tering by the normal processes, which are included in τ_P, and τ_c, is the combined relaxation time of Eq. (5). As usual, x is the dimensionless variable $\hbar\omega/KT$.

The evaluation of the correction κ_1 is in general quite complicated. In reference 1, the case of large defect scattering at low temperature (small y in the terminology of the present paper) was considered; the result obtained was

$$\kappa_1 = 7B\hbar^3/96\pi^4K^2v_sA^2. \qquad \text{(A-2)}$$

The dependence of κ_1 on $1/A^2$ does not persist when A becomes small.

We consider here the case in which the relaxation time for defect scattering is long compared to τ_N. However, since the normal processes cannot be themselves lead to a nonzero thermal resistance, the conductivity will be primarily determined by the defect scattering. Equation (A-1) has been evaluated in this limit (large y), neglecting boundary scattering and umklapp processes. The result is (retaining only the two leading terms of an asymptotic expansion in powers of y^{-2})

$$\kappa_1 = \frac{\hbar}{120\pi^2 v_s A T} + \frac{13}{462}\frac{K^2}{v_s\hbar B T^2}. \qquad \text{(A-3)}$$

The first term in (A-3), when dominant, yields a thermal resistance $120\pi^2 v_s A T/\hbar$, twenty five times as great as that obtained from Eq. (16) as a defect resistance. This result is in exact agreement with that obtained by Ziman from a variational principle.[10,14] The second term in (A-3) is of the same order as κ_p [Eq. (12)]. Combining the two, we have

$$\kappa = \kappa_p + \kappa_1 = \frac{\hbar}{120\pi^2 v_s A T} + \frac{15}{77}\frac{K^2}{v_s\hbar B T^2}. \qquad \text{(A-4)}$$

Equation (A-4) shows the extent to which the thermal resistance is overestimated by Ziman's formula, and indicates an explicit contribution from the normal processes to the conductivity. In these equations the constant B pertains to the normal processes only; Umklapp processes are neglected.

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Coloration of Pure and Doped Calcium Fluoride Crystals at 20°C and −190°C*

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Coloration of pure CaF_2 crystals with 2.5-Mev electrons at room-temperature results in bands at 580, 400, 335, and 225 mμ. In YF_3-doped crystals the bands are in the same spectral positions as in pure crystals. They are, however, enhanced and their intensity ratios are significantly changed, the 400-mμ band being predominant. NaF-doped crystals show an even more drastic change: Coloration at room temperature produces bands at 605, 385, and 330 mμ and is deeper than in either pure or YF_3-doped crystals. Since the 400-mμ band is strongly enhanced by YF_3 addition which forms F^- interstitials, it is correlated to neutral fluorine atoms in interstitial positions. Similarly, the 605-mμ band in crystals doped with NaF, which creates F^- vacancies, is correlated to electrons trapped in F^- ion vacancies (F centers). The enhancement of the 385-mμ band by NaF is explained by the reduction of the activation energy required for formation of interstitials and vacancies. Of several possible correlations the 330-mμ band is probably connected with a hole trapped in a Ca^{2+} vacancy and that at 225 mμ with an electron trapped by a Ca^{2+} interstitial. The bands at 440 and 200 mμ which appear in NaF-doped crystals only must be connected with Na ions. Coloration at −190°C produces strong changes in the absorption spectrum. In pure and YF_3-doped crystals bands appear at 550, 320, and 270 mμ while in NaF-doped crystals bands are formed at 440, 390, 315, and 200 mμ in addition to the 550-mμ band. The primary process of coloration at low temperature cannot differ from that at room temperature but the secondary processes are strongly influenced by temperature.

COLOR centers in CaF_2 can be produced just as in alkali halides, i.e., additively by heating in Ca vapor or by irradiation with γ rays, x rays, electrons, or other ionizing radiation.[1]

Additive coloration in CaF_2 usually produces two strong bands at 375 and 525 mμ (denoted by Mollwo[2] α and β, respectively), while irradiation produces four bands at 580, 400, 335, and 225 mμ.[3] In the alkali halides both methods produce identical F bands although additional bands (V bands) are formed by irradiation only. By proper control of temperature and quenching rate, either the two- or four-band system can be produced by additive coloration.[4] Crystals that have been

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

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

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

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

irradiated after heat treatment at high temperature (1200°C) show a two-band system similar to that produced by additive coloration.[5]

The optical properties of uncolored CaF_2 are affected by exposure of the crystal to oxygen or to water vapor at high temperature.[6,7] Oxygen contamination also affects the position and intensity of the color-center spectra[8,9]; other unknown impurities or defects may likewise influence the color centers.

At present there are no consistent interpretations (model proposals) of color centers in CaF_2 similar to those in alkali halides. For example, in additively colored crystals, Mollwo[2] suggested that the 375-mμ band (α) corresponds to an *F* center while Bontinck[10] concluded that it is the 525-mμ band (β) that corresponds to an *F* center. A study of the influence of known defects on color centers might give some information about their nature.

Zintl and Udgard[11] have shown that YF_3 forms a solid solution with CaF_2, the Y^{3+} ions replacing Ca^{2+} ions substitutionally and the F^- ions taking interstitial positions. Ure's ionic conductivity measurements[12] support these findings. In addition, Ure demonstrated that in NaF-doped CaF_2 the Na^+ ions replace Ca^{2+} ions substitutionally, resulting in the formation of F^- vacancies. Thus, in YF_3-doped crystals F^- interstitials, and in NaF-doped crystals F^- vacancies predominate. It therefore seemed worth while to study the influence of these defects on color centers in CaF_2 crystals.

EXPERIMENTAL PROCEDURE

Crystals of CaF_2, pure and doped, were grown by the Stockbarger[6] (Bridgman) method in graphite crucibles in an evacuated induction furnace (Fig. 1). The doping agents YF_3 and NaF (up to 1 mole %), with a few tenths of a percent of PbF_2, were mixed into the charge beforehand. The PbF_2 acts as scavenger and removes oxygen contamination by the reaction $PbF_2+CaO \rightarrow PbO + CaF_2$; PbO and excess PbF_2 evaporate completely from the melt before crystallization begins.[6] Because of the appreciable vapor pressure of NaF at the melting point of CaF_2 (1380°C) it was necessary to confine the NaF-doped melt in the crucible by means of a floating graphite plug, which reduced the open surface area of the melt and thus decreased NaF evaporation. The sliced and polished crystals were colored by electron bombardment (2.5-Mev electrons from a Van de Graff) at room (20°C) and liquid-nitrogen (−190°C) temperatures. The optical absorption was measured by means of a Beckman DK-1 spectrophotometer (range 3.5 to 0.175 μ) after coloration at temperatures from −190° to 20°C. The concentration of interstitials and vacancies was determined by measuring the density (by hydrostatic weighing[13]) and the lattice constant.[14]

Since YF_3 forms a solid solution with CaF_2,[10] the Y^{3+} ions replacing Ca^{2+} ions and the excess F^- ions taking interstitial positions, the density is

$$d_i=(4/a^3N_0)[(1-x)M_{\mathrm{Ca}}+xM_{\mathrm{Y}}+(2+x)M_{\mathrm{F}}], \qquad (1)$$

where x is the mole fraction of YF_3, which equals the mole fraction of F^- interstitials, and *M*'s are the respective atomic weights.

Similarly, NaF forms a solid solution with CaF_2 and introduces F^- vacancies, giving the density;

$$d_v=(4/a^3N_0)[(1-x)M_{\mathrm{Ca}}+xM_{\mathrm{Na}}+(2-x)M_{\mathrm{F}}]. \qquad (2)$$

From Eqs. (1) and (2) the concentration of interstitials and vacancies was computed.

Concentration of Interstitials and Vacancies

The results of the density and lattice-constant measurements for a few crystals prior to coloration are shown in Table I. The measured concentration of YF_3 shows quite good agreement with the amount added to the melt. The lattice constant shows an increase in YF^3-doped crystals as compared with pure crystals because the interstitial F^- ions expand the lattice. These measurements agree with the findings of Zintl and Udgard.[11] The only empty sites in the lattice available for interstitial F^- ions are at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ or $(0, 0, \frac{1}{2})$ in the unit cell (Fig. 2). These two positions are located at the centers of cubes formed by the simple cubic sublattice of F^- ions and therefore are equivalent. It would seem at first sight that the eight surrounding F^- ions would

TABLE I. Density, lattice constant, and computed defect concentration of pure and doped crystals.

Crystal	Density (g/cm^3)	Lattice constant (*A*)	Defect concentration (percent)
Pure CaF_2	3.1791	5.4635	...
CaF_2+0.9% YF_3 nominal[a]	3.2001	5.4650	0.85
CaF_2+1.0% NaF^2 nominal[a]	3.1779	5.4636	0.07

[a] Nominal = added to the melt.

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

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[13] A. Smakula and V. Sils, Phys. Rev. **99**, 1744 (1955).

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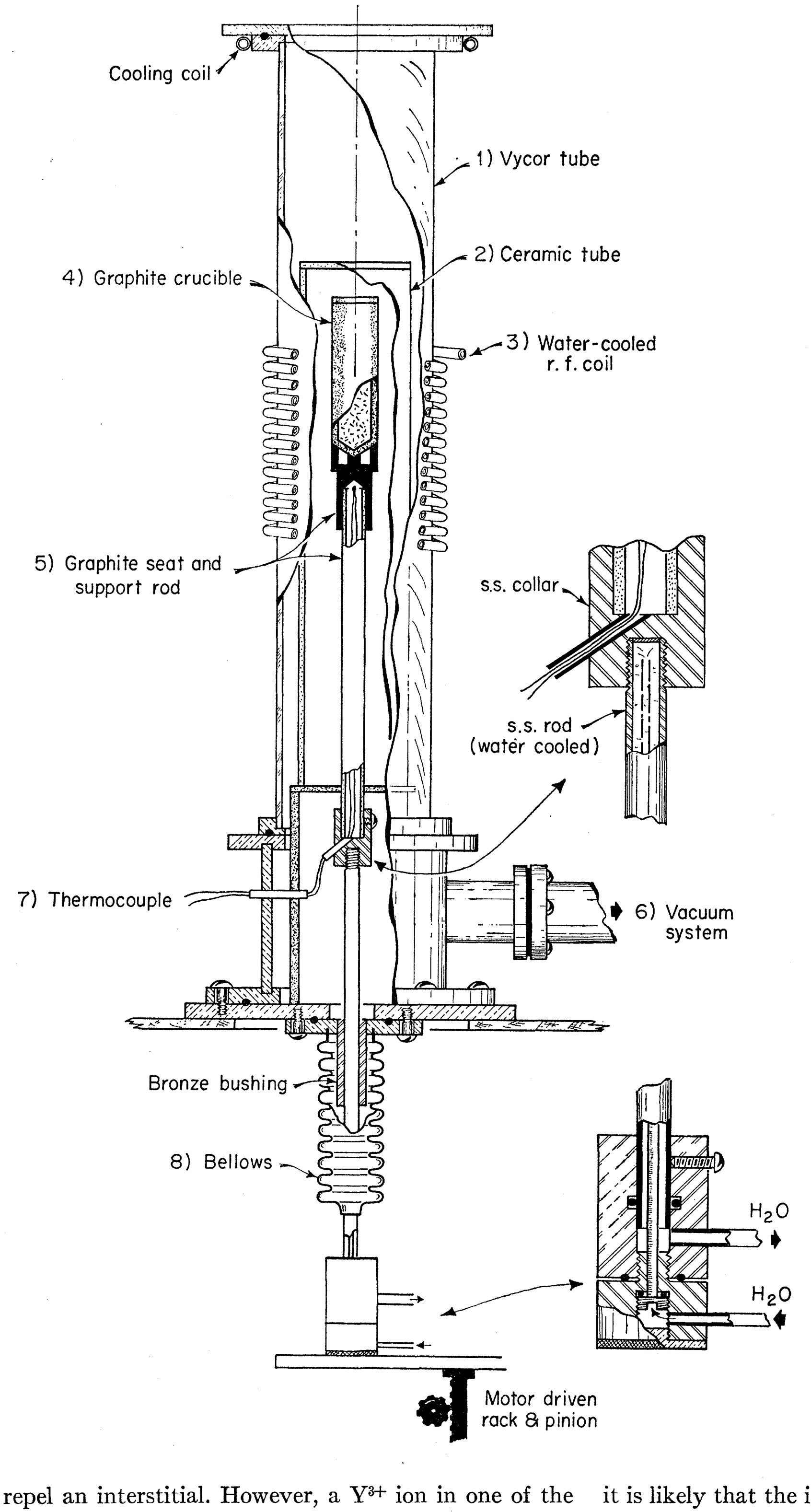


FIG. 1. Crystal-growing induction furnace.

repel an interstitial. However, a Y^{3+} ion in one of the six nearest cation sites probably aids the formation of interstitials by causing additional polarization of the adjacent anions by its extra positive charge. Therefore it is likely that the interstitial F^- ion is associated with the Y^{3+} ion. The computed F^- vacancy concentration in NaF-doped crystals is much lower than the nominal amount (Table I). This is due to the evaporation of

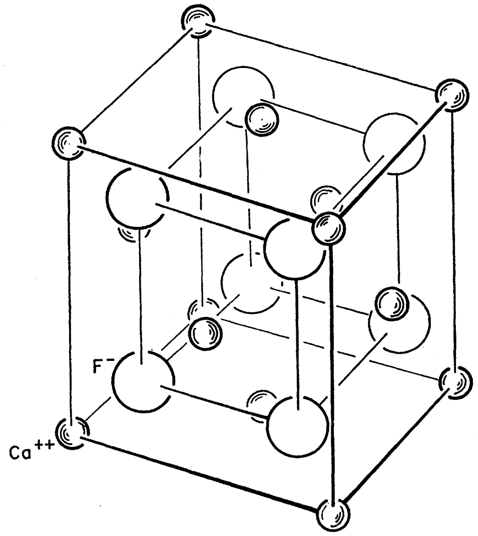


FIG. 2. Fluorite structure.

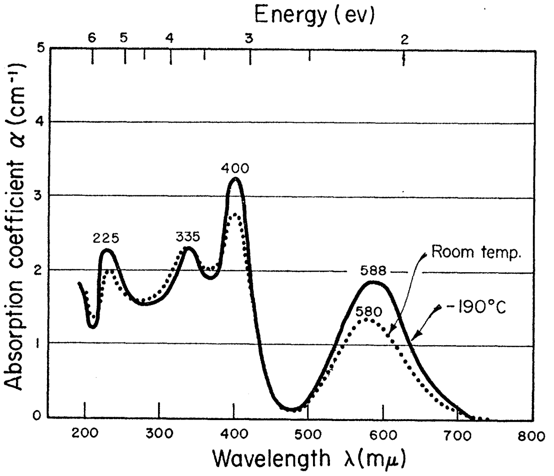


FIG. 3. Absorption of pure CaF_2 colored at 20°C by 2.5-Mev electrons (2.5×10^6 rad dose).

NaF from the melt, which is impossible to avoid completely despite precautions. The lattice constant does not change significantly, indicating that contraction due to vacancy formation is small.

If YF_3 were assumed to introduce cation vacancies instead of F^- interstitials, the difference in density from pure crystals would be only about half of that observed. If, on the other hand, NaF were assumed to introduce Na^+ interstitials instead of F^- vacancies, the density would be higher in pure crystals rather than lower, as observed. Y^{3+} vacancies or Na^+ interstitials, however, might also be present in a concentration too small to be detected by density measurements, yet large enough to play a role in coloration.

Color Centers in Pure CaF_2

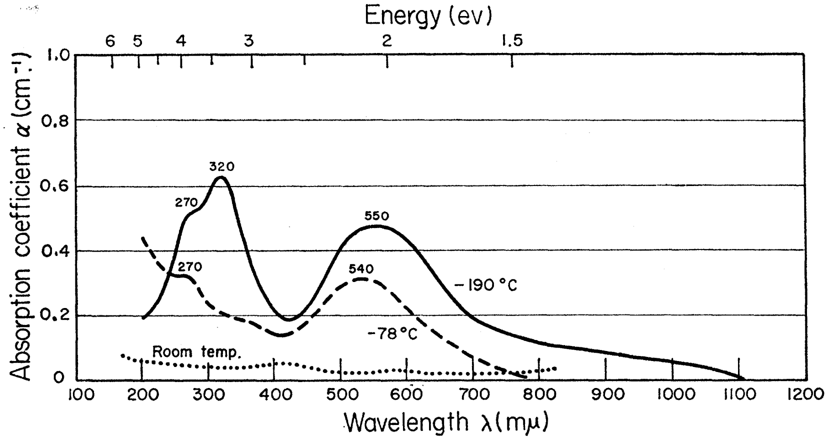
The absorption of pure crystals is plotted in Fig. 3. In agreement with previous work,[8] the 580-mμ band shifts toward longer wavelength at low temperature while the remaining bands shift very slightly toward shorter wavelength. The half-width of the 580-mμ band changes from 0.35 ev at 20° to 0.30 ev at −190°C.

Unexpected results were obtained by coloring pure crystals at −190°C. These crystals, measured at −190°C, show an absorption spectrum with peaks at 550, 320, and 270 mμ (Fig. 4). Comparing Fig. 4 with Fig. 3 shows that the spectra exhibit a certain similarity. Coloration at −190°C seems to shift all bands to the ultraviolet. The band at 550 mμ is, however, considerably broadened and the long tail indicates another weak but very broad band. Warming to −78°C bleaches all bands, particularly that at 320 mμ. After reaching 20°C the crystal exhibits a weak spectrum similar to that of crystals colored at that temperature.

Color Centers in YF_3*-Doped* CaF_2

The addition of YF_3 to CaF_2 does not change the optical transmission of uncolored CaF_2 crystals in the range from 3.5 to 0.175 μ. In colored YF_3-doped crystals

FIG. 4. Absorption of pure CaF_2 colored at −190°C by 2.5-Mev electrons (10^5 rad dose).



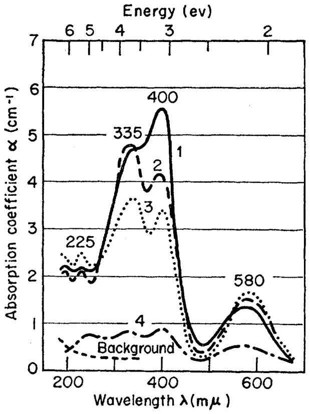


FIG. 5. Absorption of YF_3-doped CaF_2 colored at 20°C by 2.5-Mev electrons (10^5 rad dose). (1) 0.9, (2) 0.2, (3) 0.02 mole % of YF_3, (4) pure.

no new bands appear but all bands found in undoped crystals are enhanced (Fig. 5), and the intensity ratios are significantly changed (Fig. 6). At several hundredths mole % the 580-mμ band reaches a maximum and then decreases slowly; the 400-mμ band continues to increase whereas the 335-mμ band reaches saturation at about 0.2 mole % YF_3.

Thermal bleaching at room temperature seems to depend on the degree of coloration and doping but was not investigated extensively. Photochemical bleaching with 400-mμ light discolors the 400-mμ band, and to a lesser degree other ultraviolet bands, but not the 580-mμ band (Fig. 7). A small absorption increase around 500 mμ occurs during bleaching.

Coloration of YF_3-doped crystals at −190°C yields the same bands as in pure crystals colored at the same temperature (Fig. 8). Warming the crystal to room temperature (Fig. 9) changes the spectrum to that obtained by coloration at 20°C. In contrast to pure crystals (see Fig. 4), however, YF_3-doped crystals do not exhibit complete bleaching of the 320-mμ band but a shift to 335 mμ. The 400-mμ band, absent at −190°C, grows on warming, probably at the expense of the 275-mμ band which disappears.

Results show that the addition of YF_3 has two effects: a general enhancement of all bands and a very strong specific enhancement of the 400-mμ band at higher concentrations. The general enhancement may be caused by the lattice distortion manifested in the increase of lattice constant. The interstitial F^- ions may also act as a source of free electrons and holes in excess of the normal number created by irradiation. Although interstitial F^- ions are probably associated with Y^{3+} ions, the proximity of the eight surrounding F^- ions could decrease the binding force between electrons and interstitial F^- ions. The lower recombination rate of free electrons and interstitial atoms may promote color-center formation.

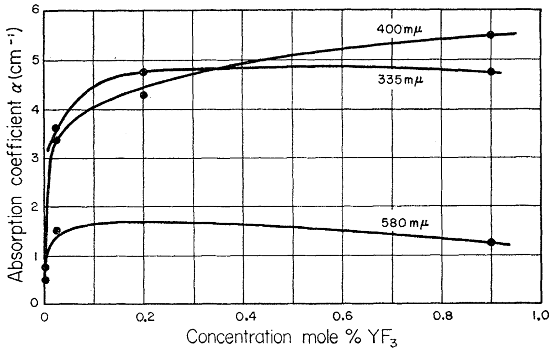


FIG. 6. Intensity of absorption bands of YF_3-doped CaF_2 colored at 20°C by 2.5-Mev electrons (10^5 rad dose) as function of YF_3 concentration.

Could it be possible that the four-band system is due to yttrium ion, which may always be present in CaF_2? The mineral yttro-fluorite occurs in nature, and the chemical properties of Ca and Y are similar. If this proposal had merit, it would have to be expected that the coloration should increase proportionally with YF_3 concentration. This is, however, not the case.

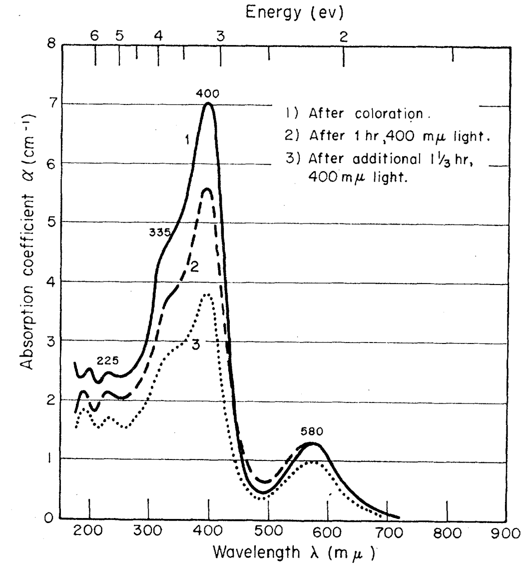


FIG. 7. Photochemical bleaching with 400-mμ light of YF_3-doped CaF_2 colored at 20°C by 2.5-Mev electrons (10^5 rad dose).

No bands appear at new positions in YF_3-doped crystals, as compared to pure crystals, nor does the light or thermal bleaching produce any. This is evidence that Z bands, as found in KCl doped with $CaCl_2$,[15] are either not present or not strong enough to be observed.

Color Centers in NaF*-Doped* CaF_2

Three features were observed in the color-center spectra of NaF-doped crystals colored at 20°C compared to pure or YF_3-doped crystals: a change in the positions and intensities of the bands, a deeper colorability for

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[15] H. Pick, Ann. Physik **35**, 73 (1939); Z. Physik **114**, 127 (1939). G. Heiland and H. Kelting, Z. Physik **126**, 689 (1949); F. Seitz, Phys. Rev. **83**, 134 (1951).

similar doses, and a delayed time dependence of the intensity of the 605-mμ band. The three bands at 605, 385, and 330 mμ (Fig. 10) resemble those at 580, 400, and 335 mμ in pure colored crystals. The first is, however, shifted toward longer and the other two toward shorter wavelengths. The intensity of the individual bands differs greatly. While in pure crystals the 580-mμ band is only half as intensive as the 400-mμ, the 605-mμ band in NaF-doped crystals is practically equal to the 385-mμ band. At low temperature the 605-mμ band shifts toward longer wavelengths, same as the 580-mμ band, and its half-width decreases from 0.33 to 0.23 ev (Fig. 11). The principal difference between the 605- and 580-mμ bands is that the former shows a time delay (of several minutes in lightly doped crystals) in its formation, i.e., it does not form during but after coloration, as indicated by a change of the crystals from pale green to dark blue. All bands increase with the concentration of NaF added but not uniformly: The enhancement of the 605- and 385-mμ bands is greater than that of the 330-mμ band. Quantitative comparison with NaF concentration was, however, not possible because of strong evaporation of the NaF during crystal growth. NaF-doped crystals show little photochemical bleaching but are particularly sensitive to slight heating (100°C) (Fig. 12). While the bands at 605, 385, and 330 mμ decreased, a new band at 500 mμ was formed, which seems to appear in the more highly doped crystals only.

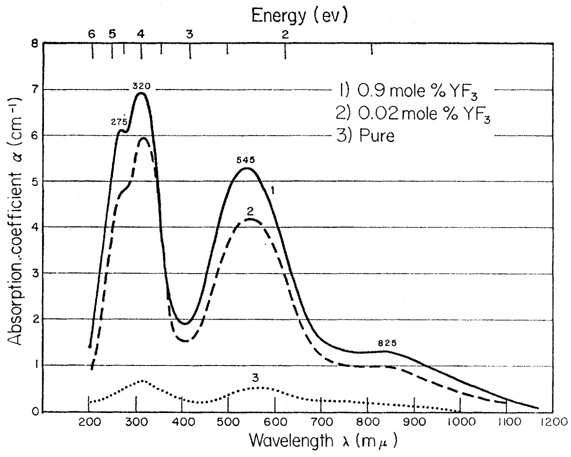

FIG. 8. Absorption of YF$_3$-doped CaF$_2$ colored and measured at −190°C by 2.5-Mev electrons (10^5 rad dose).

NaF-doped crystals showed different absorption spectra also when colored at −190°C (Fig. 11). The main difference between coloration at this temperature and 20°C is that at −190°C new bands appear at 440 and 200 mμ while the 605-mμ band is practically nonexistent. In addition, a band at 550 mμ appeared in lightly doped crystals. Upon warming, the 440- and 200-mμ bands decrease and the 605-mμ band increases, while those at 385 and 315 mμ first decrease, then increase, and finally decrease again. On reaching 20°C, the spectra are identical with those found in NaF-doped crystals colored at 20°C.

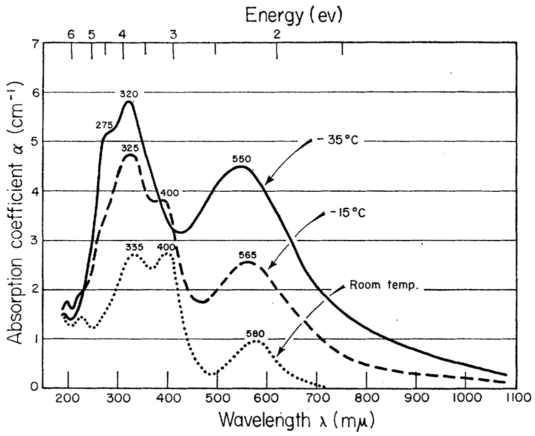

FIG. 9. Influence of temperature on YF$_3$-doped CaF$_2$ colored at −190°C by 2.5-Mev electrons (10^5 rad dose).

The absorption spectrum of NaF-doped crystals colored at 20°C is identical with the band system observed by Smakula[8] in his crystal No. 3. In addition Smakula observed, after cooling a colored crystal to −190°C, a small band at 500 mμ which was also found in this study after slight thermal bleaching. Smakula ascribes his centers to anion vacancies introduced by oxygen contamination. Since his crystals contained only traces of Na, it seems that the identity of the absorption spectra is not directly associated with NaF as such but with anion vacancies that can be formed by NaF as well as by oxygen.

Another possibility is that there is larger oxygen contamination in NaF-doped crystals than in pure crystals because of vacancies introduced by NaF which aid the diffusion of oxygen into the lattice. Oxygen, because of its double charge, in turn creates more negative ion vacancies. This hypothesis is, however, difficult to accept since the oxygen pressure in the furnace was

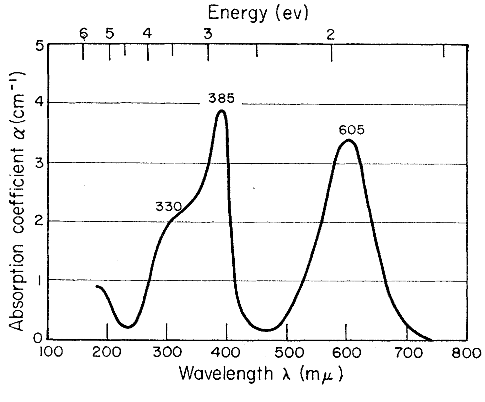

FIG. 10. Absorption of NaF-doped CaF$_2$ colored and measured at 20°C by 2.5-Mev electrons (10^4 rad dose). (1 mole % NaF added to the melt.)

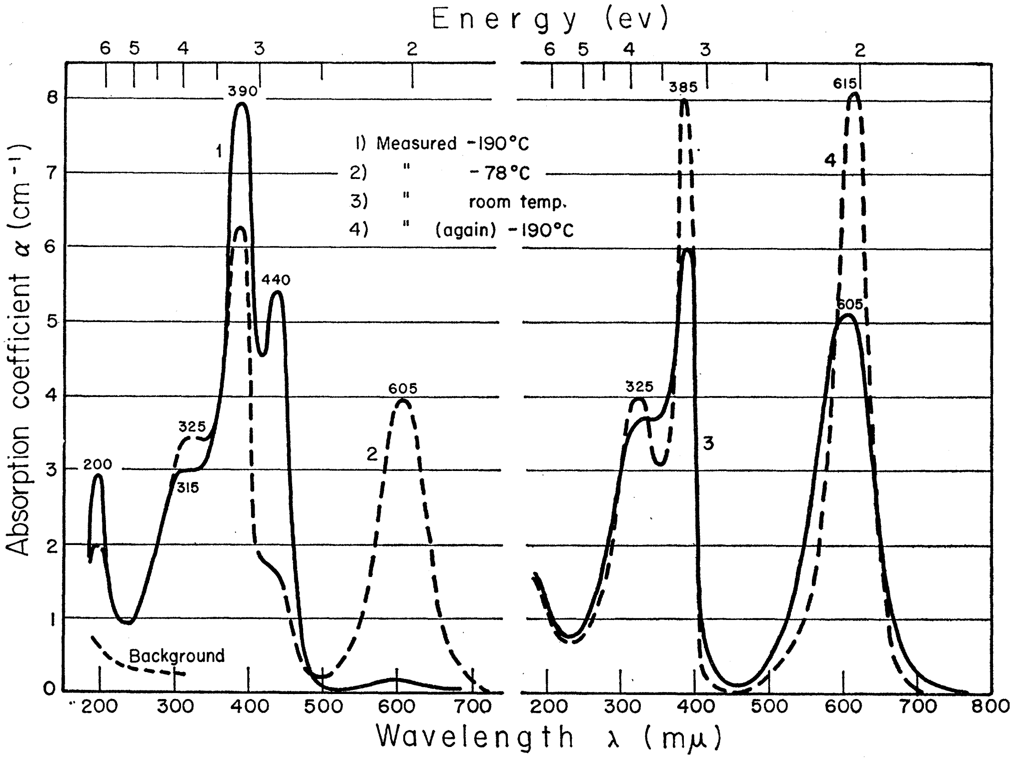

FIG. 11. Absorption of NaF-doped CaF_2 colored at $-190°C$ by 2.5-Mev electrons (2×10^4 rad dose).

less than 10^{-3} mm and the graphite crucible creates a reducing atmosphere around the crystal.

DISCUSSION

Our experimental results show that the color centers of CaF_2 crystals are strongly affected by the addition of YF_3 or NaF and by temperature of coloration. The number of bands, as well as their spectral position and intensity, is changed.

Both YF_3 and NaF additions increase the intensity of all absorption bands. This effect is caused by an increased concentration of traps for electrons and holes due to lattice distortion. In addition, the specific influence of certain bands is of particular interest.

YF_3 addition results in very pronounced enhancement of the 400-mμ band. Since YF_3 forms a solid solution with interstitial F^- ions, it may be assumed that the 400-mμ band is connected with F^- interstitials that have been neutralized by irradiation. Interstitial F^- ions seem to be present, even in pure CaF_2 crystals, and are probably created also by coloration. Thus the 400-mμ band in pure crystals is correlated to a hole connected with fluorine interstitials located in the center of the cube formed by the sublattice of eight fluorine ions (see Fig. 2).

The principal effect of NaF addition, which forms a solid solution with F^- vacancies, is a strong enhancement of the 605- and 385-mμ bands. It is quite logical to correlate the 605-mμ band with electrons trapped in F^- ion vacancies. In pure CaF_2 crystals this band is located at 580 mμ, the shift probably being due to the presence of Na^+ ions. The 385-mμ band seems to be the same as the 400-mμ band observed in pure and YF_3-doped crystals. Its shift is probably also caused by the presence of Na^+ ions.

The enhancement of the 385-mμ band by NaF addition can be explained by the presence of Na^+ ions which reduce the lattice binding of F^- ions. The activation energy for the formation of interstitial F^- ions is thereby decreased and their concentration increased.

The doping by NaF has thus two effects: the formation of F^- vacancies by replacement of Ca^{2+} by Na^+ to preserve electrical neutrality, and the formation of F^- interstitials and vacancies by a reduction of the binding energy of F^- ions. The concentration of F^- vacancies is therefore higher than that of interstitials. This corresponds to the greater increase of the 605-mμ band whose intensity equals that of the 400-mμ band in NaF-doped crystals while in pure crystals, where the number of F^- interstitials and vacancies is the same, the 605-mμ band is only half of the 400-mμ band.

The identity of the bands in NaF–doped and oxygen-contaminated CaF_2 crystals indicates that oxygen creates F^- vacancies as well as interstitials. This effect can be expected because the replacement of bivalent Ca^{2+} by monovalent Na^+ and the replacement of monovalent F^- by bivalent O^{2+} have the same effect on the lattice.

The effect of YF_3 on the 580-mμ band (Fig. 6) indicates first an increase and then a decrease of the absorption maximum. The initial increase is probably caused by general lattice distortion. The suppression at higher concentration indicated that some F^- vacancies are filled with F^- ions which are generally in interstitial positions.

The formation of the 605-mμ band in NaF-doped crystals appears to take place in two steps, as indicated by a change from pale yellow to blue immediately after coloration. The first step seems to be connected with the 440-mμ band which is stable only at low temperature. As it decreases, the 605-mμ band grows. The 440-mμ band may be connected with a Na center which decomposes into $Na^+ + e$. The free electron migrates and is finally trapped in a F^- vacancy.

A correlation of the bands located at 330 and 225 mμ is more difficult. They can be aggregates or excited states of fundamental centers or the type of α and β band centers caused by Ca^{2+} ion vacancies or interstitials. The aggregates are generally formed by photochemical or thermal bleaching. The above bands always appear simultaneously with others. The higher excitation bands should be less stable and considerably lower in intensity than the fundamentals. Our bands do not show these properties. (The α and β bands are closer to fundamental absorption than observed here.) It seems to be most probable that these bands are connected with Ca^{2+} vacancies and interstitials. The 335-mμ band in particular might be connected with electrons trapped in Ca^{2+} vacancies since it shows some decrease with concentration of the YF_3 addition. The Y^{3+} ions might fill some of the Ca^{2+} vacancies. The 330-mμ band may correspond to a hole trapped in a Ca^{2+} vacancy, and, correspondingly, the 225-mμ band may be a center created by an electron trapped by a Ca^{2+} interstitial.

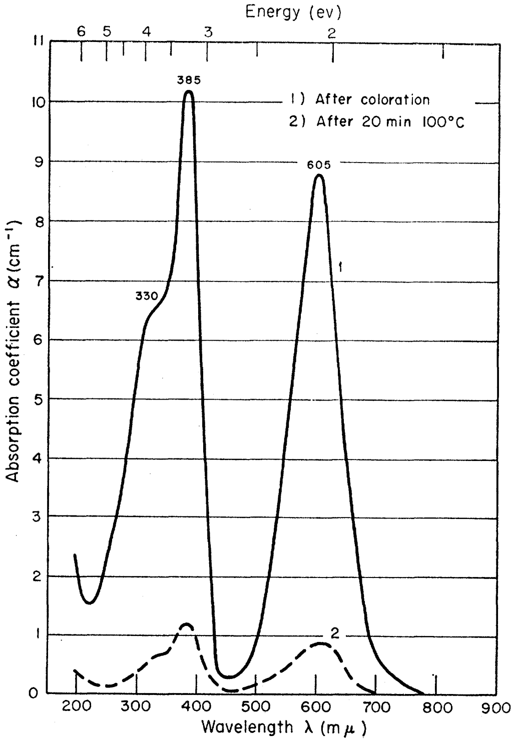

FIG. 12. Thermal bleaching of NaF-doped CaF_2 colored at 20°C by 2.5-Mev electrons (10^4 rad dose).

Temperature has several effects on color centers in CaF_2. The unusual shifting of the 580- and 605-mμ bands toward lower energy with decreasing temperature indicates a decrease of binding energy of this center, while other bands are practically unaffected by temperature. Although there is a similarity between the spectra produced at −190° and 20°C, their nature seems to be different since they do not shift continuously but transform irreversibly. The low-temperature centers are connected either with shallow traps or with the close proximity of the holes and electrons to their place of origin. In crystals colored at −190°C the strong broadening of the 550-mμ band might also be associated with a center similar to the *F′* center in alkali halides, where two electrons are trapped in a single vacancy. The 440- and 200-mμ bands in NaF-doped crystals colored at −190°C might be connected with the first and second excitation of a Na center which dissociates at higher temperature forming the 605-mμ band.

All correlations discussed are more or less speculative and must be considered tentative. The complexity of the spectra indicates the presence of several types of centers due to a variety of traps; additional study is necessary for their full explanation.

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