Lead incorporation mechanism in LiF crystals

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The **doping** process of **LiF with Pb** has been described by using structural **ab initio** modeling and **experimental** data. The intake of Pb starts in interstitial $Pb_I^{••}$ or Li-substitutional $Pb_{Li}^{•}$ sites and it is eased by charge-balancing Li vacancies v_{Li}'. The metal successively captures the vacancies to form a final stable **complex $Pb_{Li}^{•}$ +v_{Li}'**. Experimental data from X-ray Absorption Spectroscopy confirm the presence of Pb in LiF crystals in this site. A **maximum solubility** of Pb in LiF of the order of $3*10^{20}$/cm^3 can be estimated from the values of the complex formation energies.

Introduction.

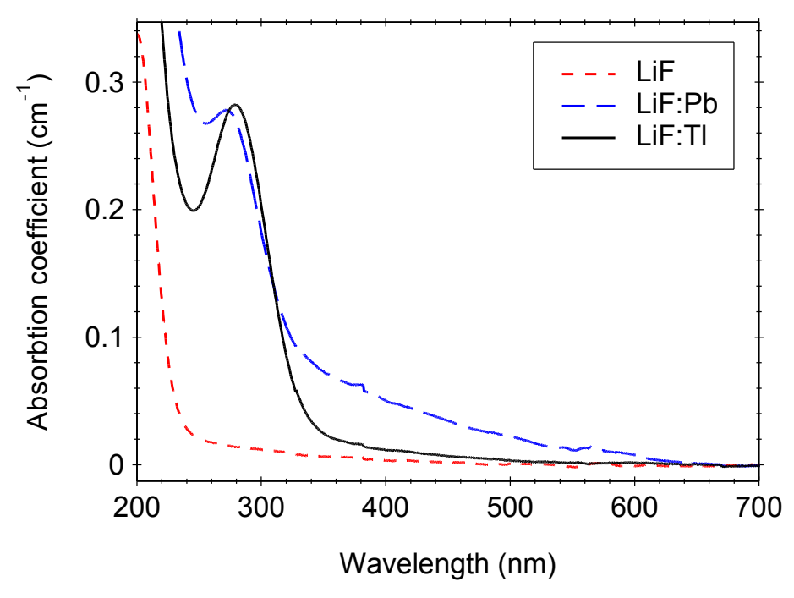
Point defects in LiF make it a very attractive radiation-sensitive material, well known for application in **dosimeters**, optically pumped solid-state lasers and miniaturized **light-emitting devices**. An interesting possibility for the development of innovative materials for infrared **colour-centre lasers** is expected from LiF crystals doped with ions like Pb and Tl.

The present study aims to describe the process of **LiF doping with Pb** using ***ab initio*** methods for **structural modeling** compared to **experimental** data from X-ray absorption Spectroscopy (**XAS**).

Sample preparation

The **growth** of Pb doped LiF crystals is a **nontrivial task** for a number of reasons. From a structural point of view there is a severe **structural mismatch** between cubic LiF and orthorhombic PbF_2 and the large **differences** between the **ionic radii** of Pb and Li result in a poor solvation of the dopant ions. A further problem is represented by the large **difference** between the **electronegativities** of dopants and the host cations, Pb^{2+} being 2.33 and Li 0.98. Our group has succeededd in preparing Pb doped LiF single crystals with the following procedure: first a LiF powder is prepared by using quasi-homogenous synthesis in aqueous solutions from LiCl and NH_4F. The powder is dried and then LiF crystals (pure and doped using PbF_2) are grown by the **Kyropoulos growth technique** in dry nitrogen atmosphere.


LiF monocrystal doped with 300 mg PbF_2 in melt

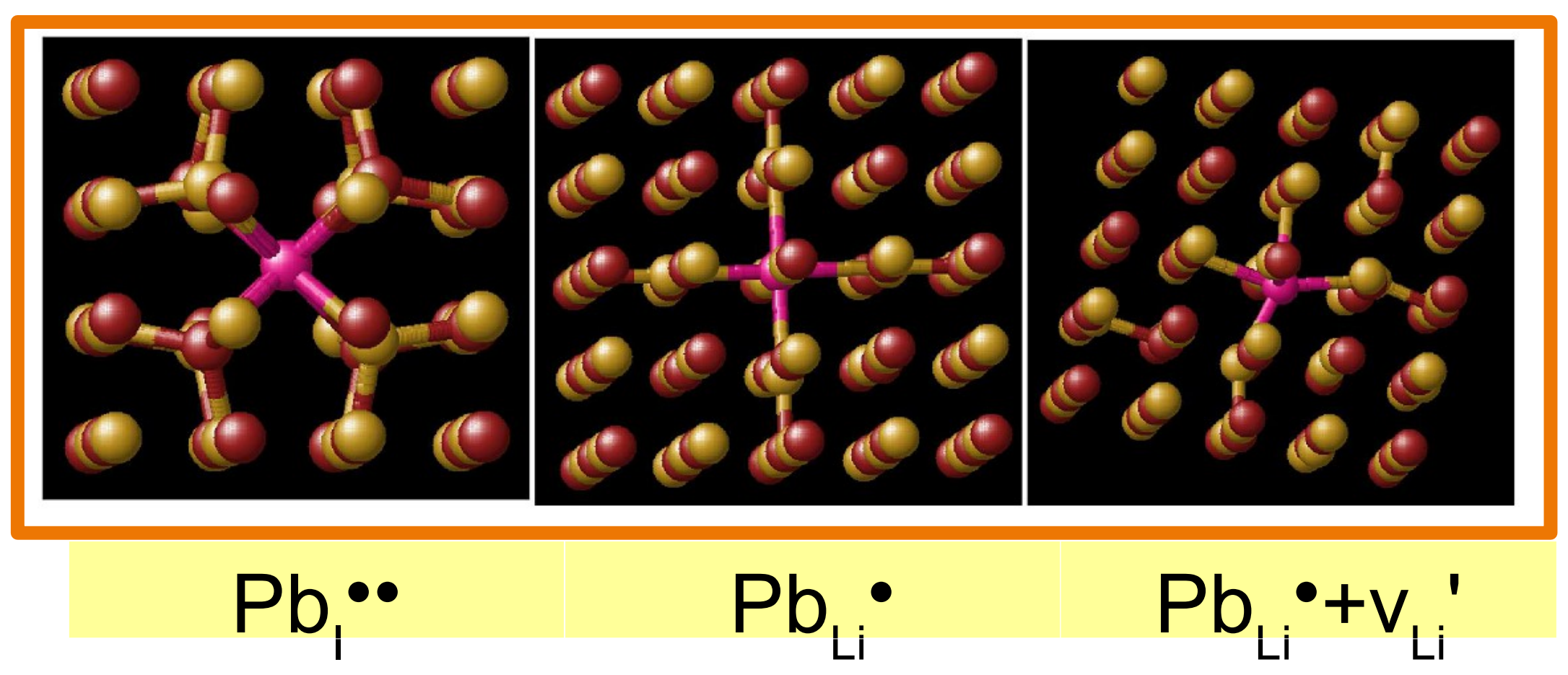


The optical absorption spectra of doped LiF crystals show a broad absorption band located around:
275nm (4.51eV) for Pb^{2+}
279nm (4.44eV) for Tl^{+}

Several crystal slices, few mm thick, are then cleaved and annealed in order to eliminate the crystallization water. UV-Vis absorption spectra exhibit an absorption line at 275 nm non present in the undoped samples.

Ab-initio structural simulations

The formation energy and local structures of various Pb complexes in LiF have been calculated with the density functional theory (**DFT**) as implemented in the VASP code. Supercells of 64 atoms (2*2*2) were considered and calculations were done with projector augmented wave pseudo-potentials, whereas the exchange-correlation functional used was the generalized gradient approximation. Different **complexes** were considered like **$Pb_{Li}^{•}$, $Pb_I^{••}$, $Pb_{Li}^{•}$+v_{Li}', $Pb_I^{••}$+2v_{Li}'**, with the vacancies taken near (second coordination shell) of far from Pb.



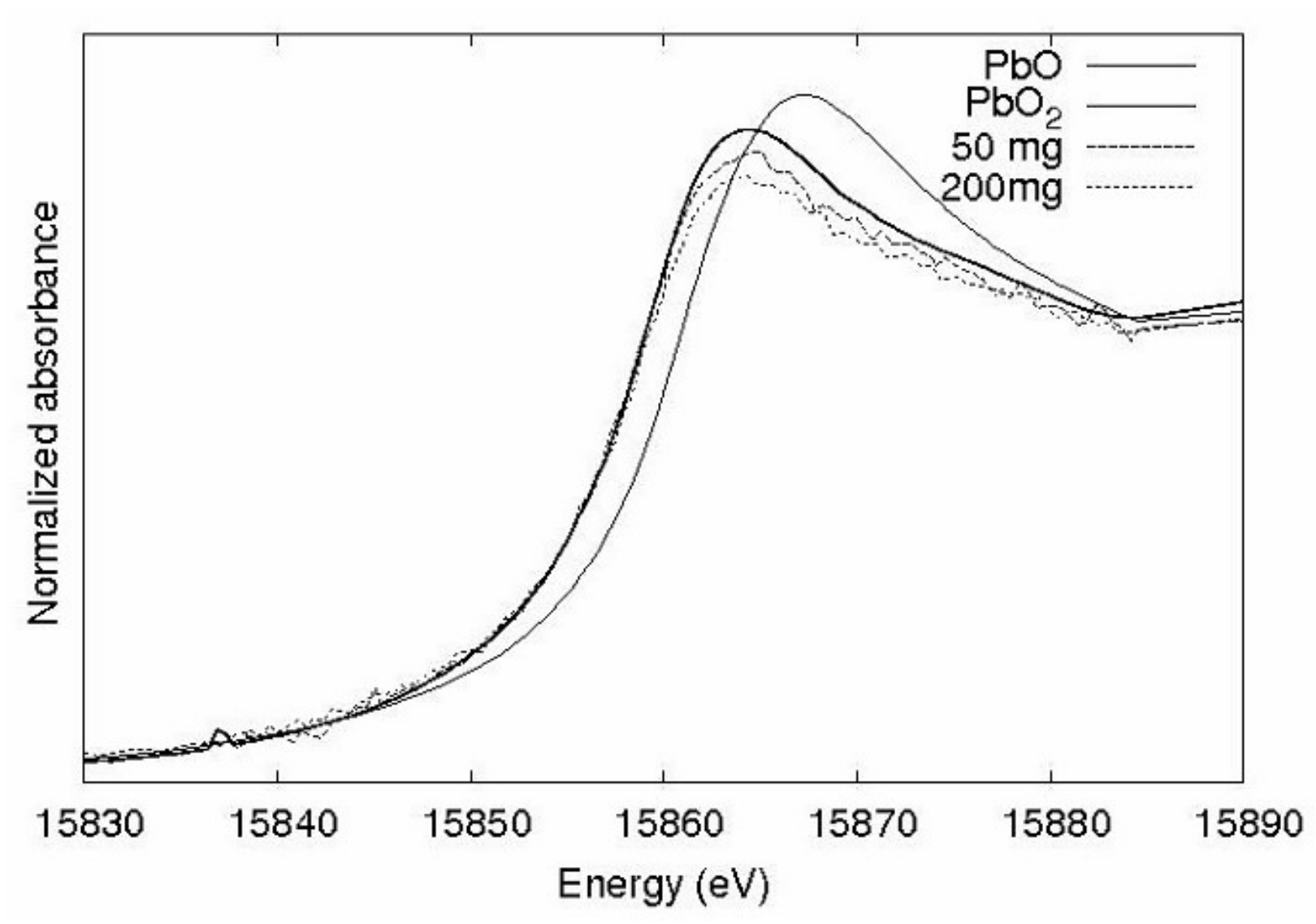
Here we show the **formation energies** for several complexes (subfix f or n stands for far or near)

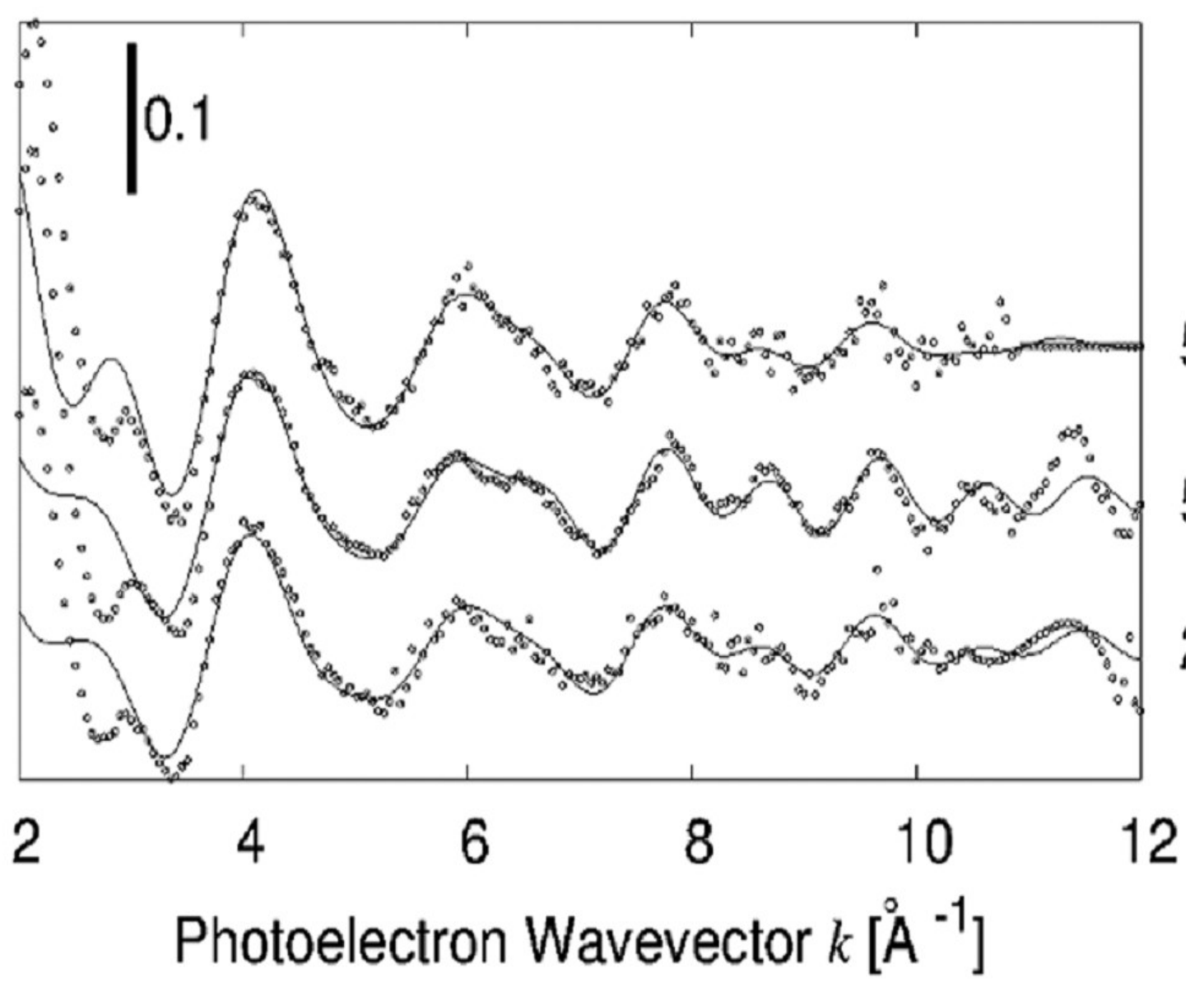
Structure	E_f (eV)	Structure	E_f (eV)
$Pb_{Li}^{•}$	9.57	$Pb_{Li}^{•} + V_{Li-n}'$	2.66
$Pb_{Li}^{•} + V_{Li-f}'$	3.14	$Pb_I^{••}$	17.05
$Pb_I^{••} + 2V_{Li-n}'$	3.07	$Pb_I^{••} + 2V_{Li-f}'$	3.12
V_{Li}'	0.48	$2V_{Li}'$	1.03

It is clear that the vacancy lowers the formation energy of either the substitutional or interstitial site and that the **lowest energy site is $Pb_{Li}^{•}$+v_{Li}'**

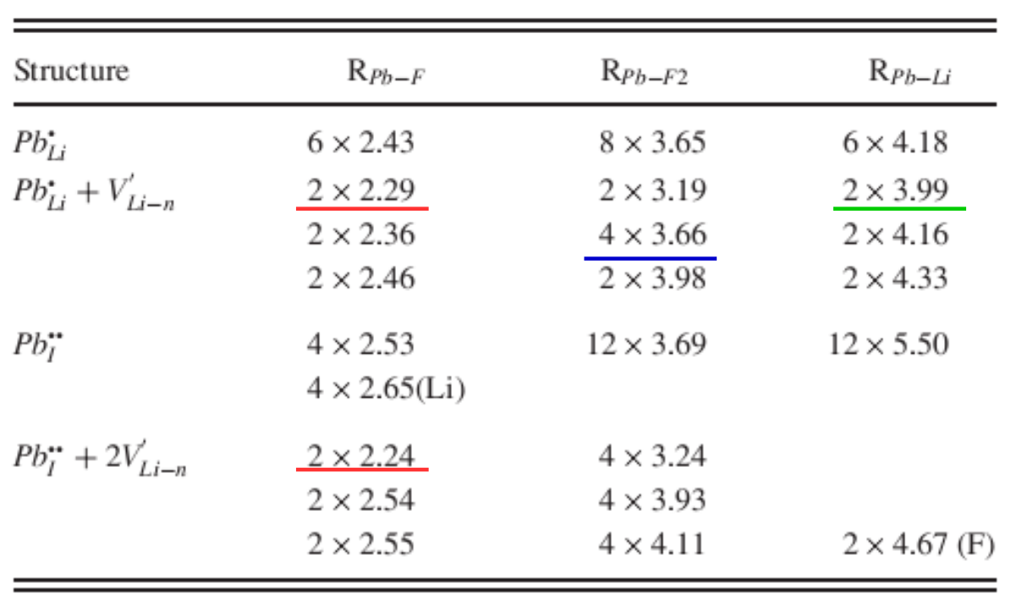
X-ray Absorption Spectroscopy

XAS at the Pb-L_3 and -L_1 edges (GILDA beamline ESRF) was used to characterize the state of Pb and its incorporation site.

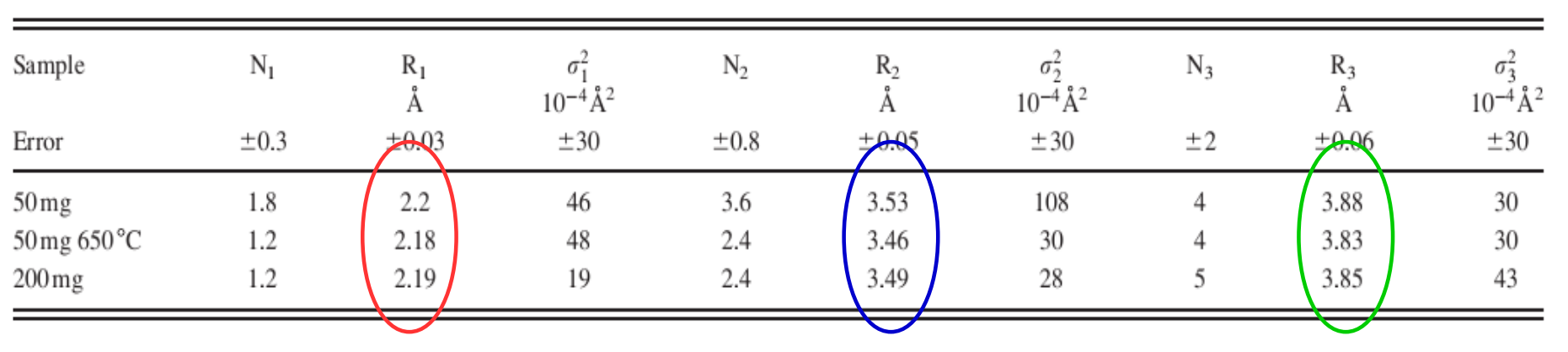




From the XANES it can derived that **Pb is in the 2+ state**. The EXAFS data can be reproduced with a Pb-F bond plus a collinear configuration Pb-F-Li



Structure	R_{Pb-F}	R_{Pb-F2}	R_{Pb-Li}
$Pb_{Li}^{•}$	6 × 2.43	8 × 3.65	6 × 4.18
$Pb_{Li}^{•} + V_{Li-n}'$	2 × 2.29 2 × 2.36 2 × 2.46	2 × 3.19 4 × 3.66 2 × 3.98	2 × 3.99 2 × 4.16 2 × 4.33
$Pb_I^{••}$	4 × 2.53 4 × 2.65(Li)	12 × 3.69	12 × 5.50
$Pb_I^{••} + 2V_{Li-n}'$	2 × 2.24 2 × 2.54 2 × 2.55	4 × 3.24 4 × 3.93 4 × 4.11	2 × 4.67 (F)



Sample	N_1	R_1 Å	σ_1^2 10^{-4}Å^2	N_2	R_2 Å	σ_2^2 10^{-4}Å^2	N_3	R_3 Å	σ_3^2 10^{-4}Å^2
Error	±0.3	±0.03	±30	±0.8	±0.05	±30	±2	±0.06	±30
50mg	1.8	2.2	46	3.6	3.53	108	4	3.88	30
50mg 650°C	1.2	2.18	48	2.4	3.46	30	4	3.83	30
200mg	1.2	2.19	19	2.4	3.49	28	5	3.85	43

Discussion

The interatomic distances found from **EXAFS data** show the better agreement with the **$Pb_{Li}^{•}$+v_{Li}' complex** i.e. that with the lowest formation energy following the ab-initio calculation. The doping of LiF with Pb can be thus resumed in the **following steps:**

- Intake of Pb in presence of vacancies. Pb can enter interstitial or substitutional sites, as the relative energy difference is low.
- Migration of the vacancies that come near to the metal. For substitutiona Pb this is already the lowest energy.
- Capture of one vacancy by the $Pb_I^{••}$+2v_{Li}'complex that is thus converted in $Pb_{Li}^{•}$+v_{Li}

At the end the material will only contain $Pb_{Li}^{•}$+v_{Li} complexes and they need a vacancy to be stabilized. From the formation energy of the vacancies we can estimate a **maximum doping level of $3*10^{20}$ Pb/cm^3** if the process is carried out just below the melting temperature of LiF.

References

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