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Color Centers, Associated Rare-Earth Ions and the Origin of Coloration in Natural Fluorites

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Abstract. Natural colored fluorites were studied by means of optical absorption and electron paramagnetic resonance (EPR). Complex centers involving rare-earth ions and/or oxygen give rise to the various colors observed. These include yttrium-associated *F* centers (blue), coexisting yttrium and cerium-associated *F* centers (yellowish-green), the (YO_2) center (rose) and the O_3^- molecule ion (yellow). Divalent rare-earth ions also contribute to the colorations, as for instance Sm^{3+} (green fluorites), or they are at the origin of strong fluorescence observed (Eu^{2+}). Strong irradiation of the crystals with ionizing radiation leads to coagulation of color centers, and to precipitation of metallic calcium colloids. There is probably no simple relation connecting the coloration and the growth process of the crystal. Thermal stability studies, however, have allowed to partially classify the colors as being of primary or secondary origin.

Introduction

Natural fluorites are probably the minerals which exhibit the largest variety of colors. Several theories have been proposed to explain the cause of these colorations since the first studies on this subject (see, e.g., Przibram, 1953; MacKenzie and Green, 1971). Invariably, however, it turned out that there is no unique cause, and that much more experimental information was needed before really reliably theoretical foundations could be constructed.

The availability of good synthetic single crystals exhibiting a wide range of optical transparency, and the increasing interest in the spectroscopic properties of pure and doped CaF_2 has led to a rapid increase of the experimental research work done in this field. Numerous technical applications have resulted, such as solid-state lasers (CaF_2 doped with Sm^{2+} was the second successful laser material discovered), and more recently photochromic materials and infrared up-converters. Our understanding of color centers is now reasonably good (Hayes, 1974). However, interaction between these and rare-earth ions is a matter of considerable complexity.

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The identification of the structure of the center responsible for a specific coloration is complicated by the simultaneous presence of many different impurities. It is in particular difficult to determine if the center is intrinsic, impurity-associated, or an impurity ion. Studies of coloration of natural material were made in several specific cases as for instance the blue-john fluorite or the rose one. A few reviews have been published recently (Bill et al., 1967; Recker et al., 1968; Hunt et al., 1972). The purpose of the present paper is to carry out a review of the recent work done in the field of color centers in the fluorites, and to add some new results on yellow and yellowish-green fluorites. Further, the colorations will be related to their thermal stability, and to the growth conditions of the host crystals.

Experimental

Crystals from more than 70 different localities corresponding to various formation conditions were examined by means of several spectroscopic techniques. These include optical absorption spectrophotometry, electron paramagnetic resonance (EPR), electron nuclear double resonance (ENDOR) and Raman spectrometry. The kinetics of thermal bleaching was investigated with the aid of isothermal heating experiments for the yellow, blue, and red colors. The stability of the other colors was studied qualitatively for comparison. Rare-earth element concentrations were determined in some zoned crystals by neutron activation analysis.

Impurity-Associated Color Centers

Two properties of the material CaF_2 contribute in an essential manner to the extraordinarily rich possibilities of creating color centers in the fluorites. For one, the material easily incorporates cation impurities, especially rare-earth ions. Then, oxygen is introduced into the crystals without much difficulty at temperatures down to 100° C by hydrolysis (Bontinck, 1958) and is possible during hydrothermal growth processes. Direct reaction with oxygen also occurs, but this seems to proceed at a much slower rate than the hydrolysis reaction.

At elevated temperature the oxygen diffuses to the impurity cations, producing thereby localized molecular structures. Crystals containing impurities show many optical absorption bands related to these when they have been irradiated with ionizing radiation at room temperature. Incidentally, extremely pure laboratory-made crystals show practically no coloration even at high doses under these conditions. The impurities present in the crystal have still another effect. They often suppress very efficiently the formation of intrinsic color centers, even when the crystals are irradiated at liquid nitrogen temperature.

1. Rare-Earth Ion-F Center Complexes

1.1. Yttrium-Associated F Center. The optical absorption spectrum shown in Figure 1 consists of four bands at 580 nm, 400 nm, 335 nm, and 224 nm. This

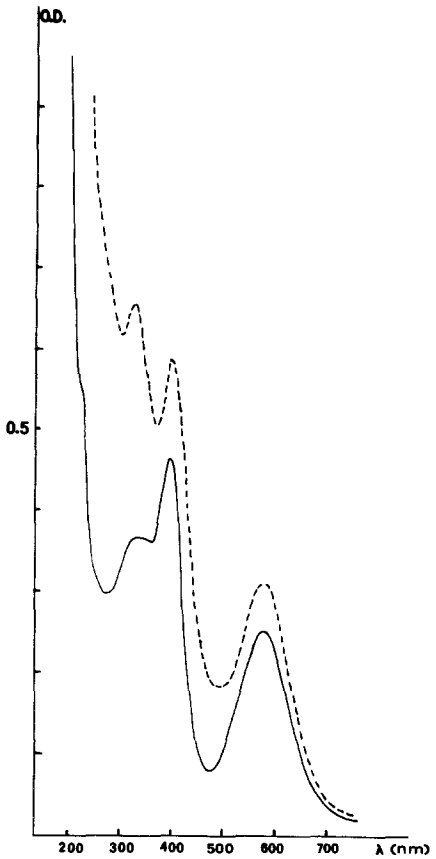

Fig. 1. Optical absorption spectra of light-blue fluorites from Moritz Mine, France *(straight line)* and Ponteaumur, France *(dashed line)*

spectrum is commonly encountered in light-colored natural fluorites (Calas, 1972) and in X-rayed synthetic crystals ("Smakula spectrum"). It was first thought to be intrinsic to CaF_2. Later, however, this spectrum was found to be enhanced by the presence of yttrium impurities (O'Connor and Chen, 1960). The discovery of a polarized luminescence (Görlich et al., 1968), and the more recent studies on the properties of the photochromic centers in CaF_2 (Staebler and Schnatterly, 1971) revealed the complex structure of this center.

The responsible center has a C_{3V} point symmetry and is aligned along a [111] axis. It can be described as an Y^{3+} ion associated with an F^- center (an anion vacancy containing two electrons). Linear dichroism experiments (Staebler and Schnatterly, 1971) and the theoretical work of Alig (1971) showed that the three low-energy bands are σ-, π-, and σ-, polarized in order of increasing energy. This is consistent with transitions from a $1A_1$ fundamental orbital singlet to $1E$, $2A_1$ and $2E$ levels respectively, arising from the overlapping of the F center wave function by the $4d$ and $5s$ orbitals of the yttrium ion (Staebler, in Hayes, 1974).

The absorption spectra show some differences among samples from different localities: some supplementary weak lines may be observed near 250 nm,

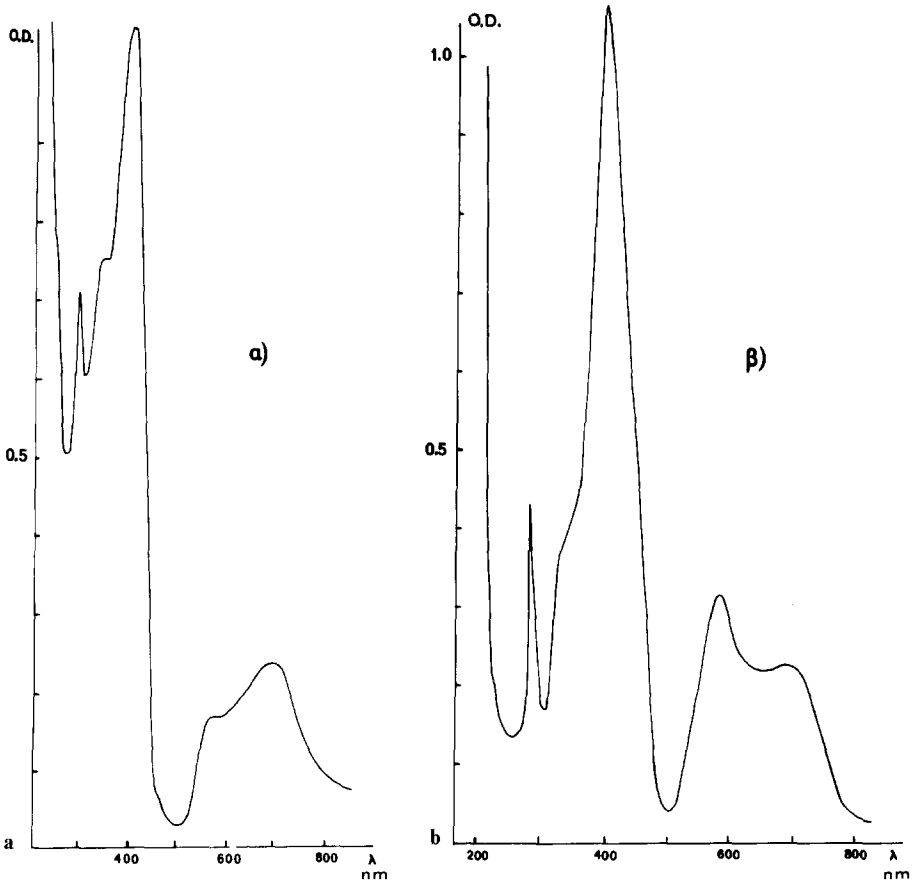

Fig. 2a and b. Optical absorption spectra of yellowish green fluorites: **a** Redruth, England, **b** Thüringen, Germany. The relative intensities of both low energy bands are opposite in (**a**) and (**b**), indicating the presence of two different centers

310 nm, and 720 nm, and the intensity of the strong absorption near 200 nm varies among the samples studied. Furthermore the exact location of the low-energy band varies, in relation perhaps with other rare-earth ions involved in similar color centers. Their presence could explain the relatively large width of the low energy band observed in the natural samples, 100–130 nm (0.4–0.5 eV) at half height, instead of 80 nm (0.3 eV) in synthetic crystals.

1.2. Coexisting Yttrium- and Cerium-Associated F Centers. We present here some results on natural fluorites exhibiting a deep green (yellowish green) color, which have never been studied before, perhaps because of their scarcity. Optical absorption spectra are given in Figure 2. They are similar to those observed in the blue fluorites, but exhibit two low energy bands and a supplementary band near 300 nm. The former are located at 590 nm and 712 nm, and correspond to the $1A_1 \rightarrow 1E$ transition of an yttrium-associated and a cerium-associated center,

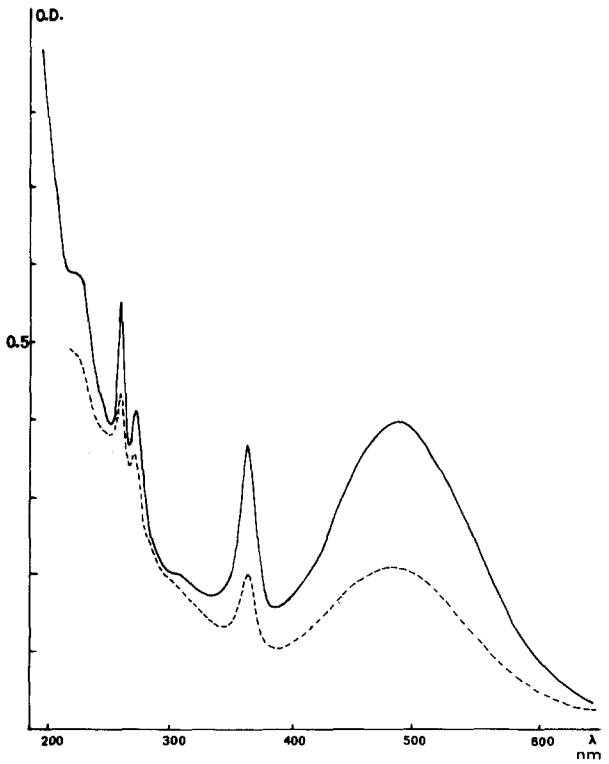

Fig. 3. Optical absorption spectra of rose alpine fluorites from Les Périades *(straight line)* and Vallée de Chamonix *(dashed line)*, France. Apart from the characteristic (YO_2) center absorption band at 485 nm, these spectra exhibit some supplementary lines, due probably to other color centers

respectively. They are in good agreement with the values published by Staebler (1969) on synthetic crystals, 580 nm, and 714 nm. The intensities of both bands are mutually independent in natural fluorites, as indicated by the comparison of Figure 2a and b, confirming the presence of two different centers. There are few variations in the position of the three other bands, at 230 nm, 335 nm, and 400 nm, as compared with Figure 1. Staebler and Schnatterly (1971) demonstrated that they remain in fact at about the same position for all the photochromic centers. The sharp band at 306 nm corresponds probably to the $4f \rightarrow 5d$ transition of the Ce^{3+} ion (Rydberg spectrum), as it was observed in synthetic cerium-doped and subsequently irradiated CaF_2 crystals (Alig et al., 1969). Manthey (1973) assigned it to the $e_g(x^2 - y^2)$ component of the $5d$ orbital. The splitting of that $5d$ orbital results from the tetragonal (C_{4V}) crystal field due to a nearest-neighbor interstitial F^- ion as charge compensator.

2. *The (YO_2) Center*

The optical absorption spectra of the rose and red alpine-type fluorites show a characteristic absorption band at 485 nm (Fig. 3), attributed to the (YO_2) center,

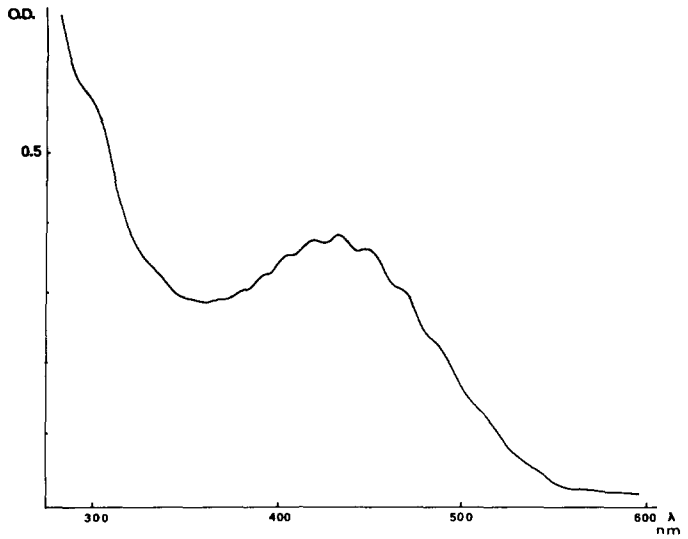

Fig. 4. Optical absorption spectrum of yellow fluorite from Valzergues, France

first called "*R* center" by Bill and Lacroix (1967). This name is however confusing because this center is not equivalent to a true *R* center, which consists in the fluorite lattice of three nearest-neighbor *F* centers aligned along [100] (Beaumont et al., 1972).

The (YO_2) center was produced in the laboratory by X-raying YF_3-doped CaF_2 crystals which had previously been hydrolyzed. Bill and Lacroix (1967) and Bill (1969a) have shown by detailed studies with EPR and ENDOR techniques that it consists of an O_2^{3-} molecular ion stabilized by an adjacent Y^{3+} ion. Many alpine fluorites exhibit some supplementary absorption bands at 225 nm, 260 nm, 270 nm, and 365 nm in their absorption spectra, in addition to the band arising from the (YO_2) center. These supplementary bands do not, however, bleach in the same manner as the 485 nm band.

3. *The "Yellow Center"*

This center, first described by Bill (1971), is at the origin of the typical coloration observed in all the yellow natural fluorites investigated in this study. The yellow color is due to the broad optical absorption band centered at 434 nm (Fig. 4). This band is resolved into a series of vibronic lines at and below liquid nitrogen temperature. The center is paramagnetic with an electronic spin $S=1/2$. A detailed investigation of its magnetic and optical properties has been carried out. It was shown that the center consists most likely of an O_3^- molecular ion which substitutes for two nearest-neighbor F^- ions. The direction of the two outer oxygen nuclei is parallel to a fourfold crystal axis. Finally the molecular ion performs librational motion. A detailed ENDOR investigation did not yield any lines which could be attributed to Na^+ or Y^{3+} or any other cationic

impurity, although a similar investigation performed on V_F centers in the same samples proved unambiguously the presence of a rather high concentration of Na^+ ions (Bill and Mareda, 1975). The structure observed in the optical absorption band is typical for a molecular center with moderate coupling between the electronic states of the center and the internal molecular vibrations, and stronger coupling to perturbed phonons of the crystal (Bill and Von Der Osten, 1976). The vibronic structure is nearly uniformly spaced in energy, with a separation of about 900 cm^{-1}.

Very often these crystals contain in addition O_2^- molecular ions (Bill, 1971). These centers produce an optical absorption band at 230 nm. EPR studies have shown a rhombic symmetry (D_{2h}) with a [100] axis. The O_2^- molecular ion substitutes for a pair of fluorine neughbors and the charge compensation is dominantly performed by substitutional Na^+ ions (see below), as shown by Bill and Mareda (1975).

Rare-Earth Ions

Rare-earth elements usually enter as trivalent ions into the crystal structure of the fluorite, in substitution for Ca^{2+} ions. The charge compensation is achieved by an F^- interstitial ion or an O^{2-} substitutional ion. These clusters imply a local symmetry which is lower than cubic. The cubic symmetry can however be observed in the case of a remote compensation: the compensating charges are disposed in the crystal at some distance from the excess charge. Other valence states also occur, the most stable being Ce^{4+} with a $4f^0$ configuration, Eu^{2+} and Tb^{4+} which both have a half-filled shell ($4f^7$) and Yb^{2+} with a filled shell ($4f^{14}$). Sm^{2+} ($4f^6$) is also stable and occurs frequently.

1. Divalent Rare-Earth Ions

Radiation-induced reduction of the trivalent rare-earth ions is only possible for the ions located at cubic sites, i.e., with remote charge compensation: Hayes and Twidell (1961) suggested a repulsive Coulomb effect of the negative charge compensator, which hinders the trapping of electrons by the adjacent rare-earth ion. The divalent rare-earth ions are thus expected to be located only at cubic sites. The characteristic optical absorption spectrum consists of intense and broad bands, due to transitions from the $4f^n$ to the $4f^{n-1}5d$ configuration (Rydberg spectra). These bands occur in the visible region because the $5d$ orbital energy is lowered relatively to the $4f$ when going from the trivalent to the divalent rare-earth ions. Their width arises from interactions between non-shielded $5d$ electrons and lattice vibrations. The strong intensity of these allowed transitions (oscillator strength of the order of 0.1) is in contrast to the weak and sharp bands resulting from the forbidden $4f \rightarrow 4f$ internal transitions. In natural fluorites, only Eu^{2+} and Sm^{2+} ions are known to have some influence on the colorations observed.

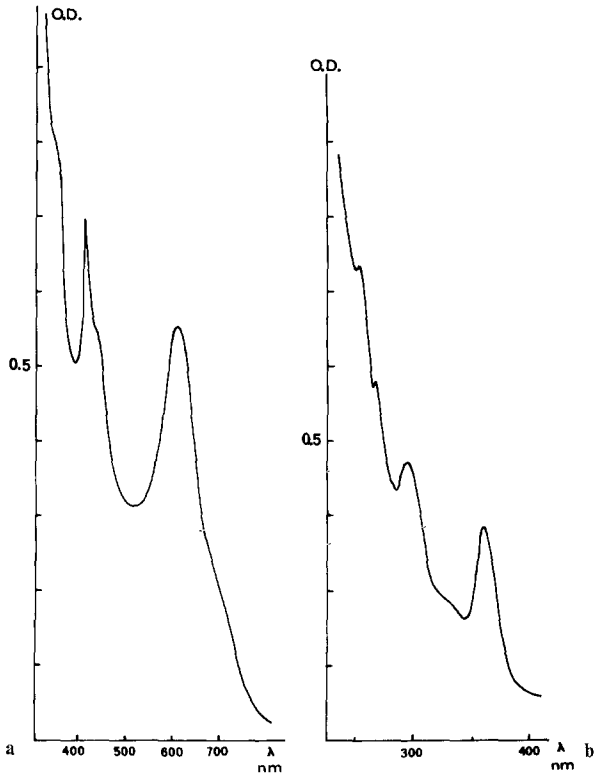

Fig. 5a and b. Sm^{2+} absorption spectrum in green fluorites from Weardale, England:
a e_g region
(sample thickness: 2.1 mm),
b t_{2g} region
(sample thickness: 0.3 mm)

Divalent europium is known to give the blue-violet fluorescence observed in the daylight at 413 nm (Recker et al., 1968). The optical absorption spectrum consists of two bands assigned to the e_g and t_{2g} components of the $5d$ orbitals in the cubic crystal field, with a superimposed structure due to the coupling of the $5d$ *orbitals* to the ^7F ground term of the $4f^6$ core (Loh, 1969; Weakliem, 1972). Although Eu^{2+} was proposed by Goldberg (1963) to be responsible for the yellow color of natural fluorites, we always observed the typical absorption spectrum of the "yellow center" in each yellow crystal we investigated.

Divalent samarium is very important as a coloring ion of natural fluorites. It is responsible for the light green color usually observed. The absorption spectrum of light green crystals is given in Figure 5 and clearly shows the conspicuous broad absorption bands characteristic of Sm^{2+}, at 690 nm, 611 nm, 440 nm, and 422 nm. First described by Feofilov (1956) in synthetic crystals, the Sm^{2+} ion was found to be the cause of the green color of natural fluorites [Goldberg (1963); Bill et al. (1967); Recker et al. (1968)]. Loh (1968) showed that these absorption bands arise from the $4f^6 \rightarrow 4f^5\,5d^1$ transitions, which include an interaction between e_g or t_{2g} components of the $5d$ orbital (in the 14,000–30,000 cm^{-1} and 30,000–40,000 cm^{-1} region respectively) and the ground multiplets of the $4f^5$ core. The U.V. part of the absorption spectrum (bands at 360 nm, 335 nm, 305 nm, 279 nm, and 260 nm in Fig. 5b) is probably perturbed by strong defect absorption (Loh, 1968).

2. EPR Results

The EPR spectrum of Gd^{3+} and Eu^{2+} was studied in CaF_2 by Ryter (1957), Low (1958), and Baker and Williams (1962). The divalent Eu^{2+} ion in fluorite is virtually always observed in cubic symmetry (see Sect. 1). Although Gd^{3+} ions occur frequently in cubic symmetry, they may however also be present as tetragonal centers because of charge compensation. The remote charge compensation observed in the case of the cubic Gd^{3+} center indicates that both the trivalent rare-earth ion and the compensating element are incorporated separately during the growth processes of the crystal.

The EPR spectra of the S-state ions are described by the spin-Hamiltonian (Abragam and Bleaney, 1970):

$$\mathcal{H} = g\beta \mathbf{BS} + \frac{b_4}{60}(O_4^0 + 5O_4^4) + \frac{b_6}{1260}(O_6^0 - 21O_6^4) + A_{\mathrm{RE}}\mathbf{I}\cdot\mathbf{S} + \sum_{\mu}\mathcal{H}_{\mu}$$

when the site is cubic, and by

$$\mathcal{H} = g\beta \mathbf{BS} + \frac{b_2^0}{3}O_2^0 + \frac{b_4^0}{60}O_4^0 + \frac{b_4^4}{12}O_4^4 + \frac{b_6^0}{1260}O_6^0 + \frac{b_6^4}{60}O_6^4 + A_{\mathrm{RE}}\mathbf{I}\cdot\mathbf{S} + \sum_{\mu}\mathcal{H}_{\mu}$$

in the case of a tetragonal Gd^{3+} center (all symbols have their usual meaning). The terms O_n^m, n=2, 4, 6, m=0, ± 4 ($|m|<n$) are spin operators transforming totally symmetrically under the appropriate point symmetry group. $A_{\mathrm{RE}}\mathbf{I}\cdot\mathbf{S}$ is only necessary for isotopes having a nonzero nuclear magnetic moment, and describes the hyperfine interaction of the electronic spin with the nucleus. (The nuclear spin of both isotopes ^{151}Eu and ^{153}Eu is $I=\frac{5}{2}$.) Finally $\sum_{\mu}\mathcal{H}_{\mu}$ describes the superhyperfine interaction with the surrounding F^- ions.

2.1. Cubic Center. The cubic EPR spectrum is well known in synthetic and natural fluorites (Ryter, 1957; Low, 1958; Vinokurov et al., 1963). The EPR spectrum of Eu^{2+} ions is more complex than the seven-line spectrum of cubic Gd^{3+}, and consists of seven groups of lines. Each of the groups is composed of two equidistant sextets of hyperfine structure of about equal intensity, due to the almost equally present ^{151}Eu and ^{153}Eu isotopes. The values observed in natural samples are reported in Table 1. Some of the lines exhibit partly resolved superhyperfine structure due to the first F^- neighbors. This interaction has been studied up to the fourth shell of F^- neighbors with ENDOR by Baker and Williams (1962) and Baker and Hurrell (1963) for Eu^{2+} ions in synthetic crystals and by Bill (1969b) for Gd^{3+} ions in natural yellow fluorites. From these results there is evidence of a nonnegligeable covalency between the rare-earth ion and the first F^- neighbors (A_{F_S} and A_{F_P} in Table 1), due to overlap of rare-earth ion $4f$ and ligand orbitals. This covalent contribution is difficult to interpret and varies in an unknown way with the distortion of the lattice, but it diminishes rapidly between nearest and next-nearest neighbors. In fact for all neighbors in the second shell, the field is almost totally dipolar.

Table 1. Spin-Hamiltonian parameters for the $^8S_{7/2}$ level in cubic Gd^{3+} and Eu^{2+} $(4f^7)$[a]

S-state ion	g	b_4 (10^{-4} cm^{-1})	b_6 (10^{-4} cm^{-1})	A_{RE} (Gauss)	A_{F_S} (Gauss)	A_{F_P} (Gauss)
Gd^{3+}	1.9918	−46.6	0.07	−	−0.66	1.808
Eu^{2+}	1.9926	−58.74	0.26	^{151}A = 36.9 ^{153}A = 16.4	−0.799	1.452

[a] A_{RE} is the hyperfine structure constant of the rare-earth ion; A_{F_S} represents the isotropic part of the superhyperfine interaction with the nearest F^- neighbors; A_{F_P} gives the anisotropic contribution

A cubic Yb^{3+} center has been identified in many yellow fluorites (Bill, unpublished). Its EPR spectrum shows up at low temperatures, typically below 20–30 K. The parameters of the spin-Hamiltonian are identical to the ones reported by Weber and Bierig (1964) for cubic Yb^{3+} ions in synthetic CaF_2 crystals.

2.2. Tetragonal Center. Gd^{3+} cubic spectrum is often accompanied by another spectrum exhibiting tetragonal symmetry particularly in green and red fluorites. A detailed study has been done on alpine red fluorites by Bill (unpublished). The parameters obtained in this case are:

$$g = 1.9925, \quad b_2^0 = 1480 \cdot 10^{-4}\ \text{cm}^{-1}, \quad b_4^0 = 23.1 \cdot 10^{-4}\ \text{cm}^{-1},$$
$$b_6^0 = 0.6 \cdot 10^{-4}\ \text{cm}^{-1}, \quad b_4^4 = 30 \cdot 10^{-4}\ \text{cm}^{-1}, \quad b_4^6 \simeq 0.$$

These values are within the same experimental errors as those obtained by Sierro and Lacroix (1960) for tetragonal Gd^{3+} in synthetic crystals. The sixth order terms in the spin-Hamiltonian are very small and comparatively inaccurately determined. This tetragonal site can be referred to as a $T_g(F_i^-)$ center, using Baker's notation (Baker, in Hayes, 1974), i.e., an interstitial F^- ion occupying the nearest interstitial site at $00\frac{1}{2}$, and this identification is supported by the similarity of the parameters to those for $T_g(H_i^-)$ definitely identified by Jones et al. (1969) from the local mode of the hydride ion. The difference between b_4^4 coefficients in cubic and tetragonal centers ($-46.6 \cdot 10^{-4}$ cm^{-1} and $30 \cdot 10^{-4}$ cm^{-1}, respectively) indicates a deformation of the local crystal field by the presence of an interstitial F^- ion. This deformation may be due to a polarization effect or to a displacement of some of the neighboring fluorine ions from their normal position.

Colloids

Calcium colloids result from the coagulation of color centers by heating additively colored fluorites (Hayes, 1974), but may also be produced by irradiating the crystals with 75 KeV electrons (McLaughlan and Evans, 1968) or 1.5 MeV protons (Kubo, 1966). It is now recognized that the presence of these colloids is responsible for the deep blue color of Blue-John-type fluorites

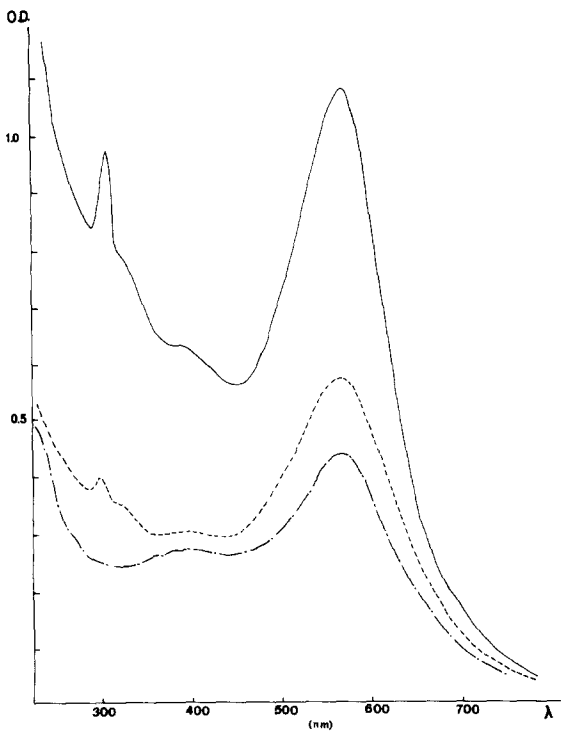

Fig. 6. Optical absorption spectra of purple fluorites from Foisches, France *(straight line)*, Fontsantes, France *(dashed line)* and Djebel el Kohol, Tunisia *(dashed-dotted line)*. Apart from the colloid absorption band near 560 nm, additional bands are visible in relation with other color centers (e.g., the 335 nm and 400 nm absorption bands of the Y-associated F-center)

(Braithwaite et al., 1973), although their formation in natural crystals still remains obscure.

The optical absorption spectrum of intense blue and deep purple fluorites, as seen in Figure 6, consists mainly of a broad absorption band with a maximum lying between 560 and 580 nm, and a width at half peak height of about 120 nm (0.5 eV). Additional weaker absorption bands occur also at 303 nm, 335 nm and 395 nm. The main band is identical to the one observed in Blue John fluorites by MacKenzie and Green (1971) and in synthetic crystals containing colloïds. The bands at 335 and 395 nm are bleached at lower temperature than the 560 nm band, and are probably due to the yttrium-associated F-center. The 303 nm band is not always encountered in natural crystals and was not described by the other authors; its origin is obscure.

The origin of the 580 nm band is not well understood. Using the Mie scattering theory (see, e.g., Przibram, 1953), it is possible to correlate the position of the absorption band and the average size of the colloids: thus, particles with dimensions between 500 and 800 Å give an absorption maximum at 540–580 nm. However, as pointed out by MacLaughlan and Evans (1968) and Braithwaite et al. (1973), no Tyndall effect is observed in those crystals. This implies for colloids encountered in natural fluorites a maximum average particle size of 300–400 Å. Thus, the deep blue or purple color seems to be due mostly to metallic calcium particles. The variability of the colors observed, from deep

purple to intense blue, seems to correspond to an increasing absorption wavelength as particle size increases.

Purple color is frequently observed in natural fluorites and is stable up to 400°–500° C. The formation of metallic colloids is due to long irradiation, and may be facilitated by the presence of numerous defects. Impurities like oxygen or sodium, by creating fluorine vacancies, are known to enhance strongly the coagulation of color centers, and hence the formation of colloids. The relation with radioactive inclusions is exhibited in many samples by the irregular distribution of the color ("pleochroic haloes") which probably arises from short penetrating radiations (Vochten and Geys, 1977). The formation of secondary electrons by γ-irradiation of natural fluorites was suggested by Braithwaite et al. (1973) to be another possible cause of colloid formation. We did not observe dichroic phenomena as those reported by Holgate (1973) and thought by him to be due to an organic chromophore. They may arise from a residual effect of a stress-induced dichroism of large *F*-center aggregates.

Discussion

1. Relation With Growth Processes

Studies of natural single crystals of fluorite by means of X-ray topography showed that the zoning was related to drastic changes in growth conditions (Calas and Zarka, 1973). Chemical analysis of the same zoned crystals were performed to uncover the relation between the growth zones and the colors observed. It can be seen from Table 2 that rare-earth ions content is higher in the yellow zones, comparatively to the blue and purple zones which have similar contents. The same difference was seen in blue-, purple-, and yellow-zoned fluorites from different localities. Sodium content also increases in the yellow zones, and can provide a local charge compensation, thus stabilizing centers like the O_2^- or O_3^- molecular ions. The presence of numerous fluid inclusions in these yellow zones, with a high salinity (Calas and Touray, 1972), may however distort chemical analysis results. The low crystallization temperature of these fluorites (130°–140° C) permitted the incorporation of these molecular ions, which are thermally unstable and cannot be incorporated into the crystal at higher temperatures.

In other samples, the change of colors is not correlated with any significant chemical variation. This is the case in green, purple, and white fluorites studied

Table 2. Rare-earths and sodium contents (in ppm) of zoned crystals from Valzergues (Aveyron, France). Analyst: G. Chaminant (C.N.E.T.)

	La	Nd	Sm	Eu	Tb	Yb	Lu	Σ La–Lu	Na
Yellow zone	2.3	12.0	8.6	5.2	1.1	0.85	0.09	30.14	365
Blue zone	1.8	4.4	1.3	1.1	0.25	0.4	0.03	9.28	77.5
Purple zone	0.8	3.1	2.3	2.1	0.5	0.4	0.03	9.23	66

by Marchand et al. (1976): the green crystals do not exhibit a correspondingly higher concentration of samarium. The role of defects or impurities like O^{2-} or OH^- may then be predominant, but remains not always explained. It must also be pointed out that in a reducing environment ions like Eu^{2+} can be incorporated directly in the divalent state during the growth processes (Guichard, 1974).

2. *Thermal Stability*

The Smakula formula (see Przibram, 1953) was used to obtain the concentration of color centers in the samples we examined, in order to study the kinetics of the thermal bleaching (Calas et al., 1972). We did not use the same formalism for all the colors we studied, but qualitative comparisons were made to deduce the primary or secondary origin of the coloration. The rare-earth ion *F*-center complexes are less stable (the activation energy for thermal bleaching is less than 1 eV), and this implies that they cannot be formed during crystal growth, but only as a result of a permanent irradiation process ("secondary origin": Calas, 1972). Rose, yellow, and green colors are more stable (with an activation energy for thermal bleaching of about 2 eV), and may have both origins: primary, if formed during crystal growth, or secondary by a later irradiation. This latter process leads to a less homogeneous color than the former process does. Purple and intense blue are more stable, up to 400°–500° C, but the high irradiation level needed for the formation of metallic colloids, as well as the usually observed inhomogeneous distribution of this color, indicate that they are related in many cases to radioactive impurities which give a permanent irradiation.

Conclusion

Color centers are nearly always found to be responsible for the colors observed in natural fluorites. However, organic matter causes the brown coloration of some samples, as in the Clay Center (Ohio) fluorites (Calas et al., 1976). We did not study all the colors cited in the literature (e.g., the orange coloration of some Australian fluorites mentioned by Bailey et al., 1974). However the results outlined in this paper give a rough idea of the structure of the most important color centers encountered in almost all the samples. Further work is needed to establish the relationship between the color centers and the geochemistry and the growth conditions of natural fluorites.

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