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(Received 17 July 2012; published 5 November 2012)

We use the dynamical mean-field theory to study a *p-d* Hubbard Hamiltonian for LaCoO₃ derived from *ab initio* calculations in local density approximation (LDA + DMFT scheme). We address the origin of local moments observed above 100 K and discuss their attribution to a particular atomic multiplet in the presence of covalent Co-O bonding. We show that in solids such attribution, based on the single ion picture, is in general not possible. We explain when and how the single ion picture can be generalized to provide a useful approximation in solids. Our results demonstrate that the apparent magnitude of the local moment is not necessarily indicative of the underlying atomic multiplet. We conclude that the local moment behavior in LaCoO₃ arises from the high-spin state of Co and explain the precise meaning of this statement.

DOI: [10.1103/PhysRevB.86.195104](https://doi.org/10.1103/PhysRevB.86.195104)

PACS number(s): 71.10.Fd, 75.30.Wx, 71.30.+h, 71.28.+d

I. INTRODUCTION

LaCoO₃ and related compounds have been much studied for half a century.¹⁻³ Their strongly temperature dependent magnetic and transport properties have been eluding complete theoretical description so far.⁴⁻¹⁰ An apparent band insulator below 50 K, LaCoO₃ exhibits a local moment magnetic response above 100 K while the charge gap continuously disappears between 450 and 600 K.¹¹⁻¹³ This behavior points to an important role played by the electronic correlations as common among transition metal oxides. The correlated nature of LaCoO₃ reveals itself also in the formation of atomic-scale inhomogeneities with large magnetic moments upon moderate hole doping.^{14,15} The picture of thermal evolution of LaCoO₃ as an entropy driven crossover from a nonmagnetic to a magnetic state of Co³⁺ ion has been generally accepted. However, the actual why's and how's are far from settled. The main open questions include the following. (i) Which atomic multiplet is responsible for the formation of local moments? (ii) Does the lattice thermal expansion actively contribute to the spin-state transition or is it merely a slave to the changes of the electronic structure? (iii) Why do the crossovers to local moment paramagnet and to bad metal happen at different temperatures? In this work we use the combination of the density functional band structures with the dynamical mean-field theory, known as LDA + DMFT,¹⁶⁻²¹ to address the former two questions. We discuss in detail the attribution of local moment behavior to a particular atomic multiplet in systems with covalent bonds, a question of general importance in oxide physics.

The magnetic susceptibility of LaCoO₃ is usually analyzed in terms of the lowest multiplets of an isolated Co³⁺ ion in octahedral crystal field:²² the low-spin (LS) ¹A₁ (*t*⁶*e*⁰), the intermediate-spin (IS) ³T₁ (*t*⁵*e*¹), or the high-spin (HS) ⁵T₂ (*t*⁴*e*²) states. The energy differences between the multiplets are controlled by the crystal-field (CF) splitting and the intra-atomic exchange *J*. While the LS singlet ground state is undisputed (at least for low temperature crystal structures) the nature of the first excited state is still a subject of debate. Goodenough²³ attributed the appearance of local moment to

population of the HS state. Heikes *et al.*,¹ on the other hand, proposed the IS scenario, which became popular²⁴⁻²⁶ after Korotin *et al.*⁴ obtained an IS ground state for expanded lattice with LDA + U calculation, contrary to a simple ligand-field theory. More recent experiments make a strong case for the HS scenario. The electron spin resonance shows a triplet excited state with a large *g* factor of 3.35–3.55, which is consistently explained in the HS scenario invoking the effect of spin-orbit coupling.^{5,27} The x-ray absorption spectra (XAS) and magnetic circular dichroism at the *L*_{2,3} edge of Co²⁸ also select the HS scenario. However, several authors^{10,28-30} pointed out that in order to interpret the magnetic susceptibility, specific heat, or XAS data in the HS scenario a rather strong temperature dependence of the crystal field has to be assumed. In other words, the experimentally deduced increase of the HS population is significantly slower than anticipated with a fixed crystal field. The implication is that the apparent crystal field grows with temperature. This is somewhat unexpected since the expansion of the Co-O bond which accompanies the spin crossover should reduce the crystal field. A possible explanation of this puzzling feature is provided by an interatomic repulsion between the HS states, which is equivalent to attraction between HS and LS states.^{10,29,30} Breathing lattice distortion proposed by Raccah and Goodenough,³ studied in detail by Bari and Sivardière,³¹ provides a mechanism. Knížek *et al.*³² used LDA + U calculations to argue for HS-LS attraction. Recently, a purely electronic mechanism of HS-LS attraction was observed by two of us³³ in a two band Hubbard model and by Zhang *et al.*³⁴ in LaCoO₃ specific calculation.

It is well known that the effective crystal field in transition metal oxides is largely due to hybridization with ligands, i.e., generated by hopping of predominantly *e_g* electrons between the metal and oxygen sites. This effect is particularly pronounced in LaCoO₃ and leads to charge fluctuations on the Co site. Therefore, it seems natural to question descriptions based on an isolated ion. How does one define and distinguish HS and IS states when sizable charge (valence) fluctuations are present? Or, more precisely, is it possible to express the *T*-dependent susceptibility as a sum of contributions from different atomic states? We will show in Sec. II C that in

a solid the answer is negative in general. However, in the insulating phase of LaCoO₃ the notion of LS, IS, and HS states can be preserved when these are generalized to include the hybridization induced charge fluctuations. The *T*-dependent paramagnetic moment can be to a good accuracy approximated by a *T*-independent HS moment multiplied by a *T*-dependent weight. Importantly, the magnitude of this effective moment differs from the free ion value.

The role of the lattice thermal expansion poses a chicken-and-egg question about the relationship between the spin-state transition and the anomalous lattice expansion.^{26,35,36} While the transition to the magnetic state, both IS and HS, weakens the Co-O bond and thus leads to its expansion, stretching the Co-O bond reduces the effective CF splitting and thus favors a magnetic state. Therefore, there is a positive feedback between these two effects. To include the lattice response directly into our calculations is not computationally feasible at the moment. Therefore, we have performed calculations for several lattices corresponding to experimental crystal structures at different temperatures. By comparing the *T* dependence of the spin susceptibilities on these lattices we find that experimentally observed variation of Co-O bond length has a pronounced effect on the electronic properties.

Inclusion of thermal effects in “first principles” density functional approaches is notoriously difficult. Therefore, the existing studies are either limited to the *T* = 0 LS phase³⁷ or assume that temperature enters only through the lattice thermal expansion.^{4,32} The only serious attempt to explicitly include temperature in such a calculation was made by Eder¹⁰ using the variational cluster approximation (VCA). The VCA and DMFT methods share many formal similarities, but involve different approximations. VCA is, in principle, an exact method for calculation of one-particle properties, but, as pointed out in Ref. 10, the relevance of multiplets populations obtained from a reference CoO₆ cluster is a conjecture, which calls for verification with other methods. DMFT, on the other hand, treats one-particle and multiparticle correlations on the same footing, but becomes exact only in the limit of vanishing nonlocal correlations (infinite dimension). Recently, DMFT was applied to LaCoO₃ to study the effect of varying interaction strength and pressure.³⁴

II. METHODS

A. Model

Multiband Hubbard Hamiltonian with the two-particle interaction within the Co 3*d* shell is used to describe LaCoO₃. The one-particle part of the Hamiltonian, which spans the Co 3*d* and O 2*p* orbitals, has been constructed from the local density approximation (LDA) to the density functional theory. The non-spin-polarized band structure obtained with WIEN2k³⁸ was transformed into the Wannier basis representation with WIEN2WANNIER³⁹ and WANNIER90⁴⁰ codes. The Hamiltonian in this representation reads

$$H = \sum_{k\sigma} (h_{k,\alpha\beta}^{dd} d_{k\alpha\sigma}^\dagger d_{k\beta\sigma} + h_{k,\gamma\delta}^{pp} p_{k\gamma\sigma}^\dagger p_{k\delta\sigma} + h_{k,\alpha\gamma}^{dp} d_{k\alpha\sigma}^\dagger p_{k\gamma\sigma} + h_{k,\gamma\alpha}^{pd} p_{k\gamma\sigma}^\dagger d_{k\alpha\sigma}) + \sum_{i,\sigma,\sigma'} U_{\alpha\beta}^{\sigma\sigma'} n_{i\alpha\sigma}^d n_{i\beta\sigma'}^d. \quad (1)$$

Here $d_{k\alpha\sigma}$ and $p_{k\gamma\sigma}$ are Fourier transforms of the annihilation operators $d_{i\alpha\sigma}$, $p_{i\gamma\sigma}$ which destroy the *d* or *p* electron with the orbital index α or γ and the spin index σ in the *i*th unit cell, $n_{i\alpha\sigma}^d$ are the corresponding occupation number operators, and $h_{k,\alpha\beta}^{ab}$ are the corresponding matrix elements of the one-particle LDA Hamiltonian.

The $U_{\alpha\beta}^{\sigma\sigma'}$ are the density-density matrix elements in the e_g - t_{2g} basis of the full Coulomb interaction⁴¹ parametrized with U (Slater parameter F_0) and Hund’s exchange J [connected with the Slater parameters F_2 , F_4 as $J = (F_2 + F_4)/14$, $F_4/F_2 = 0.625$]. The screened values of $U = 6.0$ eV and $J = 0.8$ eV have been obtained using the constrained density functional theory (cDFT), described in detail in Ref. 42. To the DFT potential an orbitally dependent term was added, which shifts by a small amount the energy of selected Wannier functions (WFs). Due to this shift, occupation of the WFs in question is changed and the Coulomb interaction parameters are then determined as a derivative of the site energy with respect to the occupation.

In the following calculations are performed with cDFT values of U and J . Calculations, where U and J were varied, are also reported to assess the stability of the results.

The h^{dd} diagonal elements were modified to account for the static part of the interaction, double-counting correction,

$$h_{k,\alpha\beta}^{dd} = h_{k,\alpha\beta}^{0,dd} - (N_{\text{orb}} - 1)\bar{U}\bar{n}\delta_{\alpha\beta}, \quad (2)$$

where \bar{n} is the average self-consistent occupancy per Co:*d* orbital, \bar{U} is the orbital averaged interaction energy, and N_{orb} is the total number of interacting orbitals on a single site (10 in our case).⁴³ This is equivalent to subtracting the orbitally averaged Hartree potential felt by the *d* electrons.

B. DMFT calculations and one-particle spectra

The one-particle Green’s function of the Hamiltonian (1) is found by iteratively solving the DMFT equations on the Matsubara contour. The auxiliary impurity problem is solved by the continuous time quantum Monte Carlo (CT-QMC) method in the hybridization expansion formulation⁴⁴ using the implementation based on free-access package ALPS.^{45,46} The Wang-Landau reweighting^{47,48} was employed in order to ensure the ergodicity of the simulations for some parameter values, in particular at low temperatures and close to the spin state transition.

Once the calculation was converged we have evaluated the one-particle spectra in real frequency and analyzed the impurity dynamics and spin susceptibility. For the former analytic continuation is necessary. To this end we have employed the maximum entropy method in two modes: (i) continuation of the local Green’s function from the imaginary time τ to real frequency ω and (ii) continuation of the local self-energy from the Matsubara frequency $i\omega_n$ to ω . For the latter we have used the statistical error estimates following Ref. 49. The former was used to cross-check the results of (ii) and the spectra are not shown in the paper. Analytic continuation of self-energy has several attractive features, such as being exact in the noninteracting limit, providing a direct access to the *k*-resolved and ligand spectra, and smearing out the lifetimes (imaginary part of the self-energy) but not the quasiparticle dispersions.

C. Susceptibility and local moments

To analyze the on-site dynamics we have studied two additional quantities. First, the state weights⁵⁰ which are the diagonal terms of the site-reduced density matrix, i.e., expectation values of the projection operators on the atomic (many-body) states $\hat{P}_\mu = |\mu\rangle\langle\mu|$. In the present case of the density-density interaction the site-reduced density matrix is diagonal in the occupation number basis. Therefore, the knowledge of the state weights allows us to evaluate the expectation value of any local operator, e.g., the instantaneous local moment $\langle\hat{m}_z^2\rangle = \sum_\mu m_z^2(\mu)\langle\hat{P}_\mu\rangle$ with $m_z(\mu) = \langle\mu|\hat{m}_z|\mu\rangle$.

Second, we define the imaginary time state-state correlation matrix $C_{\mu\nu}(\tau)$ and its time average $\Pi_{\mu\nu}$,

$$C_{\mu\nu}(\tau) = \langle\hat{P}_\mu(\tau)\hat{P}_\nu(0)\rangle, \quad (3)$$

$$\Pi_{\mu\nu} = T \int_0^\beta d\tau C_{\mu\nu}(\tau),$$

where $\beta = 1/T$ is the inverse temperature. The correlation matrix allows us to analyze the local response functions (via fluctuation-dissipation theorem) and decompose them into different contributions. In particular, we will be interested in the local spin susceptibility χ , which in the paramagnetic state can be expressed as

$$\chi = \int_0^\beta d\tau \langle m_z(\tau)m_z(0) \rangle$$

$$= \frac{1}{T} \sum_{\mu,\nu} m_z(\mu)m_z(\nu)\Pi_{\mu\nu}. \quad (4)$$

The second expression shows that in general the local magnetic response cannot be decomposed into contributions of atomic states, but pairs of states must be considered. Decomposition into individual states contributions is possible only if $C_{\mu\nu}(\tau)$ can be made diagonal, e.g., in an isolated atom.

Discussing briefly the physical meaning of these quantities we start by pointing out that in the course of time a given atom visits various quantum-mechanical states as a result of statistical (thermal) fluctuations and quantum-mechanical (causal) evolution. The weight of a given state is a relative measure of the time spent by the atom in this state, which does not distinguish between thermal fluctuations and causal evolution. The state-state correlations distinguish to some extent between these two effects as only states connected by causal evolution can have a nonzero cross term. The state weights can be obtained as row (or column) sums over $\Pi_{\mu\nu}$.

III. RESULTS AND DISCUSSION

A. Noninteracting band structure

We have considered the experimental distorted perovskite structure with $R\bar{3}c$ space group containing two formula units per unit cell. The structural parameters were taken from the x-ray measurements of Ref. 24. To assess the effect of lattice thermal expansion the calculations were repeated for the experimental structural parameters obtained at three different temperatures (denoted as τ_{lattice} in the following): 5, 450, and 750 K.

The octahedral crystal field splits Co:*d* states into six t_{2g} states at lower energy and four e_g states at higher energy.

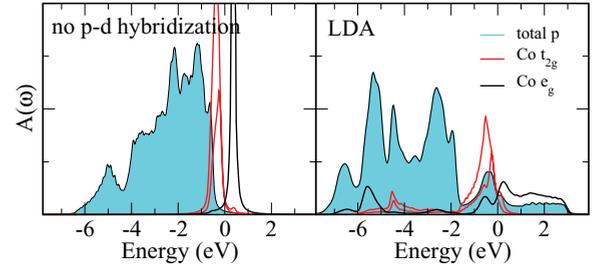


FIG. 1. (Color online) Calculated orbitally resolved spectral function [O:*p* (shaded cyan); Co: t_{2g} and e_g (red and black line)]. Left panel: the hybridization term $h_{k,\alpha\gamma}^{dp}$ of the Hamiltonian (1) is set to zero. Right panel: the LDA Hamiltonian in the Wannier basis.

The resulting orbitally resolved spectral density is shown in Fig. 1. The splitting is strongly contributed by the O:*p*-Co:*d* hybridization, as is clear from the comparison in Fig. 1, where the right and left panels show the spectral function with and without the *p*-*d* hybridization included. The on-site contribution to the crystal field splitting Δ (left panel of Fig. 1) is close to the value 0.7 eV extracted from the XAS measurements.²⁸ The *p*-*d* hybridization increases the distance between the centers of t_{2g} and e_g bands considerably. The band broadening, more pronounced for the e_g band, is another consequence. Matching O:*p* and Co:*d* features reflect formation of bonding and antibonding states. Stronger hybridization of the e_g orbitals compared to t_{2g} ones results from their larger spatial overlap with O:*p* orbitals. The t_{2g} band is further split to the e_g^{dp} doublet and the a_{1g} singlet due to a distortion from the octahedral symmetry. This splitting does not play an important role in our study, though. As in previous calculations a metallic ground state is incorrectly predicted by LDA.⁹

B. Thermal effects and lattice expansion

LDA + DMFT calculations were performed for several temperatures between 290 and 2320 K (β from 40 to 5 eV^{-1}). If not stated otherwise, the results are shown for $U = 6.0$ eV and $J = 0.8$ eV (obtained by cDFT calculations).

Local susceptibility. The local spin susceptibility χ , calculated from Eq. (4), is shown in Fig. 2(a) as a function of T . For $\tau_{\text{lattice}} = 750$ K the huge error bar at $T = 580$ K is due to a long autocorrelation time despite the Wang-Landau^{47,48} sampling. For all lattice parameters we observe an emergence of Curie-like susceptibility at high temperatures. The corresponding average spin moments $m_{\text{scr}} = \sqrt{T\chi}$ are shown in Fig. 2(b). As we calculate directly the local susceptibility (the local response to a field applied to a single site of the infinite crystal) the intersite exchange does not enter the definition of the local moment. Figure 2(b) suggests a gradual thermal population of a magnetic state. The lattice expansion clearly favors the magnetic state and the experimentally observed magnitude of the Co-O bond-length expansion has a sizable impact on our results.

Next, we discuss the temperature dependences $\chi(T)$, obtained from Eq. (4), for a fixed lattice. To get in touch with experimental observations we adopt the single ion expression

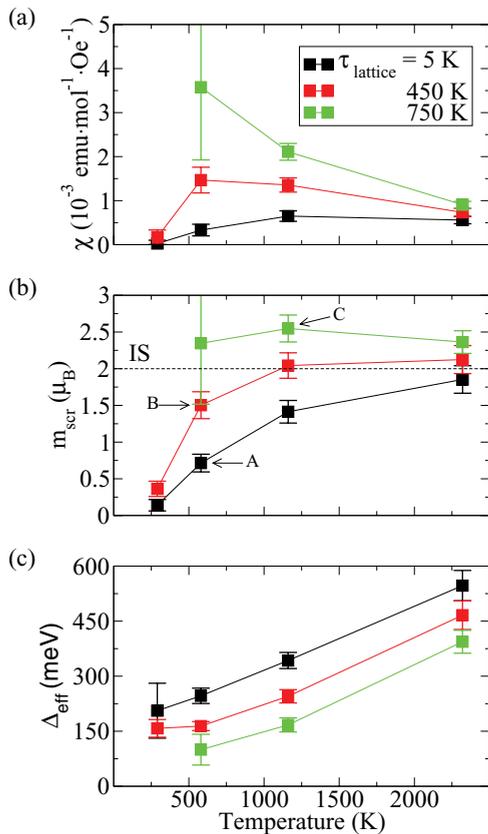


FIG. 2. (Color online) (a) Local spin susceptibility as a function of the temperature for different lattices (τ_{lattice}). (b) The corresponding screened spin moment. The dashed line indicates the value for the IS in the ionic limit. The letters A, B, C denote the solutions discussed in the text. (c) The apparent crystal field Δ_{eff} obtained from Eq. (5).

commonly used in analysis of experimental data,

$$\chi(T) = \frac{\mu^2}{T} \frac{\nu}{\nu + \exp[\Delta_{\text{eff}}(T)/T]}, \quad (5)$$

where μ and ν are the magnitude of the local moment and the multiplicity of the excited magnetic state and Δ_{eff} is the excitation energy with respect to the LS ground state. In Fig. 2(c) we show Δ_{eff} obtained from Eq. (5) using $\nu = 6$ and $\mu = 3.5$, which correspond to an Ising HS state, a choice explained later in the text. Like in the experiments^{28–30} and the VCA theory,¹⁰ our Δ_{eff} for a fixed lattice increases with temperature for the reason discussed below. In particular, the increase of Δ_{eff} by a factor of 3–5 over the spin-state crossover was deduced from XAS²⁸ and measurements of the magnetic susceptibility and heat capacity.³⁰

It is quite clear that our results do not provide an accurate quantitative description of LaCoO_3 as the spin crossover takes place at a too high temperature. This is not surprising since the present theory is unlikely to achieve the necessary ~ 10 meV accuracy without fine-tuning the material parameters by hand. The approximations of the model (such as the restriction to the density-density Coulomb interaction and neglect of the long-range or p - d interactions) limits the accuracy further. However, two important trends are revealed. First, the lattice response (expansion of O_6 octahedra around moment-carrying sites) acts as a positive feedback for generation of local

moments. Second, this is countered by a purely electronic effect, making addition of a local moment the harder the more local moments are already in the system; this is reflected in the increase of Δ_{eff} with the temperature [Fig. 2(c)]. This is another way of saying that there is a repulsive interaction between the magnetic sites in the LS background. We point out that in our calculation all O_6 octahedra are the same, which excludes a possible contribution of the breathing distortion.³ Indeed, Kyômen *et al.*²⁹ substituting Co with Al, Ga, and Rh came to the conclusion that electronegativity rather than ionic radius of the neighbors is the parameter which controls Δ_{eff} . We suggest the following picture based on the observation that a strong $\text{Co}:e_g\text{-O}$ bond favors LS state, and that in the Co-O-Co trimer the Co-O bonds share the central p_σ orbital. Due to this sharing the energy gain per Co-O bond in the trimer is less than the energy gain for an isolated Co-O bond. Therefore, breaking (weakening) one bond in the trimer makes the other bond stronger. Introducing a local moment on one Co site provides this bond breaking and strengthening the other bond favors the LS state.

Spectral functions. In Fig. 3 we compare the one-particle spectra of the low- T nonmagnetic state (left panels) and the high- T paramagnetic state (right). The orbital resolved spectra are displayed in the upper panels and the k -resolved spectra along the high symmetry directions are shown in the lower panels. The nonmagnetic spectrum resembles the LDA solution (Fig. 1), the main difference being a uniform (Hartree) shift of the e_g band. There is very little dynamical renormalization since the LS state is an approximate eigenstate of both the kinetic term (dominated by the crystal field) and the interaction term taken separately. The correlated nature of LaCoO_3 is revealed at elevated temperature. The thermal population of the excited atomic multiplets leads to a formation of local moments, which are incompatible with dispersive

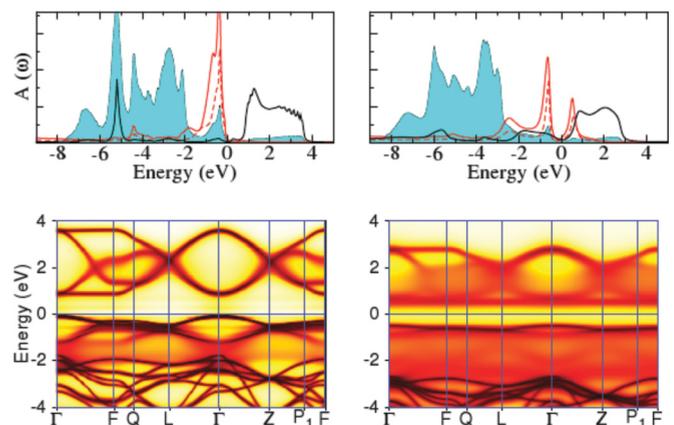


FIG. 3. (Color online) (Upper panels) Orbital-resolved spectral functions (states/eV/formula unit). $t_{2g}(e_g^\pi)$: solid red line; $t_{2g}(a_{1g})$: dashed red line; e_g : black line; $\text{O}:p$: cyan shaded area. The $\text{O}:p$ spectral function is downscaled by the factor of 2 to fit in the graph. (Lower panels) k -resolved spectral function $A_k(\omega)$ along the high symmetry directions. Left panels show the interacting nonmagnetic (low-spin) solution [denoted as A in Fig. 2(b); $T = 580$ K; $\tau_{\text{lattice}} = 5$ K] and the right panels display the paramagnetic solution (with a large content of high-spin atomic states) [denoted as C in Fig. 2(b); $T = 1160$ K; $\tau_{\text{lattice}} = 750$ K].

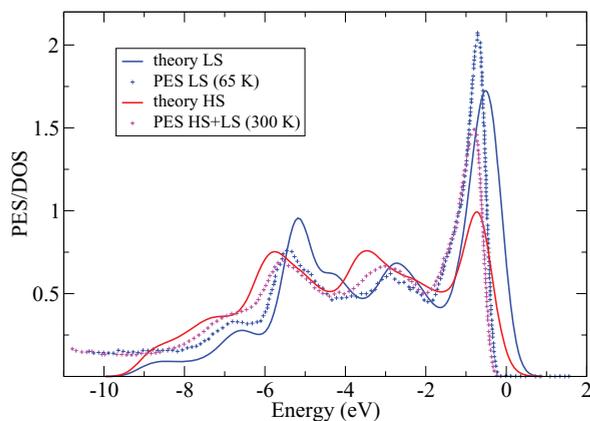


FIG. 4. (Color online) Comparison of the calculated density of states (lines) with the PES measurements (symbols). The calculated density denoted as LS is taken for $T = 580$ K, $\tau_{\text{lattice}} = 5$ K [A in Fig. 2(b)] and that denoted as HS for $T = 1160$ K, $\tau_{\text{lattice}} = 750$ K [C in Fig. 2(b)]. The measurements were taken at 65 K (denoted as LS) and 300 K (denoted as HS + LS, as the temperature is not high enough for the full spin-state crossover).

bands. As a result incoherent features appear in the spectra. The nature of the charge gap changes from a semiconductorlike gap between coherent valence t_{2g} and conduction e_g bands (left panel of Fig. 3) to a t_{2g} - t_{2g} gap (right panel of Fig. 3). The bottom of the conduction band is now defined by an incoherent t_{2g} excitation, the tail of which gradually fills the gap with the increasing temperature. The top of the valence manifold is formed by a renormalized dispersive t_{2g} band. This spectrum is consistent with the positive Seebeck coefficient^{51,52} indicating holes to dominate the electronic transport. Like the VCA results,¹⁰ the photoemission part of the spectra exhibits a transfer of spectral weight from the low-energy peak (~ 1 eV) to higher energies (~ 3 eV) observed experimentally.⁵³

In Fig. 4 we compare the calculated spectral functions to the photoemission spectra (corrected for surface effect) of Ref. 54 (Fig. 2.8). We have tuned the relative weights of the O: p and Co: d (1:5) spectra to mimic the effect of different absorption cross sections and added a Gaussian broadening of 0.2 eV to account for the experimental resolution. We find a good match of the major spectral features. We also observe consistent trends in both the O: d and Co: d parts of the spectra. The more pronounced difference of the two theoretical spectra reflects most likely a higher degree of LS to HS crossover.

C. Spin state analysis

Local state statistics. Next, we address the local dynamics at Co sites and whether it is meaningful to describe it in terms of the atomic states (such as LS, IS, and HS). The hybridization expansion CT-QMC solver is well suited to this task as it provides the site-reduced statistical operator (density matrix), referred to as state statistics.⁵⁰ This quantity describes the probability of finding an atom in a particular many-body state and the expectation value of any local operator can be easily obtained from it. We display schematically the atomic states important for the forthcoming discussion in Fig. 5.

There are many atomic states with non-negligible weights contributing to the partition function (Fig. 6). The total

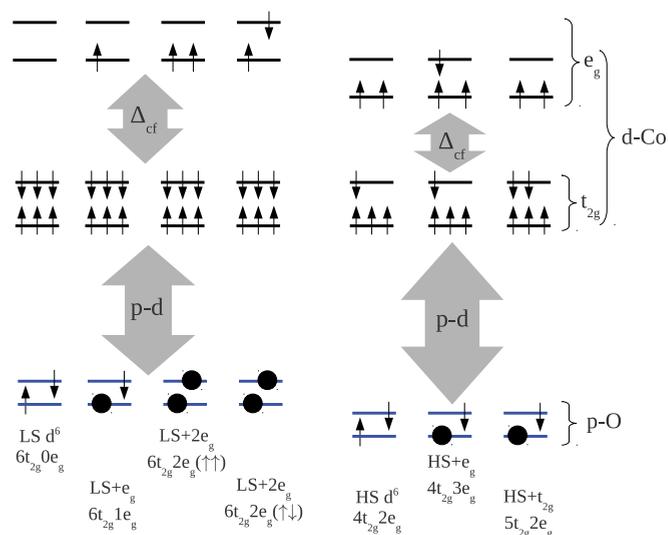


FIG. 5. (Color online) Atomic states at LS and HS configurations. The blue lines depict the oxygen p orbitals and the black circles denote the hole in O: p shell. The effects of the crystal field and Co: d -O: p hybridization are schematically depicted. In total four atomic states belong to LS block (see the left part of figure): (LS) all t_{2g} orbitals occupied, all e_g orbitals empty, (LS + e_g) in addition to LS single e_g orbital occupied, [LS + $2e_g$ ($\uparrow\uparrow$)] in addition to LS two e_g orbitals with the opposite spin orientation occupied, and [LS + $2e_g$ ($\uparrow\uparrow$)] in addition to LS two e_g orbitals with the parallel spin orientation occupied. All these states are accessible from LS via the e_g hybridization. For brevity we do not distinguish LS + $2e_g$ ($\uparrow\downarrow$) from LS + $2e_g$ ($\uparrow\uparrow$) from now on. In total three atomic states belong to HS block (see the right part of figure): (HS) all majority spin orbitals and one minority spin t_{2g} occupied, (HS + e_g) in addition to HS another minority spin e_g orbital occupied, and (HS + t_{2g}) in addition to HS another minority spin t_{2g} orbital occupied. All these states are accessible from HS via the e_g or t_{2g} hybridization.

contributions of different charge states (insets of Fig. 6) point to sizable valence fluctuations, which is related to finding substantial admixtures of $d^7\bar{L}$ and $d^8\bar{L}^2$ state to the d^6 ground state in the cluster calculations.¹² Unlike the cluster calculations, in DMFT the ligand hole does not remain coherent with the central Co atom due to the influence of the rest of the crystal. Therefore, one cannot use the CoO₆ eigenstates to analyze the local dynamics. Instead, we use the statistical description and also analyze the temporal evolution of the atomic states.

Clearly, the d^6 atomic multiplets denoted as LS, IS, and HS in Fig. 6 are not sufficient to describe the local physics in LaCoO₃. We distribute the atomic states into LS, IS, and HS blocks (Fig. 5). Although an *a priori* assignment of the blocks is not unique we later present an *a posteriori* justification of our choice. For example, the state denoted as HS + t_{2g} can, in principle, be reached by adding a t_{2g} electron to the HS state as well as by adding an e_g electron to the IS state. In Fig. 6 we present the state statistics for various lattice parameters and temperatures corresponding to the solutions denoted as A, B, and C in Fig. 2(b). Besides substantial weights of the d^7 states the figure reveals that the increasing local moment response is connected to the growing weight of the HS block, while the IS block has only minor weight.

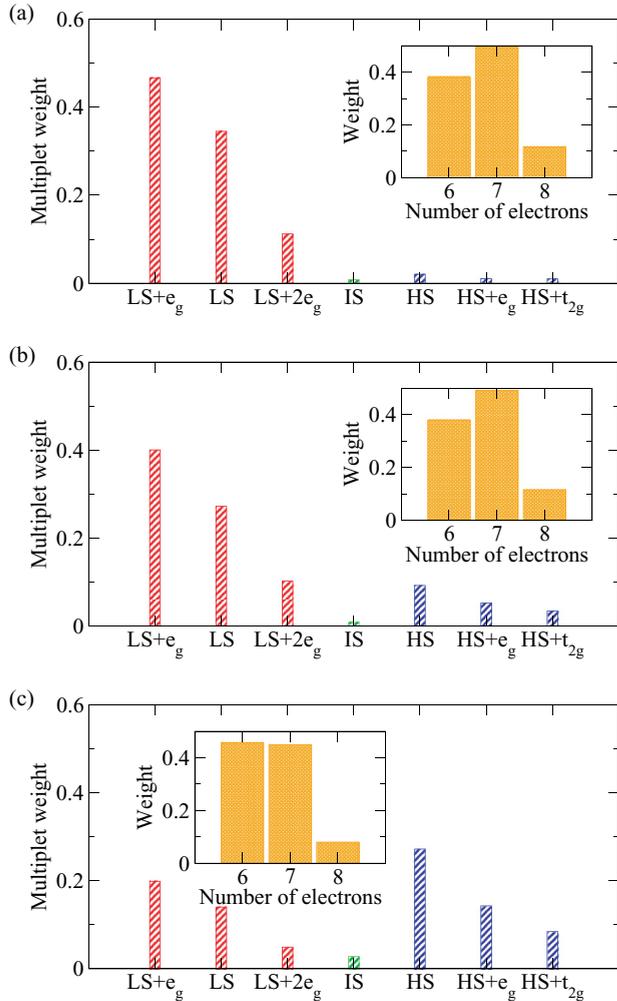


FIG. 6. (Color online) Weight of dominant atomic states for $U = 6.0$ eV, $J = 0.8$ eV. (a) Nonmagnetic solution [A in Fig. 2(b), $T = 580$ K, $\tau_{\text{lattice}} = 5$ K], (b) low- T solution [B in Fig. 2(b), $T = 580$ K, $\tau_{\text{lattice}} = 450$ K], and (c) high- T solution [C in Fig. 2(b), $T = 1160$ K, $\tau_{\text{lattice}} = 750$ K].

Correlation matrix of local states. Although we have identified the atomic states with large weights, a question arises whether their appearance is due to a unitary evolution or rather due to statistical averaging. This question is closely connected to the decomposition of susceptibility into atomic states contributions [Eqs. (3) and (4)]. States connected by a unitary evolution lead to a large off-diagonal element of the time averaged state-state correlation matrix Π and thus their individual contributions to the susceptibility cannot be well defined. On the other hand, if the weights of different states originate in statistical averaging the corresponding off-diagonal element of Π is vanishing as is its contribution to the susceptibility. Analysis of the correlation matrix $\Pi_{\mu\nu}$, displayed in Figs. 7 and 8, reveals nonzero off-diagonal elements, indicating a unitary evolution between the corresponding states. Nevertheless, the matrices can be arranged in a block diagonal form, which justifies our choice of the LS, IS, and HS blocks. As the unitary evolution between the most populated LS and HS blocks has a vanishing probability, their simultaneous population is a result

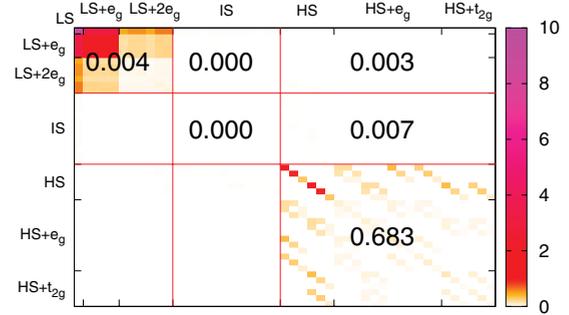


FIG. 7. (Color online) Correlation matrix $\Pi_{\mu\nu}$ between the dominant atomic states for $T = 580$ K and $\tau_{\text{lattice}} = 450$ K [solution B of Fig. 2(b)]. Color-coded values show the state-by-state relative contributions in % to the sum over all pairs. The numbers within blocks of atomic states indicate the contribution of the blocks to the local susceptibility in the units of 10^{-3} emu Oe $^{-1}$ mol $^{-1}$.

of the statistical averaging and blocks generalize the notion of atomic multiplets in isolated atoms.

The block-summed contributions to the local susceptibility are indicated by numbers inside the respective blocks in Figs. 7 and 8. In both cases the contribution of the HS diagonal block amounts around 97% of the total susceptibility. Inspecting the block contributions to the spin-spin correlation (Fig. 9) we find a finite τ -constant part of the HS contribution, leading to Curie-type susceptibility, in contrast to the rapidly decaying LS contribution. This allows us to define an effective HS moment as

$$\mu_{\text{HS}} = \frac{\sqrt{\sum_{\mu\nu \in \text{HS}} m_z(\mu)m_z(\nu)\Pi_{\mu\nu}}}{\sum_{\mu\nu \in \text{HS}} \Pi_{\mu\nu}}. \quad (6)$$

We obtain μ_{HS} of 3.52 and 3.56 μ_B in the low- T and the high- T solutions, respectively. The weak T dependence of the effective moment and its dominant contribution to the susceptibility χ justifies expressing χ as a product of Curie term μ^2/T and a T -dependent weight. Covalent Co-O bonding results in about 10% reduction of the effective moment from its atomic value of 4 μ_B .

D. Role of U , J , double counting correction

Since the form and construction of the Hamiltonian (1) is to some extent an *ad hoc* procedure it is important to understand the sensitivity of our conclusions to the particular values of U ,

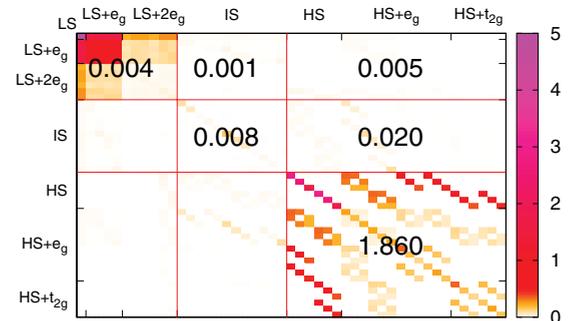


FIG. 8. (Color online) Same as Fig. 7 for $T = 1160$ K and $\tau_{\text{lattice}} = 750$ K [solution C of Fig. 2(b)].

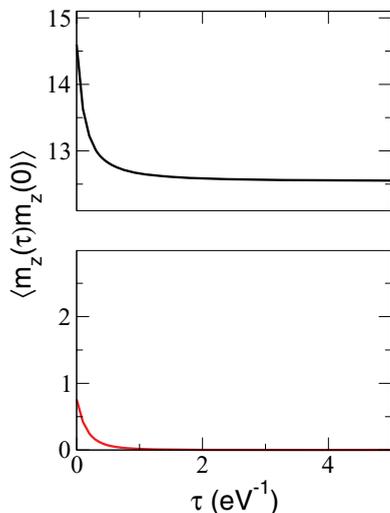


FIG. 9. (Color online) HS (upper panel) and LS (lower panel) normalized block contributions to the spin-spin correlation function, $\sum_{\mu, \nu \in \text{block}} m_z(\mu)m_z(\nu)C_{\mu\nu}(\tau) / \sum_{\mu, \nu \in \text{block}} \Pi_{\mu\nu}$, for $T = 1160$ K and $\tau_{\text{lattice}} = 750$ K [solution C of Fig. 2(b)].

J , and the double counting energy [E_{dc} is the second term on right-hand side of Eq. (2)]. Although these are not adjustable parameters in the present theory, their determination is not unique, which holds in particular for the double counting correction E_{dc} . In Fig. 10 we show the dependence of the weight of the LS block for various values of U and J . As expected J is the more important parameter. Its cDFT value falls into the spin state crossover range of 0.8–0.9 eV. Outside this range the results are insensitive to temperature or the variation of U . Variation of U inside the crossover regime has some impact as higher U suppresses the fluctuations to the $d^7\bar{L}$ and $d^8\bar{L}^2$ states. As a result the LS state is destabilized.

We have examined the role of double counting correction (E_{dc}) for $U = 6.0$ eV, $J = 0.8$ eV, $T = 1160$ K, and $\tau_{\text{lattice}} = 750$ K. We varied E_{dc} by δE_{dc} in the range of ± 5 eV around the self-consistent value of 33.56 eV. The positive values of δE_{dc} mean that the Co: d states are shifted downward in energy closer to the O: p state, which in turn enhances the hybridization and leads to preference of a LS metallic phase. The weights of the LS, IS, and HS blocks are shown in Fig. 11.

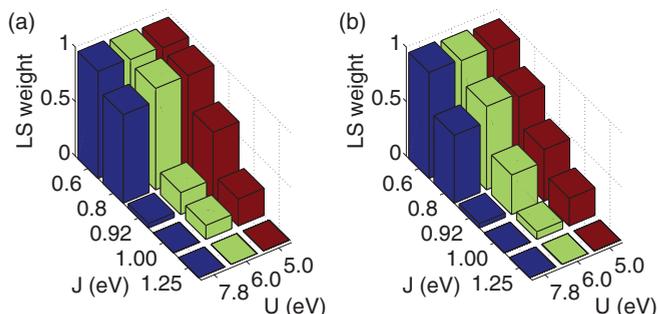


FIG. 10. (Color online) Weight of the LS block of atomic states (LS, $LS + e_g$, and $LS + 2e_g$) for various U and J at $\tau_{\text{lattice}} = 5$ K, (a) $T = 580$ K, and (b) $T = 1160$ K.

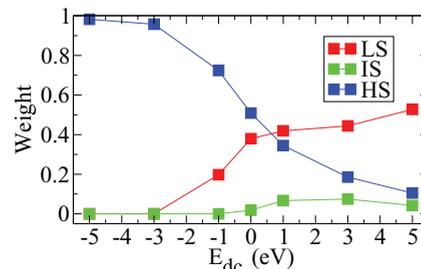


FIG. 11. (Color online) Weight of LS, IS, and HS blocks of atomic multiplets for various double counting energies for high- T solution ($U = 6$ eV, $J = 0.8$ eV, $T = 1160$ K, and $\tau_{\text{lattice}} = 750$ K). The values indicate the offset from the self-consistent value of 33.56 eV.

For $\delta E_{\text{dc}} > 1$ the system becomes metallic and the definition of the LS, IS, and HS blocks loses its justification.

Based on the one-particle spectra and the overall behavior of our results we conclude that the self-consistent value of E_{dc} provides a rather good description of the actual material. We also point out the T -dependent variation of E_{dc} is rather small and had minor effect on the T dependence of both χ and Δ_{eff} .

IV. CONCLUSION

We have studied the temperature dependence of the magnetic and spectral properties of LaCoO_3 using the LDA + DMFT approach. Our results show that the local moment response at elevated temperatures is associated with the HS state of Co ion and that there is an effective interatomic repulsion between HS atoms in the LS matrix. Our findings at this point agree with the VCA calculations¹⁰ and LDA + U cluster calculations³² as well as with the conclusions of the experimental studies.^{28–30} On the other hand, our results are inconsistent with interpretation of the intermediate temperature phase in terms of the IS state.^{4,24,26} Furthermore, since a purely electronic mechanism of the HS-LS attraction exists³³ the absence or smallness of the breathing mode distortion²⁴ does not exclude HS-LS short range ordering. The experimentally observed (anomalous) lattice expansion has a pronounced effect on the LS-HS crossover, which leads to the conclusion that the lattice provides a strong positive feedback for the crossover.

To account for the strong covalent bonding with O the notion of Co HS state has to be generalized to include not only d^6 , but also d^7 and d^8 electron configurations. This leads to reduction of the magnitude of the effective HS moment. Therefore, using the apparent magnitude of the magnetic moment as an indicator of the underlying atomic state may lead to incorrect conclusions.

Although we have varied the computational parameters in a wide range we have not found a phase that would be dominated by the IS state. Therefore, scenarios invoking HS-IS crossover^{30,32} are not consistent with our results. Guided by a similar LDA + DMFT study on metallic SrCoO_3 , it is plausible that in the metallic phase of LaCoO_3 observed experimentally above 600 K distinction between IS and HS state is not possible as those are connected by unitary evolution of the system.

Based on the above observations we propose the following scenario of LaCoO_3 physics, which is in many aspects similar to Refs. 32 and 10. At the lowest temperatures most Co ions

are in the LS state with isolated Co ions in the excited HS state. Increasing temperature assisted by the lattice feedback leads to growing density of the HS sites. Effective repulsion keeps the HS sites apart leading to a short range HS-LS order, which is responsible for the insulating behavior in the 100–500 K range, similar to the observation made in Ref. 33. We speculate that the second crossover experimentally observed around 500 K is associated with “melting” of the LS-HS order. This leads to an anomalous lattice expansion due to the breaking of attractive LS-HS bonds. The experimentally observed onset of metallicity changes the local moment character by coherently admixing some IS-like states to the dominant HS configuration. The distinction between HS and IS in the high T metallic phase is thus not possible.

ACKNOWLEDGMENTS

We thank Z. Jiráček for numerous discussions and suggestions concerning the manuscript. This work was supported by Grant No. P204/10/0284 of the Grant Agency of the Czech Republic, by the Deutsche Forschungsgemeinschaft through FOR1346, by the Russian Foundation for Basic Research (Project Nos. 10-02-00046 and 10-02-96011), and by the Fund of the President of the Russian Federation for the Support of Scientific Schools NSH-6172.2012.2.

APPENDIX: COMPARISON OF FULL AND DENSITY-DENSITY INTERACTIONS

The restriction to the density-density terms in the Coulomb interaction is an approximation which greatly reduces the computational effort. To assess the approximation to the excitation energies we compare the Tanabe-Sugano²² diagrams for the d^6 configuration obtained with the density-density and

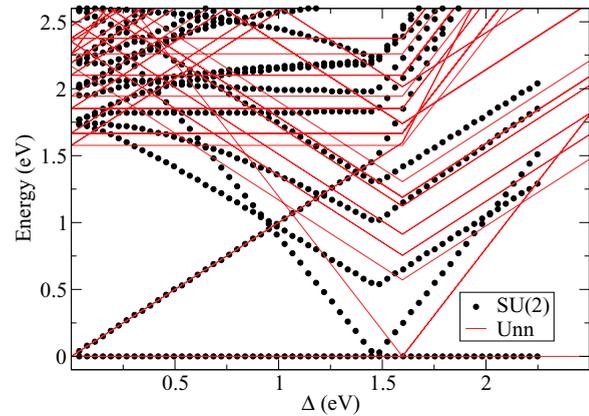


FIG. 12. (Color online) Comparison of Tanabe-Sugano diagrams for the full rotationally invariant [SU(2); black points] and density-density (Unn; red lines) Coulomb interaction. Only the low-energy multiplets are displayed for the crystal field Δ around the LS and HS multiplet crossing.

full Coulomb interaction in Fig. 12. The largest difference of the two spectra is found at zero crystal-field splitting where the off-diagonal elements, neglected in density-density approximation, play the most important role. At larger crystal fields some of the full multiplet states (e.g., LS or HS with the maximal spin projection) become dominated by a single Slater determinant and their energies are close to the density-density ones. Importantly, the degeneracies of the multiplets for the two interactions differ. Recently, the effect of the density-density interaction was studied on a similar material SrCoO₃ and good agreement was found for the multiplet-averaged state weights.⁵⁵

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