

EXAFS simulations in Zn-doped LiNbO₃ based on defect calculations

Mário E G Valerio¹, Robert A Jackson², Frank G Bridges³

1. Department of Physics, Federal University of Sergipe, São Cristavão-SE, Brazil

2. School of Physical and Geographical Sciences, Keele University, Keele, Staffordshire ST5 5BG, UK

3. Department of Physics, University of California Santa Cruz, Santa Cruz CA 95064, USA

mvalerio@ufs.br

Abstract. Lithium niobate, LiNbO₃, is an important technological material with good electro-optic, acousto-optic, elasto-optic, piezoelectric and nonlinear properties. EXAFS on Zn-doped LiNbO₃ found strong evidences that Zn substitutes primarily at the Li site on highly doped samples. In this work the EXAFS results were revisited using a different approach where the models for simulating the EXAFS results were obtained from the output of defect calculations. The strategy uses the relaxed positions of the ions surrounding the dopants to generate a cluster from where the EXAFS oscillations can be calculated. The defect involves not only the Zn possible substitution at either Li or Nb sites but also the charge compensating defects, when needed. From previous defect modelling, a subset of defects was selected based on the energetics of the defect production in the LiNbO₃ lattice. From them, all possible clusters were generated and the simulated EXAFS were computed. The simulated EXAFS were then compared to available EXAFS results in the literature. Based on this comparison different models could be proposed to explain the behaviour of Zn in the LiNbO₃ matrix.

1. Introduction and Motivation

Zn-doped lithium niobate, LiNbO₃ is an important material for photorefractive applications. LiNbO₃ has been modelled in both pure and undoped states ([1], [2], [3]), and the calculations predict that Zn will substitute on the Li and Nb sites, with the defect $3Zn_{Li}^{\square} - Zn_{Nb}'''$ being the defect with the smallest solution energy, when considering the bound defects. The defect involving charge compensation via Li vacancies, $Zn_{Li}^{\square} - V_{Li}'$, where found to have energy three times higher than the previous one. A key issue in the previous modelling results is the fact that the defects were modeled as a full defect including all components in a way that they were neutral. Two important conclusions were drawn from this approach: i – the contribution of the binding energy to the total solution energy was very important, and for the case of the $3Zn_{Li}^{\square} - Zn_{Nb}'''$ it reduced the total energy to half of the initial unbound value, and ii - the final configuration of the lattice is highly influenced by the presence of the defects and its charge compensation accompanying defects.

EXAFS (Extended X-rays Absorption Fine Structure) is a very powerful technique to investigate the symmetry of the surrounding neighborhood of the target absorbing ion in a material. Recent EXAFS studies ([4], [5]) suggest that Zn occupies the Li site, and the model was based on assuming as

a starting point the Zn ion inside of a perfect LiNbO₃ lattice and fitting the simulated EXAFS to the experimental results by varying the coordination shell distances, the disorder parameter (Debye-Waller factor) among others.

In the present paper, an alternative and complementary way of viewing the EXAFS results is proposed based on the results of previous defect modelling and the LiNbO₃:Zn system was used as a test case for such approach.

2. Modelling background

The details of the defect modelling calculations were described in previous papers [1], [2], [3] and the potential sets and defect configurations for the Zn ions in the LiNbO₃ matrix were the ones described by the Araujo, RM at al. [3]. The EXAFS simulations were done using the FEFF6 code embodied in the IFEFFit package [6].

The EXAFS simulations were carried out using clusters of radii around 8 Å that were extracted from the output of the defect modelling calculations. The clusters, thus, already include the lattice distortion around the Zn ions due to the defect generated in the LiNbO₃ lattice and since both the dopant and the charge compensating defects were included in the defect calculations, the distortion represents more accurately the system. The defect modelling calculations were done at 0K and this temperature was chosen due to the fact that the experimental data from refs [4] and [5] were measured at low temperature.

On building up the cluster to use as the input for the EXAFS modelling special attention were taken in the case of the $3Zn_{Li}^{\square} - Zn_{Nb}'''$ defect because there are 4 Zn ions in the cluster and all of them will absorb the incident X-rays in the energy range covered by the EXAFS measurements in the Zn K edge. So, 4 different clusters were built where each one of the Zn ions were set at the origin and considered the absorbing atom, while the other ones acts as scatterers. The final simulated EXAFS was taken to be the average of the four individual simulations. The Debye-Waller factor was set to 0.003 Å^{-2} that is a typical value for low temperature measurements and is close to the experimental values fitted to the EXAFS data in refs [4] and [5].

3. Results and Discussions

Figure 1 shows the simulated Fourier transform of the EXAFS oscillations (red curves) for the model where Zn substitutes for the Li site (figure 1(a)) and substitutes at the Nb site (figure 1(b)) but considering the perfect lattice site with no distortion. Figure 1 also reproduces for comparison the experimental result of LiNbO₃:Zn sample (blue curves) extracted from reference [5]. For all simulated curves, the k space used in the Fourier transform of the EXAFS oscillations is compatible with the ones used in the experiment, i.e., k in the range from 3.8 to 13.2 Å^{-1} .

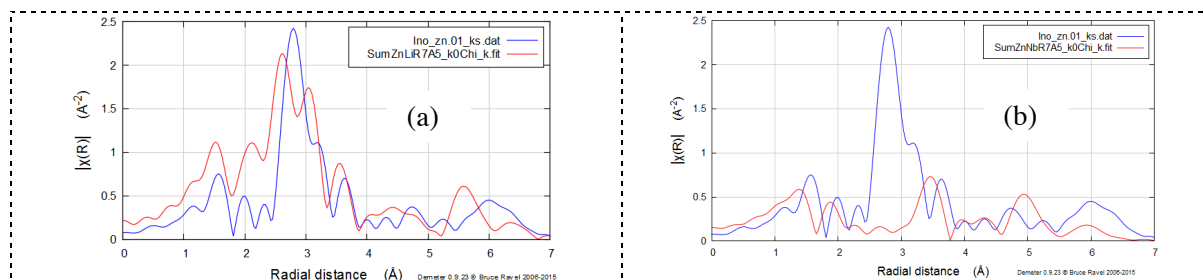


Figure 1: Comparison between the simulated Fourier Transform of the EXAFS (red curves) for Zn at a Li site (a) and Zn at Nb site (b) with the experimental measurements extracted from reference [5]. The results were expressed using k^2 weighting.

Results in figure 1 indicated that none of the models can describe the experimental results without taking into account distortion of the lattice. This is expected since Zn is a divalent metal and upon substituting either Li or Nb, the lattice will need to accommodate not only the differences on chemical behavior of the dopant in comparison to the host ions but also the charge compensating defects that will be needed. The computer modelling can be used to check how important these factors are. It is possible to consider first the effect of distortion assuming that the concentration of the dopants are low and there would be possible to have the charge compensating defect well apart from the dopant. Figures 1 indicated that the Zn substituting at the Li site seems to be closer to the experimental data than the other possibility and this was consider as a test.

Figure 2(a) shows the Fourier transform of the EXAFS simulations obtained for the Zn_{Li}^{\square} relaxed configuration (red curve) as compared to the experimental data (blue curve). It is possible to see that the lattice distortion did improve a little bit the model, as compared to the experimental results, but the simulation is still quite far from the measurement. The next step was the inclusion of the charge compensation that, as discussed earlier, is important in the case of $LiNbO_3$ defects. The first attempt would be to include the simplest possible charge compensating that is a Li vacancy, although the defect simulations presented in ref [2] did show that this is not the defect with the lower solution energy. One can argue that since the concentration of Zn in the samples measured in ref [5] is low, the Zn ions should be far apart from each other and the neutral defect that would keep the Zn isolated is the $Zn_{Li}^{\square} - V_{Li}'$ one. This can be tested by taking the relaxed lattice structure obtaining for the defect simulations of the $Zn_{Li}^{\square} - V_{Li}'$ one and computing the EXAFS for that model, and the result of such procedure is shown in figure 2(b). The simulated EXAFS was further improved with the main peak, around 3\AA showing a better agreement between the simulated and experimental curves, but the first peaks between 1 and 2\AA , due to the first shell of neighbors, typically O^{2-} ions, and the third group of peaks, around 6\AA are not described by this latter model.

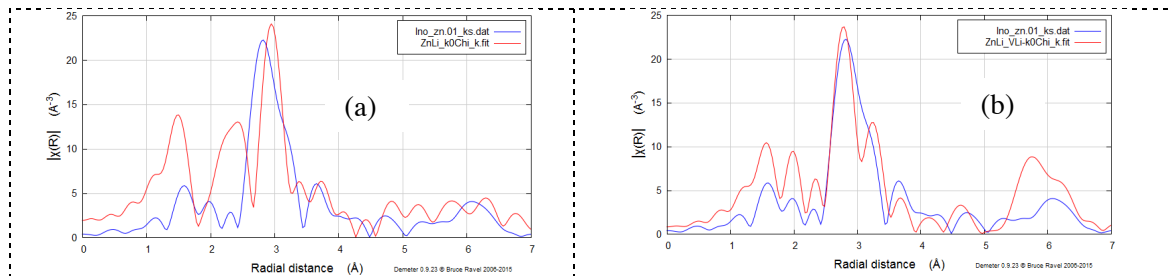


Figure 2: Comparison between the simulated Fourier Transform of the EXAFS (red curves) for the relaxed Zn_{Li}^{\square} defect (a) and $Zn_{Li}^{\square} - V_{Li}'$ relaxed defect (b) with the experimental measurements extracted from reference [5]. The results were expressed using k^2 weighting.

The next step is to test if the defect predicted by the defect modelling can improve the description of the experimental results. The defect predicted to have the smallest solution energy is the self-compensating defect $3Zn_{Li}^{\square} - Zn_{Nb}'''$ that involves 4 Zn ions in the cluster that have to be treated to simulate the EXAFS, as explained before. The result is shown in figures 3 and 4, where figure 3 shows the contribution of the individual Zn ions in the cluster and figure 4 the averaged simulated EXAFS.

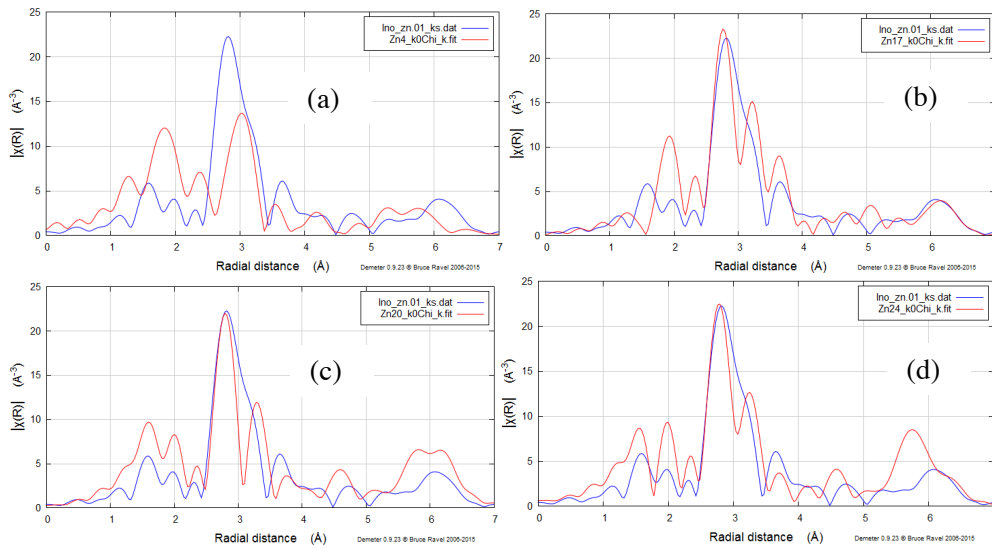


Figure 3: Comparison of the experimental measurements extracted from reference [5] with the simulated Fourier Transform of the EXAFS (red curves) for individual Zn ions in the relaxed $3Zn_{Li}^{\square} - Zn_{Nb}'''$ defect: (a) Zn_{Nb}''' and (b), (c) and (d) Zn_{Li}^{\square} . The results were expressed using k^2 weighting.

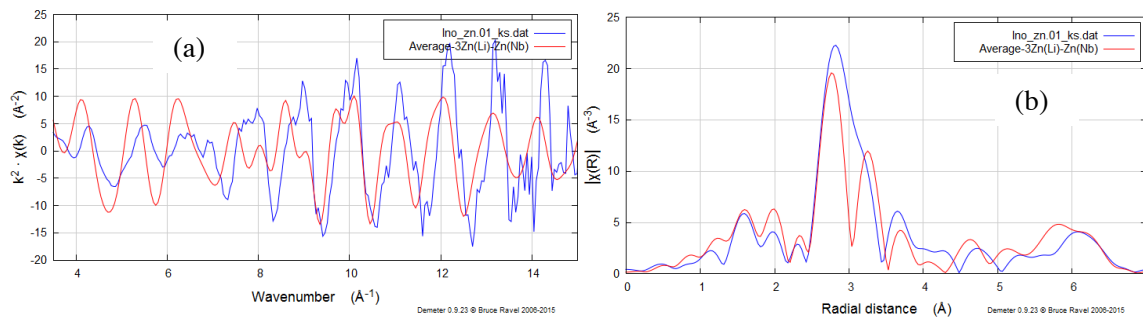


Figure 4: Comparison of the experimental measurements (blue curves) extracted from reference [5] with the simulated EXAFS oscillations (a) and Fourier Transform of the EXAFS (b) (red curves) for the relaxed $3Zn_{Li}^{\square} - Zn_{Nb}'''$ defect. The results were expressed using k^2 weighting.

Figures 3 and 4 show that the simulated EXAFS obtained for the relaxed LiNbO_3 lattice surrounding the $3Zn_{Li}^{\square} - Zn_{Nb}'''$ defect gave a better description of the experimental data. The relative intensity of the peaks in the Fourier transform curve are much closer to the experimental results. It is interesting to notice that the position of the peaks due to different shell of neighbours (group of neighbouring ions around a same average distance from the target Zn atom) are reasonably well described by the configuration of the lattice after relaxation around the $3Zn_{Li}^{\square} - Zn_{Nb}'''$ defect, although the EXAFS obtained from the contributions of the individual Zn ions are not as good as the averaged EXAFS curves.

4. Conclusions

In conclusion the combination of defect modelling with the EXAFS simulations can be a powerful tool to help the interpretation of EXFAS data mainly in quite complex systems where a simple defect or a simple initial configuration of the lattice around the target absorbing ions cannot be easily devised.

The output of the defect simulations, that takes the relaxation of the lattice around the defect into account, can be used as an initial guess for the configuration of the lattice around the ion being probed. It is important to stress that this is not an alternative to the usual way of analyzing and interpreting EXAFS data, but a different and maybe a much easier way to interpret EXAFS data mainly for the case of dopants.

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