Lord Rayleigh[7,8] for the surface vibration modes in a semi-infinite isotropic elastic continuum which bear his name. These modes are waves which propagate over the boundary surface of a solid but penetrate only a small distance into its interior. This result shows that our expressions for $2M$ and $(\delta E/E)$ contain contributions from the surface vibration modes. This is in contrast with the results obtained by Rich,[2] because the crystal model used by him in his work is too simple to give rise to surface modes.

ACKNOWLEDGMENT

We wish to thank Brenda Kagle for programming the sums in the expression for $2M$ for the computer.

---

[7] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon Press, Inc., New York, and Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1959), p. 108.

[8] A. E. H. Love, *A Treatise on the Mathematical Theory of Elasticity* (Dover Publications, New York, 1944), pp. 307–309.

PHYSICAL REVIEW VOLUME 133, NUMBER 4A 17 FEBRUARY 1964

Photochemical Study of F and M Centers in Additively Colored Alkali Halides*†‡

I. Schneider§ and M. E. Caspari

Laboratory for Research on the Structure of Matter, Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania

(Received 20 September 1963)

A study of absorption changes in the visible and near infrared spectral region, produced by F-band irradiation at 77°K which recover spontaneously when the F light is removed was made in additively colored KCl, KBr, and KI crystals containing M bands. These temporary changes are caused by a superposition of two processes. In crystals containing small M-center concentrations the tunneling of excited F-center electrons to nearby F centers could account for the temporary process. In crystals containing large M-center concentrations, the dominant process involves the transformation of M centers to related centers. In KCl, the principal M-center transitions at 801 and 546 mμ are changed to 685 and 505 mμ, respectively. Studies in crystals containing polarized M bands in which the temporary changes were produced with polarized light, show that this irradiation is not absorbed by M centers, but probably by F centers. The F-center excitation energy is then transferred locally to nearby M centers. The consistent interpretation of both processes requires the occurrence of F-center clustering during the early stages of room temperature irradiation and the formation of F and M centers in close proximity during later stages. The possible nature of the transformed M center is discussed and may involve F_2^+-center formation or the excitation of the M center into a metastable state. The recovery involves two channels: a temperature-independent process dominant below 100°K and one involving a thermal activation energy of about 0.035 eV dominant at higher temperatures.

I. INTRODUCTION

It is well known that F-band irradiation at room temperature of additively colored alkali halide crystals results in the formation of the M band.[1,2] Recent experiments have established that the M center, which gives rise to this band, consists of two nearest-neighbor F centers.[3–8] Moreover, room-temperature irradiation of crystals containing M centers with M light polarized along a [011] direction produces a dichroic F,[9] as well as M band indicating that M-center optical transitions may exist in the F-band region (M_2, M_3, etc., bands).[10]

Studies concerning M-center formation have led to the conclusion that F-center migration and clustering occurs during the earliest stages of F irradiation.[11] During subsequent stages, M centers form probably in close proximity to F centers. Effects which have been attributed to the interaction of near lying color centers include the large reduction in F' yields and F-center fluorescence in crystals which had received relatively small exposure to F irradiation near room temperature. Energy transfer from F to M centers has been proposed as a possible interpretation for the observed M-center

---

[*] This work was supported by a contract with the Electronic Technology Laboratory, Wright Air Development Division, U. S. Air Force.

[†] This work was presented in part at the Color Center Symposium, Stuttgart, Germany (August 1962) and in Solid State Communications **1**, 9 (1963).

[‡] Based on a thesis submitted by one of us (I.S.) to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[§] Now at Laboratory for Insulation Research, Massachusetts Institute of Technology, Cambridge, Massachusetts.

[1] J. P. Molnar, thesis, Massachusetts Institute of Technology, 1940 (unpublished).

[2] St. Petroff, Z. Physik **127**, 443 (1950).

[3] C. Z. van Doorn, Phys. Rev. Letters **4**, 236 (1960).

[4] B. J. Faraday, H. Rabin, and W. D. Compton, Phys. Rev. Letters **7**, 57 (1961).

[5] W. C. Holton, H. Blum, and C. P. Slichter, Phys. Rev. Letters **5**, 197 (1960).

[6] A. W. Overhauser and H. Rüchardt, Phys. Rev. **112**, 722 (1958).

[7] H. Gross and H. C. Wolf, Naturwissenschaften **8**, 299 (1961).

[8] E. Sonder, Phys. Rev. **125**, 1203 (1962).

[9] C. Z. van Doorn and Y. Haven, Phys. Rev. **100**, 753 (1955).

[10] F. Okamoto, Phys. Rev. **124**, 1090 (1961).

[11] C. J. Delbecq, Z. Physik **171**, 560 (1963).

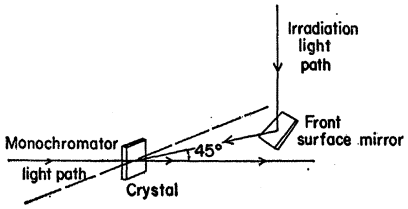

FIG. 1. Schematic arrangement of the crystal position relative to the measuring and irradiating beams.

luminescence resulting from F-band irradiation at low temperatures.[12,13]

In recent years, temporary absorption changes accompanying intense F-band irradiation at low temperatures have been observed in alkali halide crystals. These changes are temporary in the sense that the removal of the F light results in a total spontaneous recovery of the altered spectral regions. Markham, Platt, and Mador[14] attributed a transient F-band bleaching at 5°K by F irradiation in x-ray colored (300°K) KBr crystals to electron tunneling from excited to nearby F centers. Such dark recovery was absent in both freshly quenched additively colored samples and samples colored by x rays at 5°K. Their results suggest that F-center clustering occurs during room temperature x-ray irradiation.

Temporary absorption changes produced by low-temperature F irradiation have also been observed in additively colored crystals containing M and other derived centers.[15–18] This effect generally involves the reduction of the F, M, and N bands and the formation of bands on the high- and low-energy side of the F band. Compton and Klick[13] originally attributed this effect to the interaction of color centers in close proximity. This bleaching effect has more recently been attributed to an electron transfer process involving the formation of primed derived centers.[16]

In this paper, we report the results of a general study of the temporary changes due to intense F irradiation at low temperatures primarily in additively colored KCl. The purpose of this investigation was to determine the nature of the effect and hence gain a clearer understanding of both the mutual interaction and relative distribution of F and M centers in additively colored crystals.

II. EXPERIMENTAL PROCEDURES

Single crystals ($\frac{1}{4}\times\frac{1}{4}\times\frac{1}{2}$ in.) grown by the Harshaw Chemical Company were additively colored in potassium vapor, quenched to room temperature, and cleaved to thicknesses ranging from 0.3 to 3.0 mm. R, M, and N bands were introduced at room temperature by exposure to light from an intense tungsten source. To achieve uniform bleaching, crystals were mounted on a mirror-backed holder for double pass exposure and irradiated in the high-energy side of the F band (510 mμ). Dichroic M bands were produced by room-temperature M irradiation normally incident on the (100) crystal face and polarized along the $[0\bar{1}1]$ direction. Some of the samples used in experiments not involving dichroic M bands were thermally annealed to reduce or eliminate R and N bands.

Absorption measurements were made in a Cary model 14M spectrometer. For experiments performed at 77°K or above, crystals were mounted in a Pyrex Dewar and cooled by either immersion in fixed temperature baths, i.e., liquid nitrogen, or by slowly warming from low temperatures. In measurements below 77°K, crystals were cemented to the cold finger of a helium optical Dewar of standard design. Temperature measurements were made by means of copper-constantan thermocouples in good thermal contact with the samples.

A Dewar holder assembly securely housed the Dewar in the sample compartment of the monochromator and contained an optical arrangement for irradiating the crystals during or immediately preceding the absorption change measurements. The irradiation was supplied by a Sylvania 625-W type DWY tungsten lamp. Its light passed through a water cell, lens, and appropriate monochromatizing filter, and was incident on the (100) surface at an angle of about 45° with respect to the crystal normal. (Figure 1.)

For experiments involving polarized irradiation and high dc electric fields, the Cary near infrared source was used. In each case, the F irradiation passed through monochromatizing filters, and entered the (100) crystal surface with normal incidence. In the polarized irradiation experiments, properly oriented polaroids were interposed between the filters and the crystals. In the high electric field experiments, the F irradiation and monochromator beam passed through the electrodes parallel to the field. The electrodes consisted of a wire mesh cathode and an evaporated semitransparent layer of gold on the anode side of the crystal. These evaporated layers were deposited while the crystals were maintained at about 77°K prior to their room-temperature F irradiation.

In addition to the F to F' conversion and the temporary absorption changes, the low-temperature F-band irradiation produced certain permanent spectral changes which saturate after several minutes. Absorption spectra and temporary changes were recorded after these permanent changes were saturated. Temporary changes were measured relative to the F-F' photostationary state established with the same intense F light which was later used to produce the temporary changes. This photostationary state was measured after the dark decay of the temporary changes.

---

[12] J. Lambe and W. D. Compton, Phys. Rev. **106**, 684 (1957).

[13] W. D. Compton and C. C. Klick, Phys. Rev. **112**, 1620 (1958).

[14] J. J. Markham, R. T. Platt, Jr., and I. L. Mador, Phys. Rev. **92**, 597 (1953).

[15] See Refs. 12 and 13.

[16] M. Ikezawa, H. Masamitsu, and M. Ueta, J. Phys. Soc. Japan **17**, 1474 (1962).

[17] M. Ikezawa and M. Ueta, J. Phys. Soc. Japan **18**, 145 (1963).

[18] I. Schneider and M. E. Caspari, J. Appl. Phys. **33**, 3387 (1962).

III. EXPERIMENTAL RESULTS

A. Temporary Absorption Changes in Crystals Containing Unpolarized *M* Bands

The temporary absorption changes due to *F*-band irradiation at low temperatures[19] were investigated in additively colored KCl crystals with initial *F*-center concentrations varying from 4×10^{16}/cc to 1.2×10^{18}/cc. The crystals were exposed to room temperature *F*-band irradiation for times ranging from 5 sec to 80 min. Under such irradiation the *M* band first increased and then decreased after reaching a maximum value. For crystals with initial *F*-center concentrations in the 10^{17}/cc range, the *M* band reached a maximum and saturation value after about 2 and 80 min, respectively, with the light intensity and spectral distribution used.[20] Samples that were thermally annealed were maintained at temperatures from 72 to 138°C for several minutes.

Except in crystals containing relatively large *R*- and *N*-center concentrations where small temporary reductions in these bands were observed, the temporary changes due to low-temperature *F* irradiation in these moderate to densely colored crystals were found to depend primarily on the relative magnitude of the *F*- and *M*-center concentrations. [For short room temperature *F*-band irradiation times (i.e., less than 4 min) the ratio α_{M0}/α_{F0} of the *M*- and *F*-band absorption coefficients, not including the temporary changes, was approximately equal to the ratio of their corresponding concentrations.] The temporary changes for crystals containing small and large *M*-center concentrations (i.e., small and large values of the ratio α_{M0}/α_{F0}) exhibited distinctly different characteristics, as shown in Fig. 2. In this figure, curves A and C represent the absorption spectrum and the temporary absorption change values at saturation, respectively, in a crystal with $\alpha_{M0}/\alpha_{F0}=0.03$. Curves B, and D represent the corresponding curves in a crystal with $\alpha_{M0}/\alpha_{F0}=0.40$.

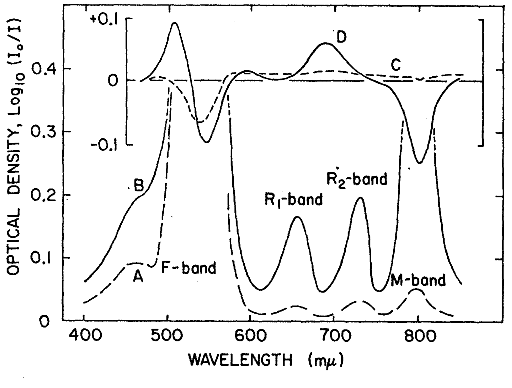

FIG. 2. Temporary absorption changes due to *F* irradiation at 77°K in two additively colored KCl samples. Curves A and B are the absorption spectra, C and D, the temporary absorption changes in crystals with α_{M0}/α_{F0} equal to 0.03 and 0.40, respectively.

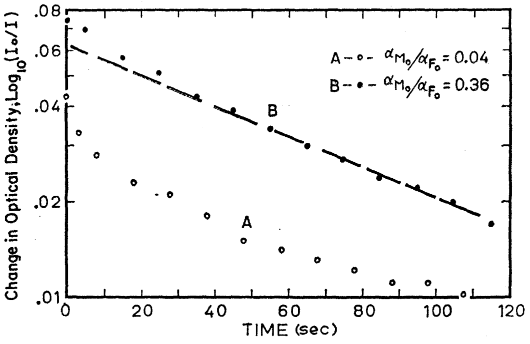

FIG. 3. The decay of the temporary *F* change (logarithm of the change in optical density as a function of time) at 77°K in two additively colored crystals containing extreme α_{M0}/α_{F0} values.

In crystals containing small α_{M0}/α_{F0} ratios ($\alpha_{M0}/\alpha_{F0}\lesssim 0.03$) one observes a prominent temporary absorption decrease in the *F* band accompanied by a small, very broad, absorption increase in the red and near infrared regions. The maximum *F* change coincides with the *F*-band absorption maximum (about 540 mμ). These characteristics were not only observed in crystals containing small α_{M0}/α_{F0} values obtained through limited room temperature *F*-band exposure, but were also observed in crystals in which the *M* band had been substantially bleached through thermal or optical treatments.

In crystals characterized by large α_{M0}/α_{F0} ratios ($\alpha_{M0}/\alpha_{F0}\gtrsim 0.3$), one observes a temporary decrease in the *F* and *M* bands denoted by $\Delta\alpha_F$ and $\Delta\alpha_M$, respectively, and the formation of new bands at about 505 and 685 mμ denoted by $\Delta\alpha_{505}$ and $\Delta\alpha_{685}$, respectively. In addition, a slight temporary increase could be observed in the background absorption extending to about 1 μ. In contrast with the case for small α_{M0}/α_{F0} the maximum *F*-band change now lies on the long-wavelength side of the *F*-band absorption maximum at about 545 mμ.

In crystals with intermediate α_{M0}/α_{F0} values an effect which is a superposition of both types was observed. Thus absorption change ratios involving $\Delta\alpha_F$ were not independent of α_{M0}/α_{F0}. The ratio $\Delta\alpha_{505}/\Delta\alpha_F$ was found to increase with increasing α_{M0}/α_{F0} for small values of α_{M0}/α_{F0}, but asymptotically approached a constant value for large α_{M0}/α_{F0}. $\Delta\alpha_F/\Delta\alpha_M$ was found to decrease with increasing α_{M0}/α_{F0}, but also asymptotically approached a nearly constant value at large α_{M0}/α_{F0}. For values of α_{M0}/α_{F0} greater than 0.34, $\Delta\alpha_F/\Delta\alpha_M$ was found to be 0.67 ± 0.05.

For all samples, the ratio $\Delta\alpha_{685}/\Delta\alpha_M$ was independent of α_{M0}/α_{F0} with a value of 0.457 ± 0.003. Both the temporary absorption changes $\Delta\alpha_M$ and $\Delta\alpha_{685}$ were

---

[19] This light was monochromatized by a series combination of a Farrand interference filter which had a maximum transmission of 47% at 552 mμ (13 mμ half-width) and a Corning 4–96 glass filter.

[20] The Cary source was monochromatized with a Farrand interference filter which had a maximum transmission of 38% at 510 mμ (13 mμ half-width).

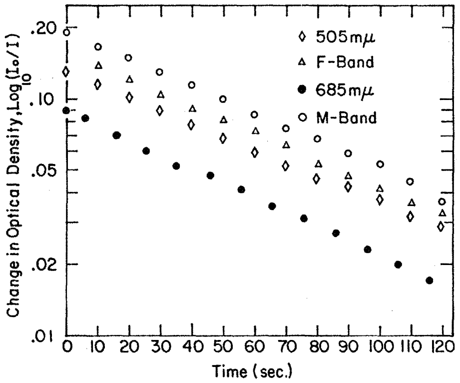

FIG. 4. The decay of the four principal temporary changes at 77°K in a crystal with $\alpha_{M0}/\alpha_{F0}=0.25$.

measured relative to the small temporary increase in background absorption. This background change was not taken into account in the determination of the maximum temporary absorption changes $\Delta\alpha_F$ and $\Delta\alpha_{505}$ since its value in these regions was unknown.

The temporary changes produced in crystals with large α_{M0}/α_{F0} values recovered spontaneously after the F light was removed with a recovery half-life of about 50 sec at 77°K. The recovery rate was greatly increased, however, if the crystal was exposed to intense red light, the rate increasing with red light intensity. On the other hand, it was found that the spontaneous recovery rate was little affected by exposure to light with wavelengths greater than 0.8 μ.

The decay from saturation of the logarithm of the temporary F-band change (or simply the F-band decay) at 77°K for a crystal with $\alpha_{M0}/\alpha_{F0}=0.04$ and with $\alpha_{M0}/\alpha_{F0}=0.36$ is shown in curves A and B of Fig. 3, respectively. Curve A is clearly nonlinear for a major portion of the decay. On the other hand, except for the small initial region, curve B can be characterized by a single time constant. This initial deviation from linearity may be due to the contribution to $\Delta\alpha_F$ of the change associated with the process dominant in crystals with small M-center concentrations.

The decay at 77°K of the 505 mμ, 685 mμ, F-, and M-band changes was measured for a crystal with $\alpha_{M0}/\alpha_{F0}=0.25$ (Fig. 4). These graphs demonstrate that the decay in each region can be characterized by a recovery time constant which is identical at each wavelength.

The recovery rate for the 685 mμ and M-band regions was also measured as a function of temperature from about 30 to 190°K, using crystals with large α_{M0}/α_{F0} values. As the crystal temperature was increased from 77° to 190°K, the absorption was continuously recorded at a fixed wavelength (805 or 685 mμ) during both irradiation and decay. Since the M-band absorption maximum varies with temperature, the absorption at 805 mμ was independently determined as a function of temperature subsequent to the decay measurements. Additional base line corrections were also required at temperatures for which the F'-band absorption in the 685 mμ and M-band regions is significant. Decay measurements above 190°K were not made because of the complicating effect of F'-center thermal instability.

The decay of the 685-mμ change for a number of temperatures greater than 77°K is shown in Fig. 5. As seen these curves are all linear in this temperature range, the recovery half-life decreasing with increasing temperature. Similar results were obtained in this range for the M-band decay. Decay curves near 30°K for the 685 mμ and M-band changes were also linear.

Figure 6 shows the variation of log τ, where τ is the recovery half-life, with $1/T$ for both the 685 mμ and M-band regions in the temperature range from 30° to 190°K. These data show that the temperature variation of the recovery half-life is identical for both spectral regions over this range. Furthermore, the logarithm of this recovery time constant increases approximately linearly with $1/T$ above 100°K,[21] levels off at about 100°K and is temperature-independent down to at least 30°K. The thermal activation energy for the temperature-dependent process is 0.03_5 eV.

B. Temporary Absorption Changes in Crystals Containing Polarized *M* Bands

When crystals containing F and M bands are exposed at room temperature to M light polarized along the $[0\bar{1}1]$ direction, the M- and F-band absorption is greatest for light polarized along the $[011]$ and $[0\bar{1}1]$ directions, respectively.[22] Unlike the anisotropy induced through polarized irradiation at 77°K, the polarizations produced in this manner were found to be completely unaffected by intense F-band irradiation at 77°K.

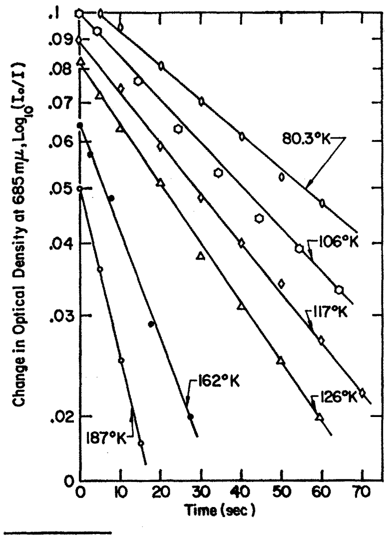

FIG. 5. The decay of temporary change at 685 mμ as a function of temperature in a crystal with $\alpha_{M0}/\alpha_{F0}=0.37$.

---

[21] This result is in general agreement with a similar measurement made in this restricted temperature range (see Ref. 16).

[22] See Ref. 9.

Dichroism was also observed in the four temporary changes.[23] The temporary *M*-band absorption change, the 685 mμ band change, and the initial *M*-band dichroism were largest when measured with [011] light. On the other hand, the temporary *F*-band absorption change, the 505 mμ band change, and the *F*-band dichroism were largest when measured with [0$\bar{1}$1] light. The wavelength of the maximum *F*-band dichroism and the maximum temporary *F*-band change coincided and was located on the long-wavelength side of the *F*-band maximum at about 545 mμ.

Assuming that the *M*-center symmetry axis lies along one of the six unit cell face diagonals (Fig. 7), the absorption coefficient for light polarized along the [011] and [0$\bar{1}$1] directions is[24]

$$\left.\begin{aligned}(\alpha_M)_1&=k[(n_M)_1+(n_M)_3]\\(\alpha_M)_2&=k[(n_M)_2+(n_M)_3]\end{aligned}\right\}, \tag{1}$$

respectively, where $(n_M)_1$ and $(n_M)_2$ are the *M*-center concentrations with symmetry axes oriented along the [011] and [0$\bar{1}$1] directions, respectively, $(n_M)_3$ is the concentration of *M* centers with axes oriented along any of the other four equivalent face diagonal directions, and k is a constant. For crystals polarized at room temperature with [0$\bar{1}$1] *M* light, the difference,

$$(\alpha_M)_1-(\alpha_M)_2=k[(n_M)_1-(n_M)_2], \tag{2}$$

is positive and nonvanishing.

If the *F*-band dichroism is due to *M*-center transitions in the *F*-band region with dipole moments perpendicular to the *M*-center symmetry axis, the difference in the *F*-band absorption coefficient is

$$(\alpha_F)_2-(\alpha_F)_1=k'[(n_M)_1-(n_M)_2], \tag{3}$$

where k' is a constant $(k'\neq k)$. The ratio of the dichroism in the *F*- and *M*-band regions, respectively, then becomes

$$\left.\begin{aligned}\Delta F/\Delta M&=[(\alpha_F)_2-(\alpha_F)_1]/[(\alpha_M)_1-(\alpha_M)_2]\\&=k'/k\end{aligned}\right\}. \tag{4}$$

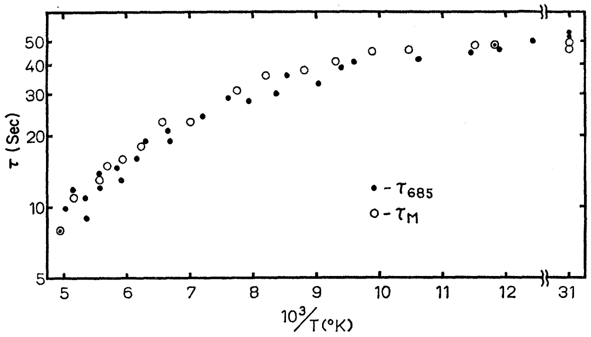

FIG. 6. A plot of the recovery half-life as a function of $1/T$ for the 685 mμ and *M*-band regions using crystals containing large α_{M0}/α_{F0} values.

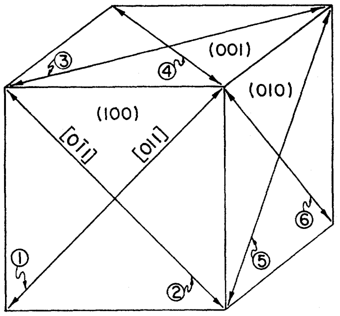

FIG. 7. Diagram of the six possible orientations of an *M*-center symmetry axis.

The ratio $(\Delta F/\Delta M)$ measured for a variety of crystals used in the absorption change measurements and exposed to polarized room temperature *M*-band irradiation for times ranging from 10 to 300 seconds was found to have a value of 0.64±0.10.

If it is assumed that the temporary change in the concentration of *M* centers oriented along a particular symmetry axis is porportional to the initial concentration along that axis with the same proportionality constant for each direction, it follows that the ratio

$$\begin{aligned}P&=[(\Delta\alpha_F)_2-(\Delta\alpha_F)_1]/[(\Delta\alpha_M)_1-(\Delta\alpha_M)_2]\\&=[(\alpha_{M_2})_2-(\alpha_{M_2})_1]/[(\alpha_M)_1-(\alpha_M)_2]\\&=\Delta F/\Delta M.\end{aligned} \tag{5}$$

Hence, the ratio P should be equal to $\Delta F/\Delta M$. Experimentally, P was found to have the value 0.54±0.03. Although this value is somewhat smaller than that obtained for $\Delta F/\Delta M$, the discrepancy may have its origin in the overlap of the temporary changes in the 505 mμ and *F* bands.

In unpolarized crystals, the concentration of *M* centers along each symmetry axis is equal. Thus, the *M* and M_2 band absorption coefficients, measured with unpolarized light would be

$$\left.\begin{aligned}\alpha_M&=2kn_0\\\alpha_{M_2}&=2k'n_0\end{aligned}\right\}, \tag{6}$$

respectively, where n_0 is the concentration of *M* centers oriented along any symmetry axis. It follows that $\Delta\alpha_F/\Delta\alpha_M$ measured in nondichroic crystals, will equal k'/k if *M*-center changes account for the entire temporary *F*-band reduction. Since the overlap effect of the temporary 505 mμ and *F*-band changes should be approximately equal in both $\Delta\alpha_F/\Delta\alpha_M$ and P, it is appropriate to compare these values. As $\Delta\alpha_F/\Delta\alpha_M$, was found to be 0.67 for the largest values of α_{M0}/α_{F0} used it is seen that for large α_{M0}/α_{F0}, at least 80% of the total temporary *F*-band change can be attributed to changes in the dichroic part of the *F* band. The discrepancy between these ratios may arise from the persistent contribution to $\Delta\alpha_F$ from the changes associated with the process which is dominant in crystals with small α_{M0}/α_{F0}.

---

[23] See Ref. 18.

[24] H. Kanzaki, Phys. Rev. **110**, 1063 (1958).

Experiments were also performed to determine the effect on the magnitude of the temporary changes of irradiating crystals containing dichroic M bands with intense polarized F light. Both the intense F light used tc produce these changes and the monochromator beam (set at 545 mμ) were incident normally on a (100) crystal face and polarized along either the $[011]$ or $[0\bar{1}1]$ direction. If one defines $(\Delta\alpha_F)_j^i$ as the temporary F-band change at saturation measured with light polarized along the j direction but produced with intense F band irradiation polarized along the i direction, the quantity $(\Delta\alpha_F)_1^1-(\Delta\alpha_F)_1^2$ will be nonvanishing if the temporary M-center changes are produced by direct absorption in the M_2 or M_3 bands.

Furthermore, if the saturation concentration along a particular orientation simply depends on the component of the light intensity along that orientation it follows that

$$(\Delta\alpha_F)_1^1-(\Delta\alpha_F)_1^2=(\Delta\alpha_F)_1^1-(\Delta\alpha_F)_2^1, \qquad (7)$$

and, hence,

$$(\Delta\alpha_F)_1^2=(\Delta\alpha_F)_2^1.$$

The results of a typical measurement expressed in terms of changes in optical density (abbreviated O.D.) were

$$\Delta(\mathrm{O.D.})_1^2=2.303d(\Delta\alpha_F)_1^2=0.14_0$$
$$\Delta(\mathrm{O.D.})_2^1=2.303d(\Delta\alpha_F)_2^1=0.07_8.$$

In all measurements the expression

$$\Delta(\mathrm{O.D.})_1^2-\Delta(\mathrm{O.D.})_2^1$$

was found to be significantly different from zero and was usually greater than the differential error by about one order of magnitude.

Since the M center may also possess optical transitions oriented along the $[010]$ direction[25] which may directly absorb the F light to produce the temporary changes, similar experiments were performed using crystals with M bands polarized at room temperature with $[010]$ M light and irradiated at 77°K with $[010]$ and $[100]$ F light. Again, the magnitude of the temporary changes at saturation were independent of the F-irradiation polarization.

C. Additional Studies

The application of a large dc electric field during F-band irradiation at 77°K leads to an increase in the number of free electrons in the crystals.[26] If the capture of free electrons by M centers played a role in the temporary bleaching effects the application of an electric field during the low-temperature F irradiation should increase the magnitude of the temporary F- and M-band changes.

It was found, however, that for crystals with a wide range of α_{M0}/α_{F0} values, the magnitude of these changes was field strength independent. Since the M band is always reduced by less than 40% in these experiments a sufficiently large number of unmodified M centers exist to produce increased temporary M-band bleaching.

Experiments were performed to determine whether M' bands form in the near infrared region from 1.0 to 2.5 μ during the F-band irradiation at 77°K. To within experimental error, temporary absorption changes were never observed in this region. In these experiments temporary M-band changes were usually of the order of 0.150 optical density units. If a primed band does form its absorption maximum must be less than the smallest detectable absorption change (less than about 0.00_2 optical density units). Furthermore, the recovery time of the temporary changes was not reduced by irradiation in this spectral region.

The 685 mμ band half-width was measured in unpolarized crystals for which the change in optical density at 685 mμ was greater than 0.05 O.D. Since the R_1 band absorption maximum lies near a 685-mμ half-width position, a temporary R_1 band reduction would reduce this half-width energy. The average half-width measured in thermally annealed crystals containing at least partially bleached R bands was $(W_{\mathrm{eV}})_{685}=0.125_7 \pm 0.001_6$. If one assumes that each temporarily bleached M center results in the creation of a single center which contributes to this 685 mμ band absorption, the ratio of the 685 mμ and M-band oscillator strengths, respectively, is

$$f_{685}/f_M \cong [(W_{\mathrm{eV}})_{685}/(W_{\mathrm{eV}})_M]\times[\Delta\alpha_{685}/\Delta\alpha_M].$$

Using $(W_{\mathrm{eV}})_M=0.066$ eV,[27] $\Delta\alpha_{685}/\Delta\alpha_M=0.457$, and $(W_{\mathrm{eV}})_{685}=0.125$, we obtain a value of

$$f_{685}/f_M=0.87.$$

For an M-band oscillator strength of $f_M=0.36$,[28] the 685 mμ oscillator strength is then

$$f_{685}=0.31.$$

A brief study of the temporary absorption changes was also made in additively colored KBr and KI at 77°K. In each crystal, M centers were introduced at room temperature with irradiation lying in the high-energy side of the F band. The temporary absorption changes due to F irradiation in KBr and KI were qualitatively similar to those observed in KCl. Four principle temporary changes, namely, F- and M-band reductions and the appearance of bands on the short wavelength side of the F and M bands again characterized the effect. A band which forms at 780 mμ in KBr and at 860 mμ in KI probably corresponds to the 685 mμ band in KCl. The recovery half-life of the temporary M-band changes was found to be about 7 sec in KBr and 2–3 sec in KI.

---

[25] See Ref. 10.

[26] F. Lüty, Z. Physik **153**, 247 (1958).

[27] Value obtained in Ref. 4.

[28] Value obtained in Ref. 4.

The wavelength of the maximum of the "685 mμ" band in KCl and the corresponding bands in KBr, KI, and NaCl[29] could be fitted to a Mollwo formula with reasonable accuracy (Fig. 8). The best fit to these experimental values is given by the relation

$$\lambda_{\max}=832d^{1.87}.$$

IV. DISCUSSION

A. The Process Dominant in Crystals with Small *M*-Center Concentrations

The data presented above clearly reveal the fact that the temporary absorption changes due to *F*-band irradiation at low temperatures consist of two distinctly different processes. Crystals receiving very short room-temperature *F* exposures resulting in small derived center concentrations exhibit a temporary decrease in the *F* band and a temporary increase in the *F*′-band region. Since the wavelength of the maximum temporary *F*-band change coincides with that of the *F*-band maximum, it is reasonable to associate the temporary absorption change with a true decrease in *F*-center concentration and this temporary effect to *F*-*F*′ conversion. Although *F*′ centers are thermally stable at 77°K, spontaneous recovery may occur if the process involves tunneling of excited *F*-center electrons to nearby *F* centers. The resulting *F*′-center electrons may then tunnel back to the neighboring negative ion vacancies and thereby account for the spontaneous nature of the recovery. Since *F* centers in freshly quenched crystals are believed to be uniformly distributed with average separations of from 50 to 100 lattice spacings (for the *F*-center concentrations used in our experiments), this interpretation would require *F*-center distributions with greatly reduced average separations. Clearly, *F*-center migration with the resultant formation of local regions of large *F* concentrations during the R. T. irradiation would favor this tunneling interpretation. Conversely, the effect may be taken as further evidence for the presence of such *F*-center clusters. The fact that the spontaneous decay cannot be represented by a single time constant indicates that the decay involves a superposition of electron tunneling events to and from *F*-center sites located at varying distances from the original excited *F* center.

Since the bleaching effect with these characteristics is also observed in crystals in which a major portion of the *M* band was either optically or thermally bleached, it is likely that such treatments simply decompose the *M* center from two *F* centers in nearest-neighbor positions to a configuration where the *F* centers are removed by several lattice distances.

The apparent independence of this process to the application of large electric fields is consistent with the above description if one assumes that the temporary *F* to *F*′ conversion between neighbors within tunneling distances is almost completely saturated by the light intensity alone.

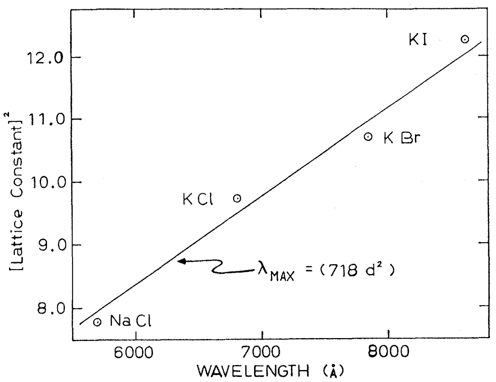

FIG. 8. Fit of the wavelength of the maximum temporary band formed on the short-wavelength side of the *M* band due to the low-temperature *F* irradiation of additively colored KCl, KBr, KI, and NaCl containing *M* centers to a Mollwo formula.

B. The Process Dominant in Crystals with Large *M*-Center Concentrations

A second process gradually replaces that described above, when the additively colored crystals are exposed to increasing doses of *F* light at room temperature. The effect in KCl crystals containing large *M*-center concentrations is characterized by temporary decreases in the *F*- and *M*-band absorption, and the temporary appearance of new bands at 685 and 505 mμ. The constancy of the ratio $\Delta\alpha_{685}/\Delta\alpha_M$ for all crystals, as well as the identical time and temperature dependence of the *M*- and 685 mμ band decays, evidently implies that the process involves the transformation of the *M* center into another center with a transition at 685 mμ. Under the assumption that the *F*-band dichroism is due to dichroic *M*-center transitions lying under the *F* band, rather than for example *F* centers polarized by local electric fields, our data qualitatively supports the view that the temporary *F*- and 505 mμ-band changes may also be associated with the *M*-center transformation. This conclusion is consistent with the following evidence:

(1) In crystals containing polarized *M* bands, the sign of the dichroism of the temporary *M*- and 685 mμ-band changes is the same as that of the original *M*-band dichroism, while the sign of the dichroism of the temporary *F*- and 505 mμ-band changes is identical to that of the original *F*-band dichroism.

(2) The saturation temporary absorption change ratios involving $\Delta\alpha_F$ and $\Delta\alpha_{505}$, such as $\Delta\alpha_F/\Delta\alpha_M$, $\Delta\alpha_{505}/\Delta\alpha_M$, approach constant values for sufficiently large values of α_{M0}/α_{F0}.

(3) The recovery rate of the temporary *F*- and 505 mμ-band changes in this process can be described by

---

[29] The 570 mμ band observed in NaCl with *F* irradiation at low temperatures, as given in Ref. 13, was used.

a single time constant which is the same as that of the temporary M- and 685 mμ-band changes.

(4) The maximum of the temporary changes in the F-band region occurs at about 545 mμ, which is near the peak of the dichroic part of the F band rather than the total F-band absorption maximum.

Furthermore, this interpretation is consistent with the quantitative fact that for the largest ratio of α_{M0}/α_{F0} used in our experiments, 80% of the observed temporary F-band changes can be accounted for by the dichroic part of the F-band region alone. It seems quite reasonable to ascribe the remaining 20% of the total temporary F-band absorption changes to the F-F' conversion process previously described.

This straightforward self-consistent interpretation of the results describes this particular process simply as the temporary transformation of the M center with its principal transition at 801 mμ to a related center with a corresponding transition at 685 mμ, and also provides further indirect evidence for the existence of optical M-center transitions under the F band. The temporary bleaching of the M center then also results in the temporary change of the 546 mμ transition of the M center to 505 mμ in the related center.

In crystals containing M bands polarized by [011] or [001] M light, the magnitude of the temporary changes at saturation was independent of the polarization of the F light used to induce the changes. This result indicates that the F-light irradiation responsible for the temporary absorption changes is not absorbed in the dichroic part of the F band, but must be absorbed by either an F or less likely some unpolarized anisotropic center.

If the irradiation is absorbed by the F center, the primary effect of the F-light irradiation at 77°K would be the production of excited F centers. It is interesting to consider on hand of our experimental results, how the formation of excited F centers can temporarily alter M centers.

It is very improbable that the M center is ionized or excited by the recombination radiation of the excited F centers with or without Stokes shift, at least if this F center is not situated in the immediate vicinity of the M center. This statement can be justified by the fact that none of the temporary changes are directly induced by irradiation in the long wavelength side of the F band.

The data, furthermore, rule out an electronic transfer from excited F centers to M centers with the formation of M' centers, through either direct ionization or tunneling. The following points may be cited in support of this conclusion:

(1) Primed bands, and in particular the M' band at 1.94 μ, were not observed during the low temperature F-band irradiation in the spectral region where these bands would be expected to form. Although these bands may be too small and broad to be detected, it was also found that the recovery rate was unaffected by irradiation with intense light lying in the near infrared region (wavelengths greater than 0.75 μ).

(2) From its spectral location it is unlikely that the 685 mμ (or 505 mμ) band represents a transition, to the first excited state of the M' center since the additional electron in an M' center should experience a looser binding than the original M electrons and should therefore be more easily ionized.

(3) The magnitude of the temporary changes was found to be independent of high electric fields applied during the F irradiation. This field application results in free electron production (greatly increased F-F' conversion) and should affect the magnitude of the temporary changes if M, bands are formed.

(4) If the temporary F-band change due to changes in M-center concentration is subtracted from the total F-band change, and it is assumed that this difference is due to changes in F-center concentration, then the number of bleached F centers is insufficient to account for the observed M-band changes by electron transfer from F to M centers. For example, if we decompose the temporary F-band change into possible contributions from the F and M center, the ratio for nondichroic crystals is given by

$$\begin{aligned}(\Delta\alpha_F/\Delta\alpha_M)_{\text{total}} &= (\Delta\alpha_F/\Delta\alpha_M)_{F\text{ center}} + (\Delta\alpha_F/\Delta\alpha_M)_{M\text{ center}} \\ &= (\Delta\alpha_F/\Delta\alpha_M)_{F\text{ center}} + (\Delta F/\Delta M).\end{aligned}$$

The ratio, $\Delta F/\Delta M$, was found to be about 0.6. $(\Delta\alpha_F/\Delta\alpha_M)_{F\text{ center}}{}'$ which represents the F-center contribution to the observed ratio, $(\Delta\alpha_F/\Delta\alpha_M)_{\text{total}}$, can be obtained by equating changes in concentration using Smakula's formula. If it is assumed that each ionized F electron destroys a single M center, this ratio becomes

$$(\Delta\alpha_F/\Delta\alpha_M)_{F\text{ center}} \cong (W_{\text{eV}})_M/(W_{\text{eV}})_F \times (f_F/f_M),$$

where $(W_{\text{eV}})_M$ and $(W_{\text{eV}})_F$ are the M- and F-band half-widths, respectively; f_F and f_M are the F- and M-band oscillator strengths, respectively. The ratio $(\Delta\alpha_F/\Delta\alpha_M)_{F\text{ center}}$ has a value of about 0.5. Thus, if the M' center were responsible for the temporary absorption changes, the experimentally measured values of $\Delta\alpha_F/\Delta\alpha_M$ should be greater than 1.1. Experimentally this ratio was less than 0.7.

It is therefore apparent that electron transfer from the excited F center to the M center cannot account for the observations. The possibility remains that the F-center excitation energy is locally transferred to an M center. This alternative requires that F and M centers exist at nearby lattice positions.

It is difficult however to come to any definite conclusions from our data with respect to the nature of the new center which is formed from the M center during the low temperature F-band irradiation. Processes involving ion or vacancy transfer are very unlikely at these low temperatures and would make it difficult to understand the complete recovery of the initial dichroism after the decay of the temporary changes.

Assuming that electronic processes are involved in the M-center transformation we may have either the excitation of the M center to a metastable state or the ionization and subsequent transfer of an M-center electron to some trapping center with the formation of an F_2^+ center. The latter process may involve the tunneling of an excited M-center electron to a nearby trap. The local transfer of excitation energy may involve phonons as well as photons, and may result in the excitation of the M center into an otherwise optically forbidden state [such as the $(1s\sigma 2s\sigma)\sum_\mu$ state]. This would account for the fact that the temporary changes do not seem to be readily induced by direct irradiation on the long-wavelength side of the F band.

If M-center ionization occurs, it probably involves electron tunneling from excited M centers to nearby traps, rather than a direct ionization process which produces free conduction electrons. In a free state, electrons may be trapped at isolated sites far removed from the initially ionized M centers, i.e., beyond electron tunneling distances. Thus, recovery can only occur through thermal activation. This channel, however, was not found to be dominant below 100°K. Furthermore, unless the ionization results from a multiple excitation process, the maximum radiant energy which can be transferred to the M center corresponds to the F-band absorption energy (if the transfer occurs before the excited F center experiences a Stokes shift). If this energy were transferred, it would not be evident why the temporary absorption changes are not produced by a direct M_2-band absorption of the radiation in the F-band region. Moreover, if this energy transfer produces an ionized M electron, it would also be unclear why stable F' centers do not form.

The difficulties associated with the free electron process are partially eliminated if one assumes that electron tunneling from excited M states to nearby traps occurs. Since the irradiation process involves tunneling, this recovery channel is available at all temperatures. Above 100°K the dominant recovery process could involve thermal ionization. The energy requirements are also somewhat relaxed. It is unknown, however, where the ionized M electrons are trapped. Since the total F-band change in this particular process can be attributed to M-center changes, these electrons do not tunnel to nearby F centers. Since M' centers have not been observed, M centers are not trapping electrons. Finally, R and N centers probably are not the electron traps as these are relatively inactive during the process. To account for the character of the recovery rate, it must be assumed that electrons tunnel to unique sites relative to the ionized M centers.

A process involving the formation of a metastable electronic state [e.g., $(1s\sigma 2s\sigma)\sum_\mu$] could also account for the general recovery characteristics. At low temperatures the recovery rate would simply depend on the extremely small transition probability from the metastable to the ground state. At higher temperatures (above 100°K), the reduction in the recovery rate may result from the thermal excitation of the excited electron to a higher state of shorter lifetime, such as an excitation from a triplet to a singlet state. Red irradiation during recovery may shorten the lifetime by either stimulated emission or an excitation to a shorter lived higher state. The principle difficulty associated with a metastable state mechanism, however, is the extraordinarily long lifetime of this state.

In theory, the choice of an F_2^+ or metastable M center may be made by comparing the experimental energy values of the temporary bands with theoretical calculations for the F_2^+ center transition energies. F_2^+-transition energies have been computed. In a calculation by Deigen and Vinetskii[30] the F_2^+ transition energy ($1s$-$2p$ optical transition) in KCl was found to be 1.91 eV. This can be compared with the experimental value of 1.81 eV. In KBr, these calculated and measured values are 1.68 and 1.59 eV, respectively. It is difficult, however, to decide whether this result can be used to justify the F_2^+-center model.

While the exact nature of the electronic process occuring in the temporary bleaching effect are not yet understood, our results and their consistent interpretation lend experimental support to the fact that F-center clustering occurs during the initial stages of room temperature F-band irradiation in additively colored alkali halides and that optical transitions of M centers occur in the F-band region.

Note added in proof. Recent paramagnetic resonance experiments by H. Seidel, Physics Letters **7**, 27 (1963), have established the excitation of the M center into a metastable triplet state as suggested above.

---

[30] M. F. Deigen and V. L. Vinetskii, Zh. Eksperim. i Teor. Fiz. **32**, 289 (1957) [translation: Soviet Phys.—JETP **5**, 226 (1957)].