Microscopic magnetic modeling for the $S = \frac{1}{2}$ alternating chain compounds
$\text{Na}_3\text{Cu}_2\text{SbO}_6$ and $\text{Na}_2\text{Cu}_2\text{TeO}_6$

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The spin-1/2 alternating Heisenberg chain system $\text{Na}_3\text{Cu}_2\text{SbO}_6$ features two relevant exchange couplings: $J_{1a}$ within the structural $\text{Cu}_2\text{O}_6$ dimers and $J_{1b}$ between the dimers. Motivated by the controversially discussed nature of $J_{1a}$, we perform extensive density-functional-theory (DFT) calculations, including DFT+U and hybrid functionals. Fits to the experimental magnetic susceptibility data.

The vibrant research on magnetic insulators keeps on delivering new examples of exotic magnetic behaviors and unusual magnetic ground states (GSs).$^{1,2}$ Two prominent examples are the spin-liquid system herbertsmithite $\text{Cu}_3\text{Zn(OH)}_6\text{Cl}_2$, featuring a kagome lattice of $S = 1/2$ spins,$^3$ or the recently discovered $\text{Ba}_3\text{Cu}_2\text{SbO}_9$, where the magnetism is likely entangled with the dynamical Jahn-Teller distortion.$^4$

Cuprates are a particularly promising playground to study low-dimensional magnetism, since they often combine the quantum spin $S = 1/2$ spins, or the recently discovered $\text{Ba}_3\text{Cu}_2\text{SbO}_9$, where the magnetism is likely entangled with the dynamical Jahn-Teller distortion.$^4$

The simplest example of a quantum GS that lacks a classical analog is the quantum-mechanical singlet. Such a GS is found experimentally, e.g., in $\text{CsV}_2\text{O}_5$ (Ref. 5), $\text{CuTe}_2\text{O}_5$ (Ref. 6), $\text{CaCuGe}_2\text{O}_6$ (Ref. 7), and $\text{Cu}_2(\text{PO}_4)_2\text{CH}_2$ (Ref. 8). All these compounds feature pairs of strongly coupled spins (magnetic dimers). An isolated dimer is an archetypical two-level quantum system, which can be solved analytically.

Compounds with sizable couplings between the dimers can exhibit diverse behaviors. For instance, the non-frustrated$^9$ spin lattice of the Han purple $\text{BaCuSi}_2\text{O}_6$ is favorable for propagation of triplet excitations, promoting a Bose-Einstein condensation of magnons, experimentally observed in the magnetic field range between 23.5 and 49 T.$^{10}$ In contrast, $\text{SrCu}_2(\text{BO}_3)_2$ features strongly frustrated interdimer couplings that give rise to a fascinating variety of magnetization plateaus.$^{11}$ The remarkable difference between the behavior of $\text{BaCuSi}_2\text{O}_6$ and $\text{SrCu}_2(\text{BO}_3)_2$ is governed by the difference in the magnetic couplings that constitute the respective spin model. Thus, the precise information on the underlying spin model is crucial for understanding the magnetic properties.

I. INTRODUCTION

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An evaluation of the microscopic magnetic model can be performed in different ways. The basic features of the spin lattice can be often conceived by applying empirical rules, such as the Goodenough–Kanamori rules.$^{12}$ Then, the resulting qualitative model is parameterized by fitting its respective free parameters to the experiment. The main challenge is the limited amount of the available experimental data that may not suffice for a unique and justified fitting of the model-specific free parameters. Thus, such a phenomenological approach is generally insecure against ambiguous solutions.

Microscopic modeling based on density-functional theory (DFT) calculations is an alternative solution. Such calculations require no experimental information beyond the crystal structure, and in contrast to the phenomenological method, provide a microscopic insight. A straightforward application of the DFT is impeded by the fact that cuprates are strongly correlated materials. Hence the effective one-electron approach of DFT generally fails to reproduce their insulating electronic GS.$^{13}$ This shortcoming can be mended in alternative calculational schemes, such as DFT+U or hybrid functionals, yet these methods are not parameter-free. Often, these parameters sensitively depend on the fine structural details of the system under investigation.

The low-dimensional $S = 1/2$ Heisenberg compound $\text{Na}_3\text{Cu}_2\text{SbO}_6$ is an instructive example that demonstrates the performance and the limitations of the phenomenological as well as the microscopic approach. This compound was initially described as a distorted honeycomb lattice, owing to the hexagonal arrangement of the...
Cu atoms in the crystal structure.\textsuperscript{14} However, this purely geometrical analysis neglects the key ingredients of the magnetic superexchange, such as the orientation and the spatial extent of the magnetically active orbitals. Indeed, as pointed out by the authors of Ref. 14, the orientation of the Cu $3d_{x^2−y^2}$ orbitals readily accentuates the chains formed by structural dimers and hints at two relevant magnetic couplings: $J_{1a}$ within the structural dimers and $J_{1b}$ between the dimers (Fig. 1), leading to the quasi-1D Heisenberg chain model with alternating nearest-neighbor couplings.

Thermodynamical measurements confirmed the quasi-1D character of the spin model,\textsuperscript{14,15} yet no agreement was found for the sign of the intradimer coupling $J_{1a}$: Refs. 14 and 15 vouch for a ferromagnetic (FM) and antiferromagnetic (AFM) exchange, respectively. The sign of $J_{1a}$ basically governs the magnetic GS: the AFM-AFM solution is a disordered dimer state, while the GS of an FM-AFM chain is adiabatically connected to the Haldane phase with nontrivial topology and sizable string order parameter.\textsuperscript{16} Therefore, for the magnetic GS, the sign of $J_{1a}$ is of crucial importance.

Notably, even DFT studies do not concur with each other: Ref. 15 reports AFM $J_{1a}$, while an alternative DFT-based method in Ref. 17 yields FM coupling. To resolve the controversy on the sign of $J_{1a}$, the authors of Ref. 18 performed inelastic neutron scattering (INS) experiments on single crystals of Na$_3$Cu$_2$SbO$_6$. The resulting values for the exchange couplings ($J_{1a} = −145$ K and $J_{1b} = 161$ K) clearly indicate the FM-AFM chain scenario. Still, the origin of ambiguous solutions in earlier experimental as well as in DFT studies has not been sufficiently clarified.

In our combined experimental and theoretical study, we evaluate the magnetic model for Na$_3$Cu$_2$SbO$_6$ and its Te sibling Na$_2$Cu$_2$TeO$_6$ (Ref. 19) using extensive DFT calculations and investigate how the magnetic GS is affected by the structural distortion within the chains. By comparing our DFT results to the earlier studies, we explain the origin of ambiguous parameterizations of DFT-based spin models in both compounds. Simulations of the momentum-resolved spectrum for our microscopic model reveal excellent agreement with the INS experiments (Ref. 18) and enlighten the ambiguity of AFM-AFM and FM-AFM solutions inferred from the thermodynamical measurements.

This paper is organized as follows. The used experimental as well as computational methods are described in Sec. II. The details of the crystal structures of Na$_3$Cu$_2$SbO$_6$ and Na$_2$Cu$_2$TeO$_6$ are discussed in Sec. III. In Sec. IV, we present our magnetic susceptibility measurements and extensive DFT calculations. Peculiarities of the excitation spectrum of the Heisenberg chain model is discussed Sec. V. Finally, a summary and a short outlook are given in Sec. VI.

\section{II. METHODS}

\textbf{Synthesis and sample characterization} Polycrystalline samples of Na$_3$Cu$_2$SbO$_6$ were prepared by solid state reaction. A stoichiometric amount of Na$_2$CO$_3$ (Chempur, 99.9+\%), Sb$_2$O$_5$ (99.999\%, Alfa Aesar) and CuCO$_3$-Cu(OH)$_2$ (Chempur) was thoroughly mixed. The homogeneous powder was pressed into a platinum crucible and annealed at 1273 K for two weeks in air. Finally the crucible was taken out of the furnace at 1273 K and cooled down to room temperature in air.

For magnetic measurements, the powder sample was pressed into a pellet and heated again at 973 K in a platinum boat for several days. The green powder was identified and characterized by powder x-ray diffraction using a high-resolution Guinier camera with Cu K$_\alpha$ radiation. The determined lattice parameters $a = 5.676$ Å, $b = 8.860$ Å, $c = 5.833$ Å and $\beta = 113.33^\circ$ are in good agreement with Ref. 20.

To control the oxygen content in the sample at different stages of the thermal treatment, we performed coulometric titration of the samples using a commercial OXYLYT device. We found that the maximal oxygen content (close to the stoichiometric Na$_3$Cu$_2$SbO$_6$) is attained right after the thermal treatment at 973 K (Fig. S3 in Ref. 21). However, a subsequent storage at room temperature and in air leads to a reduction of the oxygen content. This effect can be seen in the magnetic susceptibility by the increased amount of Curie impurity (Fig. S4 in Ref. 21). Therefore, for thermodynamic measurements, we use “fresh” samples (i.e., we performed measurement right after the thermal treatment) that feature smallest impurity contribution. Magnetic susceptibility $\chi(T)$ of Na$_3$Cu$_2$SbO$_6$ was measured using a SQUID magnetometer (MPMS, Quantum Design) in a magnetic field of 0.04 T.

\textbf{DFT calculations} For the electronic structure calculations, the full-potential local-orbital code FPLO (version FPLO8.50-32) within the local (spin) density approximation (L(S)DA) was used.\textsuperscript{22} In the scalar relativistic calculations the exchange and correlation potential of Perdew and Wang has been applied.\textsuperscript{23} The accuracy with respect to the $k$-mesh has been carefully checked.

The LDA band structure has been mapped onto an effective one-orbital tight binding (TB) model based on Cu-site centered Wannier functions (WF). The strong Coulomb repulsion of the Cu 3$d$ orbitals was considered by mapping the TB model onto a Hubbard model. In the strongly correlated limit and at half-filling, the lowest lying (magnetic) excitations can be described by a Heisenberg model with $J'_{ij} = 4U_{ij}/U_{\text{eff}}$ for the antiferromagnetic part of the exchange. Spin-polarized LSDA+$U$ supercell calculations were performed using two limiting cases for the double counting correction (DCC): the around-mean-field (AMF) and the atomic limit (AL, also called the fully localized limit). We varied the on-site Coulomb repulsion $U_{\text{3d}}$ in the physically relevant range ($4$–$8$ eV in AMF and $5$–$9$ eV in AL), keeping the on-site
performed using the pseudopotential code vasp-5.2 approximation (VCA).

HSE06 (Ref. 25) hybrid functional calculations were performed using the pseudopotential code vasp-5.2, employing the basis set of projector-augmented waves. The default admixture of the Fock exchange (25%) was adopted. We used the primitive unit cell with 2 Cu atoms and a 6×6×6 k-mesh with the NKRED=3 flag.

Simulations and fits to the experiment. We used the high-temperature series expansion (HTSE) to a Heisenberg chain with alternating nearest-neighbor couplings \( J_{1a} \) and \( J_{1b} \). For the case of AFM couplings, the parameterization is given in \( \alpha = |J_{1a}|/J_{1b} \) in Table II of Ref. 27; the parameters for the case of FM \( J_{1a} \) are provided in Ref. 28. Quantum Monte Carlo simulations were performed using the loop algorithm\(^{29}\) from the ALPS package.\(^{30}\) To evaluate the reduced magnetic susceptibility, we used 50 000 loops for thermalization and 500 000 loops after thermalization for chains of \( N = 120 \) spins \( S = 1/2 \) using periodic boundary conditions. Exact (Lanczos) diagonalization of the Heisenberg Hamiltonians was performed using SPINPACK.\(^{31}\) The lowest-lying \( S^z = 0 \), \( S^z = 1 \) and \( S^z = 2 \) excitations were computed for \( N = 32 \) sites chains of \( S = 1/2 \) using periodic boundary conditions.

III. CRYSTAL STRUCTURE

The monoclinic (space group \( C2/c \)) crystal structure of \( \text{Na}_3\text{Cu}_2\text{SbO}_6 \) (Ref. 20) features pairs of slightly distorted, edge-shared CuO\(_4\) plaquettes forming structural dimers with the Cu–O–Cu bonding angle of 95°. The dimers are connected by the equatorial plane of SbO\(_6\) octahedra and form chains running along the \( b \) axis (Fig. 1, bottom). The apical O atoms of the SbO\(_6\) octahedra mediate connections to the next CuO\(_6\) dimer chain. In this way, the magnetic layers, separated by Na atoms, are formed (Fig. 1, top).

The crystal structure of \( \text{Na}_2\text{Cu}_2\text{TeO}_6 \) (Ref. 19) features a similar motif, with the reduced number of Na atoms between the layers, to keep the charge balance. In addition, the smaller size of Te\(^{5+}\) compared to Sb\(^{5+}\) gives rise to a stronger distortion of the CuO\(_6\) dimer chains in \( \text{Na}_2\text{Cu}_2\text{TeO}_6 \). To investigate the influence of this distortion, we also computed fictitious structures with idealized planar arrangements of the CuO\(_6\) units (Fig. 1, bottom, lower panel).

IV. RESULTS

A. Magnetic susceptibility

Above 200 K, the magnetic susceptibility of \( \text{Na}_3\text{Cu}_2\text{SbO}_6 \) fits reasonably to the Curie-Weiss law with \( C = 0.442 \text{emu K/(mol Cu)}^{-1} \) and the antiferromagnetic Weiss temperature \( \theta_{CW} = 60 \pm 10 \text{K} \). The effective magnetic moment amounts to \( \mu_{eff} \approx 1.88 \mu_B \), slightly exceeding the spin-only value for \( S = 1/2 \) (1.73 \( \mu_B \)). The resulting value of the Lande factor \( g = 2.17 \) is typical for Cu\(^{2+}\) compounds. At lower temperatures, antiferromagnetic correlations give rise to a broad maximum in the magnetic susceptibility around \( T_{\text{max}} \approx 96 \text{K} \). The low-temperature upturn below 17 K is likely caused by defects, typical for powder samples of quasi-1D magnets (e.g., Sr\(_2\)Cu(PO\(_4\))\(_2\) from Ref. 32 or (NO)Cu(NO\(_3\))\(_3\) from Ref. 33), since already a single defect terminates the spin chain.

We briefly compare our susceptibility measurements with the published data. The Curie-Weiss fit from Ref. 15 yields a similar \( \theta_{CW} = 55 \text{K} \), but their \( g = 2.33 \) exceeds our estimate. This discrepancy likely originates from the difference in the magnetic field (0.1 T versus 0.04 T in our work) as well as different temperature ranges used for the fitting. Unfortunately, the authors of Ref. 14 do not provide the values of \( \theta_{CW} \) and \( g \), but a Curie-Weiss fit to their data yields \( \theta_{CW} \approx 49 \text{K} \) and \( g \approx 2.10 \), in good agreement with our findings. A bare comparison of the absolute values of \( \chi(T_{\text{max}}) \) (Table I) reveals sizable
deviations of the $\chi(T)$ data from Ref. 15 compared to the other two data sets.

For a more elaborate analysis, we adopt the AHC model and search for solutions that agree with the experimental $\chi(T)$ curve. To this end, we perform HTSE considering the physically different scenarios: both $J_{1a}$ and $J_{1b}$ couplings are AFM (“AFM–AFM”) and $J_{1a}$ is FM (“FM–AFM”). The corresponding HTSE coefficients for the two cases can be found in Refs. 27 and 28, respectively. In both cases, we obtain a solution (first row of Table II) which conforms to the experimental data.

Our solution for the FM–AFM case (Table II, first row) nearly coincides with the corresponding solution from Ref. 14 (Table II, second row), yielding $\alpha \equiv J_{1a}/J_{1b} \approx -1.25$ and a considerably smaller $g$-factor of about 2 compared to the value from the Curie-Weiss fits (2.17). For the AFM–AFM case, we obtain $\alpha \approx 0.4$ which deviates from the result of Ref. 14, but closely resembles the solution from Ref. 15 (Table II, third row). The discrepancy can originate from different parameterizations used for the HTSE fitting. In particular, the AFM–AFM solutions in Refs. 14 and 15 are obtained using the parametrization from Ref. 34. In contrast, we adopt the coefficients from a more recent and extensive study,25 valid in the whole temperature range measured.

\begin{table}[h]
\centering
\caption{Na$_3$Cu$_2$SbO$_6$: the Curie-Weiss temperature $\theta_{CW}$ (in K) and the $g$-factor evaluated using the Curie-Weiss fit for $T \geq 200$ K, as well as the experimental position $T_{\text{max}}$ (in K) of the susceptibility maximum and its absolute value $\chi(T_{\text{max}})$ [in emu (mol Cu)$^{-1}$].}
\begin{tabular}{lcccc}
\hline
\textbf{data source} & $\theta_{CW}$ & $g$ & $T_{\text{max}}$ & $\chi(T_{\text{max}})$ \\
\hline
this study & 60 & 2.17 & 96 & 2.2\times10^{-5} \\
data from Ref. 14 & 49 & 2.10 & 95 & 2.3\times10^{-5} \\
data from Ref. 15 & 55 & 2.33 & 90 & 1.7\times10^{-3} \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{High-temperature series expansion (HTSE) and quantum Monte Carlo (QMC) fits for the FM–AFM and the AFM–AFM solution of the alternating Heisenberg chain (AHC) model. Inset: difference curves emphasize the excellence of the FM–AFM solution.}
\begin{tabular}{crrrr}
\hline
\textbf{data source} & $J_{1a}$ & $J_{1b}$ & $g$ & $\chi_0$ & $C_{\text{imp}}^\text{HTSE}$ & $\theta_{\text{imp}}^\text{HTSE}$ \\
\hline
this study & -207 & 171 & 2.01 & $3\times10^{-5}$ & 4.7\times10^{-3} \\
 & 155 & 66 & 2.20 & $3\times10^{-6}$ & 6.1\times10^{-3} & 1.1 \\
Ref. 14 & -209 & 165 & 2.01 & - & - & - \\
Ref. 15 & 160 & 62 & 1.97 & $2.2\times10^{-4}$ & 2.3 \\
\hline
QMC & -217 & 174 & 2.02 & $9\times10^{-6}$ & 6\times10^{-3} & 1 \\
 & 153 & 61 & 2.19 & $3\times10^{-6}$ & 6\times10^{-3} & 1.2 \\
\hline
\end{tabular}
\end{table}

To account for the full temperature range measured, we turn to QMC simulations. Thus, we adopt the ratios $\alpha = -1.25$ and $\alpha = 0.4$ from our HTSE fitting, and calculate the reduced magnetic susceptibility $\chi^*(T/k_B J)$, which can be fitted to the experimental curve using the expression:

$$
\chi(T) = \frac{N_A g^2 \mu_B^2}{k_B} \cdot \chi^*\left(\frac{T}{k_B J}\right) + \frac{C_{\text{imp}}^\text{HTSE}}{T + \theta_{\text{imp}}^\text{HTSE}} + \chi_0,
$$

where $N_A$ and $k_B$ are the Avogadro and Boltzmann constants, respectively, $\mu_B$ the Bohr magneton, $C_{\text{imp}}^\text{HTSE}$ and $\theta_{\text{imp}}^\text{HTSE}$ account for impurity/defect contributions, $\chi_0$ is a temperature-independent term, and $J = \max|J_{1a}, J_{1b}|$. Using a least-squares fitting, we obtain the solutions listed in Table II (last row) and shown in Fig. 2.

The AFM–AFM solution shows sizable deviations at high temperatures and in the vicinity of the low-temperature upturn (Fig. 2, inset), while the FM–AFM solution yields an excellent fit to the experimental $\chi(T)$ in the whole temperature range, making the latter solution more favorable. Still, the choice is impeded by the following issues. First, the AHC model is a minimal model for Na$_3$Cu$_2$SbO$_6$, which completely neglects interchain couplings and anisotropies. Second, the $g$-factor of the FM–AFM solution deviates significantly from the estimate based on the Curie-Weiss fit, while its counterpart from the AFM–AFM solution shows a better agreement with the Curie-Weiss fit. Finally, the shape of the $\chi(T)$ curve is affected by oxygen deficiency in the sample.23

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{(Color online) Experimental (exp) magnetic susceptibility of Na$_3$Cu$_2$SbO$_6$ (circles) and the quantum Monte Carlo (QMC) fits for the FM–AFM and the AFM–AFM solution of the alternating Heisenberg chain (AHC) model. Inset: difference curves emphasize the excellence of the FM–AFM solution.}
\end{figure}
which is difficult to control during the synthesis process. Therefore, the AFM-AFM solution cannot be ruled out using the $\chi(T)$ data, only.

**B. Electronic structure and magnetic model**

To resolve the ambiguity between the FM-AFM and AFM-AFM solutions, we perform microscopic magnetic modeling of Na$_3$Cu$_2$SbO$_6$ and its Te sibling Na$_2$Cu$_2$TeO$_6$ using DFT calculations. The valence bands feature similar band width and are similarly structured in the two compounds, as revealed by the LDA densities of states (DOS) in Fig. 3. The DOS is dominated by Cu and O states down to $-8.0$ eV (see Fig. 3) is far too small to account for the green color of the powder and originates from dimerization effects. This drastic underestimation of the band gap is a well-known shortcoming of the LDA, which does not account for the strong Coulomb repulsion in the Cu 3$d$ orbitals. The missing part of correlation energy will be accounted for by resorting to a Hubbard model, as well as using DFT+$U$ and hybrid-functional calculations. Second, the orbital resolved density of states (see Fig. 4) shows small hybridization with the out-of-plane Cu-O states due to the distortion of the dimer chains. Since these contributions are small compared to the pure antibonding $dp\sigma^*$ states, the restriction to an effective TB model is still justified.

To verify the structural input, we relaxed the crystal structures within LDA. For Na$_3$Cu$_2$SbO$_6$, the relaxation results in a rather small energy gain of 33 meV per formula unit (f. u.), and the respective changes in the crystal structure are negligible. In contrast, a relaxation of the atomic coordinates in Na$_2$Cu$_2$TeO$_6$ lowers the energy by 130 meV per f. u. and alters mainly the chain buckling. Since the relaxation of Na$_2$Cu$_2$TeO$_6$ affects the magnetically relevant $dp\sigma^*$ states, we evaluated the magnetic properties for both, the experimental and the relaxed crystal structure.

The transfer integrals $t_{ij}$ (the hopping matrix elements) are evaluated by a least-squares fit of an effective one-orbital TB model to the two LDA $dp\sigma^*$ bands. Using 10 inequivalent $t_{ij}$ terms (see the bottom panel of Fig. 5, Table III, and Ref. 21) we obtain excellent agreement between the TB model and the LDA band structure. The respective fit for Na$_3$Cu$_2$SbO$_6$ is shown in Fig. 5 (top).

In both systems, the leading coupling is $t_{1b}$, which connects two neighboring structural dimers: $t_{1b} = 127$ meV for Na$_3$Cu$_2$SbO$_6$ and $t_{1b} = 162$ meV for Na$_2$Cu$_2$TeO$_6$, respectively. The coupling within the structural Cu$_2$O$_6$ dimers ($t_{1a} = 60$ meV for Na$_3$Cu$_2$SbO$_6$ and $t_{1a} = 16$ meV for Na$_2$Cu$_2$TeO$_6$) are significantly smaller. Besides, several long-range couplings that connect different chains,
are comparable to $t_{1a}$ (Table III and Ref. 21). Subsequent mapping of the TB model onto a Hubbard model (adopting $U_{\text{eff}} = 4$ eV) and a Heisenberg model, yield the following AFM contributions: $J_{\text{AFM}}^{\alpha} = 188$ K and $J_{\text{AFM}}^{\beta} = 43$ K for Na$_3$Cu$_2$SbO$_6$ and $J_{\text{AFM}}^{\alpha} = 305$ K and $J_{\text{AFM}}^{\beta} = 2$ K for Na$_2$Cu$_2$TeO$_6$, respectively.

The resulting minimal model is incomplete, since it disregards the FM contribution to the exchange integrals, which are expected to be especially large for the $J_{1a}$ coupling within the structural dimers. To estimate the total exchange integrals, comprising AFM and FM contributions, we performed LSDA+$U$ calculations of magnetic supercells. Mapping the total energies of different collinear spin arrangements onto a classical Heisenberg model yields $J_{1a} = -135 \pm 20$ K for Na$_3$Cu$_2$SbO$_6$ and $J_{1a} = -120 \pm 20$ K for Na$_2$Cu$_2$TeO$_6$, respectively. For the exchange between the structural dimers, we find $J_{1b} = 150 \pm 50$ K for Na$_3$Cu$_2$SbO$_6$ and $J_{1b} = 232 \pm 70$ K for Na$_2$Cu$_2$TeO$_6$ ($U_{3d} = 6 \pm 1$ eV). All further exchange integrals between different chains and layers are smaller than 10 K, and thus can be neglected in the minimal model.

Unlike the related compounds featuring edge-shared chains$^{35,36}$ or Cu$_2$O$_6$ dimers,$^8$ Na$_3$Cu$_2$SbO$_6$ and Na$_2$Cu$_2$TeO$_6$ exhibit a sizable influence of the Coulomb repulsion $U_{3d}$ on the exchange integrals (see Fig. 6). However, the variation of $U_{3d}$ within the physically relevant range (Sec. II) does not affect the FM nature of $J_{1a}$. Thus, Na$_3$Cu$_2$SbO$_6$ features alternating chains with the exchange integrals of nearly the same magnitude but different sign (FM $J_{1a}$ and AFM $J_{1b}$), while for Na$_2$Cu$_2$TeO$_6$, the AFM exchange between the structural dimers is dominant. The evaluated exchange integrals are listed in Table IV.

For an independent computational method, we use hybrid functional (HF) total energy calculations. The absence of the double counting problem and minimal number of free parameters makes HF calculations an appealing alternative to the DFT+$U$ methods.$^{37}$ Here, we employ the HSE06 functional to evaluate the leading couplings $J_{1a}$ and $J_{1b}$ in both compounds. In accord with DFT+$U$, we obtain FM $J_{1a}$ and AFM $J_{1b}$. For Na$_3$Cu$_2$SbO$_6$, the resulting exchange integrals are in excellent agreement with the HTSE estimates (Table IV). Similar to DFT+$U$, Na$_2$Cu$_2$TeO$_6$ features a weaker $J_{1a}$ and stronger $J_{1b}$, thus the $\alpha$ value is substantially reduced.

We are now in position to compare our results with the previous DFT-based studies. Derakhshan et al. (Ref. 15) evaluated the relevant transfer integrals using $N$th-order muffin-tin-orbital downfolding of the LDA band struc-

![FIG. 5. (Color online) Top: LDA band structure of Na$_3$Cu$_2$SbO$_6$ and the fit using the effective one-orbital TB model with ten inequivalent transfer integrals $t_{ij}$. Bottom: the superexchange pathways corresponding to the relevant $t_{ij}$ terms.]

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**TABLE III. Relevant ($>10$ meV) transfer integrals $t_{ij}$ (in meV) evaluated by fitting the LSDA band structures for the different structural models: experimental (exp), LSDA-relaxed (relaxed) and fictitious planar (planar). For the notation of $t_{ij}$, see Fig. 5 (bottom).**

| $t_i$/meV | $t_{1a}$ | $t_{1b}$ | $t_2$ | $t_{1c}^{\alpha}$ | $t_{1c}^{\beta}$ | $t_0^{a}$ | $t_0^{b}$ |
|-----------|-----------|-----------|--------|-------------------|-------------------|----------|----------|
| exp       | 60.6      | 127       | 18.2   | $-27.8$           | 17.0              | 21.8     | 17.4     |
| relaxed   | 68.2      | 134       | 18.1   | $-32.3$           | 20.6              | 20.9     | 19.2     |
| planar exp| 45.3      | 119       | 22.4   | $-7.8$            | 9.4               | 30.1     | –        |
| planar relax| 55.6     | 125       | 23.8   | $-9.2$            | 10.7              | 29.2     | –        |
| Na$_2$Cu$_2$TeO$_6$ | | | | | | | |
| $t_i$/meV | $t_{1a}$ | $t_{1b}$ | $t_2$ | $t_{1c}^{\alpha}$ | $t_{1c}^{\beta}$ | $t_0^{a}$ | $t_0^{b}$ |
| exp       | 15.6      | 162       | 16.4   | $-38.5$           | 24.7              | 13.7     | 25.5     |
| relaxed   | 42.5      | 152       | 17.3   | $-42.4$           | 26.3              | 14.5     | 23.1     |
| planar exp.| 27.3     | 152       | 29.3   | $-12.6$           | 12.4              | 25.6     | 1.3      |
| planar relax.| 45.2     | 148       | 30.0   | $-12.8$           | 12.7              | 26.0     | –        |


TABLE IV. Leading exchange integrals $J_{1a}$ and $J_{1b}$ (in K) and the alternation ratio $\alpha \equiv J_{1a}/J_{1b}$ for Na$_3$Cu$_2$SbO$_6$ and Na$_2$Cu$_2$TeO$_6$, evaluated using different methods. HTSE and QMC estimates are made based on the experimental data from the respective reference (first column). Theoretical estimates, LSDA+$U$, HSE06, and extended Hückel tight-binding (EHTB) are based on calculations for the experimental crystal structures.

| data source | method | $J_{1a}$ | $J_{1b}$ | $\alpha = J_{1a}/J_{1b}$ |
|-------------|--------|----------|----------|-------------------------|
| Na$_3$Cu$_2$SbO$_6$ | this study | LSDA+$U$ | -135 | 150 | -0.90 |
| | | HSE06 | -205 | 163 | -1.26 |
| | | HTSE | -207 | 171 | -1.21 |
| | | QMC | -217 | 174 | -1.25 |
| | Ref. 17 | EHTB | -165 | 345 | -0.48 |
| | Ref. 14 | HTSE | -165 | 209 | -0.79 |
| | Ref. 15 | HTSE | 22 | 169 | 0.13 |
| Na$_2$Cu$_2$TeO$_6$ | this study | LSDA+$U$ | -120 | 232 | -0.52 |
| | | HSE06 | -165 | 291 | -0.57 |
| | Ref. 17 | EHTB | -158 | 516 | -0.30 |
| | Ref. 14 | HTSE | -272 | 215 | -1.27 |
| | Ref. 19 | HTSE | 13 | 127 | 0.1 |

C. Influence of chain geometry

Next, we study the influence of the structural parameters onto the alternation ratio $\alpha = J_{1a}/J_{1b}$ for Na$_3$Cu$_2$SbO$_6$ and Na$_2$Cu$_2$TeO$_6$. The two compounds differ not only by the nonmagnetic ions (Sb and Te) located between the structural dimers, but also by details of their chain geometry. These subtle differences can have a substantial impact on the magnetic properties. In particular, the substitution of Sb by Te and the corresponding change of the Na content modulates the crystal field. Furthermore, the substitution of Sb by Te has a sizable impact on the buckling of the dimer chains, which is determined by the deviation of O atoms from an ideal planar arrangement. Finally, the interatomic distances in the two compounds are different. To separate these effects out, we introduce fictitious compounds containing ideal planar dimer chains (see Fig. 1), evaluate their electronic structure, and compare them with real compounds.

The direct comparison of the antibonding $dp_z^*$ bands for the experimentally observed crystal structures of Na$_3$Cu$_2$SbO$_6$ and Na$_2$Cu$_2$TeO$_6$ (Fig. 7, upper panel) reveals that these bands differ mainly by their width.
In contrast, comparing the antibonding $dp\sigma^*$ bands of Na$_3$Cu$_2$SbO$_6$ within the experimental crystal structure (distorted plaquettes) with the fictitious crystal structure (planar plaquettes) reveals similar band widths, but substantially different dispersions (compare X-Γ or X-Z in Fig. 7). The same trend is also observed for Na$_2$Cu$_2$TeO$_6$.

(i) To separate out the effect of the Sb$\leftrightarrow$Te substitution, we perform VCA calculations for the same structural model. In particular, a certain fraction $x$ of Sb atoms is replaced by Te, with a concomitant change in the Na content, in order to keep the charge balance. The band structures calculated for different Te concentrations exhibit similar dispersions and similar band width, evidencing the minor relevance of the pure substitutional effect for the magnetic exchange couplings.\footnote{The obtained hopping terms and exchange integrals are given in Tables III and V. LSDA+$U$ calculations ($U_{3d} = 6 \pm 1$ eV) yield $J_{1a} = -230 \pm 50$ K and $J_{1b} = 126 \pm 35$ K for the fictitious Na$_3$Cu$_2$SbO$_6$ and $J_{1a} = -312 \pm 80$ K and $J_{1b} = 212 \pm 45$ K for the fictitious Na$_2$Cu$_2$TeO$_6$, respectively. The dependence of the exchange integrals on the Coulomb repulsion $U_{3d}$ is depicted in Fig. 6. Analysis of the resulting exchange couplings suggests that the two structural parameters act differently: the distortion of the dimer-chains mainly influences the coupling strength of $J_{1a}$ and the coupling regime between the dimer-chains ($t_{1c}$ and $t_{1d}$), whereas the interdimer exchange $J_{1b}$ is rather insensitive to this parameter (Table V), since the respective superexchange path does not involve O(2) atoms that rule the distortion.

(ii) Comparing the total exchange integrals for Na$_3$Cu$_2$SbO$_6$ for the experimental crystal structure with the planar system discloses an increase of the NN coupling $J_{1a}$ by nearly a factor of 2, whereas $J_{1b}$ is decreased by less than 20%. This observation is in line with the intuitive picture derived from geometrical considerations comparing the experimental distorted crystal structure to the fictitious system containing ideal planar chains (compare Fig. 1, lower panel). Locking the O atoms within the chain plane directly alters the exchange path of $J_{1a}$ along Cu-O-Cu, by a change of the Cu-O-Cu bridging angle and the orientation of the magnetically active orbitals. In contrast, the superexchange path of $J_{1b}$ (Cu-O-O-Cu) is altered only indirectly by changes of the crystal-field due to the distortion of the Sb/TeO$_6$ octahedra (compare Fig. 1, lower panel).

(iii) The modulation of interatomic distances influences $J_{1a}$ and $J_{1b}$ in a similar way. The crucial impact of the interatomic distances on $J_{1b}$ manifests itself in the coupling strength of the planar model structures for Na$_3$Cu$_2$SbO$_6$ and Na$_2$Cu$_2$TeO$_6$ (see Tab. V) with the corresponding NNN Cu-Cu interdimer distance. The about 0.1 Å shorter NNN Cu-Cu distance in the fictitious planar Na$_2$Cu$_2$TeO$_6$ structure compared to the fictitious planar Na$_3$Cu$_2$SbO$_6$ increases the coupling strength by about 60%. However, comparing the experimental distorted crystal structure with the planar model structure of Na$_2$Cu$_2$TeO$_6$ the difference in the NNN Cu-Cu dis-

TABLE V. DFT estimates for the magnetic exchange integrals in Na$_3$Cu$_2$SbO$_6$ and Na$_2$Cu$_2$TeO$_6$. The AFM part of the exchange integral $J_{1b}^{AFM}$ (in K) evaluated using the effective one-orbital model (with $U_{eff} = 4$ eV) and total exchange integrals $J_{1a}$ and $J_{1b}$ (in K) from LSDA+$U$ total energy calculations (using $U_{3d} = 6.0$ eV), for the experimental (exp), the LDA-relaxed (relaxed) and the fictitious (planar) crystal structures.

| Structure | $J_{1a}$ (K) | $J_{1b}$ (K) | $J_{1b}^{AFM}$ (K) |
|-----------|--------------|--------------|-------------------|
| Na$_3$Cu$_2$SbO$_6$ | 212 | 126 | 182 |
| Na$_2$Cu$_2$TeO$_6$ | 120 | 212 | 269 |

FIG. 7. Top: LDA band structures showing the magnetically active antibonding $dp\sigma^*$ states for Na$_3$Cu$_2$SbO$_6$ and Na$_2$Cu$_2$TeO$_6$. Bottom: comparison of the LDA band structures calculated for different structural models of Na$_2$Cu$_2$TeO$_6$. The obtained hopping terms and exchange integrals are given in Tables III and V. LSDA+$U$ calculations ($U_{3d} = 6 \pm 1$ eV) yield $J_{1a} = -230 \pm 50$ K and $J_{1b} = 126 \pm 35$ K for the fictitious Na$_3$Cu$_2$SbO$_6$ and $J_{1a} = -312 \pm 80$ K and $J_{1b} = 212 \pm 45$ K for the fictitious Na$_2$Cu$_2$TeO$_6$, respectively. The dependence of the exchange integrals on the Coulomb repulsion $U_{3d}$ is depicted in Fig. 6. Analysis of the resulting exchange couplings suggests that the two structural parameters act differently: the distortion of the dimer-chains mainly influences the coupling strength of $J_{1a}$ and the coupling regime between the dimer-chains ($t_{1c}$ and $t_{1d}$), whereas the interdimer exchange $J_{1b}$ is rather insensitive to this parameter (Table V), since the respective superexchange path does not involve O(2) atoms that rule the distortion.
tance is only half as large (about 0.05 Å) as between the two planar structures and result in an about 1/4 smaller increase of $J_{1b}$. Thus, $J_{1a}$ follows a simple distance relation and scales according to $r^2$. The same relation holds for $J_{1a}$ (compare $J_{1a}$ for the two planar structures with the change of the NN Cu-Cu distance).

Based on the above considerations, we can conclude that the crucial parameter, determining the alteration ratio $\alpha = J_{1a}/J_{1b}$ for Na$_3$Cu$_2$SbO$_6$ and Na$_2$Cu$_2$TeO$_6$, is the distortion of the chains. Thus, a directed modification of the chain buckling by the appropriate substitution of ions should allow to tune the magnetism of these systems. Furthermore, the chain distortion also influences the interchain coupling regime. In the experimental structure the long-range exchanges mostly operate within the magnetic layers (in the ab-plane), whereas in the planar system the coupling between the layers is enhanced ($t_{ij}$’s in Table III).

V. ENERGY SPECTRUM

As already mentioned, the FM-AFM and AFM-AFM solutions correspond to different magnetic GSs. In the former case, the GS is similar to the Haldane chain and features sizable string order parameter $O_s = 0.36$, indicative of a topological order, while in the latter case the string order is suppressed ($O_s = 0.16$). It is thus tempting to find an observable quantity that would be substantially different in the two phases. Theoretical studies of the $S = 1/2$ AHC model suggest that this requirement is fulfilled for the momentum position of the spin gap. Indeed, the $Q = 0$ gap is characteristic for AFM-AFM chains, except for the narrow parameter range $\alpha = 0.79 - 1.00$, where the gap shifts to small finite $Q \leq 0.02/\pi$. In contrast, the spin gap in the FM-AFM chains is located at $Q = \pi$. Therefore, by measuring momentum resolved excitation spectra, the sign of $J_{1a}$ can be reliably determined.

To resolve the ambiguity between the FM-AFM and AFM-AFM cases ultimately, we calculate the low-energy excitations for $\alpha = -1.25$ as well as $\alpha = 0.4$ using Lanczos diagonalization of the respective Heisenberg Hamiltonian. The resulting $E(Q)$ dependence is plotted in Fig. 8. Although the two solutions yield similar estimates for the spin gap, its $Q$-position is very different: $Q = \pi$ and $Q = 0$, for the FM-AFM and AFM-AFM solution, respectively. Another distinct feature of the excitation spectra is the well-separated branch of lowest-energy excitations (Fig. 8). For the FM-AFM solution, this branch resembles the behavior of $\cos(Q)$, while the AFM-AFM solution yields a $\sin(Q)$-like behavior.

To compare with the experimental dispersion from Ref. 18, we scale the two spectra using the values of the exchange couplings from our QMC fits to the magnetic susceptibility (Table II, last row). This way, we find that the FM-AFM solution agrees very well with the experimental data (Fig. 8), while the AFM-AFM solution can be safely ruled out.

Fig. 8 also provides an answer to an intriguing question, why both $\alpha = -1.25$ and $\alpha = 0.4$ provide good fits to the susceptibility data. At finite temperature, magnetic susceptibility reflects the thermal-averaged magnetic spectrum integrated over the whole momentum space. Thus, at low temperatures, $\chi(T)$ is largely affected by the value of the spin gap, but is insensitive to its $Q$ position. Since the values of the spin gap for the two solutions are very similar (around 100 K), the similarity of the low-temperature $\chi(T)$ is also not surprising. Moreover, the shape of the low-energy branch is similar (but reflected around $Q = \pi/2$), thus the $Q$-integrated spectrum is nearly the same in both cases. Only at elevated temperatures, the contribution of high-lying states gives rise to the difference in $\chi(T)$. This is in excellent agreement with the enhanced deviation of the AFM-AFM solution at high temperatures (Fig. 2, inset).

VI. SUMMARY

Since the first report on the magnetism of the low-dimensional $S = 1/2$ systems Na$_3$Cu$_2$SbO$_6$ and Na$_2$Cu$_2$TeO$_6$, their spin models were controversially de-
bated in the literature. The main conundrum was the sign of the exchange coupling $J_{1a}$ operating within the structural $\text{Cu}_2\text{O}_6$ dimers. To resolve the conflicting reports, we applied a series of different computational methods, including density functional theory (DFT) band structure, virtual crystal approximation, DFT+$U$, and hybrid functional calculations, as well as high-temperature series expansions, quantum Monte Carlo simulations, and exact diagonalization.

Our calculations evidence that the magnetism of both compounds can be described by the alternating Heisenberg chain model with two relevant couplings: ferromagnetic $J_{1a}$ within the structural dimers, and antiferromagnetic $J_{1b}$ between the dimers. The alternation parameter $\alpha = J_{1a}/J_{1b}$ amounts to about $-1.25$ and $-0.55$ in $\text{Na}_3\text{Cu}_2\text{SbO}_6$ and $\text{Na}_2\text{Cu}_2\text{TeO}_6$, respectively. This parameter regime corresponds to the Haldane phase, characterized by the gapped excitation spectrum and a topological string order.

Using extensive calculations for different structural models, we find that the physically relevant ratio $\alpha = J_{1a}/J_{1b}$ is primarily ruled by the distortion of the structural chains, while the $\text{Sb}+\text{Te}$ substitution and the change in the $\text{Cu}–\text{Cu}$ distance play a minor role. A comparison of the simulated dispersion $E(Q)$ with the experimental inelastic neutron scattering data (Ref. 18) yields an unequivocal evidence for the FM nature of $J_{1a}$ in $\text{Na}_3\text{Cu}_2\text{SbO}_6$. These spectra facilitate the understanding of the similarity between the magnetic susceptibility curves for mutually exclusive solutions that involve ferromagnetic and antiferromagnetic $J_{1a}$.

It is important to note that the problem of ambiguous solutions appears in the empirical modeling, only. In contrast, the microscopic modeling based on DFT calculations readily yields a quasi-one-dimensional model with the ferromagnetic $J_{1a}$. This clearly indicates that present-day DFT calculations are a reliable tool to disclose even rather complicated cases and deliver a reliable microscopic magnetic model. Since the correctness of the magnetic model is of crucial importance for its refinement and extension, DFT calculations should be an indispensable ingredient of real-material studies.

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Supplementary information for

**Microscopic magnetic modeling for the \( S = \frac{1}{2} \) alternating chain compounds**

\( \text{Na}_3\text{Cu}_2\text{SbO}_6 \) and \( \text{Na}_2\text{Cu}_2\text{TeO}_6 \)

M. Schmitt, O. Janson, S. Golbs, M. Schmidt, W. Schnelle, J. Richter, and H. Rosner

TABLE VI. Crystal structures for \( \text{Na}_3\text{Cu}_2\text{SbO}_6 \) used in the DFT study. The experimental structure is adopted from Ref. 1. The fictitious planar structures deviate from the experimental ones only by the coordinate of the O(2) site. The relaxed structures were optimized with respect to the LDA total energy.

|             | exp.         | relaxed      |
|-------------|--------------|--------------|
| \( \text{Cu} \) | \( x/a \) 0 \( y/b \) 0.6667 \( z/c \) 0 | \( x/a \) -0.1987 \( y/b \) 0.6667 \( z/c \) 0 |
| \( \text{Sb} \) | \( x/a \) 0 \( y/b \) 0 \( z/c \) 0 | \( x/a \) 0 \( y/b \) 0 \( z/c \) 0 |
| \( \text{O}(1) \) | \( x/a \) 0.2931 \( y/b \) 0.3340 \( z/c \) 0.7750 | \( x/a \) -0.1987 \( y/b \) 0.1667 \( z/c \) -0.2234 |
| \( \text{O}(2) \) | \( x/a \) 0.2404 \( y/b \) 0.5 \( z/c \) 0.1774 | \( x/a \) -0.2619 \( y/b \) 0 \( z/c \) 0.1734 |
| \( \text{Na}(1) \) | \( x/a \) 0 \( y/b \) 0.5 \( z/c \) 0 | \( x/a \) 0 \( y/b \) -0.5 \( z/c \) -0.5 |
| \( \text{Na}(2) \) | \( x/a \) 0.5 \( y/b \) 0.3280 \( z/c \) 0.5 | \( x/a \) 0 \( y/b \) -0.1732 \( z/c \) -0.5 |

TABLE VII. Crystal structures for \( \text{Na}_2\text{Cu}_2\text{TeO}_6 \) used in the DFT study. The experimental structure is adopted from Ref. 2. The fictitious planar structures deviate from the experimental ones only by the coordinate of the O(2) site. The relaxed structures were optimized with respect to the LDA total energy.

|             | planar exp. | relaxed      |
|-------------|-------------|--------------|
| \( \text{O}(2) \) | \( x/a \) 0.2931 \( y/b \) 0.5 \( z/c \) 0.7750 | \( x/a \) -0.1987 \( y/b \) 0.5 \( z/c \) -0.2234 |

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TABLE VIII. Transfer integrals $t_{ij}$ (in meV) evaluated by fitting the LSDA band structures for the different structural models: experimental (exp), LSDA-relaxed (relaxed) and fictitious planar structures originating from the experimental ones by shifting O(2) (planar exp and planar relaxed). For the notation of $t_{ij}$, see Fig. 5 in the manuscript. ("−" $< 1$ meV)

| $t_i$/meV | $t_{1a}$ | $t_{1b}$ | $t_{2}$ | $t_{1a}^{ic}$ | $t_{1b}^{ic}$ | $t_{1a}^{il}$ | $t_{1b}^{il}$ | $t_{0}$ | $t_{1}^{d}$ | $t_{0}^{d}$ |
|-----------|----------|----------|--------|---------------|---------------|---------------|---------------|--------|----------|----------|
| exp       | 60.6     | 127      | 18.2   | -27.8         | 17.0          | 5.8           | -6.6          | 21.8   | -4.6     | 17.4     |
| relaxed   | 68.2     | 134      | 18.1   | -32.3         | 20.6          | 6.4           | -7.2          | 20.9   | -3.8     | 19.2     |
| planar exp| 45.3     | 119      | 22.4   | -7.8          | 9.4           | 14.1          | -18.8         | 30.1   | -13.2    | -        |
| planar relaxed | 55.6 | 125 | 23.8 | -9.2 | 10.7 | 17.3 | -21.7 | 29.2 | -19.9 | -        |

| $t_i$/meV | $t_{1a}$ | $t_{1b}$ | $t_{2}$ | $t_{1a}^{ic}$ | $t_{1b}^{ic}$ | $t_{1a}^{il}$ | $t_{1b}^{il}$ | $t_{0}$ | $t_{1}^{d}$ | $t_{0}^{d}$ |
|-----------|----------|----------|--------|---------------|---------------|---------------|---------------|--------|----------|----------|
| Na$_2$Cu$_2$SbO$_6$ | | | | | | | | | | |
| exp | -11.6 | (3.7) | 12.9 | (16.1) | 0.8 | 0.4 | | | | |
| relaxed | -10.7 | 13.9 | (4.7) | (18.0) | 0.9 | 0.2 | 1.2 | | | |
| planar exp | -19.7 | 10.8 | (2.1) | (14.2) | 1.0 | 0.2 | - | | | |
| planar relaxed | -19.5 | 12.2 | (3.1) | (15.7) | | | | | | |

| $J_i$/meV | $J_{1a}$ | $(J_{1a}^{AFM})$ | $J_{1b}$ | $(J_{1b}^{AFM})$ | $J_{2}+J_{tb}^{ic}+J_{tb}^{il}$ | $J_{1a}^{ic}+J_{tb}^{ic}$ | $J_{1b}^{ic}+J_{tb}^{ic}$ | $J_{0}^{d}+J_{1}^{d}$ |
|-----------|----------|-----------------|----------|-----------------|-----------------------------|-----------------------------|-----------------------------|--------------------|
| Na$_2$Cu$_2$SbO$_6$ | | | | | | | | |
| exp | -10.3 | (0.2) | 19.9 | (26.2) | 0.1 | 1.0 | 0.1 | | |
| relaxed | -10.5 | 16.9 | (1.8) | (23.1) | 0.2 | 1.0 | - | | |
| planar exp. | -26.8 | 18.2 | (0.8) | (23.1) | 1.2 | 0.5 | 0.8 | | |
| planar relaxed | -26.2 | 17.2 | (2.0) | (21.9) | 1.5 | 0.6 | - | | |

TABLE IX. Exchange integrals derived from the LSDA+$U$ total energy calculation for different structural models ($U_{3d} = 6.0$ eV). For comparison the AFM parts of exchange integrals estimated from the effective one-orbital approach (tight-binding model → Hubbard model → Heisenberg model, $U_{eff} = 4$ eV) are given in brackets. The "−" sign means that the respective coupling was not evaluated.

| $J_i$/meV | $J_{1a}$ | $(J_{1a}^{AFM})$ | $J_{1b}$ | $(J_{1b}^{AFM})$ | $J_{2}+J_{tb}^{ic}+J_{tb}^{il}$ | $J_{1a}^{ic}+J_{tb}^{ic}$ | $J_{1b}^{ic}+J_{tb}^{ic}$ | $J_{0}^{d}+J_{1}^{d}$ |
|-----------|----------|-----------------|----------|-----------------|-----------------------------|-----------------------------|-----------------------------|--------------------|
| Na$_2$Cu$_2$SbO$_6$ | | | | | | | | |
| exp | -11.6 | (3.7) | 12.9 | (16.1) | -0.01 | 0.8 | 0.4 | | |
| relaxed | -10.7 | 13.9 | (4.7) | (18.0) | 0.3 | 0.7 | - | | |
| planar exp | -19.7 | 10.8 | (2.1) | (14.2) | 0.9 | 0.2 | 1.2 | | |
| planar relaxed | -19.5 | 12.2 | (3.1) | (15.7) | 1.0 | 0.2 | - | | |
TABLE X. Comparison of representative interatomic distances (in Å) and bond angles (in deg.) for the different structures. $d_{NN}$ and $d_{NNN}$ correspond to the nearest-neighbor and next-nearest-neighbor Cu–Cu distances. Cu–O–Cu is the bond angle within the structural dimer. O–O is the shortest distance between O atoms in the neighboring structural dimers. Cu–O are the distances within the CuO$_4$ plaquette. δO is the distance (in Å) between the O(2) atom in the experimental structure and the respective atom in the ideal planar chain geometry.

| structure         | $d_{NN}$ | $d_{NNN}$ | Cu–O–Cu | O–O | Cu–O | δO  |
|-------------------|----------|-----------|----------|-----|-----|-----|
| Na$_3$Cu$_2$SbO$_6$ |          |           |          |     |     |     |
| exp               | 2.96     | 5.91      | 95.27    | 2.94| 2.021/2.000 | 0.39 |
| planar exp        | 2.96     | 5.91      | 94.22    | 2.94| 2.021/2.017 | 0   |
| relaxed           | 2.96     | 5.91      | 96.03    | 2.96| 1.986/1.988 | 0.43|
| planar relaxed    | 2.96     | 5.91      | 95.39    | 2.96| 1.988/1.998 | 0   |
| Na$_2$Cu$_2$TeO$_6$ |          |           |          |     |     |     |
| exp               | 2.86     | 5.82      | 91.27    | 2.83| 1.978/1.999 | 0.55|
| planar exp        | 2.86     | 5.82      | 95.48    | 2.83| 1.978/1.931 | 0   |
| relaxed           | 2.86     | 5.82      | 92.91    | 2.92| 1.950/1.972 | 0.53|
| planar relaxed    | 2.86     | 5.82      | 95.24    | 2.92| 1.950/1.935 | 0   |

![FIG. 9](image-url) Dependent of exchange integrals on the double-counting correction: the around-mean-field (AMF) and the atomic limit (AL). For the LSDA+$U$ calculations we adopted the experimental crystal structure (exp) and the structure with planar chains (planar exp).

![FIG. 10](image-url) Oxygen content determined by coulometric titration of a freshly annealed sample (green curve) and a sample stored at room temperature and in air (violet curve). Note the difference between the initial oxygen content in the two samples.
FIG. 11. Dependence of the magnetic susceptibility on the annealing temperature and sample history (quality) due to changes in the O occupation. External magnetic field is 0.04 T. Note the difference between the 700 °C samples stored in air ("old") and measured right after annealing ("fresh"). In the paper, we used $\chi(T)$ data for fresh samples annealed at 640 °C, i.e., the samples featuring the smallest Curie-law-type impurities and/or defects (inset).

FIG. 12. Comparison of the antibonding $dp\sigma$ band using LDA for the experimental crystal structure of Na$_3$Cu$_2$SbO$_6$ and a model compound where Sb is substituted by Te (with an concomitant change in the Na content) within the same crystal structure using VCA. The obtained bands show nearly the same band width and shape pointing to minor relevance of pure substitutional effects.