Spin-Phonon Coupling Effects in Transition-Metal Perovskites: A DFT+U and Hybrid-Functional Study

J. Hong,[1] A. Stroppa,[2] J. Íñiguez,[3] S. Picozzi,[2] and D. Vanderbilt[1]

[1] *Department of Physics and Astronomy, Rutgers University, Piscataway, NJ 08854-8019, USA.*
[2] *CNR-SPIN, L'Aquila, Italy.*
[3] *Institut de Ciència de Materials de Barcelona, Campus UAB, 08193 Bellaterra, Spain.*

Spin-phonon coupling effects, as reflected in phonon frequency shifts between ferromagnetic (FM) and G-type antiferromagnetic (AFM) configurations in cubic $CaMnO_3$, $SrMnO_3$, $BaMnO_3$, $LaCrO_3$, $LaFeO_3$ and $La_2(CrFe)O_6$, are investigated using density-functional methods [1]. We find that the phonon frequency shifts $\Delta\omega = \omega_{\rm AFM} - \omega_{\rm FM}$ strongly depend on the U value when using the DFT+U method. We propose a scheme to obtain a proper value for U 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. We find that in the $A\mathrm{MnO_3}$ materials class with (A=Ca,Sr,Ba), the Γ (R) phonon frequency shift $\Delta\omega$ decreases (increases) as the A^{2+} size increases. In LaMO$_3$ (M=Cr, Fe, Cr/Fe), the phonon frequencies at Γ decrease as spin order changes from AFM to FM for $LaCrO_3$ and $LaFeO_3$, but they increase for double perovskite $La_2(CrFe)O_6$. We discuss the prospects for bulk and superlattice forms of these materials to be useful as multiferroics.

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Contact: hongjw10@physics.rutgers.edu