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Model for reduced stability of coloration in microcrystalline powders of alkali halides

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The color centers in microcrystalline powders of alkali halides are considerably less stable than those in single crystals. The differences had been attributed to the interaction of moving dislocations, which are abundantly present in the powders with color centers. However, in the powders, the surface effects are also expected to be important. Experiments performed to distinguish between the surface effects and interactions with dislocations are reported in this paper. It is shown that the majority of the experimental evidence favors the dislocation model, although the possibility of surface effects playing some role cannot be ruled out.

I. INTRODUCTION

It is known that the colored crystals of alkali halides can be stored at room temperature in darkness without any loss of coloration for a period of several years.[1,2] In contrast to this, the coloration of microcrystalline powders of some alkali halides was found to decay within 24 h upon storage under the same conditions.[3] It was also shown[4–8] that the decay was not due to the recombination of F centers with electron-deficient centers, as was observed in the powders obtained by crushing electrolytically colored crystals which contained only F (excess-electron) centers.

The differences in the stability of electron centers in crystals and powders were attributed to the presence of dislocations in the powders in far greater abundance. It was speculated that the observed decay was due to the interaction of moving dislocations with color centers. The plastic deformations, which result in, among other things, dislocation motions, are known to cause bleaching of the color centers.[9] The dislocations strip off the charges from color centers. It was observed that the impurities inhibit the decay,[10] the magnitude of inhibition being proportional to the "misfit." This is consistent with the proposed model. The impurities are expected to pin the dislocations and thus inhibit the decay. Impurities differing most in size from the host ions are expected to be most effective in pinning the dislocations.

It was suggested that if the above explanation is valid, then the stability of coloration in microcrystalline powders, in turn, can be used to study the interaction between color centers and moving dislocations, dislocation motions, etc. It is therefore necessary to establish the earlier results and the model, and to put them on a more sound footing. It is especially important to substantiate the above model in view of the fact that the powders are rather complicated, and one may devise alternative explanations. Particularly, at the mention of "microcrystalline powders," one suspects some kind of surface effects to be present.[11] One may ascribe the decay to motions of color centers instead of dislocations. The color centers may migrate to the surface where they are annihilated.

In this paper we report the results of the experiments performed specifically to decide between the dislocation model and surface effects. The results which substantiate the previously published data are also presented.

II. EXPERIMENTAL PROCEDURES

Single crystals of various pure and doped alkali halides were grown from a melt by the Czochralski method. Guaranteed reagent-grade powders were used without further purification. The stated impurities were added to the melt in desired concentrations. The single crystals were cleaved to the required size and colored electrolytically using a previously described arrangement.[12] The crystals were heated to the desired temperature ($\simeq$600 °C), and an electric field (100 V/cm) was applied using a flat anode and pointed cathode. Thin slices were cleaved out from the central uniformly colored portion of the single crystals for optical-absorption measurements. The remaining uniformly colored pieces were then crushed to powders and sieved to required fineness. The results of Sec. III correspond to particles between 124 and 140 μm, unless mentioned otherwise.[13] The reflectance spectra of these powders were scanned on a Carl Zeiss spectrophotometer (model VSU 2P). For recording the decay, reflectance at a F-band maximum was measured at suitable intervals. Complete spectra were scanned at longer intervals (greater than 2 h). For recording the decay at temperatures other than room temperature (RT), the samples were stored in an oven or ice bath, removed at intervals, and quickly brought to RT; reflectance at the F-band maximum was measured, and the samples were replaced at the same carefully marked position in the oven or ice bath. The complete procedure required only a couple of minutes. When the readings were to be taken at longer intervals (greater than 2 h), the complete spectra were scanned in about 5 min during which time the samples remained at RT before they could be returned to the oven or ice bath.

The procedure of coloring the crystals first and then crushing them to powders must be carried out to ensure that only excess-electron color centers are produced, which in turn ensures that only the processes under discussion are responsible for the observed decay; the decay is not due to recombination with hole centers. It is not possible to color powders by electrolytic coloration (which makes it possible to introduce only excess-electron centers), and hence the rather roundabout procedure must be followed.

In the case of fluorides, the conditions under which the electrolytic coloration can be carried out are very exacting.[14] The powders colored by electrodeless discharge were used in these cases. The decay thus need not be due to "nonrecombination" processes; nevertheless the observations are useful in deciding the lower-temperature limit to which the color centers in these materials are stable.

While studying the effect of optical bleaching on decay, F light separated by employing a suitable Corning filter was used. In all cases, the results on bleached samples were always compared with samples stored in darkness under identical experimental conditions.

In one experiment, the dislocation densities in single crystals were measured by the etch-pit method. Ethanol saturated with $PbCl_2$ was used as an etchant.

III. RESULTS

The results for the optical absorption of pure and doped single crystals were not different from those reported in the literature (hence not reproduced here), indicating that the new results reported are not due to the presence of unintentional impurities.

A. Powders of pure crystals

Figure 1 shows the isothermal decay of F centers for different samples recorded at various temperatures. The decay was recorded for powders 124—140 μm. The Kubelka-Munk function $F(R)$ normalized in terms of initial value is plotted as a function of time.[15]

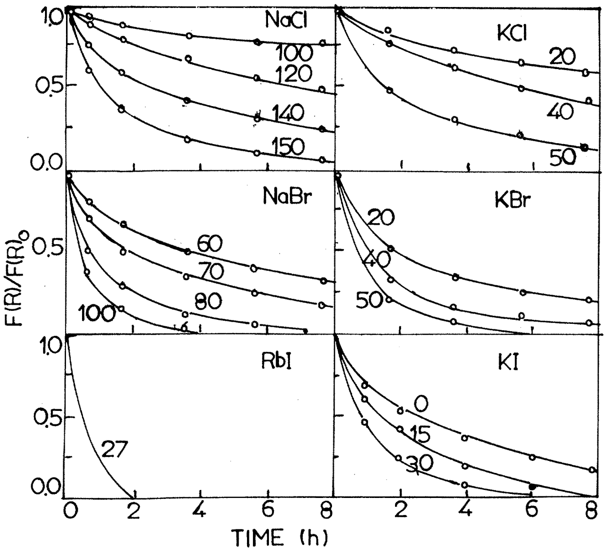

FIG. 1. Isothermal decay of F centers in microcrystalline powders (124—140 μm) of various alkali halides at different temperatures (numbers of the curves). The Kubelka-Munk function normalized in terms of initial value at the F-band maximum is plotted as a function of storage time.

It is seen that in potassium-halide powders there is rapid isothermal decay of coloration at RT over the entire wavelength region as there is no conversion of F to F-aggregate centers. The powders of other alkali halides were found to retain the coloration for a long time when stored at RT. When NaCl powder was stored at elevated temperatures there was no appreciable loss of coloration when the storing temperature was up to 80 °C. Conversion of $F \rightarrow F$-aggregates and colloids was observed when the storing temperature was 50—80 °C. Around 100 °C, the already formed aggregates and colloids disperse upon storing. Above this temperature, a genuine decay of coloration is observed without any conversion.

When NaF powder colored in an electrodeless discharge[17] was held at 175 °C, $F \rightarrow F$-aggregate, colloid, etc., conversion could be observed. A similar conversion could be observed when LiF powder was held at 400 °C (Fig. 2). This shows that genuine F-center decay does not commence at least up to 175 °C in NaF and 400 °C in LiF.

The results presented in Figs. 1 and 2 show an unmistakably regular trend. The stability of coloration of powders goes on decreasing as one proceeds along the alkali-halide series. To have a quantitative measure of this property, we plot T_s—the temperature required to induce 50% decay in 2 h—as a function of nearest-neighbor distance d (Fig. 3).

The data presented in Fig. 1 enable one to obtain the activation energy for the decay processes. The decay curves can be decomposed into two or more exponential components. One can write

$$C = \sum_j C_{j0} \exp(-\lambda_j t) , \tag{1}$$

where C is the color-center concentration and C_{j0} are the initial concentrations of centers decaying with rate λ_j. The activation energy for decay can be calculated by studying the decay rates of Eq. (1) as a function of temperature and plotting $\ln p/\lambda$ (p is the arbitrary constant) against $1/T$. A straight line with a slope of E/k results (Fig. 4). The E values obtained using Eq. (1) for the

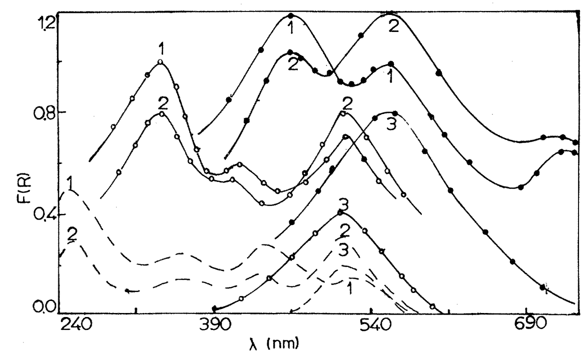

FIG. 2. F-to-colloid conversion in powders colored in an electrodeless discharge. Dashed curve: LiF—(1) as colored, (2) after 8 h at 400 °C, and (3) after 1 h at 400 °C; curve through open circles: NaF—(1) as colored, (2) after storing at 175 °C for 30 min, and (3) for 1 h; curve through closed circles: NaCl—(1) as colored, (2) after storing at 80 °C for 30 min, and (3) for 1 h.

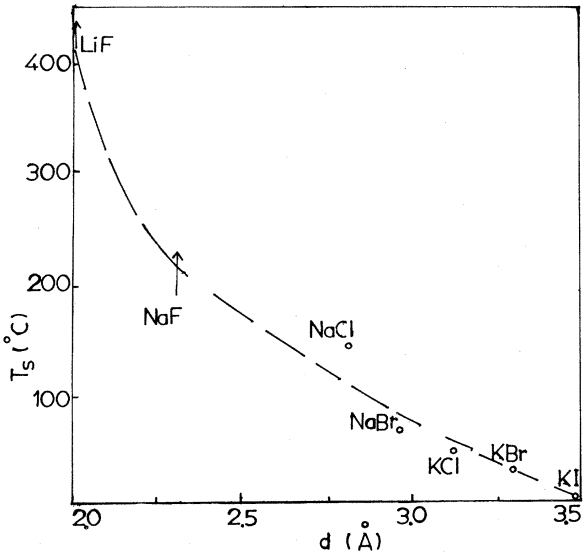

FIG. 3. Stability of coloration of microcrystalline powders of various alkali halides. Temperature T_s required to induce 50% decay in 2 h in powders 124—140 μm is plotted as a function of nearest-neighbor distance d. In the case of NaF and LiF, an estimated lower limit of T_s is shown.

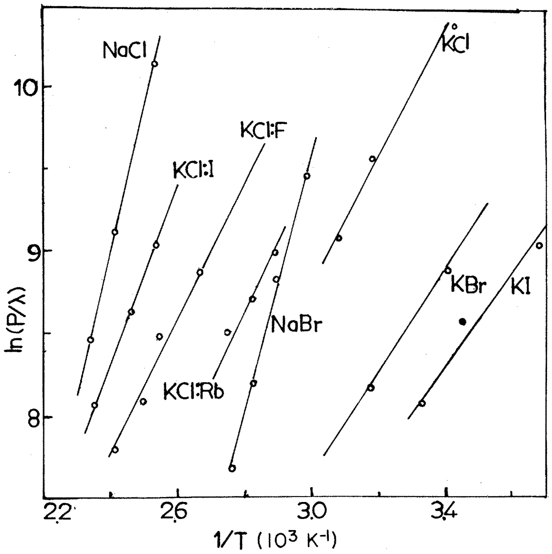

FIG. 4. Arrhenius plots for various powders. lnp/λ vs $1/T$ is plotted, where λ is the rate constant, p is an arbitrary constant, and T is the temperature (K) at which the decay is recorded. Slopes of the straight lines equal E/k.

fastest-decaying component are listed in Table I. Because the decay was interrupted for taking readings, large errors in E values are expected; still one can observe regularity. The E values decrease with increasing d. Thus it is seen that the reduction in stability of the coloration of powders shows a very regular trend, qualitatively as well as quantitatively. It was shown previously[17] that the coloration characteristics of the microcrystalline powders can be explained on the basis of the interaction between color centers and dislocations. A qualitative measure of the interaction was shown by the differences in F-band halfwidths in crystals and powders and the shape of F-aggregate bands. It was found that this interaction showed a very regular trend; being least for LiF and increasing regularly with the d value. Based on these results and interpretation, Janszky *et al.*[18] obtained distance between dislocations and color centers and arrived at acceptable values.

The results presented in Figs. 1—4 also show such regular trends. We thus suggest that the observed decay of coloration is due to interaction of moving dislocations with color centers. The activation energies obtained are adequate to represents dislocation motions.[19]

B. Doped alkali halides

If the proposed mechanism of decay based on the "dislocation model" is correct, then it implies that the impurities which pin the dislocations should inhibit the decay. Figure 5 indeed shows such results. The effectiveness of impurities in inhibiting the decay increases with misfit.

The model also implies that at higher temperatures, when the dislocations will be unpinned from the impurities, the isothermal decay of coloration should be observed in the powders of the doped crystals as well. This was indeed observed experimentally. The results are presented in Figs. 6 and 7.

It is seen that the coloration of the powders of doped crystals shows decay similar to that observed in Fig. 1, when stored at adequately high temperature. The temperatures required to induce the decay increase with misfit. The temperatures required to induce 50% decay in 2

TABLE I. Parameters indicating the stability of coloration in microcrystalline powders (124—140 μm) of alkali halides. E is the activation energy expressed in eV and T_s is the temperature in °C to reduce the F-center concentration by 50% in 2 h.

		E	T_s (°C)
LiF			≥400
NaF			≥175
NaCl		0.77	145
NaBr		0.69	65
KCl		0.35	45
KBr		0.28	20
KI		0.24	5
RbI			0
KCl:Ca		0.345	75
KCl:Sr		0.31	70
KCl:Ba		0.27	60
KCl:Li		0.32	100
KCl:Na		0.35	110
KCl:Rb		0.40	70
KCl:F		0.37	100
KCl:I		0.45	125
KCl:KBr	1:1	0.32	80
	3:1	0.40	65
	1:3	0.50	55
	5:1	0.50	50
	1:5	0.60	48

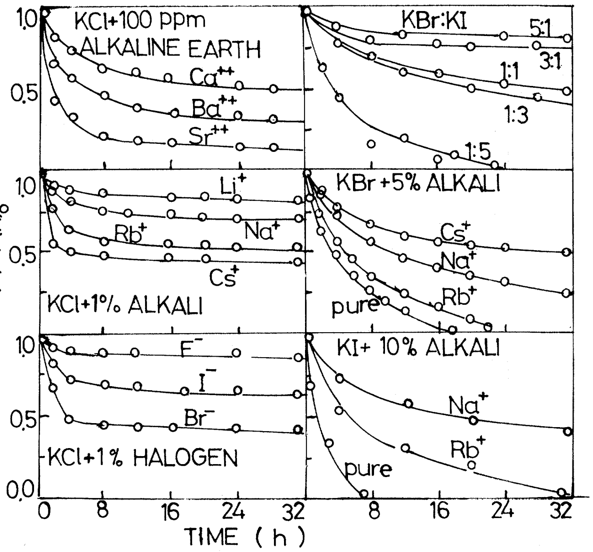

FIG. 5. Inhibition of decay by impurities. Isothermal decay of F centers in various powders at RT (after Ref. 5).

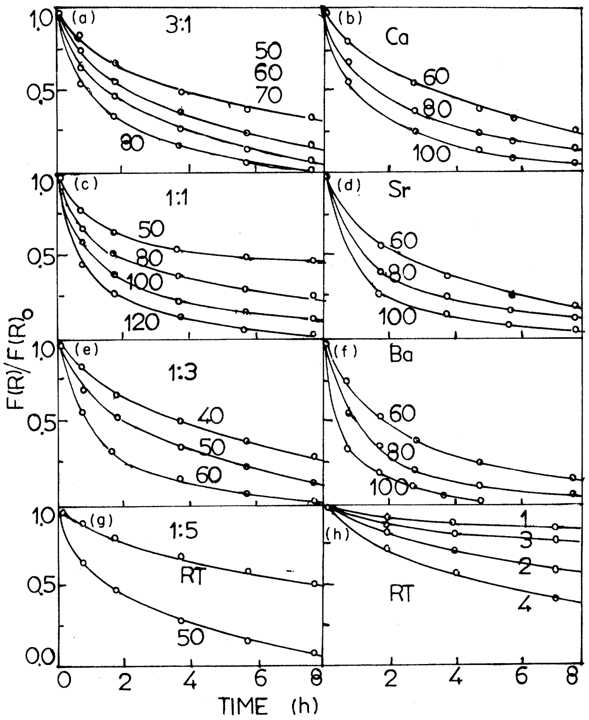

FIG. 7. Isothermal decay of F centers in KCl powders doped with various impurities at different temperatures (numbers on curves). (a), (c), (e), and (g); mixed KCl-KBr powders; (b), (d), and (f): impurity concentration of 100 ppm; (h): effect of precipitation of impurities on isothermal decay of F centers in γ-irradiated powders of KCl:Li and KCl:F; (1) as-grown KCl:Li powder, (2) powder annealed at 120 °C for 4 h, (3) as-grown KVl:F powder, and (3) powder annealed at 120 °C for 4 h.

h are listed in Table I. At RT, the stability in descending order is Li, Na, Rb, and F, I, and Br. At elevated temperatures, on the other hand, decay in KCl:Li is faster than in KCl:Na, and KCl:F is faster than in KCl:I. This may be due to precipitation of these impurities (Li,F) which are sparingly soluble during the storage at high temperature. The following experiment was performed to verify this. Powders of as-grown KCl:Li and a sample annealed at 120 °C for 4 h were colored by γ rays. Isothermal decay of these samples was then recorded at RT [Fig. 7(h)]. The decay is considerably faster in annealed powders. The results explain the fact that at RT the stability of coloration is in descending order, F, I, and Br, and Li, Na, and Rb, but at elevated temperatures KCl:Li loses color faster than KCl:Na and KCl:F loses color faster than KCl:I. From the data of Figs. 6 and 7, activation energies were obtained for the decay processes in doped powders. Arrhenius plots for some of the impurities are included in Fig. 4. The activation energies are listed in Table I.

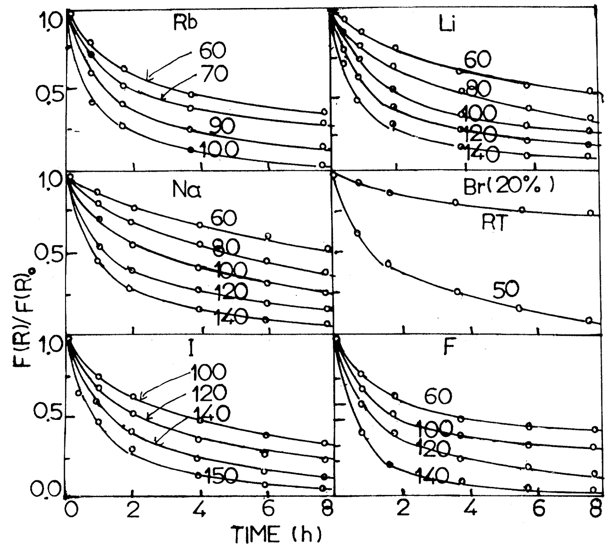

FIG. 6. Isothermal decay of F centers in KCl powders doped with various impurities (1 mol %) at different temperatures (numbers on curves).

C. Experiments related to the mechanism of decay

All the results described up until now can be satisfactorily explained by the dislocation model. However, it appears that a very simplified picture had been considered, and the explanation proposed need not be unique, but there might be other alternatives. Particularly, the powders possess not only more dislocations but also greater surface to volume ratios. Several mechanisms based on the surface effects can be offered. In the following, we state a particularly attractive mechanism based on Lehovec's results.[20,21]

Lehovec[20] has pointed out that because of (a) the difference in energy of formation of $+ve$ and $-ve$ components of either the Schottkey or Frenkel pair, and (b) the requirement of electrical neutrality in the crystal interior, there exists a defect gradient near the surface which results in the creation of cation vacancies near the surface. During crushing the single crystal to powder, a substantial fraction of the crystallite consists of the double layer which is rich in $+ve$ ion vacancies. Color centers migrate and interact with the vacancies in the double layer, forming complexes which absorb in a spectral range entirely different than that in which F centers absorb. In doped crystals, impurities form complexes with vacancies, and thus less vacancies are available for recombining with F centers. At higher temperatures, vacancies are dissociated from impurity-vacancy complexes, and are available for interacting with F centers. This regenerates the F-center decay.

Several experiments were performed to distinguish between the dislocation model and "surface-effect model." The results of these experiments are described in the following.

1. Decay of coloration by optical bleaching

The surface-effect model attributed the decay to the motion of color centers toward the surface and their subsequent recombinations with vacancies. If this explanation is correct, then the decay should be observed when the mobility of color centers is increased by other than thermal means. This can be achieved by optical bleaching. The color centers mobilized by optical bleaching should recombine with vacancies resulting in the loss of coloration. The results of optical bleaching for pure and doped KCl are shown in Fig. 8. The bleaching light corresponds to wavelengths absorbed by F as well as Z_1 centers. The inset [labeled (a)] shows the F-band concentration plotted against time.

It is seen that there is an initial rapid loss of F centers, but when the complete spectra were scanned, it was found that there was quite some conversion to F-aggregate, colloid, E, etc., bands (the E band is supposed to be due to electrons trapped in dislocation debris[22]). This is in sharp contrast to the decay reported in Figs. 5—7. These results clearly demonstrate that when color centers are made mobile, there is some interconversion observed, the decay is not uniform over the entire range. The decay under discussion, on the other hand, is genuine without accompaniment of any conversion. Again, even the genuine decay is not made any faster by moderate bleaching, as is observed for KCl:Ca bleached at 80 °C [inset labeled (b)]. All of these facts are consistent with the dislocation model. The mobile color centers can aggregate or become trapped by dislocations; only in the latter case there is a chance of annihilation. The resultant decay will be very slow compared to the one caused by dislocation motions where the whole color-center population is swept up and motion of a single dislocation suffices to destroy several color centers.

2. Particle-size effect

Transition from crystal to powder can be studied gradually by performing the experiments on particles of various sizes. The variation in decay rates with particle size is predicted differently by the two models. The dislocation model expects the stability of coloration to go on decreasing with increasing dislocation density. With increased crushing, the dislocation densities will go on increasing and after a certain size is reached, saturation in dislocation density will be attained. The stability of coloration will also follow a similar trend. It is to be noted that even in coarse particles obtained by crushing the dislocations are present in large numbers and the stability of coloration

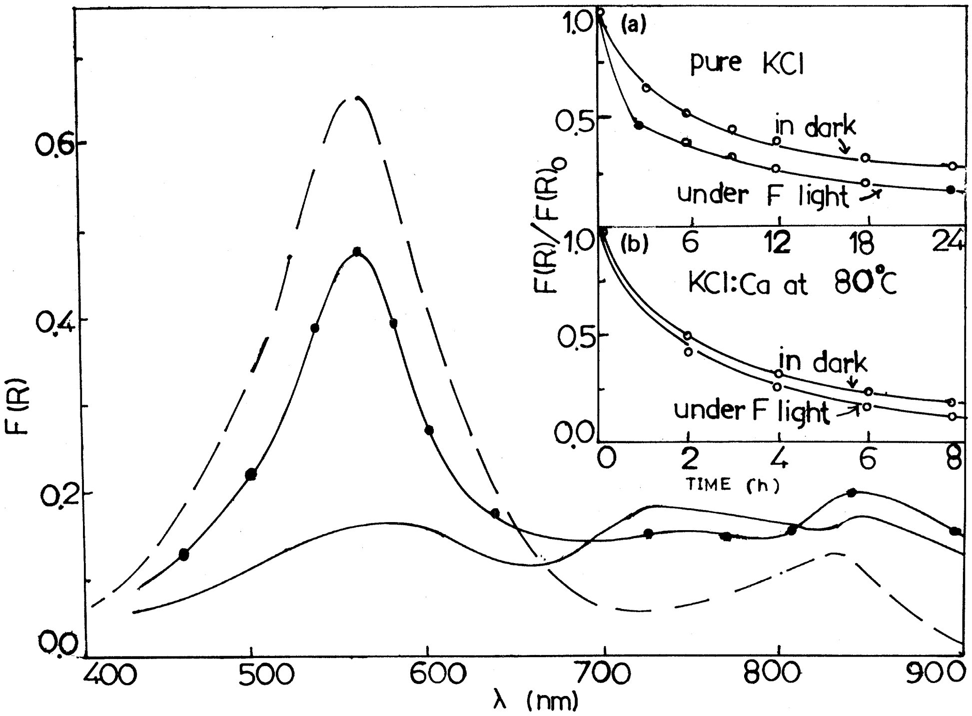

FIG. 8. Effect of optical bleaching on decay. — — —: as-colored KCl powder; —o—: after 15 min F bleaching; ——: after 6 h F bleaching. Inset (a) shows decay of F band in KCl powders stored at RT in dark and under F light. Inset (b) shows similar results for KCl:Ca powders stored at 80 °C.

should be much less compared to good single crystals.

The predictions of the surface-effect model are different. With its use, we expect that for sufficiently large particles, the stability of coloration should be as much as that of good single crystals, as the double layer is too small a fraction of the crystallite in this case to affect the stability. The S/V ratio goes on increasing with the increasing particle size, and there should be very rapid reduction in stability of coloration with the decreasing particle size.

Isothermal decay curves were obtained for KCl particles of various sizes. Figure 9(a) shows the decay recorded at RT. It is observed that decay is fastest for particles of size 105—124 μm. The decay did not become any faster for particles of smaller sizes (77—105 and less than 77 μm). In Figs. 9(b)—9(h) the decay of coloration in particles of various sizes is shown. The numbers on the curves show the temperature at which the decay was recorded and also show the particle size, respectively.

Figure 10 shows the stability of coloration as a function of particle size. The variation of the surface-to-volume ratio (which is of significance for the surface-effect model) is also plotted. The temperature required to induce 50% decay in 1 h was taken as a criterion for stability. It is seen that below 200 μm the S/V ratio is increasing fast, but stability is not reduced much. Particularly, below 100 μm, there is no change in stability though S/V is increasing steeply. Thus the results are compatible with the dislocation model and go against the surface-effect model. Particularly, the fact that crystallites as large as 850 μm are not as stable as single crystals is rather curious and goes against not only the surface-effect model considered here, but against any model that is based on purely surface effects.

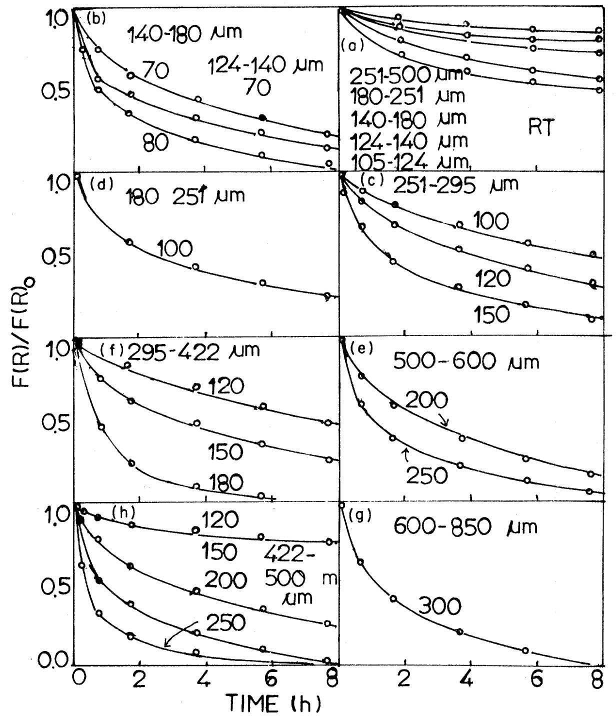

FIG. 9. Effect of particle size on stability of coloration. Isothermal decay of F centers in powders of varying fineness at different temperatures (numbers on curves) are shown in Figs. (b)—(h). In (a), isothermal decay curves for various particle sizes recorded at RT are plotted. The decay curves for powders in the range 77—105 μm and less than 77 μm are not appreciably slower than shown for 105—124 μm.

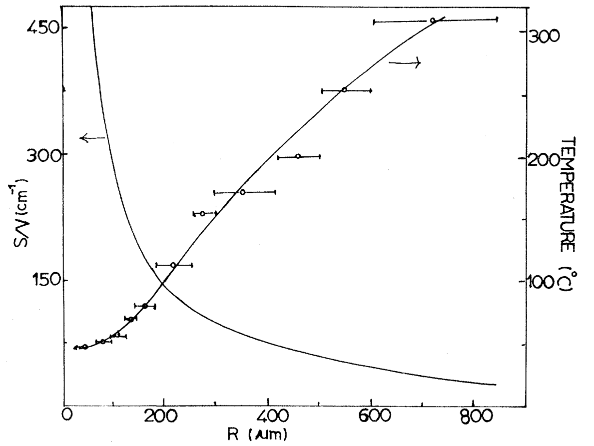

FIG. 10. Stability of coloration as a function of particle size. Temperature required to induce 50% decay in 1 h is taken as a criterion for stability. S/V ratio ($3/R$) is also plotted.

An interesting observation was made for particles as coarse as 600—850 μm which again supports the dislocation model. Small crystallites (600—850 μm) were "cleaved" from a colored KCl crystal. A part of the same crystal was crushed and particles between 600—850 μm were collected. The decay of these two samples was recorded by storing them at 300 °C. The results are shown in Fig. 11(a). For crushed particles (curve 1) most of the coloration is lost within 8 h, while in cleaved particles (curve 2) about 35% of the initially present F centers are still surviving. The remaining 65% are also not completely destroyed, but a considerable fraction has been utilized in $F \rightarrow$ colloid conversion as indicated by the well-known colloid band at 730 nm [Fig. 11(b)]. It was also observed that a few of the crushed particles retained the coloration and turned blue (colloid formation). Small residual coloration of the crushed sample is due to such particles. Under the microscope, these particles were found to be of regular square shape. Apparently these particles became cleaved during crushing and they are behaving as the cleaved particles. It is thus fairly well established that the coloration of the cleaved particles is much more stable than that of the crushed particles of the same dimensions. This cannot be explained by the surface-effect model, as the surface effects would have been the same in both the cleaved and crushed samples.

3. Dependence of stability of coloration of single crystals on the degree of perfection

From the results of Sec. III C 2 one suspects that the stability of coloration of even single crystals may depend upon their dislocation contents. Such results were indeed obtained.

The crystals containing varying dislocation densities could be obtained by changing the growth conditions; even

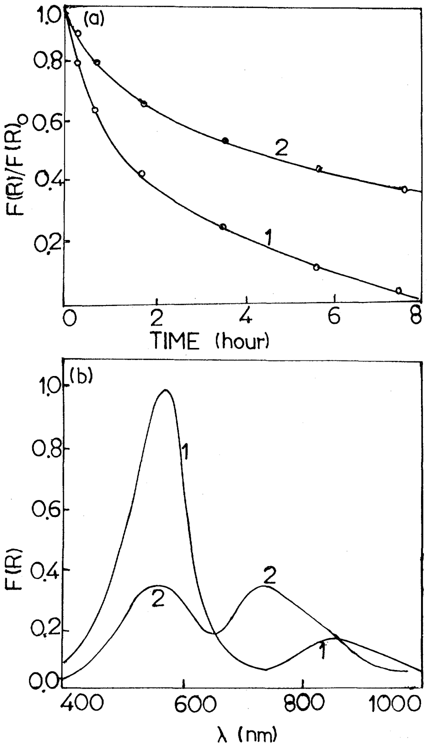

FIG. 11. (a) Isothermal decay of F centers in microcrystallites: (1) particles (600—850 μm) obtained by crushing stored at 300 °C; (2) particles of same size obtained by cleaving stored at 300 °C. (b) F-colloid conversion in cleaved crystallites. Reflectance spectra of 1, as-colored particles, and 2, after storing at 300 °C for 8 h.

during cleaving after and before coloration, coloration, etc., samples with varying dislocation densities were invariably obtained. Thin slices from crystals containing different amounts of dislocations were cleaved out and their absorption spectra were recorded. The slices were then stored in an oven, removed after some time, cooled to RT, and the spectra were again recorded. At the end of the experiment the dislocation densities were measured by the etch-pit method.

It was observed that in crystals containing 1.3×10^6 dislocation lines/cm^2, 60% coloration was retained when the crystal was held at 525 °C for 10 min. On the other hand, 85% of the coloration of the crystal containing 7.87×10^6 dislocation lines/cm^2 was lost when it was subjected to the same heat treatment. The experiments were repeated several times. It was always observed that coloration of the crystal containing more dislocations was significantly less stable. Again the results are compatible with the dislocation model and go against the surface-effect model.

4. *Dislocation motions and bleaching of color centers*

To establish the dislocation model beyond a doubt, it will be necessary to show that when the dislocations are made mobile by other than thermal means the decay of coloration similar to that of Fig. 1 results. The following experiments were performed to test this.

The dislocation motions could be achieved by applying cyclic stress with the help of an arrangement described by Ramaurt and Vennik.[23] One end of the colored crystal was glued to a rigid support and the other to a vibrator. By fixing the crystal such that its length was parallel to the vibrator, it was subject to cyclic bending. When the length was held perpendicular, cyclic compressions and elongations were achieved. In either case, the coloration was lost only partially after applying the stress, in no case the loss could be made to exceed 20%, no matter how long the crystal was subject to cyclic stress.

5. *Sundry experiments*

In the surface-effect model, the color centers migrate and form complexes with vacancies to form a defect which has optical absorption in a region far removed from that of the F-center region. In the dislocation model, the decay can be due to the formation of complexes, or the charges from color centers can be utilized in charging the dislocations or neutralizing the charges on already charged dislocations. The surface-effect model, thus, looks for complex defect absorbing in the infrared (ir). The dislocation model, on the other hand, can do with or without such a defect. The ir spectra of the colored powders from which the coloration has decayed to various extents were recorded between 900—14 000 nm. The spectra of all powders were identical. No changes in the spectra were found to accompany the decay, and thus formation of complex absorbing in ir which is expected by the surface-effect model is not borne out.

In any type of surface-effect model the color centers are expected to migrate the surface in which case a shift of the F band to longer wavelengths can be expected.[24–27] As the decay proceeds, a larger fraction of the F centers will be near the surface, and the shift should increase, at least asymmetric broadening of the long-wavelength side of the F band is to be expected. The results discussed show no such changes.

IV. DISCUSSION

The salient results presented here and in earlier papers can be summarized as the following.

(1) The coloration of powders is significantly less stable than that of single crystals; the difference increasing along the alkali-halide series beginning from LiF to RbI.

(2) The coloration decays over the entire wavelength range and there is no interconversion between F and F-aggregate centers. There is also no change in the F-band position or halfwidth during any stage of decay.

(3) The decay of the coloration is inhibited by the addition of impurities. The impurities which are the most misfit are also most effective in inhibiting the decay, provided they are soluble.

(4) In the doped powders, the decay can be observed again if the powders are stored at adequately high temperatures.

(5) When only color centers are made mobile, but not

the dislocations (e.g., by optical bleaching or by heating below the temperature of genuine decay), $F \rightarrow F$-aggregate, colloids, etc., conversion is observed without profound decay.

(6) The stability of coloration of even large crystals depends upon their dislocation contents. The crystals containing more dislocation lines/cm^2 lose their coloration more easily.

(7) When crystallites of the same size are obtained from a large colored single crystal by crushing the cleaving, the coloration of crystallites obtained by cleaving is significantly more stable than those obtained by crushing.

(8) When the dislocations are made mobile by other than thermal means, e.g., by applying cyclic stress, the color centers were bleached only partially. Bleaching to a maximum of 20% could be achieved.

The model for explaining the nonradiative decay of colore centers in microcrystalline powders should be built around the above evidence. The starting point of the model is that the decay is characteristic of the defects inherent to the microcrystalline powders. Compared to single crystals, the powders contain a large number of dislocations and grosser imperfections such as grain boundaries; they are also characterized by a rather high S/V ratio. The decay must be explained on the basis of the interaction between color centers and one or more of these defects.

It is clear from the results of Sec. III that a model based on purely surface effects will not be adequate for explaining the results, and hence the other defects such as dislocations, grain boundaries, etc., must be considered. The interaction with dislocation seems to be the most promising explanation. It has been shown[9] that the dislocation motions can result in the destruction of color centers. All of the results, with the possible exception of Sec. III C 4, can be adequately explained on the dislocation model. However, it is not yet clear why all of the color centers are not bleached when the dislocations are moved under applied stress below the breaking point. One of the reasons could be that under such conditions dislocations move mostly by glide; at RT, there is no diffusion possible, the dislocation climb will be negligible. During the isothermal decay, on the other hand, a slow dislocation climb is expected, especially at elevated temperatures. The climb motion is accompanied by the creation of interstitials or vacancies. These can interact with color centers causing the decay. In the powders the diffusion, and in turn the climb, may be made possible at temperatures considerably lower than those for single crystals, because of easier motions of ions (or vacancies) near the surface.[20] In this sense surface effects may play some secondary role.

Alternatively, the mechanism similar to the one suggested on the basis of surface effects may be operative, the dislocations taking over the role of surface—the double layer may be formed near dislocation boundaries[28] instead of the surface. It has also been shown[29] that at moderate temperatures, the glide of dislocations results in a maze substructure. At high temperatures the glide and climb of dislocations produce a system of small-angle dislocation boundaries separating a crystal into subgrains.[29] Thus the dislocations can serve as a source of increasing surface effects, this accounts for their observed role in the bleaching of color centers. Results of Sec. III C 3, and to some extent those of Sec. III C 2, can then be explained on the basis of surface effects, with the dislocations increasing the effective surface.

These are the finer details of the model. The present paper does not claim to have obtained a final answer to the problem. However, the results presented here take us quite ahead toward it. The results also indicate that study of the stability of coloration in microcrystallites will provide an indirect way of observing dislocation motions.

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