Color Centers in CsCl-Type Alkali Halides*

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A study of x-ray-induced color centers in the CsCl-type alkali halides has been made at room, liquid nitrogen, and liquid helium temperatures. The gross features of this coloration are similar to those observed in NaCl-type alkali halides, namely a principal absorption band in the visible portion of the spectrum with other absorptions at both longer and shorter wavelengths. The absorption spectra observed vary with the temperature of irradiation; the bands show characteristic thermal shifting and broadening, bleach under both thermal and optical excitation, and demonstrate much of the usual color-center behavior. At the same time some characteristics of the cesium halides appear to be unique, in particular the multiplicity in structure which makes its appearance in the principal absorption bands of CsCl and CsBr at liquid helium temperature. Since the principal absorption gives every evidence of being associated with the F center, one possible explanation of the component structure is that it arises from higher excited states of the F center.

INTRODUCTION

ALTHOUGH color centers in alkali halides have been of considerable interest for many years, the major portion of this interest has been devoted to studies of the face-centered cubic (NaCl-type) salts. The major reviews of color centers[1-4] reveal that no systematic studies of color-center formation in the simple cubic (CsCl-type) alkali halides have been pursued during the long history of the field.

Discoloration of the cesium halides was noted by a number of the early investigators of color centers including Jahoda,[5] who reported on luminescence as well as optical absorption of irradiated CsCl, and Pohl,[6] who reported the F band in additively colored CsCl. A number of the early efforts in the field have been referenced by Gmelin.[7] More recently there appears to be renewed interest in the cesium halides. In what is perhaps the first detailed observation of color centers in CsBr at low temperature, Pringsheim and Hutchison[8] described the x-ray-induced absorption spectrum produced at liquid nitrogen temperature over the range of 200 to 700 mμ. A number of brief references to color centers in CsCl-type alkali halides have appeared as part of studies which deal primarily with NaCl-type crystals, chief among which are those of Jacobs[9] and

Maisch and Drickamer,[10] who have reported on the effects of pressure on color centers in CsCl and CsBr, and Rauch and Heer,[11] who have reported on the F-band oscillator strength in CsBr. The most recent studies of color centers in CsCl-type alkali halides are those of Avakian and Smakula,[12] who have made systematic optical measurements between room and liquid nitrogen temperatures; Jacobs, Fiermans, and Van de Wiele,[13] who have investigated coloration with excess halogen; and Rabin and Schulman,[14] who have discussed structure in the F band in CsBr.

There is considerable motivation for a detailed exploration of the color center spectra of the CsCl-type alkali halides. Study of alkali halide structures other than the NaCl-type may serve to test and extend current models of color centers and current concepts of coloration processes. Conversely, the existing sizeable accumulation of knowledge of alkali halides with the NaCl-structure may be expected to give a great deal of aid in interpreting cesium halide color center spectra. Interesting questions can be raised with respect to the existence of CsCl-type analogs of the familiar NaCl-type color centers. One would expect the model of the F center to remain intact except for the adjustment required for eightfold coordination in the CsCl structure rather than the sixfold coordination of the NaCl-type lattice. The situation, however, becomes considerably more involved when one considers the more complex centers. The CsCl analogs of multivacancy centers like the M center, or of centers which involve an interstitial like the H center, are by no means easily predicted. An added feature that makes an investigation of the cesium halides timely is the fact that several associated studies of these crystals have recently been performed,

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[1] R. W. Pohl, Proc. Phys. Soc. (London) 49 (Suppl.), 3 (1937).

[2] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940).

[3] F. Seitz, Revs. Modern Phys. 18, 384 (1946).

[4] F. Seitz, Revs. Modern Phys. 26, 7 (1954).

[5] E. Jahoda, Sitzber. Akad. Wiss. Wien, Math.-naturw. Kl., Abt. IIa 135, 675 (1926).

[6] R. W. Pohl, Kolloid-Z. 71, 257 (1935).

[7] *Gmelin's Handbuch der Anorganischen Chemie* (Achte Auflange, Verlag Chemie, G.M.B.H., Berlin, 1938), Teil 25, pp. 156, 181, and 200.

[8] P. Pringsheim and E. Hutchison, Argonne National Laboratory Report ANL-5451, 1955 (unpublished), p. 12.

[9] I. S. Jacobs, Phys. Rev. 93, 993 (1954).

[10] W. G. Maisch and H. G. Drickamer, J. Phys. Chem. Solids 5, 328 (1958).

[11] C. J. Rauch and C. V. Heer, Phys. Rev. 105, 914 (1957).

[12] P. Avakian and A. Smakula, Bull. Am Phys. Soc. 5, 40 (1960); Phys. Rev. 120, 2007 (1960).

[13] G. Jacobs, L. Fiermans, and F. Van de Wiele, Physica 27, 144 (1961).

[14] H. Rabin and J. H. Schulman, Phys. Rev. Letters 4, 280 (1960).

TABLE I. Spectroscopic analysis.[a]

Element	CsCl Semi-Elements	CsCl NRL[b]	CsBr Harshaw	CsBr MIT[c]	CsBr:K Harshaw[d]	CsI Semi-Elements
Ag		FTR	TR	...	...	
Al	VW	S	VW	TR	VW	M
Ba	...	...	...	...	...	...
Ca	VW	W	TR	TR	TR	VW
Ce		...				
Cs	VS	VS	VS	VS	VS	VS
Cu	FTR	FTR	FTR	...	...	FTR
Fe	VW	M	TR	TR	FTR	W
K	VW	TR	TR	FTR	VW	VW
Li		FTR	TR	TR	FTR	...
Mg	TR	M	TR	...	TR	VW
Mn	...	W	...	TR	...	TR
Na	VW	W	VW	...	...	W
Ni	...					...
Pb	...	TR	...	...	...	...
Rb	VW	FTR	W	TR	VW	VW
Si	VW	W	VW	TR	TR	W
Sr		...	...	...	...	...
Ti	...	TR	...	...	...	VW

[a] The abbreviations and symbols used are as follows: VS—greater than 10%, S—1.0 to 10%, M—0.1 to 1.0%, W—0.01 to 0.1%, VW—0.001 to 0.01%, TR—0.0001 to 0.001%, FTR—less than 0.0001%, ... not detected. The absence of a designation indicates that a test was not made for that element.
[b] Kindly provided by L. R. Johnson and W. Zimmerman of the Solid State Division, U. S. Naval Research Laboratory.
[c] Kindly provided by Professor A. Smakula and Dr. P. Avakian of the Laboratory for Insulation Research, Massachusetts Institute of Technology.
[d] Kindly provided by Dr. W. G. Maisch of the University of Maryland, who performed the additive coloration with potassium.

in particular, studies of electrical conductivity and self-diffusion in CsBr and CsI by Lynch[15] and electron paramagnetic resonance in irradiated CsCl by Hughes and Allard.[16]

EXPERIMENTAL PROCEDURE

Crystals

The CsCl, CsBr, and CsI used in this work were all synthetic crystals[17] obtained commercially or made available by various research groups. The commercial suppliers were the Harshaw Chemical Company and Semi-Elements Inc., and the source of the privately supplied crystals is indicated in Table I. All of the crystals were prepared by melt growth with the exception of a CsCl crystal grown from water solution at the Naval Research Laboratory (henceforth referred to as the NRL crystal). All crystals used in this study are listed in Table I along with their impurity content as determined by emission spectroscopy.

Table I indicates not only the presence of a variety of impurity atoms in these crystals, but that these impurities are present in sizeable quantity in several cases. The presence of a large aluminum content in Semi-Elements CsI is presumably the result of this supplier's treatment of the raw material with aluminum oxide prior to growth; the presence of substantial

amounts of other impurities (iron, sodium, silicon) is not explained. The NRL CsCl crystal likewise shows a very large quantity of aluminum as well as sizeable amounts of iron and magnesium. This crystal was prepared a number of years ago without any attempt at attaining crystal purity but rather to study the impurities that promote its growth from solution.[18] The Harshaw CsBr which was additively colored with potassium shows an increase of roughly tenfold in potassium content over the untreated Harshaw CsBr crystal; the MIT CsBr specimen shows purity superior to both.

The presence of impurities in the crystals of Table I was indicated in their optical absorption prior to irradiation. Generally, an increasing absorption was noted in passing from the visible to the ultraviolet portion of the spectrum where the absorption joined what appears to be the tail of the fundamental absorption in the vicinity of 200 mμ. In several cases the absorption bands made their appearance as unresolved distortions of this absorption background at room temperature, and as the temperature was lowered this structure in several cases became resolved. For example, the Harshaw CsBr shows weak but resolved bands at approximately 206, 208, 217, 224, and 256 mμ upon cooling to liquid helium temperature. In a single instance, the NRL CsCl crystal, sizeable resolved absorption structure was observed at room temperature. This structure shown in Fig. 1, curve (a), consists of two large bands, one at about 244 mμ and the other at 267 mμ. These bands were observed to shift to shorter wavelength and become narrower when the temperature was reduced. The technique that was used throughout this investigation in observing color centers *produced* by irradiation was to use the pre-irradiation optical absorption of the crystal as the baseline of zero initial optical density. This baseline was then subtracted from the absorption spectra obtained after irradiation.[19] An example of this procedure can be observed in Fig. 1, curve (e) shown as a dashed line. The tacit assumption in this procedure was that the pre-irradiation structure was not altered during the irradiation process. The results generally bear this assumption out. In Fig. 1, for example, bands at 233, 252, and 281 mμ appear as a result of x-ray irradiation, but the 244- and 267-mμ bands originally in the crystal apparently have not been altered by the irradiation. The only crystal which had any history of irradiation prior to this investigation

[15] D. W. Lynch, Phys. Rev. 118, 468 (1960).
[16] F. Hughes and James G. Allard, Phys. Rev. 125, 173 (1962).
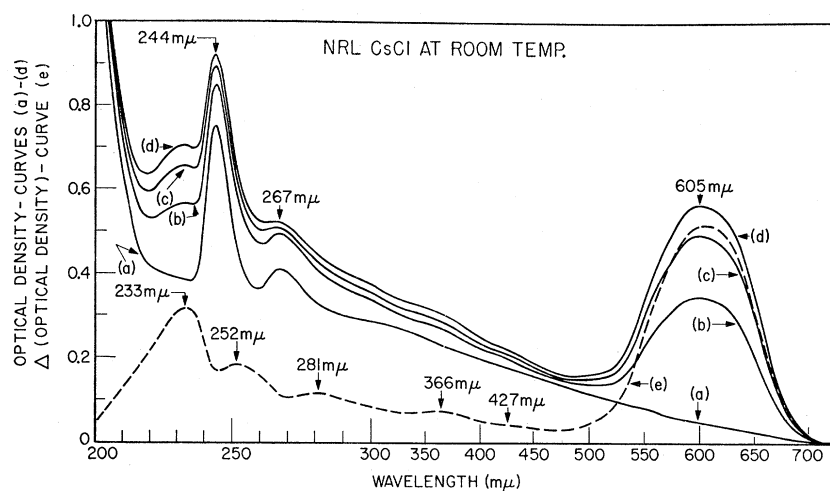[17] To the knowledge of the authors, cesium halide crystals are not found as natural minerals.

[18] The promotion of solution growth of CsCl by the addition of impurities is an established practice since the growth of the pure material is poor. Recently, the use of urea addition in the solution growth of CsCl has been reported, P. Avakian and A. Smakula, J. Appl. Phys. 31, 1720 (1960).
[19] The optical data in this paper are reported in terms of either the optical density, (OD), or the change in optical density produced by irradiation, Δ(OD)=(OD) after irradiation − (OD) before irradiation. The usual definition of optical density is used throughout this work, namely, the common logarithm of the reciprocal of the fraction of incident radiant energy of a given wavelength transmitted by the specimen.

FIG. 1. NRL CsCl at room temperature. The optical density is plotted as a function of wavelength (a) prior to x-raying, and after 15, 54, and 99 min of x-raying, (b), (c), and (d) respectively. Curve (e) gives the change in optical density after 99 min of x-raying, (d) minus (a).

was the MIT CsBr crystal which had been irradiated at MIT with 130-kv x rays for approximately five hours at $-78°C$. Optical absorption measurements indicated that previous coloration induced in the crystal was absent and that the crystal had returned to its normal, uncolored state prior to study at NRL.

Since the cesium halides used in this study did not exhibit cleavage, flat plates in the crystals were cut and ground to proper dimensions. The surfaces of the plates were then polished for optical measurement. The crystals were roughly 1 mm thick, the dimension along which both irradiations and optical measurements were made. No attempt was made to cut the crystals along specified crystallographic planes since it was uncertain that the specimens employed were single crystals. The CsCl that was melt-grown (Semi-Elements) was received in blocks of 1 cm³ which contained a number of small cracks, and additional cracking often occurred as this material was cut into plates. The supplier indicated that the cubes were originally cut from a large ingot that was highly strained owing to the crystallographic phase transition which CsCl undergoes at a temperature roughly 200° below its melting point. The crystal is transformed from a face-centered to a simple cubic lattice[20] in passing to lower temperature. Although a structure analysis of the crystal was not made at NRL, the similarity of its color-center spectrum to that of the solution-grown CsCl crystal (grown near room temperature) suggests that the transformation to the low-temperature phase was complete, as claimed by the supplier. Only one crystal in this work received a heat treatment prior to irradiation. The additively colored CsBr crystal was heated at about 450°C for about 10 sec and quenched in air at room temperature. This treatment was necessary to produce F-band coloration.

Apparatus

Color centers investigated in this work were essentially limited to those produced by x rays. X-ray irradiations and optical absorption measurements were made at room, liquid nitrogen, and liquid helium temperatures in a Hofman low-temperature Dewar. The Dewar was provided with a beryllium x-ray entrance window (approximately 0.75 mm thick) and quartz windows for optical measurement. These windows were mounted on a rotating head so that a crystal could be measured optically along the irradiation direction. The crystals were mounted on a copper block which was cooled by conduction for irradiations at liquid nitrogen and helium temperatures. Since precise temperature measurements were not made, the terms liquid nitrogen and liquid helium temperatures are approximate. In general, optical measurements were made at the same temperature as the irradiation temperature, but there are several exceptions which are noted in the text. Irradiations were performed in the dark and periodically interrupted for optical measurements in order to observe the growth of coloration as a function of x-ray exposure time. All x-ray exposures were made with a Machlett OEG-50 tungsten-target tube operated at 43 kvp and 20 ma; owing to the high x-ray absorption of the cesium halides, this beam was fully absorbed in the crystals under study. In addition to the use of x rays for color-center production, a CsI crystal was irradiated with 2-Mev electrons using a Van de Graaff accelerator, and as noted above an additively colored CsBr crystal was also investigated. The electron irradiations and associated optical measurements of CsI were performed in a separate crystal holder and Dewar described by Arnold and Compton,[21] and the additively colored crystal was optically measured in the previously mentioned Hofman Dewar.

[20] See, for example, J. W. Menary, A. R. Ubbelohde, and I. Woodward, Proc. Roy. Soc. (London) A208, 158 (1951).

[21] G. W. Arnold and W. D. Compton, Phys. Rev. 116, 802 (1959).

FIG. 2. Change in optical density of Semi-Elements CsCl at liquid nitrogen temperature (a) after 15 min x-raying measured in the visible and ultraviolet, and (b) followed by an infrared measurement. (c) is a repeat of the former measurement after optical bleach resulting from the infrared measurement.
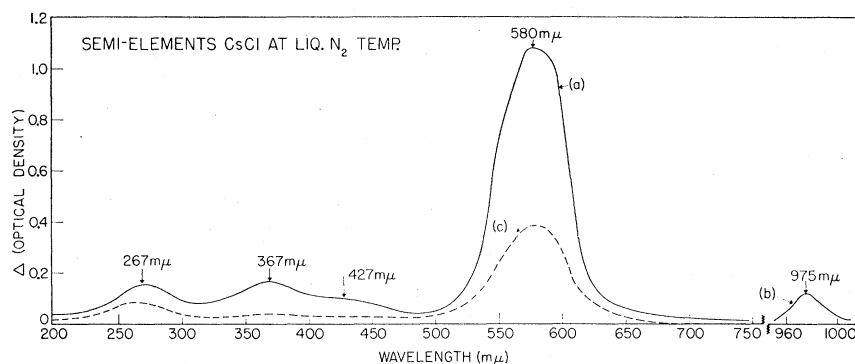
All optical measurements, covering the range 200 mμ–2.6 μ, were performed with a Cary model 14M spectrophotometer, modified slightly to accommodate the Dewars described above. Measurements over the infrared portion of this range (800 mμ–2.6 μ) resulted in a severe optical bleach of the crystal because, due to the design of the instrument, the full white light output of the tungsten lamp is incident upon the crystal. This difficulty is not encountered in the spectral range below 800 mμ since a comparatively weak, monochromatized beam passes through the crystal in this case. The procedure followed throughout this investigation was to avoid making the infrared measurement until measurements in the shorter wavelength region were concluded. Since the infrared measurement resulted in a bleach of the crystal, a repeat measurement was generally made of the shorter wavelength range following the infrared measurement to determine the effect of the resultant optical bleach. An example of this procedure is shown in Fig. 2 in which absorption was measured over the 200- to 750-mμ wavelength range, curve (a), followed by the infrared measurement, curve (b), and then a repeat measurement of the short-wavelength range, curve (c). It should be emphasized that the significance of the measurement over the infrared range is severely limited owing to the possibility of spectral changes during the process of measurement. Not only may existing optical structure be altered but new structure may be introduced. The data are included, however, because several interesting absorption bands in the range of about 800 mμ to 1.3 μ were repeatedly noted. Since no significant structure was observed in any specimens in the wavelength range beyond 1.3 μ, the data of this report omit the 1.3- to 2.6-μ portion of the spectrum.

RESULTS

Cesium Chloride

Figures 1–3 show typical absorption spectra of x-rayed CsCl at room, liquid nitrogen, and liquid helium temperatures, respectively, for NRL solution-grown and Semi-Elements melt-grown crystals. Table II gives a composite of the spectral positions of the

absorption bands in these figures, as well as additional bands for spectra not shown. Most peak positions were located by inspection, and accordingly, the wavelength assignments are approximate in cases of appreciable overlapping structure. Structure is not cited for the NRL crystal at low temperature in the spectral range below 300 mμ although there is indication that such structure exists. The separation of radiation-induced structure from the absorption background is most difficult in this case because the impurity absorption structure shows marked sharpening at low temperature. As indicated in Table II, a number of the bands which appear in Semi-Elements CsCl at liquid helium temperature were not observed in the NRL CsCl, namely, bands at 258, 515, 615, 657, and 740 mμ. Several of these (515, 657, and 740 mμ) were not observed in all Semi-Elements crystals.

Table II indicates that the centers giving rise to structure occurring at 366 and 427 mμ at room temperature appear to be also present in both crystals at liquid nitrogen temperature. At present no significance is attached to the fact that this absorption is specified

TABLE II. Spectral position of x-ray induced absorption bands in CsCl.[a]

Room temp.		Liq. nitrogen temp.		Liq. helium temp.	
NRL	Semi-Elements	NRL	Semi-Elements	NRL	Semi-Elements
233	234				
252	253				258
			267		
281					
				336	
366	369	367	367		
				366	376
				410	410
427	421	427	427		
					515
605	605	580	580	⎰558 ⎱575 588	⎰558 ⎱575 588
					615
					657
					740
	943				
		975	975		

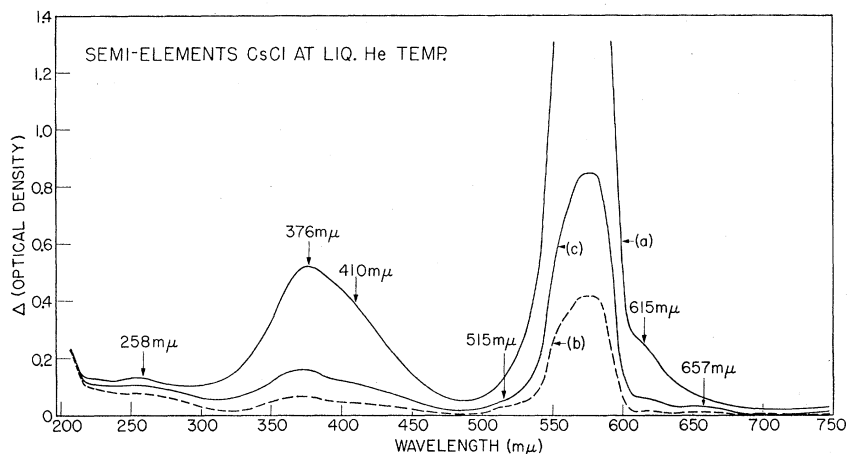[a] Recorded at the temperature of the irradiation and given in mμ.

FIG. 3. Change in optical density of Semi-Elements CsCl at liquid helium temperature (a) after 26 min x-raying, (b) followed by an optical bleach, and (c) re-irradiating for an additional minute.

at 421 mμ in the case of the Semi-Elements crystal at room temperature, owing to the weakness of the absorption and the difficulty in locating its spectral maximum in the neighborhood of strongly overlapping structure. It is questionable that the 410-mμ structure present in both crystals at liquid helium temperature is due to the same center giving rise to the 427-mμ band at higher temperatures in view of the absence of a thermal shift between room and liquid nitrogen temperatures for the 427-mμ band. In the case of the structure at about 366 mμ the results indicate that the same center is involved at both room and liquid nitrogen temperatures, with the situation at liquid helium temperature again in doubt. At liquid helium temperature, the Semi-Elements crystal shows a sizeable absorption in the neighborhood of 376 mμ as indicated in Fig. 3. In the NRL crystal, on the other hand, structure in this region is complicated by shorter wavelength absorption near 336 mμ. Since the latter absorption is not present in the Semi-Elements crystal, it is most likely an impurity absorption. Nevertheless, it greatly distorts absorption to longer wavelengths and could well account for the apparent location of the band at 366 mμ in the NRL crystal at liquid helium temperature. Accordingly, the 366-mμ band that is specified in the NRL crystal at liquid helium temperature actually peaks at longer wavelengths and is probably associated with the same center that gives rise to the 376-mμ band in Semi-Elements CsCl at this temperature. Thus the center giving rise to this structure is presumably not related to the center giving rise to the 366-mμ bands at higher temperature on the basis of its apparent location to longer wavelength (376 mμ) at liquid helium temperature.

The principal absorption which occurs at 605 mμ at room temperature gives evidence of being composed of three overlapping bands. An asymmetry in this absorption, noticeable at room temperature, becomes more pronounced at liquid nitrogen temperature, and structure is in full evidence at liquid helium temperature (Figs. 1–3). Figure 4 shows this structure at liquid

helium temperature for both Semi-Elements CsCl, curves (a)–(e), and NRL CsCl, curves (f) and (g), normalized[22] at 620 mμ. In the former case the absorption was produced by x-raying at room temperature, and the latter by x-raying at liquid helium temperature. Attempts at optical bleaching at liquid helium temperature, selectively [curves (b)–(e)] and with white light [curve (g)], resulted in a proportional diminution of the entire triplet. An approximate subdivision of the principal triplet in NRL CsCl at liquid helium temperature is shown in Fig. 5. The three components were obtained by fitting successive Gaussian curves starting at the low-energy side of the absorption envelope. The result is three components of approximately equal amplitude, with the two low-energy components of identical half-width and slightly narrower than the high-energy component. Table III summarizes the characteristics of these bands.

Figure 6 shows the growth of the principal optical absorption as a function of x-ray exposure time at room, liquid nitrogen, and liquid helium temperatures. A unit of 1.0 of the ordinate of this figure corresponds to roughly $(6.5 \times 10^{17}/f)$ centers/cm^3, where f is the oscillator strength using the Gaussian form of Smakula's formula.[23] This value is based on the assumption that a single center gives rise to the triplet structure (Fig. 5) and that the coloration was uniform over an x-ray penetration depth of 0.2 mm. The range 0.2 mm is an

TABLE III. Characteristics of the components of the principal triplet in CsCl at liquid helium temperature.

Peak position		Half-width	Relative peak	Relative
E(ev)	λ(mμ)	(ev)	height	area
2.107	588	0.064	1.00	0.30
2.155	575	0.064	1.00	0.30
2.220	558	0.088	0.99	0.40

[22] The intersections of the curves as well as their separation at the low-wavelength limit are attributed to weak overlapping structure such as that occurring at 515 and 615 mμ.

[23] D. L. Dexter, Phys. Rev. 101, 48 (1956), Eq. 27.

FIG. 4. Optical absorption spectra at liquid helium temperature of the principal absorption in Semi-Elements CsCl, Curves (a)–(e), and NRL CsCl, curves (f) and (g), normalized at 620 mμ. The Semi-Elements crystal was x-rayed (a) for 20 min at room temperature, and was thereafter selectively bleached at 590 mμ, curves (b) and (c), at 550 mμ, curve (d), and at 570 mμ, curve (e). The NRL crystal was (f) irradiated directly at liquid helium temperature for 40 min, and (g) thereafter given a white-light bleach.
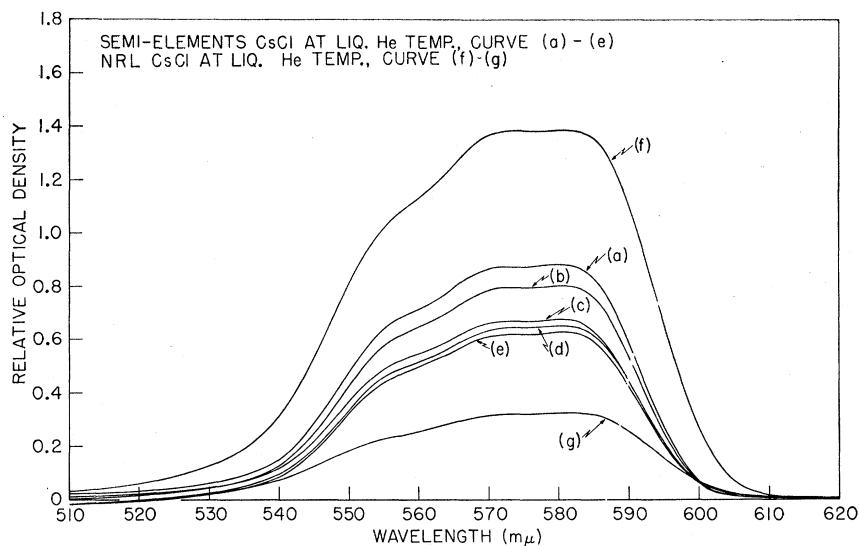
approximate computed value of the depth required for 25–40 kv x rays to be reduced in intensity to $1/e$ in the cesium halides. It is clear from Fig. 6 that the growth of the principal absorption increases markedly with decreasing temperature and that Semi-Elements CsCl is more sensitive to x rays than the NRL CsCl at all temperatures. The latter result is in accord with a previously reported[12] observation that melt-grown CsCl colors more deeply than solution-grown material.

The only structure in the infrared region (750 mμ to 2.5 mμ) consistently observed in both crystals occurs at about 975 mμ at liquid nitrogen temperature. In addition a broad absorption band appeared in the Semi-Elements crystal at room temperature at about 943 mμ. This band was observed to increase further following the infrared measurement.[24] Typical optical bleaching in the visible and ultraviolet portion of the

spectrum is shown in Fig. 2, curve (c), and Fig. 3, curve (b), also following a measurement in the infrared range. It is to be noted in the former case that the 267-mμ band gives the appearance of shifting to shorter wavelength (to approximately 263 mμ) after bleaching. A single band was found to grow upon optical bleaching; the 615-mμ band was observed to grow under conditions of a weak optical bleach (the data of Fig. 3 constitute a strong bleach).

It was found that substantially all the absorption disappears upon thermal bleaching. Absorption produced at low temperature disappears upon warming to room temperature, and the absorption produced at room temperature likewise anneals thermally in the dark at room temperature.

Cesium Bromide

Table IV lists the absorption bands observed in MIT and Harshaw CsBr x-rayed at room, liquid nitrogen, and liquid helium temperatures. Typical spectra are shown in Figs. 7–10.
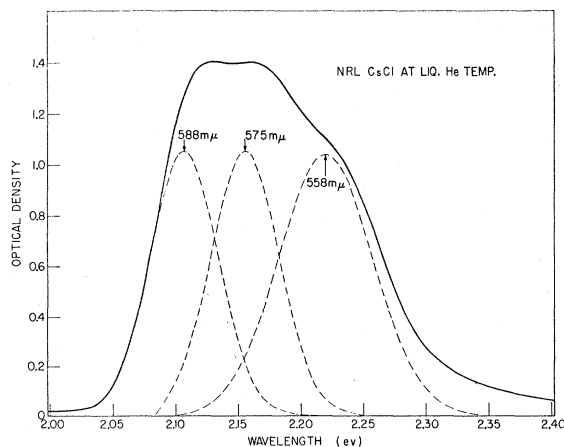

FIG. 5. The principal absorption in NRL CsCl at liquid helium temperature, subdivided into three Gaussian components.

[24] It will be recalled from above that the infrared measurement in this work results in a strong optical bleach of the crystal.
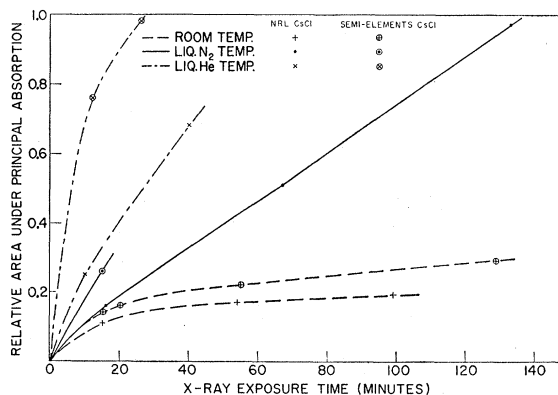

FIG. 6. Growth of the principal optical absorption in CsCl as a function of x-ray exposure time at room and low temperatures.
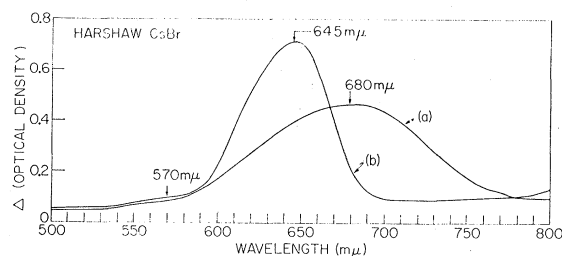
FIG. 7. Change in optical density of Harshaw CsBr at (a) room temperature and (b) liquid nitrogen temperature, following 40 min of x-raying at room temperature. The room-temperature, zero-density baseline was assumed to be unchanged at liquid nitrogen temperature.

The results at room temperature are marked by a comparative scarcity of absorption bands. The only clearly resolved room-temperature band observed in all crystals is the principal absorption. This absorption is pictured in Fig. 7 at 680 mμ at room temperature for Harshaw CsBr, curve (a), and has been shown earlier for x-rayed MIT and additively colored Harshaw crystals.[14] Curve (b) of Fig. 7 shows the principal absorption at liquid nitrogen temperature at 645 mμ following irradiation at room temperature, and the same absorption is shown in Fig. 8 for irradiation directly at liquid nitrogen temperature.

On the short-wavelength side of the principal absorption, weak structure appears in the neighborhood of about 570 mμ at both room and liquid nitrogen temperatures, Figs. 7 and 8. This structure has been observed in x-rayed Harshaw and MIT crystals (although very weakly in the case of the MIT crystal at room temperature), but appears to be totally absent in additively colored Harshaw CsBr.[14] It is not at all certain that the 570-mμ bands at room and liquid nitrogen temperature are identical. The fact that the 570-mμ band at room temperature is absent from the additively colored crystal in the presence of a reasonably strong principal absorption would further indicate that this structure was not associated with the principal absorption, at least at room temperature. The latter observation, however, is not conclusive, since data of Rauch and Heer[11] indicate the presence of a weak absorption in additively colored CsBr at room temperature at roughly the same spectral position.

In addition to the 216- and 253-mμ bands present in

TABLE IV. Spectral position of x-ray-induced and additively colored absorption bands in CsBr.[a]

Room temp. MIT	Room temp. Harshaw	Room temp. Harshaw additively colored	Liq. nitrogen temp. MIT	Liq. nitrogen temp. Harshaw	Liq. helium temp. MIT	Liq. helium temp. Harshaw	Liq. helium temp. Harshaw additively colored
			205	205	206		
216							
				235	234	235	
			245				
253							
			280	280			
			320	320			
					340	340	
							387
			395	390			
					434	435	
				450			
				480			
					490	490	490
570	570		570	570	580	580	580
680	680	680	645	645	616	616	616
					642	642	642
							840
	1050	1070	1050	1050	1050	1050	1050

[a] Recorded at the temperature of the irradiation and given in mμ.

the MIT crystal at room temperature (see Table IV), a broad absorption consisting of a number of unresolved bands in the range 260–400 mμ also appears in the MIT crystal at room temperature. When this absorption is observed at helium temperature at least two bands become discernible, 272 and 288 mμ. These bands are in addition to three others reported earlier[14] at 387, 490, and 580 mμ that result from room temperature irradiation of MIT CsBr with spectral observation at liquid helium temperature. The Harshaw crystal spectrum at room temperature is uninteresting to the short-wavelength side of the principal absorption. Again a broad absorption is observed in the ultraviolet (200–400 mμ) consisting of a number of unresolved bands which appear to bear little similarity to the structure noted in MIT material. No attempt was made to resolve the structure in this range by studying the Harshaw crystal at liquid helium temperature.

The absorptions indicated in Table IV for both MIT and Harshaw specimens show wide similarity at liquid nitrogen and helium temperatures. Liquid helium
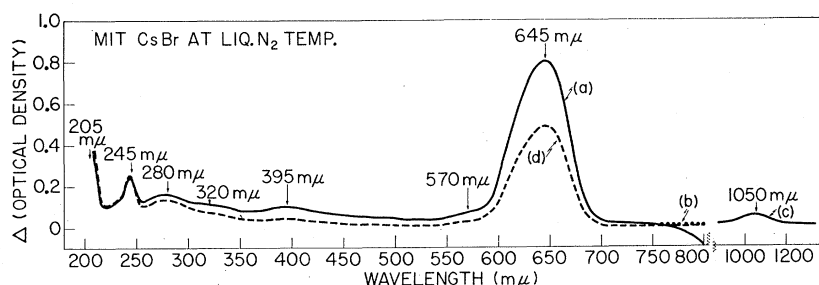
FIG. 8. Change in optical density of MIT CsBr at liquid nitrogen temperature (a) after 140 min x-raying, (b) the same as (a) except with an optical filter absorbing radiation below 730 mμ, (c) followed by an infrared measurement, and (d) a repeat of (a) after optical bleach resulting from (c).

temperature spectra are shown in Figs. 9 and 10 for Harshaw and MIT crystals, respectively. Although the 205–206 mμ band is not reported in the Harshaw crystal at liquid helium temperature (Fig. 9), its existence is suggested and it is almost certainly present. This band is indicated, however, in Fig. 8 since it was observed in an MIT crystal, other than the one shown in the figure. The absence of a 234–235 mμ band in MIT CsBr at liquid nitrogen temperature is anomalous in light of corresponding structure in Harshaw material at liquid nitrogen and helium temperatures and also MIT material at liquid helium temperature (Table IV). Moreover, the MIT sample shows the presence of a distinct band at slightly longer wavelength, 245 mμ, that seems to be absent in the other crystals at low temperature. The remaining structure in Harshaw and MIT crystals at low temperature seems to be in good correspondence with the exceptions of two bands present in additively colored Harshaw CsBr at liquid helium temperature at 387 and 840 mμ, and the 450- and 480-mμ absorptions in Harshaw material at liquid nitrogen temperature.

In a manner similar to that reported for CsCl above, the principal absorption band shows increasing asymmetry in passing from room temperature to low temperature, and at liquid helium temperature component substructure becomes apparent in the principal absorption (Figs. 9 and 10). Figure 11 shows the structure in the principal absorption band of CsBr measured at liquid helium temperature after formation under a variety of conditions, all curves being normalized at 700 mμ for comparison purposes. Curve (a) shows an additively colored Harshaw crystal, curve (b) an MIT crystal which was x-rayed at room temperature, curve (c) a Harshaw crystal x-rayed at liquid helium temperature, and curve (d) a Harshaw crystal x-rayed and thereafter optically bleached at liquid helium temperature. Thus the major substructure, consisting of two absorption bands, appears in fixed relative proportion, independent of the means of the production of the structure. The relative constancy of the structure is furthermore maintained upon successive re-irradiations at liquid helium temperature (see Fig. 10). The question arises as to whether the band occurring to the short-wavelength side of the major components at roughly 580 mμ is part of the principal structure. Owing to the weakness of this band and its overlap with the neighboring absorption, it was not possible to determine if a
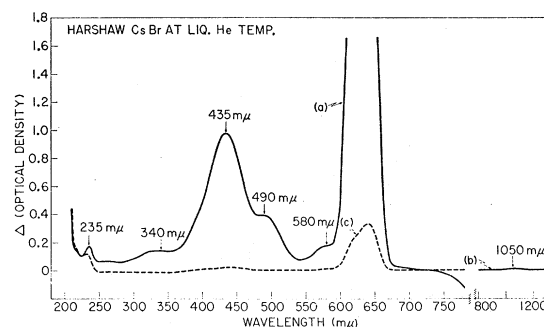

FIG. 9. Change in optical density of Harshaw CsBr at liquid helium temperature (a) after 15 min x-raying and (b) followed by an infrared measurement. (c) is a repeat of the former measurement after optical bleach resulting from the infrared measurement.

strict proportionality to the other structure were maintained. The best case for arguing that the 580-mμ band and its two neighbors form a principal absorption triplet is that the 580-mμ band is present whenever the two longer wavelength absorption bands are present, it occurs in the same spectral vicinity as the other two bands, and it provides for an analogy to the triplet structure of the principal absorption in CsCl. Table V gives the characteristics of the triplet as determined by a previous Gaussian analysis of the component structure,[14] with the 580-mμ band listed as the possible third component.

Figure 12 shows the growth of the principal absorption in CsBr at room, liquid nitrogen, and liquid helium temperatures. The relative area under the principal triplet is plotted as a function of x-ray exposure time. A value of 1.0 of the ordinate of the figure corresponds to approximately $(6.5 \times 10^{17}/f)$ centers/cm^3, where f is the oscillator strength for a Gaussian absorption, and taking the x-ray penetration depth to be 0.2 mm as in the case of CsCl. The initial growth at liquid nitrogen temperature is more rapid than that at room temperature, but the liquid nitrogen temperature growth
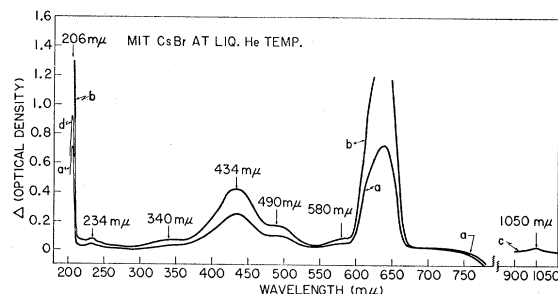

FIG. 10. Change in optical density of MIT CsBr at liquid helium temperature (a) after 2 min x-raying, (b) after 6 min x-raying, (c) followed by an infrared measurement, and (d) a repeat of the 206-mμ absorption after the optical bleach resulting from (c). This crystal was originally x-ray irradiated at room temperature, then lowered to liquid helium temperature, and the helium temperature spectrum taken as the zero density baseline for the optical density changes reported in (a) through (d) above.
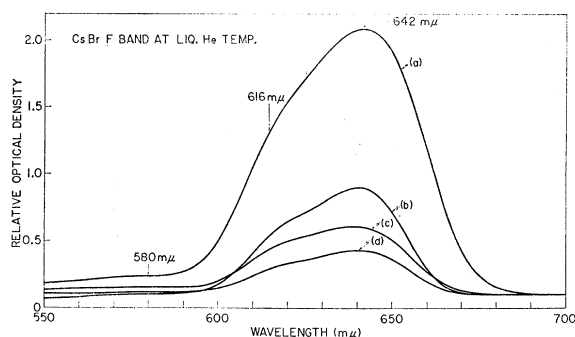
TABLE V. Characteristics of the components of the principal triplet in CsBr at liquid helium temperature.[a]

Peak position E(ev)	λ(mμ)	Half-width (ev)	Relative peak height	Relative area
2.138	580	...	~0.07	<0.10
2.013	616	0.066	0.49	0.21
1.931	642	0.110	1.00	0.69

[a] Based on the analysis of reference 14.

FIG. 11. The principal optical absorption in CsBr at liquid helium temperature normalized at 700 mμ, curve (a) Harshaw CsBr additively colored, (b) MIT CsBr x-rayed 90 min at room temperature, (c) Harshaw CsBr x-rayed 6½ min at liquid helium temperature, and (d) Harshaw CsBr x-rayed 15 min and optically bleached at liquid helium temperature.

appears to be eventually surpassed for longer exposures. Moreover, the growth rates of Harshaw and MIT specimens do not seem to be significantly different as they are for the various CsCl specimens (Fig. 6). As in the case of CsCl the production of the principal absorption in CsBr is most rapid at liquid helium temperature.

To the long-wavelength side of the principal triplet an absorption band was observed at about 1050 mμ (at 1070 mμ in the case of additively colored CsBr). This structure is reported in Table IV in all CsBr crystals with the exception of the MIT crystal at room temperature, which was not measured in this spectral range. It appears that the 1050-mμ band at room temperature in Harshaw CsBr is separate and distinct from the 1070-mμ band in the additively colored crystal and from those reported at low temperature. The band produced by x-raying at room temperature in Harshaw CsBr is quite broad, with a half-width of about 0.4 ev which essentially remains unchanged when the crystal is cooled to liquid helium temperature. In contrast the 1050-mμ band produced by irradiating directly at liquid nitrogen temperature has a half-width of only about 0.18 ev, and at liquid helium temperature the bandwidth is no broader.

As is indicated in Figs. 8–10, the absorption spectra of x-rayed CsBr at liquid nitrogen and helium temperatures shows anomalous behavior in the vicinity of 750–800 mμ, namely, the optical density recording becomes negative. It was found this behavior resulted from a violet luminescence of the crystal stimulated by the measuring light. The emission was easily observed with the unaided eye by exciting with infrared light, and with sufficient excitation the stimulated emission could be eventually depleted. Figure 8 shows the "negative absorption" resulting from the emission, curve (a), followed by a measurement of the same portion of the spectrum with a filter which absorbs strongly below 730 mμ, curve (b). After the emission is depleted by the optical bleach suffered during the

infrared measurement shown in curve (c), the spectral measurement, curve (d), is identical to the filtered spectrum, curve (b). At liquid helium temperature Fig. 9 again shows the depletion of the emission following infrared bleaching, and Fig. 10 shows that the amount of emission, measured by the magnitude of the "negative absorption," is proportional to the x-ray dose delivered. It has also been shown that the emission will not occur spontaneously in the dark but must be stimulated, and that the amount of emission is proportional to the amount of stimulation. Moreover, a crystal x-rayed at room temperature and observed at liquid helium temperature shows no stimulated emission of the type described. It does appear, however, that Harshaw CsBr x-rayed at room temperature and excited with infrared at room temperature gives evidence of luminescing in a manner similar to that observed at low temperature. However, in this case the comparatively weak room-temperature emission has only been observed visually, and has not resulted in driving the spectrophotometer to negative densities. The question arises as to the absorption structure at the wavelength of the infrared stimulation. Perhaps this absorption has not been observed as a result of being extremely weak (Avakian and Smakula[12] have reported weak structure in this vicinity) or because it is destroyed as part of the luminescence process itself. Furthermore, there is evidence that upon depleting the luminescence there is a slight increase in strength of the absorption of the principal absorption bands. The verification of this effect and its possible connection to the luminescence process will require further study.

With only a few exceptions, optical bleaching of the CsBr color-center spectrum resulted in a general diminution of all the absorption bands at all temperatures. The major exception appears to be the 245-mμ band in MIT CsBr, Fig. 8. From Figs. 8 and 9 it is not clear if the 205-mμ band bleaches optically (assuming its presence in both cases as discussed above); however, curve (d) of Fig. 10 for MIT CsBr shows quite distinctly that this band can be optically bleached at liquid helium temperature. Although the figures do not show bleaching of the 1050-mμ bands, they also have been observed to bleach under optical irradiation. The broad room-temperature 1050-mμ band is considerably more resistant to optical bleaching than the
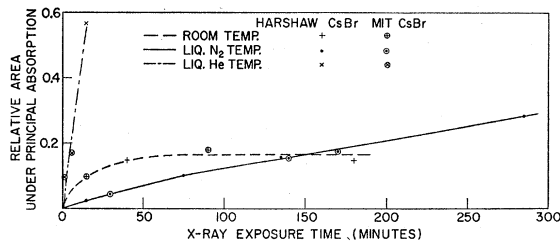

FIG. 12. Growth of the principal optical absorption in CsBr as a function of x-ray exposure time at room and low temperatures.
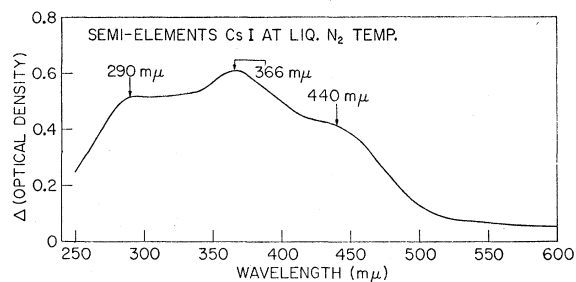
FIG. 13. Change in optical density of Semi-Elements CsI at liquid nitrogen temperature after 30 min of 2-Mev electron irradiation.

F band, and accordingly it is possible to bleach the F band almost completely and still retain a sizeable 1050-mμ absorption. In addition, all coloration produced by irradiation at low temperature is almost entirely bleached on warming the crystal to room temperature.

Cesium Iodide

Attempts to color both Harshaw and Semi-Elements cesium iodide by x-ray irradiation have not met with success. Long x-ray exposures have been equally unsuccessful at room temperature and low temperature. The only significant change noted in the CsI spectrum was a negative optical density of exactly the same type that was present in CsBr, starting from about 700 mμ and increasing to longer wavelengths. Presumably this was again a luminescence stimulated by the measuring light of the spectrophotometer. This "negative optical density" was present only at liquid nitrogen and helium temperatures and was not observed at room temperature.

In a further attempt to induce coloration in CsI, a Semi-Elements sample was exposed to 2-Mev electron bombardment at room and liquid nitrogen temperatures. This irradiation proved to be only partially successful. At room temperature again no coloration could be induced, but at liquid nitrogen temperature three overlapping absorption bands made their appearance at about 290, 366, and 440 mμ. These bands are pictured in Fig. 13. In addition a rather weak absorption was noted at about 1150 mμ. The former three bands seemed to be quite stable against optical bleaching at liquid nitrogen temperature, and also against thermal bleaching after warming to room temperature. The "negative absorption" mentioned above for x-rayed CsI was not present after electron irradiation at liquid nitrogen temperature.

DISCUSSION

The results show that the color-center spectra produced by irradiation were largely identical for specimens of the same cesium halide despite appreciable impurity variation in specimens from different sources. Moreover, in the case of CsCl, this similarity in spectra

was maintained for specimens prepared both from solution and from the melt. In cases where optical absorption was present prior to exposure to irradiation, the results indicate that this absorption did not materially interfere with the identification of radiation-induced absorptions. The luminescence observed in CsBr and CsI might well be due to the presence of impurities, but this fact has yet to be established. If the luminescence is impurity induced, the same impurity (or impurities) are apparently present in the various CsBr and CsI specimens investigated; furthermore, such an impurity either is not present or is ineffective in CsCl where there is no corresponding luminescent emission.

Undoubtedly a certain number of the absorption bands specified in Tables II and IV are the result of the presence of impurities, and it is most difficult, on the basis of the data at hand, to specify the bands which owe their origin to this source. As a first step in the identification of impurity bands, it may be assumed that absorptions which do not appear in all specimens of a given cesium halide at a given temperature are most likely due to impurity atoms. Thus the absence of a 336-mμ band in Semi-Elements CsCl at liquid helium temperature implies this band in NRL CsCl owes its origin to an impurity. Other bands can be provisionally identified as impurity bands by a similar analysis. This type of treatment can be broadened to include other published color-center data in the cesium halides, which at the present appear limited to temperatures of liquid nitrogen and above.

In the case of CsCl, the identification of the spectral position of the principal absorption at room temperature in the vicinity of 605 mμ is quite certain. It has been located at 603 mμ by Avakian and Smakula,[12] 603.9 mμ by Jacobs,[9] and in the neighborhood of 605 mμ by Pohl.[6] With the exception of the 252–3-, 281-, and 943-mμ bands in CsCl at room temperature, the remaining bands at room temperature and those given at liquid nitrogen temperature in Table II are in reasonable agreement with respective room temperature and liquid nitrogen temperature peak positions reported by Avakian and Smakula after electron irradiation at $-78°C$. Under conditions of heavy electron irradiation these authors find additional structure appearing to the long-wavelength side of the principal absorption at liquid nitrogen temperature; this is presumably absent here due to the comparatively weak x-ray doses delivered.

Data on irradiated CsBr appear to be comparatively more abundant in the literature. Pringsheim and Hutchison[8] have looked at the x-ray-induced color-center spectrum of CsBr grown from reagent-grade material at liquid nitrogen temperature. They report the presence of four bands between the F band and the α band, at 280, 320, 380, and 475 mμ, which are in reasonable correspondence with bands given in Table IV. The F band is given at 648 mμ corresponding to

the principal absorption at 645 mμ in this work, and although it is not expressly stated, the 205-mμ band (Table IV) is presumably taken to be the α band. Pringsheim and Hutchison do not draw special attention to structure on the short-wavelength tail of the principal absorption, but it is clear from their spectra that such structure exists. It is most likely the same band which has been located roughly at 570 mμ in Fig. 7. Pringsheim and Hutchison report no appreciable structure to the long-wavelength side of the principal absorption, but Avakian and Smakula indicate the presence of several longer wavelength bands.[25] Only one of these bands at liquid nitrogen temperature corresponds with structure reported here, namely the 1050-mμ band. Rauch and Heer[11] have reported long-wavelength structure at about 850 and 960 mμ in additively colored CsBr at room temperature which was not found in the additively colored crystal of Table IV; these bands, however, are in approximate agreement with weak bands reported by Avakian and Smakula at $-78°$C at 850 and 930 mμ.[26] Avakian and Smakula report the position of the principal absorption at 675 and 646 mμ at room and liquid nitrogen temperatures, respectively, corresponding to 680 and 645 mμ given in Table IV. There is some measure of agreement in the short-wavelength structure observed at liquid nitrogen temperature, but the strong 205-mμ absorption was not reported by Avakian and Smakula. Well-defined short-wavelength absorption at room temperature seems to be characteristically sparse in CsBr, as evidenced in the work of Avakian and Smakula and that reported here, with poor correspondence in the few bands which have been identified in both investigations. A further piece of work relating to CsBr coloration is that of Jacobs et al.[13] on Harshaw and Korth crystals. These investigators find two major absorptions at 275 and 925 mμ in addition to the principal absorption at 680 mμ after x-ray irradiation at room temperature. The appearance of the short-wavelength band (actually at 270 mμ) after addition of excess halogen suggests that this band is due to a V-type center, but the possibility of a simple solution of the halogen in the crystal is also considered. The 270–275 and 925-mμ bands (and other bands at 225 and 420 mμ which appear upon addition of excess halogen) are not reported at room temperature in Table IV or in the earlier work of Avakian and Smakula.

As was pointed out above, the production of coloration in CsI by ionizing radiation is quite poor. X rays have been completely ineffective in generating color

centers and electron bombardment has produced a modest amount of absorption only at liquid nitrogen temperature. It might be speculated that the electron-produced bands of Fig. 13 owe their existence to defects produced by knock-ons, but this possibility requires additional confirmation. The electrolytic method has proven most effective for coloration at CsI, producing absorption quite analogous to that observed for CsCl and CsBr between room and liquid nitrogen temperature.[12] Also, addition of excess halogen[13] to CsI has been reported effective in producing room-temperature bands at 275 and 400 mμ, the former of which appears to be present after electrolytic coloration. The principal absorption band, which is most likely the F band, occurs at 785 mμ at room temperature; for some unknown reason it has been successfully produced only by the electrolytic technique. There is no evidence of anomalous behavior of either the ionic conductivity or self-diffusion in CsI as compared to[15] CsBr to support a hypothesis that the success of the electrolytic method of coloration is related to some unique characteristic of ionic processes in CsI.

By analogy with NaCl-type alkali halides, the principal optical absorptions in both CsCl and CsBr (at 605 and 680 mμ at room temperature, respectively) give every evidence of being associated with the F center. Aside from the fact that they appear as the major optical absorptions at all temperatures, these bands bleach, shift, sharpen, and respond to ionizing radiation in a manner identical to NaCl-type F bands. The half-widths of these bands, the compatibility of their relative spectral positions with a Mollwo relation,[12] and their characteristic growth under ionizing radiation also conform with known F-band behavior. In the case of CsBr the added observation was made that the principal absorption was identical in both additively colored and irradiated specimens. If these bands are viewed solely at liquid nitrogen temperature and above, it would be concluded that they are indeed quite normal F bands, with perhaps a slight asymmetry which, however, is also known to appear in NaCl-type F bands.[27] It is, however, the resolution of component structure in these bands in the cesium halides at liquid helium temperature which differentiates them from F bands in NaCl-type crystals.

The F-band component structure at liquid helium temperature is summarized in Tables III and V for CsCl and CsBr, respectively. It should be emphasized that the separation of this structure into Gaussian components is based on assumptions, which are at best approximate, concerning the overlap of the components. Furthermore, the specification of precisely three components in both CsCl and CsBr is tentative. In CsCl it is clear that the major structure has at least three components; however, as pointed out above, the

[25] The presence of such structure is also indicated in this work by the luminescence that is stimulated by optical excitation to the long-wavelength side of the F band. The band or bands which are responsible for the absorption are yet unspecified but could be analogous to those reported by Avakian and Smakula.

[26] It might be noted that the peak position of the principal absorption in additively colored CsBr at room temperature has been indicated[11,12] at a somewhat longer wavelength, approximately 690 mμ, rather than 680 mμ given in Table IV.

[27] See, for example, J. D. Konitzer and J. J. Markham, Phys. Rev. 107, 685 (1957); J. Chem. Phys. 32, 843 (1960).

580-mμ component in CsBr is highly speculative, and moreover the possibility of additional shorter wavelength components has not been excluded.[14] Within the limits of accuracy of the subdivision it appears that the substructure in the case of CsCl is approximately evenly separated into components of roughly the same half-width and strength. The CsBr components do not appear to be evenly matched in their relative strength, but the half-widths seem to be comparable to those observed for CsCl.

The reproducibility of the component structure in the principal absorptions of the various CsCl and CsBr specimens leads to the conclusion that it is fundamental to these crystals, and moreover gives every indication of being associated with the F band. It was found that whenever and under whatever conditions this structure was observed at liquid helium temperature it existed in fixed relative proportion. As was pointed out above, the fixed proportionality is maintained in both x-rayed and additively colored specimens, independent of whether the irradiation was performed at low or high temperature. Moreover, the relative structure was not disturbed by either white-light bleaching or selective bleaching in the components (and also thereafter reirradiating). This would be a most unlikely occurrence if only a single component of the structure were related to the F band and the others were not so related. Since it was observed that the total area under the principal absorption was maintained (to within about 10%) between room temperature and liquid helium temperature, it would appear that if the liquid helium absorption is not entirely due to the F band, the assignment of the principal absorption at room temperature as the F band would likewise have to be revised.

The reason for component structure in the F band in cesium halides has not been theoretically explored. Several possibilities come to mind as possible explanations: (1) higher excited states of the F center, (2) spin-orbit splitting due to the presence of the cesium ion, and (3) a crystal field effect peculiar to the CsCl-type lattice. If a study of the F band in CsF reveals no structure, this would eliminate possibility (3), since CsF is known to have the NaCl-type structure.[28] A study of the F band in CsI at liquid helium temperature would offer the further possibility of eliminating (2) if no structure is found. The excited state explanation could be explored along optical lines parallel to those used by Lüty[29] for F-center excited states in NaCl-type alkali halides. It might be pointed out that recent electron spin resonance measurements in CsCl by Hughes[30] give no support to the possibility of ground-state splitting as an explanation of the multiple optical

TABLE VI. Efficiency for production of the principal optical absorption (the F band) in electron volts/center.

| | Room temp. | Liquid nitrogen temp. | | Liquid helium temp. | |
	(Second stage)	(Initial)	(Second stage)	(Initial)	(After bleach and reirradiation)
CsCl	$(3.9–8.1)\times10^4$	$(2.2–3.7)\times10^3$	5.4×10^3	$(5.9–15)\times10^2$	1.9×10^2
CsBr	...	2.5×10^4	4.1×10^4	8.1×10^2	3.4×10^2

structure that is noted in the F band. The g-shift results for the F band do not indicate any ground-state anomalies in CsCl in comparison to NaCl-type alkali halides.

The production efficiency (electron volts/center) of the principal or F-band absorption is given in Table VI at various temperatures using the oscillator strength of 0.26 given by Rauch and Heer[11] for CsBr as determined by magnetic susceptibility.[31] (The same oscillator strength is assumed for CsCl.) The room-temperature efficiency for CsBr is not given in Table VI due to the uncertainty in the growth curve during the second stage coloration (see Fig. 12). The apparent saturation of the coloration of this crystal, however, would imply that the efficiency is probably as large as the CsCl values for two different specimens of 3.9×10^4 and 8.1×10^4 ev/center. Corresponding determinations in NaCl-type alkali halides, namely KCl and NaCl, give somewhat higher coloration efficiencies $(0.7\times10^4$ and 1.1×10^4 ev/center).[32] The values in CsCl and CsBr at liquid helium temperature during the initial growth of coloration, however, are quite comparable with determinations in the NaCl-type crystals; moreover, this efficiency is increased during a second irradiation following an optical bleach as shown in Table VI, but by not nearly the same extent as in the case of KCl.[32] A unique characteristic of the cesium halides appears to be that the smallest energy required for production of an F center throughout the entire range of growth occurs at liquid helium temperature.

The possibilities for identifying absorption bands (other than the F band) with specific lattice defects appears remote on the basis of the limited data at hand. The general association of the various bands on the long-wavelength side of the F band with F-aggregate centers and those on the short-wavelength side with V-type centers can be made, but detailed assignments cannot be attempted with any certainty. Pringsheim and Hutchison[8] have implied that the 205-mμ band in CsBr is the α band, but this again requires confirmation. The very broad room-temperature bands that were noted at 943 mμ in CsCl and 1050 mμ in

[28] Maisch and Drickamer[10] do not indicate any anomalies in the structure of the F band in NaCl-type alkali halides which have been transformed to the CsCl-type structure by the application of high pressure.
[29] F. Lüty, Z. Physik 160, 1 (1960).
[30] F. Hughes (private communication).

[31] A private communication from E. Sonder indicates that there are other magnetic centers beside the F center in CsBr (most likely associated with structure to the long-wavelength side of the F band), thus putting a magnetically determined oscillator strength in CsBr in doubt.
[32] H. Rabin and C. C. Klick, Phys. Rev. 117, 1005 (1960).

CsBr bear similarities to the R' bands discussed by Scott and Bupp,[33] and the strong short-wavelength absorption which appears only at liquid helium temperature (376 mμ in CsCl, Fig. 3, and 435 mμ in CsBr, Fig. 9) might well be CsCl-type analogs of the NaCl-type H center,[34] but these speculations will again take additional investigation.

CONCLUSIONS

As expected, the color-center spectra of the cesium halides show many similarities to the spectra observed in NaCl-type alkali halides. At the same time there are several significant differences not only in comparison to the NaCl system but within the CsCl system as well. The unique features of the cesium halides can be briefly summarized as follows:

(1) The principal absorption band in CsCl and CsBr, which is most likely the F band, shows component substructure which is resolvable at liquid helium temperature.

(2) Unlike CsCl and CsBr, CsI seems to be insensitive to coloration by x rays at both room and low temperatures. High-energy electron irradiation has produced a limited amount of coloration at liquid nitrogen temperature, but is equally ineffective at room temperature.

(3) The least energy required for production of F centers occurs at liquid helium temperature in both CsCl and CsBr.

(4) X-rayed CsBr and CsI show luminescence which is stimulated during spectrographic measurement at wavelengths longer than about 700 mμ. This emission is of sufficient strength to produce an apparent negative optical absorption at both liquid nitrogen and liquid helium temperatures. Similar emission is not observed in CsCl.

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[33] A. B. Scott and L. P. Bupp, Phys. Rev. **79**, 341 (1950); A. B. Scott, H. J. Hrostowski, and L. P. Bupp, *ibid.* **79**, 346 (1950).

[34] W. H. Duerig and J. J. Markham, Phys. Rev. **88**, 1043 (1952); W. Känzig and T. O. Woodruff, J. Phys. Chem. Solids **9**, 70 (1959).