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$[H_2O^-]_z$ CENTRES IN LiF:OH$^-$ CRYSTALS

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Abstract—Electron-irradiated LiF:OH$^-$ crystals at −30°C exhibited a new centre absorbing in the region of F_z centre at 380 nm. The kinetics of defect formation and destruction suggest that both OH$^-$ and Mg^{++} impurities must be present in the host to propitiate its production. The isomorphism between the observed excitation spectra of this centre with the absorption of H_2O^- centres in alkali chlorides and bromides crystals, suggested that it must be of the same nature, i.e. a 'wet F_z centre', although more stable due to the intrinsic Mg^{++} effects. © 1997 Elsevier Science Ltd. All rights reserved

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1. INTRODUCTION

The high energy irradiation of OH$^-$ doped LiF crystals with e^-, γ or X-ray, primarily produces the OH$^-$ dissociation into oxygen and hydrogen atomic entities and anionic vacancy (V_a) [1]. Well after irradiation, the oxygens may get back into the vacancies producing the O$^-$ centres. The O$^-$ centre may capture a free electron and a migrating vacancy to form the O^{2-}–V_a centre, or capture a mobile atomic oxygen to produce the O_2^- centre [2]. The atomic neutral hydrogen may capture a free electron, producing the U_1 centre, or react with an F centre, forming the U centre [3]. Besides, we have seen a new defect called Y centre which was identified as a 'wet F_z centre' or $[H_2O^-]_z$, i.e. an F_z centre with a water molecule embedded.

In this paper, we report the results from an extensive investigation of the optical properties of this new centre which culminates with a configurational model proposition. The importance of this study is to supply additional information about the formation mechanism of secondary oxygen defects which is not yet well understood. The secondary products of high-energy irradiation play an important role in the stabilization of color centres as F_2^+ and F_2^- in LiF, useful for laser applications as laser medium or saturable absorbers [4, 5].

2. EXPERIMENTAL

Pure LiF and LiF:OH$^-$ used in this work were grown by Czochralski's method in our crystal growth laboratory. The concentration of OH$^-$ centres, initially present in the host, was determined by measuring the main IR absorption of OH$^-$ at 2.7 μm. The measured OH$^-$ concentration was 1×10^{18} cm^{-3}. Besides, the presence of Mg^{++} impurity contamination was found in all the used samples with a level not higher than 25 ppm.

The high energy irradiation was done at 230 K with electrons of 1.5 MeV and doses between 10 and 40 Mrads. The investigation methodology consisted of following the luminescence of the Y centre, measured at several distinct situations, using a luminescence (or excitation) spectrometer with two arms displayed at 90°. In order to have a quantitative luminescence analysis of several LiF crystals, the samples were placed in a sample holder with a mask to maintain consistent excitation and collection areas.

3. RESULTS

The e^--irradiation of LiF:OH$^-$ crystals at 230 K with 10 Mrads revealed the presence of O_2^- centres, as seen by the well known structured emission band at 470 nm (see Fig. 1). The excitation spectrum of 473.5 nm luminescence, near the O_2^- centre emission, shows the existence of a structured excitation (absorption) band at 375 nm (see Fig. 2). Only the irradiated OH$^-$ doped LiF crystals exhibit this type of absorption (excitation). The same e^--irradiation of Mg^{++} doped LiF crystals (25 ppm) produces only the F_z absorption band in that spectral region (see Fig. 2). An indication that this structured excitation band at 375 nm, produced only in irradiated LiF:OH$^-$ crystals, is due to a unique centre with several transition probabilities was obtained after following the maximum intensities of three distinct positions with

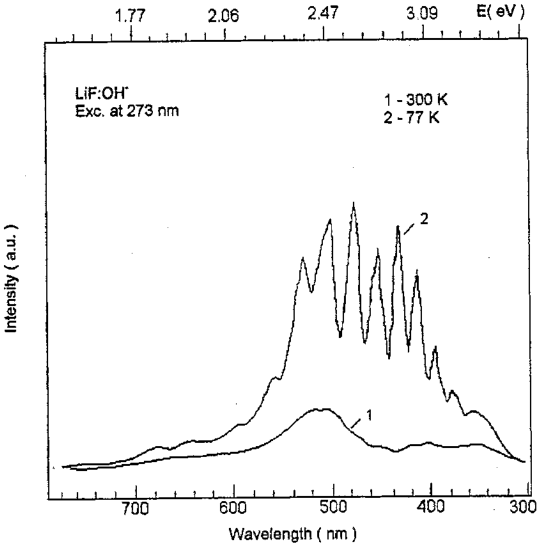

Fig. 1. Emission band of O_2^- centres produced by e^--irradiation of LiF : OH^- (1×10^{18} cm^{-3}) at 230 K with 10 Mrads. Its presence is evidenced by the well known structure at 470 nm. The excitation was done with 273 nm light at (1) 300 K and (2) 77 K.

increasing irradiation dosage. Figure 3 shows that the three excitation intensities at 356, 378 and 397 nm, are produced by a unique mechanism of defect formation, at least for doses up to 30 Mrads. After that dose value, the excitations at 378 and 397 nm start to have absorption contributions from the F_z and F_3 centres, respectively, absorbing at 378 and 380 nm. While these two excitation positions (378 and 397 nm) have a strong interference from F_z and F_3 formation after 30 Mrads, the 356 nm excitation keeps its linear increase with the dose irradiation up to 80 Mrads.

The emission spectrum of Y centre is consistent with three emissions at 420, 480 and 515 nm. The 420 nm emission clearly belongs to the Y centre and is very well separated from the others. The 480 and 515 nm emission peaks are in the positions of F_z and F_3 centre emissions, respectively (see Fig. 4). It can also be seen (curve 2 of Fig. 4) that F_3 centres are not produced in irradiated Mg doped LiF, at least for the employed doses. This is an indication that the mechanism of vacancy captured by the Mg^{++} impurity, to produce F_z centres, prevents the F_3 centres' formation.

4. DISCUSSION

The preliminary measurements indicated that the observed new centre must incorporate secondary oxygen and hydrogen products of the OH^- dissociation, since it can only be produced in irradiated OH^- doped LiF. Also, one must conclude that this centre must essentially be a perturbed F_z centre because it absorbs and emits near the F_z centre. Also it is very stable at room temperature. Besides, it can be destroyed at higher temperatures having a lifetime of 11 min at 440 K. Figure 5 shows both the excitation (Fig. 5(a)) and emission (Fig. 5(b)) spectra obtained after partial thermal destruction of Y centres at 440 K. The resultant absorption and emission curves are mainly due to F_z and F_3 centres which are more

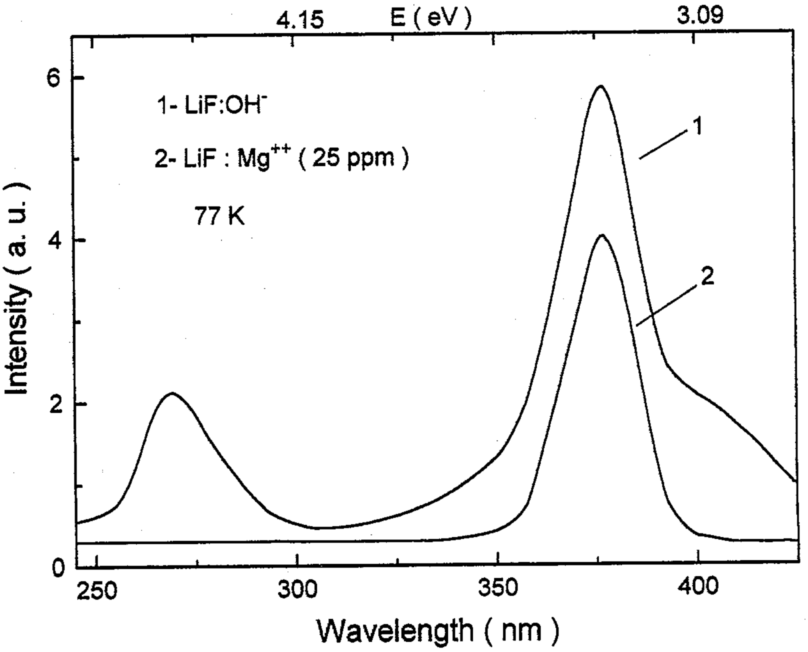

Fig. 2. Excitation spectrum of 473 nm luminescence measured at 300 K, near the O_2^- centre emission, revealing besides the existence of a structured excitation (absorption) band at 375 nm which was attributed to Y centre absorption. (1) excitation spectra obtained for LiF : OH : Mg^{++} (25 ppm), and (2) for LiF : Mg^{++} (25 ppm).

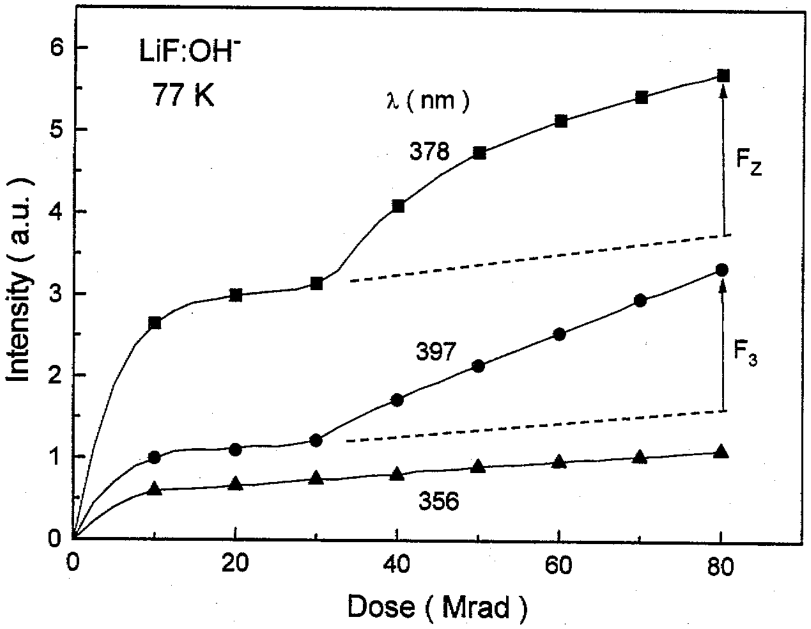

Fig. 3. Curve of Y centre formation in e^--irradiated LiF : OH^- crystal (at 230 K) with the dose increasing. Three maxima of the excitation spectrum were monitored: 356, 378 and 397 nm. After 30 Mrads, F_z and F_3 centres, contribute for the increasing of 378 and 397 nm absorptions, respectively, as indicated in the figure.

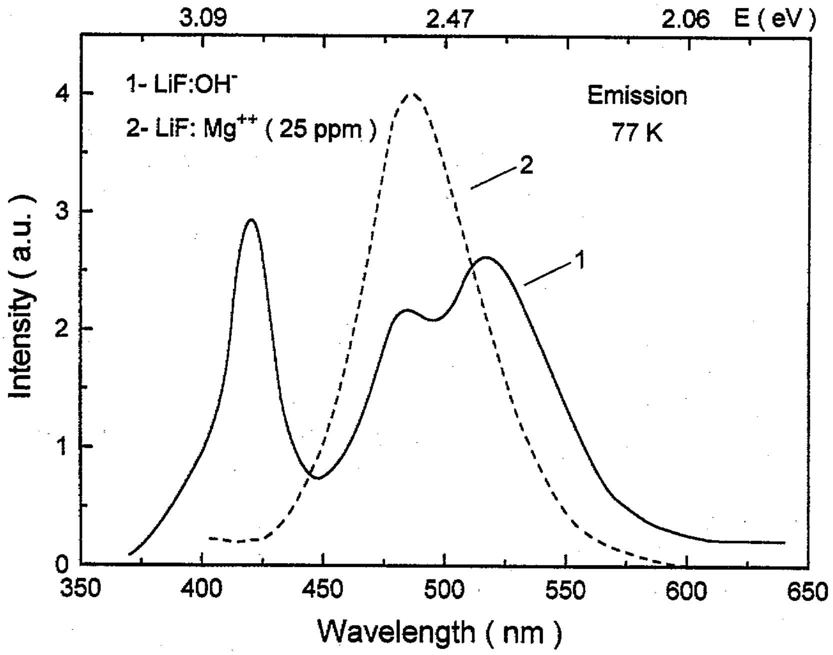

Fig. 4. Luminescence band near the F_z centre emission, excited with 370 nm monochromatic light at 77 K. (1) Emission band obtained for LiF : OH^- crystal showing three distinct emissions at 420, 480 and 515 nm (curve 1), attributed to the Y centre. (2) Emission band of F_z centres produced in LiF : Mg^{++} crystal.

stable. Figure 6 shows the difference spectra obtained after the 440 K thermal treatment (curve (1–2) of Fig. 5). By this technique we could have the real excitation and emission spectra from this new centre, without the involvement of the F_z and F_3 centre emissions which are stable in that temperature range. Both the excitation and emission spectra exhibited in Fig. 6 could be decomposed by five Gaussian bands (Fig. 6(a) and 6(b)). The peak position, half-width and relative area of each transition band is given in Table 1.

Looking at the excitation spectra of this centre, one realizes its enormous similarity with the H_2O^- defect absorptions in KCl, KBr, RbCl and RbBr [6], see Fig. 7. The observed strong isomorphism indicates that the Y centre must be a ‘wet F_z centre’ resembling

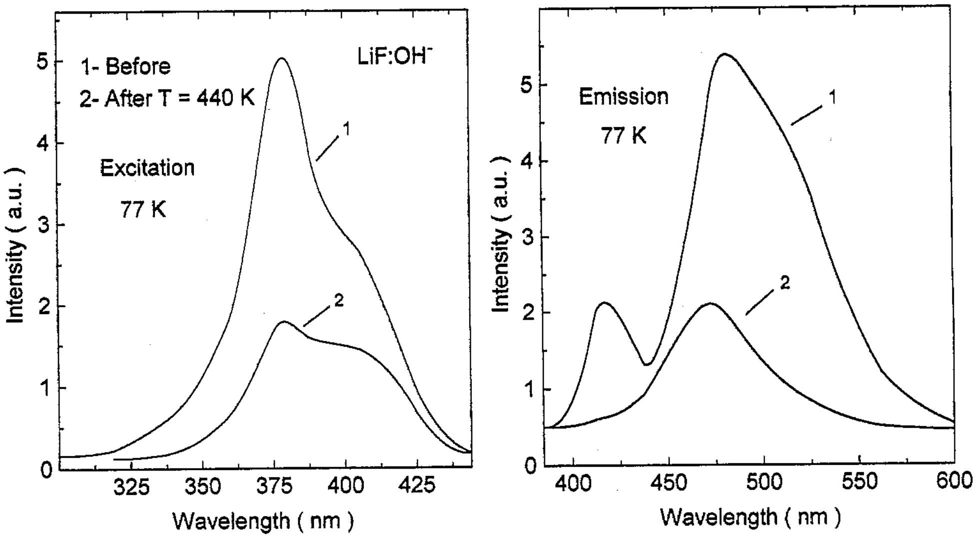

Fig. 5. Excitation and emission bands of Y centre measured for LiF : OH^- at 77 K, after the e^--irradiation with 20 Mrads at 230 K. (1) Before thermal treatment, and (2) after thermal treatment at 440 K for 11 min.

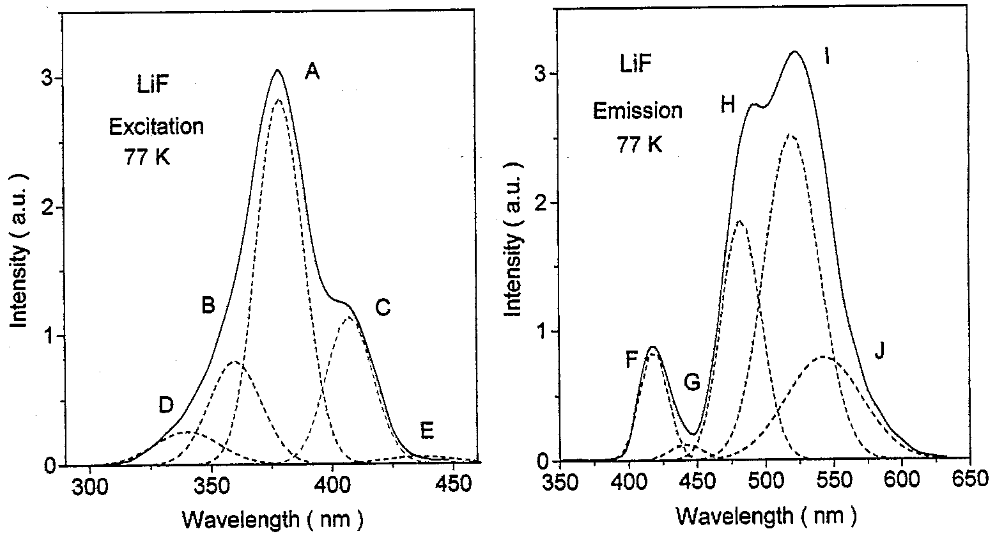

Fig. 6. Excitation and emission bands of Y centres, obtained from the spectral curves differences (1–2) of Fig. 5. The Gaussian bands represented by dashed lines were obtained from the computer best decompositions.

Table 1. Spectroscopical parameter values of $[H_2O^-]_z$ centres in LiF at 77 K. The band area of each transition (%) is relative to the total absorption (emission) area

Band	Peak position (nm)	Half width (nm)	Relative area (%)
(Excitation)			
A	380.3	24	52.9
B	360	27	16.3
C	407.5	24	21.8
D	340	34	6.9
E	436	35	2.1
(Emission)			
F	419.8	24	7.7
G	442	30	1.3
H	482.8	36	22.4
I	520	50	48.1
J	543	70	20.5

the 'wet F centre' (H_2O^- centre) produced in alkali chloride and bromide hosts.

Based on these arguments, we propose that the Y centre must be the F_z centre with a water molecule inside, exhibiting the characteristic absorption and emission bands of perturbed F_z centres with substructures produced by the electric dipole effects from the embedded water molecule.

In contrast with the 'wet F_z centre' observed in this work in LiF crystals, the H_2O^- centre ('wet F centre') is thermally unstable at 220 K and exhibits a dramatic absorption structure modification when the temperature increases towards 200 K, where it gradually shifts to exhibit only a Gaussian F type absorption [5].

Based on all these observations and phenomenological arguments one must conclude that the Y centre

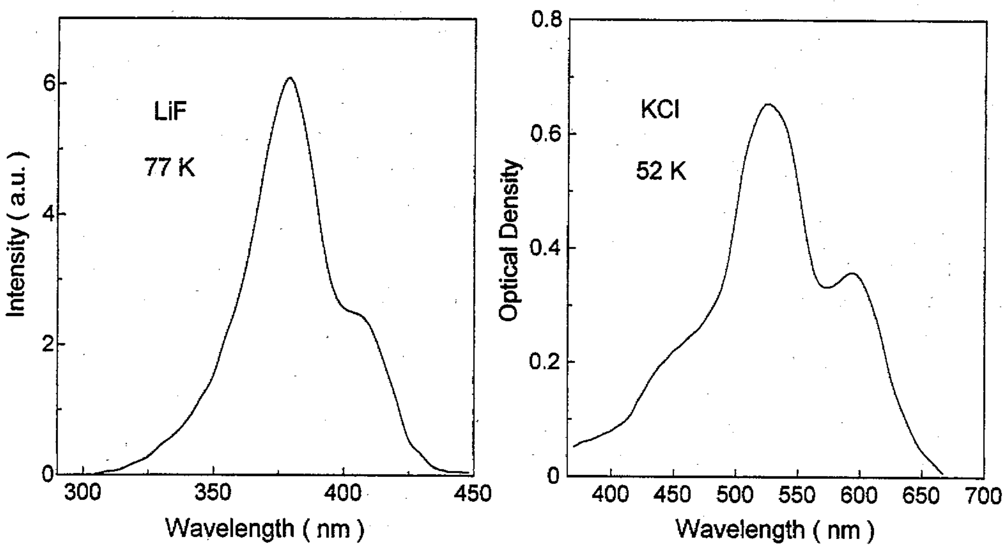

Fig. 7. Absorption band of $[H_2O^-]_z$ centers produced after high energy irradiation of OH^- doped LiF crystals with e^- at 230 K, and the absorption of H_2O^- centres produced by the OH^- photodissociation at 77 K followed by thermal annealing at 110 K, for comparison.

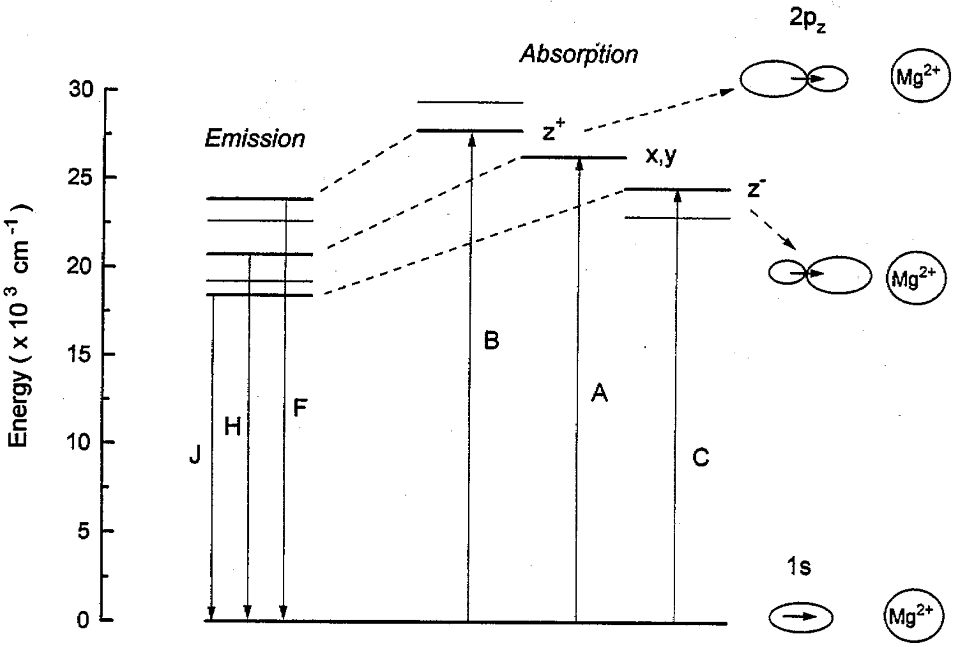

Fig. 8. Schematic energy levels diagram proposed for the absorptions and emissions of $[H_2O^-]_z$ centre in LiF, based on the spectroscopy. Only the principal transitions are indicated by solid arrows. The small solid arrow represents the orientation of the electric dipole of the water molecule trapped inside of the F_z vacancy. This dipole points in the Mg^{++} direction.

is constituted by an F_z centre with a water molecule inside having its electric dipole orientation fixed by the Mg^{++} impurity.

A proposed schematic energy level diagram for this centre is given by Fig. 8. Three optical transitions are possible: two of z-type transitions called z^+ and z^-, parallel to the molecule dipole ($1s \rightarrow 2p_z$) and a degenerate one perpendicular to it ($1s \rightarrow 2p_{x,y}$). Besides, it is possible to have sidebands due to the coupling of z-type transitions (z^+, z^-) with the scissoring mode ν_2 of water molecules ($\nu_2 = 1653.9\,\mathrm{cm}^{-1}$). By this model, the absorption band of $[H_2O^-]_z$ centre have five individual absorptions composing the absorption structure. Indeed, Fig. 6 exhibits an absorption structure which was well decomposed into five Gaussian bands named A, B, C, D and E. A is due to the degenerate $1s \rightarrow 2p_{x,y}$ transition peaking at 380.3 nm. B and C are due to the z^+ and z^- transitions with maxima at 360 and 407.5 nm, respectively. D and E are the respective sidebands having maxima at 340 and 436 nm. The measured peak differences of sidebands (D–B) and (C–E) of 1604 and 1634 cm^{-1}, respectively, are close to the pure scissoring mode value of a pure water molecule ($\nu_2 = 1653.9\ cm^{-1}$). This observation is consistent with the proposed model and also with the assumption made that D and E are sidebands of the z type transitions coupled with the ν_2 molecule mode.

Comparing the absorption areas of A band (xy-transition) with the (B + C) band, due to the z^+ and z^- transitions, one realizes that they are very close. If the ($1s \rightarrow 2p_x, 2p_y, 2p_z$) transitions had the same probability, the A band would have 66.6% of total absorption area of the centre. In the real case, the absorption area of A band is reduced to 52.9% due to dipole effect that slightly shifts the electronic charge density of $2p_{x,y}$ states towards the z direction, favouring the z type transitions.

The $[H_2O^-]_z$ centre has two main emission bands, not well separated, with maxima at 420 and 483 nm, named F and H bands, respectively. Excitation of the B band at 340 nm induces the emission from z^+ state (F band at 420 nm). Excitation of the A band mainly induces emission from (xy) states, producing the emission H band at 483 nm.

5. CONCLUSIONS

The present phenomenological model explains well the observed absorption and emission transitions of the new defect and the fact that it is formed only in irradiated LiF with OH^- and Mg^{++} impurities. The high temperature stability of the centre (1.54 eV of activation energy for centre dissociation) justifies the assumption that the oxygen and hydrogen constituents are forming a tight molecule, i.e. a pure water molecule occupying the whole vacancy volume of F_z centre. This fact guarantees a stable centre configuration and consequently a more stable absorption structure than that observed in the case of 'wet F centre', with the temperature variation.

The electron-spin resonance experiment at low temperatures is recommended for investigating the fine structure of this complex centre. It will be a difficult task because the expected ESR signal superimposes over the ones from other defects produced after irradiation (like F and F_z centres) having the spectroscopic splitting factor $g \cong 2$.

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