

Supporting Information for

⁸⁹Y Chemical Shift Anisotropy: A Sensitive Structural Probe of Layered Yttrium Hydroxides Revealed by Solid-State NMR Spectroscopy and DFT Calculations

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Chemical Shift Tensor Conventions

This magnetic shielding effect is described by a second-rank magnetic shielding tensor σ , which is a diagonalizable 3×3 matrix. For convenience, the σ is often converted to the CS tensor δ by $\delta = \sigma - \sigma_{ref}$, where σ_{ref} is the σ of a reference compound. The three eigenvectors of δ are perpendicular to each other, forming the principal axial system (PAS). The resulting diagonal elements, δ_{ii} ($i = 1, 2, 3$ or X, Y, Z), are referred to as the principal components.

The chemical shift (CS) tensor δ can be described by several conventions:

Standard convention.¹ Three principal components are defined as $\delta_{11} \geq \delta_{22} \geq \delta_{33}$. The isotropic chemical shift δ_{iso} , which is the commonly used ‘chemical shift’ in NMR experiments, is the average of three principal components, i.e., $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$.

Herzfeld-Berger convention.² Three principal components and isotropic chemical shift are the same as the standard convention. Besides, the span, $\Omega \approx \delta_{11} - \delta_{33}$, describes the maximum width of the CSA powder pattern, and the skew, $\kappa = 3(\delta_{11} - \delta_{iso})/\Omega$, describes the asymmetry of the CSA ($-1 \leq \kappa \leq 1$).

Haeberlen convention.³ Three principal components are defined as $\delta_{XX}, \delta_{YY}, \delta_{ZZ}$ following $|\delta_{ZZ} - \delta_{iso}| \geq |\delta_{YY} - \delta_{iso}| \geq |\delta_{XX} - \delta_{iso}|$. The isotropic chemical shift is $\delta_{iso} = (\delta_{XX} + \delta_{YY} + \delta_{ZZ})/3$. The largest separation from δ_{iso} is defined as anisotropy $\delta = \delta_{ZZ} - \delta_{iso}$, which can be either positive or negative. And the asymmetry is described using asymmetry parameter $\eta = (\delta_{YY} - \delta_{XX})/\delta$ ranging between 0 and 1.

Despite the differences in conventions, δ_{iso} is virtually equivalent, and the principal axes used in three conventions are also perpendicular to each other. However, only the PAS of Haeberlen convention is strictly right-handed. Since the Cartesian coordinates used in this work is right-handed, the principal axes are shown in Haeberlen convention. On the contrary, three principal components are always ordered such as $\delta_{11} \geq \delta_{22} \geq \delta_{33}$ in standard convention and Herzfeld-Berger convention, while it is not in Haeberlen convention. It is much more convenient to distinguish δ_{11} , δ_{22} , and δ_{33} experimentally. As a result, the principal components are reported in this way.

In this work, the output of SIMPSON was in Haeberlen convention, which was converted to standard convention according to:³

$$\begin{aligned} &\text{for } \delta > 0 (\delta_{ZZ} = \delta_{11}): \\ &\quad \delta_{11} = \delta_{iso} + \delta \\ &\quad \delta_{22} = \delta_{iso} - \delta(1 - \eta)/2 \\ &\quad \delta_{33} = \delta_{iso} - \delta(1 + \eta)/2 \\ &\text{for } \delta < 0 (\delta_{ZZ} = \delta_{33}): \\ &\quad \delta_{33} = \delta_{iso} + \delta \\ &\quad \delta_{22} = \delta_{iso} - \delta(1 - \eta)/2 \\ &\quad \delta_{11} = \delta_{iso} - \delta(1 + \eta)/2 \end{aligned} \quad (\text{Equation 1})$$

The output of VASP was in Herzfeld-Berger convention, which can be converted to standard convention and Haeberlen convention according to:³

$$\begin{aligned} &\delta_{22} = \delta_{iso} + \kappa\Omega/3 \\ &\delta_{33} = (3\delta_{iso} - \delta_{22} - \Omega)/2 \\ &\delta_{11} = 3\delta_{iso} - \delta_{22} - \delta_{33} \end{aligned} \quad (\text{Equation 2})$$

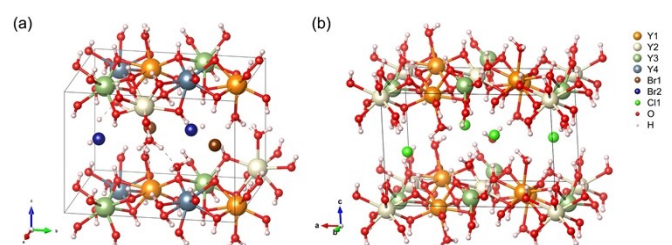


Fig. S1. Structure of (a) LYH-Br and (b) LYH-Cl.⁴ Different color of the same element corresponds to different crystallographically distinct sites.

$$\begin{aligned} &\delta = \delta_{ZZ} - \delta_{iso} \\ &\eta = (\delta_{YY} - \delta_{XX})/\delta \end{aligned} \quad (\text{Equation 3})$$

Additional Data

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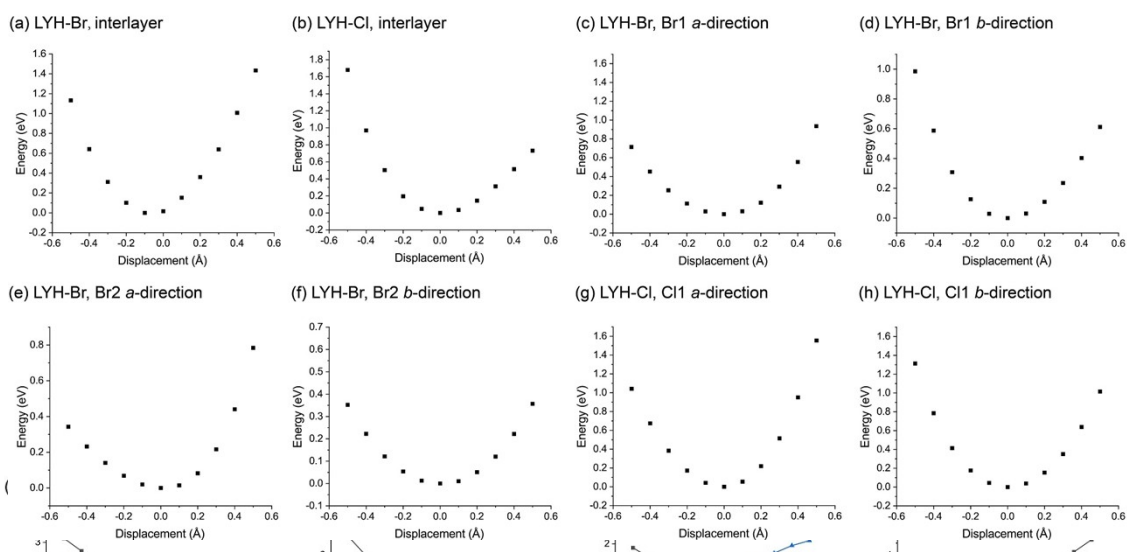
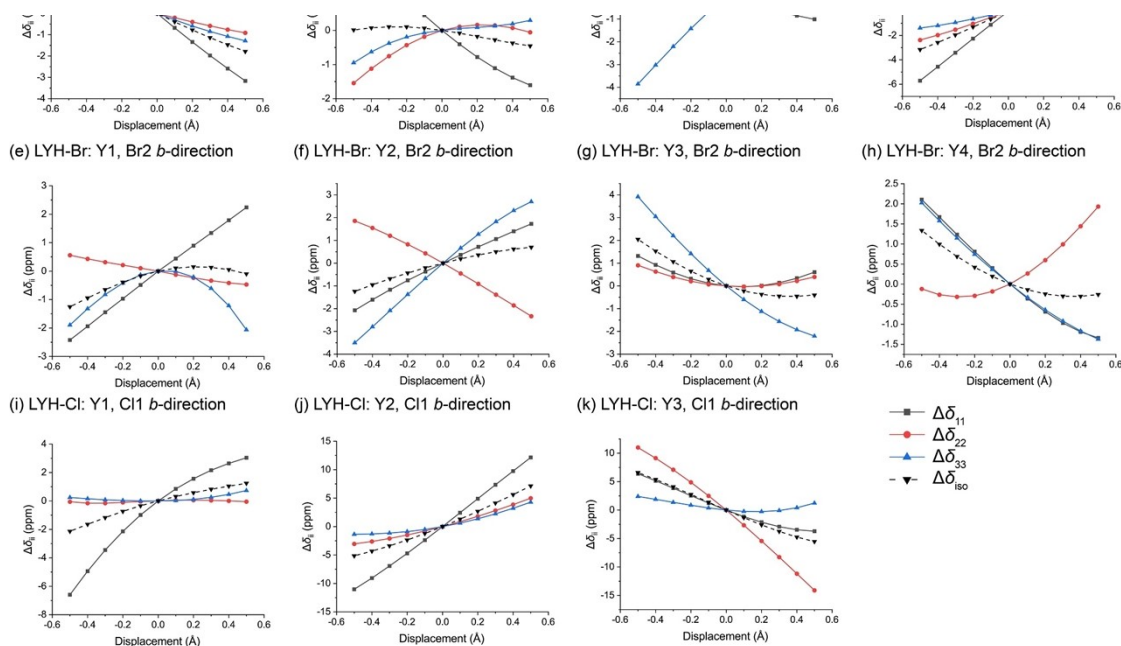
Table S1. ^{89}Y isotropic chemical shift and number of ligands on each site.

Compound	Y Site	δ_{iso} (ppm)	Number of OH^-	Number of H_2O
LYH-Br	Y1	152.9	7	1
	Y2	143.1	7	1
	Y3	107.3	8	0

LYH-Cl	Y4	29.6	8	1
	Y1	139.6	7	1
	Y2	125.6	8	0
	Y3	13.8	8	1

Table S2. Experimental and calculated ^{89}Y CSA parameters.

Compound	Y Site	δ (ppm)		η		δ_{11} (ppm)		δ_{22} (ppm)		δ_{33} (ppm)	
		Expt.	Calcd.	Expt.	Calcd.	Expt.	Calcd.	Expt.	Calcd.	Expt.	Calcd.
LYH-Br	1	129.6	129.0	0.20	0.09	282.6	261.9	101.4	74.2	75.0	62.7
	2	98.2	120.9	0.51	0.74	241.2	242.5	118.8	105.9	68.9	16.5
	3	-86.9	-84.7	0.36	0.47	166.2	171.5	134.7	131.4	20.1	24.5
	4	-58.5	-84.2	0.18	0.18	63.4	70.0	53.0	54.9	-29.5	-63.9
LYH-Cl	1	101.2	110.6	0.50	0.35	240.8	239.3	114.2	92.9	63.8	53.7
	2	-91.1	-83.3	0.63	0.66	198.6	177.7	141.2	122.9	33.2	25.3
	3	-34.4	-65.3	0.04	0.03	32.1	42.1	30.8	40.1	-20.1	-56.9

**Fig. S2** Relative energies of the structures as a function of displacement.**Fig. S3.** The changes in calculated ^{89}Y U_{iso} and principal components (U_{11} , U_{22} , and U_{33}) as a function of displacement when translating anions along the b -direction of two phases. All results are referred to with the corresponding parameters of original structure setting as zero for comparison.

Notes and references

- 1 J. Mason, Conventions for the reporting of nuclear magnetic shielding (or shift) tensors suggested by participants in the NATO ARW on NMR shielding constants at the University of Maryland, College Park, July 1992, *Solid State Nuclear Magnetic Resonance*, 1993, **2**, 285–288.
- 2 J. Herzfeld and A. E. Berger, Sideband intensities in NMR spectra of samples spinning at the magic angle, *The Journal of Chemical Physics*, 1980, **73**, 6021–6030.
- 3 U. Haeberlen, *High resolution NMR in solids: selective averaging*, Academic Press, New York, 1976.
- 4 Z. Feng, D. Xiao, Z. Liu, G. Hou and J. Xu, “X Factor” in the Structure and Anion Exchange of Layered Yttrium Hydroxides, *J. Phys. Chem. C*, 2021, **13**, 7251–7258.