

Helicoidal magnetic order in the spin-chain compound NaCu_2O_2

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We report susceptibility, specific heat, and neutron diffraction measurements on NaCu_2O_2 , a spin-1/2 chain compound isostructural to LiCu_2O_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_2O_2 . In contrast to the Li analog, substitutional disorder is negligible in NaCu_2O_2 . We can thus rule out that the helix is significantly influenced by impurities. A spin Hamiltonian with frustrated longer-range exchange interactions provides a good description of both the ordered state and the paramagnetic susceptibility.

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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.¹⁻³ 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.⁴ 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 three-dimensional-(3D)-ordered antiferromagnet⁵⁻⁷ or a spin-Peierls state,⁸ 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_2O_2 ,⁹⁻¹² 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_2O_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-one-dimensional spin-gap systems, the authors of Ref. 11 speculated that the highly disordered lattice structure of LiCu_2O_2 might play a significant part in driving helical ordering in this system.

Here we report magnetic susceptibility, specific heat, and neutron diffraction data on NaCu_2O_2 , a Mott insulator that is

isostructural to LiCu_2O_2 . However, since Na^+ is much larger than Cu^{2+} , substitutional disorder is *a priori* unlikely in NaCu_2O_2 . Chemical analysis and neutron diffraction data confirm that the Na-Cu intersubstitution is negligible in our NaCu_2O_2 samples. Below a Néel temperature T_N of 12 K, we find an incommensurate helix state similar to that in LiCu_2O_2 . 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_2O_2 . This disagrees with the spin Hamiltonian proposed for LiCu_2O_2 ,¹¹ but agrees with arguments presented in Ref. 12. 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.

Microcrystalline powder samples of NaCu_2O_2 were synthesized as described elsewhere.¹³⁻¹⁵ Powder x-ray diffraction patterns for initial characterization were collected with a Stoe STADI-P diffractometer using Cu $K\alpha 1$ and Mo $K\alpha 1$ radiation. No impurity phases were detected, except small traces of CuO and Cu_2O . The single crystals were grown by the self-flux method, as described previously.¹⁶ The crystals have a platelet shape with typical sizes of $7 \times 3 \text{ mm}^2$ and thickness of up to $100 \mu\text{m}$. X-ray diffraction from single crystals ground to powder showed no sign of impurity phases within the resolution limit. In addition, no platinum impurities were detected in our crystals by inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements. Finally, we have used ICP-AES to establish the chemical composition of our crystals as $\text{Na}_{1.00 \pm 0.02} \text{Cu}_{2.00 \pm 0.02} \text{O}_y$. The Na:Cu ratio is thus identical to the ideal stoichiometry within the experimental error. This should be compared to the samples studied in Ref. 11 whose chemical composition was quoted as $\text{Li}_{1.16} \text{Cu}_{1.84} \text{O}_{2.01}$.

For the neutron diffraction measurements, a powder sample of weight $\sim 5 \text{ g}$ was fitted into a cylindrical vanadium container and loaded in a standard helium-flow cryostat. High-resolution diffraction patterns were collected at 3.5, 23, and 300 K on the two-circle powder diffractometer

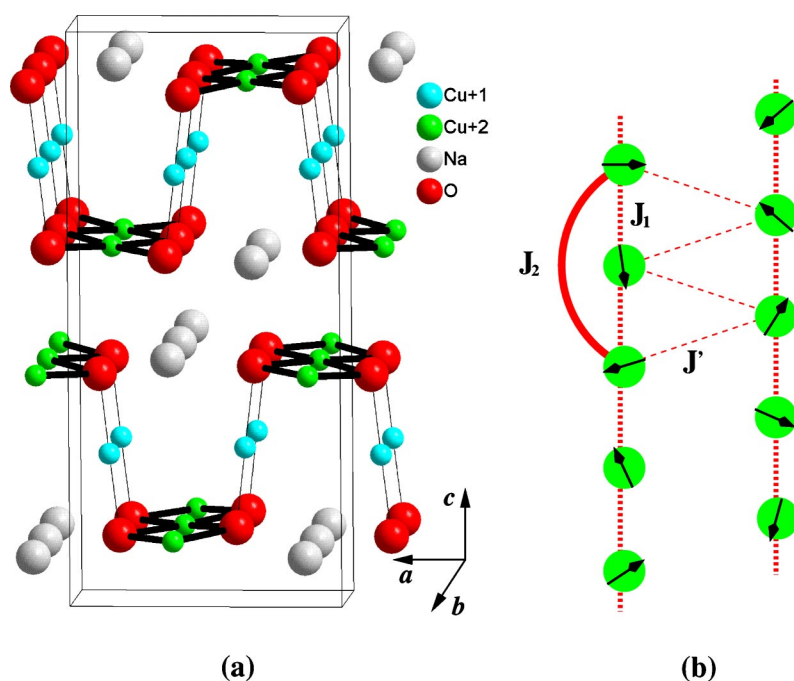


FIG. 1. (Color online) (a) Crystal structure, and (b) proposed magnetic structure of NaCu₂O₂. In panel (b), the most important magnetic interactions within a chain pair are sketched.

D2B at the Institut Laue-Langevin, Grenoble. A wavelength $\lambda = 1.5946 \text{ \AA}$ was selected by a Ge[355] monochromator. The diaphragms were set to 70/70 and the collimations to 10'-10'-10' before the monochromator, between the monochromator and sample, and between the sample and detector, respectively. Complementary neutron diffraction data were taken on the high-flux powder diffractometer D20 using a wavelength $\lambda = 2.4 \text{ \AA}$. The diaphragms were set to 70/10. Measurements of the magnetic susceptibility and the heat capacity were carried out on powder samples as well as on single crystals. The powder measurements were taken on a sample of total mass of 115 mg in a superconducting quantum interference device (SQUID) magnetometer (MPMS, Quantum Design).

A Rietveld analysis of the diffraction pattern at room temperature confirms that NaCu₂O₂ has an orthorhombic crystal structure (space group *Pnma*) with lattice parameters $a = 6.2087 \text{ \AA}$, $b = 2.9343 \text{ \AA}$ and $c = 13.0548 \text{ \AA}$, 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 NaCu₂O₂ contains four magnetic Cu²⁺ ions belonging to two pairs of copper oxide chains running along *b*. The Cu–O–Cu bond angle is 92.9°. The chains are separated from each other in the *c* direction by rows of nonmagnetic Cu⁺ ions, and in the *a* direction by Na⁺ ions. Since the two chains within one pair are shifted relative to each other by half a unit cell along *b*, each pair can also be viewed as a single zigzag chain.¹⁷ The nearest-neighbor Cu²⁺–Cu²⁺ 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 a possible Na–Cu intersubstitution, 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 Na⁺

and Cu²⁺, and it confirms the results of the chemical analysis above. In contrast to LiCu₂O₂, substitutional disorder on the copper oxide chains is therefore negligible in NaCu₂O₂.

Figure 2 shows the uniform magnetic susceptibility of a NaCu₂O₂ 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 $\Theta_{CW} = -62 \text{ K}$, indicating predominant antiferromagnetic interactions. Because of the intrinsic 1D nature of our

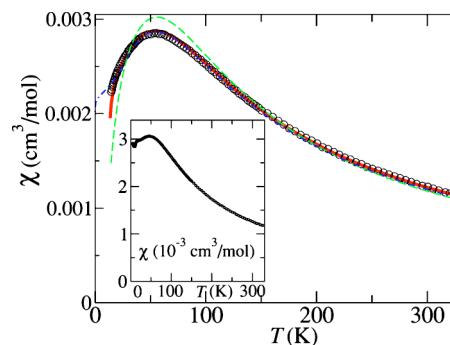


FIG. 2. (Color online) Temperature dependence of the static magnetic susceptibility of a powder sample of NaCu₂O₂ in a magnetic field $B = 0.1 \text{ T}$ (open circles). The thick red line is the result of a fit to the helix model described in the text, whereas the blue line (dot-dashed, mostly hidden by the red one) is the (exact) susceptibility of the 1D-Heisenberg chain ($J_2 = 85 \text{ K}$) (Ref. 18). For comparison, the green line represents the result of a fit to a simpler J_1 - J_2 helix model (see text). The inset shows the actually measured data, from which a Curie contribution $\chi_{Cur} = 0.0105/T$ has been subtracted to obtain the data presented in the main panel. Note that the Curie tail is very weak, providing testimony to the high quality of the sample.

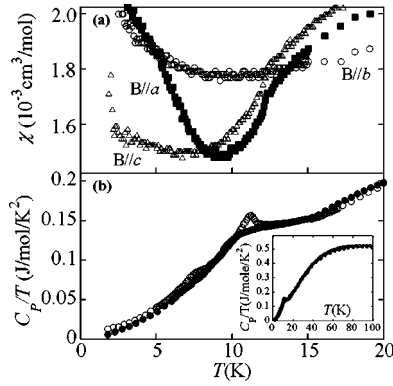


FIG. 3. Single-crystal data for NaCu_2O_2 as a function of temperature. (a) Susceptibility taken with a magnetic field of 0.1 T applied along the principal crystallographic axes. (b) Specific heat for two applied magnetic fields: 0 T (open circles) and 9 T (full circles). The inset extends the temperature range.

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 ,¹⁸ resulting from the dominant Cu-O-O-Cu exchange path. We added a diamagnetic contribution from the closed atomic shells, which we estimate as $-52 \times 10^{-6} \text{ cm}^3/\text{mol}$ from Pascal's increments.¹⁹ The fit yields $J_2=85 \text{ K}$ ($k_B \equiv 1$) and $g=2.07$, and the result is shown in Fig. 2. Our susceptibility data are thus in good quantitative agreement (except for 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. 3(a). The susceptibility in the b direction, χ_b , is not strongly affected by the 12-K transition, while χ_a and χ_c are suppressed. Below the 8-K transition, on the other hand, χ_a and χ_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 9 T [Fig. 3(b)], 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 Li_2CuO_2 .⁷

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

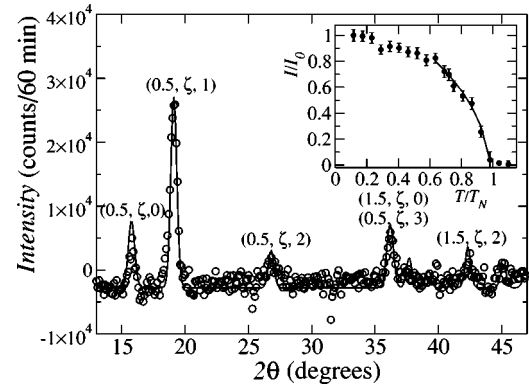


FIG. 4. Difference of neutron diffraction data collected at 2 and 20 K (open circles). The extra reflections at low temperature are all of magnetic origin. The solid line is a fit to a spiral model in the bc plane with propagation vector $(0.5, \zeta, 0)$ with $\zeta=0.227$. The temperature dependence of the $(0.5, \zeta, 1)$ reflection is plotted in the inset together with a fit of the intensity to a power law.

propagation vector $(0.5, \zeta, 0)$ with $\zeta=0.227$, which corresponds to a pitch angle $\phi_b=81.7^\circ$ 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_2O_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_2O_2 .^{11,20} The ordered moment per Cu^{2+} ion at base temperature is $0.56(4)\mu_B$.

Since the observed helical spin structure of NaCu_2O_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.⁴ 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.⁴ The classical ground state of this model is a helix whose pitch angle ϕ_b is given by the expression

$$\cos \phi_b \simeq -\frac{J_1 - 3J_3}{4(J_2 - 3J_4)}, \quad (1)$$

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,²¹ we have calculated the temperature-dependent susceptibility on chains of length $N=24$ for models where condition (1) is fulfilled, using the angle $\phi_b=82^\circ$ 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 $J_1=-16.4 \text{ K}$, $J_2=90 \text{ K}$, $J_3=7.2 \text{ K}$, and $J_4=6.3 \text{ K}$. 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 sur-

prisingly 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_2O_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 that the ground state is significantly influenced by impurities as proposed in Ref. 11 for LiCu_2O_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_2O_2 , whose Cu–O–Cu bond angle, 92.9° , is very close to the critical angle of $\sim 94^\circ$ at which the nearest-neighbor interaction is expected to change sign.⁴ Hence, the nearest-neighbor coupling J_1 is small. The magnitude of J_2 is in very good agreement with theoretical calculations for edge-sharing copper oxide chains with Cu–O bond parameters determined for NaCu_2O_2 .⁴ 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. 1(b)] 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_2O_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_2O_2 is expected to be larger than that of NaCu_2O_2 , but the next-nearest-neighbor coupling should be comparable.²³ In agreement with Ref. 12, we conclude that a scenario in which an antiferromagnetic interchain interaction of magnitude $J' \sim 70$ K significantly exceeds all of the relevant intrachain interactions¹¹ appears very unlikely.

In conclusion, the magnetic helix state and paramagnetic susceptibility of NaCu_2O_2 are in good quantitative agreement with the predictions of a model including longer-range exchange interactions. An open question concerns our use of the classical expression (1) for the pitch angle. Some theoretical work suggests that the pitch angle for quantum models deviates substantially from this expression.²² 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 1D systems.¹ 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_2O_2 and other spin chain materials is an interesting subject of further investigation.

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