Helicoidal magnetic order in a clean copper oxide spin chain compound

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We report susceptibility, specific heat, and neutron diffraction measurements on NaCu$_2$O$_2$, a spin-1/2 chain compound isostructural to LiCu$_2$O$_2$, which has been extensively investigated. Below 12 K, we find a long-range ordered, incommensurate magnetic helix state with a propagation vector similar to that of LiCu$_2$O$_2$. In contrast to the Li analogue, substitutional disorder is negligible in NaCu$_2$O$_2$. We can thus rule out that the helix is induced by impurities, as was claimed on the basis of prior work on LiCu$_2$O$_2$. A spin Hamiltonian with frustrated longer-range exchange interactions provides a good description of both the ordered state and the paramagnetic susceptibility.

Copper oxides are excellent model systems for low-dimensional spin-1/2 quantum antiferromagnets. In particular, copper oxides with magnetic backbones comprised of chains of CuO$_4$ squares have been shown to exhibit quasi-one-dimensional behavior. Two classes of copper oxide spin chain materials are known. Compounds in which adjacent squares share their corners are excellent realizations of the one-dimensional (1D) spin-1/2 Heisenberg Hamiltonian $H = -J S_i S_j$. Linear Cu-O-Cu bonds along the spin chains give rise to a large antiferromagnetic nearest-neighbor exchange coupling. In compounds built up of edge-sharing squares, on the other hand, the Cu-O-Cu bond angle is nearly 90°, so that the nearest-neighbor coupling is more than an order of magnitude smaller. Because of the anomalously small nearest-neighbor coupling, longer-range frustrating exchange interactions have a pronounced influence on the physical properties of these materials. Edge-sharing copper oxides thus provide uniquely simple model systems to test current theories of spin correlations in frustrated quantum magnets.

At low temperatures, the ground state of edge-sharing copper oxides is either a 3D-ordered antiferromagnet or a spin-Peierls state, depending on whether interchain exchange interactions or spin-phonon interactions are dominant. In the former case, the magnetic order is almost always collinear. An interesting exception was recently discovered in LiCu$_2$O$_2$, which undergoes a transition to a magnetic helix state at low temperatures. While such a state is expected for classical spin models with frustrating interactions, quantum models predict a gapped spin liquid state in the range of exchange parameters that was claimed to describe the spin system in LiCu$_2$O$_2$. Since the ionic radii of Li$^+$ and Cu$^{2+}$ are similar, chemical disorder was identified as a possible solution to this puzzle. Indeed, a chemical analysis of the sample used in the neutron scattering study of Ref. 11 showed that about 16% of the Cu$^{2+}$ ions in the spin chains were replaced by nonmagnetic Li$^+$ impurities. Since even much lower concentrations of nonmagnetic impurities are found to induce magnetic long-range order in other quasi-1D spin-gap systems, the authors of Ref. 11 attributed the unexpected helix state to the highly disordered lattice structure of LiCu$_2$O$_2$.

Here we report magnetic susceptibility, specific heat, and neutron diffraction data on NaCu$_2$O$_2$, a Mott insulator that is isostructural to LiCu$_2$O$_2$. However, since Na$^+$ is much larger than Cu$^{2+}$, substitutional disorder is a priori unlikely in NaCu$_2$O$_2$. Chemical analysis and neutron diffraction data confirm that Na-Cu inter-substitution is negligible in our NaCu$_2$O$_2$ samples. Below a Neél temperature $T_N$ of 12 K, we find an incommensurate helix state similar to that in LiCu$_2$O$_2$. Contrary to the interpretation advocated in Ref. 11, this state is thus the ground state of a spin chain system without impurities. The incommensurability along the chain axis is such that the magnetic unit cell is nearly quadrupled with respect to the chemical cell. Together with an analysis of the susceptibility data, this indicates that an antiferromagnetic next-nearest-neighbor interaction along the spin chain is the dominant exchange interaction in NaCu$_2$O$_2$. This disagrees with the spin Hamiltonian recently proposed for LiCu$_2$O$_2$. Each copper oxide chain thus contains two interpenetrating, but nearly independent 1D spin systems. A model with longer-range exchange interactions provides a quantitative description of the ground state and paramagnetic susceptibility of this spin-1/2 system.

Micro-crystalline powder samples of NaCu$_2$O$_2$ were synthesized via the azide/nitrate route in specially designed containers. The starting materials were milled, pressed in pellets under 10$^3$ mbar at 150°C for 12 h, and placed in an argon atmosphere in a tightly closed steel container provided with a silver inlay. Finally, in a flow of dry argon the following temperature sequence was applied: 25 to 260°C (100°C/h); 260 to 380°C (5°C/h), 380 to 500°C (50°C/h) with subsequent annealing for 30 hours at 500°C. Powder X-ray diffraction patterns for initial characterization were collected with a Stoe STADI-P diffractometer using CuK$_{α1}$ and MoK$_{α1}$ radiation. No impurity phases were detected, except small traces of CuO and Cu$_2$O. The single crystals were grown by the self-flux method in an argon atmosphere in platinum crucibles. The crystals have a platelet shape with typical sizes of $7 \times 3$ mm$^2$ and thickness of up to 100 μm. X-ray diffraction from single crystals ground to powder showed no sign of impurity phases within the resolution limit.
bic crystal structure (space group Pnma) with lattice parameters is shown in Fig. 1. The unit cell of NaCu in agreement with an X-ray investigation of small single crystals. The powder measurements were taken on a sample of total mass 115 mg in a SQUID magnetometer (MPMS, Quantum Design).

A Rietveld analysis of the diffraction pattern at room temperature confirms that NaCuO2 has an orthorhombic crystal structure (space group Pnma) with lattice parameters \(a = 6.2087\) Å, \(b = 2.9343\) Å and \(c = 13.0548\) Å, in agreement with an X-ray investigation of small single crystals. A pictorial representation of the lattice structure is shown in Fig. 1. The unit cell of NaCuO2 contains four magnetic \(\text{Cu}^{2+}\) ions belonging to two pairs of copper oxide chains running along \(b\). The Cu-O-Cu bond angle is 92.9°, somewhat larger than 87.2°, the equivalent angle in LiCuO2. The chains are separated from each other in the \(a\)-direction by rows of non-magnetic \(\text{Cu}^+\) ions, and in the \(c\)-direction by \(\text{Na}^+\) ions. Since the two chains within one pair are shifted relative to each other by half a unit cell along \(b\), each chain can also be viewed as a single zig-zag chain\(^{16}\). The nearest-neighbor \(\text{Cu}^{2+}\)-\(\text{Cu}^{2+}\) distances between different chain pairs are considerably larger than those within a pair. It is thus reasonable to expect that the system is magnetically one-dimensional.

In order to check for possible Na-Cu inter-substitution, we have refined the occupancies of Na and Cu sites in the Rietveld analysis of the neutron diffraction data and obtained full occupancy of both positions within an error of 2%. This finding is expected based on the different ionic radii of \(\text{Na}^+\) and \(\text{Cu}^{2+}\), and it confirms the results of the chemical analysis above. In contrast to LiCuO2, substitutional disorder on the copper oxide chains is therefore negligible in NaCuO2.

Fig. 2 shows the uniform magnetic susceptibility of a NaCuO2 powder as a function of temperature. The main feature of the curve is a broad maximum at 52 K, which is characteristic of low-dimensional spin systems and indicates a crossover to a state with antiferromagnetic short-range order. A Curie-Weiss fit of the high-temperature susceptibility for \(200 < T < 300 \text{ K}\) yields a negative Curie-Weiss temperature of \(\Theta_{\text{CW}} = -62 \text{ K}\), indicating predominant antiferromagnetic interactions. Because of the intrinsic 1D nature of our system, we have fitted the susceptibility curve to the exact solution of the S = 1/2 Heisenberg chain with a single antiferromagnetic interaction \(J_2\)\(^{17}\), resulting from the dominant Cu-O-O-Cu exchange path. We added a diamagnetic contribution from the closed atomic shells, which we estimate as \(-52 \times 10^{-6}\) cm\(^3\)/mol from Pascal’s increments\(^{18}\). The fit yields \(J_2 = 86 \text{ K}(k_B=1)\) and \(g = 2.07\), and the result is shown in Fig. 2. Our susceptibility data are thus in good quantitative agreement (except small deviations) with a model including a single antiferromagnetic interaction parameter along the spin chains (Fig. 2), supporting the view of a single chain as two interpenetrating, weakly coupled \(J_2\)-Heisenberg chains.

The low-temperature susceptibility and specific heat data plotted in Fig. 3 indicate two magnetic phase transitions at 12 and 8 K. Both transition temperatures are much smaller than \(J_2\), as expected based on the quasi-one-dimensionality of the magnetic lattice. The temperature dependent susceptibility of a single-crystal sample in the three crystallographic directions is plotted in Fig. 3a. The susceptibility in the \(b\)-direction, \(\chi_b\), is not strongly affected by the 12 K transition, while \(\chi_a\) and \(\chi_c\) are suppressed. Below the 8 K transition, on the other hand, \(\chi_a\) and \(\chi_b\) exhibit an upturn, reflecting the role of anisotropic interactions. The specific heat anomaly at the 8 K transition is weaker and obliterated by a modest magnetic field of 9T (Fig. 3b), whereas the 12 K transition is more robust. Taken together, these data suggest that the 8 K transition arises from spin canting. A similar canting transition has been observed in LiCuO2\(^{19}\).
ceptibility in terms of a spin Hamiltonian with longer-range couplings can be either ferromagnetic or antiferromagnetic. They can be indexed based on the magnetic moment per Cu$^{2+}$ ion at base temperature is 0.56(4)$\mu_B$.

Since the observed helical spin structure of NaCu$_2$O$_2$ cannot be accounted for within a simple nearest-neighbor Heisenberg model, we reanalyzed the paramagnetic susceptibility in terms of a spin Hamiltonian with longer-ranged interactions $J_d$. Such additional couplings are expected for Cu-O-O-Cu bridges in edge-sharing copper chains. We consider magnetic couplings up to a distance $d=4b$. Whereas couplings $|J_d| \geq 2$ are always antiferromagnetic, $J_1$ can be either ferromagnetic or antiferromagnetic depending on the Cu-O-Cu bond angle. The classical ground state of this model is a helix whose pitch angle $\phi_0$ is given by the expression

$$\cos \phi_0 \simeq \frac{J_1 - 3J_3}{4(J_2 - 3J_4)},$$

which is valid as long as $|J_1|, |J_3|$, and $|J_4|$ are significantly smaller than $|J_2|$. Using a finite temperature Lanczos technique, we have calculated the temperature dependent susceptibility on chains of length $N = 24$ for models where condition (1) is fulfilled, using the angle $\phi_0 = 82^\circ$ obtained in the analysis of the neutron scattering data. An excellent fit (red line in Fig. 2) is obtained for the entire temperature range from just above $T_N$ up to 330 K, with the parameters $J_1 = -16.4$ K, $J_2 = 90$ K, $J_3 = 7.2$ K, and $J_4 = 6.3$ K. The $g$-factor, $g = 2.14$, is typical for Cu$^{2+}$ in square-planar geometry. The fact that the antiferromagnetic interaction $J_2$ is by far the largest parameter in the spin Hamiltonian explains the surprisingly good fit obtained by the nearest-neighbor model discussed above. The longer-range couplings $J_3$, $J_4$ are small, as expected, yet they are essential in this context, since fits attempted with $J_3 = J_4 = 0$ ($J_1/J_2 = -0.52$ which yields the experimental pitch angle, green line in Fig. 2) are in significantly poorer agreement with the experimental data.

We have thus determined the magnetic ground state of NaCu$_2$O$_2$, a spin-1/2 chain compound without significant substitutional disorder, as a magnetic helix with a substantial ordered moment of 0.56$\mu_B$. This rules out impurity-induced magnetic long-range order, a scenario that was initially entertained because of a magnetic susceptibility of a powder sample of NaCu$_2$O$_2$ in a magnetic field of 0.1T applied along the principal crystallographic axes. Specific heat for two applied magnetic fields: 0T (open circles) and 9T (full circles). The inset extends the temperature range.

These data indicate that the magnetic ground state is more complex than suggested by the initial analysis of the paramagnetic susceptibility. In order to determine the spin configuration in the ground state, neutron powder diffraction data were taken on the high-flux powder diffractometer D20. The results are shown in Fig. 4. Several additional Bragg reflections are observed below 12 K at low scattering angles. Since no high-angle counterparts of these reflections are observed, and the intensities vanish at the magnetic ordering temperature (inset in Fig. 4), these reflections can be identified as magnetic. They can be indexed based on the magnetic propagation vector $(0.5, \zeta, 0)$ with $\zeta = 0.227$, which corresponds to a pitch angle $\phi_0 = 81.7^\circ$ along the b-axis. Since an amplitude modulation of the copper spin is not expected in a Mott insulating state, the intensities were compared to models in which the spins form a helicoidal state with identical amplitude on every Cu$^{2+}$ site, analogous to that observed in LiCu$_2$O$_2$. An excellent refinement of the peak intensities (solid line in Fig. 4) was obtained by assuming a helix polarized in the ab-plane (Fig. 1), similar to LiCu$_2$O$_2$. The ordered moment per Cu$^{2+}$ ion at base temperature is 0.56(4)$\mu_B$.
the nearest-neighbor coupling in the spin Hamiltonian for LiCu$_2$O$_2$, where a helix with a similar propagation vector was observed. The spin Hamiltonian is dominated by a large antiferromagnetic exchange parameter $J_2 \sim 90$ K, which can be identified as the interaction between second-nearest neighbors along the spin chains. The dominance of the $J_2$ coupling may at first seem surprising, but it can be understood as a consequence of the structural geometry of NaCu$_2$O$_2$, whose Cu-O-Cu bond angle, 92.9°, is very close to the critical angle of ~94° at which the nearest-neighbor interaction is expected to change sign. Hence, the nearest-neighbor coupling $J_1$ is small. The magnitude of $J_1$ is in very good agreement with theoretical calculations for edge-sharing copper oxide chains with Cu-O bond parameters determined for NaCu$_2$O$_2$. This agreement is significant, because the prediction is largely insensitive to the bond angle and hence quite robust, and because direct measurements of this parameter in other copper oxide spin chains yield comparable results. The inclusion of a small interchain interaction within a chain pair ($J'$ in Fig. 1b) marginally affects the values of the intrachain exchange parameters extracted from the susceptibility, and therefore does not change this picture qualitatively.

In view of our work on a clean, isostructural compound and the theoretical work of Ref. [4], the exchange parameters of LiCu$_2$O$_2$ should be reexamined. Because of the smaller Cu-O-Cu bond angle, the magnitude of the nearest-neighbor coupling in the spin Hamiltonian for LiCu$_2$O$_2$ is expected to be larger than that of NaCu$_2$O$_2$, but the next-nearest-neighbor coupling should be comparable. A scenario in which an antiferromagnetic interchain interaction of magnitude $J' \sim 70$ K significantly exceeds all of the relevant intrachain interactions [11] appears very unlikely.

In conclusion, the magnetic helix state and paramagnetic susceptibility of NaCu$_2$O$_2$ are in good qualitative agreement with the predictions of a model including longer-range exchange interactions. An open question concerns our use of the classical expression [11] for the pitch angle. Some theoretical work suggests that the pitch angle for quantum models deviates substantially from this expression [21]. However, one has to keep in mind that the magnitude of the ordered moment per magnetic copper site is 0.56$\mu_B$, somewhat larger than the values typically observed in 1-D systems [11]. Quantum zero-point fluctuations thus appear to be significantly suppressed in the ordered state. Large ordered moments were also observed in other corner-sharing copper oxide spin chain compounds, and were ascribed to large exchange anisotropies. A quantitative understanding of the interplay between spin anisotropies and frustration in NaCu$_2$O$_2$ and other spin chain materials is an interesting subject of further investigation.

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