Theoretical investigation of excitonic magnetism in LaSrCoO$_4$

J Fernández Afonso, A Sotnikov and J Kunes

1 Institute of Solid State Physics, TU Wien, Wiedner Hauptstr. 8, 1020 Vienna, Austria
2 Institute of Physics, Czech Academy of Sciences, Na Slovance 2, 182 21 Praha 8, Czechia

E-mail: kunes@ifp.tuwien.ac.at

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Abstract
We use the LDA+U approach to search for possible ordered ground states of LaSrCoO$_4$. We find a staggered arrangement of magnetic multipoles to be stable over a broad range of Co 3d interaction parameters. This ordered state can be described as a spin-density-wave-type condensate of $d_{xy} \otimes d_{x^2-y^2}$ excitons carrying spin $S = 1$. Further, we construct an effective strong-coupling model, calculate the exciton dispersion and investigate closing of the exciton gap, which marks the exciton condensation instability. Comparing the layered LaSrCoO$_4$ with its pseudo cubic analog LaCoO$_3$, we find that for the same interaction parameters the excitonic gap is smaller (possibly vanishing) in the layered cobaltite.

Keywords: excitonic magnetism, Co$^{3+}$, linear spin-wave approximation

(Some figures may appear in colour only in the online journal)

1. Introduction

Perovskite cobaltites from the La$_{1-x}$Sr$_x$CoO$_3$ family have attracted much attention due to their peculiar magnetic and transport properties. In particular, the physics of the $x = 0$ member with Co$^{3+}$ formal valence remains a subject of debate. Recently, we have proposed that mobility of intermediate spin (IS) excitations plays an important role in the physics of LaCoO$_3$ [1] and that the material is close to an excitonic condensation (EC) instability [2–4]. The EC scenario is also being discussed as the origin of the experimentally observed phase transition [5], in the materials from Pr$_{0.5}$Ca$_{0.5}$CoO$_3$ family [6–10].

The layered cobaltites La$_{2-x}$Sr$_x$CoO$_4$ are much less studied although they may exhibit similar physics. The parent compound La$_2$CoO$_4$, formal valence Co$^{2+}$, is an antiferromagnetic insulator with a Néel temperature of 275 K [11]. The hole doping suppresses the Néel temperature and an incommensurate magnetic order appears for $x > 1/3$. The doping range $1/3 < x < 1/2$ is particularly interesting due to a holegauge-shaped spectrum of magnetic excitations [12] invoking similarities to currate superconductors. The stoichiometric compound LaSrCoO$_4$ with Co$^{3+}$ formal valence is relatively less studied due difficulties in sample preparation [13]. The optical [14] and transport measurements [15, 16] for LaSrCoO$_4$ show a good insulator with a charge gap of about 1 eV. The inverse magnetic susceptibility has a concave shape with pseudo linear $T$-dependence below 150 K corresponding to $\mu_{eff} = 2.3–2.6 \mu_B$ and almost vanishing Weiss temperature ranging from 27 K [16, 17] to 30 K [15]. The authors of [17] reported magnetic anomaly at 7 K, which they interpreted as formation of spin glass. The specific heat data indicate only a modest entropy release of 0.06R at the supposed transition.

Theoretical studies of LaSrCoO$_4$ are even more limited. Wang et al [18] applied the unrestricted Hartree–Fock approach to a tight-binding model with Hubbard interaction in order to study various spin-state patterns and identified the high-spin–low-spin (HS–LS) order to be the most likely ground state.

In this work, we use the LDA+U density-functional method to investigate possible ordered ground states of LaSrCoO$_4$, in particular the excitonic condensate. Furthermore, we employ the strong-coupling expansion to derive a low-energy effective model in the Hilbert space spanned by the LS, IS, and HS states and compare it to an analogous model of LaCoO$_3$. Similarly to our results for LaCoO$_3$, we find a stable excitonic ground state for realistic on-site interaction parameters. Comparison to LaCoO$_3$ shows that for the same interaction parameters we obtain a smaller or vanishing excitonic gap in LaSrCoO$_4$, which implies that LaSrCoO$_4$ is closer to the excitonic instability or the excitonic condensate is actually realized.
The paper is organized as follows: in section 2 we introduce the excitonic order parameter and explain the computational methods used in this work. In section 3.1 we present DFT calculations and investigate the stability of the excitonic condensate with and without spin–orbit coupling for different interaction parameters. Section 3.2 is devoted to the strong-coupling analysis of dispersion of bosonic excitations in the normal state, the softening of which marks the onset of condensation.

2. Computational method

2.1. LDA+U

Electronic structure calculations in this paper are performed in the framework of the density functional theory (DFT) by using local density approximation (LDA) [19, 20]. The effect of Coulomb interaction within the 3d shell of Co is described by means of LDA+U scheme with the so-called fully localized limit double-counting correction [21]. The spin polarization enters the orbital-dependent potential only while leaving the LDA exchange-correlation potential unpolarized. The calculations are carried out with the WIEN2k [22] package.

The La$_2$-Sr$_x$CoO$_4$ structure consists of single layers of CoO$_6$ corner-sharing octahedra separated by a random distribution of La and Sr ions (see figure 1(a)). To simulate the LaSrCoO$_4$ compound, we employ the virtual crystal approximation (VCA) [23, 24] that sets the atomic number of La to 56.5. Anticipating the possibility of the staggered order [25], we choose a unit cell allowing for the CoO$_6$ planes. The muffin-tin radii (in bohrs) are the following: 2.50 for La, 1.91 for Co, and 1.65 for O. The plane wave cutoff is set to $R_{\text{mt}}K_{\text{max}} = 6$.

In search for possible ordered solutions we start from several different initial states with broken symmetry: the staggered excitonic and spin-state (LS–HS) orders. The calculations are performed with and without spin–orbit coupling (SOC). The anticipated EC order with the $d_{x^2−y^2} \otimes d_{xy}$ orbital symmetry is described by a three-dimensional complex vector $\phi$ with components

$$\phi_\beta = \langle \hat{O}_\beta' \rangle + i \langle \hat{O}_\beta'' \rangle = \phi'_\beta + i \phi''_\beta,$$

expressed in terms of the hermitian operators

$$\hat{O}_\beta = \sum_{\sigma,\sigma'=\uparrow,\downarrow} \tau_\beta \sigma \sigma' (c^{\dagger}_{2\sigma} c^{\dagger}_{2\sigma'} - c^{\dagger}_{-2\sigma} c^{\dagger}_{-2\sigma'})$$

and

$$\hat{O}_\beta'' = \sum_{\sigma,\sigma'=\uparrow,\downarrow} \tau_\beta \sigma \sigma' (c^{\dagger}_{-2\sigma} c^{\dagger}_{2\sigma'} - c^{\dagger}_{2\sigma} c^{\dagger}_{-2\sigma'})$$

where $c^{\dagger}_{\alpha\sigma}$ ($c_{\alpha\sigma}$) are the creation (annihilation) operators for 3d electrons on the same Co atom (the site indices are not shown for the sake of simplicity). The orbital index $m$ refers to the spherical harmonic $Y_{2m}$ basis with the $z$ quantization axis (see figure 1(b)). The Pauli matrices $\tau_\beta$ ($\beta = x, y, z$) capture the spin-triplet character of the EC order. A nonzero $\phi$ gives rise to a spin-density distribution on the Co site with vanishing spin moment per atom that is shown in figure 1(b).

2.2. Strong coupling expansion

The starting point of our strong-coupling analysis is the Hubbard Hamiltonian for the $d$-shells of Co

\[ \text{Hubbard Hamiltonian for the } d \text{-shells of Co} \]
We diagonalize the local Hamiltonian $H_{\text{lat}}^{i(\alpha)}$ to obtain atomic eigenenergies $E_\gamma^{(q)}$ and eigenstates $|\Psi^{(q)}_\gamma\rangle$, where $q$ is the number of electrons in the $d$-shell and $\gamma$ is the state index. Next, we use the set of the lowest 25 states of the $d^9$ configuration containing LS, IS, and HS as an active space and treat the non-local terms $H_{\text{int}}^{(r)}$ as a perturbation. Performing the Schrieffer–Wolff transformation [28] to the second order, we arrive at the following bosonic Hamiltonian:

$$H_{\text{eff}} = \sum_{q,\gamma,\alpha,\beta} (\varepsilon_1^{(q)} d_{\alpha i}^\dagger d_{\beta j} + \varepsilon_2^{(q)} d_{\alpha i}^\dagger d_{\beta j}^\dagger \delta_{ij}^\dagger) + H.c. + H_{\text{int}}.$$

Here, we consider the LS state as the bosonic vacuum, $|0\rangle = |\delta^0\rangle |0\rangle$, and other states from the low-energy manifold of the $d^9$ configuration as different bosonic flavors $\alpha$ characterized by the corresponding creation (annihilation) operators $d_{\alpha i}^\dagger$ ($d_{\alpha i}$) on the lattice site $i$.

In equation (6) we distinguish three types of terms. The first one with the amplitude $\varepsilon_1$ corresponds to the renormalized on-site energies of bosons (for $i = j$),

$$\varepsilon_1^{\alpha\beta} = E_\alpha^{(6)} \delta_{\alpha\beta} + \sum_{r,\nu,\nu',\pm 1} M_{\alpha\beta,\nu,\nu'}^{(r)(6+\nu)} / E_{\alpha\beta,\nu,\nu'}^{(6+\nu)},$$

and their hopping amplitudes on the LS background (for $i \neq j$),

$$\varepsilon_2^{\alpha\beta} = \frac{1}{2} \sum_{r,w,\nu,\nu',\pm 1} \left( \frac{1}{E_{\alpha\beta,\nu,\nu'}^{(6+\nu)}} + \frac{1}{E_{\beta\alpha,\nu,\nu'}^{(6+\nu)}} \right) M_{\alpha\beta,\nu,\nu'}^{(r)(6+\nu)}.$$

The second term with the amplitude $\varepsilon_2$ corresponds to the non-local pair-creation processes,

$$\varepsilon_2^{\alpha\beta} = \frac{1}{2} \sum_{r,w,\nu,\nu',\pm 1} \left( \frac{1}{E_{\alpha\beta,\nu,\nu'}^{(6+\nu)}} + \frac{1}{E_{\beta\alpha,\nu,\nu'}^{(6+\nu)}} \right) M_{\alpha\beta,\nu,\nu'}^{(r)(6+\nu)}.$$

The last term $H_{\text{int}}$ in equation (6) characterizes all other processes with nonzero amplitudes that appear due to Schrieffer–Wolff transformation. Note that the main contributions to this term originate from (density-density and magnetic/orbital exchange) interactions between different bosonic flavors. Including the effect of $H_{\text{int}}$ on the exciton dispersion/spectra is a non-trivial task and goes beyond the scope of the current paper.

Here, we focus on the excitonic instability of the normal ground state that has dominantly the LS character. The small $\varepsilon_2$ allows us to neglect the density of $d$-bosons in the ground state as well as in the lowest excited states. The elementary excitations are then approximately described by the bilinear part of the Hamiltonian (6), neglecting higher-order terms (with three and four operators $d_{\alpha i}$) contributing to $H_{\text{int}}$. Using the same argument we drop the hard-core constraint on $d$ bosons and proceed with the linearized spin-wave approach [29], which provides access to momentum dependencies of bosonic (IS and HS) excitations in the lattice. The excitation spectrum obtained in this way corresponds to one-boson excitations of the normal ground state, thus cannot account for effects originating from thermal occupation of IS and HS states.

3. Results

3.1. LDA + U calculations

LDA + U calculations without SOC lead to a non-zero $\phi'$ with staggered arrangement in the Co-O plane. We have verified that different spatial orientations of $\phi'$ are numerically equivalent. The ground state can be described as a polar excitonic condensate [30], or, more specifically, as a spin-density wave excitonic condensate in the classification of Halperin and Rice [4]. The corresponding spin-density distribution around Co site, which gives vanishing atomic moment, is shown in figure 1(b).

The stability of the EC long-range order as a function of $U$ and $J$ is summarized in figure 2. The overall shape of the phase diagram resembles the results for cubic LaCoO$_3$ [25]. We find ordered solutions in both the weak coupling (metallic) and the strong coupling regimes with a wedge of the normal phase at intermediate $U$ and small $J$. The modification of spectral density due to the excitonic condensation is shown in figure 3.

Introducing SOC breaks the spin-rotational symmetry. The non-zero value of $\langle \chi_\sigma | \hat{l}_z | \chi_\sigma \rangle / \langle \chi_\sigma | \chi_\sigma \rangle = \varepsilon^2 - \varepsilon^2$ can be viewed as a source field for $\phi''_c$ [25]. Upon inclusion of SOC, the EC state splits into two distinct stable solutions.
$\varphi \parallel j = (−1)^j(0 0 \lambda_0') + i(0 0 \lambda_0'')$, 
$\varphi \perp j = (−1)^j(\lambda_0' \lambda_0'') + i(0 0 \lambda_0'')$,

where $(-1)^j$ indicates the staggered in-plane arrangement. The $\varphi \parallel$ and $\varphi \perp$ states have different symmetries, reflected, for example, in the appearance of small but finite staggered moment $m_j \propto \varphi' \times \varphi''$ of 0.05 $\mu_B$ for $\varphi \perp \neq 0$. No ordered moment arises in the $\varphi \parallel$ solutions. The total energies shown in table 1 for $U = 3.95$ eV and $J = 0.95$ eV (the star-shaped point in figure 2) favor the $\varphi \parallel$ order. In this parameter regime we have also searched for other possible two sublattices solutions such as antiferromagnetic or spin-state order (LS-HS) [18]. All our calculations converged to the $\varphi \parallel$ solutions. The calculations were performed without lattice relaxation.

### Table 1. Comparison of the order parameters $|\varphi'|$ and $|\varphi''|$ and the energy difference $\Delta E$ (compared to the normal state) of the ordered solutions at $U = 3.95$ eV and $J = 0.95$ eV.

| Solution Approach | $|\varphi'|$ | $|\varphi''|$ | $\Delta E$ (meV f.u.$^{-1}$) |
|-------------------|---------|-----------|-----------------|
| EC LDA+U          | 0.289   | 0.000     | −14.25          |
| EC$^{\perp}$ LDA+U+SOC | 0.274   | 0.098     | −14.83          |
| EC$^{\parallel}$ LDA+U+SOC | 0.299   | 0.096     | −17.58          |

3.2. Strong coupling analysis

In figure 4 we show the set of eigenenergies $E^{(6)}_\gamma$ of the Hamiltonian (4) corresponding to the lowest atomic multiplets of LaSrCoO$_4$ as a function of the Hund’s coupling $\tilde{J}$. The three intermediate-spin $d_{xy} \otimes d_{x^2−y^2}$ states (IS$_2$) have the highest atomic energies among 25 lowest states in the region of realistic values of Hund’s coupling $\tilde{J}$ due to cubic crystal field ($\Delta = 1.594$ eV) and additional tetragonal splittings of the $t_{2g}$ and $e_g$ states (0.103 eV and 0.384 eV, respectively). This seems to prevent the IS$_2$ states from condensation. However, as we show below, the renormalization of on-site energies by virtual hopping processes reverses the order of atomic multiplets, i.e. when placed on the lattice the IS$_2$ excitations have lower energies than the IS$_1$ ones.

Next, we compute the amplitudes (7)–(9) and diagonalize the bilinear part of the effective Hamiltonian (6). In figures 5(a)–(e) we show the dispersions of elementary (IS- and HS-like) excitations of (6) obtained for different values of $\tilde{U}$ and $\tilde{J}$. While the IS excitations can move on the LS background, the HS excitations cannot, and the deviation from completely flat HS bands is due to HS-IS mixing through spin–orbit coupling. Note that the spin-orbital character of the excitations remains approximately fixed along the individual branches due to conservation of orbital and spin flavors in the nearest-neighbor kinetic exchange processes. Small mixing...
and thus momentum dependence arises due to spin–orbit coupling.

The interaction parameters were chosen so that the solution is at the verge of excitonic instability, i.e. normal solutions with a tiny gap, vanishing of which determines the phase boundary in figure 5(f). Variation of $\tilde{J}$ enters predominantly through the changes of atomic multiplet energies in figure 4. Variation of $\tilde{U}$ affects both the hopping amplitudes (bandwidths) and the renormalization of site energies (band shifts). The renormalizations of different states scale differently with $\tilde{U}$ depending of the number and amplitudes of the virtual hopping process for a given state on a LS background.

The influence of the pair-creation term is shown in the inset of figure 6. Due to bosonic nature of excitations, this term effectively acts as an ‘attraction’ between bands $\epsilon_\gamma(k)$ and their mirror images $-\epsilon_\gamma(k)$. Only when their separation is comparable or smaller than characteristic amplitudes determined by equation (9), the pair creation/annihilation processes become important. These amplitudes for the cases

![Figure 5](image5.png)

**Figure 5.** (a)–(e) Dispersions of the IS and HS excitations at different $\tilde{U}$ and $\tilde{J}$ (given in eV) and $\zeta = 56$ meV. (f) The corresponding phase diagram obtained following the disappearance of the exciton gap.

![Figure 6](image6.png)

**Figure 6.** Dispersions of the IS and HS excitations for LaSrCoO$_4$ (left) and cubic LaCoO$_3$ (right) at $\tilde{U} = 1.96$ eV, $\tilde{J} = 0.62$ eV, and $\zeta = 56$ meV. Inset: IS$_2$ dispersion with (solid lines) and without (dashed lines) pair-creation contributions.
under study are typically of the order of few meV, thus the effect becomes noticeable close to the minimum of the IS$_2$ energy dispersion.

To compare with LaCoO$_3$, we repeat the analysis for the hypothetical cubic structure of [25] and the same $\tilde{U}$ and $\tilde{J}$ values, see figure 6. We find the excitation gap is larger in the cubic structure due to narrower IS band. Moreover, the HS excitations in the layered structure are located at substantially higher energy than in its cubic counterpart. This is because the out-of-plane nearest-neighbor processes, which contribute to renormalization of the HS local energies in the cubic structure, are missing in the layered system. Similar processes play a minor role for the IS$_2$ excitations and thus the renormalizations in the cubic and layered structures are comparable.

More extensive numerical analysis confirms the general tendency that with a continuous decrease of $\tilde{U}$ and $\tilde{J}$ parameters, the EC instability first appears in the layered compound and only then in LaCoO$_3$. This agrees well with comparison of phase boundaries for critical $U$ and $J$ values in figure 2 with the values for LaCoO$_3$ published in [25] that are both obtained within the LDA+U approach.

4. Conclusions

We have performed LDA+U calculations for LaSrCoO$_4$ that amount to a static mean-field treatment of the excitonic order in this compound. We find excitonic condensate to be a stable solution with a total energy lower than the one of normal state over a large part of the studied $U$-$J$ phase diagram. The generally used $U$ and $J$ values fall close to the boundary of the region of EC stability. The stable EC solutions are of the spin-density-wave type with a $d_{x^2-y^2} \otimes d_{x^2-y^2}$ orbital symmetry and out-of-plane spin polarization. Comparison to LaCoO$_3$ by means of the linear spin-wave treatment of the effective strong-coupling model suggest that the layered cobaltite is closer to the excitonic instability or that the EC order is possibly realized. Investigations of behaviour under pressure and in high magnetic fields [31] are highly desirable.

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ORCID iDs

J Kuneš @ https://orcid.org/0000-0001-9682-7640

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