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Multi-frequency ESR in NaCu$_2$O$_2$

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Abstract. NaCu$_2$O$_2$ is regarded as an $S=1/2$ zigzag chain with competing nearest neighbor and next nearest neighbor exchange interactions. The spin structure of NaCu$_2$O$_2$ below a Néel temperature $T_N=13$ K was reported to be helical with a propagation vector $q=(0.5, 0.227, 0)$. To obtain further information on the ordered state of NaCu$_2$O$_2$, we performed multi-frequency electron spin resonance (ESR) and high field magnetization measurements on single crystal samples of NaCu$_2$O$_2$. We observed a large and some small ESR signals and a monotonical increase of magnetization with a change of the slope around 20 T. One of the ESR resonance modes from the large signal is roughly reproduced by one of the helical resonance modes calculated on the assumption of a conical spin structure.

1. Introduction

Low dimensional and geometrical frustrated small spin systems have attracted much attention because of novel physical phenomena originated from quantum effects and frustration. The $S=1/2$ antiferromagnetic zigzag-chain is one of them and theoretical studies on it have predicted that the ground state is altered by the strength and the sign of exchange constants [1]. Recently, $S=1/2$ quantum spin zigzag chains with competing nearest-neighbor (NN) and next nearest neighbor (NNN) exchange interactions, such as LiCu$_2$O$_2$ and NaCu$_2$O$_2$, have been studied by some groups [2, 3, 4, 5, 6]. LiCu$_2$O$_2$ and NaCu$_2$O$_2$ have the same crystal structure and similar magnetic properties. We tried to study magnetic properties of both compounds in high magnetic fields. In LiCu$_2$O$_2$, however, it was reported that the Li ions are not stoichiometrically contained in the compound. Thus, we examine and report here magnetic properties of NaCu$_2$O$_2$.

The NaCu$_2$O$_2$ compound crystallizes in the orthorhombic structure, space-group Pnma, with lattice constants $a = 6.210$ Å, $b = 2.937$ Å, $c = 13.070$ Å at room temperature [6]. Nonmagnetic Cu$^{1+}$ and magnetic Cu$^{2+}$ ($S=1/2$) ions coexist in the unit cell. Magnetic Cu$^{2+}$ ions form zigzag-chains along the $b$ axis and these chains are separated by nonmagnetic Cu$^{1+}$ ions along the $c$ axis and nonmagnetic Na$^+$ ions along the $a$ axis. All the magnetic susceptibilities along the principal axes show a broad maximum at about 50 K, which is characteristic of a quasi-one-dimensional antiferromagnet. NaCu$_2$O$_2$ exhibits a phase transition at about 13 K by the specific heat measurements. NMR and neutron scattering experiments revealed that the compound has an
incommensurate ground state and the spin structure below the ordered temperature was reported to be a planar helix in the \textit{ab} plane with a propagation vector \( \mathbf{q} = (0.5, 0.227, 0) \) [5]. It was expected that the helical spin structure of NaCu\(_2\)O\(_2\) is mainly caused by competing between the NN intrachain ferromagnetic exchange interaction \( J_1 \) and the NNN intrachain antiferromagnetic exchange interaction \( J_2 \) as defined in Fig. 1, but the details of these interactions have not been clarified yet [5, 6].

To obtain further information on magnetic interactions in NaCu\(_2\)O\(_2\) below 13 K, we performed multi-frequency and high field magnetization measurements on single crystals of NaCu\(_2\)O\(_2\). From similarity in NaCu\(_2\)O\(_2\) and LiCu\(_2\)O\(_2\), we also hope to get some information on the magnetic excitations in LiCu\(_2\)O\(_2\).

2. Material and Methods
Single crystal samples of NaCu\(_2\)O\(_2\) were grown similarly as described for the isomorphic LiCu\(_2\)O\(_2\) [4]. The crystal has the cleavage \textit{ab} plane. Thus, we applied magnetic field parallel and perpendicular to the \textit{ab} plane. The sample setting was carried out in a grove box under atmosphere of nitrogen gas, because the compound is very sensitive to humidity.

The ESR measurements on single crystals of NaCu\(_2\)O\(_2\) were performed by using a millimeter vector network analyzer (ABmm, France) with extensions and a 16 T superconducting magnet for the frequencies up to 700 GHz and magnetic fields up to 16 T. For high magnetic fields up to 55 T and high frequencies above 700 GHz, a non-destructive pulse magnet and a far-infrared laser were utilized. The magnetization measurements were carried out with a non-destructive pulse magnet and the magnetization was detected by an induction method with a standard pick-up coil system. All these experiments were performed at KYOKUGEN in Osaka University.

3. Results
Figure 2 shows high-field magnetization curves of NaCu\(_2\)O\(_2\). Magnetization curves for the external magnetic field \( H_{\text{ex}} \) parallel and perpendicular to the \textit{ab} plane show an abrupt increase at low fields and the change of the slope at around 20 T. We also observed a small jump at about 18 T for \( H_{\text{ex}} \parallel \text{ab plane} \). The slope of the magnetization curve for \( H_{\text{ex}} \perp \text{ab plane} \) is larger than that for \( H_{\text{ex}} \parallel \text{ab plane} \). The characteristic of magnetization at low fields is consistent with that in a previous report [6]. The abrupt increase at low fields and the change of the slope around 20 T suggest that NaCu\(_2\)O\(_2\) does not have a simple helix structure in which the magnetic moments lie in the \textit{ab} plane.
Figure 3. Frequency dependence of ESR spectra of NaCu$_2$O$_2$ for $H_{ex} \perp ab$ plane (a) and $H_{ex} \parallel ab$ plane (b) at 1.5 K.

The frequency dependence of ESR spectra for $H_{ex} \perp ab$ plane and $H_{ex} \parallel ab$ plane is shown in Fig. 3. The ESR signal with a large line width was observed above 390 GHz for both directions and the resonance position shifts to high field side with increasing frequency. The resonance field for $H_{ex} \parallel ab$ plane shifts largely as compared to that for $H_{ex} \perp ab$ plane. We observed a small signal with $g \sim 2$ indicated by a small arrow in Fig. 3, which might be attributed to magnetic impurities or Cu$^{2+}$ ($S=1/2$) ions isolated from the sample. We also measured the temperature dependence of the large ESR signal observed at about 400 GHz in Fig. 3, the resonance field of which shifted to a paramagnetic line with increasing temperature. Therefore, we conclude that the ESR signal observed below 10 K arises from a collective mode in the ordered state.

In Fig. 4, the ESR resonance fields were plotted in the frequency versus magnetic field plane for (a) $H \perp ab$ plane and (b) $H \parallel ab$ plane at 1.5 K. The highest resonance mode in Fig. 4 has an energy gap $E_g \approx 390$ GHz at zero field.

4. Analysis and Discussion

In our analyses of the resonance modes, we omit the effect of Dzyaloshinskii-Moriya (DM) interaction which was reported in a previous paper [6]. Therefore, the Hamiltonian in NaCu$_2$O$_2$ is written as follows:

$$\mathcal{H} = -\sum_{i \neq j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - \sum_{i \neq j} K_{ij} S_{iz} S_{jz} - g\mu_B \sum_i \mathbf{H} \cdot \mathbf{S}_i$$

(1)

where $J_{ij}$ is the exchange constant between $\mathbf{S}_i$ and $\mathbf{S}_j$ spins, $K_{ij}$ the anisotropy constant, $g$ the $g$-value of Cu$^{2+}$ ions, $\mu_B$ the Bohr magneton and $\mathbf{H}$ is the external magnetic field. We calculate the resonance modes with a method reported by Cooper et al. [7, 8], on assuming the helical spin structure in the $ab$-plane, the exchange interactions $J_1$, $J_2$, $J_3$, $J_\perp$, $J_{xy}$ as defined in Fig. 1 and the easy-plane type anisotropy $K<0$. The $\alpha_\perp$ mode for $H_{ex} \perp ab$ plane and the $\alpha_\parallel$ mode for $H_{ex} \parallel ab$ plane in Fig. 4 are reproduced roughly by the calculated modes denoted by $\omega^+$ and $\omega_0$ with the same parameter values $J_1=4.5$ meV, $J_2=-9.3$ meV, $J_3=-0.3$ meV, $J_\perp=-5.7$ meV, $J_{xy}=-0.8$ meV, $g_c=2.23$ and $K=-0.04$ meV as reported by Drechsler et al. [6] except $K$. An ESR signal corresponding to another resonance mode $\omega^-$ was not observed. Small ESR signals in Fig. 3 on EPR lines in Fig. 4 must come from the impurities in the compound. A further
complicated mode calculation including the DM interaction must be needed to clarify the ESR results.

In conclusion, we have performed ESR and magnetization measurements in high magnetic fields on single crystal samples of NaCu$_2$O$_2$. We observed several resonance modes and one of the resonance modes is roughly reproduced by a simple calculation based on a helical spin structure. In the magnetization curves for $H$ parallel and perpendicular to the $ab$ plane, a steep increase near zero field and an inflection at about 20T were observed. These results suggest that this compound dose not have a simple planer helical spin structure in the $ab$ plane.

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