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Formation of Color Centers in KCl:Tl by Gamma Irradiation at 21 °C[†]

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The formation of color centers in KCl, both "pure" and with thallium impurity, by Co^{60} γ irradiation at 21 °C has been carefully studied. The samples were grown from zone-refined material which had been chemically purified. The pure crystals did not contain detectable amounts of thallium, while the doped crystals were adjusted to contain from 4 to 145 ppm of Tl impurity. Presumably, Tl^+ enters the KCl lattice substitutionally and, except possibly at the highest Tl concentrations, is incorporated as an isolated ion. As the irradiation dose increases, the Tl^+ A, B, and C bands decrease; however, the F band, a broad "V-region" absorption, and, except at lowest doses, the M band all concomitantly increase. The V-region absorption is a function of the Tl content. Below $\sim 10^6$ rad the F-center formation rate increases and then decreases as the Tl content increases. Above 10^6 rad the level of the F-center absorption decreases as the Tl^+ content increases. Also, the M-center concentration is proportional to the square of the corrected F-center concentration, and the M- to-F-center ratio increases as the Tl content increases. These and other observations indicate that, with few exceptions, if any, the effects on the coloring curves produced by substituting monovalent Tl^+ ions in the KCl lattice are very similar to those produced by substituting divalent impurities such as Ca^{2+} ions. Consequently, it must be concluded that the role of monovalent and divalent metallic impurities in the coloring process is similar and is not related to the initial valence state of the impurity. In particular, it would appear that those positive-ion vacancies that are almost certainly introduced when divalent ions are substituted in the KCl lattice, to provide charge neutrality, are not essential to the impurity-related coloring mechanisms.

I. INTRODUCTION

Radiation-induced color-center formation in alkali-halide crystals continues to be an interesting subject for study, even after many years of continuing effort. The color-center formation properties which are usually described by plots of color-center concentration versus irradiation time or dose, often called growth curves, apparently involve numerous interrelated processes. At the moment, some of these are reasonably well understood but others are not. The color-center formation kinetics are sensitive to changes in a large number of experimental variables.[1] Two of the most important are the nature and the amount of any impurities present in the crystal. Other variables include plastic deformation, sample temperature during irradiation, heat treatment of the sample, radiation intensity or dose rate, and the type and energy of the coloring radiation.[2–11]

The effects on the alkali-halide coloring curves produced by purposely introducing specific impurities into the crystals have been described in several studies. Almost all of the published work is on crystals doped with divalent metals.[12–16] In comparison, there is little experimental information on color-center growth kinetics in crystals with monovalent impurities. The most pertinent reference – to the work described here – is a study of F-center formation in KI : Tl and KBr : Ag induced by electron bombardment.[17] Studies on the coloring kinetics in the particular combination of host crystal and impurity used in this investigation, namely, KCl : Tl, induced by x, γ, or electron irradiation were not found in the literature. More specifically, some of the references mentioned below include studies on the color centers produced by irradiating KCl : Tl, but they do not, other than incidentally, contain information on the rate of color-center formation.

A description of the role of metallic impurities on the coloring kinetics divides into three categories: first, "pure" crystals which really contain unknown quantities of from one to twenty or more impurities; second, pure crystals containing a purposefully introduced monovalent impurity; and third, pure crystals with purposefully introduced divalent impurity. Coloring-kinetics results for pure crystals have been summarized by Schulman and Compton.[1] However, for comparison with comments below, it is pertinent to point out that the late-stage coloring in pure crystals varies considerably and has been conclusively correlated to dislocation density or impurity content. In addition, there are indications that the coloring level attained at high-dose rates in pure crystals represents an equilibrium between one or more charge-trapping and backreactions such as electron-hole recombination.[10,11] The relatively few reports available on monovalent crystals indicate that their presence increases the first-stage coloring[1,18–20] and suppresses the late-stage coloring rate.[17] However, these effects are much more firmly established for alkali halides containing divalent impurities. Specifically, compared to the coloring rates observed in pure crystals, the presence of one of several different kinds of divalent impurities increases the initial- or first-stage coloring and decreases the late- or second-stage coloring if the crystal is exposed to either x, γ, or electron irradiation. Furthermore, different divalent impurities produced roughly equivalent effects. The mechanisms suggested to account for the impurity-related first-stage coloring differ considerably.[1,12,21,22] However, the enhancement of early-stage coloring by divalent impurities is usually, directly or indirectly, attributed to the positive-ion vacancy content assumed to be present to maintain charge neutrality. There is little understanding of the late-stage coloring other than that contained in the mechanisms proposed by Pooley[17] which include the prediction that the late-stage coloring rate should be proportional to the reciprocal of the impurity concentration, or less specifically, as the impurity content is increased the late-stage coloring rate is suppressed.

Inasmuch as there are numerous studies on the coloring of alkali halides containing divalent metal ions, it would appear to be particularly useful to make additional studies on one or more carefully purified crystals containing monovalent impurities. Furthermore, there is one especially interesting reason for studying crystals with monovalent impurities. Most likely, a monovalent ion will enter the lattice substitutionally without introducing charge compensating vacancies. Consequently, a comparision of the coloring effects observed using crystals containing monovalent impurities with crystals containing divalent impurities should give further insight into the impurity-related coloring kinetics. In particular, it should provide information useful for evaluating coloring mechanisms that are based on the presence of charge-compensating vacancies associated with divalent impurities.

Several monovalent impurities could have been chosen for this study. However, there are several compelling reasons for choosing thallium. First, as stated above, it is an ion which almost certainly replaces K^+ substitutionally in the KCl lattice. Second, KCl : Tl has been extensively studied in the past.[1] Third, because of the work of Delbecq, Yuster, and their collaborators,[23] a large amount of information is available on the absorption spectra, luminescence, stability of the color centers, etc., of KCl : Tl containing Tl as Tl^0, Tl^+, and Tl^{2+}. Fourth, chemical determinations of the amount of Tl in various charge states after γ irradiation have recently been completed.[24] They indicate that doses typically required for late-stage coloring convert a large fraction of the Tl^+ to an oxidized form, most likely Tl^{2+}. In addition, chemical determinations of the Tl^{2+} content are in reasonable agreement with the values computed from optical-absorption measurements of the Tl^+ bands.

It is also of interest to establish the chemical state of the impurity at different stages in the coloring process. It is quite clear that the impurity content is not changed during irradiation. However, the chemical and/or physical state of the impurity may change considerably, especially if the radiation dose is very large. In particular, the charge state may change. For example, it is conceivable that Tl in a crystal may exist as Tl^0, Tl^+, Tl^{2+}, or even Tl^{3+}. In solution, only Tl^+ and Tl^{3+} are observed. Also, the impurities may play an important part in the coloring process without permanently changing their valence or charge state. Such a case would occur if the Tl^+ were to act as a recombination center. In this case its charge state would change only for relatively short periods.

II. EXPERIMENTAL

A. Purification

Much of the previous work on alkali-halide coloring, conductivity, etc., has shown that even trace amounts of impurity markedly affect sample behavior. Consequently, there is a tendency to avoid using comparatively impure, commercially grown crystals. Apparently high-purity KCl crystals have been produced in several laboratories from reagent grade material by using various combinations of chemical purification, zone refining, and crystal growth.[25–31] Although small amounts of impurity might be expected to have little influence on the behavior of crystals intentionally doped with much larger amounts of a specific impurity, it was decided, at the outset of this work, to prepare highly purified undoped KCl. Material was obtained from Oak Ridge National Laboratory[32] where reagent grade material was chemically treated to produce

TABLE I. Chemical analysis of KCl at various stages of preparation.[a] All entries are in $\mu g/g$. The first six elements were determined by flame photometry, the next nine by wet chemistry, and the last six by neutron activation.

Element	Original ingot	Zone refined	Final crystal
Na	4.4	0.7	1.1
Ca	< 1	< 0.1	< 1
Sr	< 1	< 1	< 1
Mg	< 1	< 1	< 1
Rb	2.5	< 0.5	< 0.5
Pb	7.8	< 0.5	< 0.5
C	21	13	19
N	1	< 1	1
I	3	2	9
P	4	1.1	< 0.4
Al	< 1	< 1	< 1
S	< 1	< 1	< 1
Si	< 1	< 1	< 1
Br	4	3	1
Fe	< 0.2	< 0.2	< 0.2
Br	< 2	< 2	< 2
Cu	< 0.005	< 0.005	< 0.005
Na	< 0.8	0.3	0.3
Ag	< 1	< 1	< 1
Pt	< 1	< 1	< 1
Cs	< 0.4	< 0.4	< 0.4

[a] We are indebted to J. R. Russell at ORNL for providing these analyses.

large polycrystalline ingots.[30] As shown in Table I, crystals pulled from a melt of this material at Oak Ridge typically contained less than about 1 $\mu g/g$ of any foreign alkali or halide element. Conductivity measurement indicated that the total polyvalent cation content of this material was less than ~300 ppm.[30] The KCl ingots were removed from their evacuated quartz ampoules under a nitrogen atmosphere in a Plexiglass vacuum dry box, broken up, and transferred to quartz tubes for zone refining. Material was zone refined under high-purity HCl gas in an apparatus described by Warren,[29] which employed four zones simultaneously traversing the KCl. Tubes were subjected to 30–40 passes over a period of a few days after which they were evacuated, filled with high-purity nitrogen, and returned to the dry box. A selected part of the ingot (approximately the first half) was then loaded into a crucible for subsequent crystal growth. Work by Peech, Bower, and Pohl[31] has indicated that major surface contamination of zone-refined KCl occurs when it is exposed to air. Thus far, we have not made ionic-conductivity measurements on our pure crystals to determine the over-all effectiveness of the zone-refining step. The chemical analyses given in Table I indicate that the levels of a few elements are reduced, while the concentrations of the other impurities are at least as low as in the initial ingot. Only iodide ions appeared to increase.

B. Crystal Growth

Attempts were made to grow crystals using material prepared in the manner described above, without introducing any additional impurities. Zone-refined KCl was loaded into a vitreous carbon crucible, contained in a quartz ampoule, which could be attached to a high vacuum line with a Viton O-ring joint. The vacuum system was entirely greaseless. It utilized molecular sieve and vac-ion pumps, Teflon stopcocks, Viton O rings, and glass and monel tubing. While attached to this system, the molten KCl was once more treated for several hours with high-purity HCl. The crucible was then evacuated to a pressure of $\sim 5\times10^{-6}$ mm Hg and sealed off. Whenever TlCl was added (the TlCl was synthesized from Jarrel-Ash Spec-pure $TlNO_3$ using redistilled HCl and triply distilled water), it remained in a water-cooled side pocket until the quartz crucible was sealed off. Crystals ~8 cm long by 4-cm diameter were grown by the Bridgeman-Stockbarger method[33] at a rate of ~1 in. per 6 h. After growth they were annealed near the melting point for several hours and cooled to room temperature at a rate of ~20 °C/h. This method of crystal growth was selected over seed pulling purely because we required crystals doped with Tl^{204}, a β-ray emitter, and this technique enabled us to handle radioactive material without contamination problems. Both optical-absorption measurements and radiochemical determinations indicated that the thallium concentration increased by about a factor of 3 over the length of the crystal.

C. Irradiation Conditions

Samples were cleaved from the crystal ingots, ranged from 0.025 to 0.2 cm thick, and were usually 1 cm by 1 cm. Crystals were irradiated in a Co^{60} γ-ray source at dose rates which varied from 3.0 to 2.65×10^6 rad/h over the period of the experiments. They were protected from light by keeping them wrapped in Al or Pt foil at all times except when absorption spectra were being recorded. A Cary 14R spectrophotometer was used. All spectra were simultaneously recorded on a strip-chart recorder and on tape for subsequent computer processing. If the crystals were irradiated in the Al holders normally used to mount them in the spectrophotometer, they reached a temperature of 50–60 °C after several minutes in the source. However, when irradiated in thin foil wrappings, the maximum temperature reached by the samples was 21 ± 1 °C. This is the temperature maintained in the water tank containing the sources and irradiation tubes. Consequently, the thin foil covering was used for all irradiations.

III. RESULTS

A. Optical Absorption of Tl^+ Centers

The substitution of Tl^+ for a K^+ introduces three well-known absorption bands in the wavelength range from 185 to 300 mμ.[34] Designated the *A*, *B*, and *C* bands, their peaks occur at about 247, 209, and 195 mμ, respectively, when measured at room temperature. There is an additional band, the *D* band, attributed to Tl^+ which occurs at approx 169 mμ. This band is outside of the range of the spectrophotometer and could *not* be studied during this investigation. Because the *B* and *C* bands are not fully resolved at room temperature Tl^+-ion concentrations were always determined from the height of the well-resolved, but asymmetric, *A* band. It has been shown that the optical absorption of this band is proportional to the thallium content over a wide range of concentration.[34] We have verified this relationship using crystals with thallium concentrations ranging from about 3×10^{-6} to 1.5×10^{-4} moles Tl^+/mole KCl. A value of 0.077 was obtained for the *A*-band oscillator strength using the generalized Smakula equation[35]

$$N_0 f = 0.821\times10^{17}\frac{n}{(n^2+2)^2}\int \alpha_E(E)\,dE\ . \qquad (1)$$

In this equation, E is the photon energy in eV, α_E is the absorption coefficient in reciprocal centimeters, and f the oscillator strength. The actual concentration of thallium atoms present N_0 was obtained from radiochemical determinations. The refractive index n was taken as 1.594 at 247 mμ.[1] The total area under each absorption band was obtained by numerical integration.

For routine determinations of the Tl content, the thallium *A* band can be regarded as Gaussian shaped and the concentration computed from the well-known Gaussian form of Smakula's equation[35]

$$N_0 f = 0.87\times10^{17}\frac{n}{(n^2+2)^2}\,\alpha_{\max} W\ . \qquad (2)$$

In this instance, it is best to use the full width W and oscillator strength f that have been determined using the Gaussian-shape approximation. Thus, $W = 0.202$ eV and $f = 0.077$ were used for room-temperature measurements. The oscillator strength of 0.077 agrees well with the value of 0.0764 previously determined at room temperature by Wagner[34] and the approximate 0.077 given by Fukuda.[36]

B. Qualitative Changes in Absorption Spectrum of KCl : Tl

The absorption spectra of a KCl : Tl crystal, containing ~ 60 ppm[37] Tl^+, after successively increasing doses of γ irradiation are shown in Fig. 1. The *C* band is too large to be measured precisely at this doping level. The *F* and *M* bands increase steadily with dose while the *A* band gradually decreases until it does not appear as a distinct band superimposed on the observed broad absorption. The remainder of the induced absorption does not contain well-defined bands and decreases steadily from about 6.7 eV (185 mμ), the uv limit of the measurements, to about 4 eV (310 mμ).

The *V*-region absorption, which extends from 185 to 350 mμ, depends on the initial Tl^+-ion concentration. In this paper, and for crystals containing Tl^+ impurity, the *V* region is defined as the absorption remaining after the contributions of the observable Tl^+ *A*, *B*, and *C* bands have been subtracted or have been totally eliminated by an irradiation sufficient to convert all of them to other bands.

In all "pure" samples the *V* region consists of a broad band, or bands, peaking at about 210 mμ (5.9 eV). Most likely this is a large V_3 band with small contributions from other bands on both the long- and short-wavelength sides (Fig. 2). In crystals containing the lowest level of Tl^+ impurity (6.5 ppm), the *V*-region absorption, aside from that attributable to the *A*, *B*, and *C* bands, has a pronounced peak at ~ 195 mμ. In addition, the absorption, as a function of wavelength, falls off steadily to ~ 310 mμ with a slight indication of a shoulder at 236–248 mμ (5.0–5.25 eV). In samples containing 26-ppm Tl^+, this shoulder is more clearly defined, suggesting that there is a peak at 236 mμ. Its height has also increased relative to the lower energy peak. When the Tl^+ concentration is 38 ppm, there is a well-developed peak at about 225 mμ. comparable in absorption to the one at 195 mμ. Measurements on crystals containing higher Tl^+ concentrations are difficult. They have high optical densities in the *V* region and it would be necessary to use thinner samples than can be obtained by cleaving. Nevertheless, it is apparent that the character of this region is systematically changed as the thallium level is increased. The peak at 225 mμ corresponds closely in position to the peak of the V_2 band in pure KCl. Also, a peak at 198 mμ has been observed in "pure" KCl irradiated at room temperature.[38] The short-wavelength contribution to the V_3 band in our "pure" KCl could be due to a band at this energy. A similar combination of V_2 and 198 mμ bands has been observed in γ-irradiated KCl : Ca and KCl : Sr.[15] This reference indicates that the absorption edge moved to longer wavelengths with increasing irradiation and it was difficult to assess whether the 198-mμ peak was geniune, or a direct result of this movement of the band edge. It is interesting that the radiation-induced absorption changes in the same manner in crystals containing either monovalent or divalent cationic impurities.

The radiation-induced absorption bands occurring

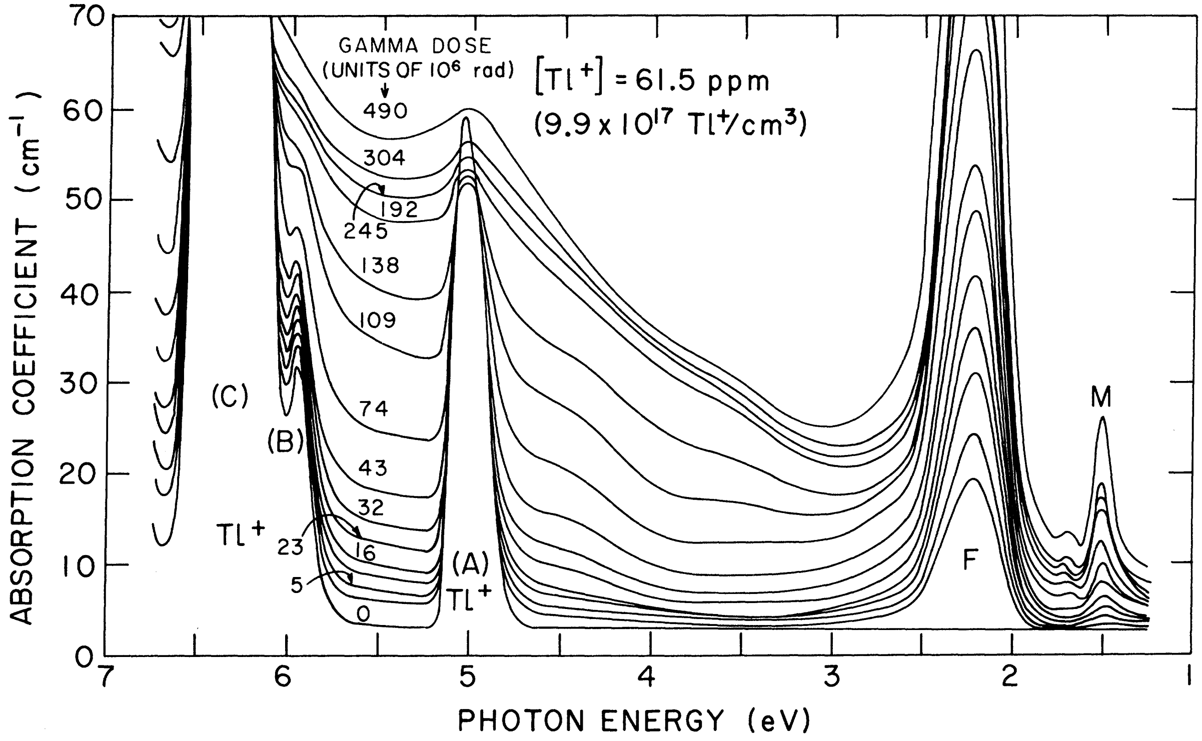

FIG. 1. Absorption spectra of a KCl crystal containing 61.5 ppm of Tl$^+$ (9.9×10^{17} Tl$^+$ ions/cm^3) after successive doses of Co^{60} γ irradiation. The crystal temperature during irradiation was 21°C and spectra were obtained at room temperature.

in the 190–240-mμ region in KCl at room temperature are not conclusively identified. However, it has been suggested that some of them may be due to interstitials and/or interstitial clusters of varying sizes, and that the cluster size distribution is temperature dependent.[38,39] In general, impurities facilitate the bleaching of these centers in at least two ways.[39,40] By trapping electrons the impurity can cause a mobile anion vacancy to have a longer lifetime which in turn can increase both the vacancy-interstitial recombination and F-aggregate formation. Second, by acting as nucleation sites, the impurities can change the distribution and average size of the clusters from that which would be formed in a pure crystal. In turn, this would alter the bleaching characteristics.

To sum up, it appears that both monovalent Tl$^+$ and divalent impurities, such as Ca^{2+}, affect the radiation-induced V-region absorption spectra of KCl in the same way. The major absorption changes occur at 198 and 220–230 mμ due presumably to the formation of V centers and possibly interstitial centers. In contrast, the major V-region absorption in "pure" KCl occurs at 215 mμ. These observations suggest that the additional cation vacancies, presumably introduced by divalent cation doping, do not contribute importantly to the mechanisms creating the V-region absorption that are usually associated with divalent impurities.

C. Changes in Tl$^+$- and F-Center Concentrations During Irradiations

When crystals of KCl : Tl are exposed to γ irradiation, the F, M, and some other centers increase while the Tl$^+$ centers decrease. Plots of F- and Tl$^+$-center concentration versus γ-ray dose (for the Tl$^+$ concentrations given in Fig. 1) are shown in Figs. 3 and 4. In these figures, except those describing early-stage coloring, the F-band absorption has been corrected for the underlying M-band absorption. The corrected absorption α_F' was obtained in accord with previous work[14] by subtracting the absorption at the M-center peak α_M from the measured α_F. During early-stage coloring α_M is small and this correction is unnecessary. F-center concentrations were calculated from the Gaussian version of Smakula's formula given above using $W = 0.36$ eV, $n = 1.49$, and $f = 0.9$.[1]

At all doping levels, the production of F-centers and the decrease in Tl$^+$ centers occur simultaneously from the onset of irradiation until either the F-center concentration reaches what is usually called stage II or the Tl$^+$ absorption bands have completely

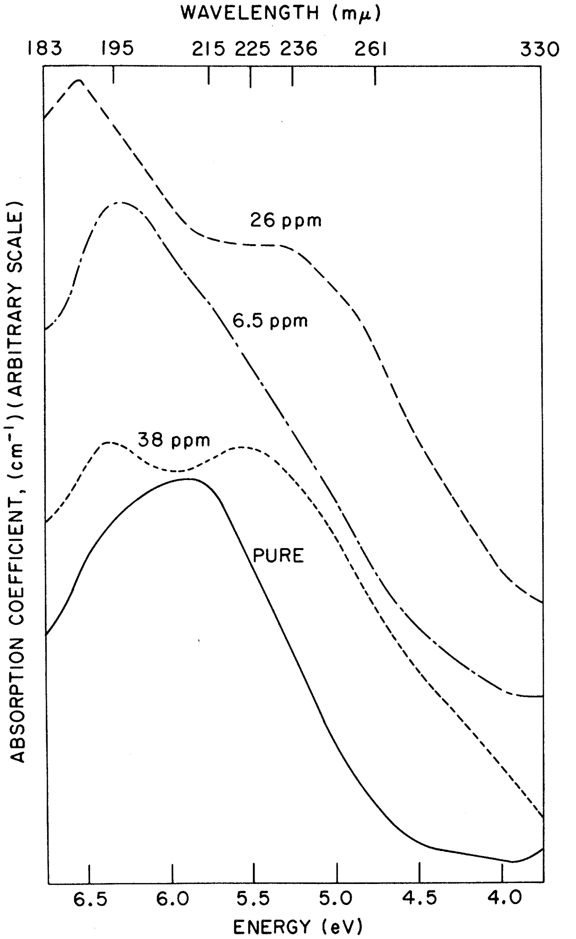

FIG. 2. *V*-region absorption spectra of γ-irradiated KCl, both doped and undoped, after Co^{60} irradiations of $3{-}3.7\times10^8$ rad. The curves were scaled to demonstrate the changes in the *V*-region absorption and the relative magnitudes are not significant.

disappeared. In crystals containing ~6 ppm of thallium, *F*-center production continues after all the Tl^+ absorption has disappeared. At 38 ppm of thallium, both processes are complete by about 360 Mrad, while at 60 and 140 ppm, the Tl^+ centers continue to decrease with increasing dose after *F*-center production has ceased. Thus, although these processes interact to some extent, when one process is complete the other can continue to occur. As the doping level is increased the ratio of the number of Tl^+ centers destroyed to the number of *F* centers formed increases considerably. Also, there is a large increase in the *V*-region absorption which increases as the thallium content is increased. This agrees with observations made on KI:Tl.[41]

Using crystals containing thallium concentrations up to 38 ppm, an attempt was made to compare the total numbers of electron and hole centers present.

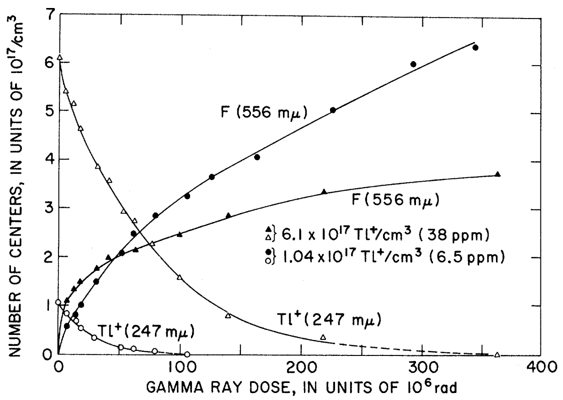

FIG. 3. Tl^+- and *F*-center—versus—γ-ray dose curves for KCl: Tl crystals containing 6.5 and 38 ppm thallium.

The total electron centers were taken as the sum of the *F*- and *M*-center concentrations. The hole-trap computations were made by the following obviously oversimplified procedure. When the Tl^+ bands are subtracted the residual *V*-region absorption curve was smooth with a peak or peaks near to the uv limit of the measurements. The curve was extrapolated on the low-wavelength side of the peak to zero absorption, yielding a roughly symmetrical *V* region. A very rough hole-center concentration was obtained by using Smakula's formula and regarding the *V*-region absorption as a single broad band. The total absorption (area) was readily measured and an oscillator strength of 0.8 and an index of refraction of 1.66 were used.

In this way it was found that in "pure" KCl and samples containing 6 ppm thallium, the electron centers exceeded the hole centers by factors of approx 2.5 and 1.5, respectively, at high γ-ray doses. In contrast, in crystals containing 26 ppm of thallium, the hole centers predominated, the

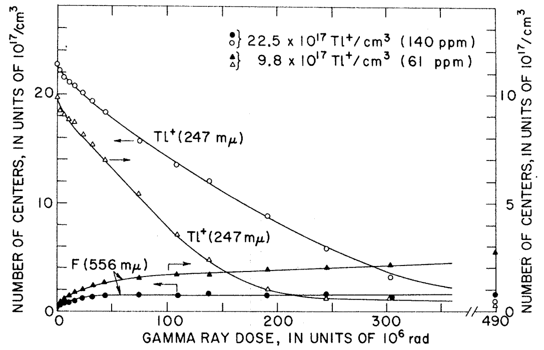

FIG. 4. Tl^+ – and *F*—center—versus—γ-ray dose curves for KCl: Tl crystals containing 61 and 140 pp, thallium.

ratio of V to electron centers was ~2.5–3.0 to 1. At higher thallium concentrations, the hole-center concentrations could not be estimated by this method. The absorption rises steeply in the uv and becomes immeasurably high. It does not contain a maximum or an indication of a peak.

The ratios of hole to electron centers given above clearly depend on the choice of the V-region oscillator strength. It would appear that the available data, for crystals containing a variety of Tl^+ concentrations, is not consistent with the idea that the total number of observable hole and electron centers are equal. In other words, to maintain charge neutrality between observable centers, a different, and for high Tl^+ concentrations a physically unrealistic, oscillator strength for the V region is required. Thus, either all of the electron and/or hole centers are not observed, or the V region contains both electron and hole centers; or alternatively, this "discrepancy" must be attributed to some other, as yet unconsidered, situation.

The values given above are for γ-ray doses sufficient to remove all of the Tl^+ bands (typically $2-3\times10^8$ rad), but the general conclusions are also valid at lower doses. The procedure used to estimate the total hole concentration attributes all of the V-region absorption to hole centers. This most likely includes an unknown amount of absorption from either Tl^{2+}, Tl^0, or even other Tl centers. While it is not entirely certain that Tl^0 or even Tl^{2+} centers are stable at room temperature,[23] the presence of a large number of Tl^0 centers, formed by electron trapping on Tl^+, would reduce the charge unbalance in crystals having high Tl content. Studies on the annealing of the radiation-induced coloring as a function of temperature may provide some useful information about this.[42]

D. Early-Stage *F*-Center Formation

The growth of F centers in various samples during the first few minutes of irradiation is shown in Fig. 5. Even 4–7 ppm of thallium causes the F-center formation to proceed more rapidly than in "pure" crystals and the rate of formation increases as the thallium content is raised to 13.6 and 36 ppm. At 131 ppm of thallium, the F-center growth, while still greater than the growth in "pure" KCl, is less than that of the 36-ppm sample. The 131-ppm thallium crystals (2.11×10^{18} Tl^+ ions/cm^3) also exhibit anomalous M- to-F-center ratios. Possible reasons for this are discussed below. The Tl^+ absorption bands decreased slightly during early stages of irradiation. Table II indicates that the initial F-center coloring may be directly related to the concentration of Tl^+ ion in the crystal. Specifically, this table shows, that at all Tl^+-doping levels, approximately one *additional F center* is formed for each Tl^+ ion which has undergone conversion to some other valence state during irradiation. *Additional F centers* are defined as the increment in F-center concentration observed in doped crystals above that observed in "pure" crystals after both kinds have been subjected to the same irradiation.

E. Late-Stage *F*-Center Growth

Typical F-band growth curves for various "pure" and thallium-doped crystals are shown in Fig. 6. For "pure" crystals, both the initial coloring rate and the F-center concentration at large doses is higher than most of the room-temperature results in the recent literature. This is probably due, at least in part, to the 21 °C irradiation temperature which is 10–15 °C below that used in other work.[10,14,15] The coloring curve for "pure" KCl grown at Oak Ridge closely follows the curve for the KCl grown in our laboratory. Clearly, as the Tl^+ content is increased the late-stage coloring is decreased.

The coloring curves for various thallium concentrations are strikingly similar to curves of oxidized thallium concentration versus γ-ray dose obtained from chemical analyses.[24] In these studies one measures, by chemical techniques, the percentage of the Tl^+ ions which are converted to an oxidized form, probably Tl^{2+}, under similar room-temperature irradiation conditions. Because of the nature of the chemical analysis, it is expected that the measured amount (percent) of oxidized thallium is not the actual amount present in the crystalline solid, but is proportional to it.[24]

The addition of ~6 ppm of thallium cuts the F-center production by a factor of 2, and 60 ppm by a factor of 4. At 140 ppm of thallium the late stage appears to be completely suppressed. This could be related to the observation that the F centers were increasingly susceptible to thermal and optical bleaching as the doping levels increased. This is characteristic of F-centers produced in the early stage of coloring.[43] This increasing suppression of late-stage colorability with increasing impurity content is similar to the effects observed with divalent Pb and Ca in KCl.[14,15]

F. Effect of Thallium on *M*- to-*F*-Center Ratio

It has previously been observed that, in "pure" KCl irradiated at room temperature, the M-center absorption coefficient α_M is proportional to the square of the corrected F-center absorption coefficient $(\alpha'_F)^2$.[10,11] This relationship was found to be valid for both our doped and undoped crystals (Figs. 7–9). The slope of the α_M-versus-$(\alpha'_F)^2$ plot was found to depend on the thallium content in the following way (Table III): The slope increased as the

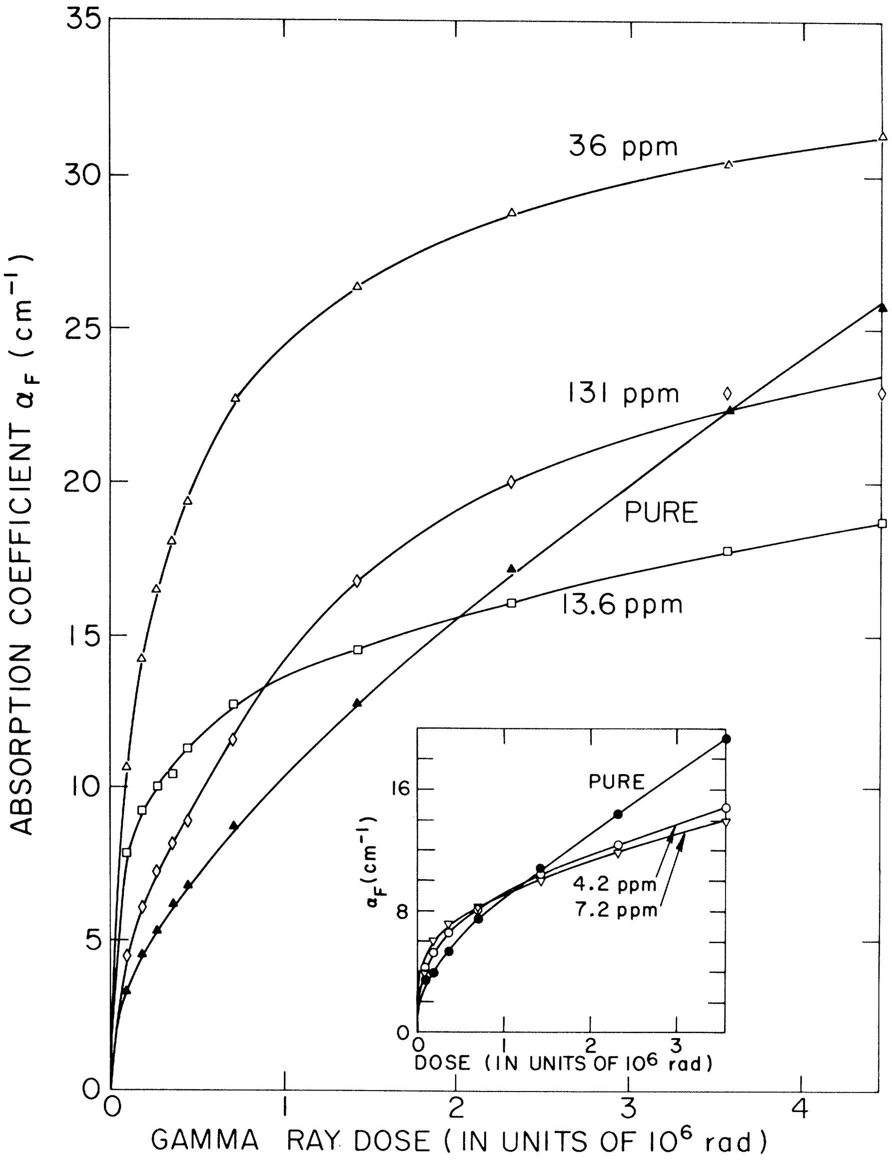

FIG. 5. Early-stage F-center–versus–dose curves for pure KCl and KCl : Tl containing the indicated thallium concentration.

thallium increased from 0 to 60 ppm. However, in crystals containing 140 ppm, the measured slope was near the value expected for a thallium concentration of ~ 20–25 ppm. Nevertheless, this slope is still approximately three times the slope found for "pure" KCl. In heavily doped crystals, the points scattered considerably at high γ-ray doses (Fig. 9). In general, these scattered points correspond to a much higher M-to-F-center ratio than would be predicted from a line drawn through the lower dose values. As has been mentioned earlier, these crystals are noticeably more susceptible to room-temperature thermal annealing and optical bleaching than the more slightly doped samples. Thus, the increased M-center content may be the result of thermally or optically induced conversion of F to M centers. Since the crystals were always shielded from light, except during absorption measurements, a thermal effect seems to be the more probable. Immediately after heavily doped crystals were removed from the Co^{60} source, they were visually observed to emit a greenish light. This emission could be an additional cause of F-to-M-center conversion process.

A similar enhancement of the α_M-to-$(\alpha'_F)^2$ ratio has been found in KCl : Pb,[14] whereas, in KCl : Ca it was reduced.[10] The crystals containing Ca impurity seem to contradict a general trend, since extensively purified crystals exhibit lower M-to-F-center ratios than commercially grown crystals.[10]

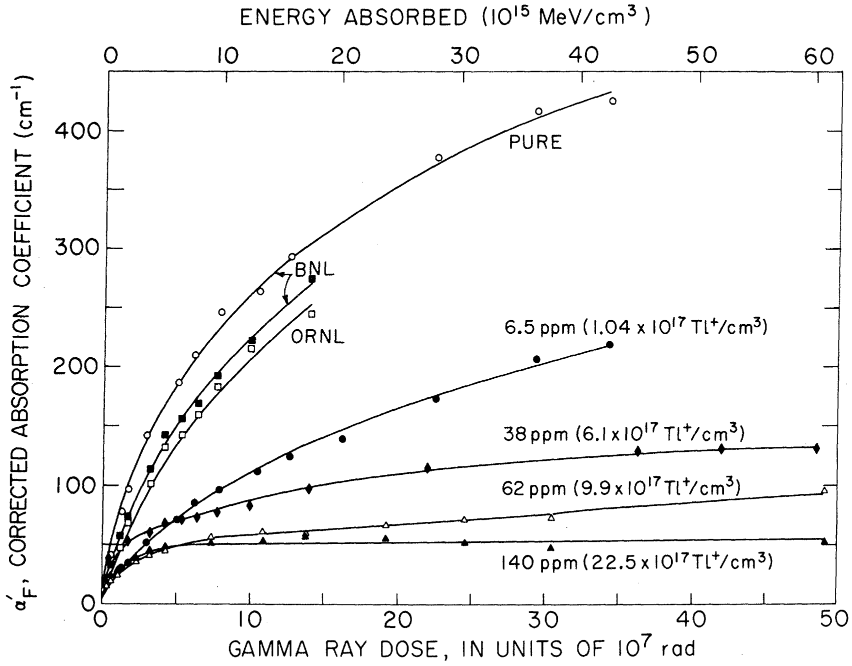

FIG. 6. Late-stage F-center–versus–dose curves for pure KCl and KCl : Tl containing the indicated amounts of thallium. The curve marked ORNL was obtained with KCl crystal grown at Oak Ridge. The two curves marked BNL were obtained with crystals grown at Brookhaven from Oak Ridge material that had been subjected to zone refining. All of the KCl : Tl crystals were grown after adding TlCl to zone-refined material.

As the actual M-to-F-center ratios for pure KCl vary considerably, meaningful comparisons between pure and doped crystals can be made only with crystals grown from the same source material. It is difficult to compare the absolute magnitudes of the slopes of α_M-versus-$(\alpha'_F)^2$ plots given in this paper with those given by other workers,[10,11] since the values vary with radiation intensity,[11] and around 25° the values are very sensitive to irradiation temperature (Ref. 11 of Ref. 11).

IV. DISCUSSION

The color-center–versus-dose or coloring curves obtained by subjecting both pure and thallium-

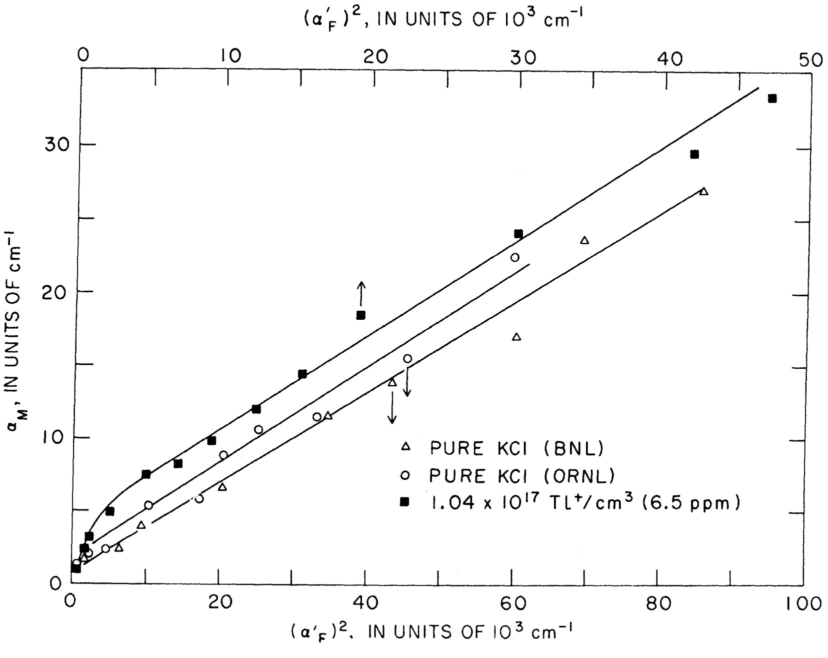

FIG. 7. Plots of α_M versus $(\alpha'_F)^2$ obtained from γ-irradiated pure KCl and a KCl : Tl crystal containing a relatively low thallium concentration of 6.5 ppm. α_M is the M-center absorption and α'_F the F-center absorption corrected for the underlying M-center absorption.

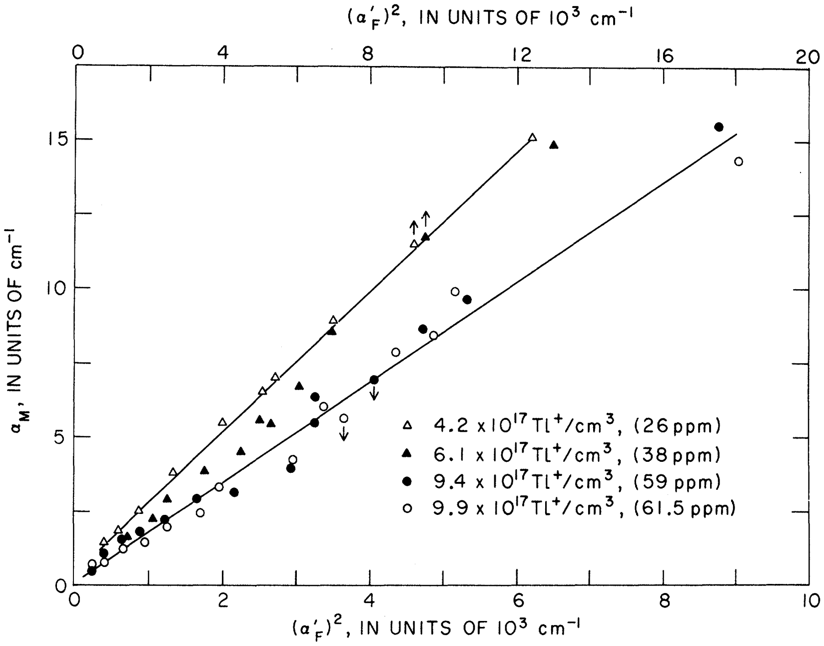

FIG. 8. A plot, similar to Fig. 7, for KCl : Tl crystals containing 26, 38, and 59–61.5 ppm thallium.

doped KCl crystals to Co^{60} γ rays at 21 °C contain results which can conveniently be discussed separately. Consider first the early-stage, or stage I, coloring. As the amount of Tl^+ in the crystals is increased the initial slope of the coloring curve increases, i.e., the coloring is enhanced. In this respect it is similar to the effect produced by divalent metal ions, such as Ca, Sr, and Pb. The close correspondence between the incremental increase in *F* centers and the decrease in Tl^+-ion concentration during early-stage coloring (Table II) indicates that the Tl^+ ions may contribute directly to the enhancement of the *F*-center coloring rate. The Tl^+ ions could facilitate *F*-center formation by acting as additional hole traps. If the number of Tl-related hole traps were large compared to the

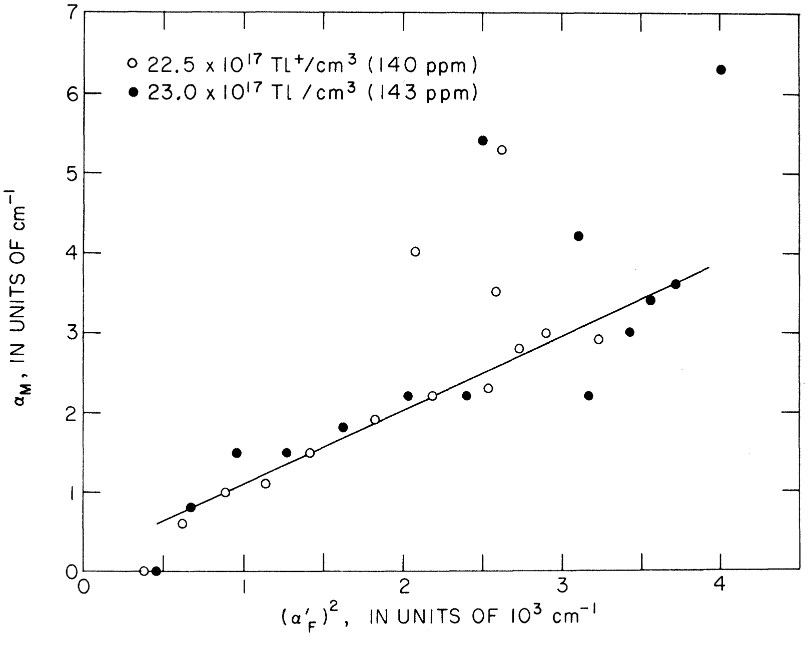

FIG. 9. A plot, similar to Fig. 7, for a KCl : Tl crystal containing between 140 and 143 ppm thallium.

TABLE II. The increase in γ-ray-induced *F*-center coloring in KCl : Tl which is in addition to the coloring observed in pure or, i.e., undoped crystals. The values given are approximate since they were determined for small changes in the Tl^+ *A* band and the slopes of the *F*-center growth curves which are difficult to determine precisely. Nevertheless, the comparisons should be valid.

Initial thallium (Tl^+) concentration ppm	Tl^+ ions/cm^3	ΔN_T [a]	ΔN_F [b]	$\Delta N_T/\Delta N_F$
4.2	6.71×10^{16}	0.59×10^{16}	0.61×10^{16}	1.03
7.2	1.16×10^{17}	0.70×10^{16}	0.71×10^{16}	1.00
13.6	2.18×10^{17}	1.6×10^{16}	$1.7-2.0\times10^{16}$	0.94–0.80
36.2	5.81×10^{17}	4.1×10^{16}	$5.7-5.8\times10^{16}$	0.72–0.71
131.0	2.11×10^{18}	2.9×10^{16}	$3.0-3.2\times10^{16}$	0.97–0.91

[a] ΔN_T is equal to the decrease in Tl^+ concentration during early-stage coloring measured by the decrease in the Tl^+ *A* band.

[b] ΔN_F is equal to the approximate concentration of early-stage *F* centers obtained by extrapolating the linear portions of α_F-versus-dose curve to zero dose and subtracting the value obtained for pure KCl in the same way.

hole traps otherwise contained in the crystal, approximately one *F* center could be formed for each Tl^+ ion oxidized. The data in Table II appear to support this.

It should be pointed out that the addition of thallium also changes the character of the *V*-region absorption. The different types of *V*-region absorption bands, and their concentrations, in the "pure" crystals may differ from those in the crystals containing thallium. In fact, the *V*-region absorption, aside from the *A*, *B*, and *C* bands, may be a function of the Tl concentration since the early-stage absorption spectra of crystals containing different amounts of Tl, and subjected to equivalent doses, cannot be superimposed by multiplying by a simple factor. The total observable hole concentration during early-stage coloring cannot be reliably estimated at present. Consequently, for this and other reasons, a more detailed analysis of the first-stage coloring was not attempted.

The absorption spectra obtained by irradiating KCl : Tl crystals at 77 °K and subsequently warming them to room temperature have been explained by proposing that both Tl^0 and Tl^{2+} are formed at this temperature.[23] The bands assigned to Tl^0 at 77 °K include a strong one at 380 mμ and weak ones at 250, 300, and 640 mμ (in addition, there are bands at 1260 and 1500 mμ which are not discussed here) and the bands attributed to Tl^{2+} are at 220, 262, 294, and 364 mμ. Also, an ESR spectrum which has been observed under similar conditions has been assigned to Tl^{2+} on a *K*-ion lattice site.[44] Both Tl^0 and Tl^{2+} centers have been observed to disappear when the crystals are warmed to 27 °C.[23] This annealing behavior appears to contradict the previously mentioned chemical studies[24] which are consistent with the idea that room-temperature γ irradiation converts a considerable fraction of the Tl^+ to a Tl^{2+} species which is stable up to 200–300 °C. Also, the annealing result[23] would indicate that relatively little Tl^{2+}, if any, should be found in crystals irradiated at 21 °C and their absorption spectra subsequently measured at ~ 25 °C.

These apparent contradictions can be explained in terms of recent measurements of the dependence of *F*-center (and other centers) annealing temperatures on the crystal impurity level. First, it has been shown the thermal stability of centers found in NaF depend on the impurity content.[45] In particular, the stability of electron excess centers is increased by adding electron donating impurities to the crystal. The conversion of Tl^+ to Tl^{2+} may be regarded as an electron-donating reaction. Second, thermal annealing studies, which will be described in another paper,[42] show that the annealing of the radiation-induced color centers in KCl : Tl depends on the Tl concentration. Specifically, if crystals containing Tl are irradiated with Co^{60} γ rays until the *A*, *B*, and *C* bands can no longer be detected, and are then heated, it is found that the temperature at which the Tl^+ bands begin to reappear decreases as the thallium content increases. The annealing data quoted above[23] were obtained with crystals containing large amounts of Tl and, consequently, it is possible that in the heavily doped crystals, the Tl^0 and Tl^{2+} centers are unstable at 27 °C. Also, the crystals used in this study contain very low Tl concentrations, and, consequently, the conversion of Tl^0 and Tl^{2+} (if these are the species actually formed) from one charge state to another may not occur completely until the crystals are heated to relatively high temperatures.

Since the results given above were obtained with crystals containing monovalent positive-ion impurity, they should be compared with similar results obtained with crystals containing divalent impurities. As previously mentioned, the two types of impurities produce surprisingly similar effects. These will be considered in turn.

TABLE III. Effect of thallium concentration on the *M*- to *F*-center ratio in γ-irradiated KCl : Tl crystals.

Initial Tl^+ concentration ppm	Tl^+ ions/cm^3	Slope of α_M-versus $-(\alpha'_F)^2$ curve
0	0	3.0×10^{-4}
6.5	1.04×10^{17}	6.4×10^{-4}
26–38	$4.2-6.1\times10^{17}$	11.8×10^{-4}
59–62	$9.4-9.9\times10^{17}$	16.9×10^{-4}
140–143	$22.5-23.0\times10^{17}$	9.3×10^{-4}

First, consider how the total number of *F* centers formed depend on the impurity-ion content. It is somewhat difficult to compare our results with the published ones since small differences in irradiation temperature and radiation intensity can produce considerable changes in impurity-controlled effects. However, except for samples containing the greatest amount of impurity, 131 ppm of thallium, the number of early-stage *F*-centers formed per divalent or monovalent impurity atom is roughly comparable. The enhancement of early-stage colorability observed when divalent atoms are introduced has been attributed to the additional cation vacancies introduced.[12,21] Furthermore, there is some experimental evidence[15,16,46] to support mechanisms, particularly the one proposed by Crawford and Nelson,[21] in which cation vacancies are converted first to anion vacancies and then to *F* centers. Both of these processes depend on the presence of divalent metallic-ion impurities. Consequently, it is surprising that very similar results are obtained with monovalent impurities; and, as mentioned above, the monovalent Tl^+ is *not* expected to increase the concentration of positive-ion vacancies.

Numerous additional comments could be made about the similarity between the results obtained with monovalent and divalent impurities but only a few are included here. First, it would be interesting to determine if the Tl doping, done in a manner used to produce the crystals used in this study, significantly increased the vacancy content of the unirradiated crystal. Second, one must consider the possibility that any impurity-controlled coloring mechanism, if it is actually responsible for the observed effects, requires the conversion of the impurity atom from one valence state to another early in the coloring process. Valence changes in two directions must be considered. First, crystals containing monovalent impurity may be converted to a divalent state in the coloring process. Once it is in the +2 state, all of the mechanisms proposed for divalent impurities may be invoked. Second, or alternatively, divalent impurities may be converted to the monovalent +1 state in the coloring process. In this case, the enhanced coloring would have to be attributed to some unknown mechanisms involving monovalent impurities.

In addition to valence changes leading to either the +1 or +2 state, other valence states must be considered. It is unlikely that an appreciable amount of stable Tl^{+3} would be formed. Hole trapping by these impurities to form triply charged ions seems unlikely[47]; and, in general, it appears to be difficult to incorporate trivalent ions into KCl. Since there are considerable data to indicate that appreciable amounts of Tl^0 are formed, one must consider seriously the possibility that neutral ions contribute importantly to the coloring processes. It is possible that ions introduced in the +1 or +2 state may be readily converted to the neutral state.

The comments in the preceding few paragraphs discuss features of the initial part of the coloring curves. Some additional comments can be made regarding the late-stage coloring. Most important is the observation that the addition of Tl^+ ions suppresses the late-stage coloring. Again, this is similar to the effects produced by introducing divalent cation impurities. The suppression per thallium ion is not as great as that for each Pb^{2+} ion. However, this conclusion is based on measurements which were not strictly comparable. In particular, the crystals containing thallium were irradiated at 21 °C and those containing lead at 34 °C.[14] The comments on the various single or multiple valence changes made above would appear to be applicable to many or all of the features associated with late-stage coloring.

The late-stage absorption spectra contain several notable features. First, at all levels of thallium doping that were studied, the Tl^+ *A*, *B*, and *C* bands were progressively reduced as the irradiation increased until, at a sufficiently high dose, they could not be detected.

Second, as the thallium content is increased, the *V*-region spectra changes and the total absorption greatly increases relative to the *F*- and *M*-band absorption. Rough estimates, described above, indicate that in crystals containing more than 20–25 ppm of thallium, there is an apparent excess of hole centers. One possible explanation for this possible imbalance of electron and hole centers is that a considerable fraction of the *V*-region absorption is due to Tl^0 or some other electron centers. As mentioned above, there is considerable evidence for Tl^0 in irradiated KCl: Tl, and that this species may be stable above room temperature under certain circumstances. Some incomplete preliminary results appear to support this conjecture. Well-resolved absorption bands previously proposed for Tl^0 or Tl^{2+} *could not* be observed at room temperature. Nevertheless, there are indications of absorption peaks at ~300 and 355 $m\mu$. The bands proposed for Tl^0 include one at ~300 $m\mu$ and the ones proposed for Tl^{2+} include one at 364 $m\mu$.[23] Also, the absorption in the vicinity of 280 $m\mu$ increases with γ irradiation, and, in addition, also increases when irradiated crystals are optically bleached by exposing them to *F* light at room temperature. Furthermore, when irradiated crystals are exposed to 280-$m\mu$ light at room temperature, the 280-$m\mu$ band and the V_2-band region decrease, while at the same time, the *F* band and Tl^+ *A* band increase. These observations are consistent with the idea that the 280-mμ band is due to a Tl^0 center formed by electron trapping on a Tl^+ site. A band with similar properties has been observed in KI: Tl by Hersh[41] who attributed it to Tl^0.

If irradiated KCl: Tl does not contain trapped-electron centers such as Tl^0, absorbing in the *V* region of the crystal, it is difficult to see how electrical neutrality is maintained. An alternative explanation for the apparent excess of trapped-hole centers is that large numbers of electrons are trapped at sites which do not produce observable absorption bands.

The results described above, especially the data contained in Fig. 6, would appear to be sufficient to evaluate the mechanisms proposed by Pooley[17] and Hersh[20] to account for the role of impurities on the *F*-center kinetics. Unfortunately, as is explained below, when carefully analyzed, these results do not provide definite conclusions. Consequently, the following discussion on mechanisms has been kept as short as possible. Also, since the Pooley mechanism is the only one containing quantitative conclusions that are susceptable to straightforward analysis, it is the only one evaluated in detail. It contains the conclusion that the "late-stage" coloring rate dF/dt, where F is the *F*-center concentration and t the irradiation time, is related to the impurity concentration n_I by the relation $dF/dt = (\mathrm{const})/n_I$. The temperature and dose rate are assumed to be constant. However, for a number of reasons, it is difficult to determine if this relation is satisfied by the data. First, the growth curves, such as those in Fig. 6, show continuous curvature except for the highest Tl^+ concentration. In the considerations that follow, the slopes attributed to nonlinear curves are the asymptotic values at large doses. Second, the thinnest samples that were feasable to prepare, containing low and intermediate thallium concentrations, color so rapidly at the lowest practical dose rates that the *F*-center concentrations in the late stage are too high to measure accurately. Thus, for these reasons, large errors in the determination of F are unavoidable and dF/dt cannot be measured accurately at low and medium Tl concentrations. Furthermore, if the thallium content is ~120 ppm or more, dF/dt is near zero and insensitive to changes in impurity content. Third, as described above in the discussion on Fig. 9, the relation between the *M*-center concentration and the square of the *F*-center concentration appears to break down for large doses and high Tl content. Thus, under these conditions the *F*-center measurements are suspect. Or more generally, it suggests that crystals with high Tl concentrations are modified in one or more respects when exposed to large doses, e.g., it is conceivable that Tl dimers are formed. When these considerations are included in the evaluation of dF/dt-versus-$1/n_I$ plots one obtains the following somewhat ambiguous conclusion. Namely, the quantity dF/dt appears to increase monotonically as $1/n_I$ increases, but it does not appear to increase linearly. However, for the reasons given above, the data are not inherently accurate enough, even if it were much more dense, to exclude the possibility that a dF/dt-versus-$1/n_I$ plot would be linear over part of the range of impurity content where this expression is supposed to be valid. In retrospect, these observations indicate that it might not be possible to make a really meaningful test of the Pooley mechanism in KCl: Tl from *F*-center concentrations-versus-dose curves obtained by γ irradiating KCl crystals containing different known amounts of Tl impurity; and if such a test were possible, it would require very accurate *F*-center-versus-dose curves for 8 or more samples containing different amounts of Tl ranging between 80 and 120 ppm.

The effect of Tl^+ doping on the *M*-to-*F*-center ratio is also similar to that observed when KCl is doped with a divalent impurity, particularly Pb^{2+}. Namely, the *M*-to-*F* ratio increases as the thallium content is increased. It is thought that the radiation first induces and then maintains an equilibrium between the *F* and *M* centers.[10,11] If the process involved in this equilibrium involves positive-ion vacancies, especially those postulated to maintain charge neutrality when divalent ions are introduced, it is surprising to find that a monovalent impurity, which presumably does not introduce vacancies, should cause effects as large as those shown in Table III. The fact that the *M*-to-*F* ratio is affected by both monovalent and divalent impurities suggests that the equilibrium processes may not involve vacancies. In other words, it is possible that these processes may involve impurities, e.g., Tl, Pb, or Ca in any of their various valence states. In addition, it is possible that the aggregation processes may accompany changes in the charge state. To give just one example, the luminescence emitted when Tl^+ acquires either a hole or electron may induce *M*-center formation in a manner analogous to the formation of *M* centers by bleaching with *F* light. Clearly, numerous possibilities of this type exist. However, at present, there is not sufficient evidence to justify an extensive discussion of the various possibilities.

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