Electronic Structures and Phonon Free Energies of LaCoO_3 using Hybrid Exchange Density Functional Theory

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Hybrid Exchange density functional theory has been used to model the electronic structure of LaCoO_3 . Based on a rhombohedral unit cell of R-3c symmetry containing two Co atoms we find a mixed spin phase, comprising alternating low and high spin Co^{+3} ions, with a total energy at 0 K just 57 meV per formula unit above that of a non-magnetic semiconducting ground state. In the mixed spin phase the high-spin Co^{+3} ion have spin moments of $3.1 \mu_B$ and the state is insulating with a band gap of 2.2 eV. Our calculations suggest that the effective on-site Coulomb repulsion energy, U_{eff} , on Co^{+3} ions are spin dependent. The U_{eff} on Co^{+3} ion is 7.1 eV and 8.5 eV for the non magnetic ground state and for the magnetic high spin state, respectively. For the mixed spin state, two different U_{eff} are estimated for two Co^{+3} ions in the unit cell having different spin states, 8.0 eV for high spin Co^{+3} ion and 7.0 eV for low spin Co^{+3} . An estimate of the harmonic phonon free energy suggests that this mixed spin phase would become the more stable phase as the temperature increases, which is consistent with experimental evidence. An alternative intermediate spin state is higher in energy at all temperatures.

I. INTRODUCTION

LaCoO_3 is a technologically important material in part because of its use as a cathode in a high temperature solid oxide fuel cells (SOFC)¹⁻⁴. It exhibits complex and temperature-dependent electronic and magnetic properties. Below about 100 K it has been reported as a nonmagnetic semiconductor, around 100-500 K as a paramagnetic semiconductor and above 500 K as a paramagnetic metal⁵⁻⁸. In this paper these three temperature ranges will be

referred to as low, intermediate and high. At the transition from the semiconducting to metallic states the electrical conductivity of the material increases by two orders of magnitude. Although, a large number of experimental and theoretical investigations have been reported^{9–38} on these temperature-dependent spin-state transitions and the semiconductor to metal transition, their origin and the related electronic structures are still unknown. The aim of this paper is to understand the nature of these phases in LaCoO_3 through combined calculations of its electronic structures and harmonic phonon free energies using hybrid exchange density functional theory. Due to the large volume of the published articles on this issue, we have referred only most relevant reports for the purpose of this paper. To get a wider view of the debate, readers are encouraged to read recent reports and references therein^{24–28,34–36}.

There are broadly two explanations in the literature for the nature of these spin state transitions as a function of temperature. In the first model^{7,8,11,13,14,24,25}, the low spin (LS) ($t_{2g}^6 e_g^0, S = 0$) ground state phase at low temperature proceeds to a higher temperature, high spin (HS) ($t_{2g}^4 e_g^2, S = 2$) phase via a mixed spin (MS) state, in which both high and low spin states coexist on different cobalt ions. We are using the notation of atomic states as a crude but convenient reflection of the situation, which in the calculations is complicated by ligand fields and structural effects. With increasing temperature it is thought that the Co ions gradually transform from LS to HS states and the nonmagnetic material becomes paramagnetic. These authors suggest that a transition from semiconducting to metallic states has occurs when most of the Co ions have switched to HS states. This model is supported by data from several experiments such as electron photo-emission spectroscopy¹³, nuclear magnetic resonance (NMR)¹¹, X-ray absorption spectroscopy (XAS), magnetic circular dichroism (MCD) at the Co- $L_{2,3}$ edge⁷ and inelastic neutron scattering (INS)⁸.

The second model is based on the presence of an intermediate spin state ($t_{2g}^5 e_g^1, S = 1$), which we denote IS, between the LS ground state and HS state. In one version of this model^{15,30,36} it is proposed that with increasing temperature the spin state of the LS Co ions gradually changes over the intermediate temperature range before transforming to a HS phase at higher temperature. Data from neutron diffraction experiments⁶, inelastic neutron scattering³¹, Raman spectroscopy, heat capacity measurements^{16,17}, electron energy loss spectroscopy (EELS) near-edge fine-structure of the O K edge³⁰, thermal expansions and SQUID magnetometer measurements³⁸ have been used to support the proposal that

an IS state is present. Data from high resolution neutron powder diffraction, on the other hand, support the existence of an alternative MS state in which some of the Co ions are in an IS state and some in a HS state⁵. The presence of the LS phase at low temperature and the HS phase at high temperature are well established, the presence of an IS state at intermediate temperature is controversial.

To understand the spin state transitions of this material, electronic structure calculations have been performed since the 1960s^{9,10,13–15,18–28,30,34–36,49}. Typically broken symmetry density functional theory calculations have been used in which different spin states can be generated by varying the initial conditions of the self-consistent field (SCF) procedure. Such stationary points in the SCF provide information about the ground state and one or more metastable states³⁴. All such calculations support the conclusion that the ground state at 0 K is LS, although the local spin density approximations (LSDA) gives a metallic LS ground state rather than the experimentally observed semiconducting state^{20,22,49}. This is typical for LSDA calculations in systems with strong electron-electron interactions and taking such interactions into account qualitatively, as in the LSDA+U, generalised gradient approximations (GGA +U) and Green function with screened Coulomb interaction approximation (U+GW) approaches, enables a description of a semiconducting state^{15,18,22,25,26,34,36,49}.

LSDA+U and GGA+U calculations^{15,18,36} also predict that an IS state ($S=1$) is metastable above the ground state, however, it is found that relative energetic stability between spin states depends on the choice of U ^{36,49}. The IS state appears at 240 meV/formula unit above LS state¹⁵ for spin independent fixed U value, however, with spin dependent U , IS state appears just 82 meV/formula unit above the LS state³⁶. Although these calculations suggest an IS state as the state observed in the intermediate temperature range, they do not reproduce its observed semiconducting nature but instead yield a metallic IS state^{15,25,36,39}. No such metastable state is found in LSDA calculations.

A HS state ($S=2$), which they calculated to be 650 meV and 450 meV higher in total energy than the LS state with spin-independent¹⁵ and spin-dependent U , respectively, has been suggested as the stable phase at high temperature, however, no thermodynamic calculation has been done to support this. Furthermore, the HS state, which is found experimentally as a metallic state appears as a semiconductor in the LSDA+U calculations.^{15,36}

Other methods, such as an empirical configuration interaction (CI) cluster model have been used to model the spectral line shape found in XAS and MCD experiments. They

suggest that at intermediate and high temperature LaCoO_3 is in an inhomogeneous MS state with simultaneous presence of Co ions of LS and HS states⁷, however, this calculation is not parameter free. In this calculation the energy difference between doubly degenerate e_g and triply degenerate t_{2g} orbitals (10Dq) for different spin configurations has been treated as a fitting parameter and it was predicted that the IS state is energetically higher state than the MS state for all possible values of 10Dq. A coherent potential approximations (CPA) method based on unrestricted Hartree-Fock has also been used to suggest that the mixing of LS and HS states is energetically more favourable than the mixing of IS and HS states²³.

To fully understand the nature of the intermediate temperature states it would be necessary to have both high quality electronic structure and thermodynamic calculations. In this paper we report the electronic structure of LaCoO_3 using hybrid exchange density functional methods (HE-DFT) as implemented in the CRYSTAL code⁴¹. The Hubbard U parameters have been estimated from calculated electronic structures using rectangular band model, finding some significant differences to previous calculations. We follow this by making estimates of the free energy versus temperature of the aforementioned phases. The qualitative features of the observed temperature dependence are reproduced by the theory, but there are still significant discrepancies in the electronic structure between theory and experiment, to which we suggest point defects make a significant contribution.

II. METHODOLOGY

We made our electronic structure and total energy calculations with the B3LYP exchange-correlation functional implemented in CRYSTAL⁴¹. This functional has been shown to provide a reliable description of geometries, phonon frequencies and electronic structures for a wide range of similar materials^{40,42–44,46}, although few exceptions for extended systems have also been reported⁴⁵. Fully optimised atom centered Gaussian type basis sets have been used. The basis sets have been optimised for the LS configuration and the same basis set has been used for all the calculations reported here.

The R-3c type (space group 167) rhombohedral structure as shown in Fig. 1 has been assumed for LaCoO_3 as indicated by neutron diffraction experiments. This unit cell consists of 10 atoms. Spin polarised calculations have been performed with 90 k-points in the

FIG. 1: (Color-online) Conventional cell structure of LaCoO₃ in R-3c symmetry.

irreducible part of the Brillouin zone. The tolerance for total energy convergence is 10^{-7} Hartree per unit cell. Full geometry optimisations have been done for all configurations. The structure was considered to be converged when the residual absolute forces along all allowed symmetry directions of the unit cell were below 2.0×10^{-4} Hartree/Bohr. The full geometry relaxations, have been done for all different spin configurations.

In order to achieve metastable states corresponding to different spin states, the spin configuration was initially constrained, namely for LS (total spin $0\mu_B$), IS and MS (total spin $2\mu_B$ per Co ion) and HS (total spin $4\mu_B$ per Co ion). Although IS and MS state both have total spin $2\mu_B$ per Co ion, the IS state is distinguished by the additional constraint that its Co ions are equivalent. These constraints on the spin configurations were removed after the first few iterations towards self-consistency, when the metastability of the desired spin state was assured and all reported data are thus from unconstrained calculations.

The HS configurations can be either ferromagnetic (HS-FM), in which all Co ions have parallel spins, and antiferromagnetic (HS-AFM), in which adjacent Co ions have antiparallel

spins. A technical limitation of our code is that we cannot constrain calculations to produce antiferromagnetic IS or MS states.

The energy-volume curves have been obtained by relaxing the internal coordinates of LaCoO_3 at each constant volume for each of the five spin configurations described above. To understand the stability of these different types of spin states as a function of temperature, it would be desirable to calculate all the contributions of harmonic and anharmonic lattice vibrations, electronic excitations, spin waves and intrinsic defects to the Gibb's Free energies, which is still a formidable task even with the availability of high-performance computing. At present we have simply calculated the main contribution, which we believe is due to volume-dependent harmonic phonons, and furthermore we have sampled only at the gamma point in the supercell, giving 24 modes of vibration. For each of our five magnetic states, the phonon frequencies have been calculated as a function of volume, and the volumes consistent with the minimum quasiharmonic free energies have been obtained as a function of temperature. In these calculations, for each volume local coordinates have been optimised while keeping volume constant and harmonic phonon calculations have been done by diagonalizing dynamical matrices using finite displacements and analytical gradient modules as implemented in the CRYSTAL code.

The linear thermal expansion for our five spin configurations has been calculated using the formula $1/3(V_i(T) - V_{LS}(0))/V_{LS}(0)$, where $V_i(T)$ is the volume of the i th spin configuration ($i = \text{LS}, \text{MS}, \text{IS}, \text{HS-AFM}, \text{HS-FM}$) at temperature T K and $V_{LS}(0)$ is the volume of the LS state at the temperature 0K.

III. RESULTS AND DISCUSSIONS

A. Ground state total energies and phonons

The calculated energy volume curves of all the spin states considered at 0 K are shown in Fig. 2. It is found that the LS state is the ground state of the material as found in experiments and other calculations^{15,18–28,30,34–36,49}. The next lowest in energy is the metastable MS state which is 57meV/formula unit higher in energy than the LS state at their respective equilibrium volumes. The HS-AFM state is 148meV/formula unit higher in energy than the LS state. The IS state and the HS-FM states are 225meV/formula unit and 458meV/formula

FIG. 2: (Color-online) Energy-Volume curves for different spin states of LaCoO_3 .

unit higher in energy, respectively.

In Table I the local structure and the phonon frequencies of the LS state are compared with published experimental results. We see that the calculated bond lengths exceed the neutron diffraction results at 5 K by less than 2%, and the bond angles are within 0.8° .

The calculated phonon frequencies differ by 12%, on average, from the experimental values, which is comparable with PBE0 based (11%)⁴⁰ but significantly better than LDA+U based (34%) calculations³⁶. The maximum difference of 31% in the phonon frequencies occurs for the Raman active A_{1g} mode, however, as the oscillator strength of this mode is found to be very small¹⁶ the experimental error in determining its correct position may be larger.

The HS-FM state is much higher in energy than the HS-AFM state at all volumes (Fig 2). The energy of the IS state with respect to the LS state is comparable to that found previously in LSDA+U calculations¹⁵. The MS state, which in our calculations has a lower energy than this IS state, has apparently not been investigated in previous theoretical work. This is not to say it is not obtainable with LSDA+U or some other functional, but finding it may depend on the choice of U. This will be discussed later in this section.

TABLE I: Structural parameters and phonon frequencies of LS state at 0K. The percentage errors of current calculations with respect to experiments have been given in parentheses.

Structural parameters			Raman active modes			IR active modes		
Parameters	Calculated	Exp ^a	Modes	Calculated	Exp ^b	Modes	Calculated	Exp ^c
				cm ⁻¹	cm ⁻¹		cm ⁻¹	cm ⁻¹
a = b (Å)	5.5131 (1.6)	5.4262	E _g	106 (25)	85	A _{2u}	169 (4)	177
c (Å)	13.1640 (1.3)	12.9910	E _g	188 (10)	171	E _u	194 (20)	242
c/a	2.3878 (0.3)	2.3941	A _{1g}	343 (31)	262	E _u	237 (22)	306
La-O (Å)	2.4559 (1.2)	2.4275	E _g	480 (11)	433	A _{2u}	287 (8)	314
La-O (Å)	3.0627 (2.1)	2.9988	E _g	571 (2)	585	E _u	341 (6)	322
La-O (Å)	2.7261 (1.4)	2.6876				E _u	448 (9)	411
Co-O (Å)	1.9571 (1.6)	1.9254				A _{2u}	475 (9)	524
∠O-Co-O	91.71 (0.2)	91.48				E _u	525 (3)	540
∠Co-O-Co	162.16 (0.5)	162.93						

^a Ref.⁵ ; ^b Ref.¹⁶; ^c Ref.⁴⁷ .

The phonon frequencies for all other spin-states are given in Table II. It is found that for all spin states IR active rotational modes with A_u symmetry are softer than that found in LS state. In the low frequency range, Raman active A_g mode is a signature of either MS state or HS-AFM state.

Experimentally, the nature of the HS state of the material is not known with certainty. It is generally assumed that the state is either HS-FM or MS, however, the stability of an HS-AFM state at high temperature has also been suggested on the basis of NMR experiments¹¹. The MS state found here has one Co ion in a LS state and the other is in a HS state. Since the unit cell used here comprises only two Co ions, this is the only kind of MS state that the calculation can access. In this state we find a 2% longer Co-O bond associated with the HS Co ion. The presence of a 50% spin mixing with alternating long and short Co-O bonds

TABLE II: Phonon frequencies of MS, IS, HS-FM and HS-AFM states at Γ point.

	MS		IS		HS-FM		HS-AFM	
Phonon Modes	Modes Calculated cm^{-1}		Modes Calculated cm^{-1}		Modes Calculated cm^{-1}		Modes Calculated cm^{-1}	
Raman Active	A_g	119	E_g	105	E_g	108	A_g	102
	E_g	128	E_g	170	E_g	174	E_g	112
	E_g	179	A_{1g}	333	A_{1g}	303	E_g	172
	A_g	285	E_g	391	E_g	418	A_g	306
	A_g	358			E_g	440	A_g	338
	E_g	422					E_g	416
	E_g	541					E_g	440
	A_g	682					A_g	651
IR Active	A_u	119	A_{2u}	124	A_{2u}	102	A_u	109
	E_u	139	E_u	158	E_u	158	E_u	156
	A_u	283	E_u	261	A_{2u}	220	A_u	271
	E_u	291	E_u	318	E_u	257	E_u	271
	E_u	324	A_{2u}	327	E_u	296	E_u	305
	A_u	380	E_u	384	E_u	340	A_u	317
	A_u	399	A_{2u}	549	A_{2u}	478	E_u	340
	E_u	412	E_u	578	E_u	548	A_u	392
	A_u	542					A_u	506
	E_u	572					E_u	559

has been suggested previously on the basis of X-ray diffraction (XRD) measurements^{7,14}.

The calculated energy of the IS state is higher than MS and HS-AFM states, suggesting that this state is unlikely to appear in experiments. In the current work no metastable state was found in calculations initiated by mixing IS and LS state Co ions; such states have been suggested previously⁵.

FIG. 3: (Color-online) The total, atom and orbital projected densities of states for low spin (LS) configuration. The star (*) denotes multiplication, i.e., the densities of states of six O^{-2} ions present in the unit cell have been denoted as $O*6$.

B. Electronic structures

In this section we discuss the calculated electronic structures of the five states we have studied, starting with the ground state LS. The calculated density of states (DOS) plot for the LS state is shown in Fig. 3. The total DOS for PBE based GGA calculations has also been shown for comparison. Local symmetry labels, e_g and t_{2g} , of the CoO_6 octahedra have been adopted as a convenience and to better reflect the effects of crystal field splitting in the various states, although, these are not representative of the full space group of the rhombohedral symmetry. This adoption is similar to other calculations^{15,22,49}.

The calculated spectral line shapes using GGA and B3LYP are similar and compared well with other reported calculations^{18,49} and experiments^{13,21}. The LS state calculated using GGA is metallic as found by other calculation^{15,18}. With B3LYP functional the state is an insulator, with a band gap of the charge transfer type, that is the top of the valence band (V) is of O-2p character with considerable hybridisation with Co-3d and the bottom of the conduction band (C) is mainly composed of the 3d orbitals of Co ions. This is consistent

with LSDA+U calculations¹⁵. The band gap is equal to 2.2eV, which is higher than the experimentally obtained band gap of 0.6eV, but such a high band gap also has been found earlier calculations^{15,33,40}. This high band gap is probably an artifact of the hybrid exchange functional used in our calculations, and may depend on the choice of U in other calculations^{15,33}.

An analysis of the Mulliken charges on ions for the LS state shows that the average charges on La, Co and O are +2, +1.9 and -1.3 respectively, which are lower than the formal ionic charges +3, +3 and -2. Similar results have been found earlier with other functionals, including LSDA, LSDA +U and GGA + U, which are due to the partially covalent nature of Co-O bonds and hybridisation of Co-3d and O-2p. Approximately 7 electrons in Co-d orbitals, rather than the 6 of the ionic model, is also a consequence of the strong hybridisation of the empty e_g orbitals with O-2p and is generally known as the d^7L configuration¹⁵.

The ionic theory predicts that in perfect octahedral symmetry the 6 electrons in the 3d orbitals of Co^{+3} ions should be paired up in t_{2g} orbitals leaving the orbitals of e_g symmetry empty. However, bonding - antibonding splitting in the energies of orbitals of both t_{2g} and e_g type are expected due to the covalency and hybridization of Co-3d and O-2p orbitals. The magnitude of splitting depends also on the departure from perfect cubic symmetry. We can see this clearly in the density of states of Fig. 3. The figure shows that both t_{2g} and e_g orbitals are split, and e_g orbitals are partially filled. The e_g orbitals, which are directed towards O-2 ions, make a σ^* antibonding, whereas t_{2g} orbitals, which are directed in between Co-O bonds, make π bonds²².

We find that the Co-3d orbitals of t_{2g} symmetry marked as 'B' in the figure contain 5 electrons per ion, while those marked as 'A' contain 0.8 electrons. The energy splitting AB may be referred to as $\Delta\pi$. Similarly the split energies of the e_g orbitals ($\Delta\sigma$) are shown in the figure as D and E. The figure shows that the magnitude of $\Delta\pi$ and $\Delta\sigma$ are almost same. Furthermore, from Fig 3 it is found also that the the energy difference between e_g and t_{2g} is small, which indicates small crystal field splitting as expected earlier from experiments¹⁴.

Of the two main peaks obtained in the LS state DOS, the one 1eV below the Fermi level is consistent with photoelectron spectroscopic observations at low temperatures^{13,21}. This peak is due to the Co-3d- t_{2g} -O-2p hybridization. The peak at 4eV below the Fermi level is due to the hybridization of O-2p with Co-3d- t_{2g} and e_g symmetry and is comparable with

the 3.5eV peak found in those experiments. The partially covalent nature of the charge distribution found in our calculations in the LS state has been suggested earlier also on the basis of photoemission experiments¹³.

The main contribution to the DOS due to the La-O covalent bond is deep in the valence band. A small overlap of La^{+3} and O^{-2} states at all energies is present up to the top of the valence band although their spectral weight is negligible in comparison with the Co-O overlap.

The DOS of the MS state is shown in Fig 4. The positive and negative values of the DOS here and for the other DOS of magnetic systems are used to indicate spin-up and spin-down electrons. There are two inequivalent Co^{+3} ions in the mixed spin state. Co1 is in a HS state and Co2 is in a LS state. The magnetic moment on a HS Co^{+3} ion is $3.1\mu_B$. The MS state is still an insulator with a band gap of 2.2eV with the top of the valence band originated from O-2p hybridized with LS-Co2-3d. In contrast to the LS state the bottom of the conduction band originates from unoccupied HS-Co1-3d- t_{2g} states. This is the magnetic semiconductor state as expected at the intermediate temperatures and shows the strongly correlated nature of the Co^{+3} ion in the LaCoO_3 .

From Fig. 4(b) it is seen that the occupied HS-Co1-3d orbitals have been pushed to about 7.0eV below the Fermi energy and the overlap with O-2p (Fig. 4(f)) is negligibly small. This indicates that the Co1 ion in HS is less covalent, which is consistent with the earlier experimental findings¹³. The valence band width of the MS state is larger than that of the LS state. This can explain the transition of Co^{+3} ions from 'localised' to 'collective' as speculated earlier by precision X-ray experiments¹⁴.

From this figure we can predict that the peak found around 6.5eV below the Fermi energy in photoelectron spectroscopy^{13,20} is due to the HS Co^{+3} ions. The O-2p related peak as speculated by experiments²¹ is found just below 4eV from the Fermi level and is due to the hybridization of O-2p and Co-3d- e_g orbitals. From the electronic structure given above we predict also that the peak 1eV below the Fermi energy is entirely from LS Co-3d, however, we see in Fig. 3 and Fig 4 that the peak 3eV below the Fermi energy can be assigned to both LS and HS Co^{+3} ions. The experimental position of the peak does not exactly match with our calculations, probably because all the electronic structures have been evaluated at the respective calculated equilibrium volumes of the different spin states and not at the

FIG. 4: (Color-online) The total, atom and orbital projected densities of states for MS state. The orbital projection of Co1 (HS state) and Co2 (LS state) ions have been shown in different panels.

volumes corresponding to finite temperatures.

Since MS state is a spin ordered state two different Co-O bond lengths are found in this state, the Co1-O (HS) bond lengths are 3% longer than the Co2-O (LS) bond lengths. And

FIG. 5: (Color-Online) The total, atom and orbital projected densities of states for IS state.

bond orders obtained from the Mulliken population analysis are 15% smaller for Co2-O than for Co1-O. This finding of alternate short and long bonds is consistent with the speculation made earlier from X-ray diffraction experiments⁴⁸.

The DOS of the IS state is shown in Fig. 5. The shape of this DOS is similar to that found by LSDA+U calculations¹⁵. The transfer of electrons from Co-3d- t_{2g} orbitals to e_g orbitals broadens the latter orbital enough to fill the bad gap and create a half-metallic state. A Mott-Hubbard type gap opens for down-spin electrons, for which the highest occupied and lowest unoccupied states both originate from t_{2g} orbitals. The overlap with O-2p orbitals has also changed. The spin-up O-2p orbitals overlap with Co-3d- t_{2g} orbitals, while beta-spin orbitals overlap with e_g orbitals. The Mulliken population analysis shows that the overlap population of the Co-O bond in the IS state is reduced by 29% from that in the LS state, although the increase in bond length is less than 2%. The magnetic moment on each Co ion is $2.0\mu_B$.

From the figure we find that the characteristic peaks of this state are situated at 2.0eV, 2.5eV, 5.5eV and 6eV below the Fermi energy. The 2.5eV peak is the Co-3d- t_{2g} -O-2p hybridisation peak and the 5.5eV peak is due to the Co-3d- e_g -O-2p hybridisation. The

FIG. 6: (Color-online) The total, atom and orbital projected densities of states for (a) HS-AFM state and (b) HS-FM state.

2.0eV and the 6eV peaks correspond to Co- t_{2g} and e_g , respectively.

The DOS for HS-AFM and HS-FM states are shown in Fig. 6. These states are competing states at very high temperatures as we find in our calculations. In both of these states the two Co ions in the cell are related by symmetry, so the DOS are plotted for only one of them. We see in both cases that the DOS of the Co is similar to that of the HS-Co1 ion in a

MS state as shown in Fig 4(b) and (c). The magnetic moments on Co ions are $3.1\mu_B$. The narrow DOS for the non-bonding and antibonding Co-3d are also apparent. The spin state of the oxygen ion is clearly very sensitive to the relative spin states of its two Co neighbours. The band gaps are of charge transfer type, in which the top of the valence band originates from O-2p and the bottom of the conduction band from t_{2g} orbitals.

Compared to the HS-AFM state, the HS-FM state in Fig. 6 (b) shows that the effect of parallel spins on the Co ions has been to broaden the non-bonding and antibonding 3d orbitals, as there will be greater overlap of the constituent spin-orbitals. Since the broadening of both occupied and unoccupied states involving t_{2g} orbitals is greater than that in the MS or HS-AFM states, the band gap is reduced to 500meV. This reduction in the band gap may be significant because the experimental high-spin state of the material is known to be metallic^{5,7,14}. A small gap for the FM state was also found in earlier LSDA+U calculations¹⁵. The band gap appearing in our calculation is probably an artifact of the hybrid exchange correlation functional, which is known to over-localise electrons. However, the metallic state of the real material might also be attributed to the presence of oxygen vacancies at high temperature or conduction through grain boundaries¹⁴.

A significant finding from Fig. 6(b) is the presence of peaks 3eV and 5eV below the Fermi level in the HS-FM state. The 3eV peak is the O-2p-Co- t_{2g} hybridization peak and the 5eV peak corresponds to the hybridization between O-2p and Co-3d- e_g . This finding is consistent with experiments^{13,21} and we can confirm the presence of HS Co ions at high temperatures.

The effective on-site Coulomb repulsion energy U and the charge transfer energy Δ are estimated from Fig.s. 3 - 6. For each spin state the U is estimated from the energy separation of the occupied and unoccupied Co-3d bands, and the Δ is estimated from the energy separation of the occupied O-2p and unoccupied Co-3d bands. Assuming a rectangular band model these energy separations are calculated from the energy differences of center of gravities of respective bands. From Fig.s. 3 - 6 it is found that Δ remains roughly constant at 7.0eV across all spin states, however, U depends on the spin state of the Co ion. For the LS state (Fig. 3) $U=7.1$ eV but for the HS-FM state (Fig. 6(b)) $U=8.5$ eV. The $U=7.2$ eV for the IS state (Fig. 7). These U values are consistent with the empirical values of U , ranging from 5.5eV to 8.6eV, assumed in LSDA+U and GGA+U calculations^{15,18,25}.

The significant finding from the MS state (Fig. 4) is the estimation of two different U

values, 8.0eV for the HS Co1(Fig. 4(b) and (c)) and 7.0eV for the LS Co2 (Fig. 4(d) and (f)) ions. In separate calculations (not reported here) we have found that effective U values depend not only on spin states but also on unit cell volumes.

The dependence of U on spin states and unit cell volumes has been found earlier for FeO using LSDA+ U method⁵⁰. In a separate report two different effective U values for a single species of transition metal ion at two different sites in a unit cell of (Mg,Fe)₂SiO₄ are predicted⁵¹. In these calculations two different spin states of the single ionic species in a unit cell have been treated as two different ions with different values of U.

For LaCoO₃ the decrease in U with the increase in unit cell volume has been reported recently⁴⁹. Using an iterative procedure authors have calculated structurally consistent U values increasing from 8.2eV to 8.6eV for decreasing unit cell volume by about 200 (atomic unit)³. These calculations have been done for LS state only.

The finding about the spin dependent U for Co ions in LaCoO₃ explains why earlier LSDA +U calculations¹⁵, using a single value of U, didn't find the spin ordered MS state as a stable state.

C. Quasiharmonic free energies

The relative quasi-harmonic free energies of the four states of higher 0 K energy with respect to the LS state are plotted in Fig.7. From the figure we see that up to about 800 K the LS state is the stable state. Above that temperature the HS-AFM state is increasingly stable, but the free energy of the HS-FM state decreases most rapidly with temperature and it eventually becomes the most stable for $T > 1500$ K. The free energy of the MS state relative to the LS ground state also decreases with temperature, but although only separated by only 15 meV/fu at 850 K, it never quite competes with the HS-AFM and HS-FM states. The IS state is not the most stable at any temperature.

The rapid decrease of the Free energy of HS states (HS-AFM and HS-FM) with temperature can be attributed to the decreasing frequencies of low frequency modes, both the Raman active rotational mode of E_g symmetry and IR active rotational mode of A_U symmetry, with increasing temperature. A decreasing frequency of this Raman active E_g mode with increasing temperature has been found experimentally¹⁶. We have found a similar de-

FIG. 7: (Color-online) Thermal stability of different spin states of LaCoO_3 obtained with respect to the temperature depended Free energy for LS state.

crease of frequency for the IR active mode rotational mode which has not yet been confirmed experimentally.

To understand further the effect of temperature on structural parameters of different spin states the linear thermal lattice expansions with respect to the volume of the LS state at 0 K are compared with reported results obtained from neutron diffraction experiments⁵ and shown in Fig. 8. An error bar is attached for each spin configuration to indicate the uncertainty in measuring the theoretical lattice expansion at that spin configuration from the calculated data. An average error of 0.5% occurred for all spin states above 0 K. 4. This average errors were calculated by estimating possible errors in the calculation of equilibrium volumes at each temperature and corresponding lattice constants. However, since only zone centre frequencies are considered the actual error can be larger than this. The result indicates that only the MS state can be the stable state in the intermediate to high temperature range, but thermal expansion for other spin states is much higher than experimental observations.

These findings are in agreement with the reported results^{7,9,10,24,34}, where it was shown

FIG. 8: (Color-online) Linear thermal expansion of different spin states of LaCoO_3 obtained with respect to the volume for LS state at 0 K.

that the IS state was far from stable for any values of the crystal field splitting, in line with other theoretical findings^{9,10,24,34}. The stability of the IS state has been found in LSDA+U calculations¹⁵, where experimental lattice constants have been used to simulate temperature dependences of different spin states. This approach cannot give the true nature of the thermodynamic stability because, as we see from the current calculations, for the temperature change 0K to 800K the increase in lattice constant can contribute only 15 meV/formula unit energy change. The main contributions to the relative stability of different spin states with temperature come from the phonon free energies. Furthermore experimental lattice constants are smaller than theoretical values, which introduces additional errors in the comparison of lattice constant dependencies of total energies in different spin states.

Although we have attempted to estimate the relative free energies of different spin states these results are rather far from reproducing the experimental phase boundaries. On the other hand they do suggest the correct trend in ordering of the structures with temperature. Given the approximations made, it seems reasonable to suggest that the phonon free energies are the main drivers of the spin state transitions at high temperatures.

It would be possible in principle to obtain a more accurate estimate of the phonon contri-

bution to the free energy by a denser sampling in k-space. Other terms not considered here include the configurational entropy term in the magnetic states, including a more complex MS state, with a variable proportion (perhaps 10-50% or more) of mixing ^{7,37}. The presence of oxygen vacancies will also be important contribution to the lowering of the free energy above 600K ⁵.

IV. CONCLUSIONS

In this paper the electronic structures and free energies of five postulated magnetic phases of LaCoO_3 have been calculated using hybrid exchange density functional theory with the B3LYP functional. Besides confirming the stability of the non-magnetic insulating phase, designated here LS, we find a metastable rhombohedral insulating phase we designate as mixed spin (MS), in which the Co ions alternately exhibit high-spin and low-spin states. The total energy of this state at 0 K is predicted to lie at 57 meV per formula unit above the LS state. Metastable high-spin antiferromagnetic (HS-AFM) and ferromagnetic (HS-FM) states are predicted to have 0 K energies 148 meV per formula unit and 225 meV per formula unit respectively above the LS state. We include in the study a metastable state of intermediate spin (IS), in which all Co ions have the same magnetic moment between 0 and the HS-FM value. This state has been previously proposed as an interpretation of the experimentally observed phase in the range 100 – 500 K; however, we find its energy to be 168 meV per formula unit above that of the MS state, which makes the latter a much more likely candidate. Our calculations show that effective on-site Coulomb energy (U_{eff}) is spin dependent. The U_{eff} on Co^{+3} ions is 7.1 eV and 8.5 eV for magnetic low spin and high spin, respectively. For mixed spin state two different U_{eff} have been found for two Co ions in different spin states. Furthermore we have made estimates of the temperature dependence of the free energy of these phases, based on the harmonic free energy of the zone centre phonons, and find that the magnetic phases decrease in free energy with temperature faster than the MS phase, which in turn decreases in free energy faster than the LS phase. The IS phase remains uncompetitive at all temperatures. This trend is qualitatively in agreement with the experimental evidence. The roles of spin waves, electronic excitations, lattice disorder and intrinsic defects on the free energy of these phases remain to be studied.

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