## Homogeneity of doping with paramagnetic ions by NMR

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# Supporting information

#### 1. Quantitative 1D <sup>1</sup>H NMR spectra of Sr<sub>1-x</sub>Eu<sub>x</sub>H<sub>2</sub> samples

We obtained quantitative <sup>1</sup>H NMR spectra on a doping series of Sr<sub>1-x</sub>Eu<sub>x</sub>H<sub>2</sub>. The NMR spectra (Fig. 1) qualitatively show a decay of signal intensity for the <sup>1</sup>H peak found in the sample with the lowest doping mole fraction  $x = 10^{-8}$ , and a broadening of the resonance with higher doping concentration x.



Figure 1: The stack plot of solid state <sup>1</sup>H MAS NMR full echo spectra of a mixture of  $Sr_{1.x}Eu_xH_2$  (peak at 6 ppm) with adamantane (peak at 1.8 ppm) with different Eu doping mole fraction.  $x_{Eu}$  equals to 0.005, 0.0032, 0.0013, 0.0005, 0.00017, 0.000005, 10<sup>-8</sup> from the top to the bottom. The peaks with the asterisk mark belong to a trace impurity phase related to the hygroscopic reaction of  $SrH_2$ . The intensity scale is adapted to the amount of sample inside each rotor, however the amount of adamantane may slighly vary.

### 2. "Box-in-a-box" Algorithm

How we set up the "box-in-a-box" algorithm of our Fortran 90 program, as shown in the Fig. 2, can be described as follows. The small box in the center is one unit cell of the PbCl<sub>2</sub>-type crystal structure of  $SrH_2^{-1}$ . The outer big box is built up based on the 3D translational symmetry around the center unit cell. The statistical doping of Eu ions is achieved by applying a system randomizer to replace Sr atoms with Eu atoms, and the probability of replacement is statistically speaking equal within the big box, including the center box. The wipe-out region of Eu ions is set up as a sphere with Eu in the center and the wipe-out radius. The visible fraction  $f_{visible}$  is thus defined as the number of H atoms within the wipe-out region divided by the total number of H atoms. When the size of the big box is significantly bigger than the wipe-out radius, the influence of boundary to the center small box can be minimized, therefore the visible fraction  $f_{visible}$  in the center box can represent the  $f_{visible}$  in a big boundless box, which is often an idealized model of crystals. To average out the fluctuation in the randomized Sr/Eu setup, the calculation is looped until  $f_{visible}$  reaches convergence (deviation less than 2%). Different wipe-out radii are assumed and different  $f_{visible}$  values are calculated accordingly.



Figure 2: The "box-in-a-box" algorithm for the Fortran90 program. The center small box is one unit cell of the crystal structure <sup>1</sup> of SrH<sub>2</sub>. The outer big box is built up based on the 3D translational symmetry around the center unit cell. The visible fraction  $f_{visible}$  is calculated as the number of H atoms within the influence region, which are spheres with Eu center and the wipe-out radius  $r_0$ , divided by the total number of H atoms.

#### 3. Error propagation for quantitative NMR

The error bars (Fig. 3) are calculated according to three error sources: (1) the mass error from the weighing process on the microbalance, which is an absolute error at around  $1\mu$ g; (2) the intensity error, which is a relative error originated from the external reference method, around 10%; (3) the fitting error, which is originating from the fitting of the peak area values from the full echo experiments. The fitting error slightly differs for different samples, but all values are around 2%.

The experimental measurements are the mass m and the peak area A.  $A_0$  is the extrapolated peak area at zero delay. External

referencing method was applied and here we define a parameter  $P = \frac{A_0}{A_{ref}}$  which relates to the stability of the spectrometer. The error

of P can be calculated from the formula (1).

$$\Delta P = \sqrt{\left(\frac{\Delta A_0}{A_{\text{ref}}}\right)^2 + \left(\frac{A_0 \Delta A_{\text{ref}}}{A_{\text{ref}}^2}\right)^2} = \sqrt{\left(\frac{A_0}{A_{\text{ref}}}\frac{\Delta A_0}{A_0}\right)^2 + \left(\frac{A_0}{A_{\text{ref}}}\frac{\Delta A_{\text{ref}}}{A_{\text{ref}}}\right)^2} = P\sqrt{\left(\frac{\Delta A_0}{A_0}\right)^2 + \left(\frac{\Delta A_{\text{ref}}}{A_{\text{ref}}}\right)^2}$$
(1)

herein  $\frac{\Delta A_{\text{ref}}}{A_{\text{ref}}} = 10\%$  and  $\frac{\Delta A_0}{A_0} \approx 2\%$ , therefore  $\frac{\Delta P}{P} \approx 0.102$ .  $f_{\text{visible}}$  can be related to the parameter P

$$f_{\text{visible}} = \frac{A_{\text{doped}}/n_{\text{doped}}}{A_{\text{non-doped}}/n_{\text{non-doped}}} = \frac{P_{\text{doped}}}{P_{\text{non-doped}}} \frac{m_{\text{non-doped}}}{m_{\text{doped}}}$$
(2)

 $A_{doped}$  and  $A_{non-doped}$  refer to the  $A_0$  values of the doped and non-doped samples, respectively. As for the mass m, there is the mass error  $\Delta m \approx 0.001 \text{ mg}$ . The final error propagation can be expressed as an equation for  $\Delta f$ , which is the standard deviation of  $f_{visible}$ 

$$\Delta f = \sqrt{\left(\frac{\Delta P_{\text{doped}}}{P_{\text{doped}}} \frac{A_{\text{doped}}}{A_{\text{non-doped}}} \frac{m_{\text{non-doped}}}{m_{\text{doped}}}\right)^2 + \left(\frac{A_{\text{doped}}}{A_{\text{non-doped}}} \frac{\Delta P_{\text{non-doped}}}{m_{\text{doped}}}\right)^2 + \left(\frac{A_{\text{doped}}}{A_{\text{non-doped}}} \frac{\Delta m_{\text{non-doped}}}{m_{\text{doped}}}\right)^2 + \left(\frac{A_{\text{doped}}}{A_{\text{non-doped}}} \frac{m_{\text{non-doped}}}{m_{\text{doped}}}\right)^2 + \left(\frac{A_{\text{doped}}}{A_{\text{non-doped}}} \frac{m_{\text{non-doped}}}{m_{\text{doped}}}\right)^2 + \left(\frac{A_{\text{doped}}}{A_{\text{non-doped}}} \frac{m_{\text{non-doped}}}{m_{\text{doped}}}\right)^2 + \left(\frac{A_{\text{doped}}}{M_{\text{non-doped}}} \frac{m_{\text{non-doped}}}{m_{\text{doped}}}\right)^2 + \left(\frac{A_{\text{doped}}}{M_{\text{non-doped}} \frac{m_{\text{non-doped}}}{m_{\text{doped}}}\right)^2 + \left(\frac{A_{\text{doped}}}{M_{\text{non-doped}} \frac{m_{\text{non-doped}}}{m_{\text{doped}}} \frac{m_{\text{non-doped}}}{m_{\text{doped}}}\right)^2 + \left(\frac{A_{\text{non-doped}}}{M_{\text{non-doped}}} \frac{m_{\text{non-doped}}}{m_{\text{doped}}}\right)^2 + \left(\frac{A_{\text{non-doped}}}{m_{\text{doped}}} \frac{m_{\text{non-doped}}}{m_{\text{dop$$



Figure 3: comparison of the visible H fraction  $f_{visible}$  calculated from experimental <sup>1</sup>H MAS NMR spectra (hollow circles) and the empirical fitted function (dashed line)  $f_{visible} = \exp[-k_1(x_{Eu})^{k_2}]$  with  $k_1 = 425 \pm 113$  and  $k_2 = 1.00 \pm 0.04$ , plotted against the Eu doping mole fraction  $x_{Eu}$  in log scale.

## 4. Estimation of the wipe-out radius from calculated data and experimental data

As the value of wipe-out radius  $r_0$  was unknown, different values were assumed and visible H fractions  $f_{visible}$  were calculated by Fortran program, based on the statistical distribution of Eu(II) ions with different doping mole fraction  $x_{Eu}$ . By comparing the obtained data set of  $f_{visible}$  with the result from quantitative NMR measurements, the estimation of the  $r_0 = 17$  Å for Eu(II) in SrH<sub>2</sub> can be achieved (see Fig. 4).



Figure 4: The comparison of the visible H fraction  $f_{visible}$  calculated from the <sup>1</sup>H MAS NMR back extrapolated full echo series experiments<sup>2</sup> with error bars, calculated according to the statistical distribution model and the fitted function  $f_{visible} = \exp(-ar_0^3 x_{Eu})$  with  $a = 0.0863 \pm 0.0016$  and  $r_0 = 17$  Å, plotted against the Eu doping mole fraction  $x_{Eu}$  in log scale. The asterisk marks, the hollow squares, the hollow circle, the hollow triangle, the solid circles, the solid squares and the dash line represent the experimental data, the calculated data at  $r_0 = 10$  Å, 16 Å, 17 Å, 18 Å, 24 Å and the function plot, respectively.

#### Reference

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