PHYSICAL REVIEW VOLUME 120, NUMBER 4 NOVEMBER 15, 1960

Color Centers in Alkaline Earth Fluorides*

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(Received July 14, 1960)

Single crystals of CaF_2, SrF_2, and BaF_2 have been colored by x rays (150 kv) and high-energy electrons (2.5 Mev). Five color-center bands in CaF_2 and SrF_2 and nine in BaF_2 have been observed in the spectral region between 0.175 and 0.8 μ. At room temperature the bands in CaF_2 are well resolved, while those in SrF_2 and BaF_2 overlap. At −190° and −255°C the bands sharpen but generally do not shift, except the 580-mμ band in 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, CaF_2, SrF_2, and BaF_2, color centers have been studied in calcium fluoride only, except for a brief investigation on BaF_2.[1] Early results[2] were however inconclusive, largely because the sensitivity of CaF_2 to oxygen was underestimated. Natural CaF_2 crystals colored electrolytically at about 800°C and quenched to room temperature show absorption bands at 375 mμ (3.30 ev) and 525 mμ (2.35 ev), designated α and β, respectively.[3] Coloration of either natural or synthetic crystals by x rays resulted in four absorption bands, located at 225 mμ, (5.5 ev), 335 mμ (3.68 ev), 400 mμ (3.09 ev), and 580 mμ (2.13 ev).[1,4,5] The same bands could also be produced by weak additive coloration of synthetic crystals. After strong additive coloration and subsequent quenching, the α and β bands appeared.[6] 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 mμ showed a strong absorption increase below 240 mμ after heat treatment at 1200°C, even in an inert atmosphere. After coloration of heat-treated crystals with x rays only two bands, at 370 and 540 mμ, developed quite close to the α and β bands. When crystals were not heat-treated, four bands appeared after coloration.[7] Subsequent studies disclosed that the four bands appear only in crystals that have no absorption down to 200 mμ prior to coloration.[8]

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.[9] The presence of oxygen has been established by infrared-absorption and chemical analysis.[10] In CaF_2 crystals it may appear in the combinations $Ca(OH)_2$, $Ca(OH)F$, CaO, and Ca_2OF_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,

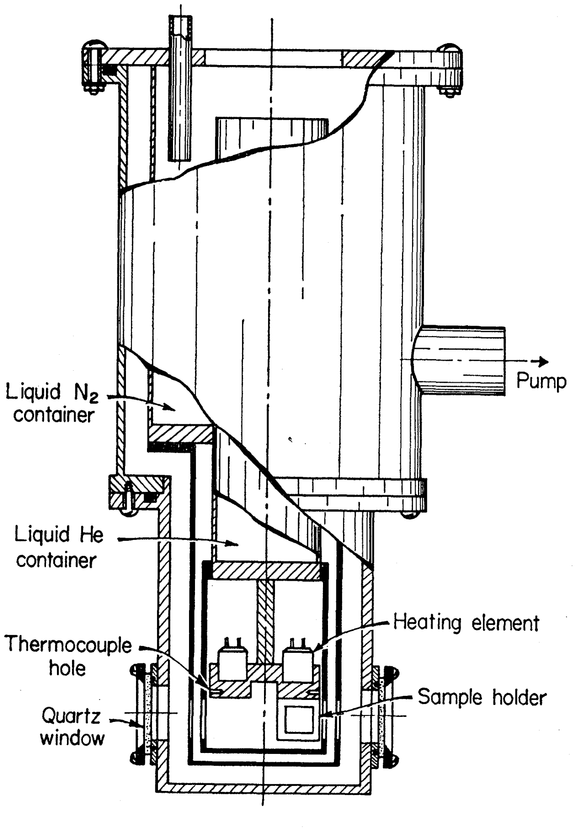

Fig. 1. Helium cryostat for coloration and absorption measurements.

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* Sponsored by the Office of Naval Research.

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[1] A. Smakula, Phys. Rev. **77**, 408 (1950).

[2] See K. Przibram, *Irradiation Colors and Luminescence* (Pergamon Press, New York, 1956).

[3] E. Mollwo, Nachr. Ges. Wiss. Göttingen, Math.-physik. Kl. **1**, 79 (1934).

[4] R. Herman and S. Silverman, J. Opt. Soc. Am. **37** 871 (1947).

[5] S. Barile, J. Chem. Phys. **20**, 297 (1952).

[6] F. Lüty, Z. Physik **134**, 596 (1953).

[7] J. H. Schulman, R. J. Ginther, and R. D. Kirk, J. Chem. Phys. **20**, 1966 (1953).

[8] A. Smakula, Phys. Rev. **91**, 1570 (1953).

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

[10] W. Bontinck, Physica **24**, 639 (1958); **24**, 650 (1958).

and 580 mμ are therefore considered pertinent to the lattice traps and not to contaminations.

A correlation of these absorption bands to definite trap configurations[3,10] 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 SrF_2 and BaF_2 and to study the color centers over a wider spectral range (from 0.175 to 3.5 μ) 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 measurements of crystals at given temperatures (Fig. 1). Four Ultrasil windows, transparent down to 0.175 μ, 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°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 kv) or electrons (2.5 Mev).

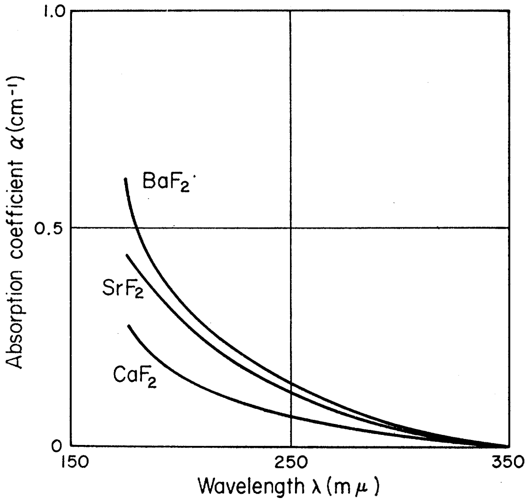

FIG. 2. Absorption of uncolored CaF_2, SrF_2, and BaF_2 crystals between 350 and 175 mμ.

For absorption measurements, a Beckman spectrophotometer (DK-1), equipped with specially selected quartz prisms and aluminum mirrors with high reflectivity below 200 mμ, was used. To prevent mirror oxidation the instrument was purged by nitrogen, which simultaneously eliminated oxygen absorption below 190 mμ. The stray light in the spectrophotometer amounted to less than 3% at 175 mμ and less than 8% at 171 mμ. Photochemical discoloration during measurement was reduced to a minimum since samples were placed in the monochromatic beam behind the exit slit.

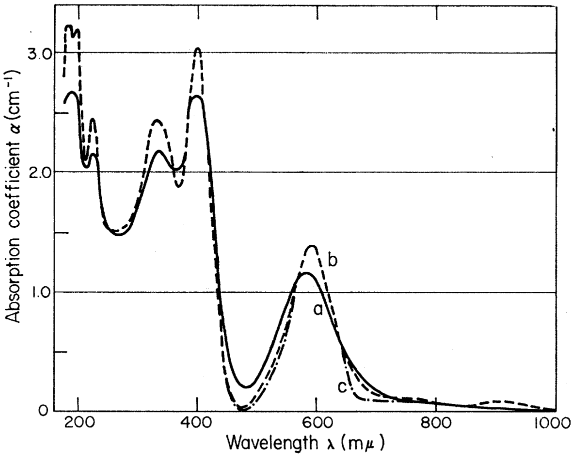

FIG. 3. Absorption of CaF_2, colored at 20°C by 3-Mev electrons (10^6 rad dose).

Figure 2 shows absorption curves of uncolored crystals. Below 200 mμ 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 CaF_2 agrees with older measurements.[11] The stronger absorption of SrF_2 and BaF_2 is caused by the shifting of intrinsic absorption in these crystals.

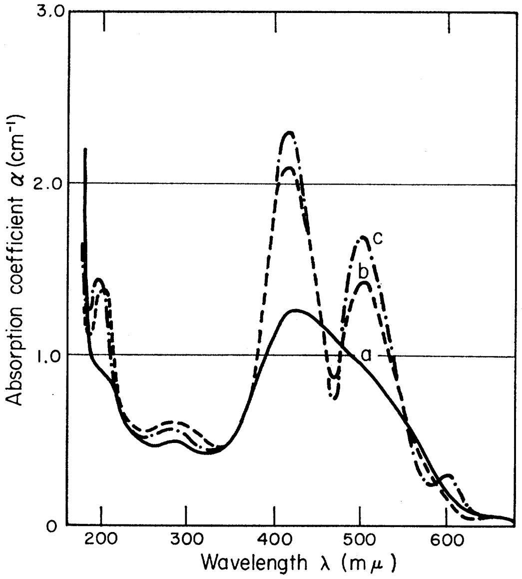

FIG. 4. Absorption of SrF_2, colored at 20°C by 3-Mev electrons (10^6 rad dose).

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[11] E. G. Schneider, Phys. Rev. **49**, 341 (1936).

TABLE I. Absorption bands of colored CaF_2, SrF_2, and BaF_2 crystals (at −255°C).

Crystal		7	6	5	4	3	2	1
CaF_2	mμ	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
SrF_2	mμ	198	290		419		505	602
	ev	6.25	4.28		2.96		2.45	2.06
BaF_2	mμ	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 CaF_2, SrF_2, and BaF_2, measured at 20°, −190°, and −225°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 CaF_2 band at ca 600 mμ, which shifts to longer wavelengths with decreasing temperature. If this band is disregarded, all three absorption spectra show a certain similarity; only that of BaF_2 is more complicated. The positions of all observed bands is given in Table I.

In colored CaF_2 in addition to the known four bands, a new double band with peaks at 186 and 194 mμ 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 mμ.

The absorption spectrum of colored SrF_2 at room temperature appears quite different from that of CaF_2. One might expect a spectrum similar to that of CaF_2 with only a slight shift of all bands toward longer wavelengths. In that case SrF_2 should absorb at wavelengths greater than 600 mμ; however, no such absorption is discernible. The broad band between 400 and 600 mμ shows no splitting; there is only a slight dip at 480 mμ. At low temperatures, however, this band splits sharply, and a new weak band appears at 600 mμ apparently shifting slightly toward longer wavelengths as temperature decreases. At 290 mμ there is a broad band which does not sharpen at low temperatures, and another sharp band at 200 mμ. An increase of absorption below 185 mμ indicates the existence of yet another band below 175 mμ.

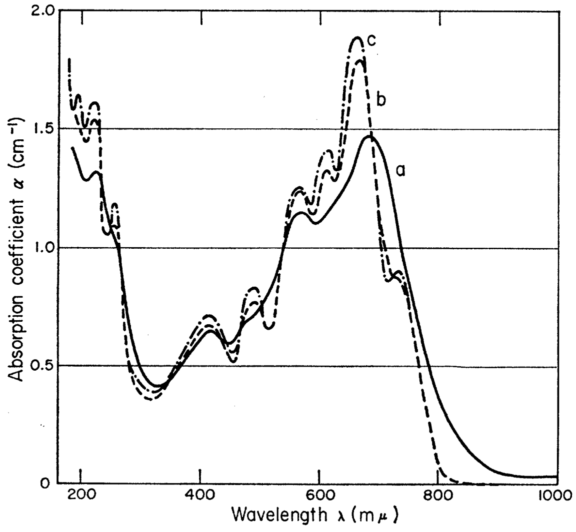

FIG. 5. Absorption of BaF_2, colored at 20°C by 3-Mev electrons (10^6 rad dose)

The absorption spectrum of BaF_2 at room temperature resembles that of CaF_2. At low temperatures, however, a structure appears which is not present in either CaF_2 or SrF_2. The band at 735 mμ seems to shift toward longer wavelengths. In this respect it is similar to the 580-mμ band in CaF_2, except for a strong overlap with other bands. The strongest band, at 662 mμ, is followed by four bands of decreasing intensity. The intensity of the next bands increases in the direction of short wavelengths.

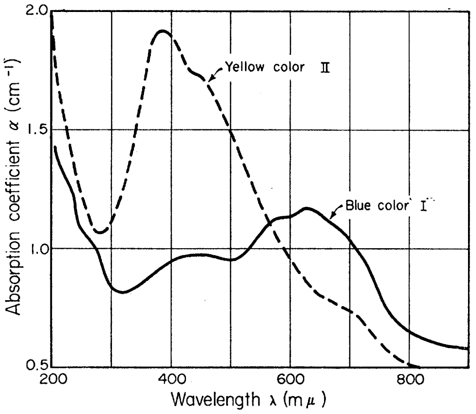

FIG. 6. Absorption of colored old and new BaF_2 crystals.

In a previous publication[1] the absorption of colored BaF_2 was shown to increase below 300 mμ 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 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.[12]

Some photochemical bleaching of the strongest absorption band has been carried out. Previous findings[8] in CaF_2 to the effect that the strongest band at 400 mμ can be bleached without any influence on other bands have been confirmed, except for the absorption around 500 mμ which increases, indicating the formation of a new band.

Bleaching of the 505-mμ band of 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 CaF_2 (Fig. 7). This difference is probably caused by the stronger band overlap in SrF_2. The bands at shorter wavelength were not affected.

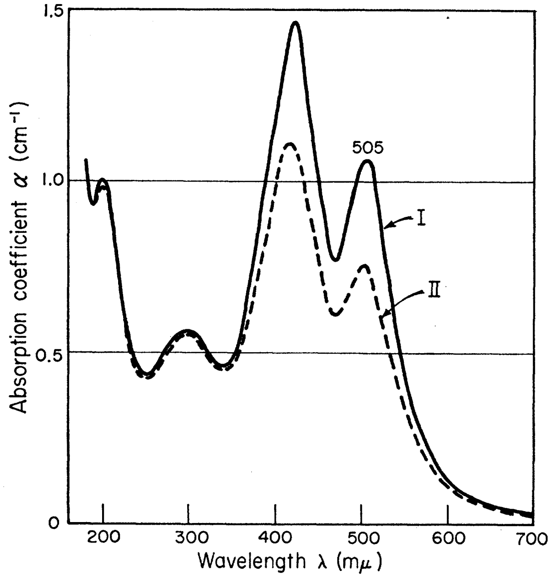

FIG. 7. Photochemical bleaching of SrF_2.

A most interesting effect has been observed on BaF_2 (Fig. 8): A monochromatic light at 680 mμ bleaches this band linearly with time. At the same time the next band, at 620 mμ, decreases, but by only half the amount. The band at 580 mμ bleaches more than that at 620 mμ but somewhat less than that at 680 mμ. The 490-mμ band, however, which appears only at low temperatures, bleaches as much as the 680-mμ band. In the shorter wavelengths only the 400-mμ 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.

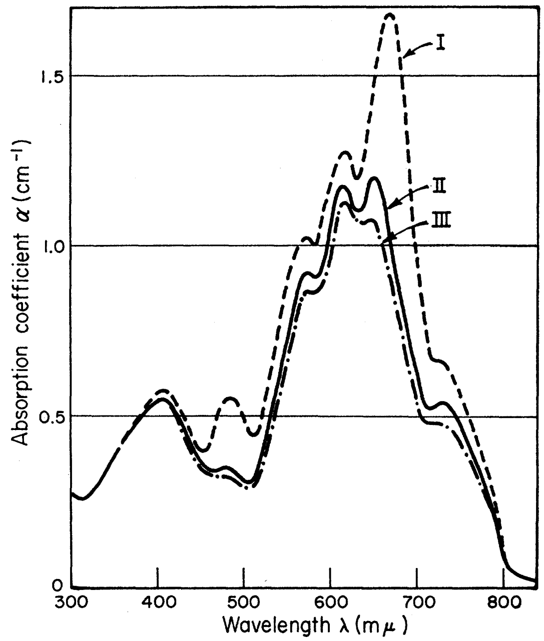

FIG. 8. Photochemical bleaching of BaF_2.

DISCUSSION

Visual observation of the spectra shows three absorption regions in CaF_2 and two each in SrF_2 and 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 CaF_2 to SrF_2 to BaF_2. Such shifting indeed exists if we disregard the 580-mμ band in CaF_2, which differs from others by shifting toward longer wavelengths at low temperature. This band seems to be present in CaF_2 alone. It may be that the 602-mμ band in SrF_2 and 735-mμ band in BaF_2

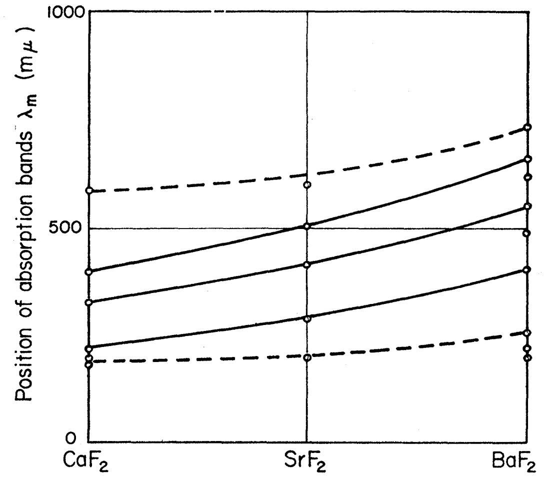

FIG. 9. Energy levels of color-center bands in CaF_2, SrF_2, and BaF_2 crystals.

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[12] A. Smakula, Z. Physik 138, 276 (1954).

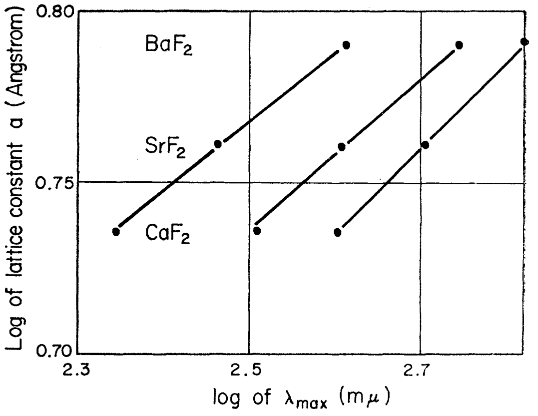

FIG. 10. Mollwo relation of color-center bands in CaF_2, SrF_2, and BaF_2 crystals.

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

The correlation of the next bands (400 mμ for CaF_2, 505 mμ for SrF_2, and 662 mμ for 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 mμ, and correspondingly those at 220, 290, and 410 mμ. Correlating other bands becomes more difficult. The 620- and 490-mμ bands in BaF_2, for example, have no apparent equivalents in the other two crystals. The 740-mμ band of BaF_2 and the 600-mμ one of SrF_2, which appear only at liquid-helium temperature, can only correspond to the 500-mμ of CaF_2, which can be formed only by bleaching the 400-mμ band. The 600-mμ band of CaF_2, which does not bleach photochemically and shifts toward shorter wavelengths with increasing temperature, does not have equivalents in either SrF_2 or BaF_2.

Similar difficulties exist in the correlation of short-wavelength bands. The 300-mμ band in BaF_2 may correspond to the 200-mμ one in SrF_2, in which case a 140-mμ band may be expected in CaF_2. There are, however, no bands in SrF_2 and BaF_2 to correspond to the double band at 190 mμ in CaF_2. The three BaF_2 bands at 255, 220, and 200 mμ may have corresponding bands in the other two crystals but these would be beyond the range of our instrument.

Bleaching the strongest bands (400 mμ in CaF_2, 505 mμ in SrF_2, and 660 mμ in BaF_2) leads to the conclusion that they are independent of the other bands. The only exception is the 490-mμ band in BaF_2 which decreases in intensity by the same amount as the 660-mμ band when the latter is bleached by light. It can therefore represent either the second excitation of the 660-mμ 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.[13] Expressed in Ivey's[14] form this relation reads

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

where λ_m is the wavelength of the absorption peak and $n \simeq 2$. 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.[15] The correlation of absorption bands of CaF_2 and BaF_2 by Ivey,[14] who used the exponents 1.00 and 1.44, was premature.[16] His predicted bands in SrF_2 do not exist. In a preceding paper[17] it was shown that the 580-mμ band in 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-mμ band by NaF addition which creates anion vacancies. In SrF_2 and BaF_2 this band either does not exist or is very weak if we consider the 602- and 735-mμ bands corresponding to it. One has to assume therefore that either there are no anion vacancies in SrF_2 and 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-mμ band in CaF_2 is strongly enhanced by YF_3 which forms anion interstitials; it was therefore correlated to neutral interstitial *F* atoms.[17] The 505-mμ band in SrF_2 and 662-mμ band in BaF_2 may correspond also to neutral interstitial *F* atoms. The 325-, 415-, and 565-mμ bands in CaF_2, SrF_2, and BaF_2, respectively, might be correlated to electrons bound to Ca^{2+} interstitials and those at 220 mμ in CaF_2, 290 mμ in SrF_2, and 410 mμ in BaF_2 to holes bound to Ca^{2+} vacancies, or vice versa. The sequence of bands in BaF_2 between 700 and 400 mμ 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.

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[13] E. Mollwo, Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., p. 97 (1931).

[14] H. F. Ivey, Phys. Rev. **72**, 341 (1947).

[15] P. Avakian and A. Smakula, Bull. Am. Phys. Soc. **5**, 48 (1960).

[16] H. F. Ivey, Phys. Rev. **89**, 322 (1953).

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