

# Spin-phonon coupling effects in transition-metal perovskites: a DFT+U and hybrid-functional study

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## Introduction

Spin-phonon coupling effects, as reflected in phonon frequency shifts between ferromagnetic (FM) and antiferromagnetic (AFM) configurations, hold promise for the discovery of new multiferroics, as demonstrated recently by Fennie and Rabe [1]. Here we take the frequency shifts  $\Delta\omega$  of low-frequency phonons between FM and AFM configurations

$$\Delta\omega = \omega_{\text{AFM}} - \omega_{\text{FM}}$$

Two first-principles methods—DFT+U and hybrid functional methods—have usually been carried out for magnetic systems. Both of them have some advantages and disadvantages:

	Pros	Cons
DFT+U	<ul style="list-style-type: none"> <li>Efficiency</li> <li>Includes Hubbard interactions</li> </ul>	<ul style="list-style-type: none"> <li>U-dependence of the calculated properties</li> <li>No good way to obtain proper U value</li> </ul>
Hybrid functionals	<ul style="list-style-type: none"> <li>Improves accuracy</li> </ul>	<ul style="list-style-type: none"> <li>Heavy computational cost</li> </ul>

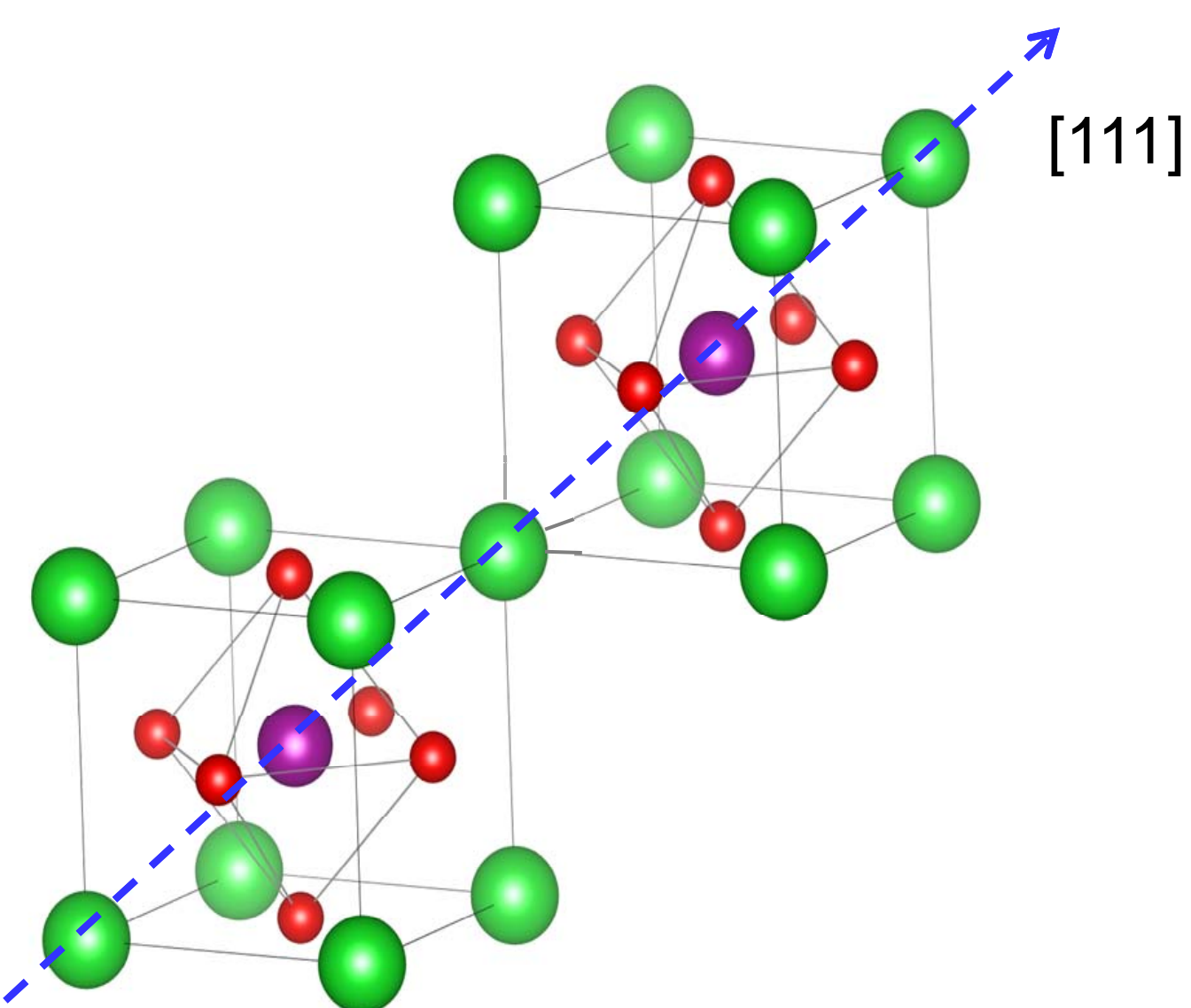
We propose a scheme to obtain the U values by fitting to hybrid-functional (HSE) calculations of energy differences between states of different magnetic order. The phonon frequency shifts obtained in this way agree well with those computed directly from the more accurate HSE approach, but are obtained with much less computational effort.

## Method

Code: VASP5.2  
GGA(PBESol) + U:  $U_{\text{eff}}=U-J$   
Hybrid functionals: HSE  
k-point:  $6 \times 6 \times 6$   
Plane-wave cutoff: 500 eV  
PAW pseudopotentials  
Frozen-ion method for phonon calculation.

Materials:  
A-site:  $\text{AMnO}_3$  (A=Ca, Sr, Ba)  
B-site:  $\text{LaMO}_3$  (M=Cr, Fe, Cr/Fe)

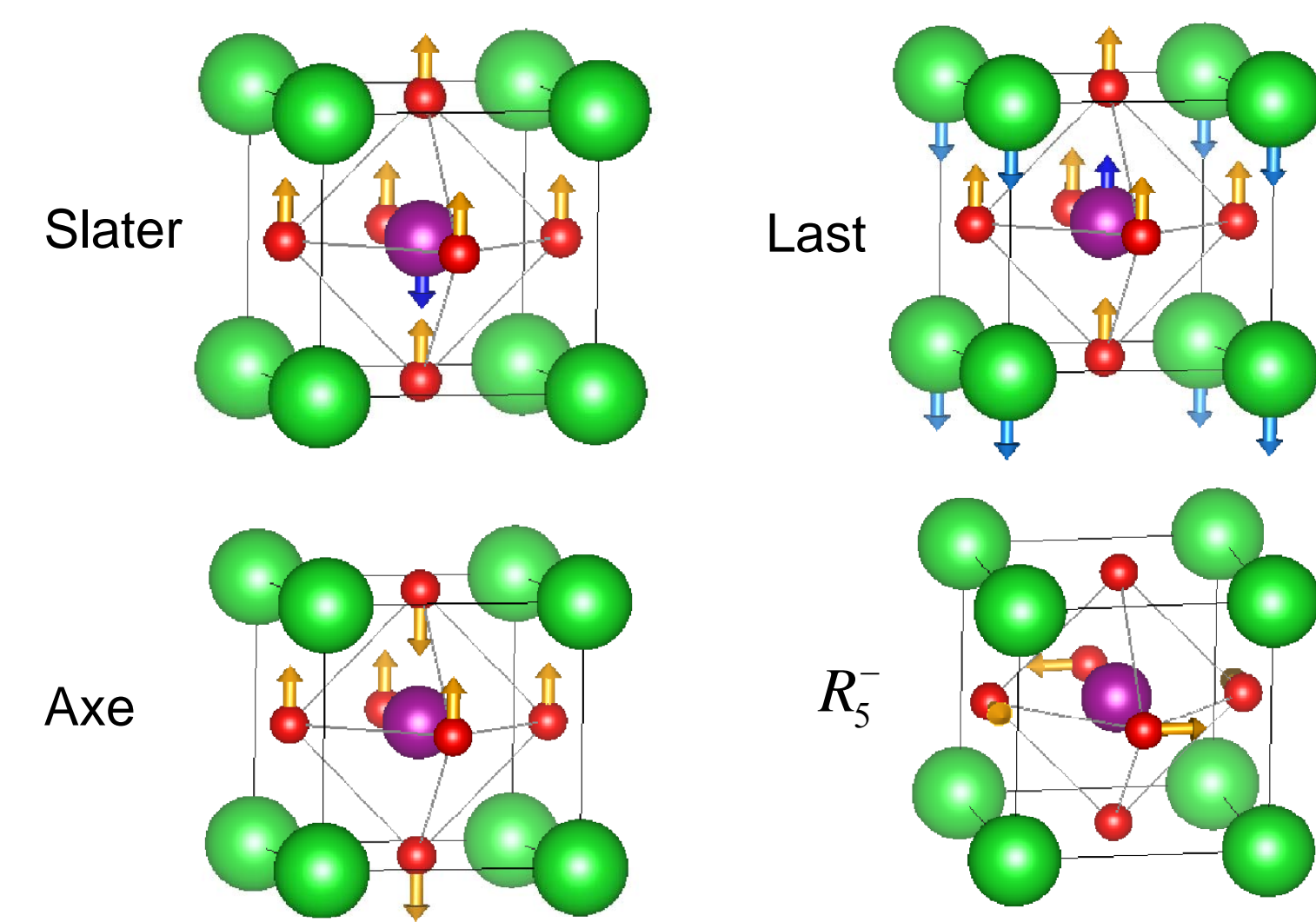
The unit cell is doubled along the [111] direction as shown in the following figure, for simulating the G-AFM magnetic ordering.



## Phonon modes

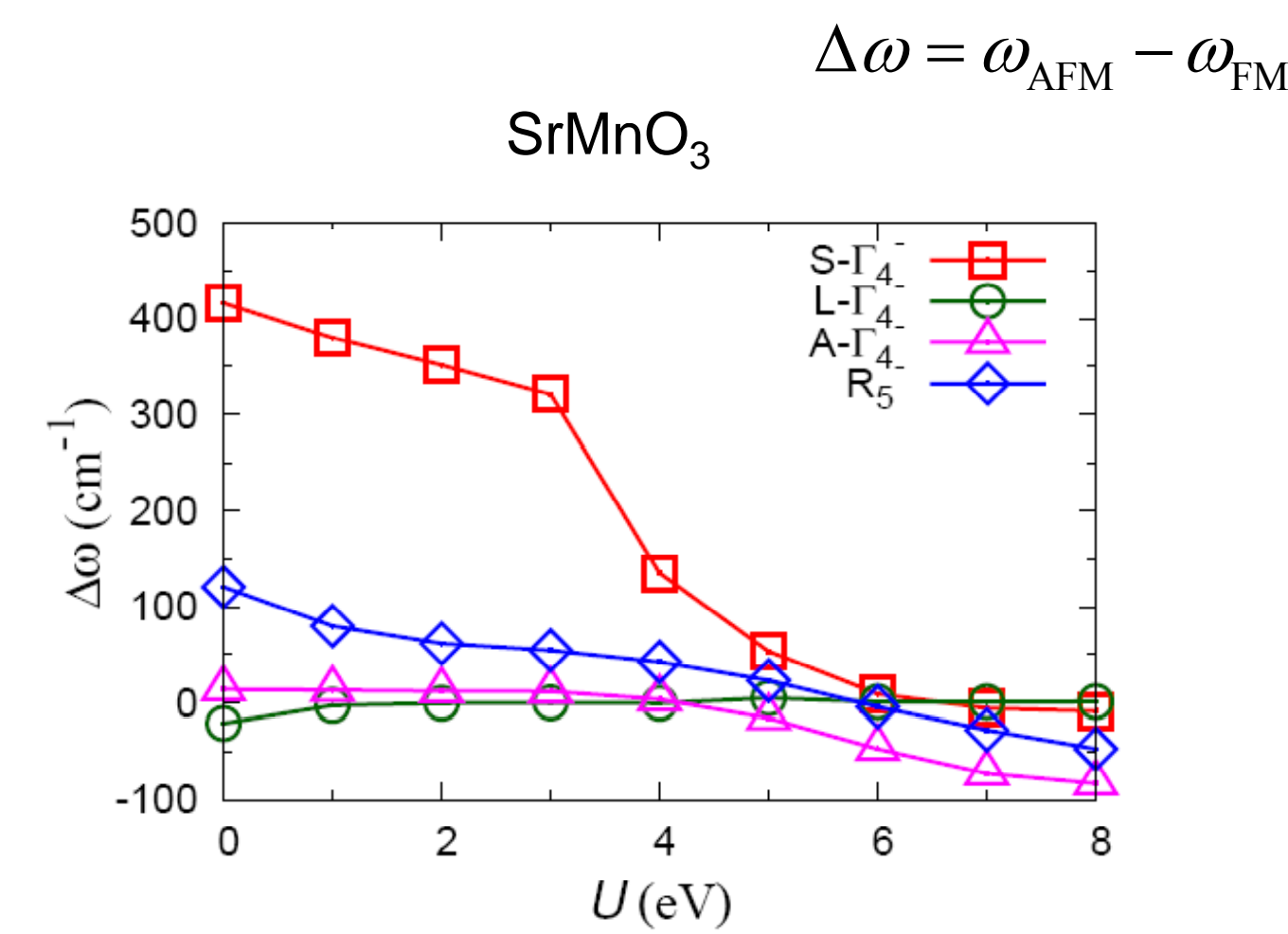
For  $Pm\bar{3}m$  perovskite cell, the zone-center phonons decompose as  $3\Gamma_4 \oplus \Gamma_5^-$  with  $\Gamma_4$  modes being polar. The zone-boundary modes at the R point decompose as  $R_5^+ \oplus R_5^- \oplus 2R_4^+ \oplus R_2^+ \oplus R_2^-$ .

As for the polar  $\Gamma_4$  phonons, these are often characterized in three idealized modes: Slater ( $S-\Gamma_4^-$ ), Last ( $L-\Gamma_4^-$ ) and Axe ( $A-\Gamma_4^-$ ). The antiferrodistortive (AFD) mode ( $R_5^-$ ). These modes are shown in the following figure.



## Effect of U on the frequency shifts

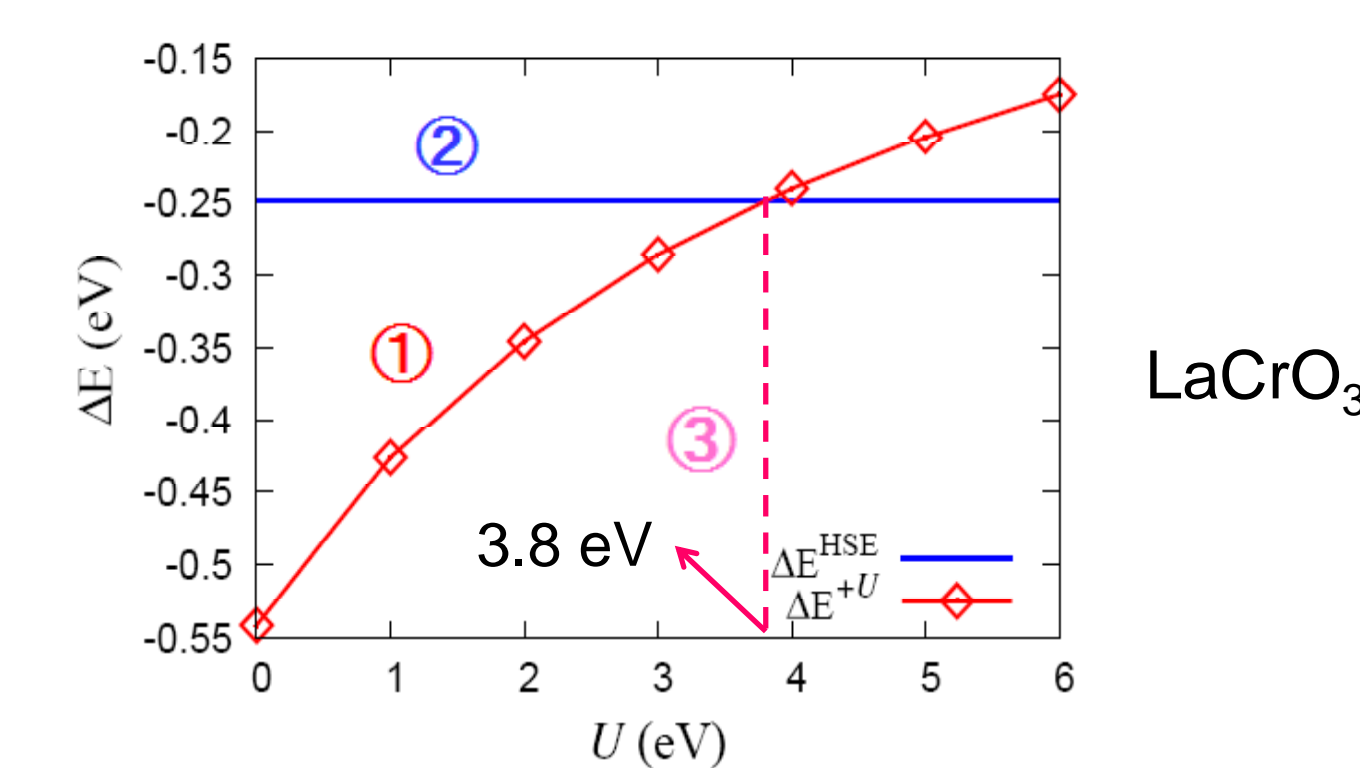
- Polar and rotation modes strongly depend on U.
- U is very important for spin-phonon couplings.



## Method to obtain U value

U is obtained by the following procedure:

- $\Delta E^{+U} = E_{\text{AFM}}^{+U} - E_{\text{FM}}^{+U}$
- $\Delta E^{\text{HSE}} = E_{\text{AFM}}^{\text{HSE}} - E_{\text{FM}}^{\text{HSE}}$
- $\Delta E^{+U} = \Delta E^{\text{HSE}} \Rightarrow U$



U values for different compounds

	CaMnO <sub>3</sub>	SrMnO <sub>3</sub>	BaMnO <sub>3</sub>	LaCrO <sub>3</sub>	LaFeO <sub>3</sub>
U (eV)	3.0	2.8	2.7	3.8	5.1

## Results

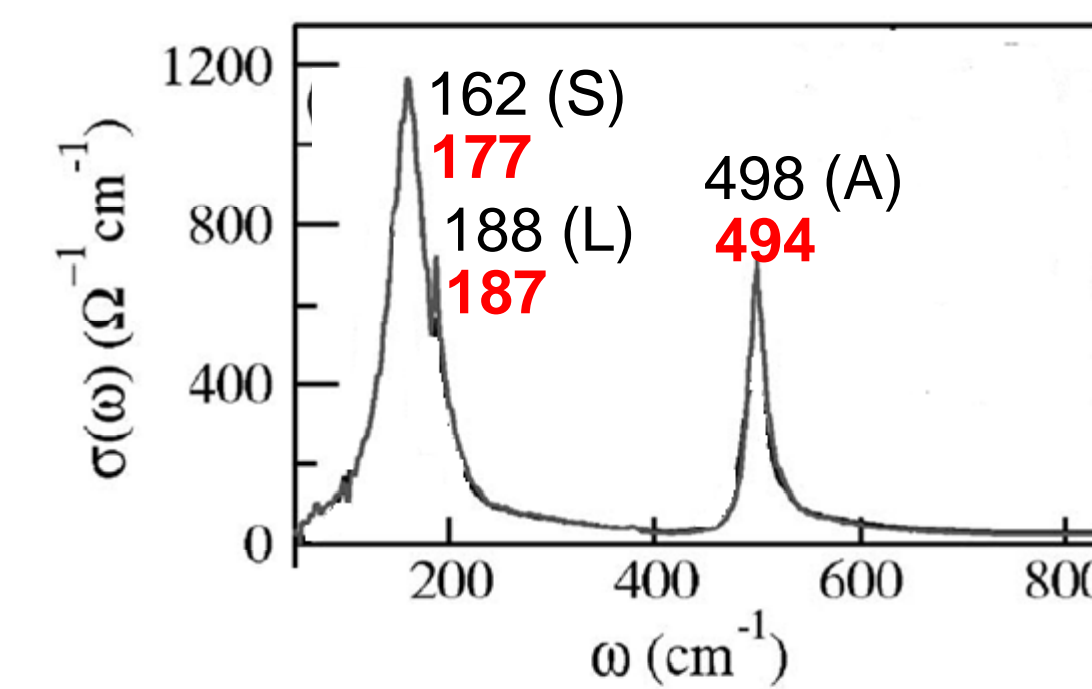
### Properties from DFT+U and HSE for AMnO<sub>3</sub> and LaMO<sub>3</sub>

	a (Å) m (μ <sub>B</sub> ) E <sub>gap</sub> (eV)			a (Å) m (μ <sub>B</sub> ) E <sub>gap</sub> (eV)			
	+U	HSE		+U	HSE		
CMO-AFM	3.73	2.79	0.35	3.87	2.86	2.01	
CMO-FM	3.74	2.84	0.00	3.88	2.84	1.70	
SMO-AFM	3.80	2.80	0.40	3.90	4.19	2.20	
SMO-FM	3.81	2.89	0.00	3.91	4.38	1.57	
BMO-AFM	3.91	2.86	0.13	3.88	2.71/4.30	1.98	
BMO-FM	3.93	3.14	0.00	3.89	3.01/4.28	2.01	
				LCFO-AFM	3.88	2.63/4.19	2.78
				LCFO-FM	3.93	4.26	2.20
					3.89	2.89/4.18	3.04

- DFT+U gives good a and m compared with HSE.

- DFT+U predicts the same metallic or insulating character as HSE, but it underestimates band gaps

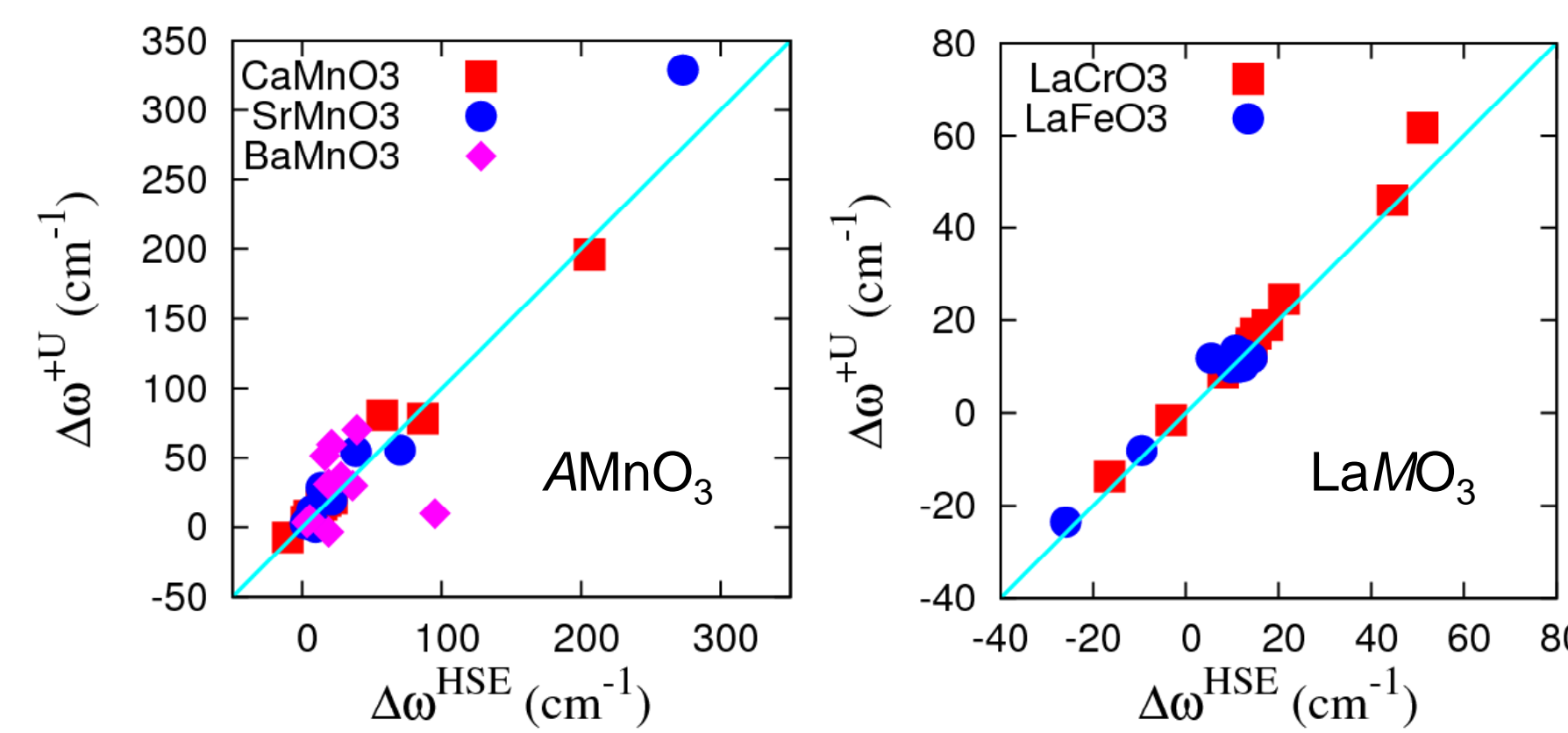
### Phonon calculation from HSE for SrMnO<sub>3</sub>



Black data from experiment (Ref.2), red data from our HSE.

- Polar mode frequencies from HSE agree well with low temperature experiment results

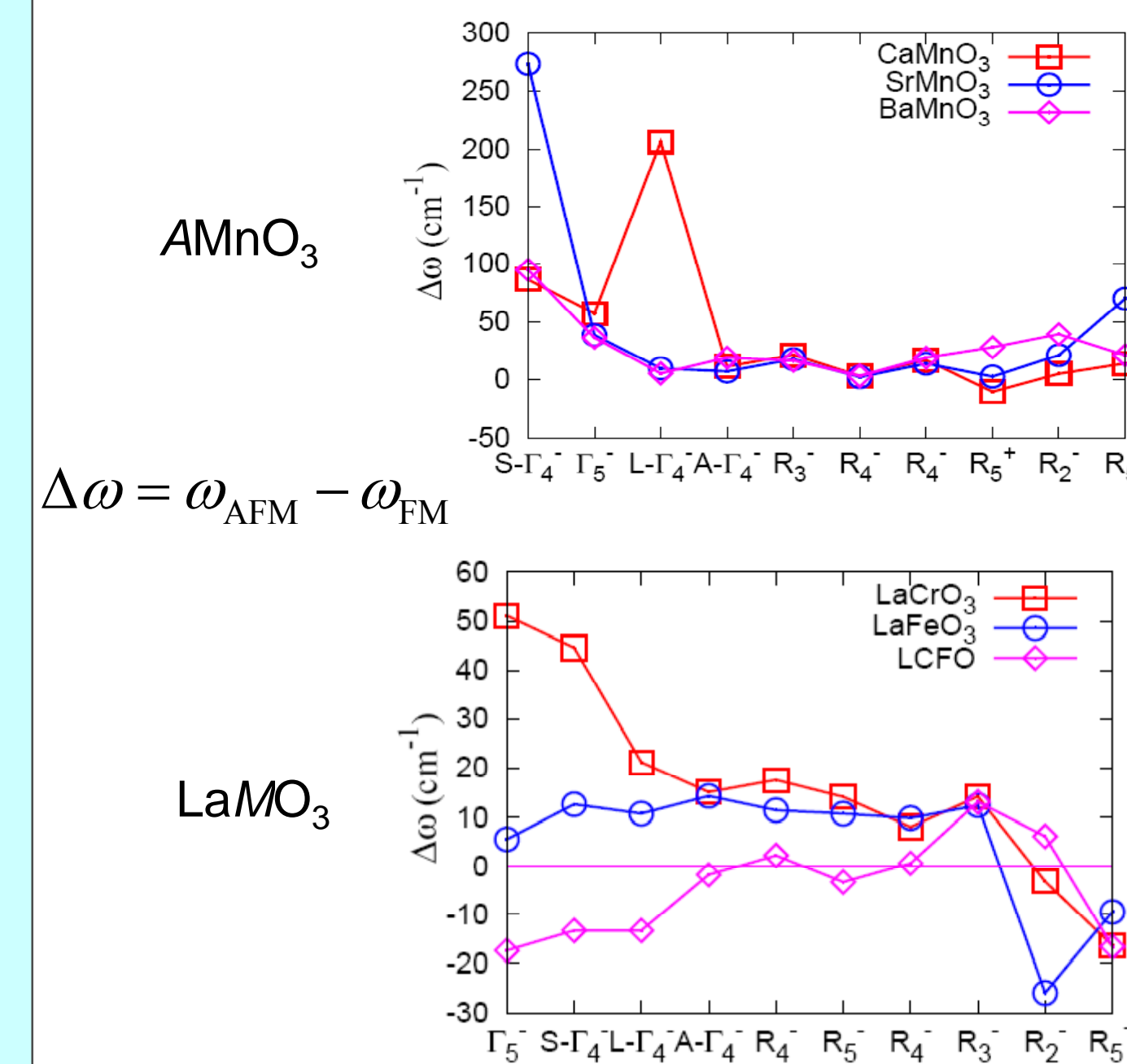
### Frequency shifts from DFT+U and HSE



- DFT+U reproduces the same spin-phonon coupling as HSE

- DFT+U has much lower cost, e.g. HSE needs ~12 days for f shift for LaCrO<sub>3</sub>, DFT+U needs only ~10 mins. (with 96 cores)

### Frequency shifts for AMnO<sub>3</sub> and LaMO<sub>3</sub>

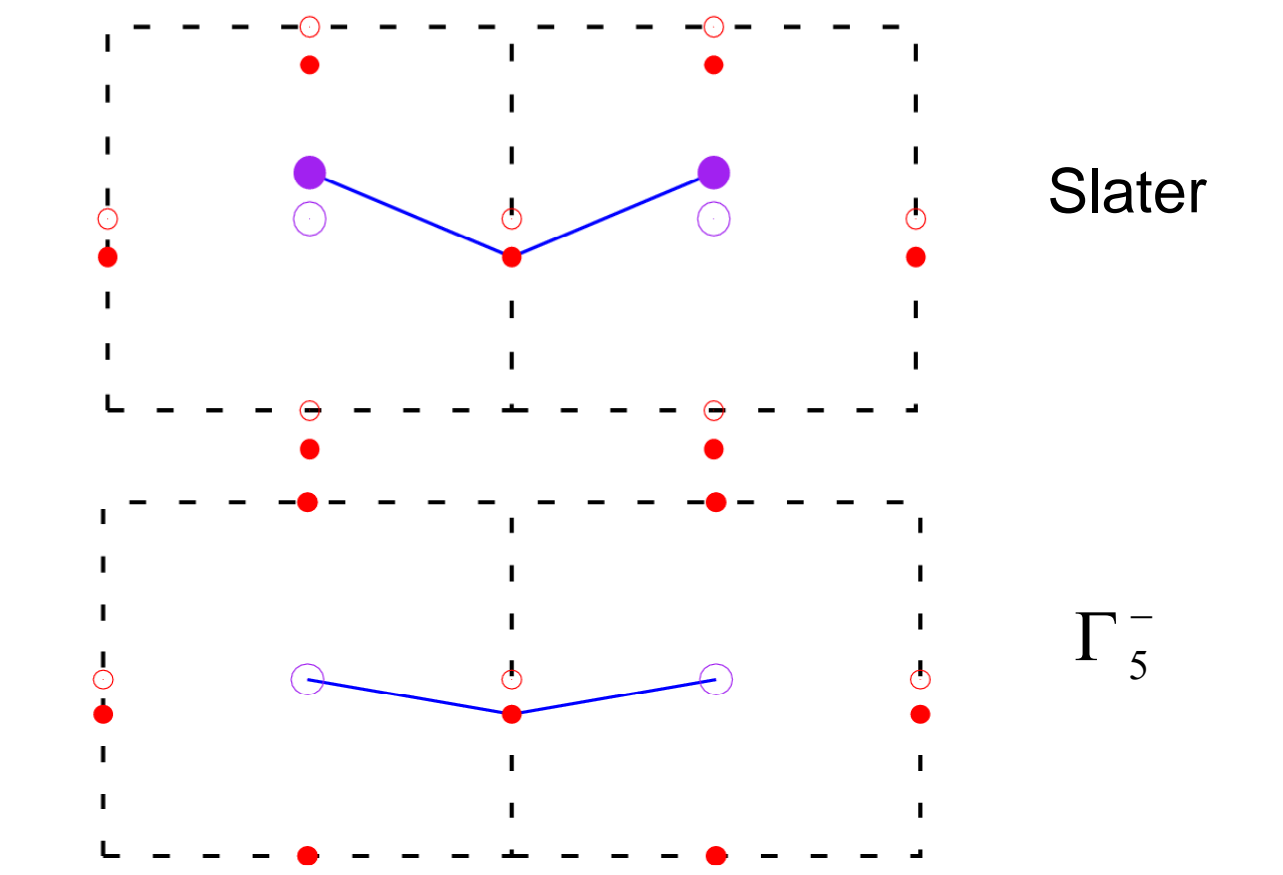


- Slater and  $\Gamma_5^-$  modes show large spin-phonon coupling for AMnO<sub>3</sub>

- LaCrO<sub>3</sub>/LaFeO<sub>3</sub>: phonon frequencies decrease as the spin order changes from AFM to FM

- La<sub>2</sub>(CrFe)O<sub>6</sub>: phonon frequencies increases instead.

### The reason of large frequency shifts for Slater and $\Gamma_5^-$



Open and solid dots indicate ideal and displaced positions, small red dots are oxygen; larger purple dots are metal atoms

- Slater and  $\Gamma_5^-$  modes involve change the Metal-O-Metal bond angles, which is critical to determine the magnitude of the magnetic interactions

## Multiferroicity in BaMnO<sub>3</sub>

Frequency which changes most with increasing size of A cation in AMnO<sub>3</sub> (FM state)

	CaMnO <sub>3</sub>	SrMnO <sub>3</sub>	BaMnO <sub>3</sub>
Slater	186	-96	-369
Rotation	-218	-6	200

- FE instability (Slater mode) becomes stronger
- Instability of rotation becomes weaker and disappears
- Perovskite BaMnO<sub>3</sub> might show multiferroicity, but it is hexagonal phase with face-sharing octahedra [3].

Two ways to induce multiferroicity in BaMnO<sub>3</sub>

- Ba<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> or Ba<sub>1-x</sub>Ca<sub>x</sub>MnO<sub>3</sub> with x large enough to stabilize the perovskite phase and small enough for the FE instability dominates over rotation modes.

Multiferroicity is found in Ba<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> solid solutions (x=0.5) [4].

- Superlattice: CaMnO<sub>3</sub>/BaMnO<sub>3</sub> or SrMnO<sub>3</sub>/BaMnO<sub>3</sub>

superlattices with varying ratios of the pure compounds, and perhaps tuning the misfit strain via the choice of substrate.

More details can be found in Ref. 5.

## Conclusions

- Spin-phonon coupling can depend very strongly on U. A practical approach is proposed to obtain U by fitting to HSE results. It reproduces the HSE results, but with much less computational cost.
- Large spin-phonon coupling effects are found in some polar modes of AMnO<sub>3</sub> and LaMO<sub>3</sub>.
- We suggest that BaMnO<sub>3</sub> is more likely to show multiferroicity by A-site substitution with smaller cation even without external strain.

## References

- C. J. Fennie and K. M. Rabe, Phys. Rev. Lett. 97 267602 (2006).
- A. Sacchetti et al, Phys. Rev. B 72, 172407 (2005)
- B.L. Chamberland et al, J. Solid State Chem. 1, 506 (1970)
- H. Sakai et al, Phys.Rev. Lett. 107, 137601 (2011).
- J Hong et al, Phys. Rev. B 85, 054417 (2012)