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Colour centres in LiF : Mg crystals

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Résumé. — Deux types de centres H^0 et un centre H^- ont été trouvés par RPE et absorption UV dans le vide, dans des cristaux de LiF : Mg irradiés aux rayons X. Les centres appelés Z_3 et Z_2 dans LiF : Mg ne peuvent pas être identifiés à aucun centre Z, ils sont plutôt en connexion avec l'impureté OH.

Abstract. — Two types of H^0 centres and one H^- centre were found by ESR and vacuum UV measurements in X-irradiated LiF : Mg. The so called Z_3 and Z_2 centres in LiF : Mg are not identical with any Z centre and are rather connected to the OH impurity.

1. Introduction. — A thorough knowledge of colour centres in LiF : Mg is necessary for understanding the TL mechanism in this thermoluminescent dosimetry material. Some authors emphasize the role of OH and O [1-4], but others are of the opinion that most important in the TL mechanism are Z centres [5-7].

The optical absorption bands at 310 and 225 nm were previously identified as Z_2 and Z_3 bands, respectively, since they follow a Mollwo-Ivey type relationship [5, 7] and since the second is produced from the first by thermoionization [6] or photoionization [7].

In X-irradiated LiF : Yb, we have shown the presence of monovalent Yb (unpublished ESR result) though Yb is a typical dopant forming Z centres in KCl [8]. But Mg ions form ordinary Z centres neither in NaCl nor in KCl [9, 10]. Therefore it was necessary to re-examine the assumptions made about Z centres in LiF : Mg.

2. Experimental. — Merck suprapure LiF was doped by 3×10^{-4} mole fraction of MgF_2 . Single crystals were grown by a vertical zone melting technique in inert atmosphere. LiF : (Mg, OH) crystals were grown in air. The annealing treatments were made in air. The X-irradiation was carried out by a THX-250 deep-therapy apparatus operated at 200 kV, 20 mA and $\sim 9\,000$ R/min. For ESR and vacuum UV measurements an ERS-XQ type spectrometer and a Beaudouin MVR-100 type monochromator were used, respectively.

3. Results and discussion. — The ESR spectrum of an as cleaved LiF : Mg crystal X-irradiated for 3 hours is very complex (Fig. 1a). Annealing this sample the intensities of some lines decrease. For annealing temperatures between 130 and 220 °C

a doublet appears (Fig. 1a). The ESR parameters of this doublet are :

$$A = (47.5 \pm 2) \text{ mT}, \quad g = 2.007 \pm 0.001.$$

This centre may be identified as a H atom, since the proton HF constant in a free H atom is 50.7 mT and the U_2 and U_3 centres (H^0 in various positions) possess similar HF constants in alkali halides [11-13].

The presence of H^0 indicates with great probability that the LiF : Mg contains OH impurities.

Rising the annealing temperature to 440 °C (Fig. 1b) the ESR spectrum consisting of lines 2, 4 and 6 becomes dominant. Measuring the same sample at lower than room temperature, one can easily see that this spectrum is still complex (Fig. 1c). Therefore the ESR parameters of the spectrum measured at RT (lines 2, 4 and 6) can be given only tentatively (Table I) using the spectra obtained for various orientations of the magnetic field relative to the crystal axes (Fig. 1c). After annealing at 500 °C the ESR spectrum disappears.

Figure 2 shows the vacuum UV absorption spectrum of a non-irradiated LiF : Mg. The band at ~ 124 nm may be due to OH impurities. The spectrum of the crystal X-irradiated for 1 hour is very complex. After annealing at 400 °C the spectrum consists of the bands at 127, 222 nm (hypothetic Z_3 band) and of absorption in the 150-190 nm range (Fig. 2).

A band at 127.3 nm was identified in LiF as a H^- ion [14], one can assume that the band at 127 nm is the same.

Repeating the measurements in LiF crystals containing various amounts of Mg and OH one can see that the absorption band at 222 nm and the RT ESR spectrum (lines 2, 4 and 6) are correlated. Thus the latter ESR spectrum is due to the so called Z_3 centre.

Paramagnetic centres of Z-type should have ESR

Fig. 1. — ESR spectra of as cleaved LiF : Mg X-irradiated for 3 hours. *a, b*) After annealing the same crystal at the temperatures indicated, $H \parallel [100]$, measured at RT; *c*) After annealing at

440 °C, $H \parallel [100]$, measured at - 100 °C (upper spectrum), the same as before but measured at RT (central spectrum), the same as before but $H \parallel [110]$, measured at RT (lowest spectrum).

Table I. — Values of various components of the HF-, g -tensor and of the peak-to-peak line widths of the ESR spectra.

Centre	Host material	$ A $ (mT)	g	ΔH (mT)	Refs.
F	LiF	—	2.000	15	[15]
	KCl	—	1.996	4.6	
Z_3	KCl	—	1.996	3.9	[16]
$\cdot OH$		$A_x = 2.6$	$g_{\perp} = 2.007$		[17]
		$A_y = 4.4$	$g_{\parallel} = 2.06$		
		$A_z = 0$			
FOH^-	aqueous	$A_x(H) = 2.5$	$g_{\perp} = 2.009$		[17]
	KF	$A_y(H) = 4.0$	$g_{\parallel} = 2.1$		
		$A_z(H) \sim 0$			
	LiF : Mg	$A_{\perp} \sim 2.0$	$g_{\perp} \sim 2.006$	~ 1.3	present work
		$A_{\parallel} \sim 0$	$g_{\parallel} \sim 2.029$	~ 2.6	

spectra similar to that of the F centre. This is really the case for the Z_3 centre in KCl (Table I). Comparing the ESR parameters of the F centre in LiF and the ESR spectrum in question, the differences are obvious. From these and the similarities to $\cdot OH$ and FOH^- radicals (Table I) one may conclude that this centre is not of Z-type but probably one connected to the OH impurity.

Further on one has to assume, that the centre from

which the so called Z_3 centre can be created by ionization, is no Z_2 centre, either.

In LiF(Mg, OH) annealed at 600 °C and X-irradiated for 3 hours a new complex ESR spectrum is produced (Fig. 3). (The same spectrum can probably be produced in annealed LiF : Mg, but its concentration is very low.) The central part of the spectrum is again the superposition of several spectra, therefore only the wing lines could be used for analysis. The

Fig. 2. — Vacuum UV spectra measured at RT of LiF : Mg (—), after X-irradiation for 1 hour and after annealing at various temperatures : 400 °C (—), 450 °C (...) and 500 °C (— — —).

splittings and intensity ratios of the HF and SHF lines could be interpreted as due to a H^0 occupying a cation site surrounded by 5 F^- ions and probably one anion vacancy. The ESR parameters can be given qualitatively because of the superpositions :

$$A(H) \sim 55.6 \text{ mT}, \quad |A_{\parallel}(F)| \sim 12 \text{ mT}, \\ |A_{\perp}(F)| \sim 7.4 \text{ mT} \quad \text{and} \quad g \sim 2.003.$$

4. **Conclusion.** — On the basis of the results presented, one can say that the LiF : Mg crystals grown in inert atmosphere are not OH-free. X-irradiation results in various centres (H^0 , H^- and OH) like in other alkali halides containing OH^- . These centres must be taken into account in the interpretation of the TL mechanism.

Fig. 3. — ESR spectra measured at RT of annealed (at 600 °C) LiF : (Mg, OH) X-irradiated for 3 hours. a) $H \parallel [100]$; b) $H \parallel [110]$. The expected spectra were calculated assuming a H^0 at a cation site surrounded by 5 F^- ions. The largest splitting is due to

the HF interaction with the proton in both spectra. Two different SHF spectra due to the interactions with F nuclei are superimposed in both orientations in accordance with the two possible different positions of the F^- vacancy.

DISCUSSION

Question. — W. A. SIBLEY.

Sometime ago Bill Johnson and John Nadean showed a direct relationship between the concen-

tration of Ca^{2+} and the OH concentration in NaCl as measured by infrared absorption ($Ca(OH)_2$). Did you measure the infrared absorption for your crystals ?

Reply. — A. WATTERICH.

T. G. Stoebe showed the IR absorption spectrum of $\text{Mg}^{2+}\text{-OH}^-$ complexes in LiF. We checked our LiF : Mg crystal and found the same line at 2.8 μ .

Question. — S. P. MORATO.

Did you correlate your ESR data with thermally stimulated luminescence data ?

Reply. — A. WATTERICH.

We checked our LiF : Mg crystal by thermoluminescence measurement and we got quite the same glow peaks as usual, but we have measured TL at RT as well.

Question. — R. J. FRIAUF.

Some years ago a student of mine (F. Pilcher) made optical absorption measurements on LiF : Mg crystals colored at high temperature (about 200 °C) by neutron irradiation. We observed a definite relationship between the height of the 222 nm band and the amount of magnesium present. There may well have been some OH^- present, but we did feel that the 222 nm band was definitely related to the presence of Mg.

Reply. — A. WATTERICH.

We don't argue against the Mg content of the colour centre giving absorption band at 222 nm.

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