The role of OH$^-$ ions in the stabilization of F$_2^+$ colour centres in LiF

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Abstract. Thermally Stimulated Depolarisation Current (TSDC) and optical methods are applied to a range of alkali-fluoride crystals in order to establish a model for the stable F$_2^+$ – like colour centres in LiF:OH$^-$. The experimental results for LiF:OH$^-$ suggest that the OH$^-$ defects are partially destroyed under ionising irradiation or during crystal growth. The low-temperature dielectric relaxation signals in LiF:OH$^-$ and LiF:Mg^{2+},OH$^-$ are attributed to highly interacting hydroxide ions and products of their destruction located in extended lattice defects. In LiF:OH$^-$, in contrast to other alkali halides, the results advocate for a defect-structure model, which considers a neutral defect (ND, probably O$_2$ or H$_2$) sited at the anion vacancy of the O^{2-}–V$_a^+$ dipole and which possibly is the "nucleus" for the F$_2^+$ centre. The proposed F$_2^+$(ND, O$^-$) model seems to better explain the dielectric results, compared to the older F$_2^+$(O^{2-}) and F$_2^+$(O$^-$) models. The estimate for the electric dipole moment derived from the experimental TSDC bands, gives a value for the F$_2^+$ – like centre in LiF:OH$^-$ between those of the F$_2^+$(O$^-$) and F$_2^+$(O^{2-}) defects, in good agreement with the proposed F$_2^+$(ND,O$^-$) model. The reduction of the activation energy barrier of the (re)orientation process of the Mg^{2+}V$_c^-$(OH$^-$) complexes in LiF:Mg^{2+},OH$^-$, and the low-temperature shift of their TSDC band, compared to the single Mg$_2^+$V$_c^-$ peak in LiF:Mg^{2+}, are tentatively ascribed to an increase in the crystal-lattice parameters owing to the presence of OH$^-$ and/or products of its destruction.

PACS. 77.22.Ej Polarisation and depolarisation – 42.55.Rz Doped insulator lasers and other solid state lasers

1 Introduction

The presence of lattice defects in ionic crystals is of decisive importance for a wide range of applications. A thorough investigation of the nature, the properties and the behaviour of lattice defects produced under specific conditions might open new subjects of interest. A typical example in ionic crystals are the alkali-halides that have a long history of application as radiation dosimeters [1,2] and relatively recently have aroused great interest as active and passive elements in quantum electronics [3–11].

Over the last two decades, alkali-halide crystals with colour centres (CC) have been used as active media for tuning lasers, and interesting results were reported in the literature. Owing to the broad luminescence band of the colour centres' spectra, ultra-short pulses in the femtosecond range are possible [8–10]. Lithium fluoride (LiF) and sodium fluoride (NaF) crystals play a special role in this area of research [5–7,11]. However, some important questions about the nature of the colour centres, whose answer could promote their applications, remain unsolved. For example the model for the F$_2^+$ – like colour centres in the well-known oxygen and OH$^-$ containing lithium- and sodium-fluoride laser crystal, has not been precisely established. Contrary to the colour centres in other alkali-halides, the F$_2^+$ – like colour centres in LiF and NaF are extremely stable at room temperature. Different models have been suggested for these centres. The F$_2^+$ – like colour centres were discovered by Lobanov, Khulugurov and Parfianovich [12], which suggested a model where the divalent oxygen (O^{2-}) impurity ion compensates the superfluous charge of the F$_2^+$ colour centres. This model was also supported by recent studies from other research groups [13–15]. However, an oxygen impurity with extra charge should cause pronounced band-shifts in the optical spectrum, in disagreement with the experimental evidence. An alternative model considers a monovalent oxygen impurity ion (O$^-$) in the neighbourhood of the colour centre [16–18]. This model is in good agreement with the

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observed shifts of the zero-phonon line, but cannot explain the high stability of the F_2^+ – like colour centres in LiF:OH$^-$ crystals. Gellermann and coworkers [19] suggested that some impurity defects are involved in the stabilization of F_2^+ centres as electron traps. These impurity defects were thought to be located far away from the F_2^+ centres and thus should not change the optical parameters (zero-phonon line, absorption- and emission-peak maxima, etc.) of the F_2^+ centre. It is obvious that the determination of a model for the F_2^+ – like colour centres, in particular in the case of LiF:OH$^-$ in which the centres show the highest stability, can have both theoretical interest and practical significance, since these centres are found in crystals that are widely used for laser tuning at room temperature.

To establish a model for the F_2^+ – like colour centres in LiF:OH$^-$ one should consider the processes for OH$^-$ destruction under ionising radiation. There exist a number of possibilities. Kerkhoff and coworkers [20] made a first proposal in their studies on photochemical processes in alkali halides doped with OH$^-$. According to them, under ultra-violet (UV) irradiation, the OH$^-$ molecules are destroyed by the reaction

$$OH^- \xrightarrow{h\nu} O^- + H_i^0 \qquad (1)$$
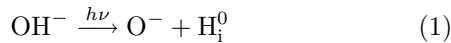
where O$^-$ is at a regular lattice site and H_i^0 is at an interstitial position. This photochemical reaction for hydroxide destruction in KCl is temperature independent, from liquid helium to $\sim$100 K [21]. At higher temperatures H_i^0 becomes unstable and binds with hydroxide ions. As a result, H_2O^- centres arise through the reaction [21]

$$2(OH^-) \xrightarrow{h\nu} O^- + H_2O^-. \qquad (2)$$
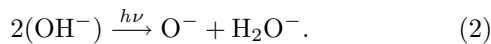
In irradiated NaF and LiF crystals doped by OH$^-$ oxyhydroxide complexes have been observed [22]. Akhvediani et al. [23] have observed the creation of U centres in alkali halides with OH$^-$ under ionising radiation. Thus, in accordance with this first approach the OH$^-$ molecules in alkali halides are destroyed under UV radiation, and U centres as well as complex O_mH_n centres may arise [22]. Another approach considers that under irradiation the OH$^-$ ions are not destroyed but that OH$^-$-X_i^0 molecular complexes with hydrogen bond form, where X_i^0 represents a halogen atom in an interstitial position [24]. A third proposal combines the previous two: the OH$^-$ molecules are destroyed or displaced to interstitial positions and hydrogen bonded complexes of OH...O, FH...O, OH...F and FH...F arise under ionising radiation [25]. Brukvina and Khulugurov [26] observed that by keeping the irradiated crystals at room temperature for one year the IR bands of OH$^-$ become stronger with the simultaneous appearance of bands (ν = 4100 cm^{-1}) due to HF molecules. These results were ascribed to the destruction of FH...O complexes forming either OH$^-$ and fluorine-atom aggregates or HF molecules and oxygen aggregates.

The aim of this paper is the investigation of the products of the OH$^-$ dissociation and their influence on the structure and properties of the laser active colour centres in LiF, using the sensitive thermally stimulated depolarisation current (TSDC) technique. Recently, we successfully implemented this technique for the study of the structure and the behaviour of a type of "red" colour centre (abbreviated as RCC), ascribed to $F_3M^{2+}V_c^-$ defect complexes, in LiF crystals with divalent impurities (M^{2+} = Mg^{2+}, Ni^{2+}, Be^{2+} and Co^{2+}) [27].

2 Experimental details

LiF, LiF:OH$^-$, LiF:Mg^{2+}, LiF:Mg^{2+}, OH$^-$, LiF:Li$_2$O, NaF and NaF:OH$^-$ crystals were investigated. Table 1 contains data on the starting materials and the specific preparation methods. The identification of the OH$^-$ impurities was performed by infrared spectroscopy at room temperature, which revealed the presence of OH$^-$ ions in LiF:OH$^-$ and NaF:OH$^-$ with vibration frequencies at 3730 cm^{-1} and 3728 cm^{-1}, respectively. LiF:OH$^-$ crystals with two different OH$^-$ ion concentrations (indicated by the absorption coefficients, 0.5 cm^{-1} and 0.1 cm^{-1}) and NaF:OH$^-$ (0.3 cm^{-1}) were used. The concentration of the OH$^-$ ions in the crystals is expected to be proportional to these absorption coefficients. In the infrared spectra of doped LiF:Mg^{2+},OH$^-$ crystals, two main bands were observed with vibration frequencies at ν_1 = 3570 cm^{-1} (strong band) and ν_2 = 3610 cm^{-1} (very low intensity band). These bands should be attributed to metal-hydroxide complexes [28]. The IR absorption spectra of LiF:Mg^{2+}, NaF and LiF:Li$_2$O do not contain optical bands ascribed to OH$^-$ ions.

The absorption spectra of the irradiated, at 195 K, LiF:OH$^-$, LiF:Mg^{2+},OH$^-$, LiF:Mg^{2+}, LiF:Li$_2$O, NaF:OH$^-$, LiF and NaF crystals include the well-known bands due to F, F_2, F_3 and F_3^+ colour centres [29,30]. Moreover, the irradiated LiF:OH and NaF:OH crystals show additional absorption bands around 600 nm in LiF, and 725 nm in NaF, due to thermo-stabilized F_2^+ – like colour centres (e.g. see Ref. [7]). A band around 400 nm, in LiF:OH$^-$, is due to F_3^+ – like centres which include products of the OH$^-$ destruction during the irradiation process [11]. The irradiated LiF:OH$^-$ crystals, after storage for one year at RT (referred to as irradiated LiF:OH$^-$ (A) crystals), exhibit a continuous increase of the concentration in F_2^+ – like centres. The increase is evidenced by the continuous, slow rise in intensity of the corresponding absorption band, with a maximum attained after one year for crystals stored at RT. From this point on, the concentration of F_2^+ – like centres begins to decrease and by the end of the second year the intensity of the absorption band has decreased by 10–15% (irradiated LiF:OH$^-$ (B) crystals; B denoting samples measured two years after preparation and irradiation). The complete destruction of the F_2^+ – like centres occurs after annealing for 5 hours at 373 K. During this time, the changes in concentration of the other colour centres are small. In the absorption spectra of LiF:Li$_2$O the F_2^+ – like centres give optical bands of very low intensity.

Table 1. Sample preparation methods and data related to the identification of OH$^-$ ions in the alkali-halide crystals used in the present work.

Materials[a]	Preparation	Starting materials	OH$^-$ identification[b] Absorption coefficients (cm^{-1})	IR bands (cm^{-1})
LiF	Bridgman method, inert atmosphere		-	-
LiF:Mg^{2+}	Bridgman method, inert atmosphere	0.05 wt % MgF$_2$	-	-
LiF:OH$^-$	Kyropoulos method, in air		0.5 0.1	3730
LiF:Mg^{2+},OH$^-$	Kyropoulos method, in air	0.05 wt % MgF$_2$	0.7 0.05	3570 3610
LiF:Li$_2$O	Bridgman method, inert atmosphere	0.1 wt % Li$_2$O	-	-
NaF	Kyropoulos method, inert atmosphere		-	-
NaF:OH$^-$	Kyropoulos method, in air		0.3	3728

[a] The concentration of metal impurities in the raw materials was less than 10^{-4} wt %.
[b] The dash indicates the absence of signals from OH$^-$ ions.

The TSDC technique has a long history of application to the study of impurity-vacancy (IV) dielectric-relaxation mechanisms in ionic crystals [31]. Alkali halides were among the first crystals studied by TSDC with significant reports on dipolar polarisation modes and the kinetics of the precipitation of impurities (formation of dipolar aggregates) [32,33]. A typical TSDC experiment starts with the polarisation of the material at a sufficiently high temperature $T_{\rm p}$ (polarisation temperature) by application of an electric field $E_{\rm p}$ (polarizing field strength) for a time $t_{\rm p}$ (isothermal polarisation time). In the next step, the temperature of the sample is lowered at a controlled rate with the electric field applied, down to $T_0 \ll T_{\rm p}$ where the non-equilibrium polarized state is "frozen-in". Finally, the sample is heated at a constant rate b, while it is short-circuited through an ammeter and the rate of depolarisation (*i.e.* the current $I(T)$) is recorded as a function of temperature. A TSDC peak results from two competing processes: the increase in the relaxation frequency of the polarized entities with temperature, which induces a current increase, and the gradual exhaustion of the dielectric polarisation, which produces a current decrease. The study of a single current peak, *e.g.* due to the uncorrelated relaxation of non-interacting dipoles in ionic crystals with low impurity concentrations, leads to the determination of the activation energy (E) and the pre-exponential factor (τ_0) using the Arrhenius equation for the relaxation time

$$\tau(T) = \tau_0 \exp\left(\frac{E}{kT}\right). \qquad (3)$$

The asymmetrical "glow curve" recorded during the TSDC experiment, is described by

$$I_D(T) = \frac{P_0 S}{\tau_0} \exp\left[-\frac{E}{k_\beta T} - \frac{1}{b\tau_0} \int_{T_0}^{T} \exp\left(-\frac{E}{k_\beta T}\right) {\rm d}T \right], \qquad (4)$$

where P_0 is the initial polarisation of the specific relaxation mode, S is the sample-surface area and k_β the Boltzmann constant. Depending on the particular chemical, structural and morphological characteristics of the dielectric, the peaks can be assigned to orientational (dipole-type relaxations), space-charge, or interfacial polarisation-relaxation phenomena (usually at relatively high temperatures).

Thermo-stimulated depolarisation currents were measured in unirradiated LiF and LiF:OH$^-$ crystals, and in crystals of LiF:OH$^-$, LiF:Mg^{2+}, LiF:Mg^{2+},OH$^-$, NaF:OH$^-$ and NaF irradiated by ^{60}Co γ-rays at 195 K, with a dose of 10^8 R, and stored at room temperature (RT) for approximately one year after irradiation (samples A). Furthermore, these crystals were stored at RT for one more year and the TSDC measurements were repeated (samples B). To recover the initial defect concentrations (as before irradiation), some samples were annealed to 873/973 K and quenched on a copper plate. The TSDC spectrum of unirradiated LiF:Li$_2$O crystals was measured shortly after crystal growth. The latter crystals were annealed at 873 K and quenched on a copper plate. All samples were provided with silver electrodes and placed in a specially designed vacuum cell, in order to perform the usual experimental procedure. The TSDC spectra were recorded in the temperature range from $\sim$10 to 340 K. Typical experimental conditions were $T_{\rm p} = 320$ K, $E_{\rm p} = (3-5) \times 10^6$ V/m, $t_p = 10$ min, $T_0 = 10$ K and $b = 5$ K/min. This provided quasi-equilibrium dielectric polarisation conditions for the relaxation mechanisms of interest. The complete TSDC experimental set-up is described elsewhere [27].
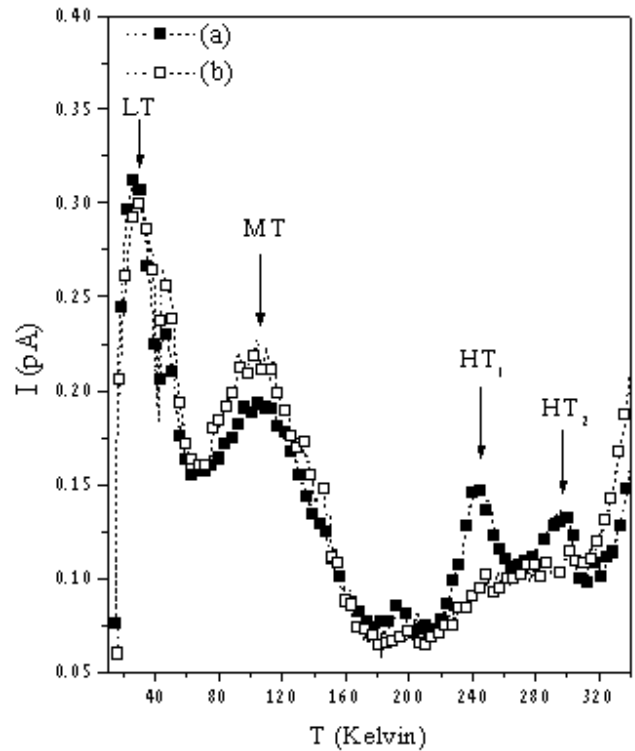
3 Results

Figure 1 presents TSDC spectra of an undoped LiF crystal (curve a), and of a LiF:OH$^-$ crystal (0.5 cm^{-1}) before (b)
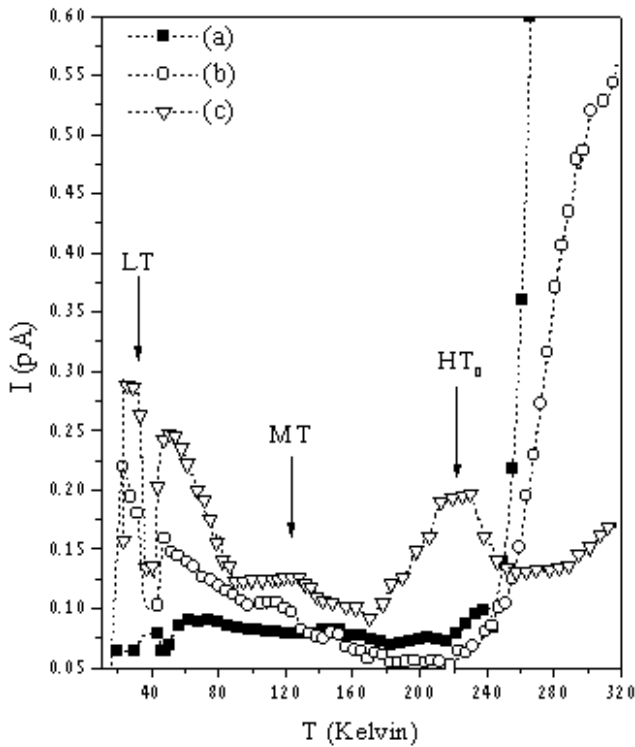
Fig. 1. TSDC spectra of: (a) the pure unirradiated LiF crystal, (b) the unirradiated LiF:OH⁻ crystal and (c) the LiF:OH⁻ crystal shortly after irradiation.

Fig. 2. TSDC spectra of: (a) the irradiated LiF:OH⁻ (A) crystal, and (b) the irradiated and annealed (at 873 K) LiF:OH⁻ (A) crystal.

and shortly after (c) irradiation. The thermograms of the LiF:OH⁻ crystal contain a broad signal below 70 K (low-temperature or LT-band). The heating cycle of the polarised sample was performed with the liquid-helium compressor on. This was preferred, as it reduces the narrow parasitic signal occurring in the range 35–45 K. The position of this signal is shown by an arrow in Figure 3. In addition, in the irradiated crystals, in particular in LiF:OH⁻, we record a weak band in the range 70 to 150 K (middle-temperature or MT-band). A broad band around 230 K (high-temperature or HT_0-band) emerges after irradiation in LiF:OH⁻ (Fig. 1c). In undoped LiF, the LT- and MT-bands are absent. LiF, in particular, presents an intense current rise above 250 K, with a maximum near the polarisation temperature T_p. From the behaviour of the band on varying T_p, we believe that it arises from a space-charge-relaxation mechanism, possibly owing to jumps of ions located near dislocations created in the cutting process.

Figure 2a illustrates the spectrum of an irradiated LiF:OH⁻ (A) crystal (0.5 cm⁻¹). The spectrum contains relatively strong LT- and MT-bands. The MT-band is considerably increased, compared to the signals in either undoped LiF or in LiF:OH⁻ before and shortly after irradiation. In addition, the spectrum of LiF:OH⁻ (A) demonstrates at least two distinct bands in the 220–320 K region (HT_1- and HT_2-bands). Annealing the irradiated LiF:OH⁻ (A) crystal (0.5 cm⁻¹) at 873 K for one hour leads to a drastic decrease of the high temperature bands with a

small change in the intensity of the low temperature spectrum (Fig. 2b).

The spectrum of a LiF:OH⁻ (B) crystal (Fig. 3a) shows that during the additional year of storage at ambient temperature significant changes take place either in the distribution or in the type of defects. More precisely, the LT-band disappears, the HT_1-band shows a drastic decrease, while the HT_2-band retains most of its original strength. The differences between the HT_2-bands of Figure 3a and 3c are most probably due to the varying contribution of the side-relaxations, *i.e.* of the 244 K band in Figure 3c. A fit of the HT_2-band of the LiF:OH⁻ (B) crystal gives the following relaxation parameters: $T_m = 310$ K, $E = 0.6$ eV and $\tau_0 = 10^{-8}$ s. Annealing the LiF:OH⁻ (B) crystal at 373 K for 5 hours, which leads to the elimination of the stable F_2^+ – like centres, results in the disappearance of the HT_2-band (Fig. 3b). The difference in area of the HT_2-bands in curves a and b, including corrections for the levels of the background current and the size of the crystals, gives an estimate of $Q = 6.14$ pC for the dielectric polarisation charge.

The spectrum of the irradiated LiF:Mg²⁺,OH⁻ (A) crystal also demonstrates the LT and MT depolarisation current bands (Fig. 4a). An interesting observation at this point is that the 10–70 K relaxation band exists both in LiF:OH⁻ (A) and LiF:Mg²⁺,OH⁻ (A) crystals, *i.e.* in crystals containing OH⁻ impurity ions. A band with maximum at 196 K emerges after annealing
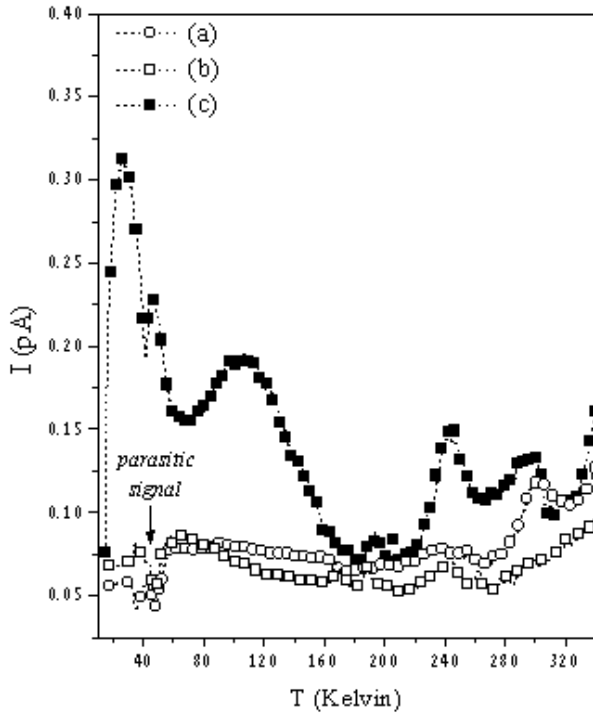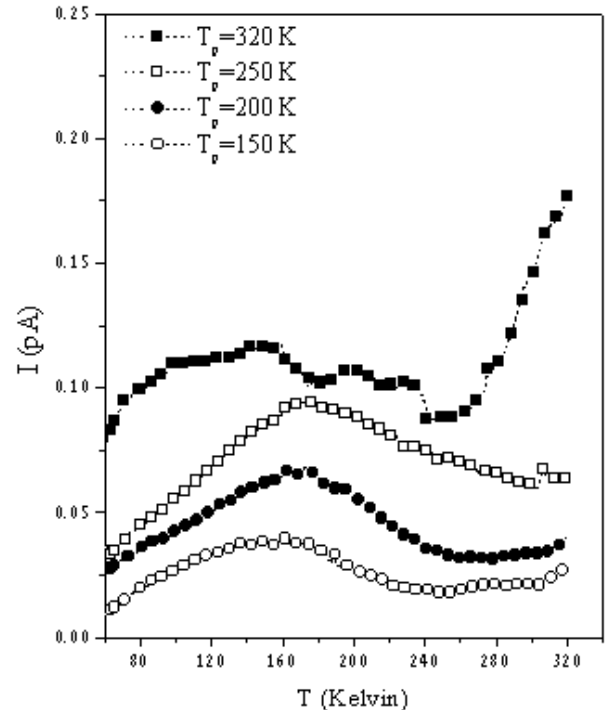
Fig. 3. TSDC spectra of: (a) the irradiated LiF:OH⁻ (B) crystal, (b) the irradiated and annealed (at 373 K) LiF:OH⁻ (B) crystal, and (c) the irradiated LiF:OH⁻ (A) crystal.
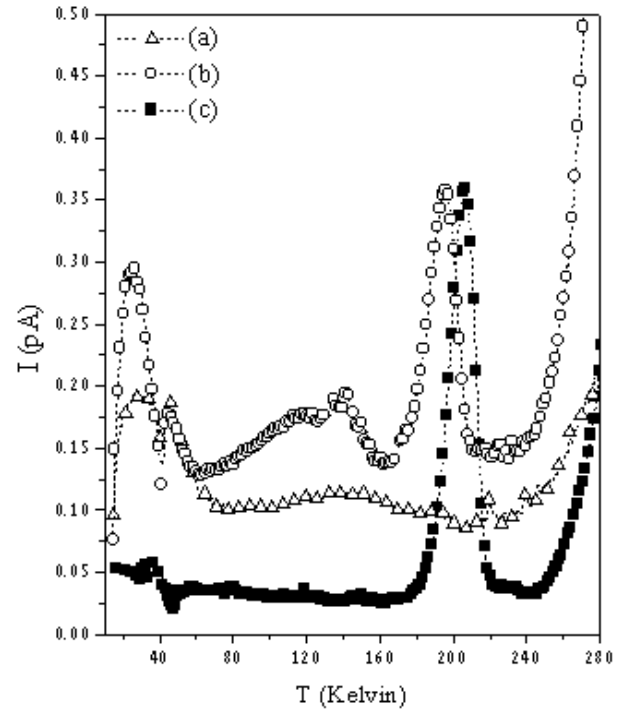
Fig. 4. TSDC spectra of: (a) the irradiated LiF:Mg²⁺,OH⁻ (A) crystal, (b) the irradiated and annealed (at 873 K) LiF:Mg²⁺,OH⁻ (A) crystal, and (c) the irradiated and annealed (at 873 K) LiF:Mg²⁺ crystal.

Fig. 5. Variation of the TSDC spectrum of the unirradiated and annealed (at 873 K) LiF:Li₂O crystal at different polarisation temperatures (details in the figure). The TSDC spectrum below 60 K (not presented here) does not exhibit the LT TSDC polarisation mode.

the LiF:Mg²⁺,OH⁻ (A) crystal at 973 K for two hours (Fig. 4b). Unlike the LiF:Mg²⁺,OH⁻ (A) crystal, in irradiated and annealed (at 873 K) LiF:Mg²⁺ (A) crystal the LT- and MT-bands are absent (Fig. 4c). The single band at $T_m = 207$ K, with relaxation parameters $E = 0.55$ eV and $\tau_0 = 0.45 \times 10^{-12}$ s, corresponds to the thermally activated (re)orientation process of Mg²⁺ – vacancy (Mg²⁺V$_c^-$) dipoles [27,34].

The spectra of LiF:OH⁻ (A) and LiF:OH⁻ (B) crystals do not seem to contain appreciable bands due to O²⁻ – vacancy (O²⁻V$_a^+$) dipole relaxations. Based on earlier TSDC reports on single O²⁻V$_a^+$ relaxations in several oxygen-doped alkali-halide and CaF₂ crystals, the O²⁻V$_a^+$ relaxation band is expected in the region 100–200 K. For instance, in KCl:O²⁻ the *single* O²⁻V$_a^+$ dipoles (re)orientation band is located at $T_m = 191$ K, in KBr:O²⁻ the O²⁻V$_a^+$ band peaks at 184 K, in KI:O²⁻ at 170 K [35], while in CaF₂ the peak maximum is at 151 K [36]. The low intensity band peaking at approximately $T_m = 190$ K in the irradiated LiF:OH⁻ (A) crystal (Fig. 2a) could be ascribed to the reorientation of O²⁻V$_a^+$ dipoles. However, its relaxation strength is rather insignificant. In addition, a *single* Debye-type O²⁻V$_a^+$ relaxation mode is not observed in spectra of unirradiated and annealed at 873 K LiF:Li₂O crystals (Fig. 5). The extremely weak and broad band around 180 K (Fig. 5) is a *complex* mechanism (*i.e.*, a relaxation mechanism with distributed relaxation parameters), as its maximum follows the variations of the polarisation temperature T_p.

4 Discussion

4.1 TSDC relaxation modes in different temperature regions

4.1.1 Thermocurrents in the 10–70 K region in LiF:OH$^-$ and LiF:Mg^{2+},OH$^-$

In LiF:OH$^-$ and LiF:Mg^{2+},OH$^-$ we observe a relatively intense LT TSDC polarisation band below 70 K. From its spectral position and the behaviour of the signal, we conclude that the corresponding relaxation mechanism is very fast. Since the experimental apparatus does not allow to observe current signals below 10 K, we cannot assess the true peak position and its relaxation parameters. The steep rise of the current signal immediately after starting the heating process suggests that the observed LT "peak" is only the high-temperature "tail" of a much stronger band with maximum below 10 K. The presence of the LT polarisation in the unirradiated, the irradiated, and the irradiated + annealed LiF:OH$^-$ (A) and LiF:Mg^{2+},OH$^-$ (A) crystals, reveals the high-temperature stability of the defects contributing to this relaxation mode. On the other hand, the absence of this LT-band in hydroxide-free LiF, LiF:Li$_2$O and LiF:Mg^{2+} crystals advocates for the association of these defects with OH$^-$ ions. In addition, the LT-band shows a significant increase after irradiation (*e.g.*, compare the low LT-signal in unirradiated LiF:OH$^-$ (Fig. 1b) with the stronger signals in the irradiated LiF:OH$^-$ crystals (Fig. 1c and 2a)). This suggests that some products of the OH$^-$ destruction in irradiated LiF:OH$^-$ (A) and LiF:Mg^{2+},OH$^-$ (A) crystals may participate to the formation of the LT-band.

In detail, the TSDC polarisation mode in the 10–70 K region of LiF:OH$^-$ crystals could be attributed to the (re)orientation, via quantum tunnelling, of non-isolated OH$^-$ molecules (OH$^-$ molecules in regular lattice sites interacting with each other) or OH$^-$ molecules interacting with some products of OH$^-$ decomposition. This assignment is supported by recent results in other fcc alkali-halide crystals [37,38]. According to An and Luty [37], the OH$^-$ defects exhibit (re)orientational tunnelling between eight equivalent $\langle 111 \rangle$ potential wells; the dominant dipole (re)orientations being nearest neighbour 70° tunneling through the $\langle 110 \rangle$ orientation. The alignment of the OH$^-$ ions in the $\langle 111 \rangle$ orientation is a result of the $\sim 12\%$ larger axial size of the OH$^-$ ion, compared to the F$^-$ host ion in alkali fluorides. Other orientations (*e.g.* the $\langle 100 \rangle$ orientation) would require high repulsion energy and stronger lattice deformation. In the above scheme, isolated "non-interacting" hydroxides in alkali halides (*e.g.* KCl with OH$^-$ or OD$^-$ concentrations of $\sim$5 ppm [39]) are defect centres that (re)orient *via* quantum tunneling at very low temperatures (≤ 1 K) [40]. The case of lithium fluoride is of special interest since in this alkali-halide crystal the OH$^-$ dipoles exhibit the highest tunnelling probability [37,38]. Such a tunneling mechanism cannot be monitored by TSDC owing to the weakly temperature-dependent character of the transition. However, according to Enss *et al.* [39], with increasing concentration of OH$^-$ the mutual interaction among pairs of defects induces a transition from coherent tunneling to incoherent tunneling. As a result, the highly interacting hydroxides (*e.g.* OH$^-$ within pairs on nearest neighbour or next-nearest neighbour sites) may present thermally-activated (re)orientation processes with dielectric relaxation bands at low temperatures. This interaction has been confirmed in the case of KCl:OH$^-$ [39] by recording isochronal (measured at 10 kHz) dielectric absorption bands at low temperatures of 1 to $\sim$70 K. The temperature region of the LT TSDC band in LiF:OH$^-$ agrees with that of the a.c. dielectric relaxation bands in the isostructural KCl:OH$^-$ crystal. The observation that the strength of the LT dielectric polarisation mode depends on the hydroxide concentration is in good agreement with the above assignment. The TSDC band in irradiated LiF:OH$^-$ increases when the concentration of OH$^-$ ions increases, *i.e.* when the intensity of the IR absorption band of the OH$^-$ stretching mode increases from 0.1 cm^{-1} to 0.5 cm^{-1}, owing to the extended OH$^-$–OH$^-$ interactions.

It is difficult at this stage to present a definite explanation for the disappearance of LT-band in LiF:OH$^-$ during the second year of crystal ageing at RT (LiF:OH$^-$ (B) crystals). Some general observations, which may help to understand this result, are given below. The red emission in unirradiated oxygen-containing LiF crystals grown in air, which presents a rich and partially repetitive vibrionic substructure resolved at low temperatures, has been assigned to (O$_2$)$_2$ dimers [41]. In addition, neutron irradiated LiF:OH$^-$ and NaF:OH$^-$ crystals reveal luminescence due to neutral oxygen molecules in the neighbourhood of the colour centres [42]. O$_2^+$ molecular ions have been observed in irradiated OH$^-$ containing Li and Na fluorides (*e.g.* in optical studies [43]) and in KCl and KBr crystals studied by electron-spin resonance (ESR) as well [44]. The above results provide evidence for the presence of molecular oxygen in both the irradiated and the unirradiated LiF:OH$^-$ and NaF:OH$^-$ crystals. A route for the creation of neutral oxygen molecules, as well as some hydrogen containing defects, is the decomposition of OH$^-$ ions in the process of crystal growth or during subsequent irradiation. Since the LT-band disappears when the irradiated crystal remains at room temperature for more than approximately two years, it is not possible to exclude that part of the mixture of the products of the OH$^-$ decomposition could be in gaseous form, located at dislocations or on other types of extended defects. In the second step of the ageing process (at RT), some of the dielectrically active products of OH$^-$ decomposition may either loose their rotational mobility or be transformed into other non-polar complexes. Examples of possible decomposition products are H$_2$, O$_2$, HF and F$_2$ molecules [25,26]. The presence of the LT-band in an aged unirradiated LiFOH (B) crystal suggests that the irradiation step, with the radiolysis of the hydroxides and the subsequent slow reactions between the initially formed O$_n$H$_m$ centres and other products of the OH$^-$ decomposition, causes irreversible and long-term changes in the initial defects of the LiF:OH$^-$ crystal.
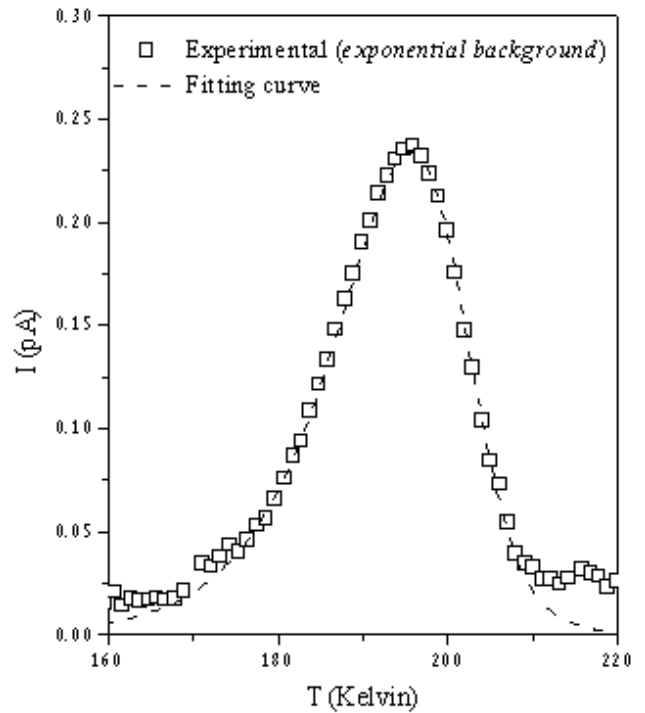
4.1.2 Thermocurrents in the 70–150 K region in LiF:OH⁻

The broad thermo-stimulated current band in the 70–150 K temperature region in LiF:OH⁻ (A) (Fig. 2) can be attributed to water molecules. The dielectric literature contains many TSDC investigations in this temperature region presenting partially or highly overlapped single-relaxation modes related to the rotational relaxation of water molecules in different environments; *e.g.*, pure ice [45], liquid electrolytes [46], biological materials [47], polymers or inorganic–organic composites [48] and natural or synthetic minerals [49]. The large temperature width of the MT-band suggests that the water molecules in lithium fluoride are not located in a single type of trapping site but at positions with varying molecular/ionic environments. It is interesting to note that in the unirradiated LiF:OH⁻ crystal the signal in this temperature range is very weak (nearly a background current, Fig. 1a); the MT TSDC band develops shortly after irradiation and it attains considerable strength one year after irradiation (Fig. 2a). The band nearly disappears upon keeping the crystal at ambient conditions for an additional year (Fig. 3a). This unexpected result can be tentatively explained by considering that relatively "unstable" water molecules are the initial products of the destruction of hydroxide in irradiated LiF:OH⁻ (*e.g.* through reaction 2), which finally transform to some other ionic or molecular form.

Fig. 6. Fit of the 196 K band of the $Mg^{2+}V_c^-(OH^-)$ complex in the irradiated and annealed LiF:Mg^{2+},OH⁻ (A) crystal with an energy-distributed relaxation with $E = 0.42 \pm 0.18$ eV and $\tau_0 = 3.0 \times 10^{-9}$ s.

4.1.3 Thermocurrents in the 150–250 K region in LiF:Mg²⁺ and LiF:Mg²⁺,OH⁻

In irradiated and annealed LiF:Mg²⁺, the current peak at $T_m = 207$ K corresponds to the thermally activated (re)orientation of Mg^{2+} – cation-vacancy dipoles ($E = 0.55$ eV and $\tau_0 = 0.45 \times 10^{-12}$ s). For irradiated and annealed LiF:Mg²⁺,OH⁻ this relaxation band is in comparison broader and it is down-shifted by 11 K ($T_m = 196$ K). The latter band should be attributed to the (re)orientation of $Mg^{2+}V_c^-$ dipoles which, as in the case of other alkali-halide crystals [28], include in their structure OH⁻ ions ($Mg^{2+}V_c^-(OH^-)$ complexes).

The optimum fitting of the experimental current (Fig. 6) was obtained by considering the TSDC curve as a complex band with a distribution in activation energies. The dielectric relaxation parameters of the $Mg^{2+}V_c^-(OH^-)$ complexes were determined to be: $E = 0.42 \pm 0.18$ eV and $\tau_0 = 3.0 \times 10^{-9}$ s. Prior to fitting, a slowly rising exponential background current was subtracted from the experimental curve. With this procedure, we effectively reduce the current contribution from the intense mechanism above ∼200 K and thus increase the accuracy of the estimate. The presence of a distributed relaxation is justified on several grounds. According to Stoebe [28], there are a number of mutually non-equivalent positions for the Mg²⁺ – cation vacancy dipoles relative to the OH⁻ ions. Thus the existence of a single dielectric

relaxation mode is highly unlikely. The IR spectrum of our LiF:Mg²⁺,OH⁻ crystal shows a strong OH⁻ band (at $\nu_1 = 3570$ cm⁻¹) which can be attributed to a particular $Mg^{2+}V_c^-(OH^-)$ complex configuration. However, the spectrum also shows several weaker absorption lines with an integrated intensity equal to about 10% of the main IR band. These signals are most likely related to other $Mg^{2+}V_c^-(OH^-)$ configurations. The existence of a distributed relaxation mechanism is also in agreement with previous optical studies, reporting multiple OH⁻ IR bands in LiF:Mg²⁺,OH⁻. For example, in earlier high-resolution FTIR studies by Capelletti *et al.* [50,51], LiF:Mg²⁺,OH⁻ crystals were shown to exhibit a complex absorption spectrum in the wave number range 3500–3750 cm⁻¹. Apart from the broad lines due to the stretching of non-interacting hydroxyl ions (at 3735.4 cm⁻¹ in LiF), many narrow lines were recorded on the lower wave-number side. These are due to the fundamental stretching-mode transitions of OH⁻ ion perturbed by Mg-related defects. A strong absorption line at 3592.5 cm⁻¹ was attributed by the authors to OH⁻ embedded in Mg-cluster (possibly an IV dipole dimer) [51].

The "characteristic" activation energy for the (re)orientation process of the $Mg^{2+}V_c^-(OH^-)$ complex in LiF:Mg²⁺,OH⁻ is clearly *lower* compared to that for the single $Mg^{2+}V_c^-$ dipole in LiF:Mg²⁺. This result gives the possibility to describe the effect that OH⁻ incorporation has on the relaxation characteristics of the

$Mg^{2+}V_c^-$ dipole. In an older study on $NaCl:Ca^{2+},OH^-$ crystals [52], a high temperature shift of the TSDC band of the $Ca^{2+}V_c^-(OH^-)$ complexes, in relation to the single IV band in $NaCl:Ca^{2+}$, has been observed. In addition, the activation energy barrier was found to be *higher* in $NaCl:Ca^{2+},OH^-$ crystals compared with $NaCl:Ca^{2+}$ crystals. Suszynska and Macalik [52] attribute the high-temperature shift to a decrease in crystal-lattice parameters owing to the presence of OH^- ions. An alternative explanation is to consider this shift as resulting from the strong electrostatic interaction between the cation (Ca^{2+}) and anion (OH^-) impurities in the NaCl host matrix. Considering the difference in ionic radii of the host anions in LiF and NaCl (1.36 Å for F^-, 1.81 Å for Cl^-) with the hydroxide, the shifts recorded in the present study in the $LiF:Mg^{2+},OH^-$ and $LiF:Mg^{2+}$ ionic systems could be connected to an increase in lattice parameters (*i.e.* to a lattice distortion) owing to the "egg-shaped" OH^-, which fits very tightly in the F^- lattice site of alkali fluorides.

4.1.4 Thermocurrents in the 220–320 K region in LiF:OH⁻

The LiF:OH⁻ crystal presents a broad and asymmetric HT_0-band shortly after its irradiation (Fig. 1c). The TSDC signals in the 220–320 K region change considerably with ageing time: in LiF:OH⁻ (A) this part of the spectrum contains two narrow bands (HT_1 and HT_2, Fig. 3c). In LiF:OH⁻ (B) the HT_1-band ($T_m = 244$ K) is appreciably smaller, while the HT_2-band ($T_m = 310$ K) is preserved (Fig. 3a). Annealing of irradiated LiF:OH⁻ (A) (0.5 cm⁻¹) at 873 K during 1 h suppresses the HT-bands (Fig. 2b). Annealing LiF:OH⁻ (B) at 373 K during 5 hours (the same conditions which lead to complete annihilation of the stable F_2^+ – like centres) leads to the disappearance of the HT_2-band (Fig. 3b). The thermal and time-evolutions of the HT_2-band are similar to those of the laser active F_2^+ – like centres in optical measurements. Thus, the HT_2 band could tentatively be assigned to the reorientation of the F_2^+ – like defect centres in irradiated LiF:OH⁻. The activation energy for this dielectric relaxation, $E = 0.6$ eV, is close to the activation energy of the V_a^+ movement in LiF, 0.67 eV, as reported by Farge *et al.* [53].

The complex HT_0-band is most likely a dielectric signal arising from colour centres and/or defects developing shortly after irradiation. The irradiation produces several F, F_2, F_3, ... as well as pure F_2^+ centres. In addition, hydroxides and oxygen-containing defects present in unirradiated LiF:OH⁻, shortly after irradiation may produce some O^{2-}-V_a^+ pairs. These pairs can partially or totally contribute to the formation of the HT_0-band which develops close to the expected temperature region for a O^{2-}-V_a^+ TSDC relaxation signal. Under storage at RT, slow reactions can create "stable" complexes. The HT_1-band at $T_m = 244$ K, with relaxation parameters $E = 0.63$ eV and $\tau_0 = 2.78 \times 10^{-12}$ s, is most likely due to a type of "complex" colour centre in the aged crystal. From the results shown in Figure 3a we conclude that these centres are much less stable than the F_2^+ - like centres (HT_2-band).

4.2 O²⁻-anion vacancy dipoles in oxygen-containing LiF

Earlier UV measurements have shown that oxygen containing LiF crystals present two bands at 10.5 and 6.5 eV [54,55]. Under irradiation with $h\nu > 9.5$ eV, these bands decrease and an F-band at 4.95 eV appears. The optical data in these crystals give results analogous to those for other alkali halides after creation of O^{2-}-V_a^+ pairs [56–62]. The TSDC spectra of Figure 5 indicate that the annealed $LiF:Li_2O$ crystals do not give O^{2-}-V_a^+ dipole-relaxation bands, in contrast to the optical results. It should be stressed that the crystals used for the optical and dielectric studies were prepared under the same conditions [54,55]. A reasonable explanation is to assume that in the LiF crystal doped with Li_2O either the main part of the oxygen impurities do not enter the crystal in the O^{2-}-V_a^+ form, or the oxygen impurities enter the crystal in the O^{2-}-V_a^+ form but the reorientation of the IV dipoles is hindered. This can be the case for a neutral defect (ND) situated at the anion vacancy of the O^{2-}-V_a^+ dipole. In the latter case the O^{2-}-V_a^+ dipoles exhibit a highly reduced rotational mobility, since the jump of the V_a^+ is not allowed, and cannot give the typical TSDC signals. Probable neutral defects in the case of $LiF:Li_2O$ could be atomic or molecular oxygen.

4.3 A model for the F_2^+ – like laser active colour centres in LiF:OH⁻

The F_2^+ – like laser active colour centres in LiF:OH⁻ have an absorption band at 600 nm and a luminescence band at 910 nm [12]. The large Stokes shift, the light polarisation behaviour and the value of the radiative lifetime of the F_2^+ – like centres are close to those of typical F_2^+ – centres [12–18]. The analogies between the optical and dielectric results suggest that the TSDC band at ~310 K (HT_2) is related to F_2^+ – like defect centres. The concentration of F_2^+ – like colour centres in LiF:OH⁻ is similar to that of laser active "red" colour centres (RCC, $F_3Mg^{2+}V_c^-$ complex centres) in $LiF:Mg^{2+}$ crystals investigated in a previous TSDC study [27]. The concentrations of the F_2^+ and the $F_3Mg^{2+}V_c^-$ colour centres was calculated using the well-known Smakula's equation

$$N = 0.87 \times 10^{17} \frac{n}{(n^2 + 2)^2} \frac{\alpha \Delta \nu}{f} \tag{5}$$

where, α is the absorption coefficients of the centre (for F_2^+ $\alpha = 2$ cm⁻¹ and for the RCC $\alpha = 3.7$ cm⁻¹), $\Delta \nu$ is the full width at half maximum of the absorption bands (for the F_2^+ band $\Delta \nu = 0.44$ eV and for the RCC $\Delta \nu = 0.25$ eV), $n = 1.39$ is the refractive index of LiF at 620 nm (the maximum of the F_2^+ absorption band is at 600 nm and that of the RCC is at 560 nm), f is the oscillator strength (for F_2^+ $f = 0.1-0.2$ [29] and for the RCC $f = 0.307$ [63]). Using equation (5), we obtain a $N_{F_2^+}/N_{RCC}$ ratio between 1.4 and 2.8, depending on the oscillator strength for the F_2^+ centre (0.1–0.2).

On the basis of this calculation, we can attempt to compare the dipole moments of these defects (F$_3$Mg^{2+}V$_c^-$ defects in LiF:Mg^{2+} and F$_2^+$ – like centres in LiF:OH$^-$) using the Langevin equation [31] for the quasi-equilibrium dielectric polarisation at $T = T_p$,

$$P_e(T_p) \approx \frac{gN_d\mu^2\kappa E_p}{kT_p} . \qquad (6)$$

In this equation g is a geometrical factor, N_d the dipole concentration, μ the electric dipole moment and κE_p the local polarising electric field. By virtue of equation (6) the charge Q released during the depolarisation step, $Q = S \times P_e(T_p)$, is predominantly controlled by the square of the dipole moment ($\mu = ed$), d being the charge distance) of the corresponding dipoles. Using the latter expressions, with equal dipole/defect concentrations ($N_d = N_{F_2^+} \cong N_{RCC}$) and polarisation temperatures (T_p), we derive the following relation

$$\frac{\mu_2^2}{\mu_1^2} = \frac{V_1}{V_2}\frac{S_1}{S_2}\frac{l_2}{l_1}\frac{Q_2}{Q_1}, \qquad (7)$$

where, μ_1 and μ_2 are the dipole moments of the defects 1 (F$_3$Mg^{2+}V$_c^-$) and 2 (F$_2^+$ – like centres), V_1 and V_2 are the electric voltages applied during the dielectric polarisation step, S_1, S_2 and l_1, l_2 are the surfaces and the thickness of crystals 1 and 2, respectively. Q_1 and Q_2 are the polarisation charges equal to the area of the TSDC peak of each defect – centre relaxation mechanism.

Using equation (7) and the point-charge approximation for the dipole moment of the F$_3$Mg^{2+}V$_c^-$ colour centre [27] we estimate for the F$_2^+$ – like centre in LiF:OH$^-$ a dipole moment $\mu = 1.5-2.1$ D. This value is approximately 6 to 8.5 times smaller than the value that can be calculated from the F$_2^+$(O^{2-}) model proposed by many researchers [12–15] with use of the point-charge approximation (*e.g.*, $\mu = ea\sqrt{7}/2$ in the case of the model in reference [14], with a the nearest-neighbour-ion distance in LiF and e the electron charge). The value $\mu \approx 2$ D is also not in agreement with the F$_2^+$(O$^-$) model suggested in references [16–18]. The dipole moment of the F$_2^+$(O$^-$) centre should be very small since it arises from a lattice distortion (see the case of the isostructural centres [64,65]). In LiF the lattice distortion around the O$^-$ impurity ion should be small because of the similarity in the ionic radii of O$^-$ and F$^-$ [66].

In the previous section, we introduced the notion of a neutral defect in the V$_a^+$ site to explain the absence of a TSDC relaxation mode from O^{2-} V$_a^+$ dipoles. The presence of V$_a^+$ in the laser active F$_2^+$ centres allows us to extend this idea in the case of the F$_2^+$ – like centres in LiF:OH$^-$. The observed high stability of these centres (centres are stable at RT during ~3 years) in comparison to the F$_2^+$ centres in other alkali halides, leads to the assumption that the structure of the F$_2^+$ – like centre in LiF:OH$^-$ includes a "neutral defect", product of the OH$^-$ ions destruction process, located at the anion vacancy. The nature of this neutral defect is ambiguous. However, from the results discussed in Section 4.1, probable candidates,

in the case of the LiF:OH$^-$ crystal, appear to be O$_2$ or H$_2$ molecules. It should be noted in addition, that some products of the lattice-ion transformation may well exist (*e.g.* fluor-atom aggregates and HF molecules [26]).

The introduction of the neutral defect in the F$_2^+$ – like centre in LiF:OH$^-$ may possibly be described as follows. At the early (first) stage after irradiation, the F$_2^+$(ND) centres could arise owing to the reaction

$$F_2^+ + ND \rightarrow F_2^+(ND), \qquad (8)$$
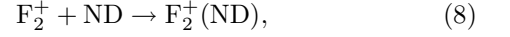
since the F$_2^+$ centres are relatively "mobile" with possible short-range (re)orientational jumps [67]. During the second long-time stage the following reaction is possible

$$F_2 + O_2^+ \rightarrow F_2^+(O_2), \qquad (9)$$
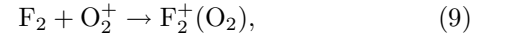
since the presence of O$_2^+$ defects has been confirmed in LiF:OH$^-$ crystals [43].

On the other hand, the creation mechanism for these F$_2^+$ – like centres could be as follows:

$$O^{2-}V_a^+(ND) + V_a^+ \rightarrow F_2^+(ND, O^-). \qquad (10)$$
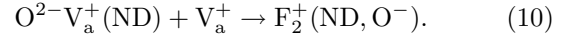
This reaction most likely starts at the irradiation step and proceeds for approximately one year after irradiation. One can see from the results presented in Figures 1 and 3 and the discussion in Section 4.1.4, that within two years after irradiation the colour centres (band-HT_1) with parameters $T_m = 244$ K, $E = 0.63$ eV and $\tau_0 = 2.78 \times 10^{-12}$ s are destroyed. Given that the reorientation activation energy of these centres, 0.63 eV, is close to the energy of the V$_a^+$ movement [53], there is high probability that these centres include an anion vacancy in their structure. During the destruction of the centres, the anion vacancy becomes free to participate in reaction (10).

The above model for the F$_2^+$ – like centre in LiF:OH$^-$ is in principle the model suggested by Salomatov and coworkers [16–18], with the addition, at variance with other alkali halides, of a neutral defect, probably an O$_2$ or H$_2$ molecule inside one of the anion vacancies which are the "nuclei" of the F$_2^+$ centre. Several positions of the O$^-$ ion, relative to the F$_2^+$ centre, have been proposed [18]. In the neighbourhood of the O$^-$ ion we do not expect significant lattice deformation. However, the presence of the bulky ND in the V$_a^+$ produces a significant displacement of the ions surrounding this vacancy, considerably higher than the lattice distortion around the adjacent "unoccupied" vacancy of the F$_2^+$(ND,O$^-$) centre. The projection of the displacements of the surrounding ions on the longitudinal F$_2^+$ axis are quite different, forming a dipole with an electric dipole moment of *e.g.* $\mu \approx 2$ D (present estimate). Owing to the greater lattice distortion, as result of the presence of the neutral defect, the dipole moment of the F$_2^+$(ND,O$^-$) centre is expected to be higher than in the case of the F$_2^+$(O$^-$) defect model [16–18]. The F$_2^+$(ND,O$^-$) model appears to be consistent with several previously published optical studies and with most experimental results presented here.

The comparison between the thermo-stimulated current responses of the irradiated sodium fluoride and

lithium fluoride crystals can be briefly summarized as follows. Contrary to the LiF crystals, the spectra of the irradiated NaF:OH$^-$ (A) and NaF (A) crystals, do not show current bands in the LT and MT spectral ranges and no indication for F_2^+ – like centres. In agreement with the TSDC results for LiF:LiO$_2$ and LiF:OH$^-$, the spectra of the NaF crystals do not record a dielectric relaxation band due to *single* O^{2-}–V$_a^+$ pairs. The latter observation is in agreement with earlier TSDC studies by Cook and Dryden [68] in NaF:O^{2-} crystals. Sodium fluoride exhibits a *complex* band in the temperature region of 200 to 320 K with the main maximum at $T_m \sim 275$ K. It is interesting to note that the structure and the spectral position of that band it not affected by the presence of hydroxide in NaF:OH$^-$. The assignment of that band to specific molecular or defect- type relaxation mechanisms is beyond the scope of the present report.

5 Conclusions

The parallel optical and dielectric studies of some OH$^-$ - containing alkali-fluoride crystals lead to the following proposals:

- The TSDC band at 196 K in the LiF:Mg^{2+},OH$^-$ crystal is attributed to the rotational relaxation of Mg^{2+}V$_c^-$(OH$^-$) dipole complexes. The low-temperature shift of this broad band and the decrease in the characteristic activation energy of the dipole (re)orientation process, compared to the single mechanism of the Mg^{2+}V$_c^-$ dipoles in LiF:Mg^{2+}, are attributed to the lattice deformation and the increase in the lattice parameters. These changes are expected owing to the presence of the longer and thinner OH$^-$ ions, compared to the F$^-$ host, and/or of some products of their decomposition. The distribution in the relaxation times of the process is related to the presence of slightly different configurations of the complex.
- The TSDC band in the 10–70 K region in LiF:OH$^-$ and LiF:Mg^{2+},OH$^-$is attributed to the reorientation, *via* quantum tunnelling, of highly interacting hydroxides (*e.g.* OH$^-$ within pairs on nearest neighbour or next-nearest neighbour sites) or OH$^-$ molecules interacting with products of the OH$^-$ radiolysis. Currents in the 70–150 K region are ascribed to the rotational mobility of some products of the OH$^-$ decomposition (*e.g.* H$_2$O$^-$ centres).
- The TSDC data support the idea that in LiF:OH$^-$, in contrast to other alkali halides, a neutral defect is located at an anion vacancy of the O^{2-}–V$_a^+$ dipole and the F$_2^+$ – like colour centre. The new F$_2^+$(ND,O$^-$) model which is tentatively proposed for the laser-active F$_2^+$ – like centres in LiF:OH$^-$ has several advantages over the older F$_2^+$(O^{2-}) and F$_2^+$(O$^-$) models. Additional theoretical calculations and experimental evidence are required to confirm the existence and the exact nature of these defects, the validity of the F$_2^+$(ND,O$^-$) model and its applicability (if at all) to other alkali halides.

References

1. M. Aguilar, F.J. Lopez, F. Jague, Solid State Commun. **28**, 699 (1978)
2. A.I. Nepomnyashchih, E.A. Radzhabov, E.V. Egranov in *Colour Centres and Luminescence of Crystals* (Novosibirsk: Nauka, 1984)
3. L.F. Mollenauer, Opt. Lett. **5**, 188 (1980)
4. C.R. Pollock, J.F. Pinto, E. Georgiou, Appl. Phys. B **48**, 287 (1989)
5. T.T. Basiev, S.B. Mirov, V.V. Osiko, IEEE J. Quantum Electronics **24**, 1052 (1988)
6. V.I. Baryshnikov, V.A. Grigorov, B.D. Lobanov, E.F. Martynovich, E.E. Penzina, V.M. Khulugurov *et al.*, Izv. An. USSR **545**, 1467 (1990)
7. S.B. Mirov, A.Y. Dergachev, in *Proceedings SPIE, Solid State Lasers VI, February 1997, San-Jose*, Vol. 2986 (1997), p. 162
8. C.P. Yakymyshyn, J.F. Pinto, C.R. Pollock, Opt. Lett. **14**, 621 (1989)
9. K. Mollmann, W. Gellermann, in *Technical Digest of Int. Conf. on Laser and Electro-Optics CLEO '94, Anaheim USA*, (1994), p. 67
10. G. Sucha, S.R. Bolton, D.S. Chemla, IEEE J. Quantum Electronics **28**, 2163 (1992)
11. I.A. Parfianovich, V.M. Khulugurov, B.D. Lobanov, Izv. An. USSR. **43**, 1125 (1979)
12. B.D. Lobanov, V.M. Khulugurov, I.A. Parfianovich, Sov. Phys. J. **21**, 476 (1978)
13. D. Wandt, W. Gellermann, F. Luty, H. Welling, J. Appl. Phys. **61**, 864 (1987)
14. E. Georgiou, J.F. Pinto, C.R. Pollock, Phys. Rev. B **35**, 7636 (1987)
15. L.C. Couroll, L. Gomes, J.M. Ranieri, Phys. Rev. B **42**, 4741 (1990)
16. V.A. Chepurnoy, S.N. Mysovskii, I.A. Parfianovich, V.N. Salomatov, A.P. Shkadarevich, Phys. Status Solidi (b) **125**, K41 (1984)
17. V.N. Salomatov, T.G. Yurieva, Sov. Phys. Solid State **33**, 1012 (1991)
18. V.N. Salomatov, T.G. Yurieva, in *Proceedings of the XII International Conference on Defects in Insulating Materials 1992* (World Scientific, 1992), p. 471
19. W. Gellermann, F. Luty, K.P. Koch, G. Litfin G, Phys. Status Solidi (a) **57**, 411 (1980)
20. F. Kerkhoff, W. Martienssen, W. Zander, Z. Phys. **173**, 184 (1963)
21. S.P. Morato, F. Luty, Phys. Rev. B **22**, 498 (1980)
22. B.D. Lobanov, N.T. Maksimova, V.M. Khulugurov, I.A. Parfianovich, Fiz. Tverd. Tela **22**, 283 (1980)
23. Z.G. Akhvlediani, K.J. Berg, G. Berg, Cryst. Lattice Defects **8**, 167 (1980)
24. P.D. Alekseev, G.I. Baranov, Fiz. Tverd. Tela **22**, 1213 (1980)
25. L.I. Brukvina, L.N. Sinitsa, V.M. Khulugurov, A.G. Shneider, preprint No 5 (Siberian Branch of Sov. Academy Science, 1986)

26. L.I. Brukvina, V.M. Khulugurov, Fiz. Tverd. Tela **32**, 288 (1990)
27. V.M. Khulugurov, V.N. Salomatov, A. Vassilikou-Dova, V.I. Baryshnikov, I.M. Kalogeras, S. Grigorakakis, S.K. Makarov, A.A. Mikhalenko, J. Phys. Cond. Matt. **11**, 7005 (1999)
28. T. Stoebe, J. Phys. Chem. Solids **31**, 1291 (1970)
29. J. Nahum, Phys. Rev. **158**, 814 (1967)
30. A. Chandra, J. Chem. Phys. **51**, 1509 (1969)
31. J. Vanderschueren, J. Gasiot, in *Field-Induced Thermally Stimulated Currents (Topics in Applied Physics)*, edited by G.M. Sessler (Springer, Berlin, 1980), p. 144
32. S. Radhakrishna, S. Haridoss, Cryst. Lattice Defects **7**, 191 (1978)
33. C. Lavergne, C. Lacabanne, IEEE Electr. Insul. Magn. **9**, 5 (1993)
34. V. Katsika, J. Grammatikakis, J. Phys. Chem. Solids **51**, 1089 (1990)
35. C. Kokott, F. Fischer, Phys. Status Solidi (b) **106**, 141 (1981)
36. P.W.M. Jacobs, S.H. Ong, J. Phys. Chem. Solids **41**, 437 (1980)
37. C.P. An, F. Luty, Phys. Rev. B **56**, R5721 (1997)
38. E. Gustin, A. Bouwen, D. Shoemaker, C.P. An, F. Luty, Phys. Rev. B **61**, 3989 (2000)
39. C. Enss, S. Ludwig, M. Kreft, C.P. An, F. Luty, Physica B **263-264**, 129 (1999)
40. F. Luty, Phys. Rev. B **10**, 3667 (1974)
41. A.G. Shneider, N.A. Ivanov, V.M. Khulugurov, Opt. Spectrosk. **83**, 102 (1997)
42. N.A. Ivanov, V.D. Inshakov, V.M. Khulugurov, J. Priklad. Spectrosc. **46**, 136 (1987)
43. N.A. Ivanov, I.A. Parfianovich, V.M. Khulugurov, A.G. Shneider, in *Proceedings XIX Union Conf. on Spectroscopy* (Tomsk, Russia, 1982, p. 228)
44. C. Jaccard, Phys. Rev. **124**, 60 (1961)
45. P. Pissis, L. Apekis, C. Christodoulides, G. Boudouris, J. Phys. Chem. **87**, 4034 (1983)
46. L. Laudat, F. Laudat, Z. Phys. Chem. **174**, 211 (1991)
47. A. Anagnostopoulou-Konsta, L. Apekis, C. Christodoulides, D. Daoukaki, P. Pissis, in *Dielectric study of the hydration process in biological materials (Biologically Inspired Physics)*, edited by L. Peliti (Plenum, New York, 1991), p. 229
48. I.M. Kalogeras, A. Vassilikou-Dova, J. Phys. Chem. B **115**, 7651 (2001)
49. J.M. Kalogeras, A. Vassilikou-Dova, Cryst. Res. Technol. **31**, 693 (1996)
50. R. Capelletti, P. Beneventi, E. Colombi, W.B. Fowler, Nuovo Cimento **15**, 415 (1993)
51. R. Capelletti, P. Beneventi, E. Colombi, S. Prato, Nuovo Cimento **20**, 859 (1998)
52. M. Suszynska, B. Macalik, Acta Phys. Polon. A **62**, 363 (1982)
53. Y. Farge, M. Lambert, R. Smoluchowski, Solid State Commun. **4**, 333 (1966)
54. E. Radzhabov, Phys. Status Solidi (b) **123**, K79 (1984)
55. E. Radzhabov, Phys. Status Solidi (b) **130**, K55 (1985)
56. F. Fischer, H. Grundig, H. Hilsch, Z. Phys. **189**, 79 (1965)
57. F. Fischer, G. Gummer, Z. Phys. **189**, 97 (1965)
58. G. Gummer, Z. Phys. **215**, 256 (1968)
59. C. Kokott, F. Fischer, Z. Phys. **249**, 31 (1971)
60. P. Hennl, Phys. Status Solidi (b) **84**, K151 (1977)
61. P. Hennl, Phys. Status Solidi (a) **46**, 146 (1978)
62. E. Radzhabov, Opt. Spectrosk. **64**, 221 (1988)
63. N.A. Ivanov, E.E. Penzina, S.A. Zilov, Phys Status Solidi (b) **213**, 197 (1999)
64. N.N. Kristoffel, V.N. Salomatov, Izv. Akad. Nauk ESSR, Ser. Fiz.-Mat. **17**, 3 (1968)
65. N.N. Kristoffel, V.N. Salomatov, Sov. Phys. Solid State **10**, 1749 (1969)
66. B.D. Lobanov, V.N. Salomatov, T.G. Yurieva, Phys. Solid State **35**, 895 (1993)
67. J. Nahum, D. Wiegand, Phys. Rev. **154**, 1000 (1967)
68. J.S. Cook, J.S. Dryden, Radiation Effects **75**, 113 (1983)