Crystallography information of species with deviation from the experimental information

Mn_2O_3
Space group $P2_12_12_1$

Site	Elements (spin direction)	Wyckoff position	x	y	z
Mn1	Mn (↑)	4a	0.498767	0	0.501022
Mn2	Mn (↓)	4a	0.287938	0	0.758195
Mn3	Mn (↑)	4a	0.785937	0	0.74197
Mn4	Mn (↑)	4a	0.0206346	0.239975	0.718515
Mn5	Mn (↓)	4a	0.515974	0.246036	0.783362
Mn6	Mn (↓)	4a	0	0.499637	1
Mn7	Mn (↑)	4a	0.258841	0.216495	0.507748
Mn8	Mn (↓)	4a	0.761263	0.216498	0.988547
O1	O	4a	0.155252	0.0859903	0.637821
O2	O	4a	0.3816	0.149303	0.923135
O3	O	4a	0.0815644	0.12388	0.360589
O4	O	4a	0.0815278	0.376423	0.858566
O5	O	4a	0.140618	0.348115	0.59384
O6	O	4a	0.354362	0.421068	0.880887
O7	O	4a	0.137604	0.149238	0.092168
O8	O	4a	0.426502	0.124852	0.651339
O9	O	4a	0.352105	0.0776471	0.382721
O10	O	4a	0.655864	0.09096	0.860356
O11	O	4a	0.927092	0.120804	0.851625
O12	O	4a	0.878631	0.149225	0.5798

a	b	c	α	β	γ
9.4773	9.5148	9.430859	90	90	90

Table S1 – Crystallography information of Mn_2O_3 employed in our calculations.

r-LiMnO$_2$

Space group $P2/c$

Site	Elements (spin direction)	Wyckoff position	x	y	z
Li	Li	2e	0	0.25	0.37441
Li	Li	2e	0	0.25	0.03479
Mn	Mn ($\uparrow$)	2f	0.5	0.25	0.86969
Mn	Mn ($\downarrow$)	2f	0.5	0.25	0.36969
O	O	4g	0.26641	0.25976	0.12145
O	O	4g	0.26641	0.25976	0.62144

a	b	c	α	β	γ
5.695706	5.410593	5.541325	90	90	90

Table S2 - Crystallography information of rhombohedral LiMnO$_2$ employed in our calculations.

LiNiO2

Space group $P2_1/c$

Site	Elements	Wyckoff position	x	y	z
Li	Li	2a	0	0	0
Ni	Ni	2d	0.5	0.5	0
O	O	4e	0.794792	0.491348	0.244974

a	b	c	α	β	γ
5.023423	2.873	9.627304	90	29.20206	90

Table S3 - Crystallography information of rhombohedral LiNiO$_2$ employed in our calculations.

CoO, sphalerite structure
Space group $\bar{1}42d$

Site	Elements (spin direction)	Wyckoff position	x	y	z
Co1	Co (↑)	4b	0.5	0.5	1
Co2	Co (↓)	4a	0	0	0
O1	O	8d	0.25	0.25	0.125

a	b	c	α	β	γ
4.307659	4.307659	9.040786	90	90	90

Table S4 - Crystallography information of CoO in sphalerite structure.

CoO, distorted rocksalt
Space group $P2_1/m$

Site	Elements (spin direction)	Wyckoff position	x	y	z
Co1	Co (↑)	2e	0.511101	0.75	0.210507
Co2	Co (↓)	2e	0.011104	0.75	0.710505
O1	O	2e	0.228033	0.75	0.007943
O2	O	2e	0.271972	0.25	0.492053

a	b	c	α	β	γ
5.39076	2.977543	4.822464	90	74.10092	90

Table S5 - Crystallography information of CoO with a magnetic structure different from the experimental.

Supercells used on phonon calculations

LiCoO$_2$

Phonon calculation is performed on a 3x3x1 diagonal supercell of the following cell.

Space group 166 = $R\bar{3}m$, conventional cell.

Element	u	v	w
Li	0	0	0
Co	0	0	0.5
O	0	0	0.23854

a	b	c	α	β	γ
2.82662	2.82662	13.9127	90	90	120

Table S6 - Crystallography information of LiCoO$_2$ supercell used for phonon calculations.

LiNiO$_2$
Space group *P2$_1$/c*

Phonon calculation is performed on a 2x4x2 diagonal supercell of the following cell.

Space group 14 = *P2$_1$/c*

Element	u	v	w
Li	0	0.5	0
Ni	0.5	0	0
O	0.71997	0.94427	0.25548

a	b	c	α	β	γ
4.9076	2.9482	4.9087	90	72.66	90

Table S7 - Crystallography information of LiNiO$_2$ supercell used for phonon calculations.

LiMnO$_2$

Phonon calculation is performed using a 2x2x2 diagonal supercell of the following cell.

Space group *P2/c*

Atom label	Elements (spin direction)	u	v	w
Li1	Li	0	0.1187	0.25
Li2	Li	0.5	0.8814	0.25
O1	O	0.25	0.6026	0
O2	O	0.75	0.8577	0
Mn1	Mn (↑)	0	0.6331	0.25
Mn2	Mn (↓)	0.5	0.3668	0.25

a	b	c	α	β	γ
5.3405	5.6848	5.3417	90	117.54	90

Table S8 - Crystallography information of LiMnO$_2$ supercell used for phonon calculations.

Vibrational contributions to thermodynamic potentials in the harmonic approximation (HA)

In the simplest case of a diatomic molecule which only has one mode of vibration a, the canonical partition function of the quantum oscillator in Maxwell-Boltzmann statistics is :

$$q_a = \sum_{j = 0,..,\infty} \exp\left(-\frac{e_j}{k_B T}\right)$$

where index j numbers the quantum states, e_j is the energy associated with state j, k_B is the Boltzmann constant and T the temperature. In the harmonic approximation, the energy associated with state j is

$$e_j = \left(j + \frac{1}{2}\right) h v_a$$

where v_a is the frequency of the mode and h is Planck's constant. Summing the geometric series leads to :

$$q_a = \frac{exp\left(-\dfrac{\theta_a}{2T}\right)}{1 - exp\left(-\dfrac{\theta_a}{T}\right)}$$

where we introduced the usual notation

$$\theta_a = \frac{h v_a}{k_B}$$

called the characteristic temperature of mode a.

In a molecule, there are not only one mode of vibration but M normal modes which, in the harmonic approximation, are independent. The probability for the oscillator to be in state $(j_1, j_2, ..., j_M)$ is the product of the individual probabilities, as in:

$$prob(j_1, j_2, ..., j_M) = prob(j_1) \, prob(j_2) ... prob(j_M)$$

Hence, the vibrational partition function of the molecule is the product of the individual partition functions of each mode:

$$Q_{vib} = \prod_{m = 1}^{M} q_m$$

The vibrational contribution to the free energy F is obtained from the partition function Q according to the general formula of statistical physics:

$$F_{vib} = -k_B T \ln Q_{vib} \qquad . \tag{1}$$

Thus, the vibrational free energy appears as a sum of the contributions of individual modes:

$$F_{vib} = \sum_{m = 1}^{M} F_{vib\, m}$$

In turn, vibrational contributions to the internal energy U, entropy S and heat capacity at constant volume C_V may be obtained from F with the usual thermodynamical relationships[1]

$$S_{vib} = -\left(\frac{\partial F_{vib}}{\partial T}\right)_V \quad , \quad U_{vib} = F_{vib} + TS_{vib} \quad , \quad C_{V\,vib} = -\left(\frac{\partial U_{vib}}{\partial T}\right)_V \tag{2}$$

where the partial derivative at constant volume denotes the fact that the frequencies ν_m are to be taken as constant. Clearly, all these quantities can be written as sums of contributions from individual modes.

In the case of an infinite perfect crystal containing N atoms per cell, the normal modes of vibration are obtained as plane waves which can be classified according to wavevectors, usually called k-points (or q-points), taken in the first Brillouin zone (1BZ). For each k-point there are $3N$ normal modes.

As for the relevant thermodynamic quantities, they are now taken as the intensive ones, such as the energy per cell and the entropy per cell. The per-cell quantities can be obtained by a uniform sampling of the first Brillouin zone.

Numerical implementation forces to choose a finite and uniform sampling of the 1BZ. This sampling is defined by a list of k-points $(\vec{k}_k, w_k)_{k=1,\ldots,K}$ where K is the number of k-points, $\vec{k}_k$ is the k-point vector of index k and w_k is its weight. In order to end up with extensive quantities corresponding for a quantity of matter equal to one unit cell, the weights are normalized by $\sum_{k=1}^{K} w_k = 1.$ The logarithm of the vibrational partition function for one unit cell is then given by :

$$\ln Q = \sum_{k=1}^{K} w_k \sum_{m=1}^{3N} \ln q_{k,m} \quad .$$

F, U, S and C_V are then obtained according to Eq (1) and Eq (2).

The CASTEP code used in this work takes as input data the crystallographic data, a sampling density of the 1BZ and the temperature T. It then automatically determines the k-point list, computes the normal modes of vibration and outputs the thermodynamic quantities F, U and S. The precision of the results strongly depends on the k-point sampling density, i.e. the larger K, the better the precision.

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[1] They may also be written as analytical expressions involving sums over the normal modes of vibrations. The formulas can be found in any statistical thermodynamics textbook.

Vibrational contributions to thermodynamic potentials in the quasi-harmonic approximation (QHA)

As described above, the HA leads to a formula for the free energy $F(T)$ which involves the frequencies $v_{k,m}$ of the vibrational normal modes for the selected k-point list $\vec{k}_k, k = 1,..,K$ and index $m = 1,...,3N$. This set of frequencies is obtained from a computation performed for an arbitrarily chosen unit cell volume V, for which it is customary to select the value at zero pressure.

In reality, all crystals are subject to thermal expansion, which means that if T is raised at a constant pressure P, the volume V changes. On the other hand one may easily observe, from 2 computations performed at different volumes, that the frequencies $v_{k,m}$ are also volume-dependent. The QHA is a simple improvement of the HA that incorporates these facts into the model.

In the QHA, the internal energy of the crystal is written as

$$U(T,V) = U_{sta}(V) + U_{vib}(T,V)$$

where we introduce the label "sta" for static contributions, i.e. results of DFT geometry optimization tasks ending with a scalar stress tensor, including the energy itself, the unit cell volume, and the pressure[2]. $U_{vib}(T,V)$ is the QHA vibrational contribution.

The QHA consists in introducing the dependency $v_{k,m}(V)$ into the vibrational partition function obtained using the HA (described in the previous Section). The necessary input data is obtained by repeating at several values of V the DFT computations of the normal modes of vibrations, as in the HA. This formally yields the QHA for the free energy as

$$F(T,V) = U_{sta}(V) + F_{vib}(T,V) \quad .$$

The internal energy U and entropy S are then obtained using relationships (2) as before.

Since the state variables are now T and V, the pressure P is given by the thermodynamic relationship

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \quad . \tag{3}$$

In general however, one is interested by the thermodynamic properties at given P, for example ambient pressure, rather than at a given V. Thus we must solve Eq (3) for V at the selected target temperature T_t and target pressure P_t. This is a simple numerical analysis problem for which a great variety of methods and numerical implementations may be used. We use the following procedure.

We arbitrarily choose a set of 3 pressures $P_i, i = 1,2,3$ between say 0 and $-15\,GPa$. CASTEP geometry optimization jobs at these (static) pressures yield the three corresponding volumes $V_i, i = 1,2,3$ and sets of phonon frequencies $v_{k,m,i}, i = 1,2,3$. Then for the target temperature T_t, the HA yields 3 numbers $F_i(T_t) = F(T_t,V_i)$ which we fit to a quadratic polynomial in the variable V in order to get an analytical

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[2] The static results are often reported in the literature as an equation of state (EOS) $P_{sta}(V)$ or the corresponding integrated EOS $U_{sta}(V)$, which are related by $P_{sta} = -dU_{sta}/dV$. When there is no explicit mention of the fact that these are static data, one should keep in mind that they differ from the actual thermodynamic properties at $T = 0K$ by the so-called "zero-point vibrational contributions" which are one of the outputs of the QHA and result from the $\frac{1}{2}hv_a$ contribution to the energy e_j of the quantum oscillator.

formula for $F(T_t,V)$ as a function of V for this specific temperature T_t. Eq (3) can then be solved analytically for V at the target pressure P_t. This gives a first estimate of the solution $V(T_t,P_t)$.

In order to make this result more reliable however, we generally iterate this procedure with different sets of pressures P_i until the estimated $V(T_t,P_t)$ lies within the volume interval containing the three V_i on which the fit is performed, while simultaneously ensuring that the polynomial fit is robust and meets a satisfactory precision.

With the volume at a given pressure and temperature, we can calculate the coefficient of thermal expansion given by

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

And finally, the heat capacity at constant pressure is written as

$$C_P = C_V + TVB\alpha^2$$

Where C_V is the heat capacity at constant volume and B is the bulk modulus, given by

$$B = V\left(\frac{\partial P}{\partial V}\right)_T$$