Magnetic properties of defect-free and oxygen-deficient cubic SrCoO$_{3-\delta}$

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(Dated: March 30, 2015)

We investigated electronic and magnetic properties of the perovskite material SrCoO$_{3-\delta}$ with $\delta \leq 0.15$ using a first-principles Green function method. This system is known from various experiments to be ferromagnetic with a Curie temperature of 260 K to 305 K and a magnetic moment of 1.5 $\mu_B$ to 3.0 $\mu_B$. Applying the magnetic force theorem as it is formulated within multiple scattering theory, we calculated the exchange parameters in this system and estimate the Curie temperature. Including correlation effects by an effective $U$ parameter within the GGA+$U$ approach, we obtained the Curie temperatures in dependence of the oxygen deficiency close to the experimental values.

PACS numbers: 61.72.jd, 71.15.Mb, 71.70.Gm, 75.47.Lx
Keywords: cobaltite, perovskite, oxygen vacancies, Curie temperature, ab initio

I. INTRODUCTION

Perovskite materials with the simple structure formula $\text{ABO}_3$ attracted attention in the last decades because of potential applications in spintronics. Especially, ferromagnetic metallic perovskites have rekindled interest, since they can be used as electrodes in complex oxide heterostructures, while conventional ferromagnetic materials such as $3d$ transition metals are hardly compatible with most of the oxides.

Over the last years, advanced experimental growing techniques allow for the growth of heterostructures and multilayer systems, with a huge variety but well designed properties, e.g. multiferroic, magnetoelectric or magnetooptic. Out of this class of materials, we concentrated on SrCoO$_{3-\delta}$ with a possible oxygen deficiency $\delta$. In its pure single-crystal composition, the experiments verify ferromagnetic behavior up to room temperature and metallic conductance. Metallic oxides are highly desired for contacts and electrodes of multi-functional heterostructures discussed above, because of a good lattice match between the electrode and the top layer oxide. Undesired distortions of thin layers could be reduced. Simultaneously, it is possible to transport an electric current, e.g. in the compounds SrCo$_{1-x}$Fe$_2$O$_3$ for $x \leq 0.5$, which are particularly suitable as electrode materials for solid electrolyte oxygen sensors. In addition, complex oxides based on SrCoO$_3$ like e.g. La$_{0.6}$Sr$_{0.4}$CoO$_3$ or SrCo$_{0.9}$Sb$_{0.1}$O$_{3-\delta}$ appear to be particularly useful as cathodes for intermediate-to-low temperature solid oxide fuel cells.

In the literature there are several experimental investigations and theoretical studies of SrCoO$_3$. They all verify the ferromagnetic and metallic behavior of this material. In theory, in particular, the electronic structure, the spin state, and possible lattice distortions are carefully discussed. Potze et al. show that SrCoO$_3$ exhibits an intermediate spin state due to the competition of intra-atomic exchange and the cubic crystal field. Such an intermediate spin state may be understood as a high spin state of a Co$^{3+}$ ion antiferromagnetically coupled to a ligand hole of $e_g$ symmetry (notation from Ref. 8): $d^9L_{eg}$. A more recent study identified this high spin state as $d^6$, but it is mixed with several other possible spin states. Also the magnetic moment (ranging from 2.6 $\mu_B$ to 3.19 $\mu_B$) is reproduced by theory and close to 3 $\mu_B$, which agrees very well with the intermediate spin state picture ($S = 3/2$). Only few earlier papers showed a smaller magnetic moment (1.691 $\mu_B$).

However, there is only one paper which discussed the Curie temperature ($T_C$) of SrCoO$_3$ from a theoretical point of view ($T_C \approx 1800 \text{K}$). This value is far too high in comparison to the experimentally measured Curie temperature, although, the range of measured values varies from 212 K to 305 K. This variation might result from different synthesis techniques and defects. Usually, the cubic and stoichiometric phase SrCoO$_3$ is prepared from the brownmillerite phase SrCo$_2$O$_4$. The oxidation is either done by a high oxygen pressure during the heating or by electrochemical oxidation. Furthermore, most samples are polycrystalline and the oxygen amount is smaller than the nominal value ($\delta \geq 0.05$). The cubic structure is only stable for a narrow range of $\delta$, since, SrCoO$_{3-\delta}$ forms a homologous series SrCoO$_{(3n-1)/n}$ for $\delta$ from 0.5 to 0 and changes its structure from orthorhombic via cubic and tetragonal to cubic again.

Even for this cubic range close to $\delta = 0$, the lattice constant increases slightly with decreasing oxygen content whereas the critical temperature decreases from 292 K to 182 K. Anyway, these values for polycrystalline samples are smaller than for a single crystal ($T_C = 305 \text{K}$ and $\delta = 0.05$). As for the $T_C$ values, the measurements of the magnetic moments vary for different experiments between 1.2 $\mu_B$ to 2.6 $\mu_B$.

Such a variation of experimental results is hard to combine into one consistent picture. Therefore, we chose for our investigation the single-crystalline results as a point of reference. The perfect crystal should be a good model for this experimental situation. In our study, we combined two methods, which have been proven to be very reliable in the particular context. The projected planewave method, the Vienna ab initio simulation package.
(VASP)\textsuperscript{22,23} was used for the calculation of total energies and the structural relaxation, to check for deviations eventually appearing from the cubic structure. For the investigation of the magnetic properties, the Korringa-Kohn-Rostoker Green’s function (KKR-GF) method was used. In both methods, we considered the electronic correlation effects for the $d$ orbitals of Co with an additional Hubbard $U$ in the GGA+$U$ approach.\textsuperscript{25} Because different $U$ values are used in the literature, we made a careful study of $U_{\text{eff}} = U - J$ in the range from 0 eV to 9 eV.

Furthermore, the multiple scattering framework of the KKR method allows us to consider randomly distributed oxygen vacancies to model a more realistic sample by applying the coherent potential approximation (CPA).\textsuperscript{26–28} Indeed, the tendency of the critical temperature agrees very well with the experiments and it is reduced with increasing amount of oxygen vacancies. In the following, we start with a detailed description of the used structure and the theoretical methods. The results are discussed at first for the defect-free SrCoO$_3$. Afterwards, we extend our study also to oxygen defects. We close this work with a summary.

II. COMPUTATIONAL DETAILS

In this work, the calculations were performed for a primitive cubic cell of SrCoO$_3$ (see Fig. 1) at the experimental lattice constant $a_{\text{exp}} = 3.835\text{\,Å}$ given by Bezdicka \textit{et al.}\textsuperscript{13} To study structural, electronic, and magnetic properties of SrCoO$_3$, we performed extensive first-principles calculations within density functional theory and used the generalized gradient approximation.\textsuperscript{29} The electronic correlation effects on 3$d$ Co electrons were taken into account using the magnetic force theorem as it is implemented within the multiple scattering Green function method.\textsuperscript{30} The study was performed within the full charge density approximation, which takes into account the non-sphericity of the charge density and improved the accuracy of calculations for complex unit cell geometries.

To investigate magnetic properties of SrCoO$_3$, we calculated the magnetic exchange constants $J_{ij}$ between the magnetic atoms at site $i$ or $j$ using the magnetic force theorem as it is implemented within the multiple scattering theory.\textsuperscript{22}

\begin{equation}
J_{ij} = \frac{1}{8\pi} \int_{E_{F}} d\epsilon \text{Im} \text{Tr}_{L} (\Delta_{i} \hat{\tau}_{ij}^{\uparrow} \Delta_{j}^{\downarrow} + \Delta_{i}^{\downarrow} \hat{\tau}_{ij}^{\uparrow} \Delta_{j}^{\uparrow}),
\end{equation}

where $\hat{\tau}_{ij}$ is the scattering path operator and $\Delta_{i}^{\uparrow} = \hat{t}_{i}^{\uparrow} - \hat{t}_{i}^{\downarrow}$ the difference between the spin-dependent single scattering operators of site $i$. The trace is taken over all relevant angular momentum quantum numbers $L = (l, m)$.

Those $J_{ij}$ enter a classical Heisenberg Hamiltonian

\begin{equation}
\hat{H} = - \sum_{i,j} J_{ij} \mathbf{S}_{i} \cdot \mathbf{S}_{j},
\end{equation}

FIG. 1: (Color online) Structure of the cubic phase of SrCoO$_3$.

FIG. 2: Experimental lattice constant change with respect to oxygen concentration for several references. The change of the volume is $\Delta V = (V - a_{\text{exp}}^{3})/a_{\text{exp}}^{3}$. The nominal and net values represent the provided and measured oxygen content in Ref. 15. 

| oxygen content $3 - \delta$ | $\Delta V$ in % |
|-----------------------------|-----------------|
| Ref. [1]                    | 1               |
| Ref. [15 (nominal)]         | 2 %             |
| Ref. [15 (net)]             | 2.2 %           |
| Ref. [16]                   | 1 %             |
| Ref. [18]                   | 1 %             |
| Ref. [20]                   | 2 %             |

2.7 2.8 2.9 3 3.1 3.2 3.3
55.84
56.4
56.97
57.53

$\Delta V$ (%)

$V$ (Å$^3$)

$\Delta V$ (%) of the stoichiometric material (see overview in Fig. 2). Therefore, we stayed consistently with Ref. [13].

(i) The electronic and magnetic structures of SrCoO$_3$ were investigated further with the first-principles multiple scattering Green function method.\textsuperscript{31} The study was performed within the full charge density approximation, which takes into account the non-sphericity of the charge density and improved the accuracy of calculations for complex unit cell geometries.
with the magnetic moments $\mathbf{S}_i$ and $\mathbf{S}_j$. The model Hamiltonian in Eq. \[2\] allows an estimate of the critical temperature $\tilde{T}$ with a Monte Carlo (MC) simulation. Here, $\tilde{T}$ might mark the transition to any kind of magnetic ground state which might result from the calculation. We crosschecked our results with the mean-field approximation (MFA) and the well established random phase approximation (RPA)\[33\] All three methods showed similar qualitative critical temperature changes and we restrict the discussion to the MC results because their quantitative results are usually considered to have the best agreement with experimental measurements. For the particular simulations, we chose 8000 magnetic atoms in a cluster with periodic boundary conditions. The temperature was reduced in steps of 5 K starting from a high-temperature disordered state above $\tilde{T}$. At every temperature, we assumed that the thermal equilibrium was reached after 20 000 MC steps and after 20 000 additional MC steps thermal averages were calculated. $\tilde{T}$ was then obtained from the fitting of the temperature dependency of the magnetic susceptibility, crosschecked by the temperature dependence of the saturation magnetization and the heat capacity. The obtained transition temperatures have been observed within an uncertainty range of $\pm 5$ K. Further computational details of our MC scheme can be found in Refs. \[23,33\]. From the orientation of the magnetic moments at low temperatures and the spin-spin correlation function, we deduced the magnetic ground state of the simulated system, which was not only ferromagnetic (FM) with the Curie temperature, $T_C$, as observed from the experiments, but also antiferromagnetic (AFM) with the Néel temperature, $T_N$, or a more complicated non-collinear ferri-magnetic spin arrangement (FiM) with a transition temperature, $T_f$, and potentially with a saturation magnetization of zero. We introduced those labels for the different magnetic transitions for the sake of clarity throughout our work and speak of $\tilde{T}$ if the ground state is not clarified.

In our calculations, we found besides the magnetic cobalt ions small induced moments also at the oxygen sites which result from the ground state calculation at 0 K. Since, those moments disappear usually at and above the magnetic transition temperature their magnetic coupling can lead to a wrong estimation of the critical temperature. We compared those results (labeled in the following with 0 K) with the $\tilde{T}$ obtained from the magnetic coupling constants at a high temperature paramagnetic state. Such state can be modeled successfully with the disordered local moment (DLM) theory\[33,43\] Here, arrangements of local magnetic moments $\{\mathbf{S}_i\}$ at the sites $i$ are thought to fluctuate independently. Above $\tilde{T}$, the orientations of those local moments are randomly distributed and the average magnetization per site is zero. Hence, the induced moments vanish. From the computational point of view, the coherent potential approximation (CPA)\[28\] as it is implemented within the multiple scattering theory\[23\] can be used to model the susceptibility or the electronic structure for such disordered magnetic systems.\[37,43\] With respect to the calculation of the $J_{ij}$ in Eq. \[1\], the scattering path operators $\hat{\tau}^{ij}$ of the perfect crystal at 0 K will be exchanged with the ones of the effective CPA media $\hat{\tau}^{ij}_C$. The random orientation of the magnetic moments in the DLM picture causes usually an increase in the size of the orbitals. So, the magnetic coupling is usually stronger in case of a DLM calculation since the strength of the magnetic coupling corresponds strongly to the overlap of those contributing orbitals. This means for the resulting transition temperature that it can become either larger or smaller depending on the type of magnetic exchange, e.g. a reduction for antiferromagnetic (super-) exchange.

To describe the oxygen vacancies in SrCoO$_3$, we applied also the CPA using a certain percentage ($\delta$) of empty spheres at the oxygen sites to mimic the vacancies. However, the vacancy may lead to substantial relaxations of the underlying crystal structure. We did not account for such structural deformations in our CPA calculations but investigated their impact on the magnetic interaction using a supercell approach. We found only minor changes of the exchange constant values and, therefore, the discussion below reports results from the ideal cubic structure.

### III. RESULTS

#### A. Defect-free SrCoO$_3$

We started our investigations with the calculation of the electronic properties of SrCoO$_3$ for the experimental lattice constant. Due to the oxygen octahedra surrounding the Co ion, the $d$ states of cobalt experience a crystal field splitting of cubic symmetry, which results in three $t_{2g}$ and two $e_g$ degenerated states. The $e_g$ states are oriented along the coordinate axes pointing to the oxygen ions and the $t_{2g}$ states are pointing to the next nearest neighbor Co ions (see Fig. 1). The local density of states (LDOS) within the GGA shows an almost fully occupied majority spin channel and a pronounced peak of the Co $t_{2g}$ spin down states at the Fermi energy (see Fig. 3). This is in a good agreement with the previous states, $\epsilon_k^\uparrow$, $t_{2g}^\uparrow$, and $\epsilon_k^\downarrow$, are below the Fermi energy and smeared over a large energy range due to a strong hybridization with the $p$ states of oxygen.

Further, we determined the magnetic moment $\mu$, the exchange coupling constants and the critical temperature $\tilde{T}$ with the pure GGA. The total magnetic moment of SrCoO$_3$ was $\mu = 2.281 \mu_B$, which is in the range of the most experimentally observed moments ($\mu \approx 2 \mu_B$) but smaller than the moments in the single crystal sample of Ref. \[1\] (2.5 $\mu_B$ at 2 K). The main contribution to the total magnetic moments originates from the Co ions. However, small moments of 0.15 $\mu_B$ and 0.04 $\mu_B$ were induced at the oxygen and strontium ions, respectively. The magnetic exchange interactions for the near-
The oxygen $p$ states at all three oxygen ions in the unit cell are three fold degenerate (only one is shown).

Although, the total moment agrees roughly with the experiments and we obtain a FM ground state, the calculated Curie temperature is more sensitive to changes in the electronic structure and does not agree with the experimental data. As we see from former studies, this in part may be due to the lack of consideration of electronic correlation effects by applying a repulsive $U_{\text{eff}}$ to the $d$ orbitals of cobalt. On the other hand, we want to describe also the oxygen-deficient material, where we expect a reduction of the critical temperature and an slight volume change. In general, all these effects might influence the transition temperature $T_c$ and we express those changes in a formula:

$$\Delta T = \left( \frac{\partial T}{\partial U_{\text{eff}}} \right)_{\delta,V} \Delta U_{\text{eff}} + \left( \frac{\partial T}{\partial \delta} \right)_{U_{\text{eff}},V} \Delta \delta + \left( \frac{\partial T}{\partial V} \right)_{U_{\text{eff}},\delta} \Delta V. \quad (3)$$

The quantity $\Delta T$ could be obtained from the experimental data.

**B. Including electronic correlation corrections**

The common way to consider the electronic correlations is to optimize the value of the repulsive $U_{\text{eff}}$ with respect to the experimental data of structural and magnetic properties of the system. As we see from former studies,
the value of $U_{\text{eff}}$ might range from 2.5 eV (Ref. [10]) to 8 eV (Ref. [12]). The constrained random-phase approximation provided a value of $U = 10.83$ eV and $J = 0.76$ eV for the Co $d$ states,[3] which seems to be too high for a metallic system.

Since the correct value of $U_{\text{eff}}$ is hardly to estimate from first-principles and the above reference values scatter quite a bit, we investigated the electronic structure and the occupation of the Co $d$ states for the whole range of $U_{\text{eff}} = 0$ eV to 9 eV (see Fig. 3). Interestingly, for the first few steps of the calculations ($U_{\text{eff}} \leq 1.5$ eV) the $d$ states preserve their degeneracy in $t_{2g}$ and $e_g$. At the Fermi energy ($E_F$) the large peak of the Co $t_{2g}$ states does not move due to an interplay of the Coulomb exchange and the crystal-field energy. Only for a larger $U_{\text{eff}}$, the degeneracy is lifted for $d_{xy}$. This state becomes occupied while the $d_{zx}$ and $d_{zy}$ are pushed above $E_F$. On the other hand, in the spin up channel the orbitals remain degenerated for the whole range of $U_{\text{eff}}$ and become strongly localized (see much higher contrast for $d_{xy}^\downarrow$ in Fig. 5). In general, the majority or minority states are pushed below or above the Fermi level, respectively. In addition, there are more subtle changes like reducing or vanishing peaks, e.g for $d_{xy}^\downarrow$ at $U_{\text{eff}} \approx 5$ eV or $d_{z^2-r^2}^\downarrow$ at $U_{\text{eff}} \approx 3$ eV.

We have to note that the particular localization of $d_{xy}^\downarrow$ is arbitrary and depends on the starting point of the self-consistent calculation. Due to the symmetric cubic structure, another localized Co $d^1$ state is also possible and was observed during the calculations. However, for a consistent description we continued throughout this work with one particular configuration (the singlet $d_{xy}^\downarrow$ state).

In order to verify this loss of degeneracy, we carried out total energy and electronic structure calculations also with VASP. We observed a similar symmetry breaking while the $U_{\text{eff}}$ values ranged from 5 eV to 7 eV. Despite this loss of orbital symmetry, the energy change is small and not sufficient to alter the positions of the atoms. So, a tetragonal distortion is not favorable and stoichiometric SrCoO$_3$ still remains in the cubic structure.

For the understanding of the critical temperature, we investigated the magnetic coupling parameters $J_{ij}$ in the ground state at $T = 0$ K and in the DLM model. Both reflect the change in the degeneracy of the Co $d$ state in the LDOS. Due to the splitting of the $t_{2g}$ states into two degenerated $t_{2g}^\|$, $t_{2g}^\perp$ and a single $d_{xy}^\downarrow$ orbital, the $J_{ij}$ with either ($\parallel$) in $x$ and $y$ direction or ($\perp$) in $z$ direction were different for $U_{\text{eff}} > 1.5$ eV (see Fig. 6). Their $U_{\text{eff}}$ dependence explains the behavior of the critical temperature but shows also more subtle features which corresponds to changes in the LDOS with increasing $U_{\text{eff}}$.

For the ground state calculation (0 K), the most domi-
nant coupling constants, $J_{01}^{\text{Co-Co}}$ and $J_{02}^{\text{Co-Co}}$, are strongly ferromagnetic (see lhs in Fig. 4). Both interactions are mediated by oxygen ions between Co ions forming either a Co-O-Co or a Co-O-Co-O-Co chain (see inset in Fig. 5). Those bonds connect mostly the O $p$ states with the Co $e_g$ states ($\sigma$ bonds). This typically antiferromagnetic (AFM) superexchange is certainly suppressed by the metallic character of SrCoO$_3$ and we observe band magnetism. In the degenerated parameter region, the coupling becomes even stronger with $U_{\text{eff}}$ until 1.5 eV because the Co $e_{g}^{\uparrow}$ and $e_{g}^{\downarrow}$ states are either pushed below or above the Fermi energy, respectively. This increases the exchange splitting and, therefore, the magnetic coupling. In contrast, the coupling between two Co ions enclosing a 90° angle ($J_{02}^{\text{Co-Co}}$) is small and AFM, while the next coupling ($J_{03}^{\text{Co-Co}}$) is very weak compared to the other interactions.

After that, in the symmetry broken regime, the competing superexchange overcomes the band magnetism and we observed an increasing localization of the $d$ states (see stronger contrast in Fig. 5). This reduces, in general, the overlap of the orbitals and the magnetic exchange interactions. It is visible e.g. for $J_{01}$ and $J_{04}$ in Fig. 6 but also for other $J_{0j}$ (not shown). On the other hand, the modifications in the coupling constants are much more complex due to the changing LDOS. However, some simple tendencies can be observed, e.g. due to the localization of the Co $d_{xy}$ states, the magnetic coupling for $U_{\text{eff}} < 4$ eV in the $x$-$y$-plane ($\parallel$) contributions in $J_{0j}$ becomes smaller than the out-of-plane ($\perp$) contributions. The $\perp$ parts of $J_{02}^{\text{Co-Co}}$ even change their character from AFM to FM.

Another significant change for all coupling constants is visible at $U_{\text{eff}} = 4.5$ eV and might be correlated with vanished states in the $d_{xy}$ LDOS indicated by a loss of contrast (see Fig. 5). At the end of the shown range, the strength of the nearest neighbor magnetic exchange coupling was only half of its starting value. It reduces further, for even higher $U_{\text{eff}}$ (not shown) and leads to an undesired antiferromagnetic ground state.

The over all tendencies for the 0 K calculations were in general also observed in the DLM picture but the changes were much stronger, e.g. at $U_{\text{eff}} = 6$ eV the $J_{0j}$ were reduced to zero and $J_{04}$ is strongly AFM. Furthermore, the loss of degeneracy was visible already for smaller $U_{\text{eff}}$ (see Fig. 6). Both changes are explained by the larger extent of the Co $d$ orbital due to the random distribution of the magnetic moments in the DLM theory as already stated in section [1]. The increasing orbital overlap enhances, on the one hand, the AFM superexchange and on the other hand, alters the competition between the crystal field and Coulomb energy which restored the degeneracy for small $U_{\text{eff}}$.

The critical temperatures follow in general a similar tendency as $J_{01}^{\text{Co-Co}}$ (see Fig. 7). Both methods show a linear increase up to $U_{\text{eff}} = 1.5$ eV. The critical temperatures obtained with the $J_{0j}(0\text{K})$ remained around 750 K with increasing $U_{\text{eff}}$ up to $\approx 3$ eV, and drops down sharply in the following while the DLM results decrease linearly immediately above 1.5 eV until the experimentally relevant range is reached. We can estimate this linear reduction with a linear fit and obtain for $(\partial T/\partial U_{\text{eff}})_{\text{exp}} = -503 \text{K}/1.25 \text{eV}$ (see Eq. (8)). Afterwards, the rate of change with respect to $U_{\text{eff}}$ is strongly reduced and $T$ stayed around 250 K.

Furthermore, we account in Fig. 7 for the magnetic ground state observed in the Monte Carlo study with different symbols, having either a FM or FiM ground state. The DLM theory predicted only a non-magnetic ground state for the range of $U_{\text{eff}}$ ($U_{\text{eff}} \approx 2.5$ eV) equivalent to experimental results. This is, however, still physically reasonable. While at the critical temperature the induced moments at oxygen might be zero, they will develop for lower temperatures. This leads to a ferromagnetic ground state obtained with the $J_{ij}(0\text{K})$ for even larger $U_{\text{eff}}$ (see blue curve in Fig. 7).

On the other hand, the total magnetic moment increases monotonously in the whole $U_{\text{eff}}$ range with different linear slopes (see red line in Fig. 7). Only for changing degeneracy for $U_{\text{eff}} > 1.5$ eV the total moment decreases slightly due to a reduction of the induced moments to 0.11 $\mu_B$ for the two oxygen ions (O$_x$ and O$_y$), which lie in the same $x$-$y$-plane as the Co ions. In the following, the linear slope changed around $U_{\text{eff}} \approx 2.5$ eV and $U_{\text{eff}} \approx 4.5$ eV. Both values correspond to fading lines in the LDOS.

In summary, we found that the theoretically observed magnetic properties agree well with the measurements for a small correlation parameter of $U_{\text{eff}} = 2.50$ eV to
2.75 eV. Still, a direct comparison was complicated due to the different experimental setups, single-crystalline or polycrystalline samples, varying growing techniques or different oxygen content.

C. Effects of oxygen vacancies

We used the coherent potential approximation (CPA) to substitute the oxygen sites with a certain concentration of empty spheres, modeling the oxygen vacancies. For a macroscopic stoichiometric sample of SrCoO₃, there is no experimental evidence for an ordering of oxygen vacancies. So, we assumed randomly distributed oxygen vacancies which matches well with the concept of the CPA.

The electronic structure of the oxygen ions is mainly dominated by the strong hybridization with the Co d states (see representative LDOS for an oxygen ion in Fig. 5). With increasing $U_{\text{eff}}$ or by including few percent of oxygen vacancies (5%), the unoccupied peak above the Fermi energy is shifted to higher energies (see Fig. 5). This can be interpreted as the ligand hole of $d_g^2$ symmetry, which is expected by Potze et al to the intermediate spin state $t_{2g}^4e_g^2 (s = 3/2)$. It is stabilized by the ligand hole state $e_g^0\tilde{L}_{zg}$, where the hole couples antiferromagnetically to another $e_g^0$ in $d_e$: $t_{2g}^4e_g^2$. We found this configuration also in our LDOS calculation with almost fully occupied orbitals for $d^7$ and $t_{2g}^4$ (see Fig. 5). Although, our method is not directly comparable with the dynamic mean-field theory (DMFT) method of Kunes et al, we note that the same spin configuration appeared also in their calculation with the highest multiplet weight.

Furthermore, we expect in general a weakening of the Co-O-Co bonds similar as an applied $U_{\text{eff}}$ parameter and, therefore, a reduction of the critical temperature. This was already observed in experiments for a polycrystalline sample. The experiments cover an oxygen content change of ±6% with respect to the stoichiometric sample (see Fig. 5). A positive value means excess oxygen which might occupy unknown interstitial sites or form more complicated point defects. This is beyond our aims and we restricted the current study to model only a negative change by the introduction of oxygen vacancies into the cubic unit cell.

Since, we mainly compare our results with the measurements at the single crystal sample, we took into account correlation corrections with $U_{\text{eff}} = 2$ eV, 2.25 eV and 2.5 eV. Those results were compared with the GGA and the net oxygen content measured in Ref. [15] (see Fig. 5). All curves except for $U_{\text{eff}} = 2.5$ eV show a linear increase of the critical temperatures with increasing oxygen content (δ = 0.45) towards the stoichiometric value. However, the latter is also linear but with different linear slopes. It follows the experimental results remarkably well and shows after a kink at δ = 2.88 a similar slope as the other curves of smaller $U_{\text{eff}}$ values (light blue or red). All those graphs reflect the expected similarity between the application of a correlation parameter or the inclusion of oxygen vacancies in the unit cell. For $U_{\text{eff}} = 2.5$ eV, the combined effects lead to a similar kink from large to small slope which was observed also for $T(\delta)$ in Fig. 5.

Again, we depicted also the magnetic ground state in our DLM model with the same symbols as in Fig. 5. Although, the relevant critical temperature values show no ferromagnetic ordering, test calculations with the J₃, at 0 K and $U_{\text{eff}} = 2.5$ eV revealed a ferromagnetic ground state at low temperatures for all considered vacancy amounts. We note the AFM coupling for $U_{\text{eff}} = 2.5$ eV and $\delta = 0.45$. This chemical composition is already close to the ordered brownmillerite structure SrCoO₂.₅, which is antiferromagnetic with a high Néel temperature.
of $T_N = 570 \text{K}$\[^{11}\] Although, the lattice structure will be not the appropriate equilibrium structure at this oxygen concentration, the different chemical composition leads already to an AFM order with higher critical temperature. On the other hand, the change might be related to the investigation of the epitaxial strain which will also effect the magnetic coupling and leads to changes in the magnetic ground state properties\[^{10}\].

While the cubic structure is only experimentally stable in a narrow range of the oxygen deficiency, we considered up to $-5\%$ oxygen vacancies. Linear fits for all theoretical results provide a slope of $(\partial T/\partial \delta)_{U_{eff},V} = (30 \pm 3) \text{K}/(1\text{ at.} \%)$ which is larger than the slope $8 \text{K}/(1\text{ at.} \%)$ for the linear fit of the measured transition temperatures (see dashed line in Fig. 9). We can investigate the larger changes with Eq. (3). The volume contribution will be neglected for the moment ($V = \text{const.}$), since, its magnitude might be small as seen in the most experiments (see Fig. 2). A possible reason for the larger change of the theoretical critical temperatures could be an overestimation of the screening by the GGA+$U$ together with the oxygen vacancies. The correlation effects might be reduced with reduction of the oxygen amount. If we assume that the $U_{eff}$ depends on $\delta$, we can derive from Eq. (4):

$$
\left(\frac{\Delta T}{\Delta \delta}\right)_{\text{exp}} = \left(\frac{\partial T}{\partial U_{eff}}\right)_{\delta} \left(\frac{\Delta U_{eff}}{\Delta \delta}\right) + \left(\frac{\partial T}{\partial \delta}\right)_{U_{eff}},
$$

So, we obtain from Eq. (4) a crude estimate for $(\Delta U_{eff}/\Delta \delta)_{\text{exp}} = +55 \text{meV}/(1\text{ at.} \%)$. The plus sign is in accordance with the expectation that the correlations become weaker for a smaller oxygen content ($\Delta U_{eff} < 0$ for $\Delta \delta < 0$).

A quantitative value for $U_{eff}$ with respect to $T_C = 305 \text{K}$ at $\delta = 0.05$ of Ref. \[^{11}\] could be in the range of $2.25 \text{eV}$ to $2.5 \text{eV}$, but remains questionable considering all the other possible influences. However, we observed a very good qualitative agreement with the experimental data.

### D. Hydrostatic volume changes

We also investigated the influence of a possible volume change due to the oxygen content as observed from the experimental references in Fig. 2. Therefore, we scaled the lattice parameters of our cubic unit cell for two cases of correlation parameter $U_{eff} = 2.25 \text{eV}$ and $2.5 \text{eV}$. At first only the volume is increased up to $1.8\%$ in order to check this effect alone (see filled triangle and upper scale in Fig. 10). A volume change (filled triangles) corresponds to a particular oxygen content linearly interpolated from Ref. \[^{15}\] in Fig. 2. However, this reference shows the largest changes and, thereby, strong changes also in $\bar{T}$. If this correspondence between the volume change and the oxygen deficiency is taken e.g. from Ref. \[^{18}\] $\delta = 0.16$ is only associated to $\Delta V = 0.6\%$ (filled squares). Those differences in the experimental results made it complicated to formulate a definite conclusion or to estimate the volume change contribution to Eq. (3) while it was neglected before.

However, some consequences can be drawn. In any case, the transition temperature is reduced for an increase of the unit cell volume. The slope of reduction is lower for $2.5 \text{eV}$ which fits to the flat region of the $\bar{T}(U_{eff})$ relation. It agrees also qualitatively with the fit of the experimental data and we might consider the volume change only for the reason of the reduction of $\bar{T}$.

Finally, we combined in our calculations the oxygen deficiency corresponding to Ref. \[^{15}\] and the matching volume change (see blue open triangles in Fig. 10). We obtained for $U_{eff} = 2.25 \text{eV}$ the slope for $\Delta T$ twice as big as before and the single contributions appeared to be accumulative. In contrast, we observed a kink again for $U_{eff} = 2.5 \text{eV}$ which appeared at an higher oxygen content than before. This shift is related again with the slighter change of $\bar{T}(U_{eff})$ for higher $U_{eff}$ and the increasing effect of $U_{eff}$ with volume change and oxygen deficiency.

### IV. CONCLUSIONS

We can conclude that for cubic SrCoO$_{3-\delta}$ a small correlation correction parameter of $U_{eff} \approx 2.5 \text{eV}$ is sufficient to describe the measured magnetic properties like the magnetic moment or in particular the Curie temperature. Such value is expected for a metallic system. The
magnetism is mainly caused by band magnetism which is reduced by oxygen mediated superexchange. The ferromagnetic ground state could only be observed if we take the induced oxygen moments into consideration in the Monte Carlo simulation. Furthermore, our calculations agree with the atomic multiplet calculations and the picture of the intermediate spin state of Potze et al.\textsuperscript{33}

Although, we had to neglect possible ordering of the defects, the simple means of the coherent potential approximation were quite successful to model qualitatively the experimentally observed changes of $T$ induced by oxygen vacancies. They are one of the most important types of defects in oxides – even single crystalline samples might be not completely stoichiometric.\textsuperscript{34} The randomly distributed vacancies weaken the Co-O-Co bonds, reduce the exchange coupling and act like the correlation parameter. A similar behavior was also observed for a possible increase of the unit cell volume.

Despite the already discussed problems of the quantitative comparison between the theoretical and experimental results, the polycrystalline samples, other defects etc., the linear tendency of $T(\delta)$ is in a good agreement with the experimental results.

V. ACKNOWLEDGMENTS

This work was funded by the Sonderforschungsbereich SFB 762, 'Functionality of Oxide Interfaces'. We gratefully acknowledge fruitful discussions with Igor V. Maznichenko and Alberto Marmodoro.

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