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Generation of Electron Traps by Plastic Flow in Alkali Halides*

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Vacancy clusters, generated by moving dislocations, act as effective electron traps and change the photographic properties of the alkali halides considerably. This has been investigated by using additively colored KCl and electrolytically colored NaCl. Electrons were released from the F-centers by irradiation of F-light. In a plastically deformed crystal these electrons are immediately trapped by vacancy clusters and have not much chance to return to a negative ion vacancy. Therefore, the F-band bleaches much faster than in the case of undeformed crystals. Measurements of the bleaching rates permit an estimation of the number of traps generated by plastic flow. About 10^{17} traps per cm^3 are formed by a plastic strain of 10 percent. The nature of the traps depends upon the time, which has passed after cold work. In the case of KCl, irradiation of F-light *during* plastic deformation gives rise to a pronounced enhancement of the M-band. Filling of the traps 48 hours *after* cold working results in the formation of a very broad band, centered near 800 mμ. The generation of F'-centers and the thermal conversion of F'-centers into F-centers are also strongly affected by the presence of these traps.

A. INTRODUCTION

IT is well known that plastic deformation has considerable influence on the electrical and optical properties of the alkali halides. Rather spectacular effects are, e.g., the enhanced darkenability for x-irradiation and the temporary rise of the electrical conductivity. Seitz has shown in detailed discussions, that the generation of vacancies by moving dislocations is the key for the understanding of these effects.[1]

In a preliminary report the present authors have shown that the generation of vacancy aggregates can be demonstrated, by using the fact that these act as effective electron traps.[2] The present paper represents an attempt to estimate the number of traps generated by plastic flow and to investigate their nature.

B. A METHOD TO ESTIMATE THE NUMBER OF TRAPS GENERATED BY PLASTIC FLOW

The basic idea underlying our method to estimate the number of traps is the following: In crystals containing essentially only F-centers (additively or electrolytically colored crystals), electrons are released by irradiation of F-light. These electrons have a chance to be captured by various kinds of traps. If, e.g., the trap is a negative ion vacancy, another F-center will be formed. All other trapping processes decrease the number of F-centers. Trapping in simple clusters of vacancies results in the formation of M-, R-, N- and more complex (unidentified) centers. The probability that an electron is captured by a given kind i of traps is proportional to the concentration n_i of these traps times the capturing cross section σ_i.[3] For a crude estimation we may assume that the trapping cross sections σ_i do not differ vastly for similar simple clusters of vacancies. Therefore, the probability that an electron becomes trapped is roughly proportional to the total number of traps per cm^3. The bleaching rate of the F-band (for a given initial concentration of F-centers and a given intensity of irradiation) is therefore proportional to the concentration of unfilled traps other than negative ion vacancies. Once the traps are filled, bleaching becomes more difficult, for direct trapping is no longer possible. Bleaching curves of additively colored KCl show clearly a region of fast bleaching and a region of slow bleaching (curve I in Fig. 1). The decrease $\Delta\alpha$ of the F-absorption in the region of fast bleaching corresponds presumably to the number of traps initially present in the crystal.

If additional traps are formed by cold work, the initial bleaching rate is enhanced. It may happen that the number of traps exceeds the initial number of F-centers. In this case, almost complete bleaching occurs in a short time (curve II in Fig. 1). The absolute concentration of traps cannot be evaluated from curve II alone. However, curve I permits evaluation of the proportionality factor between the absolute number of traps per cm^3 and the initial slope of the bleaching curve. This proportionality factor may be assumed to be valid for given experimental conditions, such as

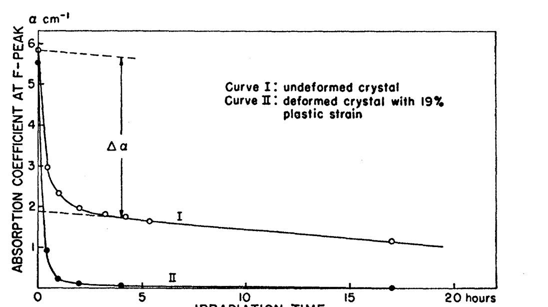

FIG. 1. Optical bleaching of the F-band in additively colored KCl crystals, measured at room temperature. Bleaching light: 546 mμ, approximately 5×10^{13} quanta sec^{-1} cm^{-2}.

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[1] F. Seitz, Phys. Rev. **80**, 239 (1950); Advances in Physics **1**, 43 (1952).
[2] M. Ueta and W. Känzig, Phys. Rev. **94**, 1390 (1954).
[3] For the sake of simplicity, we assume here that no metastable traps are present. This assumption holds for KCl at room temperature, but not for NaCl, in which case F'-centers are formed by irradiation of F-light. These are not stable at room temperature and decay with a half-life of about 10 minutes.

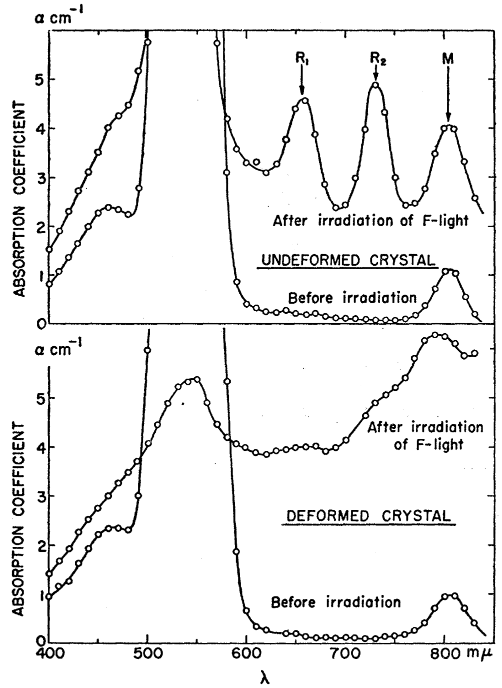

FIG. 2. (a) Formation of the M- and R-bands in an additively colored, undeformed KCl crystal by irradiation with F-light at room temperature. (b) Formation of a broad absorption band by F-irradiation at room temperature 48 hours after plastic deformation. The crystals were cut from the same colored piece and subjected to the same conditions of irradiation. The spectra were measured at liquid N_2 temperature.

initial concentration of F- centers, intensity of bleaching light, and thickness of crystal. Hence, once this factor is established, the absolute concentration of traps can be evaluated from the initial bleaching rates.

In NaCl the circumstances are somewhat more complicated, because of the formation of metastable F'-centers. It is necessary to wait, after irradiation with F-light, until the F'-centers have decayed, before the decrease of the F-band can be measured.

C. MECHANISM OF OPTICAL BLEACHING OF THE F-BAND IN ADDITIVELY COLORED CRYSTALS

The bleaching curve of Fig. 1 suggests that two different bleaching mechanisms exist: The fast bleaching corresponds probably to direct trapping of electrons in vacancy clusters already present in the crystal before irradiation. The slow bleaching is a more complex process. The traps are formed during irradiation, and migration processes are involved.

(1) Bleaching of Undeformed Crystals

The additively colored KCl crystals used in our experiments contained about 3×10^{16} traps per cm^3. Presumably most of these originate from the quenching process which the crystals have to undergo after being heated in the alkali metal vapor. The vacancies originally present combine to neutral vacancy pairs. These are very mobile and coagulate, forming quartets. The latter do not migrate and are believed to be the final clusters. If such a quartet captures an electron, a positive ion vacancy is ejected and an M-center is formed.[4,5] This process is predominant in the region of fast bleaching. The trapping of a second electron in an M-center with the formation of R-centers may also occur to a certain extent.

The slow bleaching is probably due to the following process: Positive-ion vacancies, which are left from the processes described above, or which are due to the presence of divalent impurities, migrate and join the optically ionized F-centers. New vacancy pairs and quartets can be formed this way, and the bleaching goes on. However, it is slow, because migration processes are involved. Figure 2(a) illustrates the formation of the M- and R-bands in an undeformed additively colored KCl crystal.

(2) Bleaching of the Deformed Crystals

The initial bleaching of the deformed crystal is much faster, as the number of traps is larger (Fig. 1). However, there is not only a difference in the quantity of the traps but also in their quality. Moreover, the nature of the traps depends upon the time which has passed after cold work.

(a) If an additively colored KCl crystal is irradiated with F-light 48 hours after plastic deformation, the absorption spectrum of Fig. 2(b) results: The M-band is not enhanced, and the R-bands are hardly detectable.

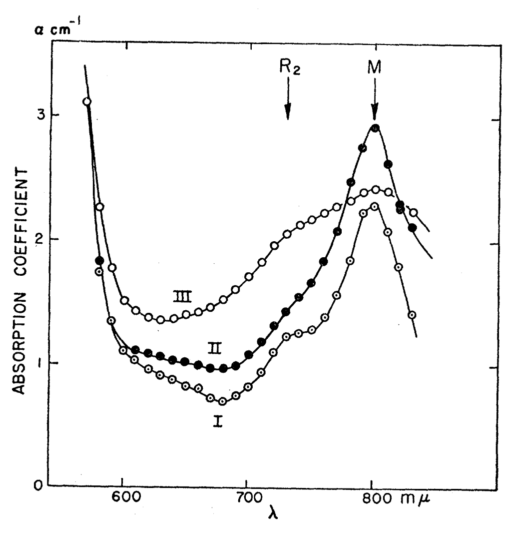

FIG. 3. Formation of a very prominent M-band in an additively colored KCl crystal by irradiation with F-light *during* plastic deformation (curve I). Growth of the M-band and decrease of the R_2 band after annealing at room temperature (curve II). Influence of the same irradiation 48 hours after plastic deformation (curve III). The spectra are measured at liquid N_2 temperature.

[4] F. Seitz, Revs. Modern Phys. **18**, 384 (1946).
[5] A. B. Scott and L. P. Bupp, Phys. Rev. **79**, 341 (1950).

A very broad absorption band is superposed on the M-band. At early and intermediate stages of F-irradiation this broad band grows very fast, whereas the M-band remains unchanged. There is no doubt that this broad band has to be attributed to electrons captured in the traps which have been generated by the plastic deformation. Very probably, it may be identified with the band, which Scott and Bupp[5] have termed the R'-band. These workers obtained it by a combined heat and optical treatment. The nature of the corresponding color centers is believed to be composite and is not known.[6]

NaCl shows a slightly different behavior.[2] The M- and R-bands are enhanced in *addition* to a broad band extending from the M-band to the F-band. This band might be due to colloids of very inhomogeneous size, or it has to be identified with the R'-band.

(b) If the crystal is irradiated with F-light *during* cold work, the absorption spectrum is entirely different from that discussed above. No R'-band is formed. The M-band is enhanced instead, and the R_2-band is formed. Curve I in Fig. 3 shows the absorption spectrum of an additively colored KCl crystal which has been plastically deformed under strong F-irradiation. A plastic strain of 20 percent was applied in 4 minutes. Then the light source was shut off, and the crystal cooled immediately to liquid N_2 temperature. For comparison, a piece cut from the same colored crystal, was subjected to the same plastic strain in the dark. Forty-eight hours after cold work it was irradiated with the same intensity and for the same time. Then the spectrum was again measured at liquid N_2 temperature (curve III, Fig. 3).

These experiments demonstrate clearly, that within the first 4 minutes of cold work a large number of quartets are present, which capture electrons and thus are converted into M-centers and R_2-centers.

If the crystal which has been irradiated during plastic deformation is annealed at room temperature for 48 hours, the R_2-band decreases and the M-band and the F-band grow (curve II, Fig. 3). Apparently the following reaction occurs: R_2-center+vacancy pair→M-center +F-center.

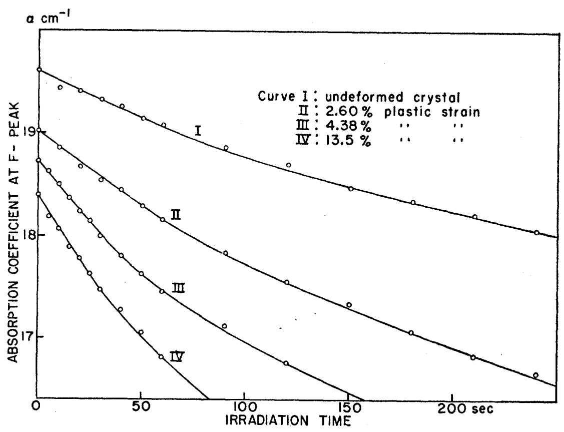

FIG. 4. Initial optical bleaching rates of the F-band in additively colored KCl crystals, measured at room temperature. Bleaching light 546 mμ, approximately 5×10^{13} quanta sec^{-1} cm^{-2}.

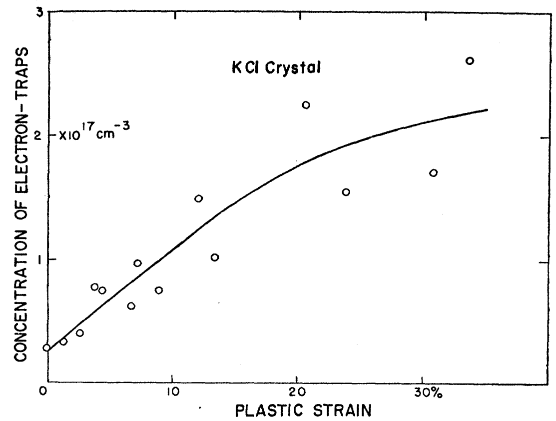

FIG. 5. Concentration of electron traps in KCl measured 2 days after cold work.

D. OPTICAL BLEACHING RATES OF THE F BAND

From the foregoing considerations it is clear that the initial bleaching rate of the F-band is a measure of the concentration of stable traps (other than negative ion vacancies) initially present in the crystal. From the fast decrease of the (ionic) conductivity during the first few minutes after cold work,[1] one concludes that the number and the nature of the vacancy aggregates changes rapidly. Bleaching rate measurements take at least a few minutes. Therefore, they cannot yield conclusive results if carried out immediately after plastic flow. All bleaching rates were measured about 2 days after cold work.

Experimental Procedure

Synthetic KCl crystals (Harshaw) were uniformly colored by heating in Na vapor at 530°C for 48 hours. The colored samples were plastically deformed in the dark by means of an elastic clamp. The rate of compression was about 10 percent per 20 minutes. The surface of the deformed samples was polished with a wet cloth. All crystals to be compared were cut from the same colored piece, ground to the same thickness and subjected to the same surface treatment. The bleaching light was the green mercury line $\lambda=546$ mμ. Approximately 5×10^{13} quanta sec^{-1} cm^{-2} were incident on the crystal. The intensity of the monochromatic light, which served to measure the absorption at F-peak, was at least two orders of magnitude smaller, and its influence could be neglected. Figure 4 shows a typical result of a measurement of initial bleaching rates.

The relation between the initial slope of the bleaching curve and the absolute concentration of traps was determined by the procedure described in Sec. B. For the

[6] F. Seitz, Revs. Modern Phys. 26, 7 (1954).

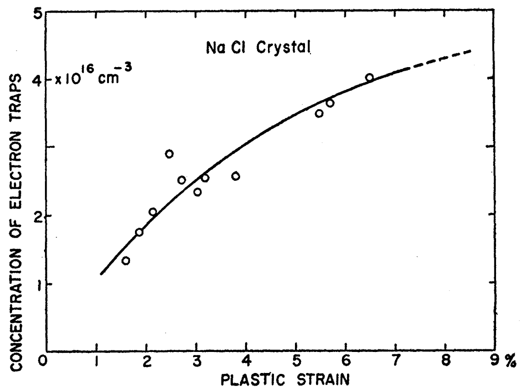

FIG. 6. Concentration of electron traps in NaCl generated by plastic deformation.

undeformed crystals we obtained trap concentrations ranging from 2.75×10^{16} to 2.85×10^{16} cm^{-3}. In Fig. 5 the total concentration of traps is plotted *versus* plastic strain.

Similar experiments were carried out with NaCl crystals. As it is very difficult to produce *F*-centers in NaCl by heating in Na vapor without considerable coagulation to colloids, we colored these crystals by injection of electrons from a pointed cathode at 530°C. The regions of fast and slow bleaching are not so clearly separated in undeformed crystals. However, a small plastic strain is already sufficient to obtain a distinct separation. Therefore, we determined the proportionality factor between the initial bleaching rate and the absolute concentration of traps, using crystals with 2 percent strain. The concentration of *F*-centers in the different samples did not differ considerably, and the same proportionality factor could be used for all samples. Figure 6 summarizes the results.

Discussion of the Results

There is no significant difference between KCl and NaCl with regard to the number of traps generated by cold work. Ten percent strain yields 0.7×10^{17} traps per cm^3 in KCl and 0.5×10^{17} traps per cm^3 in NaCl.

The number of traps is related to the number of single vacancies originally generated by the moving

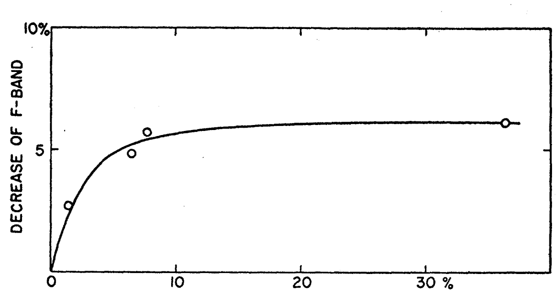

FIG. 7. Bleaching of the *F*-band in additively colored KCl by plastic deformation at room temperature.

dislocations. In order to establish this relation, definite knowledge of the nature of the traps is necessary. In the case of NaCl, the absorption spectrum reveals, that *M*- and *R*-centers are formed in addition to *R'*-centers. The former two centers are believed to contain two negative ion vacancies and one or two electrons[6] and not more than one positive ion vacancy. The character of the *R'*-centers is composite and not known. However, it is reasonable to assume that it is similar to the character of the *M*- and *R*-centers. Therefore one or two electrons are trapped per each pair of negative ion vacancies. On the other hand it is likely that equal numbers of positive and negative ion vacancies are produced. Therefore the total number of single vacancies is 2 to 4 times the number of traps. Thus, we may conclude that 1×10^{17} to 3×10^{17} single vacancies per cm^3 are produced by a plastic strain of 10 percent. These numbers are in good agreement with Seitz's

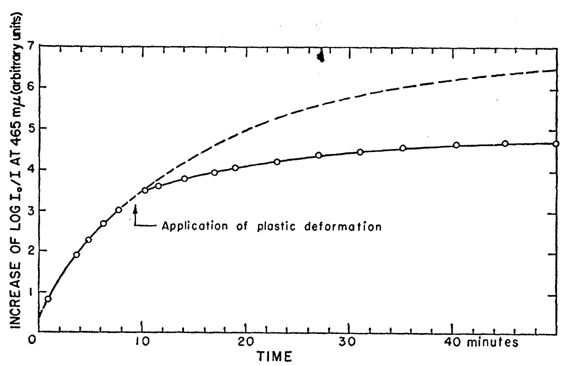

FIG. 8. Influence of cold work on the thermal conversion of *F'*-centers into *F*-centers in NaCl at room temperature. Growth of the *F*-band *versus* time. The dotted curve corresponds to the behavior of the undeformed crystal.

interpretation of the enhanced conductivity observed by Gyulai and Hartly.[7]

E. BLEACHING OF THE *F* BAND BY PLASTIC FLOW ONLY

We expect that plastic flow without subsequent irradiation of *F*-light has an influence on the absorption spectrum of additively or electrolytically colored crystals. Two essentially different mechanisms may be effective: (1) Moving dislocations generate local heating. The electron of an *F*-center can be thermally released, when a dislocation passes very close. This electron may become captured by one of the traps generated by the moving dislocation. (2) Vacancies and vacancy pairs, generated by the plastic deformation, migrate and join *F*-centers, transforming these into *M*-centers, *R*-centers, or more complex aggregates. Both mechanisms result in a bleaching of the *F*-band. Our experiments with additively colored KCl crystals show that a relatively small bleaching effect exists. In Fig. 7 the percentage of *F*-centers destroyed is plotted *versus*

[7] Z. Gyulai and D. Hartly, Z. Physik **51**, 378 (1928).

plastic strain. The curve exhibits a pronounced saturation behavior above 10 percent strain. In order to decide which of the two proposed mechanisms is more effective, the bleaching effect of cold work at liquid N_2 temperature was also investigated. Migration is negligible in this case. The decrease of the F-band is of the same order as at room temperature, indicating that mechanism (1) is at least predominant. It seems that the vacancies generated by the moving dislocations are formed in a coagulated manner or coagulate into immobile clusters before they have a chance to meet an F-center. This in turn suggests that very high local concentrations of vacancies are generated.

F. INFLUENCE OF PLASTIC FLOW ON THE F'-BAND

1. Formation of the F'-Band

An F'-center consists of an F-center which has captured a second electron. It can be formed in additively or electrolytically colored crystals by irradiation of F-light at appropriate temperatures.

In a plastically deformed crystal, however, an electron which is optically released from an F-center has considerable chance of being trapped in a vacancy cluster instead of being captured by an F-center. We found indeed that no F'-band can be formed in additively colored KCl by irradiation of F-light at dry ice temperature if the crystal previously had been subjected to plastic strain.

2. Bleaching of the F'-Band

F'-centers are metastable in NaCl at room temperature. An electron is thermally released and an F-center is left. In an undeformed crystal nearly all the thermally released electrons return to a negative ion vacancy and two F-centers are formed for every decaying F'-center.[4] This reaction is considerably perturbed if the crystal is cold worked. The growth rate of the F-band is smaller after plastic deformation (Fig. 8). Two different effects contribute to this decrease:

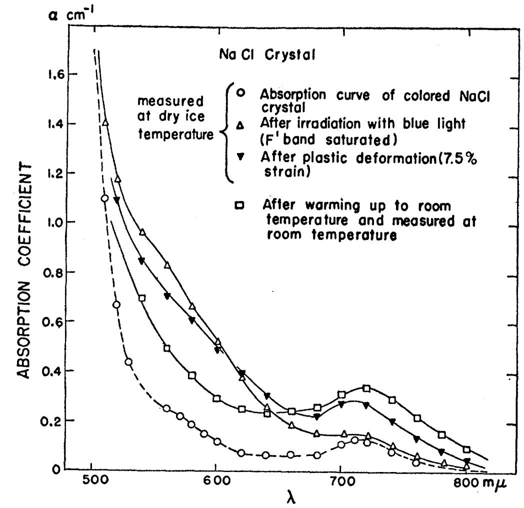

Fig. 9. Influence of cold work at dry ice temperature on the absorption spectrum of an electrolytically colored NaCl crystal containing F'-centers.

(a) F'-centers have been destroyed *during* cold work by local heating. Thus the concentration of decaying F-centers has been reduced.

(b) Part of the thermally released electrons are captured by vacancy clusters. Therefore less than two F-centers are formed for every decaying F'-center.

Process (a) was investigated separately with the crystal held at dry ice temperature when thermal freeing of electrons from F'-centers is negligibly slow (Fig. 9). The F'-band is partially bleached by cold work, and the M-band is enhanced. This confirms the conclusions made in Sec. C: The vacancies, originally generated by moving dislocations, coagulate to pairs and quartets within a few minutes. Process (b) could be observed during warming up: The F'-band bleaches completely, and the M-band grows (Fig. 9).

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