separation and recombination barriers, i.e., $P_s/P_r \propto \exp[-(E_s-E_r)/kT]$. The over-all effect of this is an exponential temperature dependence, the activation energy parameter of which is related to the interaction potential between vacancies and interstitials.

It is important to keep in mind that the "primary process" as defined by the aggregate center destruction experiments is not necessarily the same as that defined for the pulsed radiolysis measurements. As can be seen from Eq. (1), any temperature dependence cannot come from the temperature dependence of free diffusion of interstitials since the interstitial diffusion coefficient of necessity cancels in the ratio p_A/p_F. In other words, the "primary process" as defined by the aggregate-center destruction experiments consists of everything that happens during the time the members of a newly created interstitial-vacancy pair are within each others field, but does not include any free diffusion of interstitials, irrespective of whether these are in an excited or ground state. Any free diffusion is considered a secondary process whose temperature dependence is not observed.

D. Results for KBr

The results presented here for KBr and those of Saidoh *et al.*[7] yield approximately the same temperature dependence (activation energy). Aggregate center destruction experiments performed by Guillot and co-workers[16] are in even closer agreement with the results from pulsed radiolysis experiments. If indeed we assume that the two different types of measurements reflect the same temperature-dependent limiting step in the production process, we are led to some real difficulties with respect to the models discussed above. In particular, on the basis of these models, the aggregate center destruction experiments should reflect no free diffusion, whereas the pulsed radiolysis experiments should reflect interstitial diffusion in the excited state plus any vacancy interstitial interaction if present. It is difficult, in the absence of any information of time of propogation of the collision sequence, lifetime of the H-center excited state, range of vacancy interstitial interaction potential, etc., to decide if either or both of the above ideas are realistic or not. Perhaps it would be helpful to check first whether the agreement in activation energy observed for KBr is fortuitous, or if, in fact, the two types of experiments discussed here yield similar activation energies for other alkali halides.

V. SUMMARY

(a) Measurements of aggregate center destruction have yielded values for the primary production efficiency and its temperature dependence (activation-energy of the rate limiting process) for a number of alkali halides.

(b) The activation energy is only slightly dependent on the cation species in the series NaCl, KCl, RbCl, but depends strongly on the anion species in the series KCl, KBr, KI.

(c) In KI, but not in the other compounds discussed here, an additional temperature dependence is observed. This dependence can be correlated with thermal quenching of the fundamental luminescence. The two temperature dependences in KI can be resolved.

(d) The activation energy derived from aggregate center destruction in KBr is in reasonable agreement with that observed in the same compound by pulsed radiolysis. It is difficult to reconcile that agreement with the two suggestions made previously to account for the observed temperature dependence.

ACKNOWLEDGMENTS

I am grateful to N. Itoh for sending me his recent works in preprint form and to G. Guillot for informing me about his and those of his co-workers. The assistance of O. E. Schow and L. C. Templeton in maintaining and on occasion operating the electron accelerator used for this work is also gratefully acknowledged.

---

*Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corp.

[1] D. Pooley and W. A. Runciman, Solid State Commun. 4, 351 (1966).

[2] H. N. Hersch, Phys. Rev. 148, 928 (1966).

[3] J. D. Comins, Phys. Status Solidi 33, 445 (1969).

[4] E. Sonder, Phys. Rev. B 2, 4189 (1970).

[5] E. Sonder, Phys. Rev. B 5, 3259 (1972).

[6] J. D. Konitzer and H. N. Hersch, J. Phys. Chem. Solids 27, 771 (1966); D. Pooley, Proc. Phys. Soc. Lond. 87, 245 (1966).

[7] M. Saidoh, J. Hoshi, and N. Itoh, Solid State Commun. 13, 431 (1973); N. Itoh and M. Saidoh, J. Phys. (Paris) 34, C9-101 (1973).

[8] E. Sonder and W. A. Sibley, in *Point Defects in Solids*, edited by J. H. Crawford, Jr. and L. M. Slifkin (Plenum, New York, (1972), Chap. 4.

[9] See, for example, A. C. Damask and G. J. Dienes, *Point Defects in Metals* (Gordon and Breach, New York, 1963), p. 79.

[10] It should be pointed out that in previous work with KCl the variation of F-center concentration in some of the lead-containing samples (the F-center concentration was constant for the pure samples) was not taken into consideration causing the 100-ppm-Pb curve of Fig. 9 (Ref. 5) to be about 30% too low.

[11] C. J. Rauch and C. V. Heer, Phys. Rev. 105, 914 (1957).

[12] M. Ikezawa and T. Kojima, J. Phys. Soc. Jpn. 27, 1551 (1969).

[13] T. Karasawa and M. Hirai, J. Phys. Soc. Jpn. 34, 276 (1973).

[14] A. E. Hughes, D. Pooley, H. U. Rahman, and W. A. Runciman, Atomic Energy Research Establishment, Harwell, report (unpublished); a portion of that work appears in D. Pooley and W. A. Runciman, J. Phys. C 3, 1815 (1970).

[15] E. Sonder, J. Phys. (Paris) 34, C9-32 (1973).

[16] G. Guillot, A. Nouailhat, and P. Pinard, Paper presented at International Conference on Color Centers, Sendai, Japan, 1974 (unpublished).