

Effect of Plastic Deformation on the Production F Centers, M Centers, and V Centers in KCl

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The effect of plastic deformation and heat treatment on the room temperature production of F centers, M centers, and V centers by Co^{60} gamma rays was investigated. Deformation of an irradiated sample caused a reappearance of the "first stage" coloration for F centers when the sample was irradiated further. This deformation induced enhancement of the colorability could be annealed out by heat treating the samples in air at 450°C for 20 min. It was also observed that the coloration curves for the V_2 band were very similar to those for the F band, and that they were affected by deformation, heat treatment, and optical bleaching in the same way.

INTRODUCTION

THE influence of plastic deformation on the colorability of alkali halide crystals at room temperature is quite pronounced but the specific mechanism by which this increase in the colorability comes about is still not clear. Gordon and Nowick¹ and Nowick² have investigated the effect of plastic deformation on the colorability of NaCl crystals and concluded that the F -center coloration, occurring after the initial rapid first-stage coloring, was due to the generation of new vacancies at dislocations. Nowick² was able to show that the later³ stage coloration was greatly enhanced in a crystal in which the dislocation content had been increased by plastic deformation. However, if the F centers are generated at dislocations in the later stages of coloring then dislocation climb should be observed and Crawford and Young⁴ found no evidence of dislocation climb in NaCl crystals which were very heavily gamma irradiated. This suggests that the F centers are not produced at dislocations in the late stage coloring process. Moreover, Mitchell, Wiegand, and Smoluchowski⁵ have proposed that the increased coloration in deformed samples is due to the increase in the initial concentration of vacancies that are in small regions of high local concentration such as would perhaps be generated by dislocation intersections. On the other hand, Bauer and Gordon⁶ have recently presented evidence which they claim supports the idea that F centers are produced at dislocation lines and do not arise from vacancies introduced during deformation.

A test of which of these two interpretations is correct has been made by Agulló-Lopez and Levy⁷ and Bauer⁸

on sodium chloride. The results of these latter two investigations are quite interesting. Both experiments carried out the irradiation past the first-stage coloration after which the crystals were deformed by compression and the irradiation was continued. Agulló-Lopez and Levy find that the additional F -band coloration following the deformation can be separated into the same stages as one finds for a nondeformed crystal; whereas Bauer's results are not so conclusive.

Previously, it was reported⁹ that deformation does not affect the quadratic relation between the F -center- M -center concentrations and that heat treatment can eliminate the excess F -center coloration in plastically deformed specimens of Isomet KCl. In view of this and the results discussed above it was thought that a careful study of the effect of plastic deformation on the room temperature production of F centers, M centers, and V centers was necessary to supplement the information already available on this subject.

EXPERIMENTAL

In order to obtain growth curves for the color centers under investigation, cleaved plates of thickness 0.1 cm or less, were placed in light tight holders, which were equipped with slides to permit measurement of their absorption spectra in a Cary model 14R spectrophotometer. The irradiations were performed in a 3.6×10^6 $-\text{R/h}$ Co^{60} gamma source. A detailed account of the irradiation procedure has been presented previously.⁹

Most of the crystals were deformed by using an Instron Testing Machine with a compression load cell; however, specimens H:40-9, O:103C-7, and O:103C-8 were deformed in the dark while in the light tight optical sample holders. The crosshead speed of the Instron could be varied from 0.005 to 5 cm/min; therefore the effect of strain rate on the coloration properties of the crystals was studied. Heat treatments were carried out with the samples in the light tight holders and the tem-

* Oak Ridge National Laboratory is operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

¹ R. B. Gordon and A. S. Nowick, *Phys. Rev.* **101**, 977 (1956).

² A. S. Nowick, *Phys. Rev.* **111**, 16 (1958).

³ Later stage coloration means coloration occurring after the initial first-stage coloration is complete. This includes several different stages.

⁴ J. H. Crawford and F. W. Young, Jr., *J. Appl. Phys.* **31**, 1688 (1960).

⁵ P. V. Mitchell, D. A. Wiegand, and R. Smoluchowski, *Phys. Rev.* **121**, 484 (1961).

⁶ C. L. Bauer and R. B. Gordon, *Phys. Rev.* **126**, 73 (1962).

⁷ F. Agulló-Lopez and P. W. Levy, *Bull. Am. Phys. Soc.* **8**, 268 (1963). P. W. Levy, paper presented at the ASTM Symposium

on Chemical and Physical Effects of High-Energy Radiation on Inorganic Substances, June 1963 (unpublished).

⁸ C. L. Bauer, *Bull. Am. Phys. Soc.* **8**, 251 (1963).

⁹ W. A. Sibley and E. Sonder, *Phys. Rev.* **128**, 540 (1962).

perature of the holders was maintained at $450^{\circ}\text{C}\pm 3^{\circ}\text{C}$ for 20 min and then the rather massive brass holders were removed from the oven and allowed to cool.

RESULTS

A. Introduction of F Centers

A list of the samples used in the experiment, the treatments which they received, and the symbols used to identify these specimens in the figures are given in Table I. Figure 1 depicts the F -center growth curves after various treatments for samples cleaved from one large crystal ingot purchased from the Harshaw Chemical Company, and Fig. 2 is a similar graph for crystals cleaved from a large ingot obtained from the Optovac Corporation. Shown plotted are the optical absorption coefficient at the peak of the F band versus the gamma dose received. A comparison of the treatments listed in Table I with the data presented in the figures indicates three things: (1) that deformation increases the early stage coloration,^{2,4} (2) That when a sample is irradiated past the first stage and then deformed and reirradiated the additional coloration following deformation can be separated into the same stages as one finds in a non-deformed crystal.⁷ (3) If a sample is deformed and then heat treated at 450°C for no longer than 20 min, as in the case of crystals H:40-9 and O:103C-8, then the effect of the deformation on the coloration properties is eliminated. When the samples are heated in air for much longer than 20 min, there is a definite increase in the colorability of the specimen.

TABLE I. List of samples.

Sample	Symbol	Treatment
H40-0	◇	As-cleaved
H40-1	△	As-cleaved
H40-6	×	Deformed 2.7%
H40-4	+	Deformed 3.9%
H40-8	▽	Deformed 6.6%
H40-10	□	As-cleaved
H40-9	○	Irradiated 7 h; Deformed 1.9%
	●	Annealed at 450°C for 20 min after above treatment
O103-1	◇	As-cleaved
O103-3	×	Deformed 2.7%
O103-11	+	Deformed 3.4%
O103-2	▽	Deformed 3.3%
O103-10	○	Deformed 7.2%
O103-7	△	Irradiated 16 h; Deformed 3.3%
O103-9	□	As-cleaved
	■	Annealed after irradiation at 450°C for 20 min
O103-8	○	Irradiated 16 h; Deformed 2.0%
	●	Annealed at 450°C for 20 min after above treatment

Even though the strain rate was varied over three orders of magnitude, no effect on the enhancement of the coloration of the F centers outside of experimental error could be detected for the case of room temperature deformation and irradiation.

Figure 3 portrays the incremental increase in the F -center coloration after deformation as a function of total gamma dose. These curves were obtained by subtracting the "as-cleaved" curves from the "deformed" curves for specimens from the same section of the

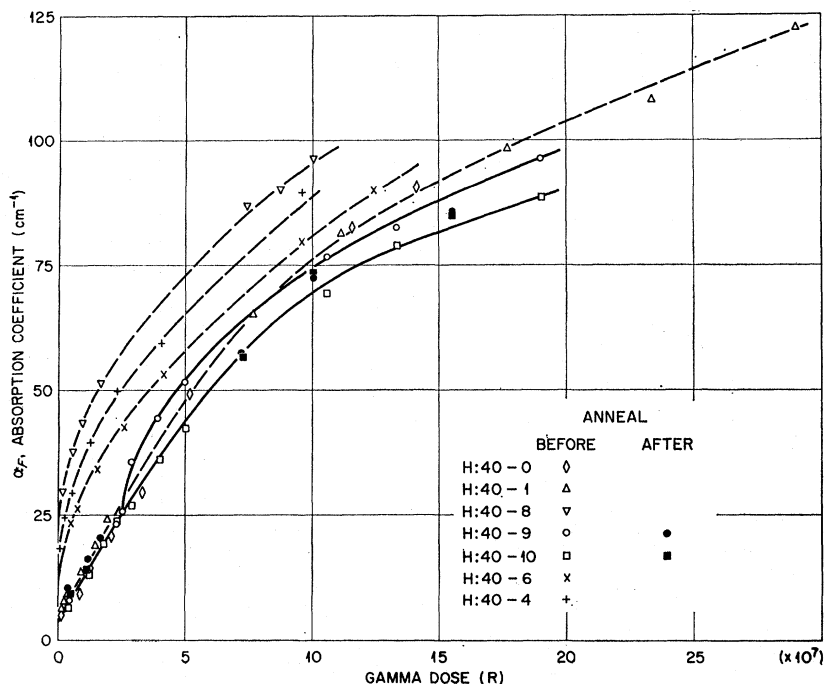


FIG. 1. F -center coloring curves for crystals from ingot H:40. The treatments for the various specimens are summarized in Table I.

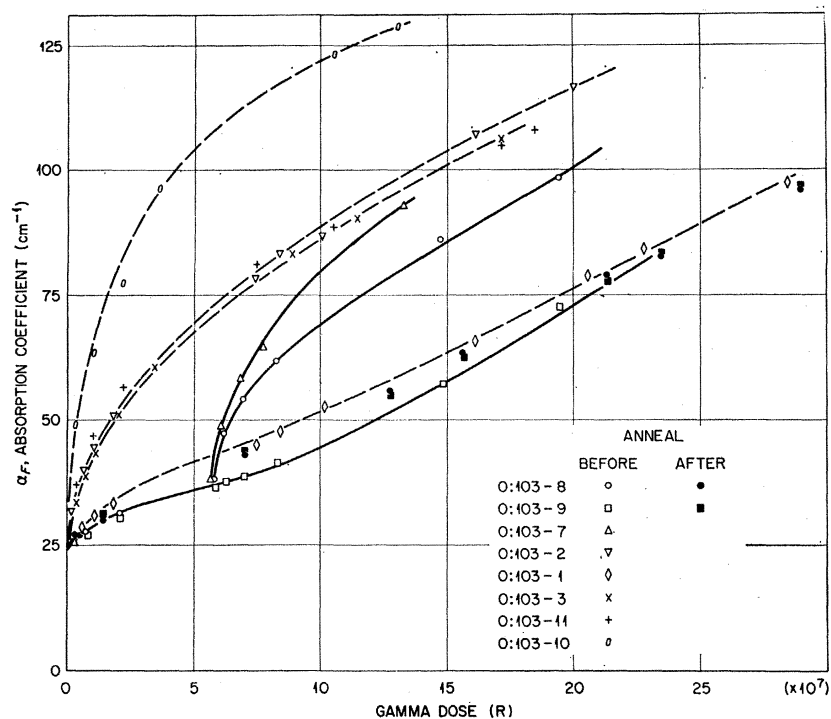


FIG. 2. F -center coloring curves for samples from ingot O:103C. The treatments for the various crystals are summarized in Table I.

ingot.¹⁰ The incremental increase is proportional, within experimental error, to the total amount of plastic deformation; but it is not possible to state whether this increase is due to the dislocations acting as sources of F centers⁶ or due to the vacancies or vacancy pairs gen-

erated by dislocation interaction during deformation.⁵ However, notice that at high doses there is a saturation tendency of the curves suggesting that either the defects are introduced in a finite amount during deformation or else that the dislocation sources tend to become inactive with time at room temperature.

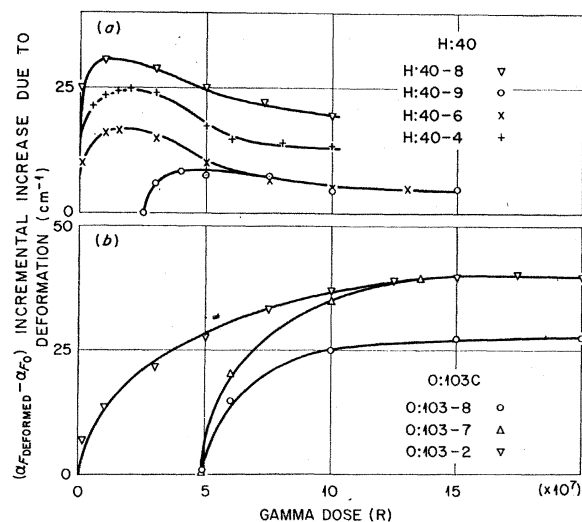


FIG. 3. The incremental increase in F -center coloration due to deformation as a function of Co^{60} gamma-ray dose.

¹⁰ It is known that crystals cleaved from different parts of the same large ingot have slightly different growth curves, and the dashed lines in the figures are for crystals cleaved from one section of the sample while the solid lines are for samples cleaved from adjacent parts of a different section. [See J. Chem. Phys. 39, 242 (1963)].

B. Introduction of V_2 Centers

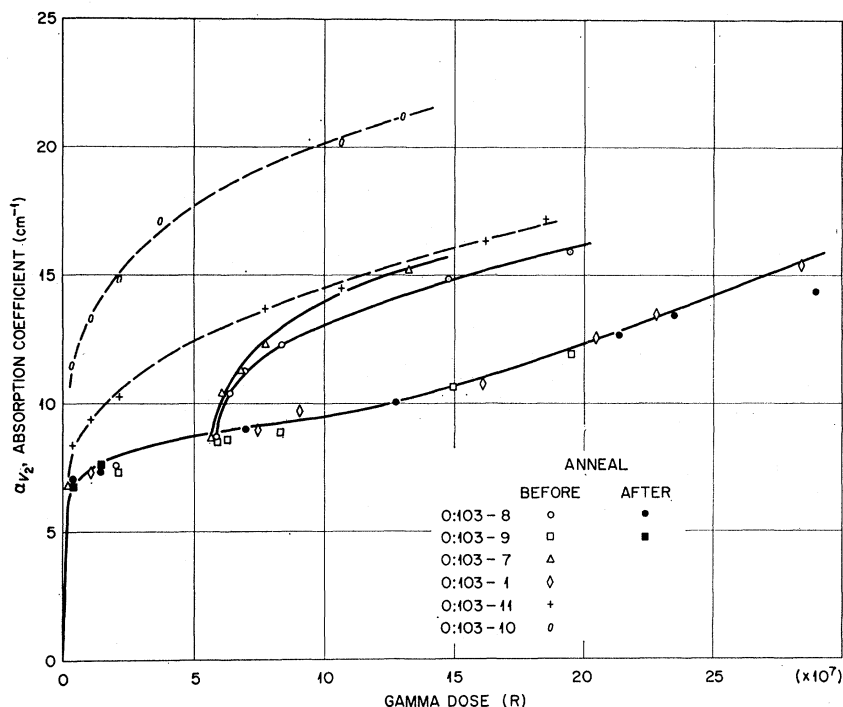
Figure 4 is a plot of the absorption coefficient at the peak of the absorption band at $230 \text{ m}\mu$ (V_2) in O:103C versus gamma dose. Notice, that the V_2 band has the same behavior in samples O:103C-7 and 8 as the F band, and that deformation prior to irradiation has the same effect on the V_2 -center production as it does on that for the F centers. This suggests a relation between the F centers and the V_2 centers; especially, since the heat treatments affect the V_2 band in the same way as they affect the F band (see Fig. 5). The V_2 band was also observed to decrease when the crystal was irradiated with F light as has been shown by Lüty.¹¹

It was not possible to make this same graph for ingot H:40 since the so-called OH^- band at $204 \text{ m}\mu$ ¹² and a band growing in under irradiation at about $195 \text{ m}\mu$ made it impossible to obtain accurate growth curves for a $212\text{-m}\mu$ (V_3) band. Lüty¹¹ has observed that crystals containing little or no OH^- show only a V_2 band when irradiated, and has attributed the $212 \text{ m}\mu$ absorption to the H^- ion in a substitutional position (U band). The

¹¹ F. Lüty, Phys. Chem. Solids 23, 677 (1962).

¹² B. Fritz, F. Lüty, and J. Anger, Z. Physik 174, 240 (1963)

FIG. 4. V_2 -center coloring curves for specimens from ingot O:103C. The treatments for the various samples are the same as those shown in Fig. 2 and listed in Table I.



H:40 ingot had an absorption coefficient of 3.5 cm^{-1} at $204 \text{ m}\mu$ which corresponds to about 15 ppm of OH^- .¹² The Optovac ingot did not exhibit an OH^- band at $204 \text{ m}\mu$ even when the absorption path length of the crystal was 4 cm long, and the absorption spectrum of the ingot over the wavelength range from 2.5 to 16μ showed no absorption. The calcium impurity concentration in both ingots was less than 5 parts per million as determined by flame photometry. The only difficulty with making accurate plots of the V_2 -center growth in the Optovac samples was a band which grew in with irradiation at about $195 \text{ m}\mu$. This band was also somewhat sensitive to deformation.

It was observed in crystals from ingot H:40 that when crystals which were heavily irradiated were heat treated at 450°C for 20 min all of the coloration disappeared and the $204\text{-m}\mu$ band was again present in the same amount as before irradiation. The specimens from ingot O:103C showed no $204\text{-m}\mu$ absorption after irradiation and heat treatment. This observation suggests that OH^- does not enter the crystal during irradiation or heat treatment.

C. The Relationship of F and M Centers

There was little or no effect of deformation or heat treatment on the slope of the $\alpha_M/[\alpha_F']^2$ curves for specimens from either of the ingots investigated. In this case α_M is defined as the absorption coefficient for the peak of the M band, and α_F' is the absorption coefficient for the peak of the F band corrected by subtracting $0.8 \alpha_M$ from it.⁹ The scatter of the points shown in Fig. 6

is unfortunately typical for samples cleaved from different parts of the same ingot, and no systematic change in the quadratic relation between M centers and F centers could be found.¹⁰

DISCUSSION

The data of Figs. 1, 2, and 3 show that deformation increases the first or early-stage coloration, but that at high radiation doses the F -center coloration curves approach the same slope as that for the undeformed samples. Moreover, the incremental increase due to deformation can be annealed out by suitable heat treatment. This suggests that the F -center coloration due to deformation is primarily due to the production of vacancies or vacancy pairs by the interaction of dislocations. Arguments can still be made in favor of the mechanism of production of vacancies at the dislocations, but these arguments must now account for the fact that the enhancement of the F -center coloration anneals out at 450°C . Therefore, the concept that dislocation motion occurs during a 20 min period at 450°C and that even without heat treatment the "new" dislocation sources tend to saturate and become inoperative must be included in the argument. On the other hand, if the idea that the coloration increase is due to vacancies or vacancy pairs produced during deformation is accepted, then some explanation of the results of Bauer and Gordon⁶ must be made. They observed that for NaCl crystals deformed 2.86%, the incremental increase in coloration due to deformation was highly temperature-dependent and that there was no increase for temperatures below 196°K . This observation, they

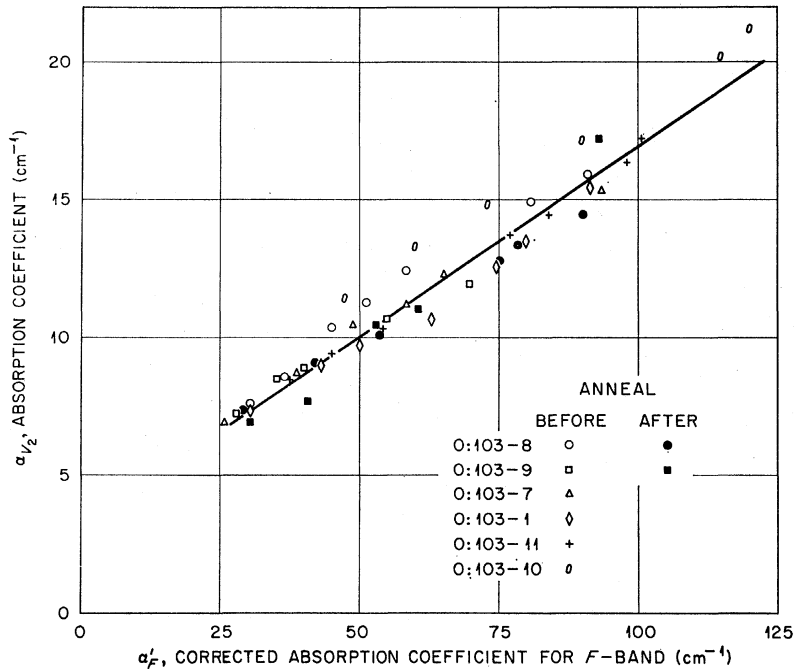


FIG. 5. The effect of plastic deformation on the ratio $\alpha_{1/2}/\alpha_F$ for crystals from ingot O:103C.

state, shows that the enhanced colorability of the deformed crystals does not arise from excess vacancies generated during the deformation process. This is certainly a valid statement if isolated negative ion vacancies are formed during the deformation process and the enhanced coloration is due merely to a filling of these vacancies with electrons. However, this is not even the mechanism for first-stage coloration in an undeformed specimen; furthermore, the deformation process in the alkali halides should favor the production of vacancy pairs rather than single isolated vacancies. Let us assume that the coloration mechanism for the formation of F centers is the same for both the first-stage production and the deformation induced production. From the work that has been done previously on the temperature dependence of the first-stage coloration^{6,13} it is clear that a temperature dependence exists and that for temperatures below 196°K the first-stage-type coloration is not very pronounced. Therefore, if both the first-stage and the deformation-induced coloration is due to vacancies, vacancy pairs, or vacancy-impurity complexes then it is reasonable to assume that the same temperature dependence should hold for both, and there should be negligible deformation induced coloration for temperatures below 196°K.

The decrease in the incremental increase of the F -center coloration due to deformation which is shown in Fig. 3 for H:40 is interesting since it does not occur for O:103C or to so large an extent for H:40 when the deformation is made after irradiation. It is known that

Harshaw KCl crystals in general exhibit a greater decay of the F band with time in the dark at room temperature than do crystals obtained from other sources,⁹ and that this decay is most pronounced for the first-stage coloration. Thus, it is possible to explain the data of Fig. 3 for H:40 by assuming that the loss rate of F centers in H:40 is greater than for O:103C. Another aspect of Figs. 1, 2, and 3 is that the incremental increase of F centers, due to deformation, per unit compression is different for the two ingots utilized. A given deformation evidently introduces about three times more potential F centers in O:103C than in H:40. This effect is not easy to explain from the point of view of either the dislocation interaction or the dislocation source mechanisms. The dislocation densities for the two ingots were about $7.1 \times 10^4 \text{ cm}^{-2}$ for H:40 and $4.3 \times 10^5 \text{ cm}^{-2}$ for O:103C, and the latter ingot had a large number of subboundaries. However, the optical specimens that were cleaved from either of the large ingots had "as-cleaved" dislocation densities of about 10^6 cm^{-2} . It is difficult to understand how two crystals deformed to about 6% could differ much in either dislocation concentration or in the number of defects introduced by the interaction of dislocations. Perhaps the reason for the large difference in the number of potential F centers introduced by the deformation in the two samples is due to something else entirely, e.g., trace impurities which exist in the crystals or which are redistributed by dislocation interaction. We have already speculated⁹ that trace impurities play a major role in the late-stage coloring of KCl crystals, and it

¹³ H. Rabin and C. C. Klick, Phys. Rev. 117, 1005 (1960).

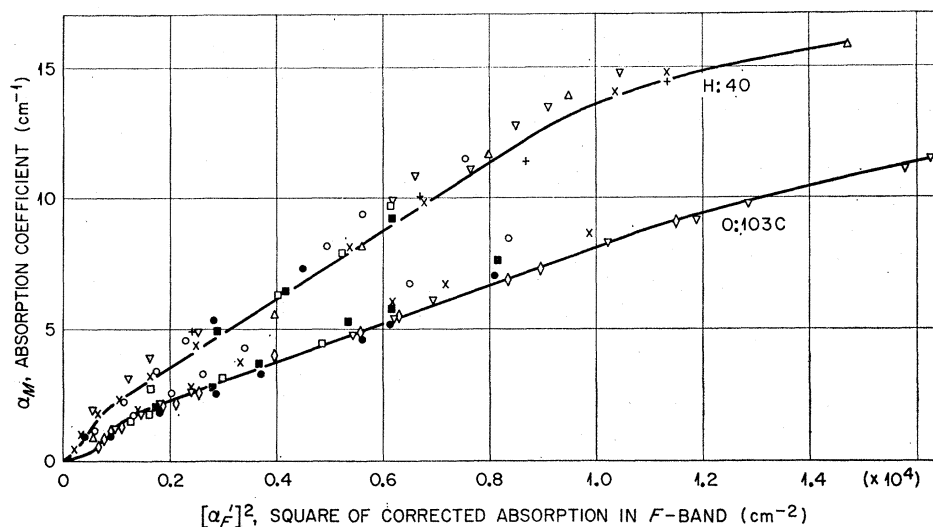


FIG. 6. The effect of plastic deformation on the ratio $\alpha_M/[\alpha_F']^2$ for crystals from ingots H:40 and O:103C. These symbols are those listed in Table I.

might be that these impurities play a part in the incremental increase of F centers due to deformation.¹⁴

Lüty and collaborators^{11,12} have done an excellent job in clarifying the V_3 band, but this spectral region is still very interesting. For example, Table II shows the apparent peak of the room temperature V -band absorption in crystals that have been used both in this present investigation and in the work of Ref. 9. The 212- $m\mu$ band, when it was present, apparently grew in very rapidly compared to the band at 230 $m\mu$. Also, in many of the crystals which were specially prepared to eliminate the OH^- band and other impurities, there is an absorption band at about 195 $m\mu$ that grows in with gamma irradiation at about the same rate as the 230- $m\mu$ band. The combination of these two bands gave a very broad absorption band with an apparent peak at about 212 $m\mu$. In these crystals which were specially treated to reduce the impurity concentrations the 230- $m\mu$ band (V_2) grew very slowly compared to samples which were known to have no 204- $m\mu$ band but which possessed other known trace impurities such as calcium. It was possible to study the growth rate of the V_2 band in samples from ingot O:103C since this band grew relatively rapidly under gamma irradiation and was much larger than any of the other bands occurring in the ultraviolet region of the spectrum. A definite relation exists between the growth of the V_2 band and the growth of the F band. This can be seen by comparing the curves in Figs. 2 and 4, and is shown more clearly in Fig. 5 which is a plot of the V_2 absorption versus the F absorption. It is not possible at this time to

identify the center responsible for the V_2 band, but it apparently is a hole center which can be introduced in concentrations proportional to the F centers by deformation.

It is important to mention that for samples from ingot O:103C no 204- $m\mu$ (OH^-) band appeared after irradiation or heat treatment, and for the H:40 samples the height of this band was the same after deformation and heat treatment as it was before. This indicates that no OH^- enters the samples during either irradiation or heat treatment unless it precipitates out at dislocation lines and does not absorb at 204 $m\mu$. Therefore, all of the U -band (212 $m\mu$) coloring in these samples (H:40) is characteristic of the OH^- present in the crystals before irradiation. The results illustrated in Fig. 6 suggest that the $\alpha_M/[\alpha_F']^2$ ratio for a given crystal is really due to a dynamic equilibrium process which presumably depends on the impurity content and the radiation dose rate and is not affected by deformation or heat treatments.

TABLE II. Ultraviolet absorption bands in gamma-irradiated KCl.

Sample	Apparent peak of the V band ($m\mu$)	Probable peaks of V bands ($m\mu$)
Ak	212	212; 230
B	195; 230	195; 230
CB	212	212; 230
H	212	212; 195; 230
I	212	212; 195; 230
O	212	212; 230
P	220	230; 195
W ₁	195; 220	195; 230
W ₂	195; 220	195; 230
D ₁	210	195; 230
D ₂	210	195; 230
CA ₁	220	230; 195
CA ₂	225	230; 195
O:103C	230; 195	230; 195
H:40	212	212

¹⁴ As a specific example consider the effect of a very effective electron trap impurity in O:103C and the absence of such a trap in H:40. This would have a threefold effect for crystal O:103C with respect H:40: (1) The production of F centers in the late stage would be suppressed, (2) the V_2 band would grow faster, and (3) the number of F centers per unit deformation would probably increase.

SUMMARY

(1) Deformation of an irradiated crystal causes a reappearance of the "first-stage" coloration for the F centers. Moreover, the coloring curve can be separated into the same stages as those present for the undeformed samples. This verifies the effect reported by Agulló-Lopez and Levy.⁷

(2) The deformation induced enhancement of the colorability can be annealed out by heat treating the samples in air at 450°C for 20 min. After this treatment reirradiation yields the same coloring curve as that characteristic of an undeformed sample. A longer heat treatment in air results in an increase in the colorability of the sample. This is possibly due to oxygen since no increase in colorability was noted for an Isomet sample

cleaved from the center of a large block which had been held at 575°C for 2 h.⁹

(3) The incremental increase in the F -center colorability due to deformation is different for crystals obtained from different sources for the same amount of deformation.

(4) In samples where the 195- and 212-m μ absorption bands grow more slowly than the V_2 band it is observed that the coloration curves for the V_2 band are very similar to those for the F band, and are affected by deformation and heat treatment in the same way.

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Nonthermal Equilibrium Fluctuations of Electrons and Holes*

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A discussion is presented on the behavior of electron and hole fluctuations under steady-state conditions. The differences between steady-state and thermal-equilibrium systems, associated with microscopic reversibility, are briefly discussed. It is concluded that so far all calculations pertained to conditions valid in (quasi-) thermal equilibrium. To illustrate the features for a nonequilibrium state, an academic model involving cyclic transitions through one set of electron traps is analyzed. The variance is shown to be super-Poissonian in the range where the photoconductance is superlinear and sub-Poissonian in the range where all traps are filled. The connection with presently accepted two-center models for phosphors and photoconductors is also indicated.

1. INTRODUCTION

DURING the past decade several methods have been developed to obtain the variances and covariances of electron and hole fluctuations in solids.¹⁻⁴ These fluctuations arise from spontaneous or induced transitions between the various energy levels in a particular solid material. A specification of these various transition rates together with the applicable constraints (e.g., charge neutrality) and *a priori* probabilities for the quantum states (generally governed by the Pauli exclusion principle) is sufficient to obtain the variances $\langle \Delta n_i^2 \rangle$ and covariances $\langle \Delta n_i \Delta n_j \rangle$. In the past two completely different procedures have been employed for materials which are in thermal equilibrium with the surroundings.

(a) Burgess¹ has shown that carrier variances are

easily calculated from the expression for the free-energy function $F(n_1, n_2, \dots, n_s)$, where $n_1 \dots n_s$ represent the carrier densities in the various electronic levels close to the equilibrium state. If $n_1 \dots n_{s-1}$ are unconstrained variables (i.e., the charge-neutrality equation has been used to eliminate n_s), then we have simply for the variances and covariances

$$\sum_j \langle \Delta n_i \Delta n_j \rangle (\partial^2 F / \partial n_j \partial n_k) = kT \delta_{ik},$$

or, in matrix notation,

$$\langle \Delta \mathbf{n} \Delta \mathbf{n} \rangle = kT [\partial^2 F / \partial \mathbf{n} \partial \mathbf{n}]^{-1}. \quad (1.1)$$

This result could also be obtained using irreversible thermodynamics, compare Ref. 3.

(b) A purely stochastic procedure was first employed by van Vliet and Blok² and later on by Lax⁴ by solving the Fokker-Planck equation or master equation, respectively. The kinetic equations are written in the form

$$\frac{dn_i}{dt} = \sum_{j=1}^s [\dot{p}_{ji}(\mathbf{n}) - p_{ij}(\mathbf{n})], \quad (1.2)$$

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¹ R. E. Burgess, Proc. Phys. Soc. (London) **B68**, 661 (1955); **B69**, 1020 (1956).

² K. M. van Vliet and J. Blok, Physica **22**, 231 (1956).

³ K. M. van Vliet, Phys. Rev. **110**, 50 (1958).

⁴ M. Lax, Rev. Mod. Phys. **32**, 25 (1960).