Itinerant metamagnetism and possible spin transition in LaCoO$_3$
by temperature/hole doping

P. Ravindran$^1$, H. Fjellvåg$^1$, A. Kjekshus$^1$, P. Blaha$^2$, K. Schwarz$^2$, and J. Luitz$^2$

$^1$Department of Chemistry, University of Oslo, Box 1033, Blindern, N-0315, Oslo, Norway
$^2$Institut für Physikalische und Theoretische Chemie, Technische Universität Wien, A-1060 Vienna, Getreidemarkt 9/156, Austria
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Abstract

The electronic structure of the perovskite La$_{1-x}$Sr$_x$CoO$_3$ has been obtained as a function of Sr substitution and volume from a series of generalized-gradient-corrected, full-potential, spin-density-functional band structure calculations. The energetics of different spin configurations are estimated using the fixed-spin-moment (FSM) method. From the total energy vs spin magnetic moment curve for LaCoO$_3$ the ground state is found to be nonmagnetic with the Co ions in a low-spin (LS) state, a result that is consistent with the experimental observations. Somewhat higher in energy, we find an intermediate-spin (IS) state with spin moment $\sim 1.2 \mu_B$/f.u. From the anomalous temperature dependent susceptibility along with the observation of an IS state we predict metamagnetism in LaCoO$_3$ originating from an LS-to-IS transition. The IS state is found to be metallic and the high-spin (HS) state of LaCoO$_3$ is predicted to be a half-metallic ferromagnet. With increasing temperature, which is simulated by a corresponding change of the lattice parameters we have observed the disappearance of the metamagnetic solution that is associated with the IS state. The FSM calculations on La$_{1-x}$Sr$_x$CoO$_3$ suggest that the hole doping stabilizes the IS state and the calculated magnetic moments are in good agreement with the corresponding experimental values. Our calculations show that the HS state cannot be stabilized by temperature or hole doping since the HS state is significantly higher in energy than the LS or IS state. Hence the spin-state transition in LaCoO$_3$ by temperature/hole doping is from an LS to an IS spin state and the present work rules out the other possibilities reported in the literature.
I. INTRODUCTION

The coupling of the charge to the spin and lattice degrees of freedom yields interesting phenomena such as the colossal magnetoresistance and high-temperature superconductivity, where the underlying mechanism is still under investigation. In the La$_{1-x}$Sr$_x$CoO$_3$ perovskite phase, cobalt spin configurations change with temperature and Sr concentration giving a rich variety of magnetic and transport properties that has attracted considerable attention over the last four decades. The simultaneous presence of strong electron–electron interaction within the transition-metal cobalt 3d manifold and a sizable hopping-interaction strength between the 3d and oxygen 2p states are primarily responsible for the wide range of properties exhibited by these compounds. LaCoO$_3$ is unique in that it is a diamagnetic semiconductor with a spin gap of 30 meV, a charge gap of 0.1 eV and a rhombohedrally distorted perovskite structure at low temperature. It undergoes a spin-state transition from a diamagnetic state to a paramagnetic state with a finite moment at 100 K and from semiconductor to metal above $\sim 500$ K. To account for the experimentally observed spin-state transition, both phenomenological explanations and *ab initio* based theories were proposed.

The magnetic properties of the cobaltites depend on the spin state of Co$^{3+}$ and Co$^{4+}$, i.e. whether they are in the low-, intermediate- or high-spin state. LaCoO$_3$ itself is a nonmagnetic insulator at low temperature, usually referred to as a low-spin state (LS, $S = 0$) because the atomic configuration ($t^6_e e^0_g$) of Co$^{3+}$ ions has no magnetic moment. Magnetic susceptibility slowly increases with temperature and reaches a maximum at $T \approx 90$ K. Above this temperature, the system shows a Curie–Weiss–law behavior, which is followed by a structural transition at 500 K. The origin of the low-temperature increase in the susceptibility is unclear at present. It is suggested that this could be due to frozen-in ferromagnetic domains which are trapped at low temperatures. Although the spin state of the Co ions and the nature of the transitions have been investigated for over 40 years these issues remain controversial. While it is generally agreed that the low-temperature phase is a nonmagnetic LS state both a high-spin state (HS, $S = 2$, $t^4_{2g} e^2_g$) and an intermediate-spin state (IS, $S = 1$, $t^5_{2g} e^1_g$) have been proposed for LaCoO$_3$ at high temperature. Most previous studies have treated the spin-state transition at 90 K as a transition from the LS state to a thermally excited HS state, which is reported to be only 10–80 meV higher in energy than the low-spin state.

The attempts to explain the spin-state transition in LaCoO$_3$ based on different experimental techniques is rather controversial. Direct magnetic measurements allow one to unambiguously identify the LS state in the temperature range below 50 K. The behavior of the magnetic susceptibility at low temperature, in the region around 100 K has been understood in terms of thermal activation of a magnetic HS state from the LS ground state. An anomalous thermal expansion associated with the spin-state transition has also been observed below 100 K. Raccah and Goodenough have emphasized that more complex supercell structures play an important role in the spin-state transition and reported the co-existence of LS and HS states of cobalt in LaCoO$_3$ and a first-order phase change at 1210 K. Rodriguez and Goodenough have suggested from magnetic and transport measurements that LaCoO$_3$ is in an LS state below 35 K, an LS-HS disordered state between 35 and 110 K, an LS-HS ordered state between 110 and 350 K and an IS-HS ordered state
above 650 K. However, a careful powder neutron diffraction study\[2\] found no evidence for any static ordering of distinct Co sites. Abbate et al. have interpreted the transition in the range 400–650 K as due to an LS-to-HS transition, based on x-ray absorption and x-ray photoelectron spectroscopy measurements.\[1\] Saitoh et al.\[2\] have argued that the 100 K transition is most likely due to an LS-to-IS transition (from analysis of photoemission spectra and magnetic susceptibility data), and also suggested that the 500 K transition is due to the population of the HS state. The XPS spectra of LaCoO\(_3\) at room temperature and 573 K along with ionic multiplet analysis suggest\[2\] that the LS and HS states co-exist at room temperatures. Polarized neutron scattering measurements\[3\] exhibit two magnetic-electronic transitions, one near 90 K and another near 500 K. The spin-state transition is maintained to occur at low temperature, and the high temperature transition is not dominantly of magnetic origin. NMR\[4\] studies also claim that the LS-to-HS spin state transition occurs at \(\sim 90\) K. Co-K-extended x-ray absorption fine structure measurements\[2\] established the occurrence of two cobalt sites above 400 K and this may be associated with two spin states for Co. Madhusudan et al.\[2\] reported that the series RCoO\(_3\) (R = Pr, Nd, Tb, Dy and Yb), all exhibit the considered LS-to-HS state transition of cobalt. Taguchi\[2\] has shown from structural and susceptibility studies that Co\(^{3+}\) in Nd(Cr\(_{1-x}\)Co\(_x\))O\(_3\) is in the low-spin state at low temperature and transform to a mixed-spin state with increasing temperature. From temperature-dependent susceptibility and Knight-shift measurements\[2\] it has been pointed out that the LS-HS model is not applicable for understanding the spin-state transition in LaCoO\(_3\) and thus a LS-IS model is more appropriate. Heikes et al.\[2\] considered an IS state to account for the effective moment obtained from susceptibility data below the \(\sim 500\) K transition in LaCoO\(_3\). From photoemission measurements it has been concluded that the hybridization of oxygen 2\(p\) orbitals and cobalt 3\(d\) states stabilize the IS state with spin \(S = 1\).\[2\]

Heat capacity measurements also support the LS-to-IS state transition.\[5\] Recent magnetic susceptibility and neutron-diffraction studies\[6\] show that LaCoO\(_3\) has the LS Co\(^{3+}\) configuration at the lowest temperatures. Below 350 K IS remains isolated and localized; above 650 K, all the trivalent Co ions are transformed to the IS state with itinerant \(d\) electrons.

Several theoretical attempts have also been made to understand the microscopic origin of the spin-state transition in LaCoO\(_3\). From an LDA+U approach (where U is the on-site Coulomb interaction) Korotin et al.\[7\] have demonstrated that the IS state is relatively stable over the HS state, as a result of the strong \(p-d\) hybridization effect as well as of the orbital ordering effect. This is in contrast to the expectation from the simple ionic model. They have also explained the semiconducting behavior above the 100-to-500 K region as a spatial ordering of orbitals associated with a Jahn–Teller distortion of an IS state and the thermal disordering of this state results in a gradual crossover to the metallic state at high temperatures. However, a controversy still exists since the calculation of Mizokawa and Fujimori\[8\] did not find the orbital-ordered state. Recent neutron diffraction measurements\[9\] also give no evidence for orbital ordering. The Hartree–Fock calculations on the multi-band lattice model\[10,11\] have also shown that the IS state is more stable than the HS state. Simulations using molecular-orbital dynamics\[12,13\] show that magnetoelastic coupling plays a very important role, the spin-state transition being mainly induced by variation of the Co–O bond length with temperature. Liu et al.\[14\] have suggested that there is a thermodynamic equilibrium between LS Co\(^{3+}\), HS Co\(^{3+}\), Co\(^{2+}\) (\(t_2g e_g^1\)) and Co\(^{4+}\) (\(t_2g e_g^0\)) in LaCoO\(_3\). The recent calculations\[15\] within the unrestricted Hartree–Fock approximation and a real space
recursion method suggest that the spin-state transition at 90 K takes place from the LS to LS-HS ordered state. Mizokawa and Fujimori showed from unrestricted Hartree–Fock calculations that the LS state is the ground state and the IS state is the first excited spin state. The Hartree–Fock calculation also shows that the total energy of the IS state can be considerably lowered on ordering of the $e_g$ orbitals. The analysis of the core-level spectrum in terms of a configuration interaction model suggests that both LS and HS states coexist at low temperature (100 K), but at 573 K there is a decrease in the LS contribution related to local structural changes.38

Much of the difficulty in reaching a consensual interpretation originates from the traditional use of an ionic, ligand-field model. In such a picture, only two distinct spin states of Co$^{3+}$ are energetically operational.39 Also most of the calculations presented in literature dealing with spin-state transition involve only a few adjustable parameters. In order to obtain a better understanding of both, the spin-state transition in LaCoO$_3$ and the origin of the paramagnetic state with local magnetic moments, it is necessary to examine the energetics of various spin-ordered states as a function of hole doping/temperature. This is the motivation for the present study.

The discovery of colossal magnetoresistance (CMR) in manganites with perovskite structure has stimulated research of compounds exhibiting large magnetoresistance. Fairly large magnetoresistance has indeed been observed in the perovskite series La$_{1-x}$A$_x$CoO$_3$ (A = Ca, Sr or Ba). The magnetic and transport properties of La$_{1-x}$Sr$_x$CoO$_3$ and CMR materials such as La$_{1-x}$Sr$_x$MnO$_3$ have common features. In both system the substitution of La with a divalent ion creates a metallic ferromagnetic state. The ferromagnetic interactions between Co$^{3+}$ and Co$^{4+}$ are supposed to arise from a double exchange mechanism like that in La$_{1-x}$Sr$_x$MnO$_3$ materials. However, the detailed mechanism of the ferromagnetism and the metal-insulator transition in cobaltites are not well understood. In metallic samples of La$_{1-x}$Sr$_x$CoO$_3$ ($x > 0.2$) the magnitude of the magnetoresistance is typically small whereas it becomes larger in the composition range $x \leq 0.2$, where the system is close to a metal–insulator transition.45

La$_{1-x}$A$_x$CoO$_3$ are of considerable interest because of the peculiar way their magnetic and transport properties change with composition and temperature. Extensive studies on electronic and magnetic properties of Sr-substituted lanthanum cobaltite, La$_{1-x}$Sr$_x$CoO$_3$ have provided many interesting results during the past four or five decades. The magnetic state of La$_{1-x}$A$_x$CoO$_3$ strongly depends on the doping concentration $x$. Jonker and van Santen studied La$_{1-x}$Sr$_x$CoO$_3$ already in 1953 by magnetization measurements and reported ferromagnetic order for an intermediate Sr concentration. They argued that the double-exchange Co$^{3+}$–Co$^{4+}$ interaction is responsible for the ferromagnetism. Bhide et al. measured the temperature dependence of Mössbauer spectra for ferromagnetic La$_{1-x}$Sr$_x$CoO$_3$ ($0 \leq x \leq 0.5$) and reported that ferromagnetic Sr-rich clusters coexist with paramagnetic La-rich regions in the same (crystallographic speaking) phase. The 3$d$ holes created by the Sr substitution are itinerant both above and below the Curie temperature ($T_C$) and all the experimental results are explained on the basis of itinerant-electron ferromagnetism. Itoh et al. studied this system by magnetization measurements at low fields and obtained a phase diagram with a paramagnetic-to-spin-glass transition for $x < 0.18$ and a paramagnetic-to-cluster-glass transition for $x \geq 0.18$. Neutron diffraction measurements showed the appearance of magnetic peaks below $T_C$ corresponding to long-range ferromag-
netic order for $x \geq 0.2$.

The doping changes the valence states of Co to give a mixture of Co$^{3+}$ and Co$^{4+}$. Using the unrestricted Hartree–Fock approximation and a real-space-recursion method, Zhuang et al.\textsuperscript{48} calculated different magnetic phases for SrCoO$_3$ and concluded that SrCoO$_3$ is in the IS $(t^2_g e^1_g)$ state. The observed spin moment in La$_{0.7}$Sr$_{0.3}$CoO$_3$ from neutron diffraction studies\textsuperscript{49} has concluded that the system will have Co$^{4+}$ in the LS state and a mixed LS and HS configuration for Co$^{3+}$. The magnetic state of La$_{1-x}$A$_x$CoO$_3$ was suggested to be a mixture of HS Co$^{3+}$ and LS Co$^{4+}$ ($t^2_g e^0_g$)\textsuperscript{50} because the measured saturation magnetic moment is only about half of the moment for HS Co$^{3+}$\textsuperscript{50,46}. From application of the numerically exact diagonalization method on Co$_2$O$_{11}$ clusters it has been shown that a coexistence of HS and IS due to strong $p$-$d$ mixing is most plausible in doped cobaltites\textsuperscript{51}. The evolution with Sr doping of the magnetic and transport data has been interpreted\textsuperscript{20} as follows. For $0 < x < 0.1$, the holes introduced into the CoO$_3$ array stabilize the IS clusters trapped at Sr$^{2+}$ at low temperatures and the IS clusters become super-paramagnetic below $T_C = 230$ K. In the range $0.1 \leq x \leq 0.18$, the IS clusters become larger, each containing several holes, and interactions between the isolated super-paramagnetic clusters give a spin-glass behavior below $T_g < T_C$. A collective freezing of the cluster moments below $T_g$ via frustrated inter-cluster interactions has been confirmed\textsuperscript{52} but whether the large IS clusters really are rich in Sr$^{2+}$ has not been established. However, our recent electronic structure calculations on La$_{1-x}$Sr$_x$CoO$_3$ with the supercell approach suggest that Co ions close to both La and Sr, are in the IS state. In the present paper we report the energetics of various spin-states of Co ions as a function of hole doping and volume in LaCoO$_3$. Based on these results we will consider the possible spin-state transition in LaCoO$_3$ on temperature and hole doping.

The rest of this paper is organized as follows. In Sec.\textsuperscript{II}, we describe the computational procedure used in the present calculation. In Sec.\textsuperscript{III}, we discuss the electronic structure and magnetic properties of LaCoO$_3$ as a function of Sr substitution and volume from the results obtained from VCA and supercell calculations using the fixed-spin-moment method. Finally in Sec.\textsuperscript{IV} the findings of the present study are summarized.

II. COMPUTATIONAL DETAILS

A. LAPW calculations

The present investigation is based on \textit{ab initio} electronic structure calculations derived from spin-polarized, density-functional theory (DFT). In particular we have applied the full-potential linearized-augmented plane wave (FPLAPW) method as embodied in the WIEN97 code\textsuperscript{53} using the scalar-relativistic version without spin-orbit coupling. The charge density and the potentials are expanded into lattice harmonics up to $L = 6$ inside the spheres and into a Fourier series in the interstitial region. We have included the local orbitals\textsuperscript{54} for La 5$s$, 5$p$, Sr 4$s$, 4$p$, Co 3$p$ and O 2$s$. The effects of exchange and correlation are treated within the generalized-gradient-corrected local spin-density approximation using the parameterization scheme of Perdew \textit{et al.}\textsuperscript{55} We have carried out test calculations with different sets of $\mathbf{k}$-points and found that the FSM curve changes considerably with the number of $\mathbf{k}$-points. For example, when we use only 4 $\mathbf{k}$-points in our calculations we obtained the ferromagnetic state lower in energy than the nonmagnetic state. To ensure convergence for the Brillouin
zone integration 110 k-points in the irreducible wedge of the first Brillouin zone (IBZ) were used for the rhombohedral structure and 84 k-points in IBZ for the cubic phase (even half the number of these k-points gave the correct result qualitatively). A similar density of k-points was used in the supercell calculations. Self-consistency was achieved by demanding the convergence of the total energy to be smaller than $10^{-5}\text{ Ry/cell}$. This corresponds to a convergence of the charge to below $10^{-4}$ electrons/atom. For all calculations the ratio between the sphere radii used are 1.25, 0.88 and 1.25 for $R_{\text{La}}$, $R_{\text{Co}}$ and $R_{\text{Sr}}$, respectively, where $R_O=1.8\text{ Bohr}$. Since the spin densities are well confined within a radius of about 1.5 Bohr, the resulting magnetic moments do not depend strongly on variation of the atomic sphere radii.

**B. The fixed spin moment (FSM) method**

Conventional spin-polarized calculations based on DFT allows the moment to float and the ground state is obtained by minimizing the energy functional, \( E \), with respect to the charge and magnetization densities, \( \rho(r) \) and \( m(r) \), under the constraint of a fixed number of electrons, \( N \). With the variational principle this corresponds to minimizing the functional

\[
F[\rho(r), m(r)] = E[\rho(r), m(r)] - \mu[\int \rho(r)dr - N],
\]

where \( \mu \) is the chemical potential. The minimization gives \( \frac{\delta E}{\delta \rho(r)} = \mu \), \( \frac{\delta E}{\delta m(r)} = 0 \) leading to effective one-electron equations which are solved by a self-consistent procedure that determines the moment which minimizes the total energy. In cases where two (or more) local minima occur for different moments, conventional spin-polarized calculations become difficult to converge or "accidently" converge to different solutions. Although LaCoO$_3$ is a nonmagnetic material, our conventional spin-polarized calculations always converged to a ferromagnetic solution with a moment of 1.2 \( \mu_B \)/f.u.

In order to reach convergence or to study spin fluctuations it is advantageous to calculate the total energy as a function of magnetic moment using the so-called fixed-spin-moment method. In this method one uses the magnetic moment \( M \) as an external parameter and calculates the total energy as a function of \( M \). In general one must release the constraint that the Fermi levels for up and down spins are equal because the equilibrium condition is not satisfied for arbitrary \( M \). The number of valence electrons \( N \) is known and \( M \) is fixed (as input parameter) determining the values for \( E_F^\uparrow \) and \( E_F^\downarrow \) from

\[
N = N^\uparrow + N^\downarrow = \int_{-\infty}^{E_F^\uparrow} D^\uparrow(E)dE + \int_{-\infty}^{E_F^\downarrow} D^\downarrow(E)dE
\]

\[
M = N^\uparrow - N^\downarrow,
\]

where \( D^\uparrow(E) \) and \( D^\downarrow(E) \) are the spin-up and spin-down DOS, respectively. At maxima and minima of the FSM curve, the two Fermi levels are equal, i.e. \( E_F^\uparrow = E_F^\downarrow \). In the FSM method Eqn.\[\text{II}\] is modified to minimize the functional

\[
F[\rho(r), m(r)] = E[\rho(r), m(r)] - \mu[\int \rho(r)dr - N] - h[\int m(r)dr - M]
\]
where \( h \) is the Lagrange multiplier which applies the constraint of having a fixed spin moment \( M \). The orbital contributions to the magnetization are neglected, since they are usually small for 3d transition-metal phases. Instead of minimizing with respect to \( \rho(r) \) and \( m(r) \), it is more illustrative to change to the spin-up, \( \rho^\uparrow(r) = \frac{1}{2} [\rho(r) + m(r)] \), and spin-down, \( \rho^\downarrow(r) = \frac{1}{2} [\rho(r) - m(r)] \), densities. Then the variational principle yields

\[
\frac{\delta E}{\delta \rho^\uparrow(r)} = \mu + h \quad \text{and} \quad \frac{\delta E}{\delta \rho^\downarrow(r)} = \mu - h.
\]

\( \mu \pm h \) may be identified as the chemical potentials for the two different spins. Thus, the condition of having a fixed spin moment corresponds to using two different chemical potentials, i.e.; two Fermi energies for one material at zero temperature. This can also be seen by rewriting of Eqn. 3 as

\[
F[\rho(r), m(r)] = E[\rho(r), m(r)] - (\mu + h) \left[ \int \rho^\uparrow(r) dr - N^\uparrow \right] - (\mu - h) \left[ \int \rho^\downarrow(r) dr - N^\downarrow \right].
\]

(5)

Therefore, the FSM method corresponds to fixing the number of electrons of the two spins separately. Given \( N \) and \( M \), \( N^\uparrow \) and \( N^\downarrow \) are defined from Eqns. 2 and 3. The associated Fermi energies are then found from the relations

\[
N^\sigma = \int_{-\infty}^{E_F^\sigma} D^\sigma(E)dE,
\]

(6)

where \( D^\sigma(E) \) and \( E_F^\sigma \) are the density of states and the Fermi energy for spin \( \sigma \), respectively.

Extensive FSM calculations have been undertaken to find theoretically the stability condition of 3d and 4d magnetic materials. Similar calculations are also extensively used to explain the magneto-volume instabilities in Invar alloys.

C. Structure

LaCoO\(_3\) has a rhombohedrally distorted pseudo-cubic perovskite structure. The space group is \( R\bar{3}c \) and each unit cell contains two formula units. \( \text{La}_{1-x}\text{Sr}_x\text{CoO}_3 \) has the rhombohedral structure with space group \( R\bar{3}c \) in the range \( 0 \leq x \leq 0.5 \) and transforms to a cubic phase with the space group \( Pm\bar{3}m \) at higher Sr contents. The rhombohedral distortion decreases with increase of \( x \). A similar variation results from thermal expansion for the parent \( \text{LaCoO}_3 \). The oxygen atoms are in the 6e \( (\frac{1}{4} - \delta x, \frac{1}{4} + \delta x, \frac{1}{4}) \) Wyckoff position with \( \delta x = 0.0522 \). Using the force minimization method we have optimized \( \delta x \) and found an optimized value of 0.0638. The FSM calculations at low temperature are made with this value for \( \delta x \) and the experimental lattice parameters corresponding to 4 K. The structural parameters for the hole-doped systems used in the present calculations are the same as those used in Ref. 56. The spin-state transition is believed to occur mainly due to the larger variation of the Co–O bond length with increasing temperature. Hence, it is interesting to study the spin-state transition as a function of lattice parameters and we have performed FSM calculations for \( \text{LaCoO}_3 \) with lattice parameters corresponding to 4 K as well as 1248 K. The structural parameters at 1248 K were taken from high-resolution powder-diffraction measurements.

D. Substitution

The hole-doping effect in \( \text{LaCoO}_3 \) has been simulated using supercell calculations as well as virtual-crystal approximation (VCA) calculations. For the VCA calculation we have
taken into account the experimentally reported structural parameter changes as a function of Sr substitution. Hence, these calculations accounted properly for the hybridization effect. In this approximation the true atom in the material is replaced by an "average" atom which is interpolated linearly in charge between the corresponding pure atoms. In the VCA calculations the charge-transfer effect is not thoroughly accounted for, whereas the band-filling effects are properly taken into account. The chosen approximation has an advantage owing to its simplicity and hence we are able to study small concentrations of Sr in LaCoO₃. However, for 50% Sr substitution we have made explicit supercell FSM calculations.

III. RESULTS AND DISCUSSION

Our current results are based on total-energy FPLAPW-band calculations utilizing the FSM procedure. We have considered only the ferromagnetic state. Each point on the $E(M)$ curves shown in Fig. 1 is derived from a band calculation in which the total moment of the phase was constrained to a given $M$ value. The FSM procedure fixes only the total moment and not the local moments. The latter are free to take whatever value that minimizes the energy. In all cases, the local moments vanish at $M = 0$; i.e., the situation $M = 0$ is never produced by a cancellation of opposite local moments.

A. DOS characteristics

The calculated DOS for LaCoO₃ are shown in Fig. 2 for the three spin arrangements LS, IS and HS. First of all, the results predict a metallic behavior for the LS state (Fig. 2c) of LaCoO₃, but the total DOS has a sharp minimum at $E_F$. This is in contrast to the semiconducting behavior observed experimentally. This kind of discrepancy may be expected in narrow-band materials due to correlation effect. However, this does not hold in the present case as our recent optical property calculations for LaCoO₃ show good agreement with experimental spectra up to 25 eV. Hence, the metallic behavior in LaCoO₃ is due to the usual underestimation of the band gap in LDA and not due to the correlation effect. We have recently reported on the bonding behavior of La$_{1-x}$Sr$_x$CoO₃ and found indications of strong covalent hybridization between O $p$ and Co $d$ in this phase. For a more detailed discussion about the bonding behavior reference is made to the preceding communication. The O $p$ and Co $d$ states are mixed with each other in the valence band. By contrast, the La spectral weight contributes mainly to the unoccupied electronic states in the conduction band. This suggests that La has more ionic character and is stabilized by the Madelung potential whereas the covalent contribution to the bonding is more prominent within the Co–O octahedra. The sharp feature at 4 eV above the Fermi level corresponds to the La 4$f$ band and the DOS segment at 4–8 eV is composed mainly of La 5$d$ states.

The Co 3$d$ states are very important and deserve to be discussed in more detail because they determine the magnetic properties. LaCoO₃ has a pseudocubic perovskite structure with a rhombohedral distortion along the (111) direction. Since the rhombohedral distortion is small, we use the concept of $t_{2g}$ and $e_g$ orbitals (as referred to in the cubic situation) in the following discussion. In an octahedral crystal field the $d$ electrons will be split into double degenerate $e_g$ and triple degenerate $t_{2g}$ states. The $t_{2g}$ and $e_g$ projected density of states of
Co in the cubic phases of LaCoO$_3$ and SrCoO$_3$ are given in Fig. 3 for the non-spin-polarized and ferromagnetic cases. The strong peak below the Fermi level corresponds to the Co $t_{2g}$ bands. These relatively non-bonding states produce weak Co–O–Co interactions which give rise to a narrow band. By contrast, the Co $e_g$ states produce very strong Co–O–Co interactions which give rise to a much larger dispersion, and result in the broader $e_g$ band observed for both LaCoO$_3$ and SrCoO$_3$. When the spin polarization is included in the calculations, the $t_{2g}$ states for the majority spin become localized compared with the non-spin-polarized case and thus the total energy calculation shows that the ferromagnetic state is lower in energy than in the nonmagnetic case. However, for the minority-spin state in Fig. 3a $E_F$ is located at a sharp non-bonding $t_{2g}$ peak. As this is not a favorable condition for stability, a rhombohedral distortion arises due to a Jahn–Teller/Peierls-like instability.

The simple ligand model predicts that for the LS state in LaCoO$_3$, that the $t_{2g}$ levels are completely filled and the $e_g$ states completely empty. In our calculation, however, the $e_g$ states are distributed over the entire valence and conduction bands. The band structure obtained from a tight-binding method also shows that the $e_g$ orbitals partly fall below the Fermi level and are mixed with the $t_{2g}$ orbitals. This feature can be understood as follows. The lobes of the $t_{2g}$ orbitals point between the oxygen ligands, whereas the $e_g$ orbitals point directly towards the ligands. Hence, the overlap with O 2$p$ orbitals will be greater for the $e_g$ states, and the increased overlap results in local repulsion between overlapping charge densities. This repulsive interaction pushes the $e_g$ orbitals to higher energy. However, some of the repulsion is compensated by hybridization in the resulting bonding states which in turn leads to considerable amount of $e_g$ state in the conduction band. The calculations show that $E_F$ lies in the vicinity of the sharp non-bonding $t_{2g}$ peak for the Co 3$d$ electrons at the ground state LS configuration. In this case, a small shift in $E_F$ leads to large changes in $N(E_F)$ and causes the ferromagnetic instability of the system. So, the presence of the high DOS close to $E_F$ and the small energy difference between the nonmagnetic and ferromagnetic state are the two main reasons for the temperature induced anomalies in the physical properties.

Considering DOS for LaCoO$_3$ in the rhombohedral structure and the LS state, it is interesting to note that $E_F$ lies in a pseudogap which separates bonding from anti-bonding states. As a result there is a gain in one-electron energy and the system stabilizes in the rhombohedrally distorted nonmagnetic phase. In the case of SrCoO$_3$, the 3$d$ DOS of Co in the non-spin-polarized case shows that $E_F$ lies in a sharp peak which originates from non-bonding $t_{2g}$ states. Here the Stoner criterion is fulfilled and the ferromagnetism appears. In the spin-polarized case these $t_{2g}$ states are exchange split as shown in Fig. 3a. Unlike LaCoO$_3$ the Co-3$d$ $t_{2g}$ states for spin-polarized SrCoO$_3$ are well separated from $E_F$ and hence stabilizing the ferromagnetic state. This is evident from the FSM curve for SrCoO$_3$ shown in Fig. 3a where the ferromagnetic state with a magnetic moment 2.6 $\mu_B$/f.u. is 0.463 eV lower in energy than the nonmagnetic state. Even though SrCoO$_3$ is stabilized in the cubic ferromagnetic phase, our calculation shows that $E_F$ falls on a shoulder of the nonbonding minority spin Co $t_{2g}$ DOS. This may be one reason for the presence of oxygen vacancies in SrCoO$_3$.

The pseudo-gap feature in the vicinity of the Fermi level disappears in the IS and HS state of LaCoO$_3$ as shown in Figs. 2a and b, respectively. In Fig. 4 the limits of the IS and HS states are represented by vertical lines. A detailed examination of energy vs. moment shows that the slope change its sign around 1 $\mu_B$. However, a flattened region is seen in
the vicinity of $1.2\mu_B$ (Fig. 1 and the inset to Fig. 1) where the ferromagnetic state gets stabilized according to our ferromagnetic spin-polarized calculations. So, we assigned a moment of $1.2\mu_B$ to the IS state. From our calculations the IS state turns out to be metallic which is consistent with the LDA+U calculation\cite{11} that leads to a half-metallic ferromagnet. Moreover our calculation predicts the HS state to be a half-metallic ferromagnet whereas according to LDA+U calculations it should be a semiconductor. The reason for the metallic behavior of the IS state is that the bands formed by $e_g$ orbitals are broad and the band splitting is not strong enough to create a gap. On the other hand, in the HS state, the $e^\uparrow_g$ band becomes completely filled and a band gap appears in the majority-spin state. DOS for the IS and HS states shows that the nonbonding $t_{2g}$ electrons are present at $E_F$ in the minority-spin state. Consequently these states are at a energetically higher level than the LS state (Fig. 1). The magnitude of DOS just below the Fermi level is lower for the IS and HS phases than for the LS phase. A similar decrease is observed with increasing values of $x$ in the XPS spectra.\cite{66} In relation to Fig. 1 it should be noted that the one electron eigenvalue sum itself explains why the LS state is lower in energy than the IS and the HS states.

**B. Hole doping effect**

It has been reported that the La$_{1-x}$Sr$_x$CoO$_3$ phase develops a ferromagnetic long-range order above $x = 0.05$ and that the metal–insulator transition takes place at $x \approx 0.2$. Optical measurements\cite{46,69,67} show that the electronic structure of the high-temperature metallic state of LaCoO$_3$ is very similar to that of the doping-induced metallic state. Hence, the FSM calculations on hole-doped LaCoO$_3$ is expected to give a better understanding about the nature of the temperature-induced spin-state transition.

For the Sr-doped system, it is natural that the Sr substitution induces a partial oxidation from Co$^{3+}$ to Co$^{4+}$. From the effective magnetic moment obtained by magnetization measurements, Taguchi and Shimada\cite{50} concluded that Co$^{3+}$ is in an HS state in La$_{1-x}$Sr$_x$CoO$_3$ and Co$^{4+}$ in an LS state becase the saturation moment in the ferromagnetic phase ($0.3 > x$) is only about half the full moment of HS Co$^{3+}$.\cite{46,50} A transition from LS to HS through doping has been suggested from NMR studies on $^{59}$Co and $^{139}$La probes and neutron scattering.\cite{59} Electron spectroscopy\cite{46,69} and magnetic measurements\cite{46,69} indicate that hole doping leads to the formation of HS rather than LS configuration. As the radius of Sr$^{2+}$ is larger than that of La$^{3+}$, it is suggested that the Sr doping favors the HS state by the introduction of Co$^{4+}$ ($3d^5$) \cite{43} The HS state of Co$^{3+}$ possesses $S = 2$, viz. a maximum magnetic moment of $\mu_{Co} = 4\mu_B$. This corresponds to the purely ionic model; hybridization of Co $3d$ orbitals with the O $2p$ orbital and the band formation in the solid states can significantly renormalize this ionic value. Hence, the calculated magnetic moments are always smaller than the ionic values (Table I), and much smaller than the HS ionic value indicating that this discrepancy cannot be accounted for as a hybridization effect. It should be noted that one can expect a discrepancy between experiment and theory above $x > 0.5$, where the oxygen deficiency is known to increase significantly (see the discussion in Ref. 56).

Recent neutron diffraction studies\cite{30} show that the doping with Sr introduces LS Co$^{4+}$ ($t^5e^0$) which in turn stabilizes IS Co$^{3+}$ on the neighbors. Ferromagnetic resonance measurements suggest that subjected to hole doping, the cobalt ions transform from a paramagnetic LS to a ferromagnetic IS state.\cite{43} Ganguly et al.\cite{43} concluded from magnetic susceptibility...
studies that the Co ions in La$_{0.5}$Sr$_{0.5}$CoO$_3$ are in the IS state. Photo-emission and x-ray absorption spectroscopic measurements combined with configuration cluster-model calculations led Saitoh et al. to suggest that it is the Co ions in the IS state which are responsible for the ferromagnetism in La$_{1-x}$Sr$_x$CoO$_3$. If both Co$^{3+}$ and Co$^{4+}$ are in the IS states in La$_{0.5}$Sr$_{0.5}$CoO$_3$, one should expect 2.5 $\mu_B$/f.u. according to an ionic picture. As in our previous study (that indicated strong covalent bonding between Co and O), we obtained 1.98 $\mu_B$/f.u. for La$_{0.5}$Sr$_{0.5}$CoO$_3$ (Table I). The FSM curves from the VCA calculations (Fig. 5) as well as the supercell calculations (Fig. 6) give similar results. One of the reasons for the stabilization of the IS state by hole doping is that the hole doping reduces the ionicity and enhances the covalent hybridization between Co and O. The observed stabilization of the IS state in hole-doped LaCoO$_3$ is also consistent with recent magnetic and transport property measurements. Comparison between the experimental Co 2$p$ x-ray absorption spectra and atomic-multiplet calculations also indicate that the ground state of SrCoO$_3$ is IS ($t_{2g}^{4}e_{g}^{1}$). For IS Co$^{4+}$ one expects 3 $\mu_B$/atom. But the hybridization effect reduces the magnetic moment and hence we obtain a value of 2.6 $\mu_B$/f.u. for SrCoO$_3$.

Early studies led to the suggestion that, in the doped samples, a paramagnetic La$^{3+}$ region co-exists with ferromagnetic Sr$^{2+}$-rich clusters in the same crystallographic phase, the ferromagnetic component increasing with $x$. The magnetic and transport properties of hole-doped LaCoO$_3$ suggest that upon Sr doping, the material segregates into hole-rich, metallic ferromagnetic regions and a hole-poor matrix similar to LaCoO$_3$. The Co ions of the ferromagnetic phase are in an IS configurations, the hole-poor region experiences a thermally induced LS to HS transition. A cluster-glass state in the region $0.3 < x < 0.5$ is also proposed from magnetization measurements. For lower Sr contents ($x < 0.2$), the magnetization measurements have clarified a spin-glass ground state, where a strong ferromagnetic short-range correlation is observed by paramagnetic neutron scattering experiments. Our spin-polarized, supercell calculations for La$_{0.75}$Sr$_{0.25}$CoO$_3$ show that the cobalt ions closer to Sr and La give significant magnetic contributions. The calculated magnetic moment for these two kinds of Co ions do not differ much, indicating that the spin state of these ions are almost the same and that the hole doping affects almost uniformly all the Co ions in the structure.

From the FSM curve obtained as a function of $x$ (Fig. 5), it is clear that the LS phase of Co$^{3+}$ is the most stable among the magnetic configurations for $x = 0$, but the LS state is found to be unstable with increasing values of $x$. This is consistent with the results obtained within the HF approximation. Further, the instability of the nonmagnetic phase on hole doping is consistent with the experimentally observed paramagnetic behavior of the susceptibility for $x \geq 0.08$. Hole doping in the LS ground state of pure LaCoO$_3$ is believed to lead to the formation of localized magnetic polarons with unusually high spin numbers ($S = 10–16$). For La$_{1-x}$Sr$_x$CoO$_3$, it has been reported that the spin-state transition around 90 K disappears with increasing $x$ and the Co ions are in a magnetic state down to the lowest temperatures. Our calculated results are consistent with these observation in the sense that the metastable state of LaCoO$_3$ disappears and a magnetic phase appears on hole doping.

The total DOS for LaCoO$_3$ in the LS state (Fig. 2) shows that $E_F$ is located in a deep valley, viz. in a nonmagnetic state. The hole doping shifts $E_F$ to the peak on the lower energy side of DOS (Fig. 3). As a result the Stoner criterion for band ferromagnetism is
fulfilled and magnetism appears. From Fig. 6 it is seen that the overall topology of the DOS curve do not change significantly on hole doping. This indicates that the band-filling effect plays a decisive role for the changes in the magnetic properties of La$_{1-x}$Sr$_x$CoO$_3$ as a function of $x$. The equilibrium spin moment for La$_{1-x}$Sr$_x$CoO$_3$ as a function of $x$, calculated according to FSM-VCA, is compared with experimental data and the results obtained by self-consistent full-potential-linear-muffin-tin orbital (FPLMTO) supercell calculations in Fig. 9. It should be noted that the calculated equilibrium magnetic moments seen from the FSM curves (Fig. 5) are in excellent agreement with the experimental findings as well as our previous FPLMTO results. This indicates that the FSM method is reliable to give correct predictions for equilibrium magnetic phases. The observation of ferromagnetism in LaCoO$_3$ by temperature/hole doping has been interpreted as originating from one of the mechanisms: (i) Ordering of HS and LS Co ions through ferromagnetic super-exchange via the intervening oxygens, (ii) Zener double exchange or (iii) itinerant-electron ferromagnetism. Our band-structure calculations are able to explain the magnetic properties indicating that itinerant-band picture (iii) is suitable for these materials. The increasing trend of magnetic moment as a function of hole doping originates for two reasons. Firstly, owing to band-filling effects the hole doping moves the Fermi level to the sharpest $t_{2g}$ peak and hence enhances DOS at the Fermi level as well as the exchange splitting. Secondly, an effect of reduced hybridization resulting from the fact that Sr$^{2+}$ is larger in size than La$^{3+}$ and the consequent expansion in lattice on increasing substitution. As a result the bands narrow which in turn enhances the spin polarization.

C. Metamagnetism

A metamagnetic transition refers to paramagnetic metallic materials which are rendered ferromagnetic by applying a sufficiently large external magnetic field. Such a possibility was first discussed by Wohlfarth and Rhodes and later extended by Shimizu. Phenomena related to band metamagnetism are observed mainly in Co-based materials such as pyrite-type phases CoS$_2$, Co(Se,S)$_2$, Laves-type phases YCo$_2$, ScCo$_2$, LuCo$_2$, hexagonal Fe$_2$P-type phases Co$_2$P, CoNiP and orthorhombic Co$_2$P-type phases CoMP (M=Mo and Ru). Metamagnetism has also been found experimentally and theoretically in UCoAl.

Itinerant-electron metamagnets possess an anomalous temperature dependence of the susceptibility which increases with temperature and then decreases after a maximum at a finite temperature ($T_m$) and usually obeys the Curie–Weiss law at higher temperatures. It has been revealed that $T_m$ is closely correlated with the metamagnetic transition field $H_m$. A maximum in the temperature dependence of the paramagnetic susceptibility has been observed for the itinerant-band metamagnets ScCo$_2$, YCo$_2$, and LuCo$_2$. LaCoO$_3$ also shows a temperature dependent magnetic susceptibility with an increasing trend at low temperature and a marked maximum around 90 K followed by a Curie–Weiss-law-like decrease at higher temperature, which is similar to that of the itinerant metamagnets. Metamagnetic transitions have been recently reported for the closely related phases Gd$_{0.5}$Ba$_{0.5}$CoO$_3$ and DyCoO$_3$.

The energy needed to enforce a given magnetic moment is given by the total energy difference $\Delta E$ with respect to the nonmagnetic case. The $\Delta E$ vs. magnetic-moment curve is shown in Fig. 10 for LaCoO$_3$ at 4 K. At low temperature, the ground state of LaCoO$_3$
corresponds to the nonmagnetic LS state. However, the minimum of the ferromagnetic IS state occurs about 32 meV above the LS state (Fig. 1). The existence of a ferromagnetic solution as a quasi-stable state implies that a discontinuous transition in magnetization would be possible by application of a magnetic field. This metamagnetic IS state is destroyed by temperature as shown in Fig. 7. In our calculation temperature is introduced via volume expansion and hence the disappearance of IS by temperature is due to the weakening of hybridization between Co $d$ and O $p$ states. Further, hole doping of LaCoO$_3$ stabilizes the metastable state (see Fig. 8). The disappearance of the metamagnetic behavior and the appearance of ferromagnetism on hole doping in LaCoO$_3$ can be understood as follows. The reduction in valence electrons by the Sr substitution shifts $E_F$ to the lower energy side of VB towards the peak position in the DOS. As a result, the Stoner criterion for band ferromagnetism becomes fulfilled and the metastable state is stabilized as a ferromagnetic state.

According to the FSM method, the spin-projected DOS are filled up to $E_F$ for spin-up and spin-down electrons in order to yield the desired externally fixed-spin magnetic moment. In effect we are dealing with a system in a uniform magnetic field $H$, which maintains the magnetic moment of the system. The difference in Fermi energy corresponds to a difference in magnetic energy $E_F^{\uparrow} - E_F^{\downarrow} = 2 \mu_B H$. Since this difference is related to the size of the external magnetic field, a vanishing difference corresponds to an extremum in the magnetic total energy. Hence, this procedure allows one to find not only stable, but also metastable magnetic states. To obtain a better description of the metamagnetism, the variation of the difference in Fermi energy for up and down spins ($\Delta E_F = E_F^{\uparrow} - E_F^{\downarrow}$) with the magnetization, is shown in Fig. 8 for LaCoO$_3$ at 4 K. The difference in Fermi energy is related to the derivative of $E(M)$ by

$$\Delta E_F(M) = -2\mu_B \frac{\delta E}{\delta M}. \quad (7)$$

Stable zero-field states exist only when $\Delta E_F = 0$ and its derivative, $\frac{\delta \Delta E_F}{\delta M}$, is negative. These solutions then correspond to what one can derive by usual spin-polarized calculations. From Fig. 8 it is seen that $\Delta E_F(M)$ nearly vanishes at the metastable magnetic state obtained in our FSM curve.

The theoretical exploration of Wohlfarth and Rhodes revealed that the metamagnetic transition originates from the sharp peak in DOS in the vicinity of $E_F$. The metamagnetic state in transition-metal phases is connected with the magnetic-field-induced splitting of the majority and minority $3d$ subbands of the transition metal. Bloch et al. have pointed out that, according to the Stoner theory, $E_F$ of the itinerant $d$ electrons lies near a minimum or on a steep decrease in the DOS curve, so that there appears anomalous temperature and magnetic field dependences in the magnetic susceptibility. It is interesting to note that the DOS curve for LaCoO$_3$ in the LS state (Fig. 2c) also shows $E_F$ in a deep valley just above the Co $3d t_{2g}$ peak. In this case the ferromagnetic state with a rather large magnetic moment can be approached by the applied magnetic field. This may be the possible origin for the appearance of the metamagnetism as well as the anomalous behavior in the temperature dependence of magnetic susceptibility.

The metamagnetic transition from paramagnetic to ferromagnetic state can be understood as follows. The applied external field shifts the up- and down-spin bands by a small
amount. As a consequence the system gains potential energy owing to the reduced Coulomb interaction, but at the same time loses energy owing to an increase in the kinetic energy. The final induced magnetic moment will be determined by the balance between these two terms. However, in some systems there will be, for a certain critical value of the applied field, a sudden gain in potential energy which is not sufficiently counterbalanced by the kinetic term. Hence, the metamagnetic spin state develops. More quantitatively, the criterion for the onset of metamagnetism may be written

\[ I \left( \frac{1}{2} D^\uparrow(E_F) + \frac{1}{2} D^\downarrow(E_F) \right)^{-1} = 1 \]

where \( I \) is the multi-band Stoner parameter, and \( D^\uparrow(E_F) \) and \( D^\downarrow(E_F) \) are DOS at \( N_F \) for the spin-up and -down bands, respectively. If the densities of the two state simultaneously attain sufficiently large values for a given applied field, a metamagnetic transition will take place. A glance at Fig. 2 shows that a small splitting of the spin band will indeed give large values of both \( D^\uparrow(E_F) \) and \( D^\downarrow(E_F) \). This explains the occurrence of the metamagnetic transition in LaCoO\(_3\).

**D. Spin-state transition**

Despite numerous studies the nature of the spin-state transition is still under debate. This is because in most earlier studies a rather ionic and ligand-field-like starting point has been assumed. Such a simplified picture does not include the possibility of an IS state and a large \( e_g \) band width. The main controversies are related to the nature of the transition, the temperature range of the transition, and to the electronic structure and hence to the energy levels involved. From the temperature dependent \(^{59}\)Co and \(^{139}\)La NMR measurements Itoh and Natori have shown that the anomalous behavior around 500 K can be interpreted as a spin-state transition between IS and HS. From electrical resistivity and neutron diffraction measurements Thornton et al. concluded that the semiconductor-to-metal transition takes place around 520 to 750 K by the stabilization of an IS state for Co\(^{3+} \) associated with a smooth transition from localized \( e_g \) to itinerant \( \sigma^* \) electrons. The polarized neutron-scattering experiments firmly supported that the spin-state transition takes place at about 90 K which is in sharp contrast to the interpretation of x-ray absorption spectroscopy data which indicates that the spin-state transition takes place in the range 400–650 K coinciding with the gradual semiconductor-to-metal transition. It is also suggested that the spin-state transition in LaCoO\(_3\) occurs in two steps. First, a conversion from the ground state LS to IS around 100 K. Second, a change from the IS state to a mixed IS–HS state around 500 K. Our calculations predicts that the energy barrier between the LS and IS states is 290 K and that the HS state is much higher in energy than IS (Fig. 1). So, the possibility of stabilizing the HS state by temperature and/or hole doping is less favorable in \( La_{1-x}Sr_xCoO_3 \). Hence, the present calculations rule out the possibility of stabilizing mixed-spin states such as LS-HS and IS-HS.

The energy difference between the LS and HS states of Co\(^{3+} \) ions is reported to be less than 80 meV and may even be as low as 30 meV. From magnetization measurements the energy difference between the LS and HS states is reported to be 6 to 22 meV. Asai et al. estimated the energies of the IS and HS states at 0 K to be 22.5 and 124.6 meV.
above LS, respectively. Our calculated value for the energy difference between the LS and IS states is 32 meV and that between LS and HS states 1113 meV (see Fig. 1). The unrestricted Hartree–Fock calculation shows that the energy of the HS state is 35 meV higher than the LS state. The Hartree–Fock calculation yields the total energy of the IS state about 0.5 eV higher than the LS state. Possible reasons for the discrepancy between the two sets of results may be that the Hartree–Fock calculations have not taken into account the structural distortions and all possible low-energy phases. Our recent electronic structure studies show that the rhombohedral distortion is important for a correct prediction of the magnetic properties in LaCoO₃ (viz. calculations predicting the cubic phase to be ferromagnetic). From Fig. 1a, the cubic phase of LaCoO₃ is found to be in a ferromagnetic IS state with a magnetic moment of 1.44 \( \mu_B \)/f.u. and this state is 82 meV lower in energy than the nonmagnetic phase.

On going through the intermediate to high temperature range, LaCoO₃ is variously believed to be in a mixed LS/HS or IS state. Softening of the lattice during the spin-state transition has also been observed in the elastic modulus and this is explained by a model involving three spin states coupled with the lattice. Using the LDA+U approach Korotin et al. found that the ground state of Co³⁺ in LaCoO₃ is a LS nonmagnetic state and found two IS states followed by an HS state at significantly higher energy. Ab initio electronic structure studies on LaCoO₃−SrCoO₃ concluded that on decreasing the crystal field LS becomes unstable, while the HS state becomes stabilized. The LS-to-HS transition model needs antiferromagnetic interaction between HS Co³⁺ in order to explain the small absolute value of the magnetic susceptibility, whereas the inelastic neutron scattering study has revealed the presence of weak ferromagnetic correlations at \( T \geq 100 \) K.

Being a \( d^6 \) phase, LS would be more stable than HS if the crystal field splitting of the 3d states into \( t_{2g} \) and \( e_g \) levels is larger than the intra-atomic exchange splitting (i.e. \( 10Dq > 2J \)). Conversely, if the exchange energy dominates, the result is an HS state with \( S = 2 \). Owing to the degenerate nature of the IS state with \( S = 1 \), it is not possible to obtain stabilization within this framework. However, if hybridization with the oxygen band is taken into account the stability of IS can be accounted for. In Fig. 1 nearly degeneracy of the LS and IS states occurs because the intra-atomic exchange splitting \( \Delta_{ex} \) of the \( S = 1 \) state is close to the crystal-field splitting \( \Delta_{cf} \). The present calculation shows that in the metastable magnetic state, La, Co and O carry moments of 0, 0.968 and 0.05 \( \mu_B \)/atom, respectively, for the experimental lattice parameters at 4 K. These values along with the contribution from the interstitial region give a total magnetic moment of 1.2 \( \mu_B \)/f.u.

It should be noted that our spin-polarized calculation for LaCoO₃ always yield a finite moment corresponding to the flat region currently obtained from our FSM calculation for 4 K. From the FSM curve in Fig. 1 the calculated magnetic field necessary to stabilize an IS state is 282 T. It is well known that Co³⁺ in the HS state have a larger ionic radius than in the LS state, and LS–HS transitions are believed to be accompanied by an increase of in volume. Keeping those features in mind we carried out the calculations for the electronic structure of LaCoO₃ with the lattice parameters for 1248 K which can imitate the influence of the temperature via thermal expansion. Fig. 1 shows the total energies as a function of magnetic moment for the expanded lattice. The HS state \( \langle M = 4 \mu_B \rangle \) lies much higher in energy than LS and IS at low as well as high temperature indicating that it is less probable
to stabilize the HS state by temperature/hole doping. However, our FSM calculations show that an IS state is always lower in energy than the HS state for hole doped LaCoO$_3$. So, theory rules out the possibility of stabilizing HS by either temperature or hole doping. Hence, the LS-to-IS spin-state transition is the more probable transition in LaCoO$_3$.

**IV. SUMMARY**

The electronic structure and magnetic properties of LaCoO$_3$ as a function of hole doping and temperature have been studied with the fixed-spin procedure using the generalized-gradient-corrected FLAPW method. The hole-doping effect has been simulated by VCA as well as through supercell calculations. From these studies the following conclusions have been arrived.

1. The nonmagnetic solution with Co$^{3+}$ in the LS state has the lowest total energy at low temperature and this is consistent with the experimental observations.

2. The FSM calculation suggests that the first excited state configuration in LaCoO$_3$ is an IS state which lies only 32 meV higher than the LS state. It is experimentally established that there is a transition from an LS nonmagnetic state to a magnetic state with increasing temperature. As this transition is experimentally reported to be around 90 K, we ascribe the nonmagnetic-to-magnetic transition in LaCoO$_3$ to the LS–IS transition. Theoretical results along with the experimental finding lead us to the conclusion that the transition near 500 K is not a spin transition, but rather a semiconductor-to-metal transition and/or a localized-to-itinerant electron transition.

3. The IS state is very sensitive to the volume and it becomes unfavorable at a volume corresponding to the experimental volume at 1248 K.

4. The HS state is expected to have a moment of 4$\mu_B$/Co$^{3+}$ within the ionic picture which is much higher in energy than the IS state at 4 K as well as at 1248 K. Hence, the possible spin-state transition in LaCoO$_3$ is from LS to IS and theory predicts that the stabilization of the HS state in LaCoO$_3$ is less probable.

5. We find that the energy barrier between LS and HS as well as between IS and HS are very large. Also our supercell calculations on hole doped LaCoO$_3$ show that the Co ions closer to La and Sr have almost the same spin polarization. Hence theory rules out the possibility of stabilizing a mixed-spin state such as LS and HS, IS and HS or the combination of these by temperature/hole doping.

6. The hole doping effect induces ferromagnetism in LaCoO$_3$ which originates from the filling of Co $t_{2g}$ levels and as a result the IS state gets stabilized over the LS state. The calculated magnetic moment for the equilibrium state as a function of hole doping is found to be in good agreement with the low temperature neutron diffraction and susceptibility data.
7. With equilibrium lattice parameters, our calculations predict the possibility of a metamagnetic transition. Hence the experimentally observed anomalous behavior in the temperature dependent susceptibility has been interpreted as a metamagnetic transition from a nonmagnetic LS to a ferromagnetic IS state. The critical field for the metamagnetic transition is estimated from the FSM curve of LaCoO$_3$ to be 282 T.

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* Electronic address: ravindran.ponniah@kjemi.uio.no

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TABLE I. Magnetic moments in $\mu_B$/Co for La$_{1-x}$Sr$_x$CoO$_3$ obtained by FSM calculations (Theory) compared with experimental neutron scattering values (Exp.), together with values obtained for LS, IS and HS configurations using an ionic model.

| Composition | LS | IS | HS | Exp. | Theory |
|-------------|----|----|----|------|--------|
| LaCoO$_3$   | 0  | 2  | 4  | 0    | 0      |
| La$_{0.9}$Sr$_{0.1}$CoO$_3$ | 0.1 | 2.1 | 4.1 | —    | 1.42   |
| La$_{0.8}$Sr$_{0.2}$CoO$_3$ | 0.2 | 2.2 | 4.2 | 1.5  | 1.57   |
| La$_{0.7}$Sr$_{0.3}$CoO$_3$ | 0.3 | 2.3 | 4.3 | 1.65 | 1.67   |
| La$_{0.6}$Sr$_{0.4}$CoO$_3$ | 0.4 | 2.4 | 4.4 | 1.85 | 1.86   |
| La$_{0.5}$Sr$_{0.5}$CoO$_3$ | 0.5 | 2.5 | 4.5 | 2.2  | 1.98   |
| SrCoO$_3$   | 1  | 3  | 5  | 1.8  | 2.60   |
FIGURES

FIG. 1. The total energy of LaCoO$_3$ as a function of constrained spin moment obtained for a volume corresponding to 4K. The zero level is chosen at the nonmagnetic energy minimum. The inset gives an enlargement for the energy interval close to IS. The extrapolation of the metastable state above 25 meV is indicated by the straight line. Vertical dashed lines represent the cross-over to IS and HS and the corresponding temperatures required to excite the system to these states are quoted.

FIG. 2. Total DOS for LaCoO$_3$ in the LS, IS and the HS states obtained for the volume corresponding to 4K. The Fermi level is marked with the vertical line at zero energy.

FIG. 3. The $e_g$ and $t_{2g}$ splitted Co-$d$ DOS for (a) LaCoO$_3$ and (b) SrCoO$_3$ with and without spin-polarization.

FIG. 4. The calculated FSM curves for the cubic phase of (a) SrCoO$_3$, (b) La$_{0.5}$Sr$_{0.5}$CoO$_3$ and (c) LaCoO$_3$.

FIG. 5. FSM curves for La$_{1-x}$Sr$_x$CoO$_3$ ($x = 0$ to 0.5) obtained by VCA calculation.

FIG. 6. Co-$d$ DOS in La$_{1-x}$Sr$_x$CoO$_3$ as a function of $x$ obtained from spin-polarized VCA calculation. For clarity the DOS curves are systematically shifted 2 states eV$^{-1}$ atom$^{-1}$ in both spin channels for each increment of 0.1 in $x$, and the DOS maxima are cut at 4 states eV$^{-1}$ atom$^{-1}$.

FIG. 7. The total energy for LaCoO$_3$ as a function of constrained spin moment obtained for a volume corresponding to 1248 K.

FIG. 8. The difference in Fermi energy of majority and minority spin states of LaCoO$_3$ as a function of magnetic moment for the volume corresponding to 4K.

FIG. 9. Calculated magnetic moments for La$_{1-x}$Sr$_x$CoO$_3$ vs $x$ obtained by supercell and VCA calculations from the generalized-gradient-corrected relativistic full-potential linear muffin-tin orbital method and from FSM calculations according to the FPLAPW method. Experimental magnetic moments are taken from neutron-scattering measurements (Ref. 17) at 4.2 K and magnetization measurements (Ref. 20) at 5 K.
DOS (states eV$^{-1}$ f.u.$^{-1}$)

Energy (eV)

(a) HS

(b) IS

(c) LS
LaCoO$_3$ and SrCoO$_3$ DOS (states eV$^{-1}$ spin$^{-1}$)
Magnetic moment (\(\mu_B\) f.u.\(^{-1}\))

Energy (eV f.u.\(^{-1}\))

(a) SrCoO\(_3\)

(b) La\(_{0.5}\)Sr\(_{0.5}\)CoO\(_3\)

(c) LaCoO\(_3\)
La$_{1-x}$Sr$_x$CoO$_3$

Magnetic moment (µB/f.u.)

Energy (eV/f.u.)

$x=0$

$x=0.1$

$x=0.2$

$x=0.3$

$x=0.4$

$x=0.5$
La$_{1-x}$Sr$_x$CoO$_3$

Co-d DOS (states eV$^{-1}$ atom$^{-1}$) vs. Energy (eV) for different values of $x$: $x=0$, $x=0.1$, $x=0.2$, $x=0.3$, $x=0.4$, and $x=0.5$. The graphs show the density of states for these compositions, with energy levels ranging from $-12$ to $12$ eV and energy (eV) ranging from $-6$ to $2$. The dashed line indicates the Fermi level.
Moment (\(\mu_B\ f.u.^{-1}\))

\[\Delta E_F\ (\text{Ry.})\]
Magnetic moment ($\mu_B$/f.u.)

La$_{1-x}$Sr$_x$CoO$_3$

- VCA calculation
- Neutron scattering
- Supercell calculation
- Magnetization
- FSM VCA calculation