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P. Mollema, H. den Hartog. COLOR CENTERS IN SrCl₂. Journal de Physique Colloques, 1973, 34 (C9), pp.C9-507-C9-510. <10.1051/jphyscol:1973985>. <jpa-00215461>

HAL Id: jpa-00215461

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Submitted on 4 Feb 2008

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COLOR CENTERS IN SrCl₂

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Résumé. — Nous indiquons les résultats des expériences optiques et EPR sur des centres colorés dans des monocristaux de SrCl₂ colorés additivement et subtractivement. Dans les cristaux colorés additivement nous pouvons obtenir des centres F seulement après trempe très rapide. Nous trouvons que dans les cristaux dopés avec O²⁻ la formation des centres F est impossible.

Des centres F sont observés avec des expériences optiques et EPR et les résultats montrent que la bande F dans SrCl₂ est située à environ 630 nm. Superposée avec le spectre EPR du centre F, formé de 15 raies, nous avons observé une étroite raie EPR, due probablement à des électrons de conduction dans de très petits précipités de Sr.

Il est impossible de colorer nos cristaux avec des rayons X à 300 K, 80 K et 4 K, ce qui montre la haute pureté de ces cristaux, spécialement par rapport à l'ion O²⁻. Nous avons trouvé que ces ions augmentent considérablement la coloration. Avec des petites concentrations de O²⁻ il était possible de colorer ces cristaux à 4 K, mais, quand nous augmentions la concentration de O²⁻, il était possible d'observer une coloration jusqu'à 140 K. Les centres formés sont principalement des centres V_K et des centres F perturbés. Les centres V_K peuvent être alignés suivant la direction $\langle 100 \rangle$; les centres F perturbés sont alignés, à 80 K et 4 K, dans la direction $\langle 111 \rangle$. Nous avons réalisé des expériences équivalentes dans SrCl₂ dopé avec NaCl, YCl₃ et SrH₂.

Abstract. — Results of optical and EPR-experiments on color centers in additively and subtractively colored SrCl₂ single crystals are reported. In additively colored crystals F-centers could be obtained only after extremely rapid quenching. It was found that in crystals doped with O²⁻ even with the very high quenching rate it was impossible to produce F-centers. The F-centers were detected both optically and with EPR and these experiments indicate that in SrCl₂ the F-band is located at about 630 nm. Superimposed on the F-center EPR-signal consisting of 15 lines a narrow EPR-line was observed, which is probably due to conduction electrons in very small Sr-precipitates.

Our pure crystals could not be colored with X-rays at RT, LN₂T and LHeT, indicating a high purity especially with respect to O²⁻-impurities. These ions were found to enhance the colorability considerably. At very low O²⁻-concentrations the crystals could be colored at LHeT but as the O²⁻-content is increased further also radiation damage can be observed at temperatures as high as 140 K. The centers formed are mainly V_K and perturbed F-centers. The V_K-centers can be aligned along $\langle 100 \rangle$; the perturbed F-centers along $\langle 111 \rangle$ at LN₂T and LHeT. Similar experiments have been performed on SrCl₂ doped with : NaCl, YCl₃ and SrH₂.

1. Introduction. — After most of the physical properties of color centers in the alkali halides were studied in great detail the research of color centers concentrated fairly extensively at the group of alkaline earth fluorides CaF₂, SrF₂ and BaF₂. Because some of the properties of color centers depend sensitively upon the lattice parameter it was useful to extend the investigation to SrCl₂ which also has the CaF₂ lattice structure.

One of the main problems encountered when one studies color centers in SrCl₂ is the very strong hygroscopicity of the material. For the preparation of samples of optical quality it is necessary to treat them in a properly dried atmosphere or in vacuum. According to the lattice structure one expects that the F-center in SrCl₂ is coordinated tetrahedrally by four Sr⁺⁺-ions (see Fig. 1) while the next shell consists of six Cl⁻-ions. The formation of pure F-centers by means of additive coloration was achieved ;

very high quenching rates had to be used owing to the extremely high coagulation rate. The F-band in additively colored SrCl₂ was found to be at 630 nm by means of a combined optical and EPR-experiment. The general features of the EPR-signal due to F-centers are fairly well understood which makes the assignation of the F-band in SrCl₂ unambiguous.

Pure SrCl₂ crystals can not be colored with X-rays at RT, LN₂T or LHeT. No selective absorption has been observed in the wavelength region 200-1000 nm after irradiation with X-rays for several hours. In crystals doped very slightly with O²⁻-ions coloration was observed at LHeT. When the concentration of O²⁻-ions is increased the threshold temperature at which coloration can be observed increases. At high O²⁻-concentrations coloration may even be observed at 140 K. The optical bands in SrCl₂ : O²⁻ are situated at 405, 580, 655 and about 750 nm. Except for one extra band the same spectra were

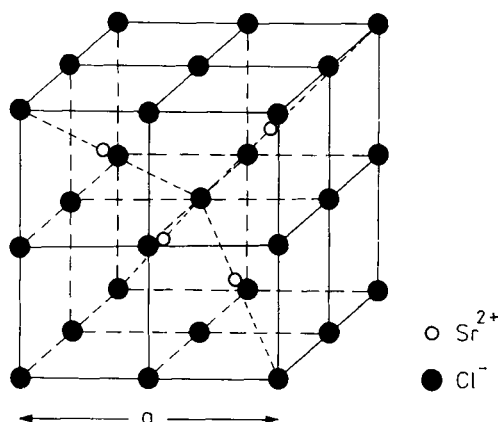


FIG. 1. — Schematic representation of the F-center in SrCl_2 .

observed for $\text{SrCl}_2 : \text{Na}^+$. A different coloration behavior was found for crystals doped with Y^{3+} and H^- -ions.

It will be shown that among the color centers produced by subtractive coloration there are no pure F-centers. There are however perturbed F-centers referred to as F^* -centers which give rise to an unresolved EPR-line and two optical absorption bands (580 and 655 nm). These two bands are due to different excitations of the center.

2. Experimental results and discussion. — Figure 2 curve 1 shows the optical absorption spectrum of an additively colored SrCl_2 sample quenched *very* rapidly. Curve 2 is the spectrum corresponding with the same sample after a few hours storage in the dark. The difference between curves 1 and 2 which is given in the box of figure 2 shows a peak at 630 nm.

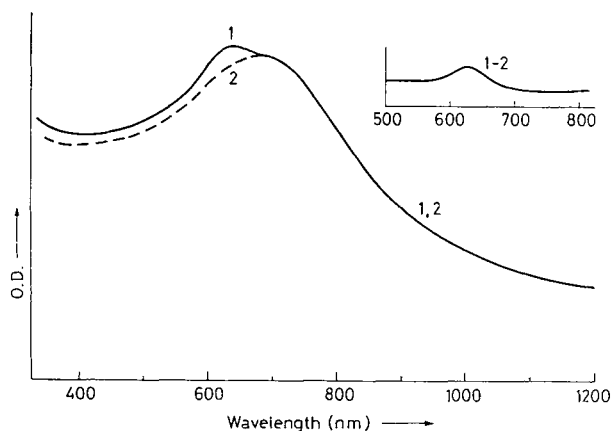


FIG. 2. — Optical absorption spectrum of an additively colored SrCl_2 crystal quenched very quickly; curve 1: immediately after quenching; curve 2: after 17 h storage in the dark at room temperature; curve 1-2: difference between curves 1 and 2.

The EPR-signal of the same sample immediately after quenching is shown in figure 3. The spectrum shows 15 approximately equidistant lines. The separation between two successive lines is 7.5 G and the

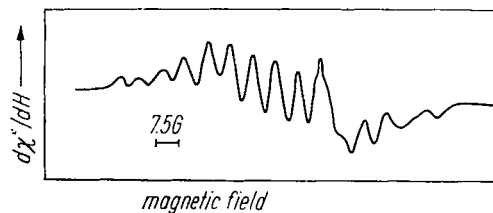


FIG. 3. — Derivative of the EPR absorption of very quickly quenched SrCl_2 measured at 300 K.

g -value of the signal is 1.989. After a few hours storage in the dark at room temperature the above described spectrum disappeared leaving only one single line at $g = 2.000$ which was also present in the original signal. Although there is no direct proof we believe that this signal is caused by conduction electrons in very small Sr precipitates. Similar signals have also been observed in improperly quenched and heat treated additively colored CaF_2 , SrF_2 and BaF_2 [1].

The resolved EPR signal can be compared with a theoretical F-center signal. The latter one is shown in figure 4. We have to take into account the fact that there are two different kinds of Cl-nuclei (Cl^{35} and Cl^{37}) both with nuclear spin $\frac{3}{2}$ but with slightly different magnetic moments. This leads to a sum of seven different signals corresponding with situations with 6 Cl^{35} , 5 $\text{Cl}^{35} + 1 \text{Cl}^{37}$, 4 $\text{Cl}^{35} + 2 \text{Cl}^{37}$..., 6 Cl^{37} -nuclei in the first shell of chlorines. From figure 4 it is obvious that the most outerlying lines are too weak and wide to be detected.

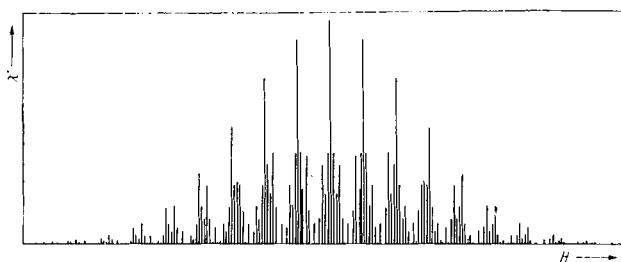


FIG. 4. — Theoretical EPR absorption spectrum of the F-center in SrCl_2 . The absorption peaks are represented by vertical lines; the length of the lines is a measure for the intensity.

The above described combined optical and EPR experiment shows clearly that the 630 nm band is correlated with the F-center EPR-signal. Therefore, the 630 nm band is the F-band in SrCl_2 . From a thermal bleaching experiment at 350 °C we found that a band at 570 nm is correlated with the narrow unresolved EPR line at $g = 2.000$ [2].

Contrary to the results obtained by Matei [3] we were not able to color our crystals by means of X-rays. The experiments were carried out at temperatures between 5 and 300 K. This result is indicative for the important role that impurities play in the radiation damage processes. When a very small amount of O^{2-} is added coloration may be obtained at the

lowest temperatures (e. g. 5 K). Increasing the amount of O²⁻ present in the crystals leads to an increase of the temperature at which coloration can be observed. Figure 5 shows the result obtained with a sample doped with a very small amount of O²⁻ X-irradiated and measured at 5 K.

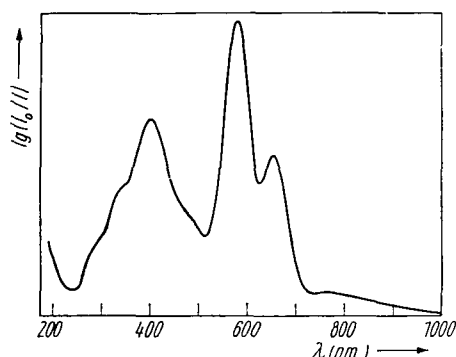


FIG. 5. — Optical absorption spectrum of a SrCl₂ crystal containing O²⁻ irradiated with X-rays for 120 min. at 5 K measured at 5 K.

The spectrum is very similar to the one obtained by Matei after irradiation at 140 K. The band at 400 nm is due to V_k-centers. This has been shown by EPR-experiments carried out in our laboratory and also by some other groups (Lefrant *et al.* [4] and Hayes *et al.* [5]).

The bands at 580 and 655 nm belong to one single type of center which turned out to be paramagnetic. The two bands can be made dichroic by means of optical bleaching with polarized light and these experiments indicate that the centers corresponding to the 580 and 655 nm-band are along < 111 >-directions of the crystal lattice.

In order to obtain more information concerning the radiation damage processes that take place in SrCl₂ we have performed experiments on crystals doped with NaCl, YCl₃ and SrH₂. In figure 6 we

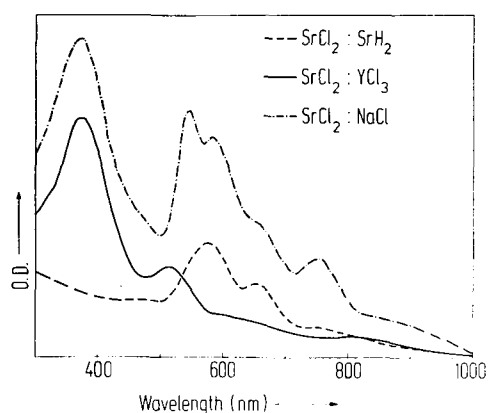


FIG. 6. — The optical absorption spectra of X-rayed SrCl₂ doped with SrH₂ (90 min. dose at 80 K); YCl₃ (150 min. dose at 80 K) and NaCl (150 min. dose at 135 K).

show the results. Apart from one extra band one observes that the spectrum corresponding with SrCl₂ : NaCl is very similar to that of SrCl₂ : O²⁻. The crystal doped with YCl₃ does not show any selective absorption at 580 and 655 nm but there is a strong band at 400 nm (V_k). The crystal doped with hydrogen does not show V_k absorption but there are strong 580 and 655 nm bands. The most important results presented here are compiled in table I.

TABLE I

Color centers in X-rayed SrCl₂

Dopant	Electron centers	Hole centers	Others
—	—	—	—
O ²⁻	F*	V _k	—
Na ⁺	F*	V _k	—
H ⁻	F*	—	H ⁰ interstitials
Y ³⁺	—	V _k	Y ²⁺ (?)
pure	—	—	—
pure additive coloration	F	—	—

The general feature of the results is that they simply correspond to a redistribution of electrons (the result for the hydrogenated crystals forms an exception). The interpretation of the optical experiments given in table I are supported by EPR experiments.

It should be emphasized that the results obtained for SrCl₂ are similar to those reported for the alkaline earth fluorides. For the latter group of materials it was observed that X-irradiation at LHeT produces perturbed F-centers, which can be aligned along < 111 >, together with V_k centers. It is possible that the pure alkaline earth fluoride crystals available now are still contaminated by O²⁻ ions.

The present experiments indicate that the radiation damage processes in the fluorite type alkaline earth halides are not yet understood completely. They suggest that the observed coloration is due to the presence of impurities like O²⁻ in nominally pure material. It is certain that the electron centers formed in SrCl₂ doped with Na⁺, O²⁻ or H⁻ are very similar. The nature of these centers has not been resolved yet, although we know that the center has a transition moment along the < 111 > direction of the crystal. Furthermore, the EPR-results suggest that this center is closely related with the F-center.

With the present knowledge we tentatively propose the following mechanism for radiation damage in SrCl₂. Only pairs of F* and V_k-centers are produced. The fact that F*-centers are not formed in pure and Y³⁺-doped samples indicate that the electron trap contains an anion vacancy. In the present mechanism the production of Frenkel pairs in the anion sublattice is not necessary because vacancies are present in

sufficient amounts in Na^+ and O^{2-} -doped crystals. In hydrogenated crystals the formation of electron excess centers is very similar to that in the alkali halides. In Y-doped crystals the anion vacancy concentration is suppressed, therefore the only electron

traps available are Y^{3+} -ions. We suggest that in these crystals Y^{2+} -ions are formed together with V_k centers. This is supported by our EPR-experiments where in addition to the V_k signal an extra narrow unresolved signal was observed which may be due to Y^{2+} -ions.

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