NMR study of quasi-1D magnetic chain in cuprates $LiCu_2O_2$ and $NaCu_2O_2$

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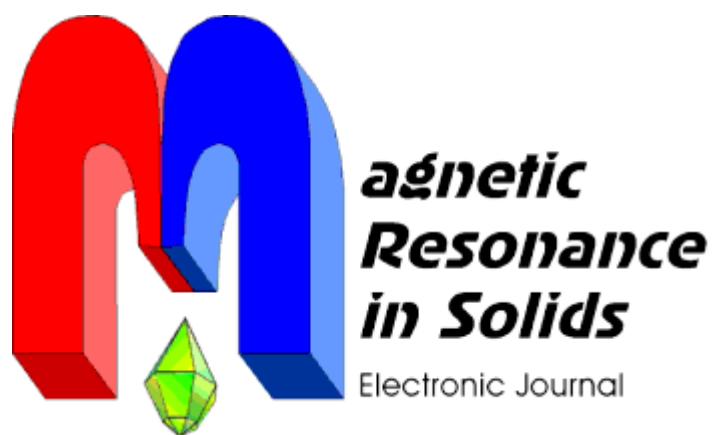[2] Institute of Crystallography RAS, Moscow 117333, Russia
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NMR study of quasi-1D magnetic chain in cuprates LiCu$_2$O$_2$ and NaCu$_2$O$_2$

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NMR investigation of magnetic structure and phase transitions in two isostructural quasi-one-dimensional cuprates LiCu$_2$O$_2$ and NaCu$_2$O$_2$ has been performed. While LiCu$_2$O$_2$ exhibits a magnetic phase transition at $T_c = 24$ K, NaCu$_2$O$_2$ orders magnetically at around 13 K. ^{6,7}Li and ^{23}Na NMR spectra in LiCu$_2$O$_2$ and NaCu$_2$O$_2$, respectively, provide an unambiguous experimental evidence that below T_c an incommensurate in-chain helical spin structure is established in both compounds. However, the features of the observed low temperature NMR are different pointing to different properties of the helical magnetic structure.

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Keywords: Nuclear magnetic resonance, quadrupole resonance, incommensurate spin

1. Introduction

The quasi-1D spin chain cuprate $LiCu_2O_2$ exhibits a unique sequence of phase transitions at $T = 24$, 22.5, and 9 K [1,2] resembling the "Devil's staircase" type behavior. Recently we have obtained the first NMR evidence for a low temperature incommensurate (IC) in-chain spin structure in $LiCu_2O_2$ [3]. It was shown that below the magnetic ordering temperature $T_c = 24$ K the ^{7}Li NMR lineshape is determined by a IC static modulation of the local magnetic field caused by spin structure of Cu magnetic moments twisted along the chain axis [3]. This result was confirmed by NMR spectra measurements on the [6]Li isotope as well as by neutron diffraction study [4].

The larger ionic radius of Na^{1+} (0.97 Å against 0.68 Å of Li^{1+}) favors the higher degree of in-chain crystallographic order and hence increasing one-dimensionality of magnetic properties in $NaCu_2O_2$. This results in lower magnetic ordering temperature $T_c = 12.6$ K [5] and lower values of local magnetic fields in the ordered state. In this paper we report first ^{23}Na NMR measurements which confirm the existence of incommensurate magnetic structure in $NaCu_2O_2$ at 3 K also seen by μSR [5]. The unusual magnetic properties of 1D chain cuprates $LiCu_2O_2$ and $NaCu_2O_2$ are discussed in terms of strong in-chain frustration and intrinsic incommensurability.

2. Experiment

Single crystals of $LiCu_2O_2$ and $NaCu_2O_2$ were synthesized according to the procedure described in Ref. [4]. The quality of the new $NaCu_2O_2$ crystal was much better than that used in our preliminary NMR measurements reported in Ref. [3]. In contrast to $LiCu_2O_2$, the $NaCu_2O_2$ single crystal shows no twinning and has no deviation from the ideal stoichiometry as confirmed by X-ray. ^{23}Na and ^{7}Li NMR measurements were performed at several temperatures in the paramagnetic and in the ordered phases of both compounds. All three principal orientations of the external magnetic field with respect to the crystallographic axes: $\mathbf{H} \parallel \mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ were used. The standard pulsed field-sweep NMR technique was applied at fixed frequency of 33.7 MHz for $LiCu_2O_2$ and 46.0 MHz for $NaCu_2O_2$.

3. Results and discussion

We present the characteristic NMR spectra of [7]Li in $LiCu_2O_2$ and [23]Na in $NaCu_2O_2$ measured both above and below magnetic ordering temperature T_c for orientation of the external magnetic field $\mathbf{H} \parallel \mathbf{c}$ (Fig.1). To make the comparison more convenient we use the same scaling of magnetic field in both panels. Above T_c in $LiCu_2O_2$ and $NaCu_2O_2$ typical first-order quadrupole perturbed NMR spectra for spin $I = 3/2$ nuclei are observed. The quadrupole splitting between the satellites in $NaCu_2O_2$ is about 200 mT, while in $LiCu_2O_2$ it is about 10 mT. Since the ratio of quadrupole moments $Q(^{23}Na)/Q(^{7}Li) = 2.7$, this large quadrupole splitting ratio means that the electric field gradient (EFG) at Na site in $NaCu_2O_2$ is almost an order of magnitude higher than the EFG at Li sites in $LiCu_2O_2$. This result reflects an enhanced role of EFG polarization effect on Na^{1+} as compared with Li^{1+}, which has only weakly polarizable $1s^2$ shell.

Below magnetic ordering temperature T_c the spectra of both compounds exhibit a dramatic change. The spectra are characteristic of IC static modulation of the local magnetic field caused by helical spin structure of Cu moments [3,6,7]. It is worth to mention, that the phase transition at T_c is much narrower in $NaCu_2O_2$ than in $LiCu_2O_2$. The formation of IC field modulation in $NaCu_2O_2$ occurs within 0.6 K while in $LiCu_2O_2$ it takes more than 2 K [3]. The asymmetric van Hove singularities of ^{23}Na NMR central transition line are very sharp and are clearly visible also on satellite transitions, which in contrast to $LiCu_2O_2$ are well separated due to the larger E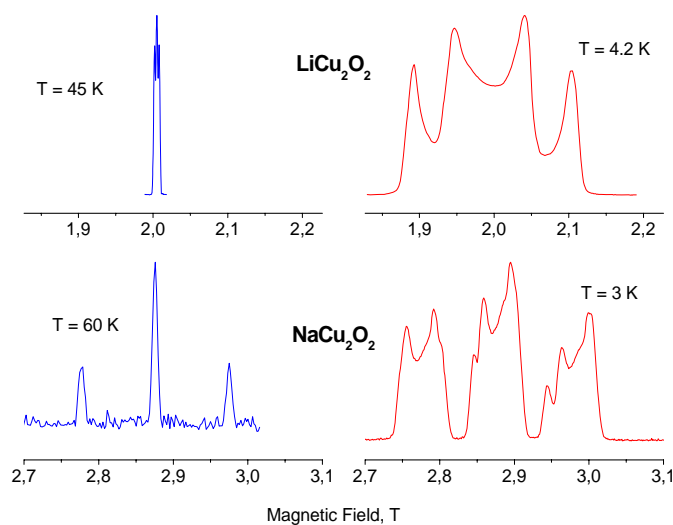FG. The lineshape of the satellite transitions follows the distribution of the Larmor frequency caused by IC local field modulation. Therefore, in the first-order quadrupole perturbation the satellite lineshape is almost the exact copy of the central transition profile.

The most striking difference between [7]Li and [23]Na spectra is that in $NaCu_2O_2$ the doublets (or degenerated quartets) are observed for all three principal orientations of external magnetic field in the magnetically ordered state. For $\mathbf{H} \parallel \mathbf{a}$ the intensities of both parts of the doublets are equal while for $\mathbf{H} \parallel \mathbf{c}$ the high field component of the doublet is more intensive. This anisotropy becomes more significant with decreasing temperature. The splitting is almost symmetric with respect to the central field determined as the resonance field of the central transition above T_c. These results are completely unlike the situation in $LiCu_2O_2$ where the ^{7}Li NMR quartet and sextet are observed for $\mathbf{H} \parallel \mathbf{c}$ (Fig.1) and $\mathbf{H} \parallel (\mathbf{a},\mathbf{b})$ [3]. The possible reason for such dissimilar behavior could be the influence of
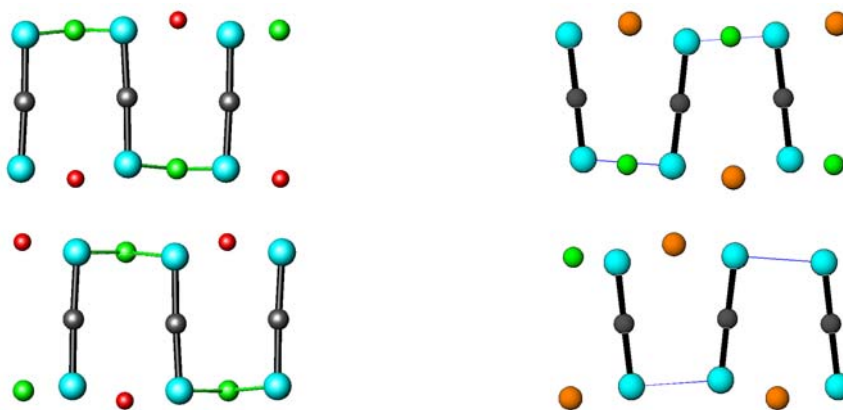

Fig.1. ^{7}Li and ^{23}Na NMR spectra measured above T_c (left spectra) and below T_c (right spectra) for H $\parallel$ c in LiCu₂O₂ and NaCu₂O₂ single crystals at 33.7 and 46.0 MHz, respectively.

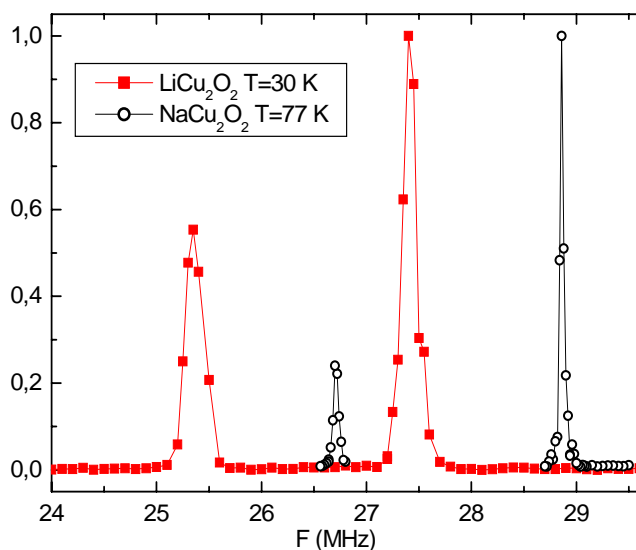**Fig.2**. Crystal structure of $LiCu_2O_2$ (left panel) and $NaCu_2O_2$ (right panel).

Fig.3. NQR spectra of $NaCu_2O_2$ (black open circles) and $LiCu_2O_2$ (red filled squares) measured above T_c on $^{63,65}Cu$ nuclei in Cu(2) site.

non-magnetic Li defects in CuO_2 chains of $LiCu_2O_2$. Due to AF character of NNN interaction the both helix phase angles θ and φ exhibit a step-like change on π in the vicinity of Li defect. This phenomenon will be analyzed in more detail elsewhere.

The value of the local magnetic field on Na site estimated as the linewidth at the base of the central transition for $\mathbf{H} \parallel \mathbf{c}$ is only 80 mT, which is a factor of 3 less than that for Li (250 mT). This is quite reasonable since the transition temperature in $NaCu_2O_2$ is lower than in $LiCu_2O_2$ pointing to a weaker inter-chain interaction in $NaCu_2O_2$.

The difference in crystal structure peculiarities of the two compounds (Fig. 2) is reflected in their NQR properties. Fig.3 shows the NQR spectra of $NaCu_2O_2$ and $LiCu_2O_2$ measured above T_c on $^{63,65}Cu$ nuclei in Cu(2) site. The right and left lines of each pair are assigned to the ^{63}Cu and the ^{65}Cu isotope, respectively. The observed frequency and intensity ratios correspond to ratios of isotope quadrupole moments and natural abundances, respectively. In the following, we will consider only the ^{63}Cu isotope NQR lines for convenience. From Fig. 3 it is clearly seen that in $NaCu_2O_2$ the NQR linewidth is a factor of 3 smaller than that in $LiCu_2O_2$. This result reflects more homogeneous EFG distribution as a consequence of higher degree of structural order in $NaCu_2O_2$. Probably for the same reason, we succeeded to find another ^{63}Cu line at 26.8 MHz originating from the Cu(1) position. It should be noted that the ^{63}Cu line at around 27 MHz has been observed earlier on the polycrystalline $LiCu_2O_2$ sample in [8], but it was falsely assigned to the Cu(1) position. In this case, the line should exist also below T_c which contradicts to our experimental findings described below.

All lines shown in Fig. 3 completely disappear below T_c. Instead, in $LiCu_2O_2$ we observed very complicated $^{63,65}Cu$ antiferromagnetic resonance (AFMR) spectrum at 4.2 K. This effect is caused by the space modulated internal magnetic field at the Cu(2) site in the ordered state of $LiCu_2O_2$. For yet unknown reason we did not find any copper AFMR spectrum in $NaCu_2O_2$. At the same time, the Cu(1) NQR line at 26.8 MHz exists even below T_c, as expected for non-magnetic Cu^+ ion at the Cu(1) site which is symmetric with respect to magnetic Cu^{2+} ions in the CuO_2 chains. Therefore, the complete cancellation of local magnetic field occurs at Cu(1) site in the ordered state of $NaCu_2O_2$.

In conclusion, ^7Li and ^{23}Na NMR spectra measured in the magnetically ordered state of the isostructural quasi-1D oxides $LiCu_2O_2$ and $NaCu_2O_2$ give unambiguously evidence for static IC modulation of local magnetic fields at the Li and the Na site, respectively. This modulation is caused by a helical spin structure of Cu moments below T_c. Due to the crystal structure peculiarities the character of the magnetic helix is dissimilar in both compounds reflected both in NMR and NQR spectra.

Acknowledgement

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