Determination of effective microscopic models for the frustrated antiferromagnets \( \text{Cs}_2\text{CuCl}_4 \) and \( \text{Cs}_2\text{CuBr}_4 \) by density functional methods

Kateryna Foyevtsova, Ingo Opahle, Yu-Zhong Zhang, Harald O. Jeschke, and Roser Valentí

Institut für Theoretische Physik, Goethe-Universität Frankfurt, 60438 Frankfurt am Main, Germany

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We investigate the electronic and magnetic properties of the frustrated triangular-lattice antiferromagnets \( \text{Cs}_2\text{CuCl}_4 \) and \( \text{Cs}_2\text{CuBr}_4 \) in the framework of density functional theory. Analysis of the exchange couplings \( J \) and \( J' \) using the available X-ray structural data corroborates the values obtained from experimental results for \( \text{Cs}_2\text{CuBr}_4 \) but not for \( \text{Cs}_2\text{CuCl}_4 \). In order to understand this discrepancy, we perform a detailed study of the effect of structural optimization on the exchange couplings of \( \text{Cs}_2\text{CuCl}_4 \) employing different exchange-correlation functionals. We find that the exchange couplings depend on rather subtle details of the structural optimization and that only when the insulating state (mediated through spin polarization) is present in the structural optimization, we do have agreement between the calculated and the experimentally determined exchange couplings. Finally, we discuss the effect of interlayer couplings as well as longer-ranged couplings in both systems.

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I. INTRODUCTION

For almost two decades the frustrated antiferromagnets \( \text{Cs}_2\text{CuCl}_4 \) and \( \text{Cs}_2\text{CuBr}_4 \) have been considered as experimental realizations of a frustrated triangular lattice \([1, 2]\). Both systems crystallize in the space group \( \text{Pnma} \) \([3, 4] \) [see Fig. 1 (a)] and are characterized by a layered arrangement of \( \text{Cu}^{2+} \) ions in a triangular pattern parallel to the \( bc \) plane. The two-dimensional character of magnetic interactions between the spin-\( \frac{1}{2} \) \( \text{Cu}^{2+} \) ions was confirmed by neutron scattering and susceptibility measurements in both systems \([5, 6] \) and was successfully modeled \([10, 11] \) by a two-dimensional Heisenberg Hamiltonian containing an anisotropic interaction term of the Dzyaloshinskii-Moriya type \([12, 13] \).

In spite of their structural similarity, \( \text{Cs}_2\text{CuCl}_4 \) and \( \text{Cs}_2\text{CuBr}_4 \) have rather different magnetic behavior. While in \( \text{Cs}_2\text{CuBr}_4 \) magnetic excitations are localized and the field dependent magnetization exhibits two well-defined plateaux \([5] \), \( \text{Cs}_2\text{CuCl}_4 \) shows fractional spin excitations and spin liquid behavior over a broad temperature range, as revealed in inelastic neutron scattering experiments \([5] \). The dissimilar behavior between \( \text{Cs}_2\text{CuCl}_4 \) and \( \text{Cs}_2\text{CuBr}_4 \) has often been attributed to their unequal degree of frustration, determined as the ratio \( J'/J \) between the inter-chain exchange coupling \( J' \) and the dominant intra-chain exchange coupling \( J \) in the underlying triangular lattice [see Figs. 1(b) and (c)].

A ratio of \( J'/J = 0.74 \) \([15] \) has been suggested for \( \text{Cs}_2\text{CuBr}_4 \) by comparing the ordering vector of a helical incommensurate structure observed in neutron elastic scattering experiments with the one obtained from inverse temperature series expansions for a spin-1/2 Heisenberg model on an anisotropic triangular lattice \([14] \). In contrast, a ratio of \( J'/J = 0.34 \) \([11] \) was derived for \( \text{Cs}_2\text{CuCl}_4 \) from comparison of spin-wave calculations for the spin-1/2 Heisenberg model with the magnetic excitation spectrum observed in neutron scattering experiments in the presence of an external magnetic field far above saturation. These observations indicate that \( \text{Cs}_2\text{CuCl}_4 \) is less frustrated and more one-dimensional than \( \text{Cs}_2\text{CuBr}_4 \).

While a large amount of work has been devoted to the description of the fractional quantum states and to understanding the phase transitions of the two-dimensional frustrated spin model with spatial anisotropy \([16, 34] \), a detailed comparative analysis of the electronic, magnetic and structural properties of these systems as well as a deep understanding of the origin of the different behavior is still missing.

In this work, we present an extensive density functional theory (DFT) study of the microscopic properties of \( \text{Cs}_2\text{CuCl}_4 \) and \( \text{Cs}_2\text{CuBr}_4 \) and compare our results with experimental data. We consider different exchange-correlation functionals in order to also investigate the dependence of the electronic, magnetic and structural properties on these choices. Our study of the performance of different exchange-correlation functionals is motivated by the fact that physical properties of recently discovered high temperature Fe-based superconductors are extremely sensitive to the details of DFT calculations \([35, 41] \). Also, DFT studies of a recently topical layered Mott insulator \( \text{TiOCl} \) \([42, 51] \) reveals that it is essential to use a suitable exchange-correlation functional in DFT calculations to describe correctly the behavior of this system.

Out of the electronic structure calculations we derive a tight-binding (TB) Hamiltonian and estimate the Heisenberg exchange coupling constants between Cu ions from total energy calculations. Our DFT derived effective models incorporate a larger number of interacting Cu neighbors compared to the models used for the experimental data analysis. We show that some of these terms
are crucial for understanding the behavior of Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$.

II. STRUCTURAL AND ELECTRONIC PROPERTIES

(a) Structural optimization schemes

In this paper, we consider the experimentally measured structures of Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$ as well as internal coordinates obtained from the structural optimization with various exchange-correlation functionals. The experimentally measured unit cell parameters of Cs$_2$CuCl$_4$ are taken from Ref. 3 and those of Cs$_2$CuBr$_4$ from Ref. 4. Both structures were measured at room temperature.

Crystal structure optimization of Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$ is required since calculations with the experimentally determined structural parameters find quite large interatomic forces, which indicates that the structures are not in equilibrium within DFT. This holds for the calculations with all the considered exchange-correlation functionals listed below. In all cases, the interatomic forces are larger in Cs$_2$CuCl$_4$ compared to Cs$_2$CuBr$_4$.

Based on our structural optimizations, we will discuss in detail the electronic properties of both compounds. For the structure optimization we apply the following schemes with different approximations to the exchange-correlation functional within DFT and different magnetic configurations: (1) the spin-independent local density approximation (LDA[nm]) \cite{52}; (2) the spin-independent generalized gradient approximation (GGA[nn]) \cite{53}; (3) the spin-dependent GGA with a ferromagnetic Cu spin configuration (GGA[fm]); (4) the spin-dependent GGA+U \cite{55} with a ferromagnetic Cu spin configuration (GGA+U[fm]). For the GGA+U[fm] calculations we considered the around mean field (AMF) version \cite{56} with values of $U$ and $J_H$ for the Cu ions of 6 eV and 1 eV respectively. The lattice constants, which are assumed to be well determined from experiments, were kept fixed for the structure relaxations while the optimization of the relative atomic positions was constrained by the symmetry of the $Pnma$ space group.

For Cs$_2$CuCl$_4$, we also considered two optimization schemes with an antiferromagnetic Cu spin configuration: GGA[afm] and GGA+U[afm] ($U = 6$ eV, $J_H = 1$ eV). The spin arrangement in this antiferromagnetic configuration is shown in Fig. 1 (d), where the Cs$_2$CuCl$_4$ unit cell was doubled in the $b$ direction along the Cu chains. In order to produce such an arrangement, the symmetry of the supercell was lowered to the space group $P21/c$, with two inequivalent Cu atoms. Our choice of this particular antiferromagnetic configuration is due to its resemblance to the experimentally observed 120° ground state configuration \cite{57}. The considered antiferromagnetic configuration is shown in Fig. 1 (d).

FIG. 1: (Color online) (a) The Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$ unit cell where the CuX$_4$ tetrahedra ($X =\text{Cl, Br}$) are highlighted. (b) Schematic triangular lattice of Cu spins. The gray lattice is below the black lattice. (c) Neighboring CuX$_4$ tetrahedra. Labels 1, 2 and 3 of the X atoms denote the three inequivalent X atoms: $X(1)$, $X(2)$ and $X(3)$. As indicated, angles $\gamma_{12}$, $\gamma_{13}$ correspond to the angles $X(1)$-Cu-$X(2)$, $X(1)$-Cu-$X(3)$, etc. (d) Cu spin configuration of a $1 \times 2 \times 1$ supercell of Cs$_2$CuCl$_4$ adopted for the structural optimization within the GGA+U[afm] scheme.
is collinear, which is beneficial in terms of computational effort, and fulfills the requirement that the strongest couplings \( J \) are satisfied and the second strongest couplings \( J' \) are partially satisfied. The optimization of the relative atomic positions with the two antiferromagnetic schemes was constrained by the symmetry of the \( P21/c \) space group.

Additionally, for both systems we completed the LDA series of structural optimizations with LDA[fm] and LDA+U[fm] optimizations. However, due to the analogous behavior of the structural properties of \( \text{Cs}_2\text{CuCl}_4 \) and \( \text{Cs}_2\text{CuBr}_4 \) observed within this series with those within the GGA series, the detailed analysis of the LDA series will be omitted here.

The DFT structural optimizations were performed with the full-potential local-orbital (FPLO) code \( \text{61, 67} \) in the scalar relativistic approximation with up to 512 \( k \)-points in the full Brillouin zone.

(b) Band gap

Before presenting the structure optimizations with the different exchange-correlation functionals, we shall consider the experimental crystal structure and discuss the electronic properties obtained with the different exchange-correlation functionals. Calculations with the GGA[nm], GGA[fm] or GGA+U[fm] exchange-correlation potentials result in the electronic structure being either gapless (GGA[nn]) or gapped (GGA[fm] and GGA+U[fm]), as shown in Fig. 2. Allowing for spin polarization opens a gap in both \( \text{Cs}_2\text{CuCl}_4 \) and \( \text{Cs}_2\text{CuBr}_4 \) [though in the latter compound the GGA[fm] gap is rather small (\( \sim 0.03 \) eV)]. Upon introducing the onsite Coulomb repulsion within the GGA+U[fm], the gaps in both systems increase considerably [Fig. 2(c) and (f)].

Spin-dependent exchange-correlation functionals provide a better description of \( \text{Cs}_2\text{CuCl}_4 \) and \( \text{Cs}_2\text{CuBr}_4 \) electronic properties as these functionals correctly reproduce the experimentally observed insulating ground state of the compounds. Moreover, as it will be shown in the next sections, it turns out that the presence of a band gap is important for the accurate determination of the equilibrium crystal structures.

(c) Structural analysis

We proceed now with the structural optimization. The crystal structures of \( \text{Cs}_2\text{CuCl}_4 \) and \( \text{Cs}_2\text{CuBr}_4 \) resulting after optimization with each of the schemes described above are presented in Appendix A. In our analysis of these structures we focus on geometry variations of the \( \text{CuX}_4 \) (\( X = \text{Cl}, \text{Br} \)) tetrahedron, which determine the strength of important exchange couplings.

In \( \text{Cs}_2\text{CuCl}_4 \) and \( \text{Cs}_2\text{CuBr}_4 \), the \( \text{CuX}_4 \) tetrahedron is distorted due to the Jahn-Teller effect and also due to the steric pressure originating from \( \text{Cs}^+ \) ions \( \text{4} \). The Jahn-Teller effect results in a squeezing of the tetrahedron such that the \( X-\text{Cu}-X \) bond angles \( \gamma_{12} \) and \( \gamma_{33} \) increase and the \( X-\text{Cu}-X \) bond angles \( \gamma_{13} \) and \( \gamma_{23} \) decrease [Fig. 1(c)]. The steric pressure by \( \text{Cs}(2) \) on \( X(3) \) causes additional symmetry lowering by increasing \( \gamma_{13} \) and decreasing \( \gamma_{33} \). In order to compare the strengths of the two types of distortions in different structures, one can define the Jahn-Teller deviation \( \Delta^{JT} \) as the difference between averages \( \frac{1}{2}(\gamma_{12} + \gamma_{33}) \) and \( \frac{1}{2}(\gamma_{13} + \gamma_{23}) \),

\[
\Delta^{JT} = \left| \frac{1}{2}(\gamma_{12} + \gamma_{33}) - \frac{1}{2}(\gamma_{13} + \gamma_{23}) \right|
\]

(1)

and the steric pressure deviations \( \delta_1^{\text{steric}} \) and \( \delta_2^{\text{steric}} \) as

\[
\delta_1^{\text{steric}} = \frac{1}{2}|\gamma_{12} - \gamma_{33}| \quad \text{and} \quad \delta_2^{\text{steric}} = \frac{1}{2}|\gamma_{13} - \gamma_{23}|
\]

(2)

As can be seen in Appendix A, the \( \text{Cs}_2\text{CuCl}_4 \) structures relaxed with GGA[fm] and GGA[afm] are very close as well as the structures relaxed with GGA+U[fm]
and GGA+U[afm]. The tetrahedron parameters in these structures are also similarly close. This demonstrates that, within the spin-dependent GGA and GGA+U, interatomic forces in Cs$_2$CuCl$_4$ are very weakly dependent on the actual Cu spin configuration and in the following we will consider only ferromagnetic spin-dependent relaxation schemes for Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$. This result is a consequence of the rather small energy scale of magnetic interactions between Cu spins, which is much smaller than the difference between total energies usually involved in structural relaxations.

In Tables I and II we present the tetrahedron parameters defined above for the experimental and relaxed crystal structures of Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$, respectively. Some of them are additionally shown in Fig. 3 in order to facilitate the comparison of the different crystal structures. In both compounds, the crystal structures of the GGA relaxation series (GGA+U[fm], GGA[fm] and GGA[nn]) are featured by a continuous variation of the Cu-X angles. In terms of these angles, the relaxed crystal structures closest to the experimental structures are the GGA+U[fm] structures for both Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$. However, in terms of Cu-X bond distances, represented here as the averaged distance $\bar{d}_{\text{Cu-X}}$, the GGA crystal structures are further away from the experimental structures than the LDA structures (see Fig. 3(a)). In the LDA structures (including the LDA[fm] and LDA+U[fm] ones, which are not listed in the tables), $\bar{d}_{\text{Cu-X}}$ are smaller than the corresponding parameters of the experimental structures, but the difference is less compared to the GGA series. Thus, the GGA relaxation tends to increase the bond distances in the CuX$_4$ tetrahedron while the LDA relaxation decreases them.

In the GGA series, the Jahn-Teller-like distortion of the tetrahedron, which we evaluate through $\Delta^{JT}$, is strongest in the GGA[nn] crystal structures of both compounds and decreases monotonically as the Cu magnetic moment in the spin-resolved calculations increases (GGA[fm], GGA+U[fm]) [see Fig. 3(b)]. The Cu magnetic moment in Cs$_2$CuCl$_4$ calculated with either GGA[fm] or GGA[afm] schemes is 0.50μ$_B$ and increases to 0.78μ$_B$ when the onsite Coulomb interaction is switched on within the GGA+U functional (Table I). In Cs$_2$CuBr$_4$, the corresponding values of the Cu magnetic moment are 0.42μ$_B$ and 0.73μ$_B$ [38] (Table I). In the LDA[nn] structures, $\Delta^{JT}$ takes the largest value. The distortion due to steric pressure, which is characterized by $\delta^{steric}$ and $\delta^{steric}$ (Figs. 3(c) and (d)), does not appear to follow any general rule.

For the further discussion of the electronic structure it

| exp | GGA+U[fm] | GGA[fm] | GGA[nn] | LDA[nn] |
|-----|-----------|---------|---------|---------|
| γ12 | 131.33    | 130.97  | 133.05  | 133.66  |
| γ13 | 101.67    | 101.60  | 100.67  | 99.69   | 98.26   |
| γ23 | 99.58     | 99.43   | 98.55   | 97.86   | 97.11   |
| γ33 | 126.79    | 127.78  | 130.41  | 134.34  | 138.56  |
| $\Delta^{JT}$ | 28.44         | 28.86   | 32.12   | 35.22   | 39.38   |
| α  | 153.99    | 153.89  | 155.21  | 157.17  | 159.28  |
| $\delta^{steric}$ | 1.76       | 1.23    | 1.00    | 0.25    | 1.10    |
| $\delta^{steric}$ | 1.04       | 1.08    | 1.06    | 0.93    | 0.59    |
| $\bar{d}_{\text{Cu-Cl}}$ | 2.232      | 2.263   | 2.263   | 2.267   | 2.227   |
| μ  | -         | 0.78μ$_B$ | 0.50μ$_B$ | 0      | 0       |
TABLE II: Tetrahedron parameters for the Cs$_2$CuBr$_4$ structures and corresponding values of the Cu magnetic moment during structural relaxation. The angles are given in degrees, the deviations $\delta^0_{\text{steric}}$ and $\delta^1_{\text{steric}}$ in percent and the averaged Cu-Br distance $\bar{d}_{\text{Cu-Br}}$ in Ångström.

|       | exp  | GGA+U [fm] | GGA [fm] | GGA [nm] | LDA [nm] |
|-------|------|------------|----------|----------|----------|
| $\gamma_{12}$ | 130.40 | 130.06 | 131.77 | 132.53 | 133.72 |
| $\gamma_{13}$ | 102.16 | 102.16 | 101.70 | 100.48 | 99.03 |
| $\gamma_{23}$ | 99.93 | 99.75 | 98.89 | 97.94 | 97.34 |
| $\gamma_{33}$ | 126.42 | 126.42 | 128.05 | 133.07 | 137.48 |
| $\Delta^\text{MT}$ | 27.52 | 27.28 | 29.62 | 33.59 | 37.41 |
| $\alpha$ | 153.21 | 153.22 | 154.03 | 156.53 | 158.74 |
| $\delta^0_{\text{steric}}$ | 1.55 | 1.42 | 1.43 | 0.20 | 1.38 |
| $\delta^1_{\text{steric}}$ | 0.96 | 1.19 | 1.40 | 1.28 | 0.86 |
| $\bar{d}_{\text{Cu-Br}}$ | 2.376 | 2.407 | 2.407 | 2.411 | 2.368 |

is useful to consider an additional structural parameter, namely, the angle in the $J$ superexchange bridge Cu-X-X-Cu, shown in Fig. 1 (c) as $\alpha$. This angle is closely related to $\gamma_{33}$ and behaves analogously in the various structures [see Fig. 3 (e) and Tab. 1]. The large variation of the superexchange coupling $J$ in different Cs$_2$CuCl$_4$ relaxed crystal structures is mainly attributed to the variation of $\alpha$, as will be discussed in Section III.

(d) Electronic structure

In this section, we present a detailed analysis of electronic properties of Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$ for the experimental and relaxed crystal structures introduced in the previous section. We show the results obtained with the spin-independent GGA exchange-correlation functional as these are also used for the tight-binding parametrization. Calculations were performed with both the FPLO code as well as the linearized augmented plane wave (LAPW) scheme, as implemented in the Wien2k code [59]. The calculations with both codes are in good agreement and the data presented here are obtained with the LAPW code.

Fig. 4 displays the density of states (DOS) for Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$ obtained using the experimental structure. In both compounds, the hybridized Cu 3d and Cl 3p/Br 4p bands occupy the energy range between -4 eV and 0 eV [see, for instance, the atomic DOS in Figs. 4 (a) and (c)]. At the Fermi level, the Cu 3d$xy$ states are half-filled as Cu is in a 3d$^9$ configuration. There are four Cu 3d$xy$ bands in the bandstructure, which corresponds to the number of Cu atoms per unit cell. A gap of approximately 4 eV separates the Cu and X (X = Cl, Br) bands from the next unoccupied states [not shown in Figs. 4 (a) and (c)], which have significant Cs contribu-

Almost no contribution from Cs atoms to the DOS near the Fermi level is observed indicating a negligible hybridization of Cu with Cs. In particular, this indicates that exchange coupling $J$ along the Cu chains in the $b$ direction arises from the Cu-X-X-Cu hybridization.

The Cu and X band manifold is an assembly of bonding states in the interval between -4 eV and -2 eV and...
antibonding states in the interval from -2 eV up to the Fermi level. The Cu antibonding states are split by the crystal field generated by X$^-$ ions surrounding a Cu$^{2+}$ ion into the energetically lower Cu $e_g$ doublet ($d_{x^2-y^2}$ and $d_{z^2}$) and the energetically higher Cu $t_{2g}$ triplet ($d_{xy}$, $d_{xz}$ and $d_{yz}$). Due to the Jahn-Teller-like uniaxial distortion of the tetrahedron, the $t_{2g}$ triplet is further split into the degenerate $d_{xz}/d_{yz}$ states and the half-filled $d_{xy}$ states. This splitting is schematically illustrated in Fig. 5 (a), and the orbital projected densities of Cu 3d states for the experimental Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$ structures are presented in Figs. 6 (b) and (d), respectively. Note that the orbital designation is given according to the local reference frame of the Cu atom, in which its orbital projected density of states is defined.

In Figs. 6 and 7 we present the total DOS and bandstructures for the experimental as well as relaxed crystal structures (GGA+U[fm], GGA[fm], GGA[nm], LDA[nn]) of Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$, respectively. In contrast to Cs$_2$CuCl$_4$, the $t_{2g}$ states in Cs$_2$CuBr$_4$ are strongly hybridizing, which is indicated by the non-separable character of the overlap of the Cs$_2$CuBr$_4$ $d_{xy}$ and $d_{xz}/d_{yz}$ bands in the bandstructure.

We now focus on the comparison between the electronic structures of Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$ calculated from different crystal structures. In both compounds, the choice of the relaxation scheme determines the degree of separation between the $d_{xy}$ and $d_{xz}/d_{yz}$ bands and the dispersion of the $d_{xy}$ band. The separation between the $d_{xy}$ and $d_{xz}/d_{yz}$ bands is reduced in the GGA[nm] crystal structure, compared to the LDA[nn] one, and keeps reducing within the GGA series as the value of the Cu magnetic moment, associated with a given relaxation functional, gets larger (GGA[fm], GGA+U[fm]). This trend is better seen in Cs$_2$CuCl$_4$, where the $d_{xy}$ band is separated by a gap (except for the GGA+U[fm] struc-

![FIG. 5: (a) A schematic splitting of Cu 3d orbitals in the crystal field. (b) The path in the Cs$_2$CuCl$_4$/Cs$_2$CuBr$_4$ Brillouin zone for bandstructure calculations (Figs. 6 and 7). (c) The local reference frame of a Cu atom, in which its orbital projected density of states is defined.](image-url)
We relate the variation of the degree of separation to the variation of the Jahn-Teller-like distortion of the CuX₄ tetrahedron. Our assumption is supported by the structural analysis in Tables II and III as one observes there that the structures possessing more distorted tetrahedra demonstrate larger \( d_{xy} \) and \( d_{xz}/d_{yz} \) band separation in the electronic structure.

Analysis of the \( d_{xy} \) band dispersion shows that the \( d_{xy} \) bandwidth does not change significantly among the Cs₂CuBr₄ structures including the experimental one (Fig. 7). In Cs₂CuCl₄, the \( d_{xy} \) bandwidth of the experimental crystal structure is significantly narrower compared to that of the relaxed crystal structures, where it stays nearly uniform (Fig. 7). The shape of the \( d_{xy} \) bands varies in details from structure to structure in both compounds. This shape variation is accompanied by a variation of the density of states distribution within the \( d_{xy} \) orbital, which is easier to quantify. Thus, in both compounds, the weight of the \( d_{xy} \) DOS gets shifted closer to the Fermi energy in the LDA[nm], GGA[nm], GGA[fm], GGA+U[fm] crystal structures sequence, which results in a more peaked appearance of the \( d_{xy} \) DOS. The DOS at the Fermi level increases correspondingly. In the experimental Cs₂CuCl₄ structure, the DOS at the Fermi level is extremely sharp also due to the flatness of the \( d_{xy} \) band.

(e) TB model for Cs₂CuCl₄

The changes observed among the various electronic structures of Cs₂CuCl₄ and Cs₂CuBr₄ can also be discussed on a quantitative level by mapping bandstructures to a tight-binding (TB) Hamiltonian:

\[
H_{TB} = \mu \sum_i \hat{c}_{i,\sigma}^\dagger \hat{c}_{i,\sigma} - \sum_{<i,j>, \sigma} \left( t_{ij} \hat{c}_{i,\sigma}^\dagger \hat{c}_{j,\sigma} + \text{h.c.} \right),
\]

where \( \hat{c}_{i,\sigma}^\dagger \) and \( \hat{c}_{i,\sigma} \) are, respectively, the creation and annihilation operators of electrons on site \( i \) and with spin \( \sigma \), \( t_{ij} \) denotes the hopping integrals and h. c. denotes Hermitian conjugate terms.

Since in Cs₂CuCl₄ the Cu 3d\( d_{xy} \) bands at the Fermi level are well separated from the rest of the t\( 2g \) manifold, its low-energy properties can be described by a one-band TB model. The hopping integrals are evaluated by Fourier-transforming the Hamiltonian Eq. (3) and mapping its eigenvalues to the four DFT Cu 3d\( d_{xy} \) bands.

In Cs₂CuBr₄, the TB procedure is complicated by the hybridization of the overlapping \( d_{xy} \) and \( d_{xz}/d_{yz} \) bands. In this case, a three-band TB model is required. Since the three-band TB model includes new electronic degrees of freedom due to electron hopping between different types of orbitals, the number of independent hopping integrals in this model is considerably larger, compared to the one-band case. With an increasing number of model parameters, the TB parametrization by means of fitting becomes less reliable, and therefore we do not apply this method to Cs₂CuBr₄ in the present work. The rest of this section will be dedicated to the discussion of the Cs₂CuCl₄ single-band TB models.

Though it was experimentally established [11] that the spin interactions in Cs₂CuCl₄ are predominantly within
the Cu layer along the J and J' paths [see Fig. 4 (b)], we observe that the electronic behavior modeled by the TB Hamiltonian show non-negligible interlayer hopping terms. We find that the d_{xy} bands of all the Cs_{2}CuCl_{4} structures can only be satisfactorily described with a minimal model that includes five hopping integrals. Three of them are the intralayer hoppings t and t' and the interlayer hopping t'' (t, t', t'' correspond to the interaction paths J, J', J'', etc.), which have been considered in previous studies in the framework of spin Hamiltonians. The two new hopping parameters are the interlayer coupling t_{3} is stable for all the structures, while t'' and t_{1} vary considerably.

We associate the variation of the hopping integral t in different Cs_{2}CuCl_{4} crystal structures with the variation of the CuCl_{4} tetrahedron geometry and, in particular, with the variation of the angle \( \alpha \) in the Cu-Cl(3)-Cl(3)-Cu interaction path. In the relaxed Cs_{2}CuCl_{4} crystal structures, larger t values correspond to larger values of \( \alpha \) and larger tetrahedron distortions. However, the experimental structure does not follow this rule; while the angles of the experimental and GGA+U[fm] relaxed structures are very similar, the t values differ by a factor of two. The reason why the experimental structure deviates from the relaxed structures might be the influence of other tetrahedron parameters, such as details of the Cu-Cl bond distances.

The observed relation between the dominant hopping integral t and the angle \( \alpha \) is reasonable since \( \alpha \) is the defining angle for the Cu 3d_{xy}-Cl 3p-Cl 3p-Cu 3d_{xy} hybridization. By considering perturbation theory on the onsite Coulomb repulsion \( U \) up to the second order, the effective Cu-Cu superexchange coupling can be obtained from t as \( J = \frac{4t^2}{U} \). Then, the relation between t and \( \alpha \) fulfills the Kanamori-Goodenough rule [62, 63], stating that \( J \) reaches a maximum when the cation-anion-cation angle equals 180°. In the present case of the cation-anion-anion-cation (Cu-Cl-Cu-Cl) bridge, the four atoms get aligned along a straight line when \( \alpha \) increases.

III. EXCHANGE INTEGRALS

(a) Computational details

The coupling integral \( J_{ij} \) of the Heisenberg Hamiltonian,

\[
H_{H} = \sum_{<i,j>} J_{ij} S_i S_j,
\]

(4)

can be obtained by means of DFT spin-resolved total energy calculations [64]. Considering the differences between the energies of the ferromagnetic configuration and various antiferromagnetic spin configurations, \( E^\text{FM} - E^\text{AFM} \), one derives a set of coupled equations for the couplings \( J_{ij} \). Following Eq. (3), antiferromagnetic exchange corresponds to positive \( J_{ij} \).
FIG. 8: (Color online) The spin exchange coupling constants as functions of $1/U$ for (a) the Cs$_2$CuCl$_4$ experimental structure calculated with the atomic limit version of the GGA+U, (b) the Cs$_2$CuCl$_4$ experimental structure (c) the Cs$_2$CuCl$_4$ GGA+U[fm] relaxed structure, (d) the Cs$_2$CuCl$_4$ GGA[fm] relaxed structure, (e) the Cs$_2$CuCl$_4$ GGA[mm] relaxed structure, (f) the Cs$_2$CuBr$_4$ experimental structure, (g) the Cs$_2$CuBr$_4$ GGA+U[fm] relaxed structure, (h) the Cs$_2$CuBr$_4$ GGA[fm] relaxed structure, (i) the Cs$_2$CuBr$_4$ GGA[mm] relaxed structure. When not specified otherwise, the exchange couplings are obtained with the around mean field version of the GGA+U. The three sets of exchange couplings correspond to $U = 8, 6$ and $4$ eV. Dashed lines mark the experimentally determined values of $J, J'$ and $J''$.

For Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$, we take into account seven important couplings corresponding to the first seven hopping integrals in Table III which are $J, J', J''$, $J_{\text{eff}}' = J'' + J_6$, $J_1, J_3$, $J_5$ and $J_8$ [see Figs. 1(b) and 1(a)]. This choice defines the number of antiferromagnetic configurations to be calculated. The combined coupling $J''_{\text{eff}}$ is introduced because the considered unit cell (which is a $2 \times 2 \times 1$ supercell) does not allow a separate calculation of the couplings $J''$ and $J_6$ but only their calculation as a sum. Since $J''$ is presumably larger than $J_6$, $J''_{\text{eff}}$ gives an approximate value of $J''$.

The choice of the supercell is dictated by the peculiarities of the Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$ magnetic sublattices. First, since the candidate for the largest coupling $J$ connects Cu atoms that belong to adjacent primitive unit cells in Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$, the primitive unit cell has to be doubled in the $b$ direction. Otherwise, $J$ would be always canceled in any $E^{\text{FM}} - E^{\text{AFM}}$ difference. Also, in order to be able to discern the inequivalent couplings $J_1$ and $J_3$, we double the unit cell once more in the $a$ direction and thus end up with a $2 \times 2 \times 1$ supercell. In the supercell, we set eight out of 16 Cu atoms inequivalent in order to be able to arrange the required seven antiferromagnetic configurations within the same unit cell space group, which is $P-1$. It is important to stay within the same space group during total energy calculations for Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$ as in these compounds the exchange couplings are small and integration over differently sampled Brillouin zones can affect the accuracy of the results.

The seven antiferromagnetic spin configurations, together with the set of coupled equations for the exchange couplings, are presented in Appendix C. The total energy calculations were performed with the FPLO code. Test calculations with Wien2k confirm the results. In the FPLO code, we chose a $5 \times 4 \times 3$ mesh of $k$-points for the supercell Brillouin zone integration and kept other settings at default. The scheme to compute magnetic exchange for a given structure consisted of a series of total energy calculations within the AMF version of the
GGA+U, with $U = 4$, 6 and 8 eV and $J_H = 1$ eV in all cases. This scheme was applied to the experimental structures of Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$ and also to the GGA[nm], GGA[fm] and GGA+U[fm] relaxed structures of the two compounds.

(b) Results

The calculated exchange couplings are plotted in Fig. 8 as a function of $1/U$. For an easy comparison, we also mark by horizontal dashed lines of corresponding colors the experimentally determined values of $J$, $J'$ and $J''$ for Cs$_2$CuCl$_4$ [11] and of $J$ and $J'$ for Cs$_2$CuBr$_4$ [12]. Additionally, the exchange coupling values are provided in Appendix D.

We first compare the Heisenberg models of Cs$_2$CuCl$_4$, derived for the experimental as well as relaxed crystal structures [Figs. 8 (a)-(c)]. The common feature for all these structures is that their spin models are two-dimensional, with $J$ being the leading interaction followed by $J'$.

For the experimental structure [Fig. 8 (b)], the ratio $J'/J$ is similar to the experimentally determined ratio $[11,65]$, while the absolute values of $J$ and $J'$, which are calculated in the present work, are off by a factor of almost 3. In this structure, the two-dimensionality is less pronounced due to the interlayer antiferromagnetic interaction $J_3$ and the ferromagnetic interaction $J_7$, which are competing with $J'$. The GGA[nm] structure [Fig. 8 (e)], on the other hand, tends to behave as a 1D rather than 2D system as here the $J'/J$ ratio is 0.15 at $U = 6$ eV. We assume that $U = 6$ eV should be close to the $U$ value for the Cu 3d electrons in the LAPW GGA+U scheme (see, for instance, Ref. [56] where the authors successfully reproduce the electric field gradients at Cu$^{2+}$ ions in a number of Cu$_2$O$_2$ oxides and halides by performing LDA+U calculations with $U_{\text{eff}} = U - J = 5$ eV). The $J'/J$ ratios at $U = 6$ eV in the experimental, GGA+U[fm] and GGA[nm] structures are, respectively, 0.30, 0.47 and 0.27. These ratios vary slightly for other $U$ values.

The differences in the $J'/J$ ratios among the relaxed structures are mainly due to a strong variation of the coupling $J$, which adopts the values 0.384, 0.568, 0.932 meV for $U = 6$ eV in the GGA+U[fm], GGA[fm] and GGA[nm] structures, respectively, whereas $J'$ decreases only slightly for the same sequence of structures.

Judging by the proximity of the theoretically derived Cs$_2$CuCl$_4$ Heisenberg model (this work) to the experimentally determined one [11], the calculations with the GGA[fm] and GGA+U[fm] optimized structures provide the most satisfactory results. In both cases, the absolute values of $J$ and $J'$ as well as their ratios are close to experiment for typical values of $U$ between 6 and 8 eV (for GGA+U[fm] $U \approx 6$ eV yields the best agreement, while in the case of GGA[fm] interpolation of the results between 6 and 8 eV results in almost perfect agreement with experiment for $U \approx 7$ eV). Moreover we find non-negligible interlayer couplings as shown in Appendix D (bold-face values).

For the spin models calculated with the relaxed Cs$_2$CuCl$_4$ structures, the ratios of antiferromagnetic exchange couplings are in good agreement with the ratios of the corresponding squared hopping integrals. This is an indication that ferromagnetic contributions to these couplings are small.

In contrast to Cs$_2$CuCl$_4$, the Cs$_2$CuBr$_4$ effective spin model derived using the experimental crystal structure [Fig. 8(f)] agrees well with the experimentally estimated model parameters in the interval of $U$ values around 6 eV. We obtain that Cs$_2$CuBr$_4$ is a two-dimensional system, with dominant antiferromagnetic couplings $J$ and $J'$ and considerably smaller interlayer couplings. At $U = 6$ eV, the obtained $J'/J$ ratio equals 0.64, which compares well with the experimental result of 0.74. Also, the model based on the GGA+U[fm] relaxed structure [Fig. 8(g)] gives similar results for the exchange parameters. The similarity between these two models is another feature that distinguishes Cs$_2$CuBr$_4$ from Cs$_2$CuCl$_4$. In the latter case, as seen above, the exchange couplings of the experimental model [Fig. 8(b)] are considerably smaller than those of the GGA+U[fm] relaxation model [Fig. 8(c)].

Overall, the Heisenberg models for Cs$_2$CuBr$_4$ obtained within the GGA relaxation series [Figs. 8(g)-(i)] follow the same behavior as the corresponding Cs$_2$CuCl$_4$ models, which is characterized by increasing $J$ and decreasing $J'/J$ in structures that have been relaxed with a smaller Cu magnetic moment.

To conclude this section, we briefly comment on the performance of the atomic limit (AL) version [54] of the GGA+U exchange-correlation functional, which is an alternative to the around mean field version. The exchange couplings of the experimental Cs$_2$CuCl$_4$ structure calculated with the AL double counting correction differ considerably from those obtained with the AMF double counting correction [compare panels (b) and (c) of Fig. 8]. The AL calculated exchange couplings $J$ and $J'$ do not behave linearly with $1/U$, as expected from the $J = 4t^2/U$ relation, valid for these antiferromagnetic couplings. Therefore, we restrict ourselves in the remaining discussion to calculations with the AMF double counting correction.

IV. DISCUSSION

From our analysis of the structural and electronic properties of Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$ we obtained the following results: Within the sequence LDA[nm], GGA[nm], GGA[fm] and GGA+U[fm] of functionals used for the structural optimization, the Jahn-Teller-like distortion of
the CuX₄ tetrahedron is reduced, which is accompanied by an increase of the Cu-X(3)-X(3) angle α in the J superexchange path. These structural changes lead to a considerable variation of the exchange coupling J and the corresponding hopping integral t.

(a) Importance of magnetism and electronic correlations

We find that the choice of the functional used in the structure optimization is crucial for the correct modeling of the properties of these two compounds, especially in the case of Cs₂CuCl₄. First of all, opening of a gap at the Fermi level by introducing various magnetic structures seems to be a necessary ingredient in the structure optimization, as can be seen from the relatively bad performance of the LDA[fm] and GGA[fm] optimizations. Since in these schemes the system is gapless, which is in stark contrast to the true ground state of Cs₂CuCl₄ observed experimentally, the strong instability at the Fermi level (visible in the peak in the DOS) has to be partially relieved by forcing an unphysically strong structural distortion, leading to an improper determination of lattice structure. Furthermore, a change of the size of the gap through onsite correlations and corresponding localization of the Cu magnetic moments also influences the results of the structure optimization. Although one might have expected a better performance of the spin-dependent optimization schemes (due to the magnetic nature of the compounds), the strong impact on the calculated exchange couplings is rather unexpected. The reason is presumably the small values of the exchange constants.

(b) Comments on the quality of the experimentally determined Cs₂CuCl₄ and Cs₂CuBr₄ crystal structures

Comparison of electronic behavior and effective models of the various relaxed Cs₂CuCl₄ structures with those of the experimental structure indicates that the experimental determination of the Cs₂CuCl₄ crystal structure was probably not sufficiently accurate, at least, as far as calculations of microscopic models are concerned. This would explain the huge differences between our derived Cs₂CuCl₄ Heisenberg model when the experimental crystal structure is considered, and the model Coldea et al. [11] obtained from fitting to neutron data and which was corroborated by a number of studies [10] [19] [27] [69]. Accurate determination of the Cs₂CuCl₄ crystal structure might be complicated due to the presence of non-stoichiometric hydrogen containing compounds, presumably HCl or HO₂, detected in this material and not detected in Cs₂CuBr₄ [3] [68].

The experimentally determined Cs₂CuBr₄ crystal structure, on the other hand, is accurate enough. We suggest therefore that Cs₂CuBr₄ can be regarded as a reference system for choosing the relaxation scheme, suitable also for describing Cs₂CuCl₄. We conclude from the data analysis and from the physical considerations that such a relaxation scheme is the GGA[fm]|(GGA+U[fm]), with 0 ≤ U ≤ 6 eV.

(c) Comparison with the experimentally determined microscopic models

In view of the arguments presented above, one should refer to the results obtained with either GGA[fm] or GGA+U[fm] relaxed structures when discussing the realistic spin model for Cs₂CuCl₄. Our calculations confirm for both systems that their spin models are 2D, with the intraplane J and J′ being the leading interactions, and Cs₂CuBr₄ showing a higher degree of frustration than Cs₂CuCl₄. The model from Coldea et al. [11], with J = 0.374 eV and J′/J = 0.34, is close to our DFT models derived with the GGA[fm] and GGA+U[fm] relaxed structures and remains a valid model for Cs₂CuCl₄. In Cs₂CuBr₄, where the experimental crystal structure seems to be much more reliable, we can propose an approximate DFT model, obtained as a generalization of the models of Figs. [3](f) and (g) for U ≈ 6 eV: 0.8 ≤ J ≤ 0.9, 0.5 ≤ J′/J ≤ 0.65. This model is quite close to the model by Ono et al. [15], with J = 0.97 eV and J′/J = 0.74. Additionally, in view of the recent theoretical studies by Starykh et al. [27] [69], who demonstrated the important role of the relatively weak Dzyaloshinskii-Moriya interaction and interlayer coupling in determining the magnetic behavior of Cs₂CuCl₄, our results for the effective Cs₂CuCl₄ model reveal a possible relevance of a number of interlayer couplings, besides J″, which are of comparable strength (J₁, J₃ and J₇). Also, we find the next-nearest chain neighbor hopping integral t₁₄ to be quite large, thus supporting another suggestion by these authors.

Finally, it is important to emphasize that the electronic TB models for the two compounds involve sizable interlayer hoppings, comparable with the intralayer ones, so that in terms of electronic degrees of freedom the two compounds have 3D behavior. In the case of Cs₂CuBr₄, this can be seen from the large dispersion of the bands along the a∗ direction in k-space, even though we didn’t derive a TB model for this material.

(d) Structural relaxation

Finally, we comment on our decision to perform structural relaxations with fixed lattice constants and using
the room temperature data. It is generally known that the GGA tends to overestimate the unit cell volume while the LDA underestimates it. Therefore, we preferred to rely on the experimental lattice constants, which are usually determined with high accuracy. We performed a test GGA[nm] relaxation of the Cs$_2$CuCl$_4$ crystal structure with lattice constants measured at 0.3 K [11] and found that the electronic structure and the TB model of the resulting Cs$_2$CuCl$_4$ structure are close to the electronic structure and the TB model of the GGA[nm] Cs$_2$CuCl$_4$ structure, relaxed with the room temperature lattice constants. Therefore, all calculations have been performed with the room temperature lattice constants for both compounds.

V. SUMMARY AND CONCLUSIONS

In summary, we have performed DFT calculations for Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$. Our study shows that the exchange coupling constants of these compounds exhibit a strong dependence on subtle details of the crystal structure, especially on the geometry of the CuX$_4$ tetrahedra. Depending on the structural model, we observe a large variation of the derived exchange couplings and their ratios, resulting in completely different spin model Hamiltonians. One reason for this unusual sensitivity are the fairly small absolute values of the exchange couplings, with the largest coupling constant $J$ being below 5 K.

One important motivation for our detailed study is the failure of the experimental structure published in Ref. [3] to correctly describe the magnetic behavior of Cs$_2$CuCl$_4$. Calculations with the experimental structure provide too small exchange coupling constants with fairly strong interlayer couplings in contrast to the pronounced 2D character observed in experiment. This indicates (together with the fairly large forces acting on the atomic positions) that a better characterization of the Cs$_2$CuCl$_4$ crystal structure is necessary. Only after structural optimization with spin-dependent GGA and GGA+U functionals, we obtain an overall good agreement with the exchange couplings obtained from experiment [11].

In contrast, the leading exchange couplings for Cs$_2$CuBr$_4$ obtained from our calculations are in good agreement with those derived from experiment, independently of whether we use the experimental structure or structures from spin-resolved optimizations.

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APPENDIX A: STRUCTURAL PARAMETERS OF CS$_2$CUCI$_4$ AND CS$_2$CUBR$_4$ OBTAINED WITHIN DIFFERENT OPTIMIZATION SCHEMES

Below, we provide the Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$ relative atomic positions obtained after structural optimization within different schemes. For a quick reference, we also cite Ref. [3] for the experimentally found structure of Cs$_2$CuCl$_4$ and Ref. [4] for that of Cs$_2$CuBr$_4$.

In the case of Cs$_2$CuCl$_4$, for the experimental structure and structures relaxed with non-spin-resolved and ferromagnetic calculations, the lattice constants are $a = 9.769$ Å, $b = 7.607$ Å, $c = 12.381$ Å and the space group is Pnma. The structures relaxed with antiferromagnetic calculations (GGA[afm] and GGA+U[afm]), for which the relaxation was constrained by the symmetry of the $P2_1/c$ space group in a supercell, were found to eventually belong to the same space group $P2_1/c$ but in a reduced cell, with the same unit cell parameters as those of the original full-symmetry unit cell of the compound.

LDA[nm]

|          | $x$    | $y$    | $z$        |
|----------|--------|--------|------------|
| Cs(1)    | 0.1322 | 0.25   | 0.1005     |
| Cs(2)    | 0.9837 | 0.75   | 0.3287     |
| Cu       | 0.2322 | 0.25   | 0.4149     |
| Cl(1)    | 0.0115 | 0.25   | 0.3692     |
| Cl(2)    | 0.3494 | 0.25   | 0.5697     |
| Cl(3)    | 0.2824 | 0.9772 | 0.3654     |

GGA[nm]

|          | $x$    | $y$    | $z$        |
|----------|--------|--------|------------|
| Cs(1)    | 0.1329 | 0.25   | 0.1050     |
| Cs(2)    | 0.9864 | 0.75   | 0.3321     |
| Cu       | 0.2320 | 0.25   | 0.4165     |
| Cl(1)    | 0.0045 | 0.25   | 0.3751     |
| Cl(2)    | 0.3507 | 0.25   | 0.5743     |
| Cl(3)    | 0.2878 | 0.9779 | 0.3615     |
In the case of Cs$_2$CuBr$_4$, the lattice constants are $a = 10.195$ Å, $b = 7.965$ Å, $c = 12.936$ Å and the space group is $Pnma$.

|            | x     | y     | z     |
|------------|-------|-------|-------|
| **LDA[nm]**|       |       |       |
| Cs(1)      | 0.1244| 0.25  | 0.1030|
| Cs(2)      | 0.0142| 0.25  | 0.6638|
| Cu         | 0.2345| 0.25  | 0.4159|
| Br(1)      | 0.0090| 0.25  | 0.3715|
| Br(2)      | 0.3497| 0.25  | 0.5751|
| Br(3)      | 0.2882| 0.5267| 0.3649|

|            | x     | y     | z     |
|------------|-------|-------|-------|
| **GGA[nm]**|       |       |       |
| Cs(1)      | 0.1272| 0.25  | 0.1072|
| Cs(2)      | 0.0117| 0.25  | 0.6619|
| Cu         | 0.2322| 0.25  | 0.4168|
| Br(1)      | 0.0001| 0.25  | 0.3756|
| Br(2)      | 0.3499| 0.25  | 0.5787|
| Br(3)      | 0.2921| 0.5257| 0.3603|

|            | x     | y     | z     |
|------------|-------|-------|-------|
| **GGA+U[nm]**|       |       |       |
| Cs(1)      | 0.1260| 0.25  | 0.1059|
| Cs(2)      | 0.0060| 0.25  | 0.6628|
| Cu         | 0.2312| 0.25  | 0.4187|
| Br(1)      | -0.0002| 0.25  | 0.3773|
| Br(2)      | 0.3456| 0.25  | 0.5818|
| Br(3)      | 0.2977| 0.5197| 0.3570|

|            | x     | y     | z     |
|------------|-------|-------|-------|
| **Experimentally determined structure**|       |       |       |
| Cs(1)      | 0.1340| 0.25  | 0.1031|
| Cs(2)      | 0.9433| 0.75  | 0.3252|
| Cu         | 0.2302| 0.25  | 0.4182|
| Br(1)      | 0.0050| 0.25  | 0.3820|
| Br(2)      | 0.3433| 0.25  | 0.5739|
| Br(3)      | 0.2936| 0.9881| 0.3550|

|            | x     | y     | z     |
|------------|-------|-------|-------|
| **GGA+U[fm]**|       |       |       |
| Cs(1)      | 0.1318| 0.25  | 0.1042|
| Cs(2)      | 0.9903| 0.75  | 0.3308|
| Cu         | 0.2311| 0.25  | 0.4178|
| Cl(1)      | 0.0039| 0.25  | 0.3768|
| Cl(2)      | 0.3479| 0.25  | 0.5764|
| Cl(3)      | 0.2918| 0.9823| 0.3588|

|            | x     | y     | z     |
|------------|-------|-------|-------|
| **GGA[fm]**|       |       |       |
| Cs(1)      | 0.1321| 0.25  | 0.1026|
| Cs(2)      | 0.9948| 0.75  | 0.3302|
| Cu         | 0.2320| 0.25  | 0.4175|
| Cl(1)      | 0.0043| 0.25  | 0.3791|
| Cl(2)      | 0.3442| 0.25  | 0.5779|
| Cl(3)      | 0.2961| 0.9848| 0.3556|

|            | x     | y     | z     |
|------------|-------|-------|-------|
| **GGA+[afm]**|       |       |       |
| Cs(1)      | 0.1317| 0.2503| 0.1044|
| Cs(2)      | 0.9899| 0.7504| 0.3309|
| Cu         | 0.2312| 0.2502| 0.4177|
| Cl(1)      | 0.0037| 0.2497| 0.3765|
| Cl(2)      | 0.3483| 0.2507| 0.5762|
| Cl(3a)     | 0.2912| 0.5181| 0.3591|
| Cl(3b)     | 0.2916| 0.9823| 0.3595|

|            | x     | y     | z     |
|------------|-------|-------|-------|
| **GGA+[fm]**|       |       |       |
| Cs(1)      | 0.1321| 0.2501| 0.1029|
| Cs(2)      | 0.9946| 0.7501| 0.3302|
| Cu         | 0.2319| 0.2501| 0.4175|
| Cl(1)      | 0.0037| 0.2499| 0.3790|
| Cl(2)      | 0.3446| 0.2501| 0.5777|
| Cl(3a)     | 0.2959| 0.5151| 0.3591|
| Cl(3b)     | 0.2959| 0.9851| 0.3595|

|            | x     | y     | z     |
|------------|-------|-------|-------|
| **GGA+[afm]**|       |       |       |
| Cs(1)      | 0.1340| 0.25  | 0.1031|
| Cs(2)      | 0.9433| 0.75  | 0.3252|
| Cu         | 0.2302| 0.25  | 0.4182|
| Cl(1)      | 0.0050| 0.25  | 0.3820|
| Cl(2)      | 0.3433| 0.25  | 0.5739|
| Cl(3)      | 0.2936| 0.9881| 0.3550|

|            | x     | y     | z     |
|------------|-------|-------|-------|
| **GGA+U[afm]**|       |       |       |
| Cs(1)      | 0.1318| 0.25  | 0.1042|
| Cs(2)      | 0.9903| 0.75  | 0.3308|
| Cu         | 0.2311| 0.25  | 0.4178|
| Cl(1)      | 0.0039| 0.25  | 0.3768|
| Cl(2)      | 0.3479| 0.25  | 0.5764|
| Cl(3)      | 0.2918| 0.9823| 0.3588|

|            | x     | y     | z     |
|------------|-------|-------|-------|
| **GGA+U[fm]**|       |       |       |
| Cs(1)      | 0.1321| 0.25  | 0.1026|
| Cs(2)      | 0.9948| 0.75  | 0.3302|
| Cu         | 0.2320| 0.25  | 0.4175|
| Cl(1)      | 0.0043| 0.25  | 0.3791|
| Cl(2)      | 0.3442| 0.25  | 0.5779|
| Cl(3)      | 0.2961| 0.9848| 0.3556|
Experimentally determined structure

| Element | x     | y   | z     |
|---------|-------|-----|-------|
| Cs(1)   | 0.1290| 0.25| 0.1058|
| Cs(2)   | 0.0049| 0.25| 0.6694|
| Cu      | 0.2311| 0.25| 0.4187|
| Br(1)   | 0.0010| 0.25| 0.3819|
| Br(2)   | 0.3440| 0.25| 0.5797|
| Br(3)   | 0.2960| 0.5138| 0.3546|

APPENDIX B: FURTHER INTERACTION PATHWAYS IN Cs$_2$CuCl$_4$ CONSIDERED IN THE TB MODEL

The interaction pathways for spin exchange coupling constants $J_7$, $J_6$, $J_{14}$, $J_{18}$ and $J_{22}$ are shown in Fig. 9(a).

APPENDIX C: ANTIFERROMAGNETIC SPIN CONFIGURATIONS AND CORRESPONDING $E_{FM} - E_{AFM}$ EQUATIONS FOR DERIVING EXCHANGE CONSTANTS IN Cs$_2$CuCl$_4$ AND Cs$_2$CuBr$_4$

Given that the Cu atoms in the $2 \times 2 \times 1$ supercell of Cs$_2$CuCl$_4$ or Cs$_2$CuBr$_4$ are labeled as shown in Fig. 9(b), the seven antiferromagnetic (or ferrimagnetic) spin configurations, considered in order to calculate exchange couplings $J$, $J'$, $J''_{\text{eff}}$, $J_1$, $J_3$, $J_7$ and $J_8$ by the total energy difference method, are the following:

- **conf. 1:** $\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$
- **conf. 2:** $\downarrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$
- **conf. 3:** $\uparrow \uparrow \uparrow \uparrow \uparrow \downarrow \uparrow \downarrow$
- **conf. 4:** $\uparrow \uparrow \uparrow \uparrow \downarrow \uparrow \downarrow \uparrow$
- **conf. 5:** $\uparrow \downarrow \downarrow \uparrow \uparrow \downarrow \uparrow \downarrow$
- **conf. 6:** $\downarrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$
- **conf. 7:** $\uparrow \downarrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow$

Each of these spin configurations leads to a corresponding equation:

$$2J + 2J' + J_1 + J_3 + 4J_8 = E_1/4,$$
$$2J' + J''_{\text{eff}} + J_1 + J_3 + 2J_8 = E_2/8,$$
$$2J' + J''_{\text{eff}} + J_1 + 2J_8 + J_7 = E_3/4,$$
$$2J + 2J' + J''_{\text{eff}} + J_1 + J_3 + 2J_8 + 2J_7 = E_4/4,$$
$$4J' + J''_{\text{eff}} + J_1 + J_3 + 2J_8 + 2J_7 = E_5/4,$$
$$4J + 8J' + 6J''_{\text{eff}} + 3J_1 + 3J_3 + 8J_8 + 4J_7 = E_7,$$

where $E_i = E_{FM} - E_{AFM}^i$, $i = 1, \ldots, 7$, with $E_{FM}$ being the energy of the supercell in the ferromagnetic configuration of Cu spins and $E_{AFM}^i$ being the energy of the supercell in the antiferromagnetic configuration $i$.

APPENDIX D: EXCHANGE COUPLINGS

The exchange couplings provided below for the experimental as well as the GGA[nm], GGA[fm] and GGA+U[fm] relaxed Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$ crystal structures are given in meV. We have marked in bold face the parameter values that should provide a realistic description of the spin models for Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$. 
|       | Cs$_2$CuCl$_4$: experimental structure [Fig. 8 (b)] | Cs$_2$CuBr$_4$: experimental structure [Fig. 8 (f)] |
|-------|--------------------------------------------------|--------------------------------------------------|
| $U=4 \text{ eV}$ | $J$ 0.2170 0.1128 0.0413 | $J$ 1.6597 0.7911 0.2756 |
|        | $J'$ 0.0548 0.0333 0.0169 | $J'$ 1.0427 0.5064 0.2030 |
|        | $J''_{\text{eff}}$ 0.0112 0.0061 0.0048 | $J''_{\text{eff}}$ 0.0868 0.0336 0.0127 |
| $J_1$  | 0.0085 -0.0039 -0.0046 | $J_1$ 0.1525 0.0516 0.0143 |
| $J_3$  | 0.0229 0.0160 0.0070 | $J_3$ 0.0675 0.0599 0.0273 |
| $J_8$  | 0.0057 0.0035 0.0018 | $J_8$ -0.0147 -0.0002 0.0019 |
| $J_7$  | -0.0152 -0.0081 -0.0030 | $J_7$ -0.0266 -0.0116 -0.0040 |

|       | Cs$_2$CuCl$_4$: GGA+U[fm] relaxed structure [Fig. 8 (c)] | Cs$_2$CuBr$_4$: GGA+U[fm] relaxed structure [Fig. 8 (g)] |
|-------|--------------------------------------------------|--------------------------------------------------|
| $U=4 \text{ eV}$ | $J$ 0.8517 | $J$ 2.0358 |
|        | $J'$ 0.3736 0.1788 0.0779 | $J'$ 1.0223 0.4821 0.1815 |
|        | $J''_{\text{eff}}$ 0.0266 0.0137 0.0089 | $J''_{\text{eff}}$ 0.0589 0.0238 0.0105 |
| $J_1$  | 0.0210 0.0039 0.0010 | $J_1$ 0.1268 0.0436 0.0119 |
| $J_3$  | 0.0008 0.0147 0.0046 | $J_3$ 0.0685 0.0694 0.0307 |
| $J_8$  | -0.0039 -0.0005 0.0011 | $J_8$ -0.0142 -0.0011 0.0012 |
| $J_7$  | -0.0219 -0.0172 -0.0065 | $J_7$ -0.0308 -0.0204 -0.0086 |

|       | Cs$_2$CuCl$_4$: GGA[fm] relaxed structure [Fig. 8 (d)] | Cs$_2$CuBr$_4$: GGA[fm] relaxed structure [Fig. 8 (h)] |
|-------|--------------------------------------------------|--------------------------------------------------|
| $U=4 \text{ eV}$ | $J$ 1.2632 0.5679 0.2095 | $J$ 2.7229 |
|        | $J'$ 0.3207 0.1556 0.0702 | $J'$ 0.9234 0.4382 0.1682 |
|        | $J''_{\text{eff}}$ 0.0224 0.0175 0.0118 | $J''_{\text{eff}}$ 0.0554 0.0219 0.0122 |
| $J_1$  | 0.0308 0.0127 0.0031 | $J_1$ 0.1467 0.0492 0.0166 |
| $J_3$  | 0.0435 0.0302 0.0108 | $J_3$ 0.1710 0.1101 0.0468 |
| $J_8$  | -0.0043 -0.0010 0.0011 | $J_8$ -0.0158 -0.0005 0.0004 |
| $J_7$  | -0.0222 -0.0172 -0.0067 | $J_7$ -0.0394 -0.0183 -0.0089 |

|       | Cs$_2$CuCl$_4$: GGA[fm] relaxed structure [Fig. 8 (e)] | Cs$_2$CuBr$_4$: GGA[fm] relaxed structure [Fig. 8 (i)] |
|-------|--------------------------------------------------|--------------------------------------------------|
| $U=4 \text{ eV}$ | $J$ 2.1036 0.9321 0.3440 | $J$ 5.1309 |
|        | $J'$ 0.2873 0.1418 0.0656 | $J'$ 0.8025 0.3872 0.1540 |
|        | $J''_{\text{eff}}$ 0.0076 0.0089 0.0112 | $J''_{\text{eff}}$ 0.0356 0.0129 0.0115 |
| $J_1$  | 0.0424 0.0150 0.0061 | $J_1$ 0.1980 0.0696 0.0246 |
| $J_3$  | 0.0919 0.0468 0.0185 | $J_3$ 0.3723 0.1907 0.0741 |
| $J_8$  | -0.0047 0.0006 0.0010 | $J_8$ -0.0196 -0.0015 0.0011 |
| $J_7$  | -0.0247 -0.0138 -0.0065 | $J_7$ -0.0521 -0.0190 -0.0083 |

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