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Spin polarization of the magnetic spiral in $NaCu_2O_2$ as seen by nuclear magnetic resonance spectroscopy

A. A. Gippius
Moscow State University, 119991 Moscow, Russia
and Max-Planck-Insitut für Chemische Physik fester Stoffe, 01187 Dresden, Germany

A. S. Moskvin
Ural State University, 620083 Ekaterinburg, Russia
and Leibniz Institut für Festkörper- und Werkstofforschung Dresden, D-01171 Dresden, Germany

S.-L. Drechsler
Leibniz Institut für Festkörper- und Werkstofforschung Dresden, D-01171 Dresden, Germany

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The incommensurate (IC) spin ordering in quasi-one-dimensional edge-shared cuprate $NaCu_2O_2$ has been studied by ^{23}Na nuclear magnetic resonance spectroscopy in an external magnetic field near 6 T applied along the main crystallographic axes. The NMR line shape evolution above and below $T_N \approx 12$ K yields a clear signature of an IC static modulation of the local magnetic field consistent with a Cu^{2+} spin spiral polarized in the *bc* plane rather than in the *ab* plane, as reported from earlier neutron diffraction data.

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The magnetic phase transitions observed at low temperature in several edge-shared chain cuprates (e.g., $LiCu_2O_2$, $LiVCuO_4$, and $NaCu_2O_2$) are considered as evidence for an incommensurate (IC) helicoidal order with propagation along the chain direction.[1] This picture based on the strong in-chain frustration is supported by NMR and neutron diffraction measurements.[2–5] However, many significant details of this spin-ordered state have not been settled so far. In particular, the orientation of the spin rotation (within the probably simplified picture of a planar spiral) is under hot debate due to the recent observation of a multiferroic behavior induced by the spin ordering in $LiVCuO_4$ and $LiCu_2O_2$.[6–10] In fact, the appearance of a spiral itself and its orientation are of crucial importance for all proposed mechanisms and phenomenological approaches to multiferroicity.[11] However, multiferroic behavior in $NaCu_2O_2$ isomorphic to $LiCu_2O_2$ has not been reported. Hence, the spiral order seems to be not directly related to multiferroicity. For both $LiCu_2O_2$ and $NaCu_2O_2$, an *ab* spin polarization has been deduced from earlier neutron diffraction measurements.[3,4] This was also supported for $LiCu_2O_2$ by later ESR data.[12] However, the observation of spontaneous ferroelectric polarization $\mathbf{P} \| c$ axis below T_N by Park *et al.*[9] raised doubts of the *ab* spin polarization in $LiCu_2O_2$ in favor of a *bc* spin polarization, which was partially supported by very recent neutron diffraction measurements by Seki *et al.*[10] To find support for the *bc* polarization, these authors have pointed to the paper by Capogna *et al.*[4] on the isomorphic $NaCu_2O_2$ where contradictory orientations have been reported.[13] Thus, we arrive at the puzzling situation that we have seemingly no reliable data regarding the spin polarization in two isomorphic IC chain cuprates $LiCu_2O_2$ and $NaCu_2O_2$. The present-day $LiCu_2O_2$ samples still exhibit significant nonstoichiometry with both nonmagnetic Li impurities in the CuO_2 chains and magnetic Cu^{2+} impurities positioned in between chains.[3] These impurities have not been considered in previous papers. However, the recently observed multiferroic behavior in $LiCu_2O_2$ can be consistently explained if the exchange-induced electric polarization on the out-of-chain Cu^{2+} centers substituting for Cu^+ ions are taken into account[14] (see also Ref. 15 on $LiVCuO_4$). Interestingly, regular spiral chains spin polarized in the *ab* plane induce on these Cu^{2+} centers a spin polarization along the *c* axis. This can explain some seeming inconsistencies recently found in neutron diffraction data[10] but without any all-out negation of an *ab* plane spiral. Due to a larger ionic radius of Na^+ (0.97 Å versus 0.68 Å of Li^+), substitutional disorder is *a priori* unlikely in $NaCu_2O_2$ and we deal here with a higher degree of in-chain crystallographic order and hence increasing one dimensionality of magnetic properties. In contrast with $LiCu_2O_2$, the $NaCu_2O_2$ single crystals exhibit no twinning and no deviation from the ideal stoichiometry, as confirmed by x-ray and thermogravimetric analysis. The $^{63,65}Cu$ nuclear quadrupole resonance lines in $NaCu_2O_2$ in the paramagnetic state are a factor of 3 more narrow than those in $LiCu_2O_2$ reflecting the higher degree of crystallographic order.[16] Likely, $NaCu_2O_2$ samples are more relevant to compare the data provided by different techniques. The $^{63,65}Cu$ NMR (Ref. 5) and our preliminary ^{23}Na NMR data[16] have confirmed the IC ordering in $NaCu_2O_2$. However, both groups did not cast doubt on the *ab*-plane spin spiral polarization reported earlier in Ref. 4 on the basis of neutron diffraction. Below in this Rapid Communication we report comprehensive data of ^{23}Na NMR measurements in $NaCu_2O_2$ for different field orientations and provide strong arguments for the *bc*-plane rather than the *ab*-plane spin polarization in contrast with that neutron data.[4,13]

The single crystalline samples of orthorhombic $NaCu_2O_2$ used in our experiments were grown, as described in Ref. 3. The unit cell[17] contains four magnetic Cu ions belonging to two pairs of CuO_2 chains running along the *b* axis and interconnected by Cu^{1+} in O-Cu-O dumbbells (Fig. 1). $NaCu_2O_2$

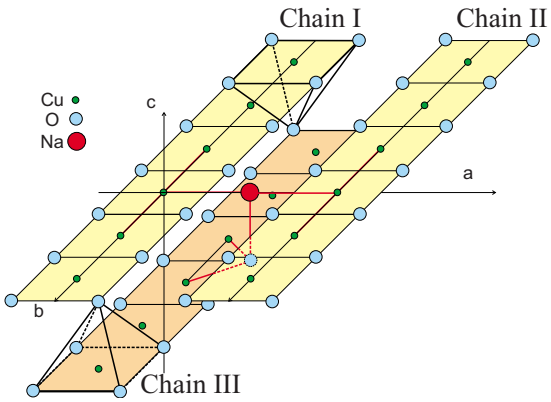

FIG. 1. (Color online) Schematic view of the active triple $Cu^{2+}O_2$ chain structure of $NaCu_2O_2$. The nonmagnetic Cu^+ ions are omitted. The hyperfine coupling geometry is shown by bold lines.

is a magnetic insulator with a magnetic phase transition to a spiral state below $T_N=12-13$ K.[4,18] The first experimental evidence of magnetic IC order in isostructural $LiCu_2O_2$ and $NaCu_2O_2$ was independently obtained by Gippius *et al.*[2] and Masuda *et al.*[3] for $LiCu_2O_2$ from ^{6,7}Li NMR and neutron diffraction measurements, respectively, and by Capogna *et al.*[4] and Horvatić *et al.*[5] for $NaCu_2O_2$ from the neutron diffraction measurements and ^{63,65}Cu NMR, respectively. The reported fit of the neutron data[3,4] means that all spins are confined to the *ab* plane and form a planar spin helix $\mathbf{S_i}=\mathbf{S}(\cos\theta_i,\sin\theta_i,\mathbf{0})$, where $\theta_i=\mathbf{q}\cdot\mathbf{r}_i+\alpha$, α is a phase shift, and $\mathbf{q}$ is the propagation vector. Actually, both spin anisotropy and external magnetic field may distort a classical spin helix. Anisotropy in the spin plane perturbs the spin helix adding higher-order even harmonics.[19] An external magnetic field applied perpendicular to the spin helix plane (transverse field) preserves the in-plane spiral order and induces spin canting toward the field direction producing an umbrella spin structure of the form $\mathbf{S_i}=\mathbf{S}(\cos\gamma\cos\theta_i,\cos\gamma\sin\theta_i,\sin\gamma)$ with $\sin\gamma=H/H_s$, which remains up to the saturation field H_s. Its effect on the NMR line shape reduces to a decrease in splitting $\propto\cos\gamma$ and to a rigid shift $\propto\sin\gamma$. An external magnetic field applied in the spin plane (longitudinal field) perturbs the spin helix adding odd higher-order harmonics.[19] For the easy axis and the external field both directed along the *a* axis, we arrive at the transformation

$$\theta_i=\mathbf{q}_i\cdot\mathbf{r}_i-\theta_H\sin(\mathbf{q}_i\cdot\mathbf{r}_i)-\theta_{an}\sin(2\mathbf{q}_i\cdot\mathbf{r}_i), \qquad (1)$$

where the deviation angle θ_H linearly depends on the external field.

The hyperfine (HF) field induced by a classical planar spin helix on a nucleus positioned at site $\mathbf{R}$ near a CuO_2 chain is directly related to the local spin polarization on the neighboring sites $\mathbf{S}(\mathbf{R}+\mathbf{r})$: $\mathbf{h}(\mathbf{R})=\Sigma_{\mathbf{r}}\hat{A}(\mathbf{r})\mathbf{S}(\mathbf{R}+\mathbf{r})$, where $\hat{A}(\mathbf{r})$ is the anisotropic HF tensor taking into account the magnetic dipole and the supertransferred Cu-O-Na HF interactions. The local field on a Na nuclei is induced by a superposition of at least three neighboring spin spirals (I, II, and III in Fig. 1). The local field on the ^{23}Na nuclei, which is induced by the isotropic supertransferred HF interaction from the antiferromagnetically coupled chains, is strongly canceled. This makes the anisotropic interaction a main contributor. Moreover, symmetry considerations point to A_{ab} as being the only nonzero component of the net HF tensor for coupling to chains I and II. Generally speaking, the HF field on an out-of-chain nucleus can be written as follows:

$$h_{x,y,z}=A_{x,y,z}(q)\cos(qy+\alpha_{x,y,z}), \qquad (2)$$

with the effective HF coupling parameters $A_{x,y,z}$ and the HF phase shifts $\alpha_{x,y,z}$ which may differ from the spin spiral phase shift α. In a continuum approximation, the resultant NMR line shape associated with a single nuclear $\Delta m_I=\pm 1$ transition can be calculated straightforwardly by a simple summation (integration),

$$F(\mathbf{H})\propto\int_0^{2\pi}\exp(-(|\mathbf{H}+\mathbf{h}(\phi)|-H_L)^2/2\delta^2)d\phi, \qquad (3)$$

where $\mathbf{H}$ and H_L are the external and the resonance Larmor fields, respectively, $\phi=qy$, and δ denotes the homogeneous linewidth. A symmetrically bunched umbrellalike spin spiral for the transversal field geometry provides a symmetric line shape of the NMR response, while an asymmetrically bunched spin spiral for the longitudinal or in-plane field geometry yields an asymmetric NMR line shape.[20] This simple relation can be used for a fast assignment of the spin spiral polarization. It should be noted that the character of the NMR line shape asymmetry depends both on the sign of the HF coupling constant and the phase shift.

We have performed ^{23}Na NMR measurements on a $NaCu_2O_2$ single crystal in the paramagnetic and in the ordered phase by sweeping an external field $\mathbf{H}$ at a fixed frequency of 70.0 MHz. The external field was oriented along the main crystal axes $\mathbf{H}\|\mathbf{a},\mathbf{b},\mathbf{c}$. The signal was obtained by integrating the spin-echo envelope. The experimental spectra are presented in Figs. 2–4. In order to discuss them, we start with the case of a $\mathbf{H}\|\mathbf{c}$ geometry. At a first glance, this implies a relatively simple symmetric picture of ^{23}Na NMR signal induced by the *ab*-plane polarized spin helix, as reported in Ref. 4. Indeed, in this case, an external magnetic field applied perpendicular to the spin helix plane should preserve the in-plane spiral order and should induce a spin canting toward the field direction resulting in a rigid shift of NMR frequency. However, our experimental results point to a completely different picture as we will explain below. At $T>T_N$, a first order quadrupole perturbed NMR spectrum typical for spin $I=3/2$ was observed (Fig. 2). It contains three lines, nearly equally spaced by a quadrupolar coupling to the local electric field gradient. The central line and the two satellites show an intensity ratio close to the theoretically expected one: 3:4:3. The quadrupole splitting $\nu_Q^c=0.103$ T does not reveal a noticeable temperature dependence. However, for $T<12$ K, a dramatic change of the ^{23}Na NMR spectrum is observed with a continuous and identical splitting of the quadrupole triplet components. This is a textbook signature of an infinite number of magnetically nonequivalent ^{23}Na sites typical for an IC static modulation of the local magnetic fields.[20] Indeed, the magnetic component of the IC line shape is dominantly given by the central tran-

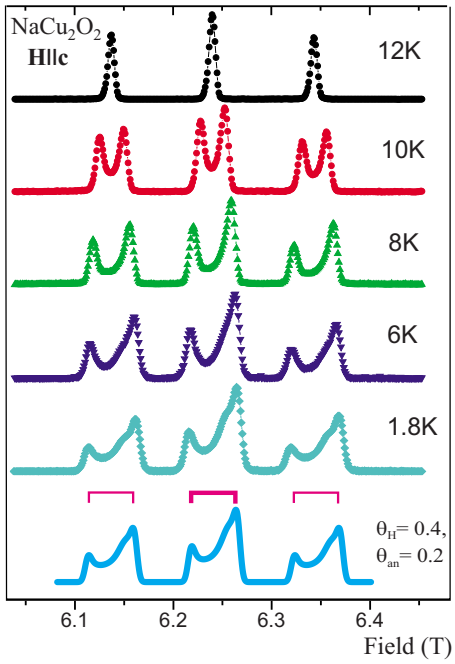

FIG. 2. (Color online) The ^{23}Na NMR spectrum for $\mathbf{H}\|\mathbf{c}$ with resonance frequency of 70.0 MHz. Bottom: Theoretical simulation with a simple asymmetrically bunched plane spiral ($\Delta_M^c=0.06$, $\nu_Q^c=0.103$ T). Rectangular brackets indicate here and below in Figs. 3 and 4 the magnetic splitting of the central (thick) and satellite transition lines.

sition. Since the same line shape is observed for all the lines, the quadrupolar coupling is not modulated, and we conclude that the origin of the modulation is only magnetic. Obviously, such a static IC modulation of the local magnetic field is caused by the helical spin structure of the Cu magnetic moments similarly to the structure observed in $LiCu_2O_2$.[2] At variance with the ^{7}Li NMR in lithium cuprate, the ^{23}Na NMR spectrum in $NaCu_2O_2$ shows a nice picture of practically identical line shapes of the satellite transitions, which are here clearly observable due to a comparable magnitude of quadrupole and magnetic splittings. However, the ^{23}Na NMR line shape is strongly asymmetric, especially at low temperatures (Fig. 2). It cannot be explained in the framework of an *ab*-plane spin polarization. Instead, it points to the NMR response of an *ac*- or *bc*-plane polarized spin spiral. In fact, the ^{23}Na NMR line shape at $T=1.8$ K can be successfully simulated assuming such a situation ($\theta_{an}=0.2$, $\theta_H=0.4$) with a magnitude of a magnetic splitting $\Delta_M^c=2|A_z|=0.06$ T (Fig. 2). Of course, such a proposal has to be tested with an external field applied along the *a* and *b* axes, respectively.

The $\mathbf{H}\|\mathbf{b}$-axis NMR spectrum (Fig. 3) shows a noticeable asymmetry of the NMR line shape, which clearly implies a non-*ac*-plane spin polarization. The quadrupole splitting $\nu_Q^b=0.022$ T is small as compared to ν_Q^c; however, the magnetic splitting saturates at an intermediate value of 0.09 T. A clear visual detection of magnetic splitting is hindered by the small quadrupole splitting. We found that the ^{23}Na NMR line shape can be simulated within a "single bunched spiral model" with parameters $\Delta_M^b=2|A_y|=0.09$ T, $\nu_Q^b=0.022$ T, $\theta_H=0.4$, and $\theta_{an}=0.2$.

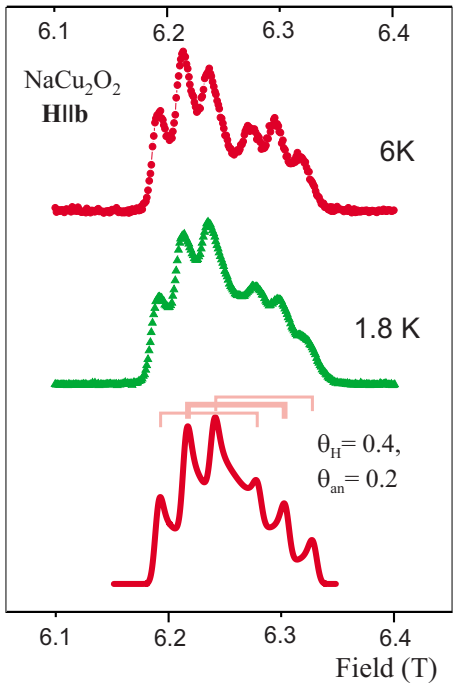

FIG. 3. (Color online) The ^{23}Na NMR spectrum below T_N for $\mathbf{H}\|\mathbf{b}$ with resonance frequency of 70.0 MHz. Bottom: Theoretical simulation with a simple asymmetrically bunched plane spiral ($\Delta_M^b=0.09$, $\nu_Q^b=0.022$ T).

Thus, after excluding the possibility of *ab* and *ac* polarization planes based on the discusion of the measured NMR spectra in $\mathbf{H}\|\mathbf{c}$ and $\mathbf{H}\|\mathbf{b}$ geometries, only the *bc* plane remains as a possible spin polarization plane. Indeed, for an external field applied along the *a*-axis $\mathbf{H}\|\mathbf{a}$, we arrive at a

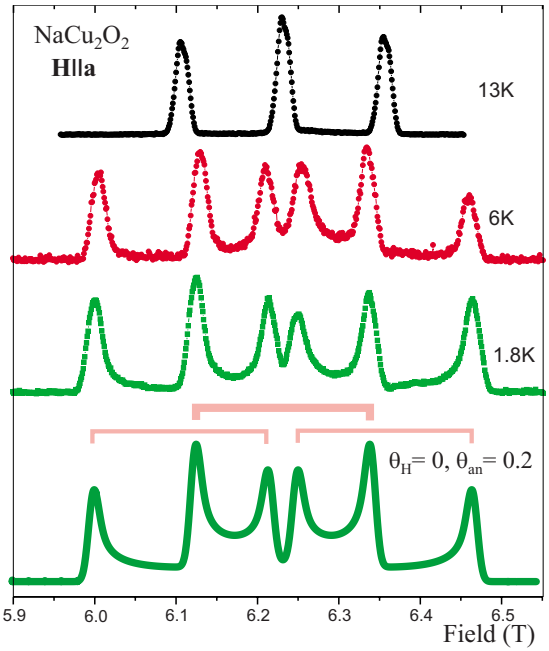

FIG. 4. (Color online) The ^{23}Na NMR spectrum below T_N for $\mathbf{H}\|\mathbf{a}$ with resonance frequency of 70.0 MHz. Bottom: Theoretical simulation with a simple symmetrically bunched *bc*-plane spiral ($\Delta_M^a=0.22$, $\nu_Q^a=0.125$ T).

highly symmetric ^{23}Na NMR line shape (Fig. 4), which can be well described in terms of a simple planar spiral model with $\Delta_M^a = 2|A_x| = 0.22$ T, $\nu_Q^a = 0.125$ T, $\theta_H = 0$, and $\theta_{an} = 0.2$. The quadrupole splitting[22] is slightly larger than ν_Q^c; however, the magnetic splitting saturates at a considerably larger value of 0.22 T. Therefore, in an $\mathbf{H} \| \mathbf{a}$ orientation, the magnetic splitting overlaps the quadrupole splitting in contrast to the $\mathbf{H} \| \mathbf{c}$ geometry (Fig. 2). Finally, we see that not an *ab*-plane but a *bc*-plane polarized spin helix is robust with respect to the application of a rather strong external magnetic field of about 6 T. The magnetization measurements for another sample of the same batch in an external field along *a*, *b*, *c* axes shows no signatures of spin-orientational transitions for the fields up to 7 T (Fig. 2 in Ref. 18). Obviously, the *bc* plane is an easy spin plane in $NaCu_2O_2$. Of course, a spin-flop transition is expected to occur too but for higher fields. Starting with the *bc*-plane polarized spin spiral, we have estimated the magnetodipole contribution to the maximal magnetic splitting of the ^{23}Na NMR line to be $\Delta_M^a = 0.109$ T$/\mu_B$, $\Delta_M^b = 0.050$ T$/\mu_B$, and $\Delta_M^c = 0.027$ T$/\mu_B$ given the pitch angle of 81.7°. The magnetodipole mechanism predicts qualitatively correctly the anisotropy of the magnetic splittings; however, its contribution explains only a fourth of the net effect given the magnetic moment of $\sim 0.6\ \mu_B$ per Cu^{2+} ion.[4] In other words, our experimental data point to a significant effect of anisotropic Cu-O-^{23}Na supertransferred HF coupling, which seems to be more pronounced as compared to the similar Cu-O-^{7}Li bonds in Li_2CuO_2.[23]

In conclusion, the ^{23}Na NMR line shape in $NaCu_2O_2$ shows clear signatures of an IC static spin structure consistent with a spiral modulation of the Cu magnetic moments polarized in the *bc* plane in contrast to the *ab*-plane polarization reported earlier. It is the first experimental indication for a polarization in an edge-shared cuprate with spins lying in a plane perpendicular to the plane of the basic CuO_4 plaquette. We have found the values of magnetic $\Delta_M^{a,b,c}$ and quadrupole $\nu_Q^{a,b,c}$ splittings that provide a starting database for a further detailed study of magnetic and electric HF interactions in this cuprate. Our results obtained for a clean system should be of considerable interest both for the magnetic anisotropy, in general, and the symmetry aspects of possible multiferroicity[11,21] in chain cuprates.

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