EXAFS Study of the local structure at Eu^{2+} ions doped into CaF_2

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X-ray storage materials and X-ray scintillators doped with various rare earth ions are presently intensively investigated. The properties of Eu^{2+} ions doped in various matrices are of special interest because of their favourable emission properties, especially in crystalline host matrices ($BaCl_2$, CaF_2) or in glasses or a combination of both [1-5]. The properties of these Eu-doped materials were investigated with various optical methods [2-5] as well as with ^{151}Eu-Mössbauer spectroscopy [6]. The latter method can immediately deliver the relative amount of Eu^{2+} and Eu^{3+} ions [6,7]. In addition, the spectral shape of the ^{151}Eu-spectra exhibit a strong dependence on the Eu concentration [6,7], a phenomenon observed already in early Mössbauer investigations of CaF_2:Eu systems [7]. This behaviour, together with a seemingly anomalous variation of the isomer shift was speculatively attributed to oxygen neighbors [7], substituting one or more fluorine neighbors of the Eu^{2+} ions. Since such oxygen neighbors should induce strong distortions within the first neighbor shell of the Eu^{2+} ions on Ca^{2+} sites, we performed an EXAFS study at the Eu-L_{III} edge on two CaF_2:Eu samples, one doped with 2% Eu and the other with 0.1% Eu. The studies were performed at the beamline E4 at room temperature and around 100 K in transmission geometry. To obtain sufficient statistical accuracy, we had to add up 5 absorption spectra for the CaF_2:Eu(2%) sample and up to 10 spectra for the CaF_2:Eu(0.1%) sample. Typical absorption spectra are shown in Fig.1.

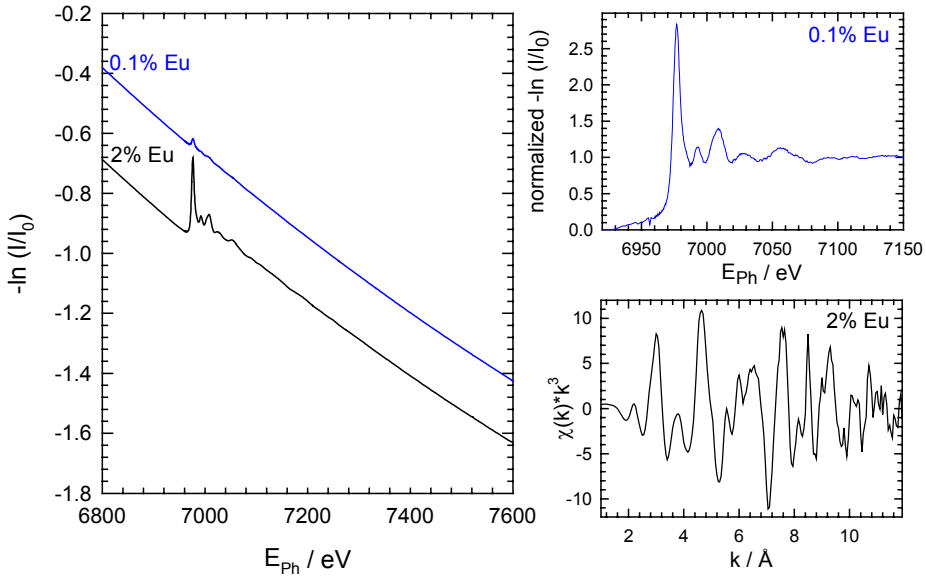

Fig.1. Typical XAS spectra and EXAFS function of CaF_2:Eu samples with different Eu concentration (as indicated).

Visual inspection of the absorption spectra already indicated a very similar surrounding of the Eu^{2+} ions in both samples. This is strikingly confirmed in the Fourier transforms of the two samples shown in Fig. 2 together with a preliminary fit of the first two neighbor shells assuming a regular surrounding with 8 F ions in the first and 12 Ca ions in the second neighbor shell. The fit was performed using the ARTEMIS [8] and FEFF6 [9] code. In Tab. 1 the derived parameters for the

distances R_1 and R_2 are given, which show a behaviour expected for the larger Eu^{2+} ionic radius in comparison to that of Ca^{2+}. The data will be further evaluated taking into account also the information obtained from the ^{151}Eu-Mössbauer studies of the same samples [6], for instance a small (3%) content of Eu^{3+}-ions as well as a 19% occupation of the Ca^{2+} sites by Eu^{2+} ions in the second neighbor shell for the CaF_2:Eu(2%) sample. We can already state that, in accordance with our Mössbauer studies [6], oxygen neighbors do not play that dominant role as suggested in [7].

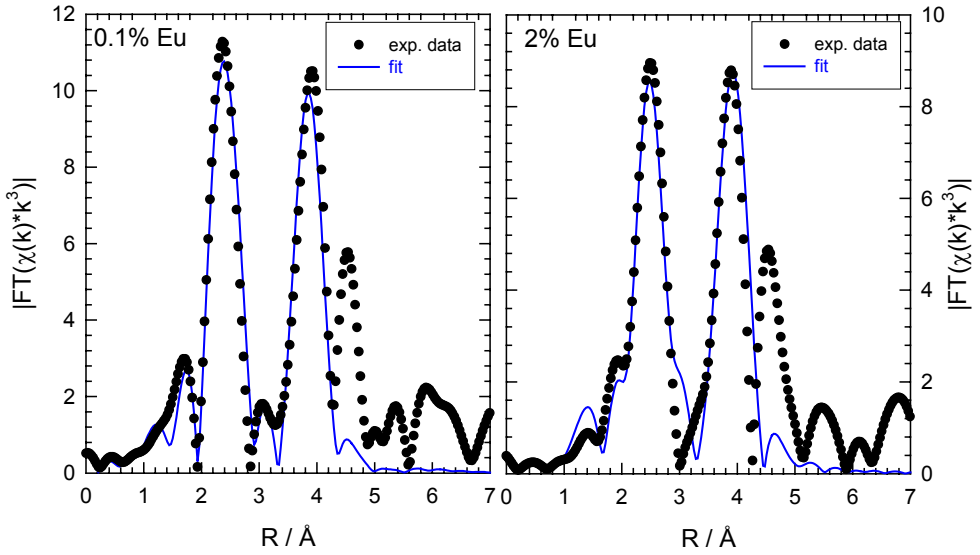

Fig.2. Fourier transformed signal (k^3-weighted) obtained form the EXAFS measurements for the Eu doped CaF_2 samples (symbols, Eu concentration as indicated) and respective fits using the first two single scattering shells. The EXAFS measurements were performed at room temperature.

Table 1. Structural parameters - interatomic distances R and Debye-Waller factors σ^2 – and the corresponding statistical goodness-of-fit (R-factor) obtained for the first two NN shells of the Eu doped CaF_2 samples by using only the first two single scattering path for the fitting procedure.

	1st NN: $Eu^0 \rightarrow F^1 \rightarrow Eu^0$		2nd NN: $Eu^0 \rightarrow Ca^2 \rightarrow Eu^0$		
	R_1 / Å	σ^2 / Å^2	R_2 / Å	σ^2 / Å^2	R-factor
0.1% Eu	2.413 ± 0.027	0.0054 ± 0.0044	3.879 ± 0.032	0.0055 ± 0.0038	0.069
2% Eu	2.462 ± 0.029	0.011 ± 0.0051	3.911 ± 0.029	0.0086 ± 0.0037	0.054

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