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# Theoretical study of the magnetic properties of the $\text{CoCu}_2\text{O}_3$ compound

Julien Lévêque,<sup>1,2</sup> Elisa Rebolini,<sup>3</sup> Marie-Bernadette Lepetit,<sup>2,3,\*</sup> and Andrés Saúl<sup>1,†</sup>

<sup>1</sup>*Centre Interdisciplinaire de Nanoscience de Marseille, CNRS UMR 7325, Marseille, France*

<sup>2</sup>*Institut Néel, CNRS UPR 2940, Grenoble, France*

<sup>3</sup>*Institut Laue Langevin, Grenoble, France*

In this work we present a theoretical study of the magnetic properties of the  $\text{CoCu}_2\text{O}_3$  compound. The magnetic effective exchange interactions and zeroth-field splitting were computed using *ab-initio* methods, then the magnetic order and transition temperature were determined using classical Monte-Carlo simulations. We showed that, unlike other members of the  $\text{ACu}_2\text{O}_3$  family, the presence of an additional magnetic atom, associated with a large folding of the puckered layers in the  $(\vec{a}, \vec{b})$  directions, induces a magnetic pattern based on coupled 3-leg ladders, quite different from the 2-leg structural ladders. The propagation vector has been found to be  $\vec{q} = (0, \frac{1}{2}, \frac{1}{2})$ . It is associated to a doubly-degenerated ground state suggesting a doubling of the unit cell. The large  $\text{Co}^{2+}$ -ion anisotropy was shown to be of crucial importance in the high transition temperature observed in this compound.

## I. INTRODUCTION

Following the discovery of high temperature superconductivity in  $\text{Ba}_x\text{La}_{5-x}\text{Cu}_5\text{O}_{5(3-y)}$  by Müller and Bednorz [1], cuprates have attracted a lot of attention over the last decades. Apart from superconductivity, a large number of compounds of the cuprate family have been studied for their low-dimensional quantum magnetism. Indeed, the  $S = 1/2$  character of the  $\text{Cu}^{2+}$  ion, and the directionality of the associated 3d magnetic orbital, are responsible for a tendency to form one- or two-dimensional magnetic systems with quantum character. For example, the  $A = \text{Sr}$  member of the  $\text{ACu}_2\text{O}_3$  family, a two-leg ladder compound has been extensively studied in the recent decades [2–8] for its one-dimensional properties.

Very few cuprates exhibit a three-dimensional magnetic ordering at a reasonable temperature (i.e. close to room temperature or higher). Among them, one can however cite the  $\text{CuO}$  oxide, that exhibits an antiferromagnetic long-range ordering below 220 K [9, 10]. Another example is the  $A = \text{Mg}, \text{Ca},$  and  $\text{Co}$  members of the  $\text{ACu}_2\text{O}_3$  family that exhibit a high temperature three-dimensional (3D) character, and that, in contrast to  $\text{CuO}$ , have been little studied. Interestingly, the  $\text{MgCu}_2\text{O}_3$  compound presents a 3D spin-ordering at 95 K [11], and the mixed  $\text{Ca}_{1-x}\text{Co}_x\text{Cu}_2\text{O}_3$  compounds show ordering temperatures that range from 27 K for pure  $\text{Ca}$  ( $x = 0$ ) [12] to 215 K for pure  $\text{Co}$  ( $x = 1$ ) [13].

The room temperature crystal structure of this family is orthorhombic ( $Pmmn$  or  $Cmmm$ ). The copper atoms are located at the center of  $\text{CuO}_4$  corner-sharing square-plaquettes, arranged in two-leg ladders along the  $\vec{b}$  direction (see Fig. 1a). In each unit cell there are two symmetry-related ladders along the  $\vec{a}$  direction (represented in blue and green). These two-leg copper ladders

are zig-zag coupled, and form planar ( $\text{Sr}$  compound) or puckered ( $\text{Mg}, \text{Ca}, \text{Co}$ ) layers in the  $(\vec{a}, \vec{b})$  directions (see Fig 1b). These layers are connected along the  $\vec{c}$  direction, by  $\text{AO}_6$  octahedra ( $A = \text{Mg}, \text{Ca}, \text{Co}$ ), or  $\text{AO}_8$  cubes ( $A = \text{Sr}$ ), sharing corners with the  $\text{CuO}_4$  plaquettes from adjacent copper-ladder layers (see Fig. 1b).

At this point one should note that the  $\text{Sr}$  compound also differs from the  $\text{Mg}, \text{Ca}, \text{Co}$  ones by its magnetic properties. Indeed, while the latter ones present a 3D magnetic order below its Néel temperature, the  $\text{Sr}$  compound remains essentially 1D [3]. It thus seems that the puckering of the  $(\vec{a}, \vec{b})$  layers plays a major role in the dimensionality of the magnetic ordering.

In this article we will study the magnetic properties of the  $\text{CoCu}_2\text{O}_3$  compound, the member of the  $\text{ACu}_2\text{O}_3$  family with the highest 3D ordering temperature. After the evaluation of the effective exchange interactions using *ab-initio* calculations, we will compute the associated magnetic order by classical Monte-Carlo methods.

This paper is organized as follows. Section II details the computational methods. Section III is devoted to the calculations of the exchange interactions and single ion anisotropy. In Section IV we discuss the magnetic order at zero and finite temperature. Finally, we conclude in Section V.

## II. COMPUTATIONAL DETAILS

### A. *Ab-initio* calculations

As the magnetic interactions are intrinsically exchange-correlation effects, we will use a multireference configuration interaction method to compute them, namely the Selected Active Space plus single excitation (SAS+S) method [15]. Indeed, this method insures that the following effects are treated explicitly i) the correlation effect within the 3d magnetic orbitals, ii) the ligand-to-metal charge transfers mediating the magnetic interactions, and iii) the screening effects on all

\* Marie-Bernadette.Lepetit@neel.cnrs.fr

† andres.saul@cnrs.fr

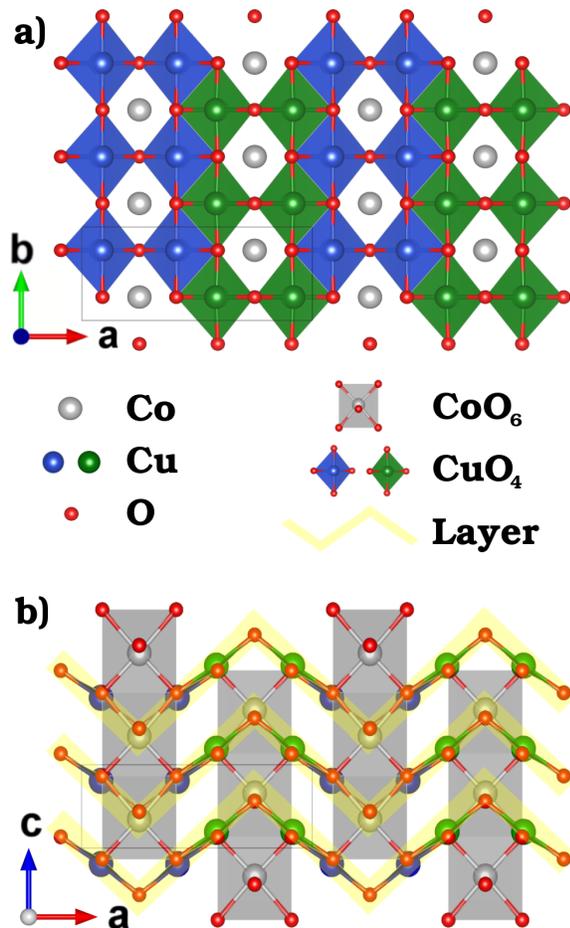


Figure 1. Schematic representation of the crystal structure of  $\text{CoCu}_2\text{O}_3$ . a) along the  $\vec{c}$  and b)  $\vec{b}$  axes. The Cu atoms form two-leg ladders along the  $\vec{b}$  direction and there are two symmetry-related ladders along the  $\vec{a}$  direction. The Cu atoms were represented either in blue or in green to more easily visualize the two equivalent structural ladders. The Co atoms are in light gray, and the O in red. Atomic structures were drawn with VESTA [14].

the previous configurations (as configuration-dependent hole-particle excitations and their coupling).

As such configuration interaction methods require the diagonalization of large matrices, they can only be used on formally finite-size systems. We thus designed, for each magnetic integral, suitable fragments embedded in a set of renormalized charges [16] and Total Ions Pseudopotentials (TIPS) [17], in order to reproduce the effects of the rest of the crystal on the quantum fragment. The TIPS reproduce the exclusion effects due to the electrons of the first layers surrounding the fragment, and the set of charges is chosen in order to reproduce the Madelung potential seen by the fragment with an error smaller than 0.1 meV. The quantum fragments were chosen in order to include the magnetic atoms associated with the desired interaction, their first coordination shell, and any additional bridging ligands.

The fragment orbitals were optimized within a Complete Active Space Self Consistent Field [18] (CASSCF) calculation on the 3d electrons of the magnetic atoms, using the MOLCAS package [19]. We used a valence basis set of  $3\zeta + P$  quality, associated to relativistic core pseudopotentials of the Stuttgart group [20]. The SAS+S calculations were then done using the RelaxSE code [21]. The latter provides the fragment low-energy excitations, from which the effective exchange integrals can be deduced.

The anisotropy calculations were performed using the same method on a single ion embedded cluster, for the spin-orbit-free description, and the RASSI/ANISO [22] modules of MOLCAS for the spin-orbit part. More details are available in the supplementary material [23]

The crystal structure used in all calculations is the room temperature X-Ray given in Ref. 24.

## B. Monte-Carlo calculations

The Monte Carlo (MC) simulations were performed on the model magnetic Hamiltonian derived from our *ab-initio* effective exchange interactions and single ion anisotropies. We computed both the order parameters and the magnetic transition temperatures. For this purpose we used the standard Metropolis algorithm [25] on a classical approximation of the spin Hamiltonian. The calculations were performed using supercells up to  $10 \times 20 \times 20$  (24000 magnetic atoms). The thermodynamical averages were performed with 4000 Monte Carlo steps per atom. More details are available in the supplementary material [23]

## III. RESULTS OF THE AB-INITIO CALCULATIONS

### A. Magnetic integrals

The formal charge analysis of  $\text{CoCu}_2\text{O}_3$  yields  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$ , corresponding respectively to  $3d^9$  and  $3d^7$  electronic configurations. The corresponding magnetic moments are  $S_{Cu} = \frac{1}{2}$  and  $S_{Co} = \frac{3}{2}$ , because the Co ion is in a high-spin configuration (as expected for such an ions and by continuity from the partially substituted compounds,  $\text{Mg}_{1-x}\text{Co}_x\text{Cu}_2\text{O}_3$  for  $x = (0.05, 0.10, 0.15, 0.50)$  [26], and confirmed by our calculations).

The magnetic exchange interactions were obtained from the *ab-initio* calculations, by mapping the computed magnetic spectra onto the energy spectra of a Heisenberg Hamiltonian on the same fragments.

$$\hat{H} = - \sum_{\langle i,j \rangle} J_{ij} \hat{S}_i \cdot \hat{S}_j \quad (1)$$

where  $\hat{S}_i$  and  $\hat{S}_j$  are the quantum spin operators associated to sites  $i$  and  $j$  respectively. The  $J_{ij}$  are the effective exchange interactions, positive and negative values



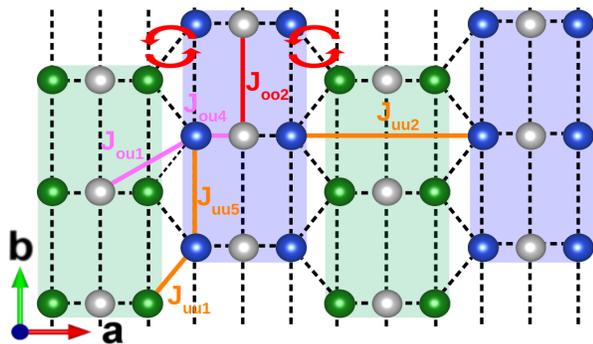


Figure 3. Schematic representation of the magnetic interaction pattern in  $\text{CoCu}_2\text{O}_3$ . This pattern is obtained from the structural pattern (Fig. 2a) by the exchange of the legs of neighboring ladders, as pictured by the red arrows. The main interactions are added for easy comparison. The dash black line represent the magnetic puckered layers including the Co atoms, the dash gray line show the rungs of the structural ladders and blue or green boxes show the magnetic ladders.

and magnetic two-leg ladders. On the contrary the  $\text{CaCu}_2\text{O}_3$  system presents a large bending of the Cu-O-Cu angle, namely of  $123^\circ$  [28] in the structural-ladder rungs. It results in a strongly reduced magnetic interaction (nevertheless still AFM (-11.5 meV) [27]) leading to a quasi-1D magnetic structure of coupled chains. In the present system the Cu-O-Cu angle is again reduced compared to the  $\text{CaCu}_2\text{O}_3$  ( $105^\circ$  [24]) and much closer to  $90^\circ$ , yielding an enhanced reduction of the AFM term, and resulting in a FM interaction of  $J_{uu2} = 9.7$  meV. This result is in agreement with the ferromagnetic ordering, experimentally observed (along the rungs) by neutron diffraction on the  $\text{MgCu}_2\text{O}_3$  compound [29], where the angle is also  $105^\circ$  [30]

To better understand the importance of the Cu-O-Cu angle bending, one should remember that the effective magnetic exchanges are the result of three terms [31] :

- a direct exchange term between the magnetic atoms ( $J_d$ ), this term is always FM and depends exponentially on the metal-metal distance,
- a through-space (also named kinetic or Anderson's superexchange) super-exchange term ( $J_{ss}$ ), issued from electron transfers between the two magnetic atoms, this term is AFM and decreases exponentially with the metal-metal distance, it is thus very small in systems where the metal-metal bond is bridged by a ligand,
- finally the through-bridge super-exchange term ( $J_{sb}$ ), issued from electron transfers between the bridging ligand and the magnetic atoms, this term is AFM and depends exponentially on the metal ligand distance and as the square of the cosine of the metal-ligand-metal angle ( $\theta$ ) ; it is the largest term in AFM bridged systems.

In a first approximation, the effective magnetic exchange can thus be assumed to be

$$J = \underbrace{J_d(d_{\text{Cu-Cu}})}_{\text{FM, scales as } e^{-\alpha d}} + \underbrace{J_{sb}(R_{\text{Cu-O}}, \theta_{\text{Cu-O-Cu}})}_{\text{AFM, scales as } e^{-\beta R} \cos^2 \theta} \quad (2)$$

The bending of the Cu-O-Cu angle thus increases the FM term  $J_d$ , as it is associated with a reduction of the Cu-Cu distance. Simultaneously it strongly reduces the AFM through-bridge super-exchange term when going from  $180^\circ$ , where the latter is maximum, to  $90^\circ$  where it cancels out. One thus sees that the Cu-O-Cu angle is a crucial parameter for the magnetic properties of the  $\text{ACu}_2\text{O}_3$  family.

Let us now focus on the magnetic character of the A-site in our compound. Structurally the  $\text{CoCu}_2\text{O}_3$  and  $\text{MgCu}_2\text{O}_3$  are very similar. However, the magnetic character of the  $\text{Co}^{2+}$  ion transforms the coupled chain magnetic pattern found in the Mg compound, into a coupled three-leg ladder system in  $\text{CoCu}_2\text{O}_3$  (see Fig. 3). Let us remember that the second largest magnetic energy is brought by the copper-cobalt  $J_{ou4}$  interaction and the next one by the Co-Co ladder legs ( $J_{oo2}$ ).

Analyzing the interactions in the puckered layers a bit closer one sees that there are two frustrating magnetic interactions, namely the  $J_{uu1}$  FM interactions between the ladders, and the FM  $J_{ou1}$  interactions between the Co atoms and the Cu atoms of the neighboring magnetic ladders (see Fig. 3). Both interactions bring frustration with the AFM interaction along the ladder legs.

Finally, the interactions between the magnetic puckered layers are conveyed by the FM  $J_{ou3}$  and AFM  $J_{oo1}$ . As can be seen in Table I the remaining interactions can be considered negligible.

## B. Anisotropy

As the  $\text{Cu}^{2+}$  ion is in a  $S = 1/2$  quantum spin state, the anisotropy of the compound is due to the  $\text{Co}^{2+}$  ion. We thus computed the cobalt easy axes and zeroth-field splitting tensor on embedded  $\text{CoO}_6$  fragments.

The zeroth-field splitting tensor is derived from the eigenstates and energies of the many-body, *ab-initio*, electronic plus spin-orbit Hamiltonian on the  $\text{CoO}_6$  embedded fragment, using the pseudo-spin method of L. Ungur and L. F. Chiboratu [22].

We found that in our system the main anisotropy axes are along the crystallographic directions,  $\vec{b}$  is the easy axis and  $\vec{c}$  the hard one. They are associated with a strong anisotropy. Indeed, the zeroth-field splitting tensor can be written as

$$\hat{H}_{\text{ZFS}} = \mathcal{D} \left[ \left( \hat{S} \cdot \frac{\vec{b}}{b} \right)^2 - \frac{S(S+1)}{3} \right] + \mathcal{E} \left[ \left( \hat{S} \cdot \frac{\vec{c}}{c} \right)^2 - \left( \hat{S} \cdot \frac{\vec{a}}{a} \right)^2 \right] \quad (3)$$

with  $\mathcal{D} = -10.60$  meV and  $\mathcal{E} = 2.10$  meV. These values are comparable to some of the strongest magnetic exchange interactions. As a consequence one can expect

the anisotropy to play a major role in the magnetic ordering.

#### IV. MAGNETIC PROPERTIES

##### A. Magnetic order at $T = 0$ K

As previously seen, the three exchange interactions with the strongest energy contributions, namely  $J_{uu5}$ ,  $J_{ou4}$  and  $J_{oo2}$ , form 3-leg ladders along the  $\vec{b}$  direction that do not correspond to the structural ones (see Fig. 3). These three AFM interactions, ( $J_{uu5}$ ,  $J_{ou4}$  and  $J_{oo2}$ ) do not bring any frustration resulting in antiferromagnetically ordered three-leg ladders. Moreover, the large anisotropy of the Co ions aligns the spins along the  $\vec{b}$  axis.

The next non-frustrated contribution to the magnetic energy comes from the FM interaction  $J_{uu2}$ , which connects second neighbor magnetic ladders, forming two independent magnetic puckered planes in the  $(\vec{a}-\vec{b})$  directions. These two independent subsystems are pictured in blue and green on Fig 3. One should note that the two subsystems are related by the  $2_1^y$  or  $i$  symmetry operations. The different planes are then connected by the AFM  $J_{oo1}$  and FM  $J_{ou3}$  interactions, leading to two magnetically-independent, 3D, non-frustrated sub-systems. Both sub-systems are associated with a  $\vec{q} = (0, \frac{1}{2}, \frac{1}{2})$  propagation vector. The two subsystems are coupled by the remaining non-negligible exchange interactions (see Table I), namely the FM  $J_{uu1}$  and  $J_{ou1}$ . These two interactions are frustrated and thus do not contribute to the magnetic energy in the proposed  $T = 0$  magnetic order (see Fig. 4).

At this point the question is whether the above 2-fold degenerate magnetic ordering (pictured in Fig 4) is the ground state. It is easy to show that these two magnetic orders correspond to minima of the classical magnetic energy : nil gradient and positive Hessian.

Let us note, that both the  $\text{CaCu}_2\text{O}_3$  [12] and the  $\text{MgCu}_2\text{O}_3$  [29] compounds also exhibit degenerate ground states, however with different sub-systems and magnetic orders.

Doubly-degenerate ground states are very rare in real compounds, as any perturbation, coupling the two states, lifts the degeneracy. In  $\text{CoCu}_2\text{O}_3$  such a coupling does not exist in the present crystallographic space group and unit cell. One can however see that to couple the two ground states and reduce the magnetic frustration, one should double the crystallographic cell along the  $\vec{b}$  direction. Indeed, such a symmetry reduction could allow lowering of the frustration brought by the inter magnetic-ladders interactions,  $J_{uu1}$  and  $J_{ou1}$ . Let us remember that spin-1/2 chains could exhibit spin-Peierls transitions and that the dominant magnetic interaction in  $\text{CoCu}_2\text{O}_3$  is, by far, the AFM exchange along the Cu ladder leg. One can thus expect that such an effect is also at play in  $\text{CoCu}_2\text{O}_3$  producing the dimerization that doubles the

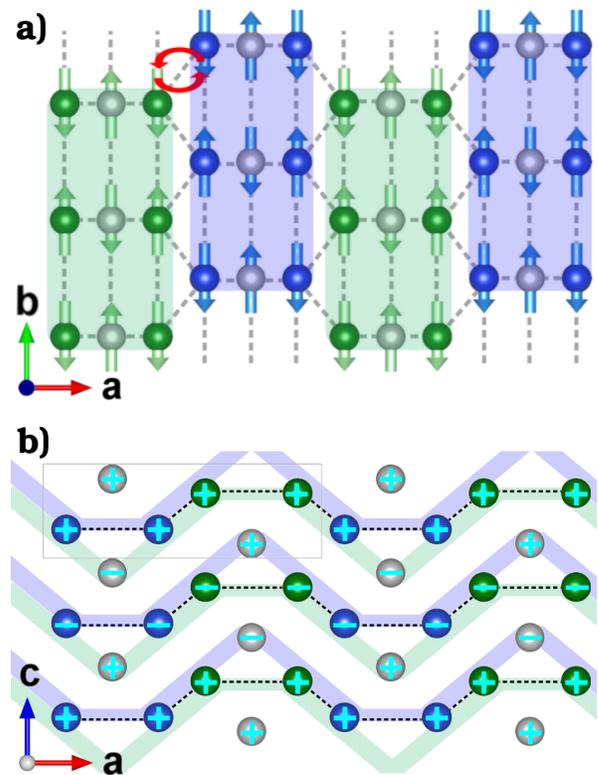


Figure 4. Schematic representation of the magnetic structure of  $\text{CoCu}_2\text{O}_3$ . (a) Order on the puckered magnetic layers. (b) Order in the structural arrangement. The Co atoms are in light gray and the Cu in blue or green according to the magnetic sub-system they belong to. The latter are outlined by blue and green boxes. Atomic structures were drawn with VESTA [14].

unit cell and lowers the energy.

Comparing the magnetic orders of  $\text{CoCu}_2\text{O}_3$  with  $\text{CaCu}_2\text{O}_3$  and  $\text{MgCu}_2\text{O}_3$ , one sees that in addition to different magnetic ladders, as discussed in the previous section, these compounds also exhibit different propagation vectors. Indeed, the  $\text{CaCu}_2\text{O}_3$  is dominated by an incommensurate order  $\vec{q} = (0.429, \frac{1}{2}, \frac{1}{2})$  [28] and  $\text{MgCu}_2\text{O}_3$  by the commensurate  $\vec{q} = (\frac{1}{2}, \frac{1}{2}, 0)$  [29] propagation vector. This is due to the non magnetic character of the Ca and Mg ions that probably induces a weakly AFM interaction between the ladders, mediated by these closed-shell ions.

##### B. Magnetic properties at finite temperature

To study the thermodynamic properties at finite temperature, we performed classical Monte-Carlo (MC) simulations. We computed both the specific heat,  $C_p$ , and the long-range order parameter,  $LRO$ , characteristic of the  $\vec{q} = (0, \frac{1}{2}, \frac{1}{2})$  magnetic order identified in the previous section. The calculation was done using the Heisenberg Hamiltonian defined from the exchange interactions given in Table I, complemented with the zeroth-field splitting

tensor of the Co ions, as provided in Section III.

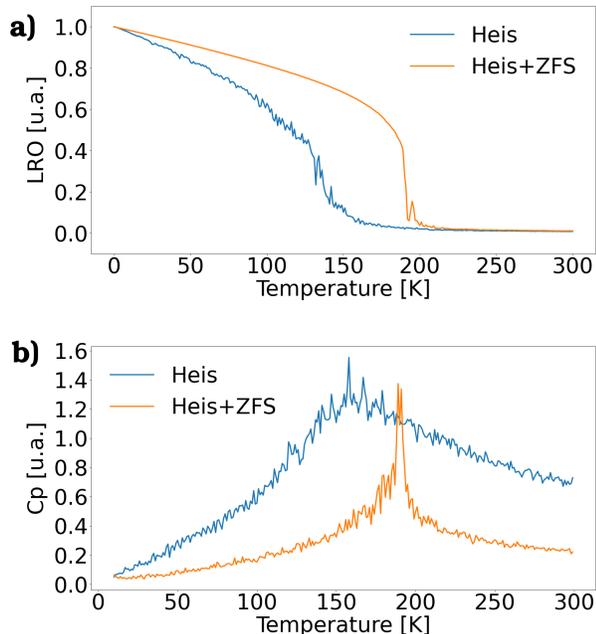


Figure 5. Results of Monte-Carlo simulations. (a)  $LRO$  and (b) Specific heat versus temperature. The two curves represent our MC results with (orange) and without (blue) the  $\text{Co}^{2+}$  zeroth-field splitting contribution to the model Hamiltonian.

Figures 5a) and b) display respectively  $LRO$  and  $C_p$  as a function of temperature. When the Heisenberg and zero-field splitting terms are considered, one can see that both quantities (in orange in both panels) exhibit a clear transition at  $T_N \simeq 190$  K confirming the magnetic order proposed in the previous section. The magnetic frustration brought by the inter magnetic-ladders effective exchanges do not bring any noticeable canting of the spins in the MC results. All spins remain aligned along the  $\vec{b}$  direction. When decreasing the temperature we obtain a MC average energy of about -259.8 meV/cell, in good agreement with the theoretical ground-state classical magnetic energy

$$\begin{aligned}
 E_{\text{cell}} = & (2J_{oo2} + 2J_{oo1}) S_{Co}^2 + 2\mathcal{D} \left[ S_{Co}^2 - \frac{S_{Co}(S_{Co} + 1)}{3} \right] \\
 & + (4J_{ou4} - 4J_{ou3} + 4J_{ou5}) S_{Cu} S_{Co} \\
 & + (4J_{uu5} - 2J_{uu2} + 4J_{uu6} + 4J_{uu3} + 4J_{uu7}) S_{Cu}^2 \\
 = & -260.2 \text{ meV/cell} \quad (4)
 \end{aligned}$$

As suggested in the previous section the frustrating interactions  $J_{uu1}$ ,  $J_{ou1}$ , (as well as  $J_{ou2}$  and  $J_{uu4}$ ) do not contribute to the energy. The very small interactions, neglected in our previous analysis, namely  $J_{uu6}$ ,  $J_{ou5}$  and  $J_{uu7}$ , have positive contributions to energy, i.e. these interactions are frustrated but their effect is negligible.

Let us note that, despite the quantum character of the spin-1/2 Cu ions, the obtained transition temperature is

close enough to the  $T_N = 215$  K value observed in magnetic susceptibility and specific heat measurements [13]. In fact the Co anisotropy plays a major role, its inclusion in the model Hamiltonian breaks the rotational symmetry, transforming  $\text{CoCu}_2\text{O}_3$  in an Ising-like magnetic system. Indeed, in MC simulations where only the exchange interactions are taken into account (see blue curves in Figure 5), long range magnetic order is obtained by the 3D character of the Heisenberg Hamiltonian provided by the inter-plane interactions  $J_{uu3}$ ,  $J_{ou3}$  and  $J_{oo1}$ . As the leading interactions of the system are quasi-2D, the symmetry breaking of the rotational invariant Hamiltonian is numerically more difficult to achieve, and the transition appears less clear in Fig. 5 but definitively takes place at lower temperature ( $T_N \approx 150$  K). Nevertheless, the magnetic order remains identical, apart from the general spin orientation.

## V. CONCLUSION

In this paper we theoretically determined the magnetic order and transition temperature of the  $\text{CoCu}_2\text{O}_3$  ladder compound. We first computed the effective magnetic interactions and anisotropy parameters using an *ab-initio* multi-reference configuration interactions method (SAS+S [15, 21]). With these parameters, we constructed a model Hamiltonian that has been used to determine the magnetic order at  $T = 0$  K and at finite temperature.

Compared to other members of the  $\text{ACu}_2\text{O}_3$  family the  $\text{CoCu}_2\text{O}_3$  compound is characterized by puckered layers with a large folding angle, and by a supplementary magnetic ion ( $\text{Co}^{2+}$ ). These two aspects have strong consequences on the magnetic properties of the system. Indeed, our results allow us to predict that the magnetic ladders strongly differ from those of the other members of the family. First, not only they are not identical to the structural ladders, but they exhibit three and not two legs. Second, these magnetic ladders are strongly connected, both in the layers and between the layers, resulting in a two-fold degenerated ground state. Finally, there is the strong  $\text{Co}^{2+}$  easy axis along the  $\vec{b}$  direction, that not only reduces the otherwise infinite degeneracy, to a two-fold one, but also explains the strong increase (compared to the other members of the family) of the temperature at which the long-range magnetic order sets in. It would be nice if our predicted magnetic order could be experimentally verified, for instance by neutrons diffraction.

We would like to conclude on the magnetic frustration responsible for the degenerated ground state. This degeneracy is due to the existence of two 3D subsystems only coupled by frustrated interactions. One thus expects that a structural distortion should occur to lower this frustration and couple the two subsystems. Our analysis yields that the expected distortion should be a doubling of the unit cell along the  $\vec{b}$  direction. Indeed, not

only such a symmetry breaking would lower the magnetic frustration, but it would also allow the Cu chains (ladder legs) to display a spin-Peierls transition as expected in spin-1/2 chains. Such a transition is reasonably expected at, or close to, the magnetic ordering temperature, however no structural transition has been seen in X-Ray diffraction in the 115-300 K range, as stated in Ref. 13. One should however remember that the energy associated with the magnetic frustration (issued from  $J_{uu1}$  and  $J_{ou1}$ ) is small compared to the other energy scales in the system. As a result the atomic displacements associated with the symmetry breaking can be expected to remain weak, and thus difficult to see with diffraction techniques

(as was learned over the last years by the study of multiferroic systems). Most probably only lattice dynamic studies will be able to clarify this point.

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