

ORIGIN OF COLORATION IN SOME FLUORITES¹

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ABSTRACT

Electron paramagnetic resonance and optical absorptions of some natural fluorites correlate with the color of the specimen. This led to the identification of the impurity (YO_2) responsible for coloration of the red fluorites of Switzerland, and to the identification of the probable impurity (Sm^{2+}) responsible for coloration of the green fluorites from Weardale (England) and the Dürschrennenhöhle (Switzerland).

INTRODUCTION

Many papers have been published contributing to the explanation of the origin of the coloration of natural fluorites. Among recent publications, a book written by K. Przi Bram (1956) suggests models of the structures responsible for coloration in natural fluorites and contains an abundant supply of references.

The most widely spread tools in this branch of research are optical absorption and fluorescence spectrometry, X-ray fluorescence spectrometry, thermoluminescence, electron paramagnetic resonance (EPR) and the microscope. In the case of CaF_2 few workers have used EPR, although many of the proposed models imply a resulting electronic magnetic moment.

We have especially studied red fluorites originating from the Gotthard and from the Grimsel (Switzerland) and yellow ones from Cavin Rock (Illinois, USA), Wölsendorf (Germany), Baslerjura (Switzerland) and Puy de Dôme (France) with EPR. Among the red ones we have looked at 55 samples from nine different origins, and among the yellow ones 25 samples from six different origins. We also investigated green fluorites: eight samples from two different crystals from Weardale (Durham, England) and eight samples from two different crystals from the Dürschrennenhöhle am Säntis (Switzerland).

EXPERIMENTAL TECHNIQUES

The resonance measurements were performed on a Varian X-Band EPR spectrometer at room temperature or at the temperature of liquid nitrogen. For low temperature measurements we used a cryostat built at the institute. The magnetic field of the Varian nine-inch magnet was measured with a self-made NMR-equipment with either built-in 100 kHz standard or a Hewlett-Packard 524c frequency counter. The microwave frequency was measured with a Hewlett-Packard 540b transfer oscillator together with the HP frequency counter.

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For optical work we used a Beckman DK2A double beam spectrophotometer. The optical measurements were all performed at room temperature.

We irradiated the samples with X-rays from Philips tubes (50 kV/20 mA or 24 kV/40 mA); the distance between the crystal and the window of the tube being three to six centimeters.

Bleaching experiments were done between 100°C and 370°C in an oil bath furnace. After the desired interval, the samples were cooled with forced air or in alcohol at room temperature. The temperature of the oil bath was measured with a mercury thermometer (0–400°C) and was held constant to $\pm 1.5^\circ\text{C}$ merely by regulating the current of the furnace by hand.

The synthetic crystals necessary for our investigation were grown by the Bridgmann-Stockbarger method at our laboratory.

RESULTS AND DISCUSSION

We have classified the crystals according to colour. Table 1 gives the detected and identified magnetic complexes found in EPR work and the optical absorption bands measured between 1000 and 210 $m\mu$ at room temperature.

The impurity concentrations are precise to about a factor of five. They were established with EPR by comparing the lines with a standard substance of known concentration of the magnetic centre (pitch in KCl supplied by Varian).

Red fluorites. All the red samples at our disposal showed an EPR spectrum arising from what we call the *R* center. This center was first observed and reported by Sierro (1963).

Comparison of the intensity of the EPR spectrum of the *R* center with the intensity of the coloration of the different samples led to the assumption of a relation between them. Bleaching experiments on different samples with simultaneous measurement of the height of the EPR lines and the intensity of the optical absorption peak at 483 m showed quantitative correlation *e.g.*, the two arise from the same structure, the *R* center.

Very detailed EPR measurements made it possible to establish its local magnetic symmetry and to evaluate the constants of the appropriate spin-Hamiltonian. The symmetry is orthorhombic and the electronic magnetic moment has its principal axes along a four-fold and two mutually perpendicular two-fold axes which lie in a plane perpendicular to the four-fold one. Furthermore magnetic data show the interaction of the electronic magnetic moment with two equivalent nuclear moments along the four-fold axis and with a third one along a two-fold axis.

Within the error of measurement the EPR and optical data of the *R* center showed to be the same as those which Bill and Lacroix (1966) had determined on a center in artificial CaF_2 crystals. This center appears when pure CaF_2 crystals, doped with YF_3 , were hydrolysed and afterwards X-irradiated. The density obtainable from centers grows with

TABLE 1. EPR AND OPTICAL MEASUREMENTS OF FLUORITES

No. of group	Colour	Origin	Treatment	EPR results	Optical Results (Wavelengths in $m\mu$)
1	red	Goescheneralp, Juchli, Grimse, Grimsehöllen +6 different crystals of unknown origin in Switzerland.	None. X irradiated at room temp. Bleached.	R center, ^a sometimes Gd^{3+} in tetragonal symmetry, ^{b,c}	483/272/263. Often some weak suppl. lines in IR and UV. The above absorptions together with four new bands ^e at 570/400/330/225.
2	green-violet	Wearidale.	None.	R center disappears, also Gd^{3+} . $Eu^{3+}Cd^{2+}$ in cubic symmetry ^d (about 90% of Gd^{3+}) and Gd^{3+} in tetrag. symmetry (about 10%). Concentration of both elements in the order of 0.01%.	Absorption at 483 and the four bands at 570/400/330/225 disappear.
3	pale green	Dürschrennenhöhle am Säntis.	None.	Gd^{3+} in cubic and in tetragonal symmetry (about same intensity of both spectra).	690/609/440/422/353/333/305.2/277/255/217: intensity of absorption growing with diminishing wavelength in UV.
4	yellow	Cavin Rock, Wölsendorf, Pay de Dôme, Baslerjura.	None Bleached.	Yellow center, ^e Gd^{3+} in cubic symmetry in very varying concentration ($\leq 0.01\%$). Yellow center destroyed irreversibly; most of the Gd^{3+} resonance disappears.	690/605/442/422/360/305/281/258: intensity of absorption growing with diminishing wavelength in UV. 433/294.
Artificial	green	$CaF_2 : SmF_3$ (0, 01%)	Bleached and X-rayed at room temperature X irradiated. Hydrolysed and X irradiated	Vr center ^f appears, center not stable at room temperature.	Absorption at 433 has disappeared irreversibly. Crystal is colored blue, color not stable at room temperature. 680/610/440/422/396/355/305.5/281/255/240/(218). 691/612/440/421/370/355/305.5/: strong absorption in UV, intensity growing with diminishing wavelength.

EPR measurements all at X-band. When not otherwise stated results given were measured at room temperature.

^a Bill, Lacroix (1966) ^b Baker, Bleaney and Hayes (1958). ^c O'Connor, Chen (1963). ^d Rytter (1957). ^e Sierro (1963).

^f Sierro (1965).

growing Y content of the CaF_2 crystals. Furthermore Bill and Lacroix have shown that the presence of both yttrium and oxygen is necessary to produce the center. They applied the same procedure as is to crystals containing *other* metal fluorides and never found this spectrum. Tentatively they proposed the following model: in a CaF_2 crystal, which has the symmetry O_h^5 , Ca ions are replaced by Y ions. At the cubes formed by F^- ions surrounding the Y ions two adjacent F^- ions are replaced by two oxygens. X rays eject an electron from the oxygen ions, which on their part now form like a molecule O_2^{3-} stabilized by the trivalent yttrium. The ejected electron is trapped somewhere in the crystal.

The correspondence between the measurements on the artificial crystals with those on the natural ones gives the explanation of the nature of the *R* center in fluorites. Chemically speaking, the *R* center is an association of an yttrium ion with two oxygen ions placed as an impurity in the crystal and ionized in course of time by natural radiation.

Measurements on a JEOL X-ray microanalyzer (Kontron 1966) have confirmed the simultaneous presence of yttrium and oxygen in the red fluorine samples examined.

The bleaching experiments performed on the natural red crystals gave the following supplementary information:

Not all of the samples showed the same bleaching temperature, especially those which had been X-irradiated. Probably the same electron-trapping mechanism is not always effective, *e.g.* according to their thermal stability the different electron-trapping centers release their trapped electron at different temperatures. This electron combines then with an *R* center.

The association of oxygen ions with yttrium is stable at least up to 700°C because crystals which had been heated to this temperature under high vacuum conditions show the center again after X irradiation.

After X irradiation, many of the red fluorites show four supplementary optical absorption bands (Table 1). This proves the existence of yttrium ions not implicated in *R* centers. Irradiation converts these trivalent ions into divalent ones which are responsible for the appearance of the four bands (O'Connor and Chen 1963). There is a possible explanation why the four bands appear only after X-irradiation of the crystals in the laboratory. Different workers have shown (Blanchard, 1966) that most of the natural fluorites show feeble radioactivity. This activity is responsible for the ionization of the yttrium-oxygen cluster, producing the *R* center. During the same time the yttrium not implicated in *R* centers is reduced to the divalent state. But the Y^{2+} ions bleach thermally at room temperature (O'Connor and Chen 1963), so the coloration mechanism is bal-

anced by the bleaching mechanism. As the radiation level is very low, undetectably few supplementary Y^{2+} ions are present without supplementary strong X irradiation.

Green Fluorites. The green crystals (Weardale, Dürrschrennenhöhle) do not show any resonance spectrum correlated with the coloration of the crystals, but optical measurements show a pronounced spectrum common to both groups. This same spectrum has been measured by Görlich, *et al.*, (1961) in artificial fluorite crystals doped with Sm. We have reproduced it in very pure CaF_2 crystals doped with 0.01 weight percent SmF_3 . After X irradiation, the crystals showed a green coloration with the spectrum given at the end of Table 1.

Hydrolysis followed by X irradiation of the crystals enhances greatly the coloration but does not change the position of the main absorption bands except that the absorption in the UV grows strongly towards shorter wavelengths. On the basis of this observation we attribute the green coloration of groups 2 and 3 of our fluorites to the presence of Sm^{2+} in the crystals. This ion, being diamagnetic, does not give EPR signals. It is perfectly stable at room temperature in the fluorite matrix (O'Connor and Chen 1963). By heating the green samples to about $300^\circ C$ the color bleaches and Sm^{2+} is converted to the trivalent state.

Yellow fluorites. All the yellow crystals present an EPR spectrum which we call a *yellow center*. It was observed for the first time by Mme A.M. Germanier. Sierro (1963) determined the angular variation of the center and found that the EPR center and the yellow coloration disappeared together upon heating the crystals. The EPR measurements show an electronic spin $S = \frac{1}{2}$. The symmetry of the center is approximately axial with the axis along one of the three non-equivalent four-fold cube axes. Our pulse annealing experiments have shown quantitatively the correlation between the optical absorption at $433 m\mu$ which produces the yellow coloration and the EPR signal.

The center is irreversibly destroyed by heating the crystal to about $300^\circ C$. Further experiments on this center are in progress. Most of the studied crystals contain Gd^{3+} and many Eu^{2+} also. As the two ions do not have any optical absorption bands in the visible region, they do not contribute to coloration of natural fluorites.

SUMMARY

For the red fluorites from Switzerland we propose a center which is responsible for the coloration of those crystals *e.g.*, a YO_2 complex. In the green ones from Switzerland and from Weardale Sm^{2+} is probably responsible for the green coloration. Both centers are radiation-induced. In

the yellow crystals we have established correspondence between the optical absorption peak at $433 \text{ m}\mu$ and an EPR spectrum designated *yellow center*.

Work is continuing in this domain.

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REFERENCES

- BAKER, J. M., B. BLEANEY AND W. HAYES (1958) Paramagnetic resonance of S-state ions in calcium fluoride. *Proc. Roy. Soc. London Ser. A*, **247**, 141.
- BILL, H. AND R. LACROIX (1966) EPR of a centre in Y^{3+} doped artificial CaF_2 crystals. *Phys. Lett.* **22**, 250.
- BLANCHARD, F. N. (1966) Thermoluminescence of fluorites and age of deposition. *Amer. Mineral.* **51**, 476.
- GÖRLICH, P., H. KARRAS AND R. LEHMANN (1961) Über die optischen Eigenschaften der Erdalkalihalogenide vom Flussspat-Typ (I). *Phys. Stat. Sol.* **1**, 389.
- HAYES, W. AND J. W. TWIDELL (1962) The Self-trapped Hole in CaF_2 , *Proc. Phys. Soc. London* **79**, 1295.
- O'CONNOR, J. R. AND J. H. CHEN (1963) Color centers in alkaline earth fluorides. *Phys. Rev.* **130**, 1790.
- PRZIBRAM K. (1956) *Irradiation Colours and Luminescence*, Pergamon Press, London.
- RYTER, C. (1957) RPE de l'europium et du gadolinium soumis à un champ cristallin cubique. *Helv. Phys. Act.* **30**, 353.
- SIERRO, J. (1963) RPE de Gd^{3+} dans CaF_2 , BaF_2 , SrF_2 . *Helv. Phys. Act.* **36**, 505.
- (1965) Paramagnetic Resonance of the V_F Centre in CaF_2 . *Phys. Rev.* **138A**, 648.
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