Supporting Information

Ab Initio DFT+U Analysis of Oxygen Transport in $LaCoO_3$: The Effect of Co^{3+} Magnetic States

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S1. Phonon Analysis of Low Spin $LaCoO_3$

The ability of different density functional theory (DFT) based methods to describe the vibrational spectrum of $LaCoO_3$ has garnered significant interest in recent years.[S1-3] These studies have employed LDA+U, PBE0, and B3LYP calculations to compute the gamma point frequencies for $LaCoO_3$ and compare them with experiment. To augment the existing literature, we report frequencies for low spin $LaCoO_3$ computed with LDA+U and GGA+U (table S1).

We briefly revisit the computational details here. We performed DFT+U calculations using the local density and generalized gradient approximations (LDA and GGA).[S4] We employed the Vienna ab initio Simulation Package (VASP) version 5.2.2 for our calculations. The calculations used a planewave basis set kinetic energy cutoff of 750 eV. The projector-augmented wave method (PAW)[S5] was used to replace the nuclei and core electrons leaving 9 valence electrons for Co, 11 for La, and 6 for O. We used the 'regular' PAW potential from the VASP library for our calculations (not the commonly used and less accurate 'soft' potential). For more accurate forces, we used a denser k-point mesh (8 × 8 × 8 Monkhorst-Pack)[S6] and converged the electronic energy to lower than 10^{-8} eV in each ionic iteration. The Hessian matrix was constructed using finite differences of forces calculated with displacements of 0.02 Å. While VASP reports the frequencies, we used Phonopy[S7] (version 1.8.3.2) to diagonalize the Hessian matrix at

the gamma point of the Brillouin zone. Using Phonopy allowed us to assign symmetries to the obtained frequencies for comparison with the existing literature.[S1-3] The Phonopy frequencies agreed with those reported by VASP.

Table S1. Gamma point phonon frequencies (in cm^{-1}) for low spin $LaCoO_3$ obtained with LDA+U and GGA+U calculations. For comparison, experimental[S8-9] and theoretical frequencies[S1-3] from the literature are also reported. All calculations were performed with planewave basis sets unless otherwise noted with the LCAO (linear combination of atomic orbitals) designation. The values in parentheses are the percentage errors with respect to the experimental frequencies.[e,f]

	Experiment	LDA+U[a]	GGA+U[a]	PBE0[b]	PBE0 – LCAO[b]	B3LYP – LCAO[c]	LDA+U[d]
Raman Active							
e_g	86[e]	93 (+8)	80 (-8)	57 (-34)	104 (-21)	106 (-23)	78 (-9)
e_g	172[e]	176 (+2)	173 (+1)	178 (+3)	178 (+3)	188 (+9)	174 (+1)
a_{1g}	261[e]	280 (+7)	298 (+14)	280 (+7)	257 (-1)	343 (+31)	253 (-3)
e_g	432[e]	433 (+.2)	431 (-.2)	438 (+1)	448 (+3)	480 (+11)	409 (-5)
e_g	584[e]	628 (+8)	550 (-6)	613 (+5)	631 (+8)	571 (-2)	448 (-23)
Infrared Active							
a_{2u}	177[f], 174[g]	168 (-5)	139 (-21)	151 (-14)	171 (-4)	169 (-5)	73 (-59)
e_u	177[f], 174[g]	182 (3)	162 (-8)	177 (0)	193 (+9)	194 (+10)	54 (-69)
e_u	242[f], 240[g]	223 (-8)	211 (-13)	247 (+2)	273 (+13)	237 (-2)	79 (-67)
a_{2u}	315[f], 328[g]	267 (-15)	259 (-18)	305 (-3)	329 (+4)	287 (-9)	532 (+69)
e_u	315[f], 328[g]	338 (+7)	312 (-1)	351 (+11)	362 (+15)	341 (+8)	111 (-65)
e_u	411[f], 411[g]	437 (+6)	423 (+3)	441 (+7)	433 (+5)	448 (+9)	158 (-62)
a_{2u}	540[f], 550[g]	566 (+5)	487 (-10)	513 (-5)	536 (-1)	475 (-12)	652 (+21)
e_u	540[f], 582[g]	579 (+7)	511 (-5)	532 (-1)	551 (+2)	525 (-3)	412 (+31)
Acoustic Modes							
e_u	0	0.1i	0.2i	4i	0.7i	----	----
a_{2u}	0	0.1i	0.1i	5i	0	----	----
Inactive Modes							
a_{2g}	----	148	129	----	----	----	144
a_{1u}	----	365	344	----	----	----	162
a_{2g}	----	329	317	----	----	----	325
a_{1u}	----	431	432	----	----	----	530
a_{2g}	----	724	654	----	----	----	577

[a] This Work
[b] Ref. S1
[c] Ref. S2
[d] Ref. S3
[e] Ref. S8 at 5 K
[f] Ref. S9 temperature not specified
[g] Ref. S10 at 9 K

For the Raman modes, both LDA+U and GGA+U show respectable agreement with experiment.[S8] The LDA+U values differ from experiment by at most 8%, while the GGA+U frequencies deviate by a maximum of 14% from experiment. Generally, the LDA+U frequencies exceed experiment while the GGA+U values fall below experiment. This trend agrees with the fact that LDA+U overbinds the crystal while GGA+U slightly underbinds the crystal (see main text, table 1). The results obtained with LDA+U and GGA+U agree with experiment as well as the values obtained with the hybrid PBE0 functional in a planewave basis set.[S1] Using a Gaussian basis set seems to have little effect on the accuracy of the frequencies obtained with the PBE0 functional.[S1] Using the B3LYP hybrid functional to predict the Raman frequencies of $LaCoO_3$ is an exercise in futility as three of the five frequencies have greater than 10% deviation from experiment.[S2] The B3LYP functional was not designed for solid state systems containing transition metals, so we are not surprised to see it struggle with a system such as $LaCoO_3$. Finally, comparing our LDA+U results to the literature values for LDA+U[S3] computed with a different U_{eff} value (7.8 eV) and different pseudopotentials yielded frequencies which have nearly the same accuracy as our results. Our LDA+U frequencies exceed the experimental frequencies (as expected due to overbinding) whereas ref. S3 reports frequencies below experiment, which is not expected from an LDA-derived theory. This becomes especially noticeable for the highest frequency Raman mode where ref. S3 deviates from experiment by 23%. Taken together, these results provide evidence that our *ab initio* U_{eff} value is superior to the higher value used in ref. S3.

The assignment of the symmetries to the infrared frequencies reported by experiment is a difficult task. Indeed, neither ref. S9 or S10 explicitly combines the symmetries with the reported frequencies. Instead, ref. S9 discusses five peaks in the infrared reflection spectrum in terms of 3(A2u+Eu) + 2Eu modes. The three (A2u+Eu) modes are assigned to the external (177 cm^{-1}), bending (315 cm^{-1}), and stretching (540cm^{-1}) modes arising from the cubic perovskite lattice. Based on our reading of ref. S9, the a_{2u} and e_u components of these modes should be lumped together because they are not reported separately. The additional modes arise from zone folding because the rhombohedral unit cell contains two formula units (compared to the one formula unit in the cubic perovskite cell). Therefore, these are two

independent e_u modes at 242 cm^{-1} and 411 cm^{-1}, respectively. We next analyze the six infrared modes reported in ref. S10 and attempt to assign their symmetries. While eight phonon modes should be visible in rhombohedral $LaCoO_3$, ref. S10 only observed six frequencies. These are described as belonging to three bands of phonon frequencies in the range of 180 cm^{-1}, 330 cm^{-1}, and 600 cm^{-1}. Since these three bands are assigned to the external, bending, and stretching modes of the cubic perovskite cell, we take the frequencies closest to these ranges and assign them to the $3(a_{2u} + e_u)$ combinations like we did for ref. S9. In this case, that means the external mode is assigned to the peak at 174 cm^{-1}, the bending mode to the peak at 328 cm^{-1}, and the stretching mode to the peaks at 550 cm^{-1} and 582 cm^{-1}. This leaves the 240 cm^{-1} and 411 cm^{-1} modes as zone folding modes, in good agreement with reference S9. Note that our assignments differ from those in ref. S1.

When compared with our LDA+U and GGA+U results, we see that these assignments have merit although problems remain. Specifically, the lowest a_{2u} and e_u modes (corresponding to the external mode) are split by ~33 cm^{-1}. This is not a large splitting, but it casts doubt on the validity of assigning the same frequency to the a_{2u} and e_u components of the external mode. For the external mode, our LDA+U results agree well with experiment while our GGA+U results are slightly below the experiments. For the bending mode, we again see significant splitting between our a_{2u} and e_u modes (71 cm^{-1} and 53 cm^{-1} for LDA+U and GGA+U, respectively). The e_u mode agrees well with experiment in both cases; however, we predict that the a_{2u} mode should lie significantly lower than the assigned experimental frequencies. The stretching mode has the highest frequencies and the LDA+U results seem to agree pretty well with experiment again while the GGA+U results remain below the experimental frequencies. For the zone folding modes, both the LDA+U and GGA+U show reasonable agreement with experiment. Given the uncertainty in assigning the experimental infrared frequencies, both our LDA+U and GGA+U frequencies give respectable agreement with experiment.

Compared to other functionals, our GGA+U results are slightly worse than hybrid DFT for the infrared active modes. Our LDA+U results have approximately the same accuracy as the hybrid DFT results. The B3LYP and PBE0 functionals give approximately the same accuracy for the infrared

frequencies. The previously reported LDA+U infrared frequencies are vastly different from experiment. The errors most likely arise from numerical issues with the pseudopotentials used, the high U_{eff}, or failure to converge the energies to a sufficiently tight threshold (e.g., 10^{-7} eV) when computing the forces. For our results and the reported hybrid DFT results, the maximum deviation is between 12-21%. The GGA+U has the largest deviations of this data set (excluding the LDA+U results from ref. S3). However, these deviations are not so different from the hybrid DFT deviations to necessitate using the far more expensive hybrid functionals (they require approximately 100 times the computational time as a GGA+U calculation).

In conclusion, comparing our LDA+U and GGA+U gamma point phonon frequencies with experimental values demonstrates that the DFT+U method provides reasonable predictions of vibrational frequencies. The obtained Raman modes had a maximum deviation of 14% from experiment. This is far lower than the maximum deviation for any hybrid functional reported in the literature. Our LDA+U frequencies show better agreement with the experimental infrared frequencies; however, the GGA+U results also seem reasonable. The hybrid functionals perform slightly better on the infrared modes, but the gain in accuracy is not worth the increased computational cost. Finally, the LDA+U results from ref. S3 fail to accurately predict the infrared frequencies of $LaCoO_3$ likely due to some numerical problem or choice of parameters. This analysis establishes that the DFT+U method provides reasonably accurate frequencies for $LaCoO_3$.

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