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Color Centers in CsBr Single Crystals Irradiated at Liquid-Helium Temperature.

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The principal absorption bands induced by irradiation at liquid-helium temperature with x rays in CsBr crystals are the complex *F* band and two overlapping *V* bands at 435 and 497 mμ. In view of the dichroic properties of these *V* bands, the most obvious model seems to be a Br_2^- molecule-ion lying in the ⟨100⟩ directions. The two observed absorption bands would be due to two transitions in the same center. Regarding the bleaching properties, the *F* center cannot be the only color center responsible for the structure of the complex absorption band. Hypotheses are proposed about the interactions between the *V* and *F* centers.

I. INTRODUCTION

In the last few years an increased interest has arisen in the study of color centers in cesium halides in order to find out to what extent the ideas developed for NaCl-type crystals can be extrapolated to the cesium halides and which new features are inherent in this structure. One of the unexpected results is the structure in the *F* band, discovered by Rabin and Schulman[1] at liquid-helium temperature (LHT). Hughes and Allard[2] studied the EPR signal of CsCl crystals irradiated with 2-MeV electrons and found a center with all the properties of an *F* center. The same authors found, in a Tl-doped crystal, a center resembling the Cl_2^- center found by Castner and Känzig[3] in KCl. It could be produced by irradiation at liquid-nitrogen temperature (LNT), and bleaching occurred at higher temperatures.

Suffczynski[4] studied the spin-orbit splitting of the *F* band. An estimate of the contribution to the spin-orbit splitting in the excited state arising from the 6*s* state of cesium showed that this effect was several orders of magnitude too small to account for the observed *F*-band splitting. Knox[5] suggested that the three absorption bands of the *F* center are due to the fact that the cesium halides would have three conduction-band branches. He bases his argument upon the complicated structure of the exciton bands of the cesium halides. In the electron-transfer model this corresponds to a transfer of the *F*-center electron to *p* states of the cesium as well as to the *s* states. The same idea was suggested by Klick and Kabler[6] to explain the properties of the *L* bands in the NaCl-type alkali halides. As no band calculations have been made for the cesium halides, all these considerations can only be qualitative and tentative. Another theoretical study of the spin-orbit splitting of the first optically excited state of the *F* center was made by Smith.[7] The splitting arises from the spin-orbit interaction of the electron with the shielded electric fields of the neighboring ions. Explicit calculations for NaCl agree with the splittings observed by the methods of circular dichroism and Faraday rotation. Smith suggests that the cesium halide *F* band structure is due, at least in part, to a spin-orbit splitting. Recently, Moran[8] was able to show that the structure of the *F* band in the cesium halides can be explained by the instantaneous distortion of the *F* center's environment induced by the motion of the lattice. The calculated optical-absorption line shapes have three components and can be brought into agreement with the experimental results. The observed circular dichroism and Faraday rotation can also be explained by this theory.

Besides the *F* band several other bands have been found in the irradiated crystals as well as in additively colored ones. Of these we only mention the bands situated on the short-wavelength side of the *F* band, since this is the only region we examined. In Table I[9,10] we sum up these results because some of these bands have been assigned to impurities, and the absence of some of them may give indications of the purity of the crystals examined. The additively colored crystal bands assigned by the authors to impurities are put in

Table I. Spectral position of absorption bands in CsBr.

	LNT		LHT		
Avakian Smakula Ref. 9	Rabin Schulman Ref. 1	Present Authors	Rabin Schulman Ref. 1	Present Authors	Additively colored crystals Lynch Ref. 10 (measured at LNT)
	205		206	205	(224)
	(235)		234	234	(239)
241	(245)				(243)
270				260	(258)
	280				(266)
315			340	340	(322)
390	390	390		390	(390)
	(450)	(450)	435	435	
480	(480)				480–500
			490	497	
			580	580	
646	645	645	*F* 616	617	646
			642	637	

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[1] H. Rabin and J. H. Schulman, Phys. Rev. Letters **4**, 280, (1960); Phys. Rev. **125**, 1584 (1962).

[2] F. Hughes and J. G. Allard, Phys. Rev. **125**, 173 (1962).

[3] T. G. Castner and W. Känzig, J. Phys. Chem. Solids **3**, 178 (1957).

[4] M. Suffczynski, J. Chem. Phys. **38**, 1558 (1963).

[5] R. S. Knox, Phys. Rev. **133**, A498 (1964).

[6] C. C. Klick and M. N. Kabler, Phys. Rev. **131**, 1075 (1963).

[7] D. Y. Smith, Phys. Rev. **137**, A574 (1965).

[8] P. R. Moran, Phys. Rev. **137**, A1016 (1965).

[9] P. Avakian and A. Smakula, Phys. Rev. **120**, 2007 (1960).

[10] D. W. Lynch, Phys. Rev. **127**, 1537 (1962).

parentheses, as well as those which do not appear in all the crystals examined by Rabin and Schulman.

The 243-mμ band is considered by Lynch as a possible *U* band.

In this paper we deal mainly with the properties of the 435–497-mμ bands, which we consider *V*-type bands. Dichroic bleaching of these bands was observed. Their optical bleaching caused partial bleaching of the *F* band and vice versa.

II. EXPERIMENTAL PROCEDURE

The crystals used in this research originated from K. Korth, Kiel, Germany. They were oriented with an accuracy of about 2° on an x-ray goniometer and sawn in the desired direction, ground, and polished. Laue diagrams were made afterwards to check the correctness of the orientation. Carefull optical polishing appeared to be necessary, as otherwise a polycrystalline layer remains on the surface of the sample. This would give rise to misinterpretations in experiments on dichroic bleaching, due to the small penetration depth of the x rays used. The samples were irradiated through a Be window with 40-kV, 20-mA x rays from a copper-target tube installed at a distance of about 10 cm.

The crystals were mounted on a copper sample holder attached to the tail of a helium cryostat. The temperature of the sample was measured with a gold (cobalt)–normal-silver thermocouple inserted in the crystal. The thermocouple was calibrated with an N.B.S.-calibrated platinum resistance thermometer. The absorption spectra were determined with a Cary model 15 recording spectrophotometer. This limits the absorption spectra on the long-wavelength side to 800 mμ. For all the irradiations with light for optical bleaching, the spectrophotometer itself was used. In bleaching experiments with polarized light, the incident beam was polarized with a Glan prism. In all the results the absorption of the polarizers and the uncolored crystals was subtracted.

III. RESULTS

Optical Bleaching with Unpolarized Light

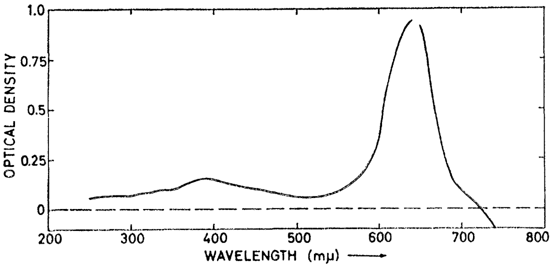

FIG. 1. Absorption spectrum after 90-min x-ray irradiation at liquid-nitrogen temperature.

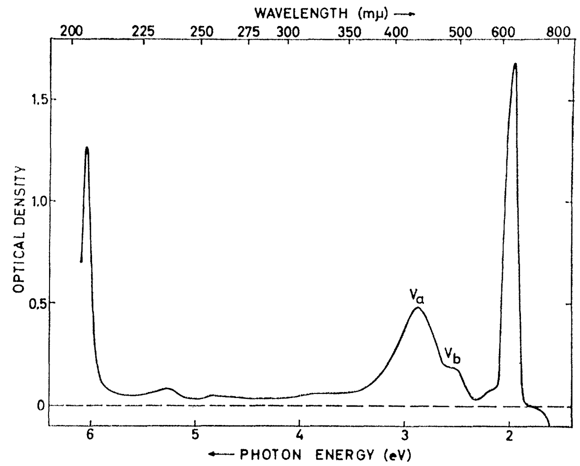

FIG. 2. Absorption spectrum after 15-min x-ray irradiation at liquid-helium temperature.

The uncolored crystals used in this study exhibited an absorption band at 255 mμ and weak bands at 233, 223, and 217 mμ; in some of them the 255-mμ band was, however, much weaker. Figures 1 and 2 show a typical absorption spectrum for a CsBr crystal irradiated with x rays, respectively, for 90 min at liquid-nitrogen temperature and for 15 min at liquid-helium temperature. The measurements are made at the same temperature as the irradiations. In Fig. 1 the only large absorption band is the asymmetric band which peaks at 645 mμ and which is recognized as the *F* band. On the long-wavelength side of the *F* band the same "negative absorption," due to luminescence and reported by Rabin and Schulman,[1] is observed. Between the *F* band and this "negative-absorption" region an absorption band was seen after irradiation at liquid-nitrogen temperature but not after irradiation at liquid-helium temperature. On the short-wavelength side of the *F* band there is a broad background absorption which extends to the ultraviolet and on which only a band at 390 mμ can clearly be distinguished. The most prominent effect of irradiation at liquid-helium temperature is the appearance of the bands at 435 and 497 mμ. We shall temporarily call these bands V_a and V_b, because their exact nature is not known, and in order to avoid confusion with known *V* bands in NaCl-type alkali halides. However, as will be seen, they behave like positive-hole bands. Another smaller band shows up at 234 mμ, as well as some still weaker bands which may be due to impurities. In Fig. 3 the *F* absorption at liquid-helium temperature is seen on a larger scale (curve a). It was decomposed graphically in its two main components at 617 and 637 mμ. The 580-mμ band is not shown. The ratio of the 617- and 637-mμ absorption at liquid-helium temperature is 0.64, as compared with 0.49 found by Rabin and Schulman. However, this difference may be due to the graphical determination of the subbands. The half-widths are 0.062 and 0.082 eV for the 617- and 637-mμ bands,

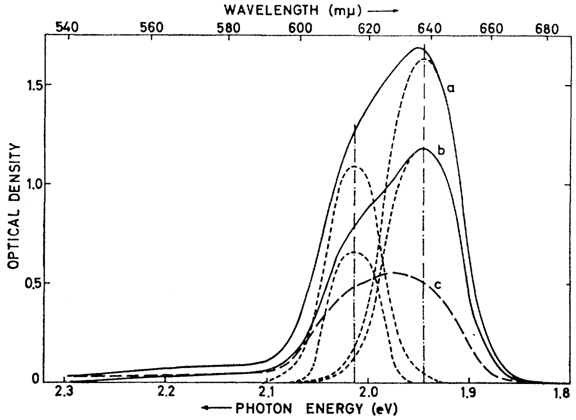

FIG. 3. Absorption spectrum curve a after 15-min x-ray irradiation at liquid-helium temperature, curve b after 150-min illumination in the V_a band. Curve c is the difference between curves a and b. Dashed curves give graphical decomposition of the components at 617 and 637 mμ.

whereas Rabin and Schulman found 0.066 and 0.110 eV, respectively.

By illumination in the F band either at liquid-nitrogen temperature or at liquid-helium temperature this band bleaches partially. When the experiment is done at liquid-helium temperature the V_a and V_b bands bleach partially at the same time. This is shown for the F and V_a bands by curves a and b of Fig. 4. By this procedure the V bands cannot be bleached completely. However, both V bands can be bleached completely (taking the background into account) by illumination either in the V_a or in the V_b band. At the same time the F band decreases. This is represented in Fig. 4 by curves c and d for irradiation in the V_a band and by curves e and f for irradiation in the V_b band. The decrease of the V_b band is not shown because the poor resolution and the background absorption did not allow sufficient accuracy. It should be noted that after the V bands are completely bleached the F band can be further bleached to a certain extent with F light.

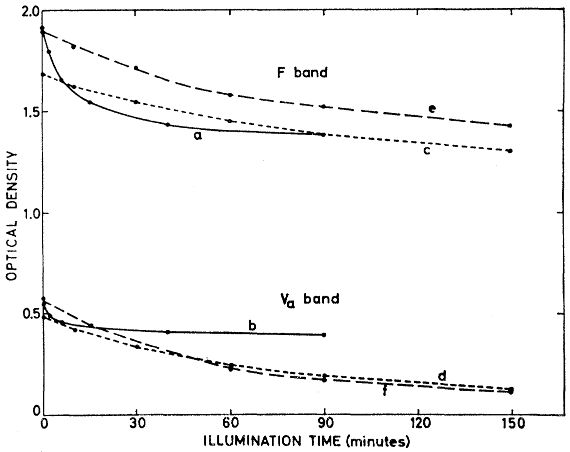

FIG. 4. Optical density of the F and V_a bands as a function of the illumination time: (a, b) in the F band; (c, d) in the V_a band; (e, f) in the V_b band.

All these curves were taken with the same crystal, although the initial absorption was not always the same. Curve b in Fig. 3 shows the absorption spectrum in the F-band region after illumination in the V_a band. Curve c of the same figure represents the difference between curves a and b. It is clear that the 617-mμ band is bleached more than the 637-mμ band. This indicates that the F-band complex cannot be due to a single color center. The same effect is seen after illumination in the V_b band instead of the V_a band.

By bleaching the V_a and V_b bands an underlying absorption band at 390 mμ can be observed. This band was not optically bleachable, as will be seen further in Figs. 5 and 7. It is possible, although not certain, that this is the same band which is observed after irradiation with x rays at liquid-nitrogen temperature.

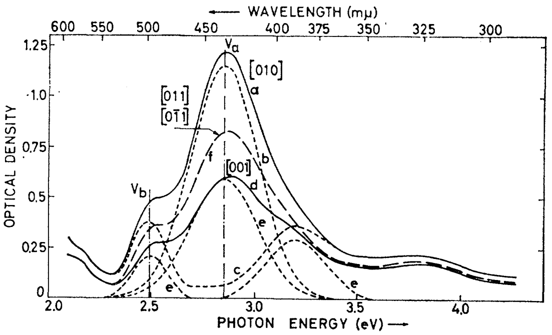

FIG. 5. Curve a absorption spectrum after 75-min x-ray irradiation at liquid-helium temperature. Absorption spectrum after 120-min illumination with [001] light in the V_a band for curve a [010] light, curve d [001] light, curve f [011] and $[0\bar{1}1]$ light. Curves b and c are the components of curve a. Curve d is decomposed in the curves e.

Irradiation of a crystal with x rays at liquid-helium temperature also gives rise to an absorption band at 205 mμ. This band did not bleach optically in the spectrophotometer. It is also not affected by illumination in the V bands, but it does increase slightly upon illumination in the F band. This would support the suggestion of Pringsheim and Hutchison (see Ref. 1) that the 205-mμ band is an α band. However, this band may be complex. Its increase is about 11% for a decrease of 26% at 637 mμ. Furthermore it appears also when the crystal is irradiated at liquid-nitrogen temperature.

Thermal Bleaching

In order to verify whether the V_a and V_b bands belong to the same center, the decrease of these bands has been followed when a crystal was warmed up from liquid-helium temperature. For both bands the maximum bleaching rate was at 14°K. The largest part of both bands thus bleaches at the same temperature.

At the same time a part of the F band disappears. Furthermore, there seem to be some smaller bands under the V bands which bleach at higher temperatures. A further study of the thermal bleaching of the absorption spectrum is in progress.

Optical Bleaching with Polarized Light

In the experiments the dichroic behavior of the V_a and V_b bands was examined. Crystal plates having, respectively, (100) and (110) as main faces were cut. The two cases will be considered successively.

a. (100) Crystals

In a first series of experiments a crystal was irradiated with x rays for 75 min and illuminated in the [100] direction with light of wavelength 435 mμ polarized in the [001] direction for 120 min. Spectra were taken with light polarized in the [001], [011], $[0\bar{1}1]$, and [010] directions. The result is shown in Fig. 5. Curve a is the original curve after irradiation. The spectrum taken in the [010] direction was unchanged after illumination. The bleaching of the background absorption makes it difficult to decompose the spectrum into its Gaussian components. The decomposition shown in the figure is therefore tentative. Curve c is obtained by subtraction of the Gaussian curve b from a. Here the 390-mμ band shows up clearly. Curve d, the spectrum in the [001] direction after illumination, has been decomposed into the three curves e. Taking into account the bleaching of the background, it is seen that the 390-mμ band is not bleached. The half widths of the V_a and the V_b bands are, respectively, 0.38 and 0.21 eV. Curve f represents the spectra taken in the $[0\bar{1}1]$ and [011] directions. Figure 6 shows the optical density at the peak of the V_a and V_b bands as a function of the time of illumination when measured with light polarized in the [001] direction. The curves of Fig. 7 concern an experiment similar to the previous one but with illumination at 490 mμ. Here the bleaching was prolonged. The subscripts have the same meaning as in Fig. 5. The spectra measured in the [011] and $[0\bar{1}1]$ directions are not drawn, but they have the same behavior as in Fig. 5. Illumination in the V_a band bleaches the V_b band and vice versa, and as far as one can tell, considering the background absorption, the bands remain in the same ratio.

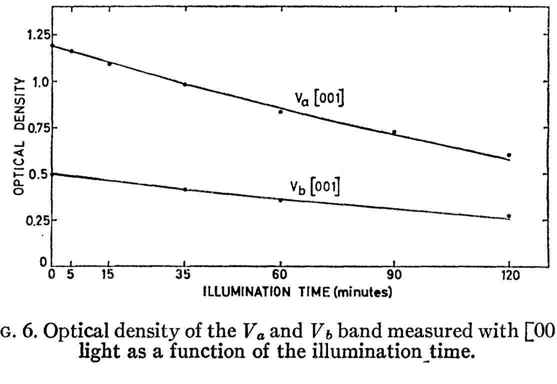

FIG. 6. Optical density of the V_a and V_b band measured with [001] light as a function of the illumination time.

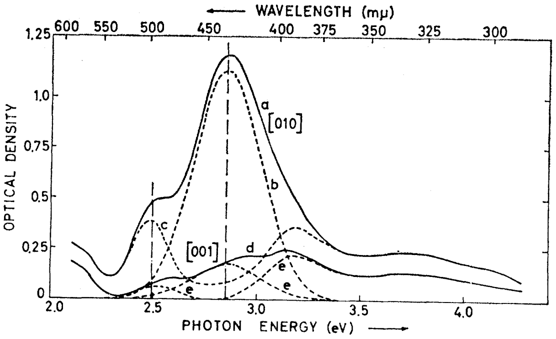

FIG. 7. Curve a absorption spectrum after 60-min x-ray irradiation at liquid-helium temperature. Absorption spectrum after 170-min illumination with [001] light at 490 mμ for curve a [010] light, curve d [001] light. Curves b and c are the components of curve a. Curve d is decomposed in the curves e.

Irradiated (100) crystals have also been illuminated in the V_a and V_b bands with light polarized in the [011] direction. Again spectra were measured in the [001], [010], [011], and $[0\bar{1}1]$ directions. No dichroism was observed as expected for color centers with transition moments in the ⟨100⟩ directions.

All these data on bleaching with polarized light are consistent with the idea that the V_a and V_b bands belong to one or two types of color centers with a transition moment oriented in the three equivalent [100] directions. To verify this picture, crystals with the principal face parallel to the (110) planes were also examined.

b. (110) Crystals

(110) crystals, irradiated as before, were illuminated in the 435-mμ band with light polarized in the [001] direction, and spectra were measured in the [001], $[1\bar{1}1]$, $[1\bar{1}0]$, and $[\bar{1}12]$ directions. The spectrum taken in the $[1\bar{1}0]$ direction was unchanged after illumination. The greatest decrease in absorbance was observed in the [001] direction and the lowest in the $[1\bar{1}1]$ direction. This confirms the idea that the centers responsible for the V_a band have a transition moment oriented in the ⟨100⟩ directions.

No reorientation of the V centers was observed in any of the experiments described in this section.

IV. DISCUSSION AND CONCLUSION

Irradiation with x rays of crystals of the cesium chloride type at liquid-helium temperature induces an absorption spectrum which is more complicated than in the case of NaCl-type crystals. The nature of the V centers could be determined by electron spin resonance. So far one can only make a guess about the structure of the corresponding centers. In view of the dichroic properties, the most obvious model is an asymmetric color center lying in the ⟨100⟩ directions and having transition moments in the same directions. This is to be compared with the V_K centers and H centers in the ⟨110⟩ directions in the NaCl-type crystals. The distance between the bromine ions in the [100] direction in CsBr is 4.29 Å. In the case of KCl and KBr the distance between neighboring halogen ions is respectively 4.44 and 4.66 Å. Although the existence of an H center in the CsBr lattice would rather be expected in the ⟨110⟩ directions (considering the larger interionic distance), it is not excluded that it could lie in the ⟨100⟩ directions. Indeed, in this direction the distance between neighboring bromine ions is not very different from the distance between bromine ions in KBr. This would easily explain the existence of the two bands V_a and V_b. However, when thermally bleached, these two bands disappear at the same temperature within the experimental error. This suggests that the two bands would be due to two transitions in the same center, probably the Br_2^- molecule-ion. Furthermore, the two bands seem always to bleach in the same ratio. The splitting between the two bands is 0.35 eV, whereas the energy difference between the two main exciton bands is 0.4 eV according to Eby.[11] Consequently they could be ascribed to two excited states corresponding to two valence bands. It seems preferable to postpone further speculations until electron-spin-resonance experiments have been performed. In this respect it is surprising that Hughes and Allard found an EPR signal corresponding to a Cl_2^- molecule in the ⟨110⟩ directions in CsCl above liquid-nitrogen temperature.

There is certainly a close relationship between the bands at 617 and 637 mμ. However, the fact that irradiation in the V bands bleaches the 617-mμ band considerably more than the 637-mμ band shows that the F center cannot be the only color center responsible for the structure in this absorption region, as suggested by several authors. From Fig. 4 one sees that irradiation with F light bleaches the same fraction of the F band and the V_a band. If the reaction is a trapping of an F electron by a self-trapped hole, an α center could eventually be formed. As mentioned before, the 205-mμ band increases somewhat at the same time. However, nothing is known about the stability of the α center in the cesium halides. Bleaching by illumination of the V bands was slower. This could be due to the smaller number of incident photons per second in this wavelength region. In this case all the V centers could be bleached. A tentative explanation is that, upon illumination in the F band, only neighboring F centers and V centers would react by tunneling, the electrons not being excited in the conduction band at liquid-helium temperature. On the other hand, illumination in the V band would make the holes mobile so that all the V centers could be bleached. This implies that only about 25% of the V centers are close enough to the F centers to allow tunneling. It should be noted here, however, that hole conductivity has never been observed in NaCl-type crystals. After complete bleaching of the V bands with V light, the F band could be further partially bleached with F light. No other changes are then seen in the visible and ultraviolet part of the spectrum. F aggregates can be formed, however, giving rise to absorption bands in the infrared.

Further experiments will be necessary to verify the proposed hypothesis about the interactions between the V and F centers.

ACKNOWLEDGMENTS

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