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:

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<th>DFT+U</th>
<th>Hybrid functional</th>
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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 functional: HSE
k-point: \( 6 \times 6 \times 6 \)
Plane-wave cutoff: \( 500 \text{ eV} \)
Pseudopotentials

Frozen-ion method for phonon calculation.

Materials:
A-site: \( \text{AMnO}_3 \) (A=Ca, Sr, Ba)
B-site: \( \text{LaMnO}_3 \) (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.

Effect of U on the frequency shifts

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

For \( Pn\overline{3}m \) perovskite cell, the zone-center phonons decompose as \( 3 \Gamma_r \oplus 3 \Gamma_f \) with \( \Gamma_r \) modes being polar. The zone-boundary modes at the R point decompose as \( R \oplus 2R \oplus 2R \).

As for the polar \( \Gamma_r \) phonons, these are often characterized in three idealized modes:

- Slater (S-\( \Gamma_r \)), Last (L-\( \Gamma_r \)) and Axe (A-\( \Gamma_r \)). The antiferrodistortive (AFD) mode (\( R \)). These modes are shown in the following figure.

Phonon modes

The reason of large frequency shifts for Slater and \( \Gamma_f \):

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

More details can be found in Ref. 5.

Conclusions

1. 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.
2. Large spin-phonon coupling effects are found in some polar modes of \( \text{AMnO}_3 \) and \( \text{LaMnO}_3 \).
3. We suggest that \( \text{BaMnO}_3 \) is more likely to show multiferroicity by A-site substitution with smaller cation even without external strain.

Phonon calculation from HSE for SrMnO

Frequency shifts from DFT+U and HSE

Frequency shifts for \( \text{AMnO}_3 \) and \( \text{LaMnO}_3 \)

References