

## Color Centers in Alkaline Earth Fluorides\*

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Single crystals of  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$  have been colored by x rays (150 kv) and high-energy electrons (2.5 Mev). Five color-center bands in  $\text{CaF}_2$  and  $\text{SrF}_2$  and nine in  $\text{BaF}_2$  have been observed in the spectral region between 0.175 and  $0.8\ \mu$ . At room temperature the bands in  $\text{CaF}_2$  are well resolved, while those in  $\text{SrF}_2$  and  $\text{BaF}_2$  overlap. At  $-190^\circ$  and  $-255^\circ\text{C}$  the bands sharpen but generally do not shift, except the  $580\text{-m}\mu$  band in  $\text{CaF}_2$  which shifts toward longer wavelengths. Photochemical bleaching of the strongest band shows a certain influence on the others. Three bands could be correlated to the Mollwo relation with the exponent 3.85. A possible correlation of the absorption bands to certain models is discussed.

OF the three cubic alkaline earth fluorides,  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$ , color centers have been studied in calcium fluoride only, except for a brief investigation on  $\text{BaF}_2$ .<sup>1</sup> Early results<sup>2</sup> were however inconclusive, largely because the sensitivity of  $\text{CaF}_2$  to oxygen was underestimated. Natural  $\text{CaF}_2$  crystals colored electrolytically at about  $800^\circ\text{C}$  and quenched to room temperature show absorption bands at  $375\text{ m}\mu$  (3.30 ev) and  $525\text{ m}\mu$  (2.35 ev), designated  $\alpha$  and  $\beta$ , respectively.<sup>3</sup> Coloration of either natural or synthetic crystals by x rays resulted in four absorption bands, located at  $225\text{ m}\mu$  (5.5 ev),  $335\text{ m}\mu$  (3.68 ev),  $400\text{ m}\mu$  (3.09 ev), and  $580\text{ m}\mu$  (2.13 ev).<sup>1,4,5</sup> The same bands could also be produced by weak additive coloration of synthetic crystals. After strong additive coloration and subsequent quenching, the  $\alpha$  and  $\beta$  bands appeared.<sup>6</sup> The appearance of both types of bands was explained by the presence of unknown impurities correlated with the four bands.

However, uncolored crystals having no absorption down to  $220\text{ m}\mu$  showed a strong absorption increase below  $240\text{ m}\mu$  after heat treatment at  $1200^\circ\text{C}$ , even in an inert atmosphere. After coloration of heat-treated crystals with x rays only two bands, at  $370$  and  $540\text{ m}\mu$ , developed quite close to the  $\alpha$  and  $\beta$  bands. When crystals were not heat-treated, four bands appeared after coloration.<sup>7</sup> Subsequent studies disclosed that the four bands appear only in crystals that have no absorption down to  $200\text{ m}\mu$  prior to coloration.<sup>8</sup>

It was shown more recently that the difference in coloration is caused by oxygen which may be initially present or introduced by heat treatment before or

during coloration.<sup>9</sup> The presence of oxygen has been established by infrared-absorption and chemical analysis.<sup>10</sup> In  $\text{CaF}_2$  crystals it may appear in the combinations  $\text{Ca}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})\text{F}$ ,  $\text{CaO}$ , and  $\text{Ca}_2\text{OF}_2$ . We can thus expect a variety of traps depending on the nature of the contamination. The simplest and most reproducible coloration can be obtained only in crystals not exposed to high temperatures before or during coloration. The four absorption bands at 225, 335, 400,

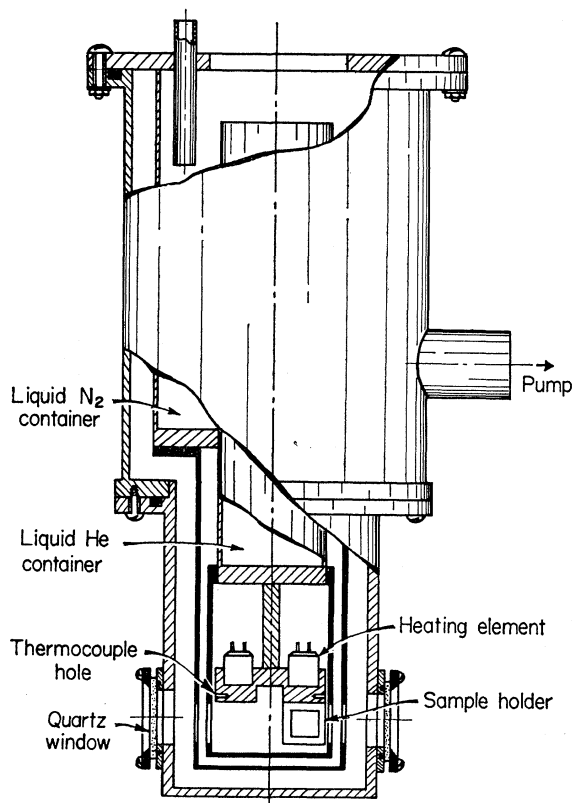


FIG. 1. Helium cryostat for coloration and absorption measurements.

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<sup>1</sup> A. Smakula, *Phys. Rev.* **77**, 408 (1950).

<sup>2</sup> See K. Przibram, *Irradiation Colors and Luminescence* (Pergamon Press, New York, 1956).

<sup>3</sup> E. Mollwo, *Nachr. Ges. Wiss. Göttingen, Math.-physik. Kl.* **1**, 79 (1934).

<sup>4</sup> R. Herman and S. Silverman, *J. Opt. Soc. Am.* **37**, 871 (1947).

<sup>5</sup> S. Barile, *J. Chem. Phys.* **20**, 297 (1952).

<sup>6</sup> F. Lüty, *Z. Physik* **134**, 596 (1953).

<sup>7</sup> J. H. Schulman, R. J. Ginther, and R. D. Kirk, *J. Chem. Phys.* **20**, 1966 (1953).

<sup>8</sup> A. Smakula, *Phys. Rev.* **91**, 1570 (1953).

<sup>9</sup> H. Adler and I. Kveta, *Sitzber. Oesterreich. Akad. Wiss., Math.-naturw. Kl., Abt. II*, **166**, 199 (1957).

<sup>10</sup> W. Bontinck, *Physica* **24**, 639 (1958); **24**, 650 (1958).

and  $580\text{ m}\mu$  are therefore considered pertinent to the lattice traps and not to contaminations.

A correlation of these absorption bands to definite trap configurations<sup>8,10</sup> of electrons and holes is at present uncertain because of oxygen contamination. It was expected that a study of related crystals of similar structure might provide additional information. We therefore decided to extend our investigations to  $\text{SrF}_2$  and  $\text{BaF}_2$  and to study the color centers over a wider spectral range (from  $0.175$  to  $3.5\text{ }\mu$ ) and at lower temperatures (to liquid helium).

## EXPERIMENTAL PROCEDURE

### Coloration

For coloration and subsequent absorption measurements at low temperatures, a portable helium cryostat was built to permit irradiation and absorption measure-

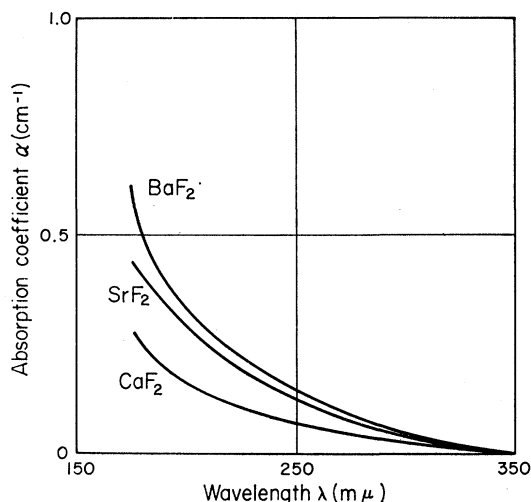


FIG. 2. Absorption of uncolored  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$  crystals between  $350$  and  $175\text{ m}\mu$ .

ments of crystals at given temperatures (Fig. 1). Four Ultrasil windows, transparent down to  $0.175\text{ }\mu$ , for absorption measurements and two beryllium windows for irradiation with x rays or electrons were mounted at right angles to each other. The crystals were rotated by  $90$  degrees in vacuum, from the irradiation to the absorption-measurement position. Temperatures could be kept constant or changed continuously from room temperature to  $15^\circ\text{K}$  by means of a precision temperature-control unit. A calibrated thermocouple of copper-constantan served for temperature measurements. Crystals were colored by either x rays ( $150\text{ kv}$ ) or electrons ( $2.5\text{ Mev}$ ).

For absorption measurements, a Beckman spectrophotometer (DK-1), equipped with specially selected quartz prisms and aluminum mirrors with high reflectivity below  $200\text{ m}\mu$ , was used. To prevent mirror oxidation the instrument was purged by nitrogen, which simultaneously eliminated oxygen absorption below

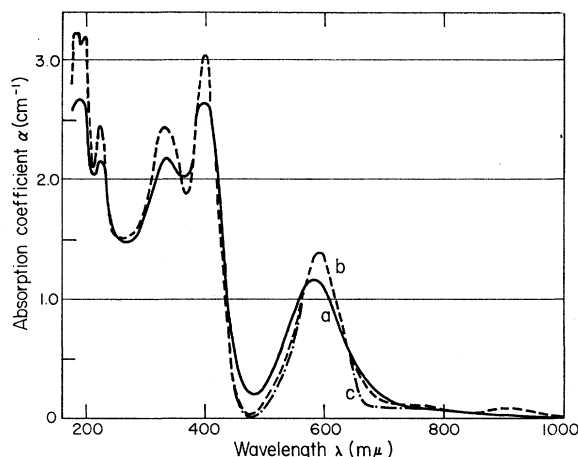


FIG. 3. Absorption of  $\text{CaF}_2$ , colored at  $20^\circ\text{C}$  by  $3\text{-Mev}$  electrons ( $10^6\text{ rad dose}$ ).

$190\text{ m}\mu$ . The stray light in the spectrophotometer amounted to less than  $3\%$  at  $175\text{ m}\mu$  and less than  $8\%$  at  $171\text{ m}\mu$ . Photochemical discoloration during measurement was reduced to a minimum since samples were placed in the monochromatic beam behind the exit slit.

Figure 2 shows absorption curves of uncolored crystals. Below  $200\text{ m}\mu$  all three crystals showed only a slight continuous absorption increase and no selective absorption, indicating absence of any oxygen contamination. The increase of absorption toward shorter wavelengths is caused by intrinsic absorption bands. The absorption of  $\text{CaF}_2$  agrees with older measurements.<sup>11</sup> The stronger absorption of  $\text{SrF}_2$  and  $\text{BaF}_2$  is caused by the shifting of intrinsic absorption in these crystals.

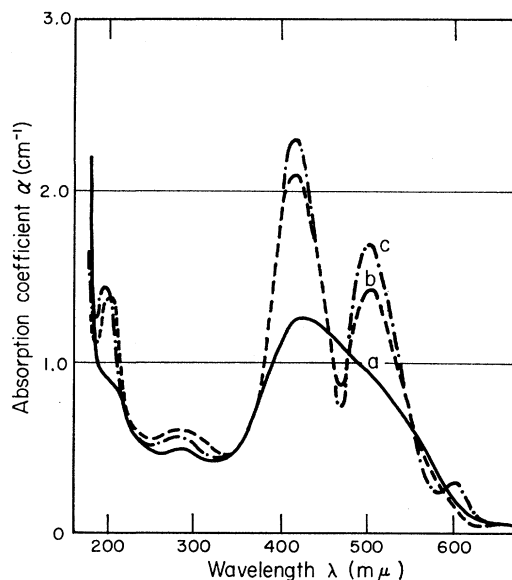


FIG. 4. Absorption of  $\text{SrF}_2$ , colored at  $20^\circ\text{C}$  by  $3\text{-Mev}$  electrons ( $10^6\text{ rad dose}$ ).

<sup>11</sup> E. G. Schneider, Phys. Rev. **49**, 341 (1936).

TABLE I. Absorption bands of colored  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$  crystals (at  $-255^\circ\text{C}$ ).

Crystal		7		6		5		4		3		2		1	
$\text{CaF}_2$	$m\mu$	186		194		220		265	285			332		400	586
	ev	6.66		6.38		5.63		4.68	4.35			3.73		3.10	2.12
$\text{SrF}_2$	$m\mu$		198			290						419		505	602
	ev		6.25			4.28						2.96		2.45	2.06
$\text{BaF}_2$	$m\mu$	198	220	255		411		490		565	618	662		735	
	ev	6.26	5.63	4.86		3.02		2.53		2.19	2.03	1.872		1.685	

The absorption spectra of colored  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$ , measured at  $20^\circ$ ,  $-190^\circ$ , and  $-225^\circ\text{C}$  are plotted in Figs. 3, 4, and 5. In all three crystals, low temperature produces sharper absorption bands. There is practically no shifting of peaks except for the  $\text{CaF}_2$  band at ca  $600 m\mu$ , which shifts to longer wavelengths with decreasing temperature. If this band is disregarded, all three absorption spectra show a certain similarity; only that of  $\text{BaF}_2$  is more complicated. The positions of all observed bands is given in Table I.

In colored  $\text{CaF}_2$  in addition to the known four bands, a new double band with peaks at  $186$  and  $194 m\mu$  has been established. At liquid-nitrogen temperature this band shows some splitting which becomes slightly more pronounced at liquid-helium temperature. There is also weak indication of another two bands at  $265$  and  $285 m\mu$ .

The absorption spectrum of colored  $\text{SrF}_2$  at room temperature appears quite different from that of  $\text{CaF}_2$ . One might expect a spectrum similar to that of  $\text{CaF}_2$  with only a slight shift of all bands toward longer wavelengths. In that case  $\text{SrF}_2$  should absorb at wavelengths greater than  $600 m\mu$ ; however, no such absorption is discernible. The broad band between  $400$  and  $600 m\mu$  shows no splitting; there is only a slight dip at  $480 m\mu$ . At low temperatures, however, this band splits sharply, and a new weak band appears at  $600 m\mu$  apparently

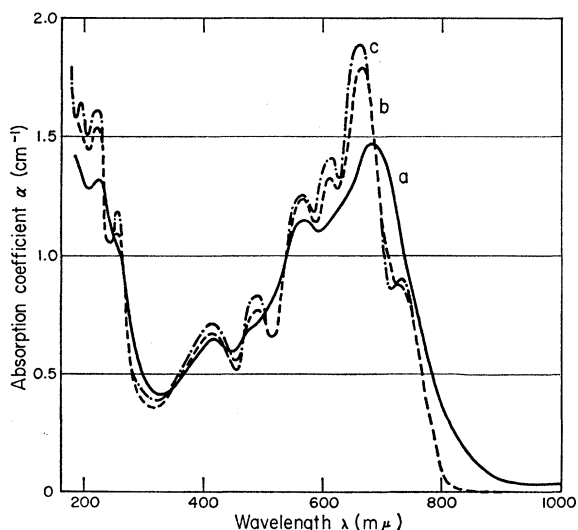


FIG. 5. Absorption of  $\text{BaF}_2$ , colored at  $20^\circ\text{C}$  by 3-Mev electrons ( $10^6$  rad dose)

shifting slightly toward longer wavelengths as temperature decreases. At  $290 m\mu$  there is a broad band which does not sharpen at low temperatures, and another sharp band at  $200 m\mu$ . An increase of absorption below  $185 m\mu$  indicates the existence of yet another band below  $175 m\mu$ .

The absorption spectrum of  $\text{BaF}_2$  at room temperature resembles that of  $\text{CaF}_2$ . At low temperatures, however, a structure appears which is not present in either  $\text{CaF}_2$  or  $\text{SrF}_2$ . The band at  $735 m\mu$  seems to shift toward

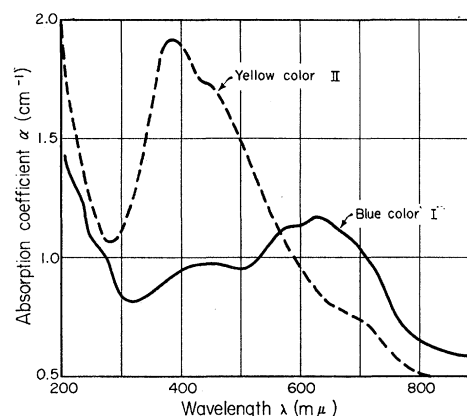


FIG. 6. Absorption of colored old and new  $\text{BaF}_2$  crystals.

longer wavelengths. In this respect it is similar to the  $580\text{-}m\mu$  band in  $\text{CaF}_2$ , except for a strong overlap with other bands. The strongest band, at  $662 m\mu$ , is followed by four bands of decreasing intensity. The intensity of the next bands increases in the direction of short wavelengths.

In a previous publication<sup>1</sup> the absorption of colored  $\text{BaF}_2$  was shown to increase below  $300 m\mu$  and to have three strongly overlapping bands at longer wavelengths. Our new material shows a quite different absorption (Fig. 6), which is shifted toward longer wavelengths. Its colorability is only half that of the old material; this indicates, in analogy to  $\text{CaF}_2$ , that the old material was contaminated, probably by oxygen.

### Bleaching

The color centers of the alkaline earth fluorides are much more stable than those of the alkali halides. Thermal bleaching at room temperature requires a

period of many days before discoloration becomes apparent. No bleaching studies at higher temperatures have yet been made. Older investigations showed that in pure crystals all bands decrease simultaneously while in contaminated crystals each bleaches individually and some new bands appear.<sup>12</sup>

Some photochemical bleaching of the strongest absorption band has been carried out. Previous findings<sup>8</sup> in  $\text{CaF}_2$  to the effect that the strongest band at 400  $\text{m}\mu$  can be bleached without any influence on other bands have been confirmed, except for the absorption around 500  $\text{m}\mu$  which increases, indicating the formation of a new band.

Bleaching of the 505- $\text{m}\mu$  band of  $\text{SrF}_2$  with light of this wavelength resulted principally in decreasing this band, but a neighboring band was also affected, in contrast to observations in  $\text{CaF}_2$  (Fig. 7). This difference

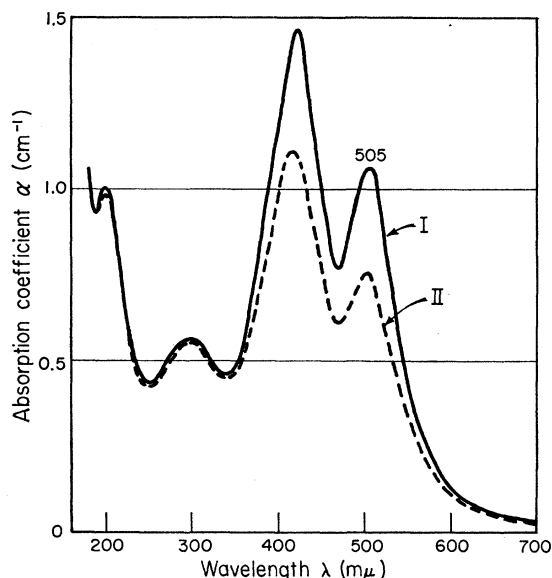


FIG. 7. Photochemical bleaching of  $\text{SrF}_2$ .

is probably caused by the stronger band overlap in  $\text{SrF}_2$ . The bands at shorter wavelength were not affected.

A most interesting effect has been observed on  $\text{BaF}_2$  (Fig. 8): A monochromatic light at 680  $\text{m}\mu$  bleaches this band linearly with time. At the same time the next band, at 620  $\text{m}\mu$ , decreases, but by only half the amount. The band at 580  $\text{m}\mu$  bleaches more than that at 620  $\text{m}\mu$  but somewhat less than that at 680  $\text{m}\mu$ . The 490- $\text{m}\mu$  band, however, which appears only at low temperatures, bleaches as much as the 680- $\text{m}\mu$  band. In the shorter wavelengths only the 400- $\text{m}\mu$  is affected slightly.

Photochemical bleaching depends on temperature in all three crystals. At liquid-nitrogen temperature no bleaching could be achieved by using the same light energy as at room temperature.

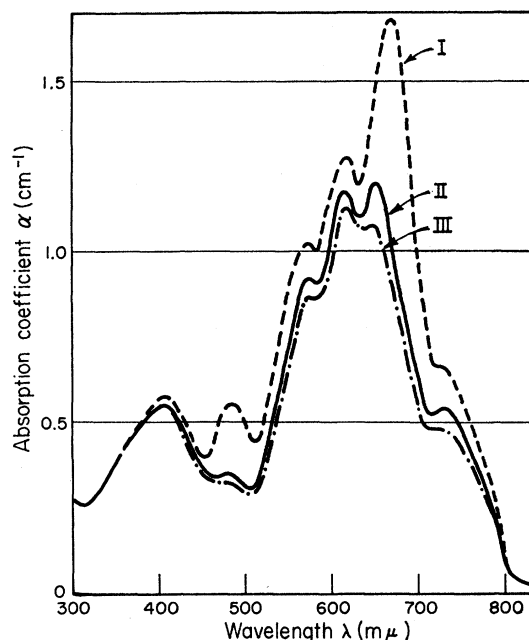


FIG. 8. Photochemical bleaching of  $\text{BaF}_2$ .

#### DISCUSSION

Visual observation of the spectra shows three absorption regions in  $\text{CaF}_2$  and two each in  $\text{SrF}_2$  and  $\text{BaF}_2$ . Since all three crystals have the same crystallographic structure, there must be a correlation between the corresponding bands. In analogy to alkali halides one can expect a shift of corresponding absorption bands toward longer wavelengths, going from  $\text{CaF}_2$  to  $\text{SrF}_2$  to  $\text{BaF}_2$ . Such shifting indeed exists if we disregard the 580- $\text{m}\mu$  band in  $\text{CaF}_2$ , which differs from others by shifting toward longer wavelengths at low temperature. This band seems to be present in  $\text{CaF}_2$  alone. It may be that the 602- $\text{m}\mu$  band in  $\text{SrF}_2$  and 735- $\text{m}\mu$  band in  $\text{BaF}_2$

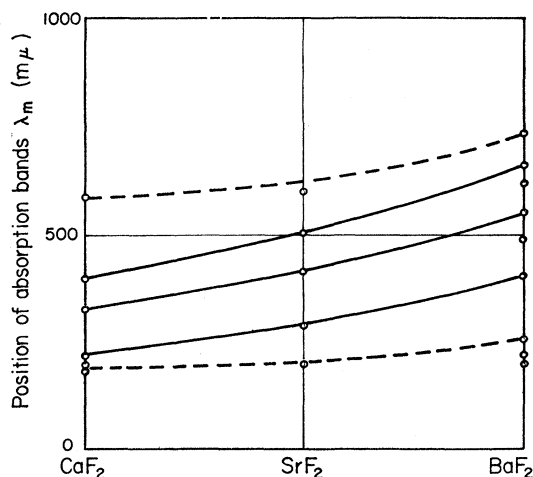


FIG. 9. Energy levels of color-center bands in  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$  crystals.

<sup>12</sup> A. Smakula, *Z. Physik* **138**, 276 (1954).

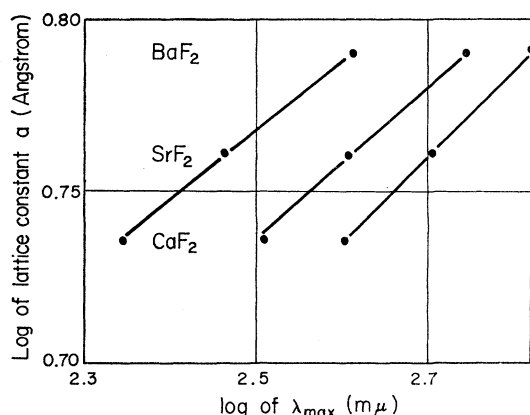


FIG. 10. Mollwo relation of color-center bands in  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$  crystals.

are corresponding bands but they are very weak and not as well defined.

The correlation of the next bands (400  $m\mu$  for  $\text{CaF}_2$ , 505  $m\mu$  for  $\text{SrF}_2$ , and 662  $m\mu$  for  $\text{BaF}_2$ ) is more evident; they have the highest intensity and bleach photochemically. The position of the bands for the three crystals is plotted in Fig. 9. These three maxima lie along a slightly curved line, similarly to the corresponding bands in alkali halides. Using this line as a guide we can correlate the bands at 332, 419, and 565  $m\mu$ , and correspondingly those at 220, 290, and 410  $m\mu$ . Correlating other bands becomes more difficult. The 620- and 490- $m\mu$  bands in  $\text{BaF}_2$ , for example, have no apparent equivalents in the other two crystals. The 740- $m\mu$  band of  $\text{BaF}_2$  and the 600- $m\mu$  one of  $\text{SrF}_2$ , which appear only at liquid-helium temperature, can only correspond to the 500- $m\mu$  of  $\text{CaF}_2$ , which can be formed only by bleaching the 400- $m\mu$  band. The 600- $m\mu$  band of  $\text{CaF}_2$ , which does not bleach photochemically and shifts toward shorter wavelengths with increasing temperature, does not have equivalents in either  $\text{SrF}_2$  or  $\text{BaF}_2$ .

Similar difficulties exist in the correlation of short-wavelength bands. The 300- $m\mu$  band in  $\text{BaF}_2$  may correspond to the 200- $m\mu$  one in  $\text{SrF}_2$ , in which case a 140- $m\mu$  band may be expected in  $\text{CaF}_2$ . There are, however, no bands in  $\text{SrF}_2$  and  $\text{BaF}_2$  to correspond to the double band at 190  $m\mu$  in  $\text{CaF}_2$ . The three  $\text{BaF}_2$  bands at 255, 220, and 200  $m\mu$  may have corresponding bands in the other two crystals but these would be beyond the range of our instrument.

Bleaching the strongest bands (400  $m\mu$  in  $\text{CaF}_2$ , 505  $m\mu$  in  $\text{SrF}_2$ , and 662  $m\mu$  in  $\text{BaF}_2$ ) leads to the conclusion that they are independent of the other bands. The only exception is the 490- $m\mu$  band in  $\text{BaF}_2$  which decreases in intensity by the same amount as the 660- $m\mu$

band when the latter is bleached by light. It can therefore represent either the second excitation of the 660- $m\mu$  band or a corresponding hole.

In NaCl-type crystals of the alkali halides, corresponding bands are related to the interionic distance  $d$  by the Mollwo relation.<sup>13</sup> Expressed in Ivey's<sup>14</sup> form this relation reads

$$\lambda_m = \text{const } d^n,$$

where  $\lambda_m$  is the wavelength of the absorption peak and  $n \approx 2$ . The corresponding maxima of alkaline earth fluorides obey this rule, but with an exponent  $n = 3.85$  (Fig. 10). No explanation for this great difference can be given. An even more surprising fact is that in cesium halide crystals the exponent is 2.85.<sup>15</sup> The correlation of absorption bands of  $\text{CaF}_2$  and  $\text{BaF}_2$  by Ivey,<sup>14</sup> who used the exponents 1.00 and 1.44, was premature.<sup>16</sup> His predicted bands in  $\text{SrF}_2$  do not exist. In a preceding paper<sup>17</sup> it was shown that the 580- $m\mu$  band in  $\text{CaF}_2$  very probably corresponds to electrons trapped in anion vacancies, i.e., to the  $F$  band. This correlation is based on the strong enhancement of the 580- $m\mu$  band by NaF addition which creates anion vacancies. In  $\text{SrF}_2$  and  $\text{BaF}_2$  this band either does not exist or is very weak if we consider the 602- and 735- $m\mu$  bands corresponding to it. One has to assume therefore that either there are no anion vacancies in  $\text{SrF}_2$  and  $\text{BaF}_2$ , which is very improbable, or that the trapped electrons are very unstable. Additional study is necessary to decide between these possibilities. The 400- $m\mu$  band in  $\text{CaF}_2$  is strongly enhanced by  $\text{YF}_3$  which forms anion interstitials; it was therefore correlated to neutral interstitial  $F$  atoms.<sup>17</sup> The 505- $m\mu$  band in  $\text{SrF}_2$  and 662- $m\mu$  band in  $\text{BaF}_2$  may correspond also to neutral interstitial  $F$  atoms. The 325-, 415-, and 565- $m\mu$  bands in  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$ , respectively, might be correlated to electrons bound to  $\text{Ca}^{2+}$  interstitials and those at 220  $m\mu$  in  $\text{CaF}_2$ , 290  $m\mu$  in  $\text{SrF}_2$ , and 410  $m\mu$  in  $\text{BaF}_2$  to holes bound to  $\text{Ca}^{2+}$  vacancies, or vice versa. The sequence of bands in  $\text{BaF}_2$  between 700 and 400  $m\mu$  indicates that they may originate from the same ground state. The color centers in alkaline earth fluorides are quite different from those in alkali halides, partly because of the different lattice structure and partly because of the presence of interstitials in addition to vacancies. The partial correlation of the spectra can be preliminary only; further study is required for safe interpretation.

<sup>13</sup> E. Mollwo, *Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl.*, p. 97 (1931).

<sup>14</sup> H. F. Ivey, *Phys. Rev.* **72**, 341 (1947).

<sup>15</sup> P. Avakian and A. Smakula, *Bull. Am. Phys. Soc.* **5**, 48 (1960).

<sup>16</sup> H. F. Ivey, *Phys. Rev.* **89**, 322 (1953).

<sup>17</sup> W. J. Scouler and A. Smakula, *Bull. Am. Phys. Soc.* **5**, 185 (1960); [preceding paper, *Phys. Rev.* **120**, 1154 (1960)].