Lattice effects on the formation of oxygen vacancies in perovskite thin films

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We use first-principles methods to investigate the effects of collective lattice excitations on the formation of oxygen vacancies in perovskite thin films. We find that phonons play a crucial role on the strain-mediated control of defect chemistry at finite temperatures. In particular, zero-temperature oxygen vacancy formation trends deduced as a function of epitaxial strain can be fully reversed near room temperature. Our first-principles calculations evidence a direct link between the lattice contribution to the oxygen vacancy free energy and the volume expansion that the system undergoes when is chemically reduced: The larger the resulting volume expansion, the more favorable thermal excitations are to point defect formation. However, the interplay between the vibrational vacancy entropy, or equivalently, chemical expansion, and epitaxial strain is difficult to generalise as this can be strongly influenced by underlying structural and magnetic transitions. In addition, we find that vacancy ordering can be largely hindered by the thermal lattice excitations.

Point defects can affect considerably the structural, magnetic, and transport properties of perovskite-structure materials with chemical formula ABO$_3$. Oxygen vacancies (V$_O$), for example, enable ionic conductivity in perovskite-based solid solutions to be used for electrochemical applications such as solid oxide fuel and electrolysis cells [1–3]. Likewise, V$_O$ can significantly distort the equilibrium arrangement of atoms and hence modify the superexchange interactions between neighboring magnetic ions [4–6]. The presence of point defects in perovskite oxides also is known to induce an increase of volume, the so-called “chemical expansion” [7–10]; such an effect is caused by atomic underbonding due to the extra electrons provided by the oxygen vacancies, which are located in nonbonding transition-metal orbitals (Fig. 1a). Engineering of defect properties in perovskite oxides, therefore, emerges as a likely avenue for the design of new materials with tailored functionality.

Recently, it has been experimentally demonstrated that strain engineering can be used to tune the content of oxygen in some perovskite oxides [2, 11–14]. For example, in SrCoO$_{3-\delta}$ thin films a moderate epitaxial strain of about +2% produces a $\sim 30\%$ reduction in the oxygen activation energy barrier, which makes it possible to stabilise oxygen-deficient samples at annealing temperatures close to ambient conditions [12]. Also, in multiferroic SrMnO$_3$ thin films the formation energy of oxygen vacancies is decreased by 0.25 eV at a epitaxial strain of +3.8% [16].

First-principles computational methods have been used to unveil the atomistic mechanisms behind strain-mediated V$_O$ formation at zero temperature (i.e., neglecting possible thermal effects) [15–17]. Interestingly, Aschauer et al. [15] have shown that the formation energy of oxygen vacancies in CaMnO$_3$ thin films is strongly favored by tensile (positive) epitaxial strain. This finding has been rationalised in terms of general electrostatic arguments based on the fact that the accompanying electron-electron repulsion is effectively reduced along elongated Mn-Mn distances. Nevertheless, experiments performed in CaMnO$_3$ thin films covering a wide range of epitaxial states have not evidenced any preference for V$_O$ formation at tensile conditions [18]. Further, recent measurements in SrCoO$_{3-\delta}$ thin films by Hu et al. [14] have revealed a nonmonotonic saw-tooth dependence of the critical reduction temperature on epitaxial strain with a marked peak at moderate tensile stresses, which suggests the presence of V$_O$ contributions other than purely electrostatic.

In this Letter, we employ first-principles methods based on density functional theory (DFT) to quantify the effects of thermal lattice excitations on the formation en-

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**FIG. 1**: (Color online) Sketch of the chemical expansion occurring in ABO$_3$ perovskites due to oxygen reduction (a). (b) The 20-atom $\sqrt{2} \times \sqrt{2} \times 2$ simulation cell used in our zero-temperature energy calculations; red, blue, and black spheres represent O, B, and A atoms, respectively. Equatorial and apical oxygen positions are noted in the figure.
energy of $V_O$ in perovskite thin films. We select $\text{SrCoO}_3$–$\delta$ (SCO) and $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$–$\delta$ (LSMCO) as the reference systems in which to perform our calculations because these materials exhibit one of the highest oxygen-deficient stoichiometries observed to date at ambient conditions in a simple perovskite $[20]$. Our computational results show that (1) thermal lattice excitations play a crucial role on the strain-dependence of oxygen vacancy formation, as they can fully reverse the energy trends deduced at zero temperature; (2) the larger the chemical expansion experienced by the system the more favorable vibrational entropy contributions are to $V_O$ formation; and (3) the vibrational vacancy entropy depends on the defect symmetry, that is, whether is equatorial or apical (Fig. 1b), which in some systems may oppose to vacancy ordering at medium and high temperatures.

We compute the quasi-harmonic Gibbs free energy associated to the formation of a neutrally-charged oxygen vacancy, $G_{\text{vac}}^{\text{qh}}$, as a function of epitaxial strain, $\eta = (a - a_0)/a_0$ (where $a_0$ represents the equilibrium in-plane lattice parameter) and temperature, $T$. This quantity can be expressed as $[14]$: $G_{\text{vac}}^{\text{qh}}(\eta, T) = E_{\text{vac}}(\eta) + F_{\text{vac}}^{\text{qh}}(\eta, T) + \mu_O(T)$, (1) where subscript “vac” indicates the quantity difference between the defective and perfect systems (in SCO, for instance, $A_{\text{vac}} \equiv A_{\text{SrCoO}_3} - A_{\text{SrCoO}_3}$), $E_{\text{vac}}$ accounts for the static contributions to the free energy ($T = 0$), $F_{\text{vac}}^{\text{qh}}$ the vibrational contributions to the free energy ($T \neq 0$), and $\mu_O$ is the chemical potential of the free oxygen atom. The vibrational energy of the defective and perfect systems are computed with the formula $[22]$:

$$F_{\text{vac}}^{\text{qh}}(\eta, T) = \frac{1}{N_q} k_B \sum_{q_s} \ln \left[ 2 \sinh \left( \frac{\hbar \omega_{qs}(\eta)}{2 k_B T} \right) \right] ,$$

(2)

where $N_q$ is the total number of wave vectors used for integration within the Brillouin zone (BZ), and the dependence of the phonon frequencies, $\omega_{qs}$, on epitaxial strain is explicitly noted.

We use the generalised gradient gradient approximation to DFT due to Perdew, Burke, and Ernzerhof $[23]$ as implemented in the VASP package $[24]$. A “Hubbard-U” $[25]$ scheme is employed for a better treatment of transition-metal $d$ electrons, and the ionic cores are represented with the “projector augmented” method $[26]$. Wave functions are represented in a plane-wave basis truncated at 600 eV. For the determination of equilibrium geometries we use a 20-atoms simulation cell that allows to reproduce the usual ferroelectric and antiferrodistortive distortions in perovskite oxides $[27]$ (Fig. 1b); defective configurations are generated by removing one oxygen atom either in an equatorial (Eq) or apical (Ap) position (case $\delta = 0.25$). For our phonon frequency calculations we employ the so-called “direct approach” as implemented in the PHON package $[28]$. Additional details of our $E_{\text{vac}}$ and $F_{\text{vac}}^{\text{qh}}$ calculations can be found in the Supplemental Material $[29]$ and Refs. $[30] [32]$.

FIG. 2: (Color online) Zero-temperature calculations done in perfect and nonstoichiometric ($\delta = 0.25$) SCO thin films. Total energy results expressed as a function of magnetic spin ordering, epitaxial strain, and oxygen content are shown in (a) and (b). The zero-temperature vacancy formation energy is enclosed in (c). Both equatorial (Eq) and apical (Ap) oxygen vacancy positions are considered and analogous results obtained in bulk are shown for comparison.

It is well known that estimation of $\mu_O$ with DFT+U methods contains large errors $[33] [34]$. Notwithstanding, as the oxygen chemical potential does not depend on epitaxial strain, we can safely base our following analysis on the results obtained for the thermodynamically shifted Gibbs free energy:

$$G_{\text{vac}}^{\text{qh}}(\eta, T) = G_{\text{vac}}^{\text{qh}}(\eta, T) - \mu_O(T) .$$

(3)
for deduced from \( G \) tetragonal affect considerably the vibrational vacancy entropy (i.e., our results show that although anharmonic corrections to the vibrational entropy results exponentially shift the calculated Gibbs vacancy free energy calculated at zero temperature. This is explicitly shown in Fig. 3, where at the highest temperature considered is easiest to create oxygen vacancies in compressively strained thin films (i.e., \( G^\text{inh} \) is minimum).

In Fig. 3, we enclose the chemical expansion results obtained in SCO thin films. It is observed that \( \Delta V \) is largest at compressive strains and that a small kink appears at the point in which the stoichiometric system undergoes a magnetic phase transition. As the vibrational properties of crystals largely depend on volume (i.e., the \( V \)-dependence of phonon frequencies, \( \omega_q \), normally can be described with the Grüneisen parameter \( \gamma_q = -\partial (\ln \omega_q) / \partial (\ln V) \)), we can reasonably correlate the observed \( F^\text{inh} \) strain dependence to the accompanying chemical expansion: the larger \( \Delta V \) is, the more preferable lattice contributions to \( V \) formation result. We comment again on this point below.

**La\(_{0.5}\)Sr\(_{0.5}\)Mn\(_{0.5}\)O\(_{2.5}\) thin films**—Our DFT calculations predict an orthorhombic Pbnm ground state for bulk stoichiometric LSMCO that is characterised by FM spin ordering and oxygen octahedral rotations \( (a''-a'-a') \), as expressed in Glazer’s notation \[57\] (i.e., antiphase within the substrate plane and in-phase in the tensile or compressive (negative) strains. With regard to \( E_{\text{vac}} \), we find that (at \( T = 0 \)) equatorial vacancies can be created more easily than apical vacancies [i.e., \( E_{\text{vac}} (\text{Ap}) - E_{\text{vac}} (\text{Eq}) \sim 10 \text{ meV/f.u.} \)] and that their formation energy decreases almost linearly with increasing strain (Fig. 2). For instance, at \( \eta = +2\% \) the (Eq) vacancy formation energy is reduced by 30 and 52 meV/f.u. as compared to the unstrained and \(-2\% \) cases, respectively. We note that these results are consistent with those reported by Tahini et al. in analogous systems \[17\], and by Aschauer et al. in CaMnO\(_3\) thin films \[13\].

In view of the outcomes shown in Fig. 2, one might guess that, provided that the thermal contributions to the \( V \) free energy were more or less independent of epitaxial strain, tensile strain should favor the formation of vacancies at \( T \neq 0 \) conditions. However, as we have noted before, this is not what has been experimentally observed by Hu et al. in SrCoO\(_3\)-\( \delta \) thin films \[14\].

FIG. 3: (Color online) Quasi-harmonic free energy calculations performed in perfect and nonstoichiometric (\( \delta = 0.25 \), equatorial vacancies) SCO thin films. Vibrational and thermodynamically shifted Gibbs vacancy free energy results expressed as a function of temperature and epitaxial strain are enclosed in (a) and (c), respectively. The accompanying chemical expansion, \( \Delta V = V_{\text{const}} - V_{\text{perf}} \), expressed as a function of epitaxial strain is shown in (b).

Namely, rather than trying to adopt experimental values for \( \mu_O \) and applying empirical corrections to the calculated \( G^\text{inh} \), we have arbitrarily set the oxygen gas chemical potential to zero. Meanwhile, we have estimated the size of anharmonic corrections to \( F^\text{inh} \) by using thermodynamic integration techniques from harmonic reference calculations \[29\] and Refs. \[35\] [36]; our results show that although anharmonic corrections affect considerably the vibrational vacancy entropy (i.e., by \( \sim 0.01 \) eV per formula unit), the main conclusions deduced from \( G^\text{inh} \) are robust.

**SrCoO\(_{3-\delta}\) thin films**—According to our DFT calculations, the ground state of stoichiometric SCO is a tetragonal \( P4/mmb \) phase with an equilibrium lattice parameter of \( a_0 = 3.89 \) Å and ferromagnetic (FM) spin ordering \[30\]. At \( \eta \sim +2\% \), the system undergoes a magnetic phase transition to an antiferromagnetic state displaying C-type spin ordering (i.e., spins in the plane parallel to the substrate align antiparallel, whereas spins in planes perpendicular to the substrate align parallel, Fig. 2). In the presence of oxygen vacancies, the magnetic properties of SCO change noticeably: the ground state becomes antiferromagnetic of G-type (i.e., spins align antiparallel both in the substrate plane and perpendicular to it, Fig. 2b) either at moderately

![Graph](image-url)
perpendicular direction). At a tensile epitaxial strain of $\sim +1\%$ the system undergoes a first-order transition to a monoclinic (and centrosymmetric) $P2_1/m$ phase, characterised also by FM spin ordering and $O_6$ rotations $(a^-a^-a^0)$ [i.e., octahedral tiltings along the direction perpendicular to the substrate disappear, Fig. 4b]. In the presence of oxygen vacancies the magnetic properties of LSMCO thin films remain invariant. With regard to $E_{\text{vac}}$, we also find that (at $T = 0$) equatorial vacancies are created more easily than apical vacancies [i.e., $E_{\text{vac}}(\text{Ap}) - E_{\text{vac}}(\text{Eq}) \sim 10$ meV/f.u.] although in this case the corresponding formation energy is quite insensitive to the strain conditions (Fig. 4b).

Fig. 4b shows our vibrational entropy results obtained for an equatorial vacancy, $F_{\text{vac}}^{\text{eq}}$, under compressive, neutral, and tensile strains expressed as a function of temperature. It is observed that lattice contributions to $V_O$ formation now are practically identical in the unstrained and $\eta = -2\%$ cases, and that $F_{\text{vac}}^{\text{eq}}$ is smallest for tensile strains. This behavior suggests that at finite temperatures equatorial vacancies in LSMCO thin films will be created more easily at $\eta > 0$ conditions, as it is explicitly shown in Fig. 5b, due essentially to lattice effects. In this case we also find that the chemical expansion of the crystal (Fig. 5b) and vibrational vacancy entropy are strongly correlated. In particular, the $\Delta V_{\text{vac}}$ values computed in the unstrained and $\eta = -2\%$ cases are almost identical and so are the corresponding $F_{\text{vac}}^{\text{eq}}$ curves. Meanwhile, the chemical expansion is larger at tensile strains, due to the underlying $Pbnm \rightarrow P2_1/m$ phase transition occurring at $\eta \sim +1\%$, and simultaneously the vibrational vacancy entropy becomes more favorable. Our ab initio results obtained in SCO and LSMCO thin films clearly evidence a direct link between quantities $\Delta V_{\text{vac}}$ and $F_{\text{vac}}^{\text{eq}}$.

Finally, it has been recently suggested, based on the results of zero-temperature $E_{\text{vac}}$ calculations, that epitaxial strain could be used as a means to engineer vacancy ordering in perovskite oxides [13]. In fact, this appears to be the logical conclusion coming up from Figs. 2 and 4b. However, as we have already shown, thermal excitations can play a critical role on $V_G$ formation at finite temperatures. In order to quantify the effects of lattice vibrations on possible vacancy ordering, we calculate the vibrational entropy of an apical (Ap) vacancy in SCO thin films at different strain states (Supplemental Material 24). Our $F_{\text{vac}}^{\text{ap}}$ results show that (i) the vibrational entropy of Ap vacancies follows the same strain dependence than Eq vacancies, and importantly (ii) lattice excitations strongly favor the creation of Ap vacancies over Eq: specifically, at medium and high temperatures we find that $F_{\text{vac}}^{\text{ap}}(\text{Ap}) - F_{\text{vac}}^{\text{ap}}(\text{Eq}) \sim -10$ meV/f.u., which in absolute value is of the same order of magnitude than the corresponding static difference $E_{\text{vac}}(\text{Ap}) - E_{\text{vac}}(\text{Eq})$. For instance, at $\eta = -2\%$ and $T = 600$ K the vibrational entropy of Ap vacancies is about 25 meV/f.u. smaller than that of Eq, and consequently $G_{\text{vac}}(\text{Ap}) \approx G_{\text{vac}}(\text{Eq})$. Therefore, lattice vibrations can hinder vacancy ordering

FIG. 4: (Color online) Zero-temperature calculations done in perfect and nonstoichiometric ($\delta = 0.25$) LSMCO thin films. Total energy results obtained in stoichiometric systems expressed as a function of epitaxial strain are shown in (a). The zero-temperature vacancy formation energy is enclosed in (b). Both equatorial (Eq) and apical (Ap) oxygen vacancy positions are considered and analogous results obtained in bulk are shown for comparison.

FIG. 5: (Color online) Quasi-harmonic free energy calculations performed in perfect and nonstoichiometric ($\delta = 0.25$, equatorial vacancies) LSMCO thin films. Vibrational and thermodynamically shifted Gibbs vacancy free energy results expressed as a function of temperature and epitaxial strain are enclosed in (a) and (c), respectively. The accompanying chemical expansion, $\Delta V_{\text{vac}} = V_{\text{monotol}} - V_{\text{perf}}$, expressed as a function of epitaxial strain is shown in (b).
(analogous results are found also in LSMCO thin films, Supplemental Material [29]). We note that this conclusion remains valid when configurational vacancy contributions to \( G_{\text{vac}}^{\text{th}} \) are taken into account, which always favor the formation of Eq vacancies over Ap, as those amount to only few meV/f.u. in the temperature interval of interest (Supplemental Material [29]). We note that this conclusion remains valid when configurational vacancy contributions to \( G_{\text{vac}}^{\text{th}} \) are taken into account, which always favor the formation of Eq vacancies over Ap, as those amount to only few meV/f.u. in the temperature interval of interest (Supplemental Material [29]). 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