

Incommensurate Spin-Density Modulation in a Copper Oxide Chain Compound with Commensurate Charge Order

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Neutron diffraction has been used to determine the magnetic structure of $\text{Na}_8\text{Cu}_5\text{O}_{10}$, a stoichiometric compound containing chains based on edge-sharing CuO_4 plaquettes. The chains are doped with $2/5$ hole per Cu site and exhibit long-range commensurate charge order with an onset well above room temperature. Below $T_N = 23$ K, the neutron data indicate long-range collinear magnetic order with a spin-density modulation whose propagation vector is commensurate along, and incommensurate perpendicular to, the chains. Competing interchain exchange interactions are discussed as a possible origin of the incommensurate magnetic order.

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The interplay between the magnetic and electric properties of copper oxides has recently been the subject of intense research activity. For instance, states with collinear and noncollinear magnetic order are currently under discussion in the contexts of ferroelectricity in undoped copper-oxide chain compounds [1] and of the anomalous transport properties of underdoped high temperature superconductors [2,3]. Since theoretical methods are well established in one dimension (1D), compounds with quasi-1D electronic structure are particularly suitable as model systems to obtain a detailed understanding of this interplay. However, research on the effect of doping in copper-oxide chain compounds has been limited by the scarcity of materials that support a significant density of holes on the chains. Most of the attention has been focused on the “telephone number compounds” $(\text{La}, \text{Sr})_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ (LSCCO), which contain chain and ladder systems based on edge-sharing CuO_4 square plaquettes [4–10]. Experiments have revealed intricate charge and spin ordering patterns on the chain subsystem, which depend strongly on the hole content. However, complications originating from the presence of two distinct electronically active subsystems with different hole concentrations and from the random potential of substituents (for $x \neq 0$) partially mask the intrinsic behavior of the copper-oxide chains. Moreover, recent work has shown that the magnetic properties of this material are strongly influenced by an incommensurate structural modulation arising from a mismatch of different units constituting the crystal lattice [8–10]. $\text{Ca}_{2+x}\text{Y}_{2-x}\text{Cu}_5\text{O}_{10}$ (CYCO), a class of materials containing only copper-oxide chains, also exhibits a complicated structural modulation unrelated to charge ordering [11,12]. In addition, the magnetic properties of doped chains in this material appear to be influenced to a large extent by substitutional disorder and/or oxygen nonstoichiometry [13].

Na_xCuO_2 , a recently synthesized family of compounds with very low chemical disorder, offers new perspectives in

this regard [14–16]. This material consists entirely of electronically inert Na^+ ions and chains built of edge-sharing CuO_4 plaquettes similar to those in LSCCO and CYCO (Fig. 1). Holes donated to the chains by the Na ions form long-range ordered superstructures that are generally incommensurate with the Na sublattice. However, in contrast to other copper oxides with dopable chains, incommensurate structural modulations due to purely steric constraints are not present, so that commensurate charge order can be established if x is a rational number. By carefully adjusting the chemical synthesis conditions, a state with $x = 1.60$, corresponding to a hole filling factor of $2/5$ on the chains, has recently been stabilized [16]. The stoichiometric compound created in this way, $\text{Na}_8\text{Cu}_5\text{O}_{10}$, is a unique testing ground for theories of magnetism in doped copper oxides, without complications arising from substitutional disorder and/or incommensurate lattice distortions.

We have determined the magnetic structure of $\text{Na}_8\text{Cu}_5\text{O}_{10}$ below its Néel temperature $T_N = 23$ K by neutron powder diffraction. We find that the spins are collinear and exhibit an incommensurate spin-density modulation that is unusual for magnetic insulators. A possible origin is a network of competing interchain exchange interactions. An investigation of the mechanisms stabilizing this state compared to the helicoidal states found in the undoped analogues $(\text{Na}, \text{Li})\text{Cu}_2\text{O}_2$ [17–19] may provide important insights into the competition between collinear and noncollinear magnetism in other copper oxides of topical interest [1–3].

Powder samples of $\text{Na}_8\text{Cu}_5\text{O}_{10}$ with weight ~ 4.5 g were synthesized in a single batch as described previously [14]. Their magnetic susceptibility was found to be in good agreement with prior reports [14,15]. In particular, a magnetic transition temperature $T_N = 23$ K was obtained by analyzing the derivative of the magnetization as a function of temperature. As $\text{Na}_8\text{Cu}_5\text{O}_{10}$ is sensitive to air, the samples were sealed in air-tight vanadium cans, which

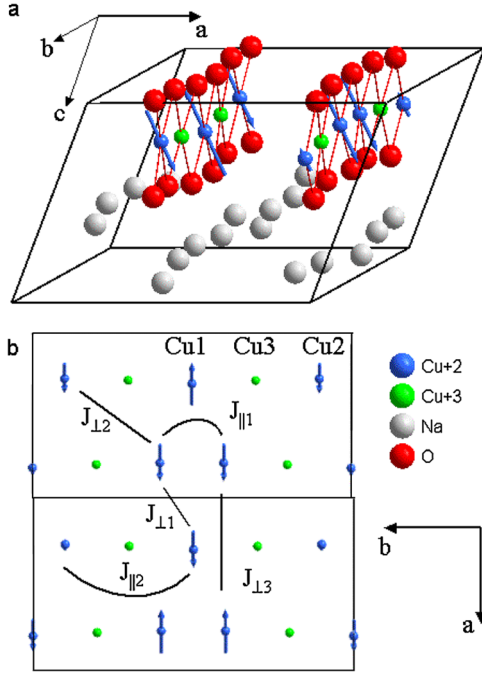


FIG. 1 (color online). (a) Nuclear unit cell and spin structure of $\text{Na}_8\text{Cu}_5\text{O}_{10}$. (b) Cut of the lattice structure along the ab plane, showing inequivalent copper sites and superexchange parameters, as explained in the text.

were loaded into a helium flow cryostat. The neutron diffraction data were taken at the Laboratoire Leon Brillouin in Saclay, France. In order to determine the nuclear structure, we used the high-resolution diffractometer 3-T-2 with a neutron wavelength of 1.23 Å. The data for the magnetic structure determination were taken on the high-flux cold-neutron diffractometer G-4-1 with a neutron wavelength of 2.43 Å.

Figure 2 shows a high-resolution powder diffraction pattern obtained at room temperature. The nuclear intensities for both samples were refined with the program Fullprof [20] on the basis of the monoclinic space group Cm . The unit cell parameters $a = 8.23492 \pm 0.00014$ Å, $b = 13.92889 \pm 0.00020$ Å, $c = 5.71324 \pm 0.00010$ Å, and $\beta = 111.91 \pm 0.004^\circ$ and atomic positions obtained from the refinement agree with the results of earlier x-ray diffraction studies [14,16]. The resulting diffraction pattern yields an excellent description of the experimental data (Fig. 2), as indicated by the goodness-of-fit-parameter $R_F = 0.0854$. This confirms that the sample is chemically homogeneous, and that the lattice structure is commensurate. Another sample prepared under nominally identical conditions yielded substantially worse refinements, and data on a sample consisting of batches of powder material synthesized in different reactions could only be fitted by a superposition of different charge ordering patterns. These findings confirm that slight deviations from the ideal composition result in incommensurately modulated structures [16].

The atomic positions within the unit cell are displayed in Fig. 1. The unit cell comprises ten copper ions, which are

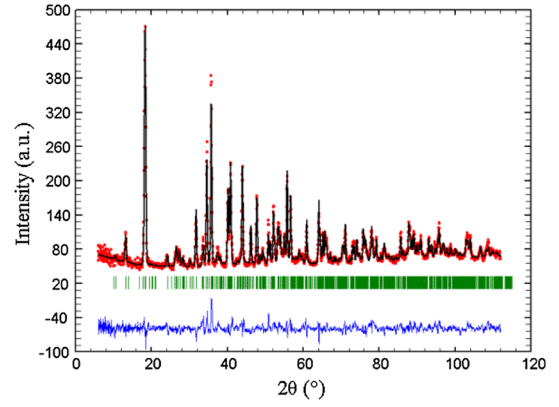


FIG. 2 (color online). High-resolution neutron powder diffraction pattern of $\text{Na}_8\text{Cu}_5\text{O}_{10}$ at room temperature. The upper line shows the result of the Rietveld refinement discussed in the text. The positions of nuclear Bragg reflections are indicated. The bottom curve gives the difference between the calculated and measured intensities.

organized in two parallel CuO_2 chains pointing along the b axis. The chains are separated by Na ions. Four of the copper ions in each unit cell [Cu3 in Fig. 1(b)] were found to exhibit bonding patterns characteristic of spinless Zhang-Rice singlet states with formal valence 3+ (Ref. [14]). The Cu-O bond lengths of the remaining six copper ions indicate a valence state of Cu^{2+} with spin 1/2. The Cu^{2+} ions are located in two inequivalent sites, which are surrounded by two Cu^{3+} ions (Cu1), and one Cu^{3+} ion and one Cu^{2+} ion (Cu2), respectively. Nominally di- and trivalent copper ions are ordered in the sequence 2 – 2 – 3 – 2 – 3 – 2 – 2 – 3 – ... along the chains (Fig. 1). The charge order is stable up to temperatures well above room temperature [14,15].

Figure 3 shows the low-angle segment of the high-flux powder pattern measured at $T = 1.4$ K taken to determine the magnetic structure. Two of the peaks shown vanish above $T_N = 23$ K identified from the anomaly in the uniform susceptibility and hence originate from magnetic scattering. The temperature dependence of the magnetic Bragg intensity is well described by a power-law fit without detectable rounding near T_N (Fig. 4), which indicates homogeneous magnetic long-range order in the low-temperature phase. This conclusion is supported by the refinement described below, which shows that the widths of the magnetic Bragg reflections are limited by the instrumental resolution.

The magnetic structure was refined using the software package Fullprof [20] based on the magnetic structure factor

$$\vec{F}_m(\vec{h}) = \sum_{j=1} O_j f_j(\vec{h}) T_j^{\text{iso}} \times \sum_s M_{js} S_{\vec{k}j} T_{js} \exp\{2\pi i[\vec{h}\{S|\vec{r}_{js}\vec{r}_j - \Psi_{\vec{k}js}\}]\}, \quad (1)$$

where \vec{h} is the scattering vector, \vec{k} is the propagation vector

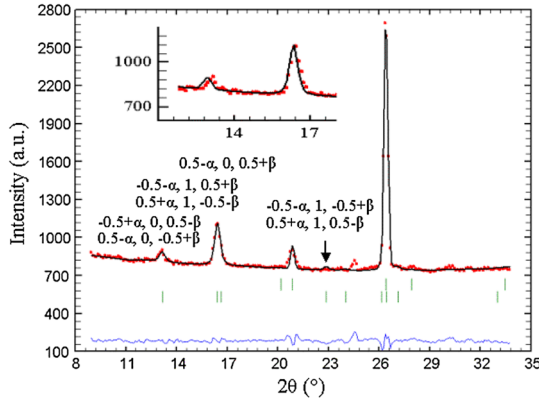


FIG. 3 (color online). Low-angle segment of the high-flux powder diffraction pattern measured at 1.4 K (red points). The upper line shows the results of the Rietveld refinement discussed in the text. The upper (lower) marks indicate the positions of nuclear (magnetic) Bragg reflections. The bottom curve gives the difference between the calculated and measured intensities. The inset shows the result of a refinement based on a commensurate spin structure.

of the magnetic structure, j enumerates the symmetry-inequivalent magnetic ions at positions \vec{r}_j in the magnetic unit cell, the index s runs over the magnetic symmetry operators, M_{js} is an operator that transforms the Fourier components $\vec{S}_{\vec{k}_j}$ of the magnetic moments according to a given symmetry, $\{S|\vec{r}_j\}_s$ generates the positions of all symmetry-equivalent magnetic ions in the unit cell, and $\Psi_{\vec{k}_j s}$ is a phase factor. The refinements are based on the isotropic form factor $f_j(\vec{h})$ of the Cu^{2+} ion. The occupation factor O_j as well as the Debye-Waller factors, T_j^{iso} and T_{js} , were set to unity.

The positions of the magnetic Bragg peaks indicate an approximate doubling of the unit cell along a and c , whereas the magnetic and nuclear unit cells coincide along the spin-chain axis b . A systematic shift away from scattering angles corresponding to commensurate Bragg reflections (inset in Fig. 3) reveals that the magnetic structure is incommensurate. Note that this shift can be extracted with high confidence, because the reference lattice param-

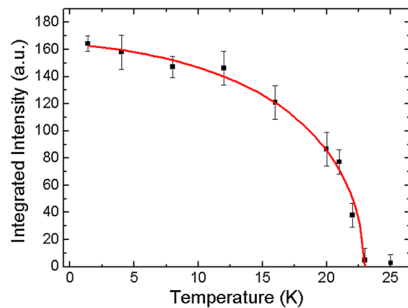


FIG. 4 (color online). Integrated intensities of the $(\mp 0.5 \mp \alpha, 1, \pm 0.5 \mp \beta)$ - and $(0.5 - \alpha, 0, 0.5 + \beta)$ magnetic Bragg reflections as a function of temperature. The line is the result of a power-law fit.

eters are determined by many Bragg reflections over a wide range of scattering angles (Fig. 2). The propagation vector resulting from the refinement is $(-0.5 + \alpha, 0, 0.5 - \beta)$ with $\alpha = 0.089(3)$ and $\beta = -0.030(1)$ (at 1.4 K). The Miller indices of the magnetic Bragg reflections are shown in Fig. 3. The asymmetric line shape of the magnetic peak at higher scattering angle is well explained as a consequence of the superposition of two resolution-limited, nearly coincident incommensurate Bragg reflections.

Although only three inequivalent magnetic Bragg reflections are visible, the diffraction pattern imposes strong constraints on the magnetic structure. Because of the large unit cell and the incommensurate magnetic modulation, most possible spin arrangements generate additional Bragg reflections with intensities well outside the experimental error bars, where none are observed. By far the best agreement with the data (Bragg $R = 0.049$, magnetic $R = 0.114$) was obtained based on a collinear spin structure in which the two Cu^{2+} moments on Cu2 sites directly adjacent along the chains are parallel, whereas Cu1 and Cu2 moments separated by Cu3 ions are antiparallel. The magnetic moment on the Cu3 site was refined to zero, consistent with the Zhang-Rice singlet state inferred from the bond-length analysis of Ref. [14]. The incommensurate propagation vector perpendicular to the chains modulates the magnitude of the Cu^{2+} moments. The modulation amplitude was refined as $0.84 \pm 0.10 \mu_B$ on both Cu1 and Cu2 sites, consistent with a spin-1/2 state. The spin direction resulting from the refinement is $(0.86 \pm 0.39, 0, 0.92 \pm 0.07)$. An additional refinable parameter is the phase difference $\Psi_{12} = 44.6 \pm 4.5^\circ$ of the modulation on Cu1 and Cu2 sites. The spin arrangement within the nuclear unit cell is displayed in Fig. 1. The corresponding diffraction pattern is in excellent agreement with the data (Fig. 3).

A comprehensive set of alternative collinear and non-collinear spin structures was also tested, but the resulting refinements were unsatisfactory. In particular, the diffraction patterns of the circular helix structure that yields the best agreement with the data generates prominent Bragg reflections $(\pm 0.5 \pm \alpha, 1, \pm 0.5 \mp \beta)$ at 22.9° , where the Bragg intensity vanishes within the error (arrow in Fig. 3). The corresponding magnetic R -factor is 0.354, much worse than that of the collinear state. If the refinement is generalized to include elliptical helix structures, the length of the minor axis of the ellipse ($0.061 \pm 0.165 \mu_B$ along b) is consistent with zero, and the magnetic R factor does not improve significantly compared to the collinear state. Although a small noncollinear component due to helicity or canting cannot be ruled out, the incommensurate modulation therefore predominantly affects the moment amplitude.

The observed spin amplitude modulation is formally analogous to spin-density waves in metallic systems, but the insulating nature and robust charge order of $\text{Na}_8\text{Cu}_5\text{O}_{10}$ imply that it cannot arise from a Fermi surface instability. We therefore discuss our data in terms of superexchange

interactions between local magnetic moments, focusing first on the commensurate spin structure along the chain axis b . The spin alignment along this axis indicates a ferromagnetic nearest-neighbor (nn) exchange interaction $J_{\parallel 1}$ and an antiferromagnetic next-nearest-neighbor (nnn) interaction $J_{\parallel 2}$ [Fig. 1(b)], in agreement with electronic structure calculations for edge-sharing copper-oxide chains [7,15,21–24] and with the conclusions of experiments on a variety of undoped compounds including LiCu_2O_2 [17,19] and NaCu_2O_2 [18], which contain undoped chains with similar bond lengths and angles as the ones in $\text{Na}_8\text{Cu}_5\text{O}_{10}$. Since the Cu-O-Cu bond angle in the edge-sharing chain geometry is close to 90° , $J_{\parallel 1}$ is anomalously small, and the competing nnn coupling $J_{\parallel 2}$ is comparable or larger in magnitude. The undoped spin systems of $(\text{Li, Na})\text{Cu}_2\text{O}_2$ respond to the resulting frustration by forming incommensurate, helical magnetic order propagating along the chains [17–19]. In $\text{Na}_8\text{Cu}_5\text{O}_{10}$, charge ordering lifts this frustration and gives rise to a commensurate spin structure along the chains, as predicted by model calculations [15].

The situation is different for interactions between different chains. For simplicity, we first ignore the small incommensurability along c and consider the magnetic bonding pattern in the ab -plane [Fig. 1(b)], including both interactions between directly adjacent chains within the same unit cell ($J_{\perp 1}$, $J_{\perp 2}$) and interactions between nnn chains ($J_{\perp 3}$). The simplest explanation for the approximate doubling of the unit cell along a is that $J_{\perp 3}$ is dominant and antiferromagnetic, leaving the interactions between nn chains frustrated. In principle, the spin system can respond to the frustration by establishing either noncollinear magnetic order, as observed in $(\text{Na, Li})\text{Cu}_2\text{O}_2$, or periodic spin-singlet correlations, as found in models of frustrated and/or doped 1D [4,6] and 2D [3] quantum antiferromagnets. An admixture of such correlations is a possible mechanism underlying the observed spin-density modulation in $\text{Na}_8\text{Cu}_5\text{O}_{10}$. To obtain a crude estimate of the magnitude of the interchain interactions in the framework of this scenario, we consider collinear classical spins coupled by sinusoidally modulated exchange bonds with amplitudes shown in Fig. 1(b). Minimization of the exchange energy with respect to the phase shift Ψ_{12} of the modulation on the Cu1 and Cu2 sublattices then yields $J_{\perp 1}/J_{\parallel 2} = \sin\Psi_{12}/2 \sin(\frac{1}{2}k_x a + \Psi_{12}) \sim -0.7$, where k_x is the component of the incommensurate propagation vector along the a axis determined by the competing interactions between nn and nnn chains. While a full quantum-mechanical calculation is required to assess the viability of this scenario, this simple estimate indicates that the exchange interactions between CuO_2 chains along a are comparable to those within the chains, as observed for other copper-oxide chain compounds [22,23,25]. The smaller incommensurability along c suggests weaker exchange interactions in this direction.

In view of the helicoidal states observed in $(\text{Li, Na})\text{Cu}_2\text{O}_2$, the collinear spin-density modulation in $\text{Na}_8\text{Cu}_5\text{O}_{10}$ may seem surprising. However, as other cuprates with undoped edge-sharing chains exhibit collinear spins [12,25], the energy balance between both types of order appears to be quite subtle. This is confirmed by *ab initio* calculations [22,24]. Anisotropic exchange [5,25] and/or order-from-disorder mechanisms [26] may be responsible for tipping the balance towards collinear order in $\text{Na}_8\text{Cu}_5\text{O}_{10}$.

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