

# Vibrational and Thermodynamic Properties of Layered $\text{LiM}_{0.5}\text{Ni}_{0.5}\text{O}_2$ (M=Mn, Co) Cathode Materials for Li Ion Batteries

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As the potential electrode materials, the layered lithium mixed transition metal oxides have received wide attention in the lithium ion battery (LIB) research field. In this work, the vibrational and related thermodynamic properties of  $\text{LiM}_{0.5}\text{Ni}_{0.5}\text{O}_2$  (M= Mn, Co) are systematically studied by using density functional perturbation theory (DFPT) and quasi-harmonic approximation (QHA). The phonon dispersion and the thermodynamic functions of  $\text{LiM}_{0.5}\text{Ni}_{0.5}\text{O}_2$  (M= Mn, Co) yield similar results for the local density approximation with the Hubbard model correction (LDA+*U*) and generalized gradient approximation with the Hubbard model correction (GGA+*U*), except for a slight difference for the  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  system. No imaginary frequency is observed in the phonon spectra of  $\text{LiM}_{0.5}\text{Ni}_{0.5}\text{O}_2$  (M= Mn, Co), indicating that the compounds are dynamically stable. Furthermore, the thermodynamic quantities as a function of temperature of  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  have almost the same trend with that of  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ , suggesting the insensitivity of the thermodynamic properties of  $\text{LiM}_{0.5}\text{Ni}_{0.5}\text{O}_2$  (M= Mn, Co) compounds to the types of the transition metal elements. Our results are helpful to understand the finite-temperature thermodynamic properties of the lithium mixed transition metal oxides as electrode materials, in turn to accurately describe the performance of LIB.

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**Keywords:** Lithium ion battery; Lattice vibrational property, Thermodynamic property; Density functional perturbation theory

## 1. INTRODUCTION

The exploration and study of layered lithium mixed transition metal oxides for rechargeable lithium ion batteries (LIBs) is always a major field of materials research. Particularly, the Ni-containing lithium transition metal oxides (such as  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  and  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$  compounds) are the main investigated objects from the experimental and theoretical aspects in terms of their operating voltage, capacity, cycleability, safety, and materials economy when compared to the commercial

LiCoO<sub>2</sub> cathode material.[1,2]. Previous work by Rossen *et al.* [3] studied the synthesis and electrochemical properties of solid solution LiMnO<sub>2</sub>-LiNiO<sub>2</sub>. Islam *et al.* calculated the structural and electronic properties of LiMn<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub> using the spin-polarized generalized gradient approximation.[4] Ohzuku and Makimura [5] carried out their work on the LiMn<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub> system, indicating a rhombohedral structure, a sloping discharge profile, and a reversible capacity (150 mAh/g) within the voltage range 2.5-4.3 V. In addition, FTIR and Raman experimental analysis has also confirmed the layered rhombohedral structure for the LiMn<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub>. [6] On the other hand, Ohzuku and Broussely both reported solid solution phase synthesis of LiCo<sub>1-x</sub>Ni<sub>x</sub>O<sub>2</sub> by applying solid-state chemistry and electrochemistry methods.[7,8] It was shown experimentally that Co replacement of Ni ions in a reasonable concentration in LiCo<sub>1-x</sub>Ni<sub>x</sub>O<sub>2</sub> can enhance the thermal stability and cycling performance.[9] J. M. Wang *et al.* studied the structural and electronic properties of LiCo<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub> by the first-principles calculations. It is found that that the Jahn-Teller distortion in LiNiO<sub>2</sub> is substantially suppressed by Co atoms that replace Ni atoms in the lattice.[10] Recently, we have systematically studied the structural and electronic structure of LiMn<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub> and LiCo<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub> by using the GGA+U method.[11]

With the rapid development and improvement of computational methods, the exact prediction on the properties of materials are obtained from the accurate calculations. So far, most of calculations and simulations for the materials in LIBs are mainly concentrated on the ground state properties. Thermodynamic forecast at finite temperature for the material, especially for the complicated compounds, is still relatively rare. Although we have made the theoretical description of the structural and electronic properties of LiM<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub> (M= Mn, Co) compounds[11], their vibrational and thermodynamic properties are still not established. It is well known that a wide variety of physical properties of solids depend on their lattice vibrational properties, including phase transition, specific heats, thermal expansion, thermal conductivity and so on.[12] In order to accurately simulate the physics and electrochemical properties of LiM<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub> (M= Mn, Co) at finite temperature, i.e. operation temperature, thus, we need to compute the phonon spectrum first. With the phonon density of states, the thermodynamic properties, such as the specific heat capacity, vibrational entropy, vibrational free energy, can be obtained easily.

To the best of our knowledge, the lattice vibrational and thermodynamic properties of LiM<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub> (M= Mn, Co) have not been investigated by using any theoretical and experimental methods. Motivated by this, we perform a systematic theoretical study on the vibrational properties of LiM<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub> (M= Mn, Co), and then obtain the finite-temperature thermodynamic properties using first-principles calculations. In our calculations, local density approximation (LDA) and generalized gradient approximation (GGA) with Hubbard model corrections (LDA+*U* and GGA+*U*) are both employed, and yield similar results. Our study will provide the fundamental information for future experimental and theoretical investigations.

## 2. COMPUTATIONAL DETAILS

The present calculations are carried out by using the first-principles density functional pseudopotential package, VASP,[13] with LDA and GGA exchange correlation potential. In the VASP

code we use the projector augmented-wave (PAW) method [14,15] for the electron-ion interaction, and a cutoff energy of 550 eV for the plane-wave basis expansion. The atomic pseudopotentials treat the Li-2s<sup>1</sup>2p<sup>0</sup>, O-2s<sup>2</sup>2p<sup>4</sup>, Co-3d<sup>8</sup>4s<sup>1</sup>, Mn-3d<sup>6</sup>4s<sup>1</sup>, and Ni-3d<sup>9</sup>4s<sup>1</sup> shells as valence states. The Brillouin zone is sampled with 3×3×1 Monkhorst–Pack *k*-point grid [16]. The convergence criteria for the total energies and ionic forces are set to be 10<sup>-8</sup> eV and 10<sup>-5</sup> eV/Å in the formula unit. Generally, GGA and LDA underestimate the localization of transition metal 3*d* electrons due to the inadequate description of the strong exchange correlation effects for the 3*d* electrons. To address this problem, thus, GGA+*U* and LDA+*U* methods are usually used to calculate the electronic structure of the system with transition metal atoms.[17,18] Herein, the effective Coulomb repulsion parameters  $U_{\text{eff}}$  are 3.9, 3.5, and 5.3 eV for the *d* orbital of Co, Mn and Ni, respectively, which agree with the previous literatures.[19,20] The phonon frequencies are computed by using PHONOPY code,[21] which utilizes the force constants obtained from density functional perturbation theory (DFPT)[22] as supplemented in VASP.

The thermodynamic quantities as a function of temperature (*T*) for a give system could be derived from the phonon spectrum when the vibrational contribution is considered. To obtain the temperature dependence of vibrational Helmholtz free energy (*F*), vibrational entropy (*S*), and constant-volume specific heat capacity (*C<sub>v</sub>*), the integration over the phonon density of states (PDOS) is performed within the quasi-harmonic approximation (QHA) according to the following equations,[23]

$$F(T) = 3nNk_B T \int_0^{\omega_{\max}} \ln \left\{ 2 \sinh \left( \frac{\hbar \omega}{2k_B T} \right) \right\} g(\omega) d\omega, \quad (1)$$

$$S(T) = 3nNk_B \int_0^{\omega_{\max}} \left[ \left( \frac{\hbar \omega}{2k_B T} \right) \coth \left( \frac{\hbar \omega}{2k_B T} \right) - \ln \left\{ 2 \sinh \left( \frac{\hbar \omega}{2k_B T} \right) \right\} \right] g(\omega) d\omega, \quad (2)$$

$$C_v(T) = 3nNk_B \int_0^{\omega_{\max}} \left( \frac{\hbar \omega}{2k_B T} \right)^2 \text{csch}^2 \left( \frac{\hbar \omega}{2k_B T} \right) g(\omega) d\omega \quad (3)$$

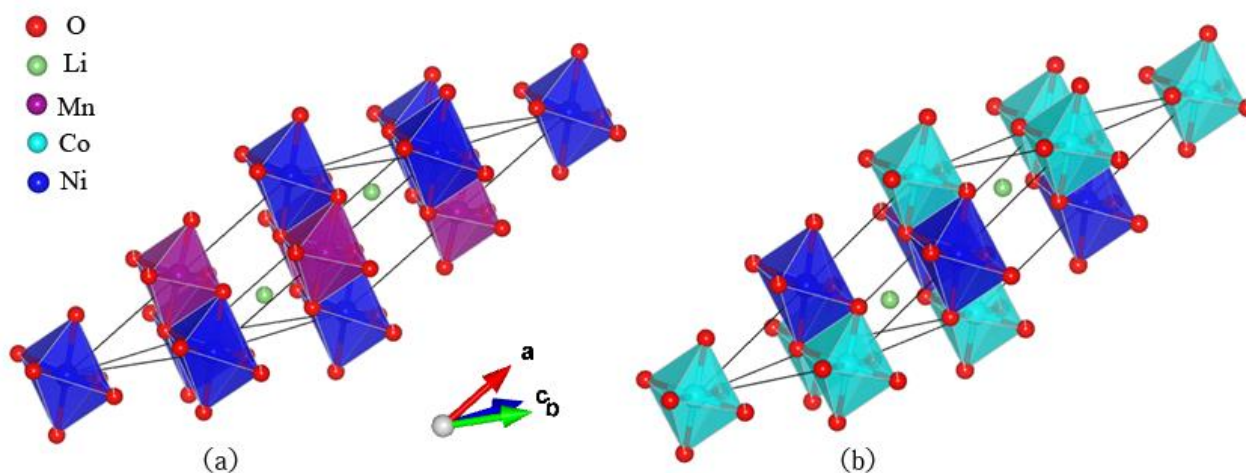
where  $k_B$  is the Boltzmann constant,  $\omega_{\max}$  is the largest phonon frequency, *n* is the number of atoms per unit cell, *N* is the number of unit cells, and  $g(\omega)$  is the normalized PDOS with  $\int_0^{\omega_{\max}} g(\omega) d\omega = 1$ . In our calculations, the thermodynamic quantities are also calculated by using PHONOPY code.

### 3. RESULTS AND DISCUSSION

#### 3.1 Structure

In order to construct the model of LiCo<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub>, we first introduce the primitive cell of LiCoO<sub>2</sub> (space group  $R\bar{3}m$ ) with one Li, one Co, and two O atoms. Then the 2×1×1 supercell of LiCoO<sub>2</sub> is obtained by repeating the primitive cell along the direction of one lattice vector. After this, one of the two Co atoms is replaced by a Ni atom. The lattice parameters of the LiCo<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub> primitive cell, which has eight atoms, is optimized entirely. The relaxed structure and the

corresponding structural parameters are shown in Fig. 1(a) and Table 1, respectively. It is worth to mention that the optimized structures in Fig. 1 are based on the GGA+ $U$  method. Actually, the effect of the exchange-correlation approximations on the metal oxides is nontrivial since it has been reported that the lattice parameters and bond lengths of metal oxides with LDA calculations agree better with experiments than GGA method.[24-26]. Therefore, the results with LDA+ $U$  method are also given in Table 1. As the LDA+ $U$  gives the usual overbinding of cohesive energy and small lattice constants, while the GGA+ $U$  corrects the cohesive energy and tends to expand the lattice constants by a small amount[27], the lattice constants and the bond lengths between transition metal atom and the nearest neighboring O atoms ( $d_{\text{TM-O}}$ ) for  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$  calculated by GGA+ $U$  method are larger than that by LDA+ $U$  method. In addition, the same approach with that for  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$  is used for constructing  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  compound, and the similar results could also be found in Fig. 1(b) and Table 1.



**Figure 1.** Schematic views of the atomic structures of (a)  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  and (b)  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ .

**Table 1.** Optimized lattice parameters of  $\text{LiM}_{0.5}\text{Ni}_{0.5}\text{O}_2$  (M=Mn, Co) layered oxides.  $d_{\text{TM-O}}$  is the distance between transition metal atom and the nearest neighboring O atoms.

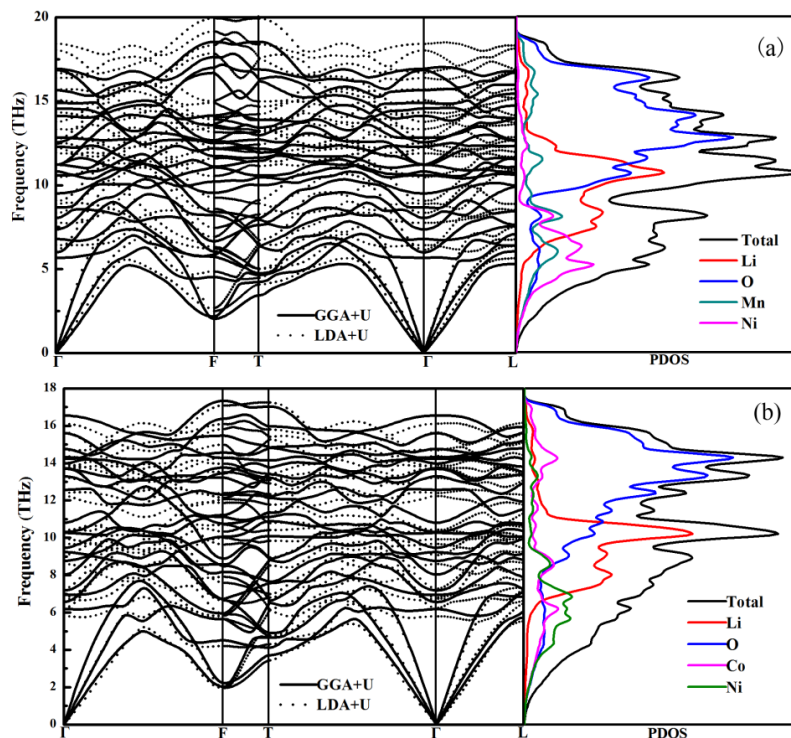
System	Method	Lattice parameter	$d_{\text{TM-O}}$ (Å)
$\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$	GGA+ $U$	$a=10.115$ $\alpha=33.383$	Mn-O $4\times 1.958$ $2\times 1.936$
		$b=c=5.079$ $\beta=\gamma=33.678$	Ni-O $4\times 2.069$ $2\times 2.082$
	LDA+ $U$	$a=9.789$ $\alpha=33.648$	Mn-O $4\times 1.913$ $2\times 1.891$
		$b=c=4.906$ $\beta=\gamma=33.828$	Ni-O $4\times 2.006$ $2\times 2.020$
$\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$	GGA+ $U$	$a=10.016$ $\alpha=33.402$	Co-O $4\times 1.926$ $2\times 1.899$
		$b=c=4.999$ $\beta=\gamma=33.765$	Ni-O $4\times 2.014$ $2\times 2.066$
	LDA+ $U$	$a=9.833$ $\alpha=32.889$	Co-O $4\times 1.883$ $2\times 1.890$
		$b=c=4.848$ $\beta=\gamma=33.278$	Ni-O $4\times 1.867$ $2\times 2.009$

### 3.2 Lattice vibrational properties

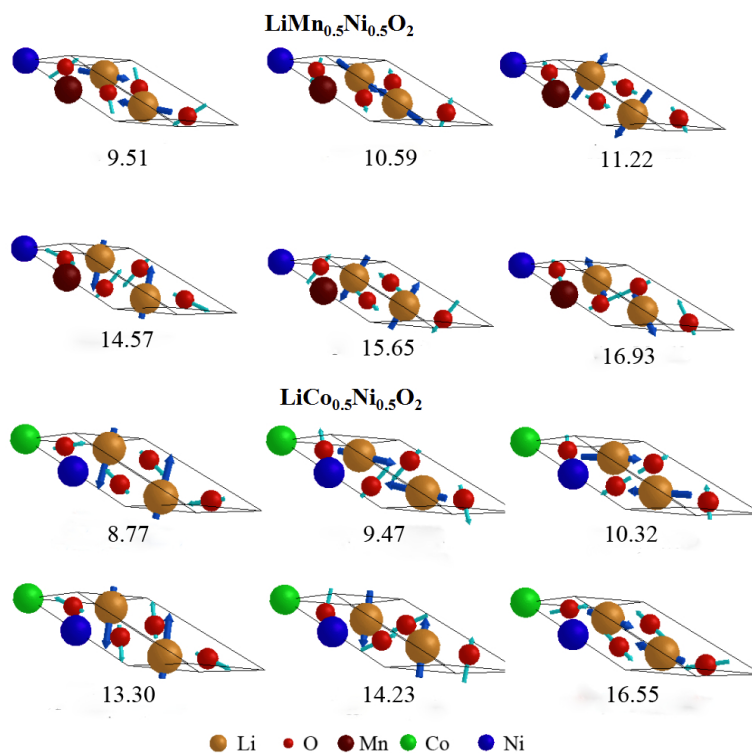
Phonon dispersion curve provides important information on the lattice and atomic dynamical properties of materials. Phonon dispersion curves give a criterion to judge the crystal stability. On the other hand, through the prediction of soft modes, it also provide information on possible phase transitions. Indeed, if all phonon square frequencies  $[\omega^2(j,q)]$  are positive, the crystal is locally stable. If it appears that some  $[\omega^2(j,q)]$  are negative (soft modes), however, the structure is unstable.

The obtained phonon dispersion curves along the principal symmetry direction of the Brillouin zone (BZ) and the corresponding PDOS for  $\text{LiM}_{0.5}\text{Ni}_{0.5}\text{O}_2$  ( $M = \text{Mn, Co}$ ) structures are illustrated in Fig.2. As the unit cell of  $\text{LiM}_{0.5}\text{Ni}_{0.5}\text{O}_2$  ( $M = \text{Mn, Co}$ ) structure contains eight atoms, a total of 24 phonon branches, including 3 acoustic branches and 21 optical branches, are observed. The calculated phonon dispersion curves do not contain any soft mode, which suggests that the two compounds  $\text{LiM}_{0.5}\text{Ni}_{0.5}\text{O}_2$  ( $M = \text{Mn, Co}$ ) are dynamically stable. Furthermore, Fig. 2 shows that the phonon dispersion curves of  $\text{LiM}_{0.5}\text{Ni}_{0.5}\text{O}_2$  ( $M = \text{Mn, Co}$ ) with GGA+ $U$  method are similar to those with LDA+ $U$  method. Compare with  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ , the phonon frequencies of  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  from LDA+ $U$  method are basically higher than those obtained from GGA+ $U$  method, which is in agreement with other recent work [20,28]. On the right side of the phonon dispersion curves, the corresponding total and partial PDOS are also plotted (see Fig.2), which are based on the GGA+ $U$  results. The PDOS for the  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  and  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$  structures indicate clearly similarity. Specifically, it is seen that the low frequency region (about  $< 8$  THz) is dominated by the displacements of transition metal atoms, while the high frequency region (about  $> 10$  THz) by the displacements of oxygen atoms, which is similar to that of the single phase  $\text{LiMO}_2$  ( $M = \text{Ni, Co, Mn}$ ) [20]. Additionally, lithium atom motions mainly contribute to the medium frequency region (about 6~12THz). In fact, the difference for the phonon frequencies of  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  between GGA+ $U$  and LDA+ $U$  methods mainly exhibits on the higher frequency part. There are two factors that result in this. On the one hand, it is due to the general underestimation of bond length according to LDA+ $U$  calculations when compared with GGA+ $U$  method, thus leading to the stronger bond and higher vibrational frequencies. On the other hand, the effect of the bond strength on the light atoms (Li, O) is larger than that on the heavy atoms (Mn, Co, Ni). Therefore, the high frequency part is easier to be affected since the high frequency part is from the motion of Li and O atoms. By contrast, for the low frequency part (i.e. acoustic regime) the LDA+ $U$  method are almost the same with that of GGA+ $U$  method. From comparison of the lattice vibration frequency of the  $\text{LiM}_{0.5}\text{Ni}_{0.5}\text{O}_2$  in the present work and the frequency of  $\text{LiCoO}_2$  reported in reference [29] and  $\text{LiMO}_2$  ( $M = \text{Ni, Co, Mn}$ ) reported in reference [20], we can see that the highest vibration frequency of the optical branches is obviously higher in compounds with Mn, namely the  $\text{LiMnO}_2$  and  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  compounds have higher frequency than other compounds. This shows that the Mn-O bonds are stronger comparing with that of the Co-O and Ni-O bonds, which is in consistent with the results from electronic structure analysis [10-11, 30].

In order to further understand the lattice vibration form of  $\text{LiM}_{0.5}\text{Ni}_{0.5}\text{O}_2$  at high frequency region, six optical vibration modes with high frequency at the zone center are selected for  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  and  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ , respectively, which are shown in Fig.3. The vibrational directions of atoms in the unit cell are represented by arrows.



**Figure 2.** Phonon dispersion and PDOS of (a)  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  and (b)  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ .

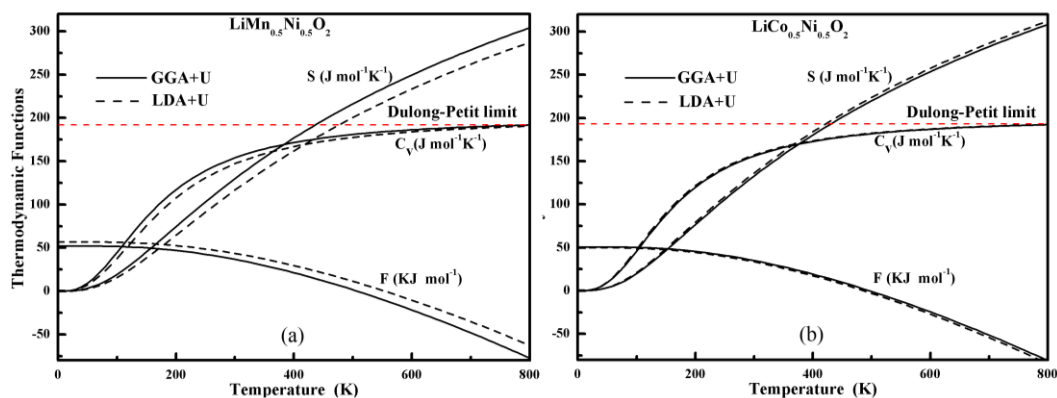


**Figure 3.** The selected vibrational modes of  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  and  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ . The corresponding phonon frequencies (in unit of THz) are given below the vibrational picture. The arrows represent the vibrational directions of the atoms. Li, O, Mn, Co, and Ni atoms are represented by brown, red, dark purple, green, and blue spheres, respectively.

From Fig.3, it is found that all these optical vibration modes with high frequency merely involve the motion of Li and O atoms, whereas not including the motion of transitions metal atoms (Mn, Co, Ni), which agrees well with the results of PDOS. It is worth mentioning that the atomic motion for these vibrational modes by GGA+ $U$  and LDA+ $U$  methods are almost the same.

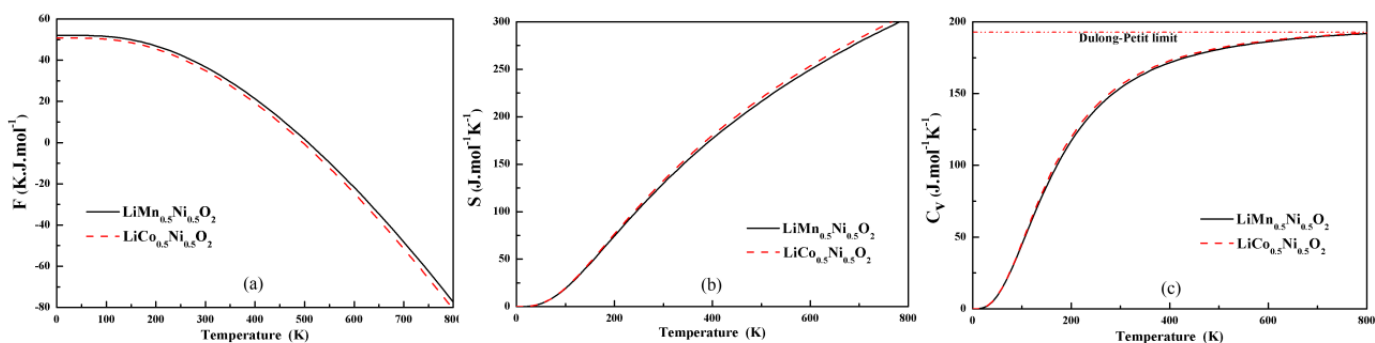
### 3.3. Thermodynamic properties

For the electrode materials of LIBs, the thermodynamic properties are the problems we are concerned about. According to eqs (1)-(3), the thermodynamic quantities, such as vibrational Helmholtz free energy ( $F$ ), vibrational entropy ( $S$ ), and constant-volume specific heat capacity ( $C_v$ ), as a function of temperature ( $T$ ) is able to be calculated. The obtained results for  $\text{LiM}_{0.5}\text{Ni}_{0.5}\text{O}_2$  ( $M=\text{Mn, Co}$ ) compounds are plotted in Fig. 4 and Fig. 5. Fig. 4 (a) and (b) show the corresponding thermodynamic functions of  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  and  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ , respectively. Both GGA+ $U$  and LDA+ $U$  results are provided. For  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ , the curves of the thermodynamic quantities by GGA+ $U$  method almost coincide with that by LDA+ $U$ . Compared with  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ , the curves of the thermodynamic quantities for  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  by GGA+ $U$  and LDA+ $U$  methods show the difference to some extent. The vibrational entropy and specific heat at a given temperature of  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  by GGA+ $U$  are slightly higher than that by LDA+ $U$ , while vibrational free energy is lower for GGA+ $U$  method. Clearly, these results of the thermodynamic properties are directly related with that of aforementioned PDOS, thus, can be understood easily. To better compare the thermodynamic properties of  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  to those of  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ , the thermodynamic quantities  $F$ ,  $S$ , and  $C_v$  of  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  and  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$  as a function of temperature are respectively shown in Fig.5(a), (b), and (c). These results are based on the GGA+ $U$  calculations. As can be seen from Fig.5, the temperature-dependent thermodynamic quantities of  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  are extremely similar to that of  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ . Interestingly, we also mention here that these properties of the mixed binary  $\text{LiM}_{0.5}\text{Ni}_{0.5}\text{O}_2$  ( $M=\text{Co, Mn}$ ) cathode is very close to that of the single phase  $\text{LiCoO}_2$  [29] and  $\text{LiMnO}_2$  ( $M=\text{Ni, Co, Mn}$ ) cathodes [20], indicating that the thermodynamic performance of the layered materials are similar.



**Figure 4.** Thermodynamic functions of vibrational entropy  $S$ , vibrational Helmholtz free energy  $F$  and constant-volume specific heat  $C_v$  of (a)  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  and (b)  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$  calculated by GGA+ $U$  and LDA+ $U$  methods.

Therefore, the thermodynamic properties of  $\text{LiM}_{0.5}\text{Ni}_{0.5}\text{O}_2$  ( $M=\text{Mn, Co}$ ) compounds are insensitive to the types of transition metal elements. The vibrational free energy and vibrational entropy decreases and increases gradually with the increase of the temperature, respectively. The calculated values of entropy at room temperature (300K) are 129.822 and 132.805  $\text{J mol}^{-1} \text{K}^{-1}$  for  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  and  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ , respectively. We found that no obvious difference are observed between the binary compounds and single phase materials. The vibrational entropy of the single phase  $\text{LiCoO}_2$  at 300 K is calculated to be about 136.3  $\text{J mol}^{-1} \text{K}^{-1}$  (correlated to the same unit cell size) in Ref. [29], which is very close to the results of the  $\text{LiM}_{0.5}\text{Ni}_{0.5}\text{O}_2$  ( $M=\text{Co, Mn}$ ) in the present work. In addition, within the temperature range of 0~400 K, the calculated heat capacities increase very rapidly with increasing the temperature, while increasing slowly after 400 K. The constant-volume specific heat capacities at room temperature are 153.872 and 155.871  $\text{J mol}^{-1} \text{K}^{-1}$  for  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  and  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ , respectively. Finally, the heat capacity would be close to the Dulong–Petit limit when the temperature is high. The constant-volume specific heat capacities of the two compounds all tend to the limit value of 199.55  $\text{J mol}^{-1} \text{K}^{-1}$  (3NR, where N is the number of atoms in the unit cell and is equal to eight in our case, R is the gas constant measured in  $\text{J mol}^{-1} \text{K}^{-1}$ ). Up to now, there are no experimental and theoretical data available for comparison with our results. Therefore, it is hopeful that the results in our study are tested in future, experimentally or theoretically, as these materials are important for the future use in fundamental research as well as application. Although no experimental data available in literature, we can compare these data with theoretical data of similar compounds.



**Figure 5.** Comparison of the thermodynamic quantities of (a) vibrational Helmholtz free energy  $F$ , (b) vibrational entropy  $S$ , and (c) constant-volume specific heat  $C_v$  for  $\text{LiM}_{0.5}\text{Ni}_{0.5}\text{O}_2$  ( $M= \text{Mn, Co}$ ) with GGA+ $U$  method.

#### 4. CONCLUSION

The presented results on the lattice dynamical and thermodynamic properties for  $\text{LiM}_{0.5}\text{Ni}_{0.5}\text{O}_2$  ( $M= \text{Mn, Co}$ ) structures are obtained by using the first-principles calculations based on density functional perturbation theory with GGA+ $U$  and LDA+ $U$  methods. We calculated the phonon dispersion curves and phonon density of states for  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  and  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ . There is no soft mode at any wave vector for the calculated phonon spectra, which shows the dynamical stability of



these two systems. Based on the phonon density of states, the important thermodynamic quantities such as vibrational Helmholtz free energy, vibrational entropy, and constant-volume specific heat capacity are derived within the quasi-harmonic approximation. Either for vibrational properties or for thermodynamic properties, the results from GGA+*U* method is very similar to that from LDA+*U* one. In addition, the calculations of finite-temperature thermodynamic functions also show the extreme similarity for the LiM<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub> (M= Mn, Co) systems. Therefore, the thermodynamic properties of LiM<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub> (M= Mn, Co) compounds are basically independent of the mass of the transition metal. Our calculations for the present compounds will be helpful for further experimental and theoretical investigations on lithium mixed transition metal oxides in the future.

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