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Temperature Dependence of *F*-Center Production and Aggregation in NaCl[†]

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The temperature dependence of the vacancy production rate and of the *F*-aggregate-center equilibrium ratio has been measured for electron-irradiated NaCl. The onset of the dose-rate dependence has also been observed. Temperatures obtained from these measurements are compared with the thermal annealing temperature of self-trapped holes and with the temperature at which *F*-aggregate centers form spontaneously in the dark. The maximum vacancy production efficiency occurs near 210 °K; the dose-rate dependence can be observed above 175 °K. These temperatures are significantly below 260 °K at which aggregation occurs. Thus different processes appear to be rate controlling for radiation-defect production on one hand and aggregation on the other. The results support the suggestion that electron-hole recombination at non-defect-producing sites limits defect production at temperatures at which holes are mobile. They also support the idea that aggregate-center formation in the presence or absence of irradiation is determined by motion of *F*⁺ centers.

INTRODUCTION

When KCl is irradiated in the vicinity of room temperature, both the rate of defect production and the *F*-center-*F*-aggregate-center equilibrium depend upon trace impurities,^{1,2} irradiation temperature,^{3,4} and dose rate.^{5,6} It is tempting to try to find a common explanation for the room-temperature defect-production behavior and *F*-center aggregation. The suggestion has been made that mobile negative-ion vacancies (*F*⁺ centers⁷) are involved in defect annealing during irradiation⁴; it also appears probable that these mobile negative-ion

vacancies cause *F*-center aggregation. Recent studies^{8–12} have shown that in a number of alkali halides, *F*⁺ centers become mobile in an experimentally convenient temperature range, between 200 and 300 °K. Thus the study of the temperature dependence of *F*-center production and of *F*-center aggregation appears a very attractive method of testing the thesis that both the net *F*-center production rate and the aggregation are determined by *F*⁺-center mobility.

Several experiments have been performed, mainly with KCl. Comins and Wedepohl¹³ have reported that the production rate for *F* centers increases with

temperature up to approximately 210 °K and then drops as room temperature is approached. It is usually assumed that a dose-rate dependence, present at room temperature and absent at 80 °K, begins in the same range of temperature as that where the maximum production rate occurs. Aggregation of F centers to form F_2 (or M) centers has been measured as a function of temperature both by warming irradiated KCl in the dark⁸⁻¹⁰ and by observing the radiation equilibrium between F and F_2 centers.^{14,15} In all these experiments the concentration of aggregates increases rapidly in the temperature range 220–280 °K.

If the F^+ center were the only defect to become mobile near 200 °K, there would be no difficulty in interpreting the above results. Unfortunately, in KCl, the material for which almost all these measurements have been made, the self-trapped hole becomes mobile just below 200 °K, so that explanations based upon hole mobility may be equally valid. In fact, Pooley has suggested¹⁶ that the decrease of F -center production efficiency in KCl and KI as room temperature is approached is due to short circuiting of the primary production mechanism when radiation-produced electrons and holes can both move to impurity sites to recombine without producing defects. This short circuiting is frozen out at low temperatures where holes are self-trapped.

It is easier to decide which one of the above-mentioned mobile defects (holes or F^+ centers) is the pertinent one if measurements are made for a material in which these two defects become mobile at more widely differing temperatures than they do in KCl. Dawson and Pooley¹² have reported that in KI, where the hole becomes untrapped near 100 °K¹⁷ but the F^+ center is stable to 240 °K, the F -center production efficiency decreases with temperature significantly below 200 °K. NaCl is another alkali halide in which holes become mobile at significantly lower temperatures than do F^+ centers.^{10,18,19} Measurements at low dose rate of the initial (first stage) F -center production efficiency^{20,21} suggest that the maximum occurs at temperature not too different from that at which F^+ centers become mobile. In an attempt to clarify this apparent difference between KI and NaCl, we have performed a number of irradiation and annealing experiments on NaCl irradiated into the "intrinsic" late stage.

EXPERIMENTAL PROCEDURES

Three types of experiments were performed. The first consisted of measuring the total negative-ion vacancy concentration resulting from electron irradiation at a number of temperatures. To do this, a cryostat was used in which the sample holder was connected to a refrigerant bath by a stainless-steel tube which could either be electrically heated

to raise the sample temperature above that of the refrigerant or be filled with refrigerant to cool the sample rapidly. Production curves were obtained by alternately irradiating at a given temperature in the dark, then cooling and measuring the absorption spectra. A maximum energy deposition rate of 6×10^{18} eV/cm³ sec was used. This was measured in an auxiliary experiment with an isolated dummy sample, the heating rate of which was determined during irradiation.

In the temperature range of interest not only F centers are produced, but F^- centers and probably F^+ centers as well. The F^- centers give rise to a broad absorption band (F' band) below the F band; the area and height of this band can be estimated by curve fitting, using parameters given in the literature.²² We found that an appreciable fraction of F^- (and presumably an equal number of F^+ centers²³) could be converted to F centers by bleaching in the Cary spectrophotometer with 560-nm light while the sample was held at a temperature between 150 and 240 °K. The ratio of the decrease of F^- band to the increase of F band ($-\Delta\alpha^-/\Delta\alpha$) appeared to be independent of F -center concentration, irradiation conditions, and bleaching temperature, so that we felt confident that the bleaching simply rearranged electrons, moving them from F^- to F^+ centers. Moreover, from the ratio ($-\Delta\alpha^-/\Delta\alpha$) we could estimate how many vacancies were represented by a given height of F^- band. Once we knew how many vacancies corresponded to a given F^- -band height, it became unnecessary to bleach the F^- band completely after every irradiation. The constants we used to obtain the total²³ vacancy concentration n produced by the irradiations are as follows:

$$n = 4.1 \times 10^{15} \alpha + 1.2 \times 10^{16} \alpha^- ,$$

where α and α^- are the absorption coefficients at the peak of the F and F^- bands, respectively, measured at 145 °K. For irradiation near room temperature, where F_2 centers were produced, we included these aggregated vacancies as well.

The reason for measuring the total vacancy concentration rather than simply the fraction that was in the form of F centers was that we wanted to observe not only the slope and shape of the production curves, but also the temperature of onset of a dose-rate dependence. Since the electron distribution among the vacancies may be affected by the dose rate (and we indeed noticed this to be the case), the neglect of any one of the vacancy charge states would have produced a false indication of dose-rate dependence.

The second type of experiment consisted of a series of isochronal anneals after irradiation at 140 °K with measurement of F_2 -band heights after every heat pulse. Annealing times of 15 min at

each temperature were used. The optical measurements were performed at 140 °K.

In the third type of experiment the steady-state ratio during irradiation, $\alpha_2/(\alpha_1)^2$, where α_2 and α_1 refer to F_2 - and F -band absorption, respectively, was measured as a function of temperature. To ensure that we actually measured the radiation steady state and not an aggregation condition attained thermally after the end of the irradiation, the samples were quenched to a lower measuring temperature within a few seconds of cessation of irradiation. Errors due to thermal aggregation could be observed above approximately 260 °K if the samples were held at the irradiation temperature for a few minutes before measuring or cooling.

The samples used for these experiments were commercial NaCl purchased from Harshaw or Isomet Corporation.

RESULTS

A. Vacancy-Production Curves

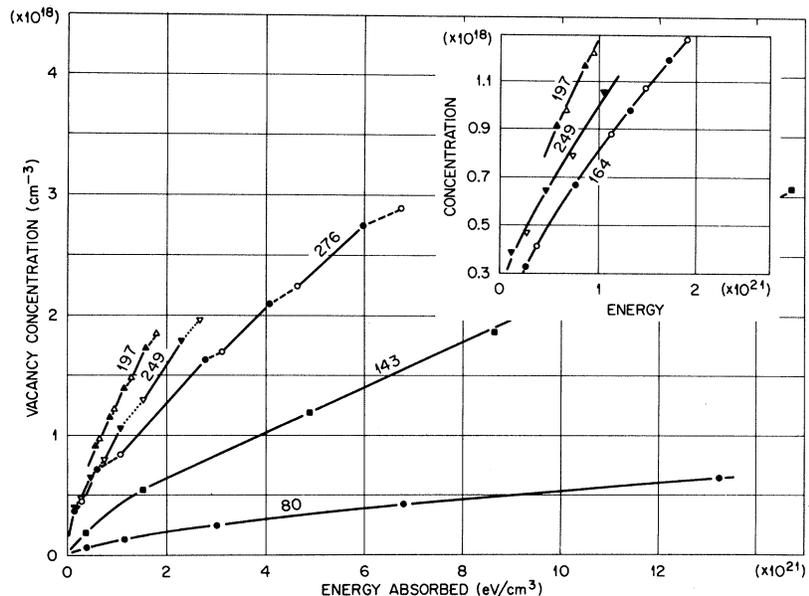
Plots of the number of vacancies produced by electron irradiation are presented in Fig. 1. The curves are labeled with the temperatures in degrees K at which the irradiations were performed. It is clear that the production efficiency increases rapidly with increasing temperature below 200 °K and then decreases above that temperature.

The curves also show the effect of changing the dose rate. The solid portions of the curves and filled point symbols indicate that an irradiation dose rate of 6×10^{18} eV/cm³ sec was used; the open point symbols and broken lines indicate dose rates reduced to $\frac{1}{2}$ (dashed lines) or $\frac{1}{18}$ (dotted lines) of the maximum value. It is evident that above 200 °K

an appreciable dose-rate dependence is present, as indicated by the change in slope (production efficiency) when the dose rate is changed. In order to demonstrate more closely the temperature of onset of this dose-rate dependence, we have expanded parts of the 197 and 249 °K curves in the inset and added data produced by irradiation at 164 °K. In the inset we have drawn smooth curves through the points; it is clear that for 197 and 249 °K all high dose-rate data points (filled point symbols) fall above and all low dose-rate points fall below these curves; however, for irradiation at 164 °K the points fall on the curve with only random scatter, irrespective of the irradiation dose rate. Thus the onset of the dose-rate dependence for NaCl is between 164 and 197 °K.

A clearer picture of the change of production efficiency with temperature and of the onset of dose-rate dependence appears when the slopes of the curves in Fig. 1 (taken for uniformity at the points when 1×10^{18} vacancies have been produced) are plotted versus temperature. This is shown in Fig. 2, where two curves for dose rates of 6×10^{18} and 5×10^{17} eV/cm³ sec have been drawn. The low dose-rate point at 247 °K is an estimate obtained by assuming a production efficiency proportional to dose rate. This was necessary because the actual experimental result, shown dotted, was obtained at a dose rate of 3×10^{17} eV/cm³ sec. The maximum production efficiency (minimum energy per produced vacancy) occurs slightly above 210 °K for the high dose rate and slightly below that temperature for the low dose rate. The dose-rate dependence becomes observable above approximately 175 °K.

FIG. 1. Negative-ion vacancy concentration versus absorbed electron dose. The numbers labeling the curves refer to the temperature during irradiation. Broken lines and open point symbols indicate reduced radiation dose rates; solid lines and filled point symbols indicate the maximum dose rate.



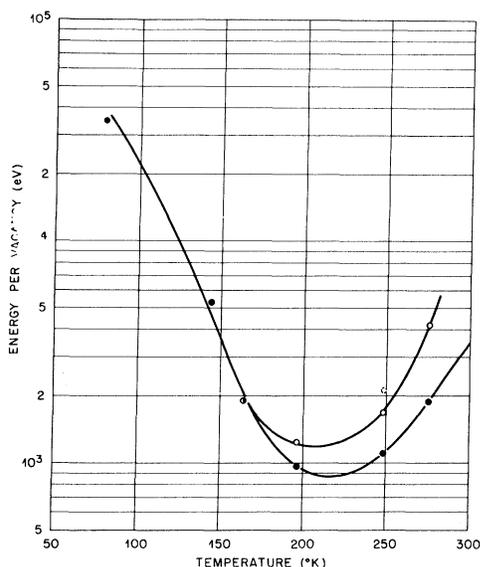


FIG. 2. Energy per vacancy versus temperature. The data depicted by solid point symbols are for a dose rate of 6×10^{18} eV/cm³sec; the data depicted by open point symbols are for a dose rate of 5×10^{17} eV/cm³sec.

B. F_2 -Center Growth in the Dark

Figure 3 shows how F -aggregate bands grow when NaCl is warmed to various temperatures after a 2-h electron irradiation at 145 °K. The circled points indicate the peak absorption coefficient for the 715-nm band; the squares represent the 1000-nm band. The 715-nm band is known to be due to F_2 centers. By comparing the position and thermal behavior of the 1000-nm band with corresponding properties of similar bands in KCl and LiF we can be fairly confident that the 1000-nm band in NaCl is due to F_2^+ centers. To make sure that this is actually the case, we bleached samples exhibiting this band as well as the F^- band. Bleaching in the F^- band at temperatures between 80 and 145 °K led to a decrease in 1000-nm and F^- absorption and to an increase in F_2 and F absorption. Since none of the negative-ion vacancy centers can move at these low temperatures, it is clear that the F^- -center electrons freed by the illumination annihilated the positive charge of the F_2^+ centers, thus forming F_2 centers.

The figure shows that very little thermal growth of the F_2 and F_2^+ bands occurs below 230 °K. The F_2^+ -center maximum for 15-min anneals appears near 260 °K and the maximum F_2 -center growth occurs in the same temperature range, perhaps 10 deg higher.

C. Radiation Equilibrium between F and F -Aggregate Centers

In preliminary experiments we found that the ratio α_2/α_1^2 , where α_2 refers to the peak absorp-

tion in the F_2 -center absorption band, was strongly sample dependent, even for samples cleaved from the same large ingot. For that reason, the data shown in Fig. 4 were obtained on one sample as follows: A 10-min electron irradiation (dose rate of 6×10^{18} eV/cm³ sec) sufficed to produce approximately 2×10^{18} F centers. At these concentrations the production rate becomes relatively slow. It thus allows one to perform a number of short irradiations during which the defect concentration changes no more than approximately a factor of 2. By irradiating for 3–4 min repeatedly we were able to observe the equilibrium F - and F_2 -center band heights at a number of temperatures between 246 and 302 °K. We varied the temperature in an essentially random order, so that any change in equilibrium ratio with total defect concentration appeared as scatter rather than an erroneous slope.

The results of plotting the log of the equilibrium ratio, $\alpha_2/(\alpha_1)^2$, versus inverse temperature are shown in Fig. 4; the data fit a straight line, the slope of which yields an experimental reaction energy of 0.6 eV. For comparison we also include published results¹⁴ for KCl; for these the slope corresponds to 0.5 eV.

As has been pointed out by Faraday *et al.*,²⁴ there will be a small concentration of F_2 centers, even in the absence of aggregation, simply due to the fact that in a random distribution of F centers some will exist in adjacent lattice sites. This statistical distribution would yield a ratio $\alpha_2/(\alpha_1)^2$ of approximately 1×10^{-6} . It is evident from Fig. 4 that only for a radiation temperature above 250 °K is

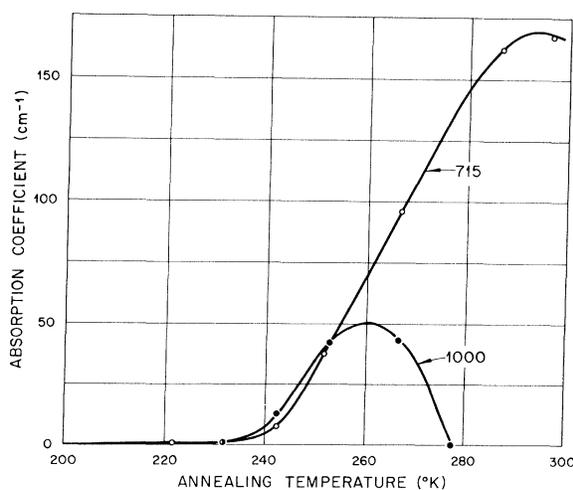


FIG. 3. Aggregate-band formation upon warming irradiated NaCl. Annealing times at each temperature were 15 min; measurements were made at 145 °K. The curve labeled 715 nm is for the F_2 band; the curve labeled 1000 nm is presumably for the F_2^+ band.

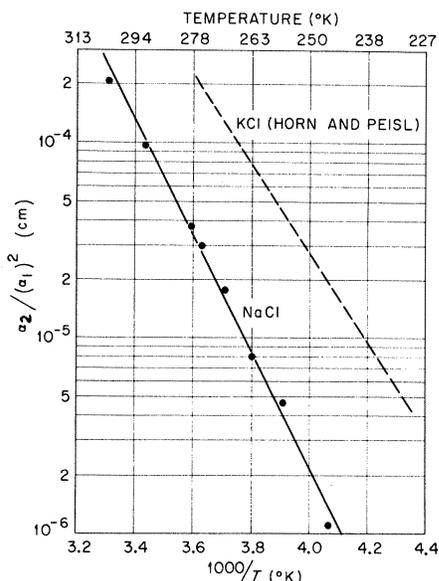


FIG. 4. Radiation equilibrium ratio $\alpha_2/(\alpha_1)^2$ versus inverse temperature. Data obtained by Horn and Peisl for KCl are included for comparison.

there any significant increase of the ratio above that statistical value. (Note that for KCl, that temperature is approximately 220°K.)

SUMMARY AND DISCUSSION

Comparison of Fig. 2 with Figs. 3 and 4 shows clearly that the production rate of defects begins to saturate and to exhibit a dose-rate dependence more than 80°K below temperatures at which aggregation processes become significant. Thus, just from these data alone we can conclude that different thermally activated processes determine, respectively, the net vacancy production rate and vacancy aggregation.

Recent reports^{18,19} indicate that holes in NaCl become mobile between 150 and 160°K. This suggests that perhaps the appearance of dose-rate dependence and the beginning of saturation of the increase of production efficiency depicted in Fig. 2 are determined by hole mobility, as stated by Pooley.¹⁶ We can in fact estimate whether self-trapped holes that begin to move near 155°K will be sufficiently mobile to cause the observed maximum in the production efficiency near 220°K. From the temperature range in which the holes disappear, we estimate²⁵ an activation energy E near 0.4 eV; we also assume that, in annealing experiments performed to observe the decay of self-trapped hole absorption bands, approximately 10^{16} holes annihilate at electron traps in a few minutes. In order to reverse the increasing trend in production efficiency depicted in Fig. 2, a significant fraction of the holes produced by our irradiation must

be able to annihilate at electron traps. At the dose rates we have used, of the order of 4×10^{17} electron-hole pairs per second²⁶ are produced. This is 4000 times as large as the annealing rate observed in hole-decay experiments. Thus to have sufficient electron-hole annihilation at the trap sites a hole mobility 4000 times as great as that observed in hole-decay experiments is necessary. This requires a temperature T_2 according to the expression $4000 = e^{E/kT_1 - E/kT_2}$, where T_1 is the temperature at which trapped-hole annealing is observed. For an E of 0.4 and T_1 of 155°K we obtain a T_2 of 214°K; this result is consistent with the observed maximum production rate in Fig. 2.

It thus appears that short circuiting of the production mechanism accounts not only for the decrease in production efficiency of KI, as reported,¹² but is more general, causing the dose-rate dependence and decreasing production efficiency above 200°K in NaCl, and probably in other alkali halides as well.

On the other hand, thermal aggregation of F centers and the radiation equilibrium of F centers and F -aggregate centers appear to depend on F^+ -center mobility. The fact that an F_2^+ band forms and later decays when NaCl is warmed suggests that F_2 -center formation occurs in two steps, the first being the combining of mobile F^+ and F centers, the second being the trapping of electrons at these positively charged defects. This is identical with what has been observed in KCl,¹¹ NaF,⁹ and LiF²⁷; and as has been done for the case of these other materials, we deduce from the annealing measurements that the F^+ center becomes mobile near 260°K. The temperature at which the equilibrium ratio significantly exceeds the statistical value is the same as the temperature at which we deduce the F^+ center to become mobile. This indicates that F^+ -center mobility is rate limiting in the radiation equilibrium.

We conclude from these and from previous results obtained with KI that short circuiting limits F -center production when holes can move. On the other hand, it has been demonstrated that F centers can be destroyed by radiation in KCl at room temperature,²⁸ and mobile holes cannot permanently destroy F centers, unless the so-produced F^+ centers can move to annihilation sites. Thus both hole- and F^+ -center processes must be taken into consideration in analyzing defect production and aggregation in the vicinity of room temperature.

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Pressure-Induced Phase Transitions in Solids: BaF₂[†]

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Similarities between the pressure dependences of the elastic constants of BaF₂ and RbI suggested that a pressure-induced phase transition should obtain in BaF₂. This transition has been observed. With increasing pressure at 295 °K the transition occurs at 26.8 kbar. The transition pressure decreases with increasing temperature, and at sufficiently high pressure the transition can be induced by raising the temperature. The possible lattice dynamical nature of the transitions in RbI and BaF₂ is discussed.

I. INTRODUCTION

The study of phase transitions in solids and the interpretation of such transitions in terms of the

dynamics of the crystal lattice are of prime importance. The general conditions for lattice stability are discussed by Born and Huang.¹ One distin-