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An EXAFS study of the Ni dopant site in BaLiF₃

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Abstract. Extended x-ray absorption fine-structure measurements show that the Ni²⁺ dopant in BaLiF₃ predominantly substitutes on the Li⁺ site of the host lattice. Quantitative analysis of the results yields the details of the local environment of the Ni²⁺ ion.

1. Introduction

BaLiF₃ is a new material that has potential technological applications when doped with divalent cations. The most important use would be as a tuneable vibronic laser material in the near-infrared region (around 1.5 μm) suitable for telecommunication devices. The important optical properties which make the material useful were studied by Prado *et al* [1] in Pb²⁺ doped crystals, by Martins *et al* [2] in Ni²⁺ doped crystals and by Duarte *et al* [3] in Co²⁺ doped crystals. The crystal structure of BaLiF₃ [4, 5] can be viewed as an inverted fluoroperovskite where the cations Ba²⁺ and Li⁺ occupy inverted positions as compared with other fluoroperovskites such as KMgF₃. It belongs to the space group *Pm3-m* where both the Ba²⁺ and the Li⁺ sites have cubic symmetry (O_h) but the coordination number is six for the Li⁺ site and 12 for the Ba²⁺ site. The lattice parameter is 3.995 Å [4] and the unit cell is shown in figure 1.

The positions of dopant divalent cations are still a matter of debate although some indirect evidence from optical studies suggests that Ni²⁺ ions are in a local octahedral environment [2], i.e. on the Li⁺ site of the host lattice. Extended x-ray absorption fine-structure (EXAFS) spectroscopy [6, 7] has proved an ideal technique for locating the positions of atoms in condensed matter. The technique has been successfully used to locate the positions of dopants in ionic crystals [8] and oxides [9]. In this paper we have used Ni²⁺ K-edge EXAFS measurements to identify the Ni²⁺ location in BaLiF₃.

The crystallographic data suggest that if the Ni²⁺ ion predominantly occupies either a Li⁺ or a Ba²⁺ site in BaLiF₃ the two possibilities should be readily resolved by the EXAFS technique. The local site geometries are very different: in particular there are large differences in the numbers and distances of the nearest F⁻ neighbours. The Li⁺ site is surrounded by six F⁻ ions at 1.998 Å whereas the Ba²⁺ site is surrounded by 12 F⁻ ions at 2.825 Å. Since EXAFS measurements monitor the local environment of the *average* target atom it is difficult to interpret the spectra when the target atom is in more than one local environment. Hence if the Ni²⁺ ion occupied both Li⁺ and Ba²⁺ sites to a significant

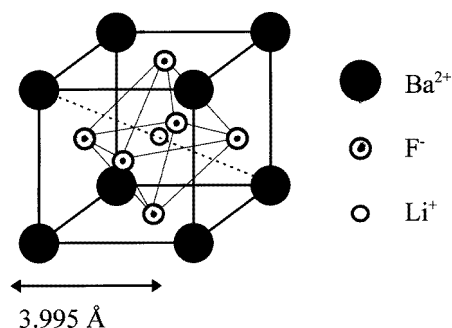


Figure 1. The unit cell of BaLiF₃.

degree the situation in terms of EXAFS analysis would be complicated. However, we will show below that this is not the case and the EXAFS for the system is qualitatively very simple. The Ni²⁺ predominantly occupies the Li⁺ site and the results have been analysed to yield quantitative information on the Ni²⁺ local environment.

2. Experimental details

The sample was a piece (~8 mm × 7 mm × 2 mm) from a BaLiF₃ single crystal doped with a low level of Ni. The crystal was grown by the Czochralski technique and was of good optical quality. The Ni concentration was determined spectrographically as 0.95 ± 0.05 mol%. EXAFS measurements on the Ni K-absorption edge were performed on station 9.3 at the CCLRC Daresbury Synchrotron Radiation Source. The synchrotron has an electron energy of 2 GeV and the average current during the measurements was 200 mA. A double-Si(220)-crystal monochromator was employed and the harmonic rejection was set at 50%. The spectra were collected at room temperature in fluorescence mode with a 16-element solid-state detector. A total of eight scans were collected and averaged to improve the signal-to-noise ratio. The useful *k*-space data range was restricted to *k* ~ 11 Å⁻¹. The data were processed in the conventional manner using the Daresbury suite of EXAFS programs: EXCALIB, EXBACK and EXCURV92 [10]. Phase shifts were derived from *ab initio* calculations using the von Barth–Hedin–Lundqvist scheme within EXCURV92. The Fourier transforms that are displayed in the figures were corrected with the phase shift of the first shell (F⁻). The programme allows various parameters in a structural model to be varied until a best fit to the experimental EXAFS is obtained. In the present work the key parameters were the coordination number, CN, radial distance, RD, and Debye–Waller factor, 2σ².

3. Results and discussion

Initial analysis of the EXAFS data involved assuming that the Ni²⁺ ion occupied either the Li⁺ or the Ba²⁺ crystallographic sites in the BaLiF₃ structure. In each case a model EXAFS and its Fourier transform were derived from the crystallographic data assuming the Ni²⁺ ion substituted on the given site with no change in the coordination numbers or the radial distances. The models extended to the first four coordination shells and all the Debye–Waller factors were set at a standard value of 0.01 Å². The results of this analysis are shown in figures 2 and 3. Simple visual inspection shows that the assumption of the

Ni²⁺ ion occupying the Li⁺ site gives the closest agreement with the experimental result. This model reproduces the frequency of the EXAFS oscillations and the positions of the two dominant peaks in the Fourier transform. In contrast, assuming the Ni²⁺ is on the Ba²⁺ site gives a model that strongly disagrees with the experimental result. The key differences in the two models are the distance from the Ni²⁺ to the first shell of F⁻ ions (1.998 and 2.825 Å for the Li⁺ and Ba²⁺ sites, respectively) and to the closest shell of Ba²⁺ ions, which are strong back-scattering atoms (3.460 and 3.995 Å for the Li⁺ and Ba²⁺ sites, respectively).

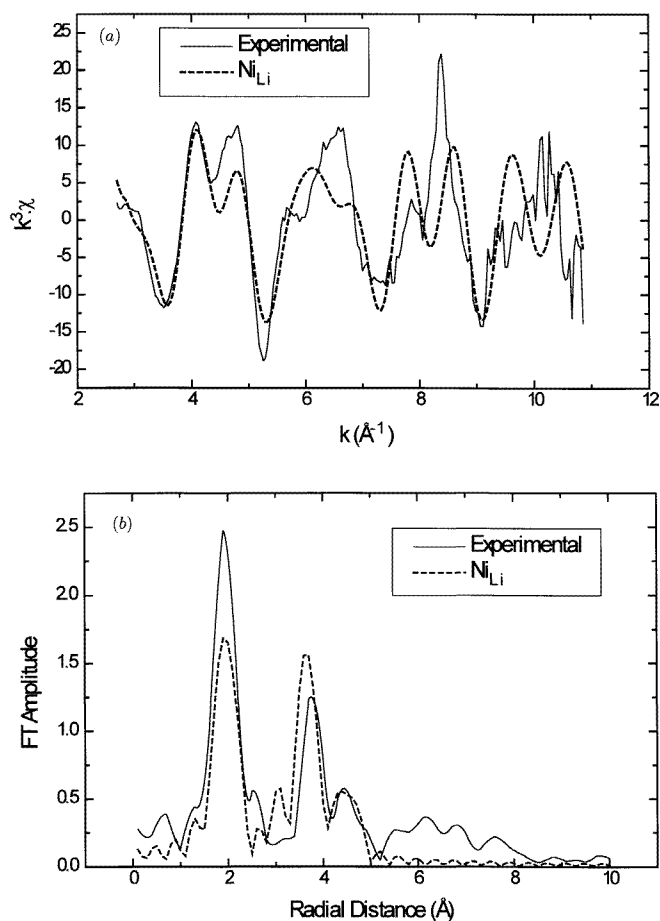


Figure 2. The experimental Ni K-edge EXAFS for Ni²⁺ doped BaLiF₃ (solid line) and the EXAFS predicted for Ni²⁺ on a Li⁺ site (dashed line). (a) The normalized EXAFS k^3 weighted. (b) The Fourier transform corrected with the phase shift of the first shell (F⁻).

The simple ‘fingerprinting’ approach described above clearly shows the Ni²⁺ ion prefers the Li⁺ site, and the next stage was to iterate the parameters, namely the radial distances and the Debye–Waller factors, within the model until a best fit to the experimental result was achieved. The coordination numbers were held constant in the fitting. This refined model included the first four coordination shells and the results are shown in figure 4 and listed in table 1. The radial distances show small variations compared to the original crystallographic

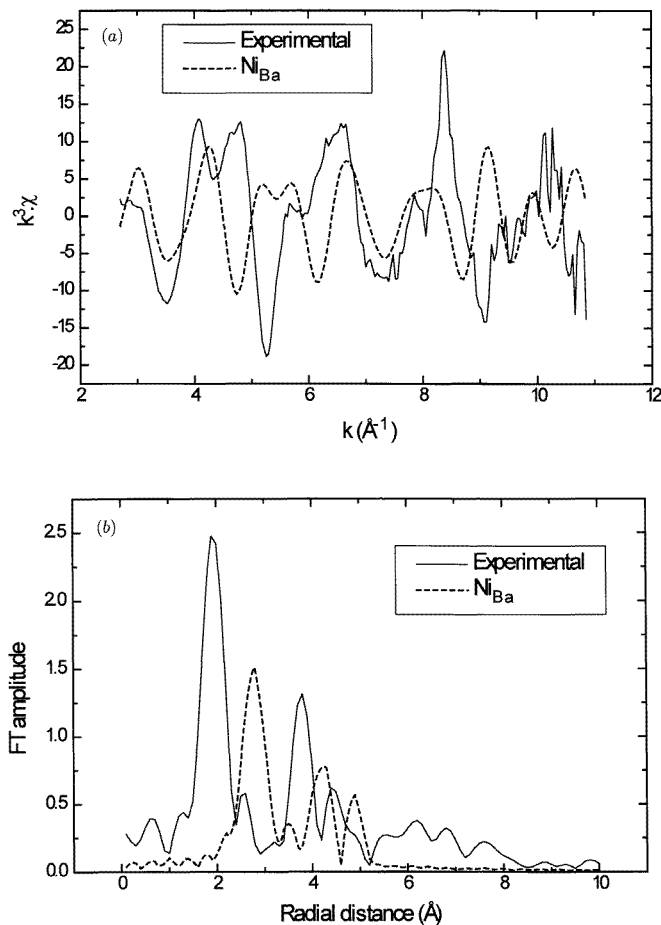


Figure 3. The experimental Ni K-edge EXAFS for Ni^{2+} doped BaLiF_3 (solid line) and the EXAFS predicted for Ni^{2+} on a Ba^{2+} site (dashed line). (a) The normalized EXAFS k^3 weighted. (b) The Fourier transform corrected with the phase shift of the first shell (F^-).

data, but they are in the expected directions for the replacement of a $1+$ cation by a $2+$ cation: the anions relax inwards and the cations relax outwards. The Debye–Waller factor for the first F^- shell is small, indicating a well ordered immediate local geometry. The Debye–Waller factors for the shells beyond this shell are relatively large and probably indicate the presence of static disorder in these shells. This could be due to the presence of charge compensating defects in one of these shells. These could be either an Li^+ ion on a Ba^{2+} site or an Li^+ vacancy or an F^- interstitial. The EXAFS data would not be sensitive enough to distinguish between these defect types.

An estimate was made of the proportion of Ni^{2+} ions on the Li^+ site by fitting the EXAFS to a mixed site model. A shell of 12 F^- ions was introduced at 2.825 \AA , i.e. the first shell around a Ba^{2+} . The fitting was repeated and the coordination numbers, radial distances and Debye–Waller factors of the two nearest F^- shells were allowed to float. The best fit was slightly improved on that provided by the parameters given in table 1. The parameters for the F^- shell at 1.977 \AA (around the Li^+ site) changed marginally from those

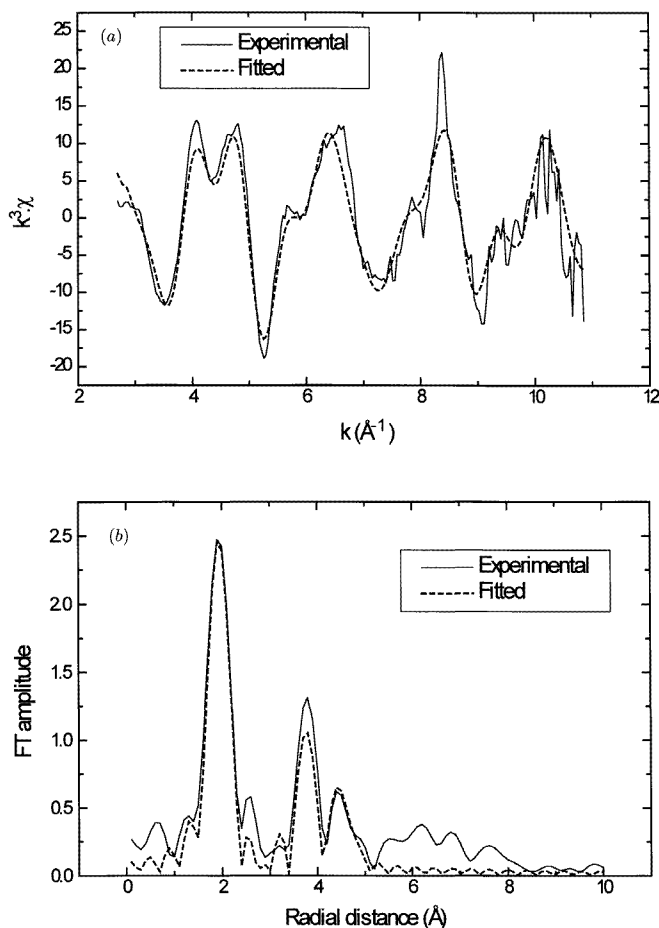


Figure 4. The experimental Ni K-edge EXAFS for Ni²⁺ doped BaLiF₃ (solid line) and the EXAFS predicted by the best-fit structural parameters given in table 1 (dashed line). (a) The normalized EXAFS k^3 weighted. (b) The Fourier transform corrected with the phase shift of the first shell (F^-).

listed in table 1. The fitted coordination number for this shell was 6.16 ± 0.38 . The extra F^- shell moved inwards to 2.703 ± 0.025 Å, as might be expected for the smaller Ni²⁺ ion replacing the Ba²⁺ ion, and the fitted coordination number was 1.37 ± 0.47 . The thus-estimated maximum degree of occupancy of the Ba²⁺ site is $\sim(1.37 + 0.47)/12$, around 15%.

Intuitively it is not too surprising that the Ni²⁺ ion prefers the Li⁺ site in BaLiF₃. The simplest argument would be that any divalent cation would substitute on the Ba²⁺ site as this would not require the formation of charge compensating defects. However this ignores the effects of ionic radii and the crystal chemistry of the dopant. Ni²⁺ has a radius of 0.69 Å [11] which is much closer to the radius of Li⁺ (0.90 Å) than that of Ba²⁺ (1.49 Å). In addition, in other Ni–F structures the Ni²⁺ ion has an octahedral shell of F⁻ ions (e.g. NiF₂ [12] and KNiF₃ [13]) which is only provided at the Li⁺ site in BaLiF₃.

Finally it is worth noting that the success of the present EXAFS work indicates that

Table 1. The best-fit structural model to the Ni K-edge EXAFS. The model assumes the Ni²⁺ substitutes on the Li⁺ site. Coordination numbers were not iterated in the fitting. The distances listed in square brackets are the distances from a Li⁺ ion in pure BaLiF₃ from crystallographic data.

Atom type	Coordination number	Distance (Å)	2σ ²
F ⁻	6	1.977 ± 0.002 [1.998]	0.0033 ± 0.0004
Ba ²⁺	8	3.554 ± 0.005 [3.460]	0.0182 ± 0.0009
Li ⁺	6	4.083 ± 0.109 [3.995]	0.0200 ± 0.0111
F ⁻	24	4.486 ± 0.007 [4.665]	0.0181 ± 0.0020

similar measurements would be extremely useful in studying the sites of other dopants in BaLiF₃. A particularly interesting case would be Pb²⁺ doping where the larger ionic radius might suggest that it occupies the Ba²⁺ site, a preference indicated in the computer simulations.

4. Conclusions

In conclusion, the present work clearly locates the dopant Ni²⁺ ion as being predominantly (at least 85%) on the Li⁺ site in BaLiF₃. The current EXAFS work will provide a good model for the computer simulations of doped BaLiF₃ that are now in progress [14]. Given the success of the present study EXAFS measurements should prove very fruitful in locating the sites of other dopants in BaLiF₃.

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