Color Centers in Additively Colored CsBr

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Color Centers in Additively Colored CsBr

Abstract
Color centers have been studied in CsBr single crystals additively colored with potassium or cesium. More than ten absorption bands were produced, most of which had previously been found in crystals colored by ionizing radiation. All bands produced by irradiation at or above liquid nitrogen temperature appear to arise from trapped electrons. The most prominent bands in the additively colored crystals are the F band at 642 mμ (liquid nitrogen temperature) and a band at 243 mμ which appears to be due to an impurity. Optically bleaching the F band at 200°K produces bands analogous to the M and R bands in other alkali halides while bleaching at liquid nitrogen temperature yields a broad band identified as the F′ band. Evidence that the asymmetry of the F band arises from several states of the F center is presented.

Keywords
absorption spectrum, potassium, cesium, bleaching

Disciplines
Atomic, Molecular and Optical Physics | Optics

Comments
INTRODUCTION

Color centers have been studied in many alkali halides but primarily those of the NaCl structure. It is of interest to extend these studies to alkali halides of the CsCl structure to see if the different lattice structure has any effect on the color centers. Such a study can be aided by the large body of knowledge in existence on color centers in NaCl-type salts and also may provide a test for some of the color center models currently used. Smakula and Avakian,1 and Rabin and Schulman2 have reported on color centers in irradiated cesium halides and the latter workers have also examined the F band in additively colored CsBr. Avakian and Smakula observed at least ten absorption bands in irradiated CsBr, the two most prominent bands being at 241 μ and 646 μ at liquid nitrogen temperature (LNT). The latter band, corresponding to the F band in other alkali halides, is asymmetric. Rabin and Schulman having decomposed it into three components at liquid helium temperature. In CsCl they find the corresponding band also has three components.3 The present work was undertaken to determine which of the bands of reference 1 result from trapped electrons and to study further the properties of some of these bands.

Recently two more papers on color centers in cesium halides have appeared.4,5 The work of Rabin and Schulman deals primarily with color centers produced by ionizing radiation, including the result of irradiating at liquid helium temperature. The work of Hughes and Allard describes the electron spin resonance spectra of the F center and a hole center in CsCl.

EXPERIMENTAL

Harshaw and Korth single crystals were used. These crystals showed traces of thallium absorption bands6 (α ~ 0.1 cm⁻¹, λ = 260 μ, and 212 μ at LNT) and evidence of hydroxyl ions (see later). They also contained from 100 to 1000 ppm of Na, 100 ppm of Rb, and 50 to 100 ppm of K, Ag, Cu, Fe, Mg, and Si were also detected spectrographically. The absorption at wavelengths less than 260 μ was not characteristic of pure crystals. There was structureless absorption to at least 220 μ, the limit of reliable measurement.

The crystals were colored for 12 h at 500°C with potassium or cesium vapor whose equilibrium temperature was between 350 and 450°C. All bands except a colloid-like band appeared to be independent of the two metals used for coloring. After polishing, the 1 to 3 mm thick crystals were heated in air to 500°C for 1 to 2 min on a platinum-clad steel block and quenched on a copper block. During and after this procedure the only light allowed on the crystals was from a 15 W lamp covered with several layers of blue cellophane transmitting between 350 and 500 μ, and beyond 1000 μ. Optical absorption measurements were made on a Beckman DU spectrophotometer. Using an oscillator strength of 4.06 and assuming a Gaussian shape for the entire F band gave color center densities between 3 x 10¹⁰ and 1.6 x 10¹² cm⁻³.

RESULTS

Figure 1 shows the absorption spectrum of an additively colored crystal about a half hour after quenching.

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1. Contribution No. 1110. Work was performed at the Ames Laboratory of the U. S. Atomic Energy Commission.
impurity but probably not thallium since additive coloration to low levels left the height of the 260-µm thallium band unchanged.

243-µm band  This band appears prominently in all crystals, but has a different shape in different crystals due to overlap with the Tl band and probably the band at 239 µm. If a colored crystal is cooled slowly from the temperature of coloration only the 243-µm band and a “colloid” band occur. Irradiation in the 243-µm band at room temperature bleaches it slowly giving rise to the F band. Subsequent optical bleaching of the F band leads to the normal products of such a bleach; the 243-µm band is not restored. Irradiation at LNT bleaches the 243-µm band very slowly (3 h with 2-mm slits on spectrophotometer removed 12%), but no new bands produced by this bleach could be found. When, instead of being optically bleached, the slowly cooled crystal was reheated and quenched, a large F band occurred and the 243-µm band was smaller. In the thinner samples quenching removed the 243-µm band completely.

This band might be the U band (due to substitutional H⁻ ions) because its behavior closely resembles that of the U band in other alkali halides. Etzel and Patterson7 showed that the U band was always present if crystals containing OH⁻ ions were additively colored. No OH⁻ absorption could be resolved in these crystals with the present equipment but the absorption in the tail of the fundamental absorption band was somewhat high (Figs. 1 and 7 of reference 1 show a slight shoulder at 225 µm and 240 µm, respectively, the former in the region where OH⁻ absorption would be expected). However the introduction of hydrogen into the colored crystals by heating them at 500°C in hydrogen at several atmospheres pressure until the blue color disappeared failed to yield any new absorption in the ultraviolet, so the identification of the 243-µm band as the U band cannot be made with certainty. The band is somewhat more removed from the absorption edge than is the U band in other alkali halides.

Two different crystals showed a band at 243 µm having twice the normal width. There was a trace of a shoulder on the short wavelength side of this band in these crystals. In these crystals an unusually large 239-µm band probably occurred simultaneously with the 243-µm band.

258- and 266-µm bands  These small bands do not occur in all crystals and are probably due to impurities. Tl gives a band at 260 µm in uncolored crystals, which remains after coloration. No band at 280 µm was seen. The width of the 270-µm band of reference 1 (Table I) may be attributed to the overlap with the 258-µm band.

322- and 390-µm band.  These are not present in all crystals and are very weak in all cases. There is a considerable difference in the widths reported for the 322-µm band (Table I).

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Table I. Spectral positions and widths of absorption bands in CsBr.

<table>
<thead>
<tr>
<th>Wavelength (λ) of maximum (µm)</th>
<th>Additively coloreda</th>
<th>Irradiatedb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present work</td>
<td>Reference 1</td>
</tr>
<tr>
<td>Full width (W) at half maximum (ev)</td>
<td>λ (µm)</td>
<td>W (ev)</td>
</tr>
<tr>
<td>224</td>
<td>0.13</td>
<td>205</td>
</tr>
<tr>
<td>239</td>
<td>0.15</td>
<td>245</td>
</tr>
<tr>
<td>243</td>
<td>0.25</td>
<td>245</td>
</tr>
<tr>
<td>258</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>266</td>
<td>0.1</td>
<td>280</td>
</tr>
<tr>
<td>322</td>
<td>0.1</td>
<td>320</td>
</tr>
<tr>
<td>390</td>
<td>0.3</td>
<td>395</td>
</tr>
<tr>
<td>481-500</td>
<td>0.1</td>
<td>570</td>
</tr>
<tr>
<td>646</td>
<td>0.22</td>
<td>645</td>
</tr>
<tr>
<td>761</td>
<td>0.1</td>
<td>780</td>
</tr>
<tr>
<td>821</td>
<td>840</td>
<td></td>
</tr>
<tr>
<td>1045</td>
<td>0.03</td>
<td>1055</td>
</tr>
</tbody>
</table>

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a Measured at LNT.

b Irradiated and measured at LNT.

c Outside the wavelength region of the present investigation.

d Not found in all crystals by Rabin and Schulman.

*Observed in the present investigation, but included in the 646-µm band.

Nine of the ten bands observed by Avakian and Smakula in irradiated CsBr are seen here. (Their λ₉ was a weak band on the long-wavelength side of the F band, suggesting that it is a band similar to the R bands in other alkali halides.) Table I lists the characteristics of these bands and compares them with the bands of references 1 and 3. Other characteristics of these bands are described below.

224-µm band  This band does not occur in all crystals but was found in some Harshaw crystals which exhibited a step at 225 µm in the absorption spectrum before coloration. The absorption at 224 µm was increased by the coloring process (not just the quenching), and the band was several times higher than the original step. Since it did not occur in all crystals, this band is probably due to an impurity. “Not occurring in all crystals” means that the bands were found in all samples cut from the same block of crystal, but not in samples cut from other blocks. Two Harshaw crystals, purchased at different times, gave different ultraviolet absorption bands after additive coloration. These bands usually occurred in different samples from one block despite different thermal histories and coloration levels.

239-µm band  In some crystals grown in the laboratory from Dow CsBr a band at 239 µm occurred upon additive coloration and quenching. These crystals contained about ten times as much thallium as the Harshaw or Korth crystals and were probably less pure with respect to other impurities. This band is due to an
500-μm band. This band was found in all crystals but with varying degrees of prominence. It could be bleached by 500-μm light at room temperature but not at LNT. At both temperatures the 500-μm light reduced the F band, but this could be due to a tail on the F band extending to 500 μm. The 500-μm band occurred upon slow cooling of the crystal and was made more prominent by quenching. There was no correlation between the height of the 500-μm band and that of the F band. In some crystals this band peaked at 480 μm instead of 500 μm. This band was present in all crystals and may be caused by a genuine color center, although there are impurities common to all samples. Further study, especially of the dependence of this band on the thermal history of the sample, is needed.

642-μm band. This band will be called the F band because of its similarity to the F band in other alkali halides. Rabin and Schulman have presented arguments for identifying this band as the F band. They have shown that this band possesses structure and could consist of three components. Analogous decomposition of this band can be made at LNT and the relative areas of the components are about the same as in reference 3 for liquid helium temperature (65:30:5 for the 1.905, 2.01, and 2.08 eV components at LNT). The shape of the F band at about 15°C agrees with that obtained by Rabin and Schulman. At dry ice temperature (DIT) and room temperature (RT) the sub-bands overlap so severely that such a decomposition is useless. The high-energy component lies at the position of the K' band that Drickamer et al. find in CsBr under pressure.

They find that as the pressure is increased the F band diminishes and the K' band grows. Illumination in either the F or K' band bleaches both bands. In other alkali halides such as KI, the K' band appears at pressures sufficient to make the CsCl structure more stable. The “K' component” of the F band appears to be a property of the CsCl lattice, not of the Cs nearest neighbors to the F center.

The F band in a freshly quenched crystal decays slowly in the dark. A quenched crystal subsequently heated in the dark to 90°C for 18 h showed a smaller F band and an increased “colloid” band. The F band can be optically bleached rapidly at RT, the ultimate product being a “colloid” band although thermally unstable K- and M-like bands can be detected. (However, see the section on the “colloid” band.) At DIT the optical bleach yields the R- and M-like bands (see Fig. 2, Result of bleaching at dry ice temperature with F-band light. Spectra measured at liquid nitrogen temperature. A. No bleach. B. 5-min bleach. C. 60-min bleach. Bleached at 645 μm with 0.1-mm slits on spectrophotometer.)

FIG. 2. Result of bleaching at dry ice temperature with F-band light. Spectra measured at liquid nitrogen temperature. A. No bleach. B. 5-min bleach. C. 60-min bleach. Bleached at 645 μm with 0.1-mm slits on spectrophotometer.

FIG. 3. Result of bleaching at liquid nitrogen temperature with F-band light. The optical density after the bleach minus the optical density before the bleach is plotted. The plot shows the F' band created and the F band lost.
Fig. 2) while a bleach at LNT gives a broad band analogous to the \( F' \) band (Fig. 3).

Partially bleaching the \( F \) band in an oriented crystal with polarized light produced no 100, 110, or 111 dichroism in the \( F \) band. This bleach took place at LNT with light in the long wavelength component of the \( F \) band.

1045-\( \mu \) band This band formed upon optical bleaching of the \( F \) band at DIT-RT (Fig. 2), but disappeared in several hours in the dark at RT. It was occasionally found in unbleached crystals, but this was attributed to inadvertent optical bleaching of the \( F \) band. It appears to correspond to the \( M \) band in other alkali halides. The full width at half maximum is about 0.026 eV at LNT and about 0.017 eV at about 15°K. Although the band is narrow, it still shifts considerably to higher energy with decreasing temperature (see Table II). Because of its narrowness, accurate determination of the \( M \) band shape is difficult, but it appears not to be Gaussian, being skewed somewhat toward long wavelengths, and perhaps having a long wavelength tail. The band bleaches optically at DIT, partially restoring the \( F \) band and also reducing the band at 821 \( \mu \) (when present) formed by the \( F \) bleach. It cannot be bleached at LNT. Figure 2 also shows that as the \( M \) band grows, the asymmetry of the \( F \) band grows. There appears to be a second and possibly a third transition of the \( M \) center at 2.0 and 2.08 eV or a new center formed by \( F \)-light bleach.

821-\( \mu \) band This band grows slowly upon DIT \( F \) bleach after a prominent \( M \) band has formed. It is unstable at RT and contributes to the restoration of the \( F \) band.

700, 761, and 905 \( \mu \) bands These small bands are produced by prolonged \( F \) light bleach at DIT, and are also unstable at RT, and are smaller than the 821-\( \mu \) band. The band at 700 \( \mu \) occasionally formed upon \( F \) light bleaching at RT and LNT. It appeared similar to the 615-\( \mu \) band in CsCl (Fig. 3 of reference 3). Conditions for its occurrence were not determined.

\( F' \) band Irradiation in the \( F \) band at LNT produced the changes shown in Fig. 3. The broad band peaking at about 775 \( \mu \) but extending from 480 \( \mu \) to above 1200 \( \mu \) appears analogous to the \( F' \) band in other alkali halides. None of the bands on the red side of the

<table>
<thead>
<tr>
<th>Approximate temperature (°K)</th>
<th>Wavelength of maximum (( \mu ))</th>
<th>Full width at half maximum (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1037</td>
<td>0.017*</td>
</tr>
<tr>
<td>90</td>
<td>1045</td>
<td>0.026-0.034</td>
</tr>
<tr>
<td>260</td>
<td>1057</td>
<td>0.035</td>
</tr>
<tr>
<td>300</td>
<td>~1080</td>
<td>~0.08</td>
</tr>
</tbody>
</table>

* Two measurements only.


**DISCUSSION**

The present work shows that nearly all bands produced by irradiation at or above LNT arose from trapped electrons. This can be seen from Table I where nearly all bands which occur in all irradiated crystals are seen to occur in at least some additively colored crystals. The exceptions are the 205-\( \mu \) band and possibly the 280-\( \mu \) band. This latter band may be the 266- or 270-\( \mu \) band in the other columns of Table I. With these possible exceptions no \( V \) bands were found.
at LNT by Avakian and Smakula, and by Rabin and Schulman. Jacobs et al. have additively colored CsBr with bromine and found a band at 275 µm which may be a V band. This band does not correspond to a prominent band in irradiated CsBr reported by others, although it lies at the position of a large band produced by x-irradiation by Jacobs and co-workers. Data taken at low temperature on bromine-colored CsBr after proper quenching are needed to relate this band to V centers. Fairly large bands at 435 and 490 µm and a smaller band at 340 µm were produced by Rabin and Schulman by irradiation at liquid helium temperature. These bands do not occur in additively colored crystals and could arise from trapped holes.

An important feature of the F band is its substructure. Rabin and Schulman cite evidence for the structure's being due to several transitions of one center. Additional evidence in favor of this view is the fact that bleaching the F band at LNT gives an F' band and a reduced F band with the same shape as before. Bleaching the F' band restores the F band with its original shape. This eliminates the possibility that part of the F-band structure arises from another center whose concentration is proportional to the F center concentration, e.g., the F2+ center, unless vacancies or F centers are mobile at LNT. Production of the F band with the same structure by irradiation at liquid helium temperature also speaks against this reason for the structure.

The accepted model for an F center in other alkali halides is an electron trapped in an anion vacancy. The F band arises from transitions from a 1s state to the degenerate 2p-like states. The possibility that in the cesium halides the structure is due to 1s-2p, 1s-3p, 1s-4p (or 1s-continuum) transitions is unlikely because the oscillator strengths should diminish for the higher energy transitions and this is not observed. In CsCl the three sub-bands have about equal areas. In CsBr the second component has about half the area of the first, but this could be assumed to be two unresolved bands of equal area, making three components of equal area as in CsCl. The structure could then arise from a transition to a 2p state split into three levels. (This decomposition of the F band in CsBr ignores the 580 µm component (Drickamer's K' band). Because this component is so small and is overlapped by the larger components of the F band it is impossible at present to know whether the 580-µm absorption arises from the F center.)

If all the F centers were sufficiently perturbed the degeneracy of the p-like first excited states would be lifted and structure in the F band would be expected. This splitting could lead to more than one luminescent emission band from the center and the emission should be polarized upon excitation with polarized light. A perturbation with sufficiently low symmetry to split the p state into three levels in all crystals of the CsCl structure is puzzling.

The experiment with polarized light appears to eliminate two possibilities for such a perturbation: the proximity of a dislocation to all F centers and the proximity of impurities to all F centers to form centers like the A center. Spectrographic analysis revealed enough sodium and potassium in all crystals to associate several ions of these impurities with each F center at all levels of coloration. The work of Drickamer also tends to eliminate impurities as the cause of the K' part of the structure. He observed the K' band in Harshaw KI and KBr, both presumably purer than CsBr, as soon as they assumed the CsCl structure.

The splitting could be due to a local distortion (ionic displacement) about the F centers. The low activation energy for anion vacancy motion in CsBr and CsI would tend to make distortions about F centers more likely in these salts than in most NaCl-type alkali halides. If this distortion is not static at LNT no dichroism would be expected upon partial bleaching with polarized light. There would also be no anisotropy in the F center electron spin resonance. (None was observed in CsCl at LNT but this may have been due to not having a good single crystal.) The fact that the F center in CsCl exhibits a g shift comparable to that of nearly spherically symmetric F centers in NaCl-type alkali halides remains to be explained, since a distortion strong enough to split the 2p levels as much as they appear would also mix considerable amounts of higher angular momentum components into the 1s ground state.

A peculiar aspect of the F-center structure is its relationship with the K' band of Drickamer et al. Drickamer et al. found the areas of the F and K' bands to be in the ratio of about 10:1 at 20,000 atm and 1:10 at 50,000 atm. (The compression was not perfectly hydrostatic and it is difficult to assess the importance of this in the changes they observed.) Such a dramatic change in oscillator strength needs explanation and data between 1 and 20,000 atm are needed to relate the K' band to the structure of the F band. If indeed the F band in CsBr has three components of equal area then the small additional part of the F band, related to the K' band, may have nothing to do with the F center.

The M band is one of the narrowest color center bands known. At about 15°K its full width at half maximum is only 0.017 eV. This corresponds to the energy of one longitudinal optical phonon, 0.016 eV in CsBr (estimating the restrahl peak to be at 120µ). This narrowness is a characteristic of M bands observed in other alkali halides. In NaCl, Klick and Compton found the M band width to be 0.09 eV at 77°K and

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estimated the ground-state configuration coordinate frequency to be $1.7 \times 10^8$ cps or about one-fifth the longitudinal optical mode frequency. In CsBr the corresponding ground-state frequency ($0.77 \times 10^8$ sec$^{-1}$) is about one-fifth the longitudinal optical mode frequency ($4.1 \times 10^8$ sec$^{-1}$) which is much lower in CsBr than in NaCl.

The appropriate model for the $M$ center appears to be two $F$ centers.\textsuperscript{19} It is surprising that the $M$ band in CsBr, if it too arises from two adjacent $F$ centers, does not exhibit the structure of the $F$ band. Other aggregate bands, especially the $R$, do not develop to a great extent in CsBr; the bands located between the $F$ and $M$ bands are weak at all times. No "negative absorption"\textsuperscript{19} occurred in the region between the $F$ and $M$ bands. Irradiation seems necessary in order for luminescence to be stimulated in this wavelength region.

ACKNOWLEDGMENTS

The author wishes to thank R. W. Major who aided in the early stages of the experimental work and Dr. Ronald Fuchs for several helpful discussions.

\textsuperscript{19} C. Z. van Doorn and Y. Haven, Philips Research Repts. 11, 479 (1956), and C. Z. van Dorn, Philips Research Repts. 12, 309 (1957).