

# IMPURITIES AND THERMOLUMINESCENCE.

## Titanium-related defects in LiF : Mg, Ti

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**Résumé.** — La résonance électronique du spin (R.E.S.) et la conductivité ionique ont été utilisées afin de définir les états de défauts possibles du Ti en LiF. Le spectre de la R.E.S. indique des raies dues à des groupes de défauts d'équilibre particulier contenant des ions  $Ti^{3+}$  et des centres F, et une raie large provoquée par l'ion  $Ti^{3+}$  dans la phase précipitée. Aucun ion  $Ti^{2+}$  n'a été observé. Les interactions possibles entre les défauts induits par Mg et Ti ont été discutées et rapprochées au mécanisme de TL en LiF.

**Abstract.** — Electron spin resonance (esr) and ionic conductivity have been used to define the possible defect states of Ti in LiF. The esr spectrum shows lines due to specific equilibrium defect complexes containing  $Ti^{3+}$  and F centers, and a broad line due to  $Ti^{3+}$  in a precipitate phase. No  $Ti^{2+}$  ions are observed. Possible interactions between Mg and Ti-related defects are discussed and related to the TL mechanism in LiF.

1. **Introduction.** — The thermoluminescent (TL) properties of LiF : Mg, Ti are well known, and the basic mechanisms for the TL process have been established [1]. The presence of Mg impurity ions in this material has been shown to be responsible for electron trapping, while the Ti ions are involved in the recombination processes occurring during TL [1-4]. In addition, OH impurities have been shown to play an important role in the TL process [5], forming defect complexes with both Mg and Ti impurities [6]. Irradiation causes decomposition of hydroxide ions into substitutional oxygen ions, U-centers and F centers [7, 8].

Two recent studies [9, 10] have concentrated on the electron spin resonance (esr) spectrum of Ti in LiF. Davies' esr results at 4 K in LiF : Ti indicated the presence of a  $Ti^{3+}$  center at  $g = 1.971$  [9]; from symmetry arguments, Davies argued that three of the nearest neighbor fluorine ions to the  $Ti^{3+}$ -ion must be absent, possibly replaced by oxygen ions. Hoffman and Poss also identified several esr signals in LiF : Ti [10]: A signal centered at  $g = 2.0227$  was interpreted as  $Ti^{3+}$ -ions interacting with five neighboring fluorine ions; the sixth nearest neighbor site is seen as being an anion vacancy. Another spectrum centered at  $g = 1.9756$ , undoubtedly the same as Davies' signal, is interpreted as a  $Ti^{3+}$ -ion with one nearest neighbor oxygen ion and one nearest neighbor anion vacancy. Both Davies and Hoffman and Poss also see the strong F-center band at  $g = 2.017$ .

The present work was undertaken to provide a more consistent lattice defect picture of the role of Ti in LiF. The LiF single crystals were grown from Baker starting material with 82 ppm Ti by weight added to the melt. These samples also contain

30 ppm Mg by weight and a small concentration of OH ions. Additional powdered samples of LiF (TLD-100) were also used: this material is known to contain about 200 mole ppm Mg and about 10 mole ppm Ti. Esr spectra were obtained using a JEOL spectrometer and later a Varian EPR spectrometer at x-band frequencies.  $g$  factors for observed signals were determined using the known signal position of DPPH as the calibration point; line widths are reported as peak to peak width on the derivative signal. Ionic conductivity was measured using the techniques described earlier [6].

2. **Results.** — Ionic conductivity plots were made for several as-grown LiF : Mg, Ti samples and compared with similar LiF : Mg samples. In no case was any additional ionic conduction observed that could be attributed to the addition of Ti to the sample. This indicates that any vacancies present for charge compensation are bound to the Ti-ion. This also means that  $Ti^{2+}$ -ions are absent, since the extrinsic vacancies introduced by divalent cations are well known to increase the conductivity of such materials [1].

Esr results for Ti-doped single crystal, obtained immediately after growth, showed a low intensity broad absorption band centered near  $g = 2.2$ , discussed in more detail below. Upon irradiation to  $10^6$  R, a complicated sharp line spectrum developed near  $g = 2$ , as shown in figure 1. Here most of the lines with indicated  $g$  values at or below 2.02 are identifiable with  $Ti^{3+}$ , except the line near  $g = 2.01$ , identified as the F-center. The lines observed at  $g > 2.03$  have been attributed to other paramagnetic impurities by Hoffman and Poss [10].

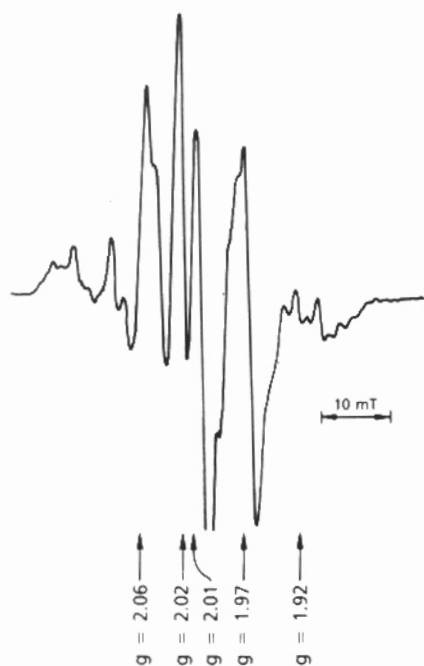


Fig. 1. — Esr signal from virgin, laboratory-grown single crystal of LiF : Mg, Ti after irradiation to  $10^6$  R. Signals discussed in text.

These Ti-doped samples were aged for 4 years at room temperature, then re-examined. In the aged condition, they exhibited a strong, broad esr line centered at  $g = 2.9$  with a width of about 50 mT, and only faint indications of lines near  $g = 2$ . After annealing at 400 °C for one hour and irradiating to  $10^3$  R the broad line is seen centered at  $g = 2.2$  with a line width of 25 mT. In the latter case, the F band and one or two  $Ti^{3+}$  lines are also seen. The sharp line spectrum of figure 1 could not be resurrected by any annealing or irradiation treatment.

The esr spectra of powdered LiF (TLD-100) samples were examined in several samples. Virgin samples irradiated to  $10^6$  R showed a broad esr line centered near  $g = 2.2$  with a width of nearly 100 mT, and additional sharp line structure near  $g = 2$ , as is seen in figure 2. A subsequent anneal at 400 °C for 1 hour eliminates the F band and  $Ti^{3+}$  signals, but does not change the broad band. LiF (TLD-100) powder that had been through several irradiation and annealing cycles shows the same broad band as above when in the annealed condition; in this case, the  $Ti^{3+}$  bands no longer disappear completely but remain after the 400 °C annealing treatment.

Another annealing treatment of interest in LiF is a 280 °C treatment for 15 min., which is known optically to destroy 75 % of the F band and create  $Z_3$  centers. The effect of this treatment on the esr spectrum in the irradiated virgin sample is shown in figure 3. As may be observed in figure 3, the treatment decreases the F band intensity and causes broadening (from 2.4 to 2.9 mT) due to the addition of a new signal. Some of the other signals present in the irradiated state in this sample are seen to disappear after this annealing treatment.

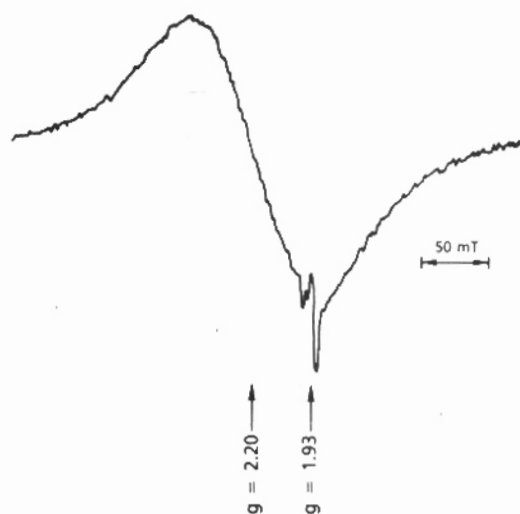


Fig. 2. — Esr signal from LiF (TLD-100) powder sample after irradiation to  $10^6$  R.

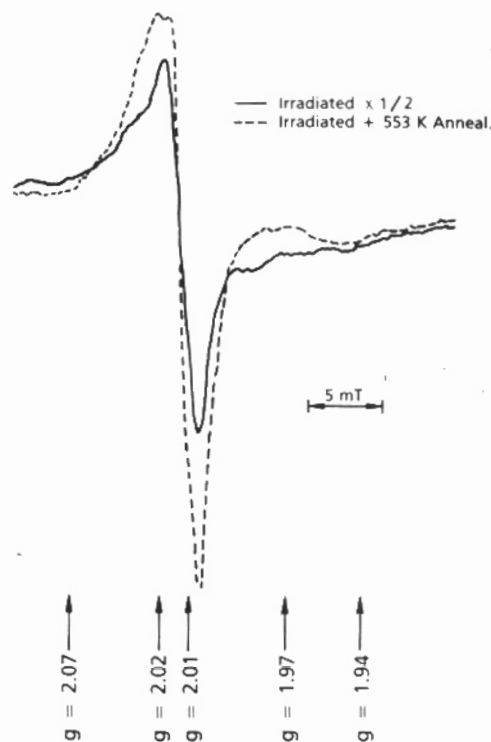


Fig. 3. — Central esr signals from LiF (TLD-100) powder after irradiation to  $10^6$  R (shown at half intensity) and after annealing at 280 °C for 10 min.

**3. Discussion.** — The mechanism of TL requires the Ti-related activator to be a generally available recombination site. The defect involved should be a hole trap after irradiation and should be plentiful enough to trap holes continually in proportion to the irradiation dose. Further, the constancy of the TL mechanism dictates that the activator be present in equilibrium in the solid. Using Kroger's nomenclature [11], several possible lattice defects meeting these criteria are listed in table I. This list is not

Table I. — *Equilibrium lattice defects containing Ti<sup>4+</sup> and Ti<sup>3+</sup> in LiF. Ti<sup>4+</sup> defect shown in left column; Ti<sup>3+</sup> defect produced by absorbing an electron during irradiation is shown in right-hand column. Only Ti<sup>3+</sup> defect is observable using esr. Changes denoted relative to the Li<sup>+</sup>F<sup>-</sup> lattice: x is neutral, ' is negative, . is positive relative to each cation (m) or anion (x) site.*

Defect No.	Ti <sup>4+</sup> defect	Ti <sup>3+</sup> defect	Remarks
1	$[Ti_m(V'_m)_3]^x$	$[Ti_m(V'_m)_3]'$	
2	$[Ti_m(O'_x)_3]^x$	$[Ti_m(O'_x)_3]'$	Davies defect
3	$[Ti_m V_x]^{x..}$	$[Ti_m V_x]^{x..}$	Hoffman defect 1
4	$[Ti_m V_x O'_x]^{x..}$	$[Ti_m V_x O'_x]^{x..}$	Hoffman defect 2
5	$[Ti_m(V'_m)_3 V_x O'_x]^x$	$[Ti_m(V'_m)_3 V_x O'_x]'$	Modified Hoffman defect 2
6	$[Ti_m(V'_m)(O'_x)_2]^x$	$[Ti_m V'_m(O'_x)_2]'$	Modified defect
7	$[Ti_m Mg_m V'_m(O'_x)_3]^x$	$[Ti_m Mg_m V'_m(O'_x)_3]'$	With Mg

meant to be exhaustive but rather to be a typical set of equilibrium Ti<sup>3+</sup> and Ti<sup>4+</sup> defects related to one another by electron and hole capture.

The most practical activator would be one that traps holes during TL and traps electrons during radiation to reset itself. The defects listed in table I, except for nos. 3 and 4, are of this type. Defects 3 and 4 seen by Hoffman and Poss are electron traps as listed; they could act as competing recombination centers but could not easily be reset by irradiation.

The broad esr band reported in this work is present in very low intensities in as-grown LiF : Mg, Ti samples and grows during the first few irradiation cycles to an apparent saturation value. It seems likely that this is due to Ti<sup>3+</sup>-ions in a precipitate phase or colloid center, which causes a line shift and broadening due to dipole-dipole interactions. These could be similar to the metastable Suzuki phase precipitates seen in several alkali halide systems [12] and studied in some detail in LiF : Mg [13]. That these precipitates form during radiation indicates that defects generated during radiation aid in the precipitation process.

The F center bands at  $g = 2.01$  in figures 1, 2 and 3 are relatively narrow (2-2.5 mT), while those in the literature are broad with well defined hyperfine structure [14]. These narrow lines were seen in several LiF : Mg, Ti and LiF : Mg, Ti, OH samples in this study, while broader lines of widths of 3.5-4.5 mT were seen in a pure Harshaw and in LiF : Mg, Ti samples purified of OH. This may indicate that neighboring OH or its radiation-generated decomposition products interact with F centers to reduce the esr line width in OH-doped samples.

In figure 3, the Ti-related bands disappear after the 280 °C anneal, as they do during the first few 400 °C annealing cycles in all LiF : Mg, Ti tested.

After several cycles, however, the Ti-related bands no longer disappear after annealing. This indicates that during the first few cycles, only enough Ti<sup>3+</sup> defects are present for recombination with the holes released to TL, but that after several radiation cycles, additional Ti<sup>3+</sup> is available that is not used during the TL readout. This could be due to defect rearrangement during the radiation cycle, perhaps related to the precipitation process involved in figure 2.

In well-used LiF (TLD-100) after a 400 °C anneal and irradiation to 10<sup>5</sup> R, the small peak seen at  $g = 1.94$  is more pronounced than shown in figure 3. This is probably the same peak as seen by Davies at  $g = 1.93$  in LiF : Mg, Ti. This peak is reduced in intensity by an 80 °C anneal prior to radiation, a treatment known to destroy traps responsible for lower temperature peak 2 of the TL spectrum; at the same time, the 80 °C anneal enhances the esr signal at  $g = 1.97$ . The mechanism of destruction for these peak 2 traps is probably the aggregation of Mg-cation vacancy-related traps into higher complexes. This aggregation could also remove Mg-cation vacancy dipoles from defects of type 7 in table I, reducing the  $g = 1.94$  esr signal at the expense of that at  $g = 1.97$ . This would be consistent with Davies' model for the  $g = 1.97$  trap.

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## DISCUSSION

*Question.* — J. L. ALVAREZ RIVAS.

Have you observed whether the glow peaks are correlated with the F centre or 310 nm band thermal annealing steps ?

*Reply.* — W. LAS.

No. We have not done these measurements.

*Question.* — J. S. DRYDEN.

In your model are the individual Mg ions and Mg-ion vacancy pairs acting as electron traps ?

*Reply.* — W. LAS.

No. In our model the Mg-cation vacancy dipoles associated with titanium act as hole traps.

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