

Effect of Plastic Deformation on the Colorability of "Pure" and "Doped" KCl Crystals*

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The effect of plastic deformation on the room-temperature production of F centers and M centers by Co^{60} gamma rays in KCl: pure, KCl: Ca, KCl: Pb, and KCl: Sr crystals was investigated. It was found that the deformation-induced enhancement of the colorability was very sensitive to impurity type and concentration, and that there was little enhancement of the F -center concentration in the "pure" samples. The blue coloration which has been observed previously to occur at dislocation boundaries in specimens that have been deformed, irradiated, and then bleached was present in the KCl: Ca crystals but not the KCl: Pb samples. This suggests that the coloration along these boundaries is not due only to vacancy clusters produced through deformation but also depends upon certain impurities.

INTRODUCTION

FOR a number of years the interrelationship between line and point defects in alkali-halide crystals has been a topic of considerable interest. Originally much of the interest resulted from the central conceptual position occupied by dislocations and dislocation jogs as the source of radiolytic F centers.¹ More recently, however, the role of jogs in the bulk coloration process has been called into question²⁻⁵ with the result that the problem of the influence of dislocations and, hence, plastic deformation on the coloration process needs a closer examination.

The general feeling arising from much of the recent work is that most, if not all, of the deformation-induced coloration is associated with dislocation debris⁶ and probably not with the production of F centers at jogs. However, this viewpoint is not unambiguous, because of the number of apparent inconsistencies found in comparing the experimental results.^{3,7-9} Moreover, recent findings by Davidge and Pratt² have indicated that the extent of the enhancement of coloration in deformed crystals may be dependent upon the energy of the radiation employed. They noted that enhanced first-stage coloration was much greater for hard radiation (200-kV-peak x rays) than for soft (50-kV x rays).

They also found that after a high dose of hard x rays, a high density of color centers was formed along dislocation boundaries in the deformed samples. On optical bleaching, blue bands were formed along these boundaries while the rest of the crystal was completely bleached. Their primary conclusion was that very different effects can occur depending upon whether hard or soft radiation is used, and that a new interpretation of the main source of vacancies formed during these processes must be made.

The main purpose of this paper is to show that the deformation-enhancement of the colorability is strongly dependent on impurity type and concentration, and that the apparent diverse observations in the literature can be explained by this dependence. The observations of Davidge and Pratt are also considered in the light of existing information on the influence of radiation intensity¹⁰ and specimen purity,¹¹ rather than energy, on the coloration process.

EXPERIMENTAL

The specimens used in this investigation were cleaved from large single crystals grown by the Kyropoulos method in our laboratory, and from a zone-refined crystal ingot.¹² Details on the growth of the crystals grown by us have been given previously,^{11,13} and a list of the samples used in the experiment, their major impurity concentrations, and the amount they were deformed is given in Table I.

In order to obtain the color-center growth curves, 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 optical absorption in a Cary model 14R spectrophotometer. The holders were also equipped with a deformation device by which the samples could be deformed in the dark within the

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¹ F. Seitz, *Rev. Mod. Phys.* **26**, 7 (1954).

² R. W. Davidge and P. L. Pratt, *Phys. Status Solidi* **3**, 665 (1963).

³ W. A. Sibley, *Phys. Rev.* **133**, A1176 (1964).

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

⁵ M. Geudeke and W. G. Burgers, *J. Phys. Chem. Solids* **24**, 667 (1963).

⁶ The term dislocation debris covers a spectrum of defects including single point defects, clusters of defects, and dislocation dipoles. Interstitials, vacancies, and impurities fall in the category of defects for this case.

⁷ C. L. Bauer, *Bull. Am. Phys. Soc.* **8**, 251 (1963).

⁸ 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).

⁹ T. Mumaw and A. Paiche, *Bull. Am. Phys. Soc.* **9**, 262 (1964); D. A. Wiegand, *ibid.*

¹⁰ E. Sonder and W. A. Sibley, *Phys. Rev.* **129**, 1578 (1963).

¹¹ W. A. Sibley and E. Sonder, *Phys. Rev.* **128**, 540 (1962); W. A. Sibley, E. Sonder, and C. T. Butler, *ibid.* **136**, A537 (1964).

¹² Kindly supplied by R. Pohl and J. Peech of Cornell University.

¹³ W. A. Sibley and J. R. Russell, *J. Appl. Phys.* **36**, 810 (1965).

TABLE I. List of samples, their major impurity concentration, and percent deformation.

Sample	Impurity (ppm)					Deformation (%)
	Ca	Sr	Na	Br ₂	S ₂	
0227-a	<2	<3	7	3	5	0
-b	<2	<3	7	3	5	1-½
LZ4-a	Knee of ionic conductivity curve occurs at about 250 °C					0
-b						2
52 ppm Ca-a	52	<3	<6	32	<2	0
-b	52	<3	<6	32	<2	1-½
123 ppm Ca-a	123	<3	10	37	14	0
-b	123	<3	10	37	14	2
440 ppm Ca-a	440	<3	13	60	19	0
-b	440	<3	13	60	19	3
-c	440	<3	13	60	19	2-½
5 ppm Pb-a	<2	<3	The Pb concentration was determined from the height of the 272 mμ absorption band (see Ref. 7b).			2
-b	<2	<3				2
-c	<2	<3				3
60 ppm Pb-a	<2	<3	6			0
-b	<2	<3	6			1-½
270 ppm Sr-a	<2	270	6	39	7	0
-b	<2	270	6	39	7	½

holders. The samples were typically the order of 1.3 cm long and 0.8 cm wide, and were compressed in the long direction to a total deformation of 1.5-3.0%. The irradiations were performed in a 3.1×10^6 -R/h Co⁶⁰ gamma source with the crystals at 34°C. A more detailed account of the irradiation procedure has been presented previously.¹¹

RESULTS

Introduction of *F* Centers

The effect of deformation on the *F*-center coloration for a number of "pure" and "doped" KCl crystals is illustrated in Figs. 1 and 2. Shown is the corrected optical-absorption coefficient α_F' for the peak of the *F* band¹⁴ versus the gamma dose received. The full symbols will always be used for the data on deformed specimens while the data for the undeformed samples are shown by open symbols. The small arrows in the figures indicate the gamma dose at which the samples were deformed. Figure 1 shows the data for a zone-refined KCl: pure, a KCl: Sr, and several KCl: Pb crystals. These data suggest that the effect of deformation on the colorability of the zone-refined crystal is small and tends to disappear at high doses, and that there is a noticeable enhancement in the coloration of deformed KCl: Sr and KCl: Pb crystals. Heavy doping (60 ppm Pb) apparently tends to suppress this enhancement. In Fig. 2 the growth curves for a pure sample (0227) and several KCl: Ca crystals are depicted.

¹⁴ It is known that the *M* center gives rise to absorption bands in the *F*-band region. An attempt has been made to eliminate this *M*-center contribution by subtracting the height of the *M*-center absorption at 825 mμ from the height of the *F*-center absorption. $\alpha_F - \alpha_M = \alpha_F'$.

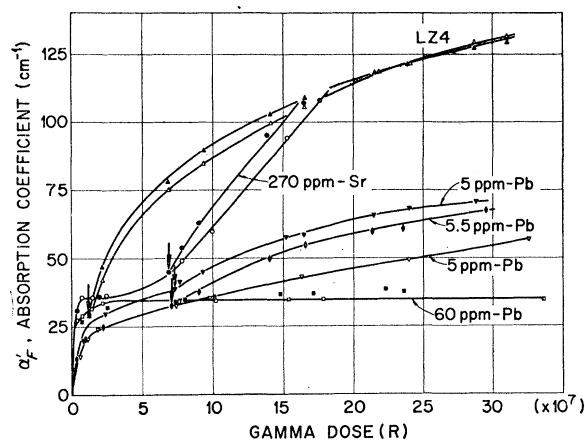


FIG. 1. *F*-center coloring curves for samples LZ4 (zone-refined), KCl: Sr; KCl: Pb were deformed. The curve showing the effect of deformation on the colorability for the 5-ppm Pb-doped specimen (\blacktriangledown symbol) has a higher early-stage coloration than that shown for the untreated 5-ppm KCl: Pb crystal (∇ symbol). This is because it was prestrained $\sim \frac{1}{2}\%$ during mounting.

Table I shows that the KCl: Ca samples have considerable Br₂ impurity, but previous work¹³ indicates that the colorability is not very sensitive to this impurity. It is clear that small amounts of Ca impurity enhance the deformation effects, whereas higher doping levels will suppress it. The effect of deformation on the *F*-center colorability of 0227 is even less pronounced than for LZ4, suggesting that deformation does not appreciably enhance the colorability of pure samples. It should be noted that there is a difference in the effectiveness of the Ca, Sr, Pb impurities, and this observation together with the fact that the pure samples do not show a deformation-induced increase in *F*-center concentration helps to explain some of the variations

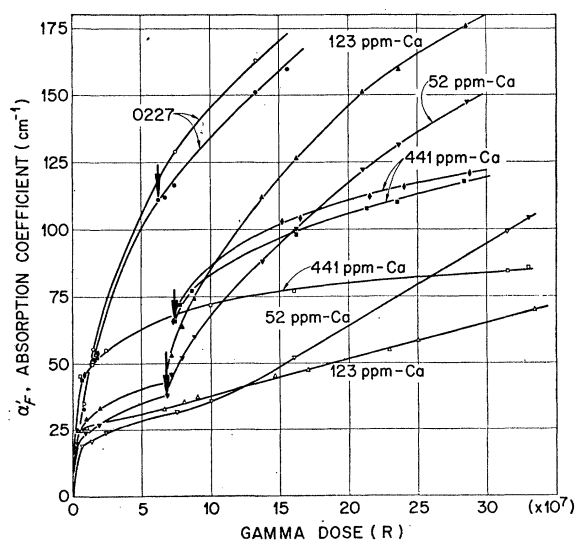


FIG. 2. *F*-center coloring curves for specimens 0227 (pure) and KCl: Ca.

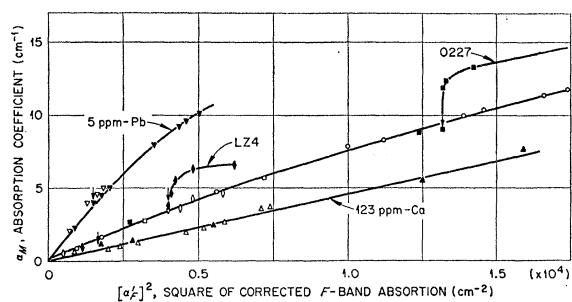


FIG. 3. The effect of plastic deformation on the ratio $\alpha_M/[\alpha_{F'}]^2$ for KCl: pure (0227 and LZ4), KCl:Pb, and KCl:Ca crystals.

in the effect of deformation on the colorability which have been reported.^{3,7-9} Moreover, we know that the effect of impurities on the magnitude of the colorability of KCl is intensity-dependent,¹¹ and this means that the amount of enhanced colorability shown in Figs. 1 and 2 might well vary with radiation intensity. The amount of deformation of the crystals is apparently not as important as the impurity concentration, but for a series of samples doped with the same concentration of impurity the incremental increase in coloration increases with increasing deformation. The strong dependence of the deformation-induced colorability on impurity means that for crystals containing certain impurities cleavage strains or mounting strains can affect the early-stage coloration. In Fig. 1 a comparison of the height of the early-stage coloration for the two 5-ppm Pb-doped samples suggests that prestraining can have an effect (see figure caption). The same effect can be seen in Fig. 2 by comparing the coloration curves of KCl:Ca specimens containing the same impurity concentration. This indicates that when quantitative measurements of early-stage coloration are important special care must be taken to avoid prestraining the specimens.

Introduction of Other Centers

Previous results^{3,11} suggested that there was little or no effect of deformation on the ratio of F and M centers. However, we present evidence here that there is an effect in the pure crystals. Figure 3 is a graph of the absorption coefficient at the peak of the M band versus the square of the corrected absorption coefficient at the peak of the F band. There is practically no effect of deformation on the slope of the α_M versus $[\alpha_{F'}]^2$ curves for the doped specimens; however, the pure samples (0227 and LZ4) show a marked increase in M -center production relative to F -center production. This increased concentration of M centers is apparently only temporary since as the irradiation is continued the α_M versus $[\alpha_{F'}]^2$ ratio appears to return to that characteristic of the undeformed specimens. More data points are available for sample 0227 than are illustrated in Fig. 3, and the line connecting the data points for the deformed crystals is drawn to pass through two data

points taken at higher F -center concentrations than are shown. The rate of destruction of the excess M centers would be expected to be intensity dependent,¹⁰ and perhaps at lower irradiation intensities the effect would be even more obvious.

Figure 4 is a plot of the absorption coefficient at 220 $m\mu$ (V_2 region) versus gamma dose for some of the crystals. Sample 0227 (not shown in figure) did not exhibit an increased absorption in this spectral range with deformation. For those specimens which show an enhanced absorption, the center apparently introduced by deformation which absorbs in this region does not seem to be the usual V_2 center. It is known that the V_2 band bleaches with the F band at room temperature,¹⁵ and in the case of the KCl:Ca undeformed samples this is observed. However, in the deformed samples, it appears that only that part of the absorption at 220 $m\mu$ which is associated with the early-stage coloration in KCl:Ca crystals can be bleached. For example, in the deformed crystals containing 52 and 123 ppm Ca, only a small part of this absorption band can be bleached, whereas in the crystal with 440 ppm Ca almost all of the band is bleachable.

Brilliantow and Obreimow¹⁶ and Davidge and Pratt² have reported that colored bands are formed along dislocation boundaries in irradiated crystals which have been subsequently bleached. We have seen this same coloration in Ca-doped crystals, but not in Pb-doped or pure specimens. The pure samples do not bleach as completely as either the Ca- or Pb-doped ones. Therefore, it may not be possible to distinguish the colored bands in these samples, but these bands should have been detectable in the Pb-doped crystals. Their absence in material which is not Ca-doped suggests that the centers responsible for this coloration are in some way connected with specific impurities. Moreover, the bands form only if a sample is irradiated after being deformed. If a crystal is irradiated and then deformed and

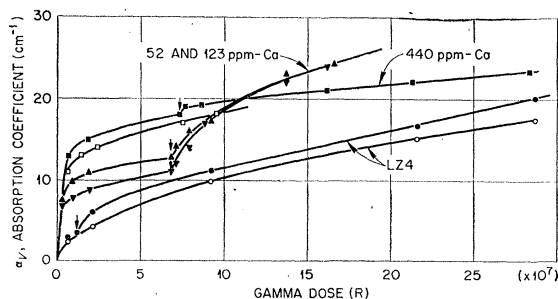


FIG. 4. V -center coloring curves for LZ4 and KCl:Ca samples. There was no effect of deformation on either the F band or V band for crystal 0227. The absorption coefficient was measured at about 220 $m\mu$ and is not necessarily a measure of the peak height of a particular band.

¹⁵ J. H. Schulman and W. D. Compton, *Color Centers in Solids* (The Macmillan Company, New York, 1962).

¹⁶ N. A. Brilliantow and I. W. Obreimow, *Physik. Z. Sowjetunion* 12, 7 (1937).

bleached, no evidence of coloration along dislocation boundaries can be found. Further irradiation and subsequent bleaching of these specimens, however, produces the colored bands.

DISCUSSION

Recent experimental evidence²⁻⁵ suggests that dislocation debris is responsible for most of the enhanced coloration observed in deformed samples. The production of one type of debris (vacancies and vacancy clusters) by dislocation interactions during plastic deformation has been studied by several groups.¹⁷⁻¹⁹ Davidge and Pratt¹⁸ have found that deformation of NaCl causes a decrease in the density of the crystal, the rate of decrease with deformation being less at low strains than at high strains. This is to be expected from deformation theory since the number of dislocation intersections produced during unit deformation is much larger when multiple slip systems are active, which occurs for high deformation, than for slip on a single system, which occurs for small strains. Dislocation interactions should generate equal concentrations of positive and negative vacancies and, because of electrostatic interactions between these, one would expect primarily vacancy pairs to be formed. Now the question arises whether these defects can be transformed into *F* centers or *M* centers and, therefore, whether they can account for the increase in coloration after deformation.

From the work of Davidge and Pratt¹⁸ some idea of the magnitude of the change in vacancy concentration accompanying deformation may be obtained. They found that the rate of density change in NaCl corresponded to the introduction of about 7×10^{16} vacancy pairs cm^{-3} per percent deformation for strain less than 4%. The data of Figs. 1, 2, and 3 indicate that the incremental increase in *F*-center and *F*-aggregate-center concentrations for the pure specimens (*LZ4* and *0227*) is no greater than 7×10^{16} cm^{-3} , which is well within this expected range provided the response of KCl is similar to NaCl. Thus, it appears that it is possible for the vacancies and vacancy clusters formed by dislocation intersections to be transformed into color centers by irradiation. Since most of the vacancies will probably be present as vacancy-pairs, as discussed above, enhanced *M*-center and *R*-center concentrations are to be expected with little increase in *F*-center concentration, at least initially. Figure 3 shows that there is a large increase in the production of *F*-aggregate centers in the pure crystals after deformation. The small incremental increase in *F*-center concentration after deformation seen for sample *LZ4* could be primarily due to the break up of *F*-aggregate centers by radiation, which

would explain the apparent induction period evident in Fig. 1.

The KCl:Pb crystals behave in a similar way as the pure specimens, and the dominant mechanism again appears to be vacancy cluster formation by deformation and the breakup of these clusters by irradiation. However, the marked enhancement of *M*-center formation is not evident for the Pb-doped samples. This could be because a large relative *M*-center-to-*F*-center ratio already exists, or it could be that the impurities which are present interact with the vacancies in such a manner that vacancy-impurity clusters are produced. This latter possibility is reasonable since many impurities are present in the lattice and since the impurity clouds around dislocations are broken up by dislocation motion, and the impurities are then available for recombination. The heavily doped KCl:Pb samples (60 ppm) do not show an appreciable increase in *F*-center production after deformation (see Fig. 1). This could be due to electron-hole recombination at Pb impurities.¹¹ It can be seen from the figure that even for the undeformed, heavily doped sample the late stage coloration is completely suppressed; therefore, it is not surprising that the addition of vacancies or vacancy clusters causes no enhancement of the colorability.

The KCl:Ca crystals show a quite different behavior from the KCl: pure and KCl:Pb ones. The most striking differences are the magnitude of the effect and the absence of an induction period for the enhanced *F*-center production after deformation. Notice that the 123-ppm Ca-doped specimen exhibited an incremental change of more than 4.5×10^{17} cm^{-3} after a deformation of 2.2%. This is considerably greater than the 7×10^{16} cm^{-3} observed for the pure samples and amounts to about a factor of two more *F* centers than would be expected from Davidge's and Pratt's results on NaCl. In view of the fact that some differences in the deformation response between NaCl and KCl may exist, one cannot rule out completely defect generation by interacting dislocations as the basis for the observed enhancement even in the KCl:Ca-doped crystals. However, the great difference in incremental increase of coloration between the pure and Ca-doped specimens and the *M*-center increase in the pure samples suggests that other factors can play a major role.

A possible explanation of this difference between the pure and Ca-doped crystals is that the impurities aid the multiple cross-glide mechanism²⁰ of deformation and, thus, in the impure samples more vacancies are produced per unit deformation. If this were the case, one would expect that the deformation-induced enhancement of the *F*-center concentration would depend on the flow stress of the samples. The flow stress of Ca- and Pb-doped crystals containing comparable amounts of impurity is very nearly the same, but the

¹⁷ W. H. Vaughan, W. J. Leivo, and R. Smoluchowski, *Phys. Rev.* **110**, 652 (1958).

¹⁸ R. W. Davidge, C. E. Silverstone, and P. L. Pratt, *Phil. Mag.* **4**, 985 (1959). R. W. Davidge and P. L. Pratt, *Phys. Status Solidi* **6**, 759 (1964).

¹⁹ M. Ueta and W. Känzig, *Phys. Rev.* **97**, 1591 (1955).

²⁰ J. J. Gilman and W. G. Johnston, *Solid State Phys.* **13**, 148 (1962).

F -center enhancement is much less for the KCl:Pb crystals. Moreover, the flow stress of the 440 ppm Ca-doped samples is twice that of the 52-ppm Ca-doped specimens, but Fig. 2 indicates that the less heavily doped samples give the greater enhancement. In view of this fact, it appears that the impurities themselves and their chemical state are important.

The most likely explanation of the results for the KCl:Ca samples is that the defect clusters, such as associated vacancy-impurity pairs and higher agglomerates, can be broken up and isolated vacancies produced during deformation. This would lead to an enhanced early-stage type coloration which would result in a large increase for the calcium-doped crystals. As is the case for Pb-doped crystals, the deformed Ca-doped ones show no detectable deviation from the M - to F -center relation obtained before deformation and because of the low concentration of M centers, any enhancement of M -center density relative to F -center concentration would be readily apparent. The absence of an enhancement suggests that either the deformation products in the doped crystals are different, or that the impurities in some way prevent an alteration in the M - to F -center relationship after deformation.

The V -center coloration in KCl crystals and particularly in deformed samples is extremely complex. It was possible to use a Cary 15 spectrophotometer to extend our measurements further into the ultraviolet. The apparent ultraviolet absorption edge shifts to longer wavelengths as a function of radiation dose and may move from as low as 175 $m\mu$ to as high as 183 $m\mu$. This shift results in an apparent increase in the V -center-region absorption and can be quite misleading. Also, several absorption bands are evident in this region and they overlap to such an extent that resolution is very difficult. Therefore, it is not possible at this time to make any definitive statements about V -center production.

The blue coloration along dislocation boundaries occurs in KCl:Ca samples which have been deformed,

irradiated, and bleached in that order. Davidge and Pratt² have tentatively attributed these bands to cluster centers, as opposed to colloids. The failure of KCl:Pb specimens to show dislocation boundary coloration suggests that certain impurities are necessary for its existence, and the fact that a post-irradiation deformation does not produce this coloration indicates that the irradiation itself is important. Perhaps a reasonable suggestion would be that cluster centers of the Z and R types are primarily responsible for this coloration. This interpretation would be consistent with the data of West and Compton,²¹ Cappelletti *et al.*,²² and Nowich,²³ and Davidge and Pratt.²

In addition to the blue coloration along dislocation boundaries, Davidge and Pratt also found a difference in the effect of 50-kV- and 200-kV-peak x rays on the colorability of deformed NaCl crystals. They suggested that this difference was due to the energy of the radiation used; however, it is equally probable that the difference they observe is due primarily to the intensity dependence of the colorability.^{10,24} In fact, a comparison of their data with that of Harrison²⁴ strongly suggests that the later case obtains. Furthermore, it is known that the height of early-stage coloration is radiation-intensity-dependent,¹¹ and so it is not unreasonable to suggest that there may be an intensity dependence of the incremental increase in F -center coloration due to deformation.

ACKNOWLEDGMENTS

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²¹ E. J. West and W. D. Compton, *Phys. Rev.* **108**, 576 (1957).

²² R. Cappelletti, L. Dalla Croce, and R. Fieschi, *Phys. Status Solidi* **3**, 1347 (1963).

²³ A. S. Nowick, *Phys. Rev.* **111**, 16 (1958).

²⁴ P. G. Harrison, *J. Chem. Phys.* **37**, 388 (1962).