NMR study on the quantum spin ladder NH_4CuCl_3

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Abstract

Cu-NMR study in the field up to 30T has been performed on the two-legged quantum spin ladder system NH_4CuCl_3 which shows the two-stepped plateaus in magnetization. By analyzing the angular dependence of the peak shift, observed Cu-NMR spectra are assigned to the singlet site with a very small magnetic shift. The temperature dependence of this shift does not reflect that of the macroscopic magnetization, indicating that the excited triplet sites in NH_4CuCl_3 have a tendency to be immobile at low temperatures.

Key words: Quantum spin ladder, NMR, magnetization plateau

Generally, even-legged quantum spin ladders with the antiferromagnetic interaction are expected to have a non-magnetic ground state due to the formation of singlet dimers. One of the good prototypes is $SrCu_2O_3$, having a large spin excitation gap of a few hundreds Kelvin, which cannot be collapsed by a magnetic field within reach[1].

The two-legged spin ladder NH_4CuCl_3 with an edge-sharing-type Cu_2Cl_6 plane has a very weak exchange interaction between Cu-3*d* spins around a few tens Kelvin, allowing one to investigate the excited states under steady magnetic field within reach. The spin excitation gap of this compound has been reported to open and close repeatedly with increasing field, leading to magnetization plateaus at 5∼12.8 and 17.9∼24.7T at low temperatures[2]. Though theoretical models for the plateau have been proposed so far[3], a microscopic state of spins is still in veil. We report in this paper our recent Cu-NMR study on the spin state of NH_4CuCl_3 under the magnetic field in and outside of the magnetization plateau.

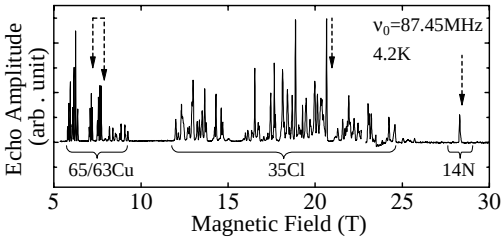

Fig. 1. Field-swept spectra of NH_4CuCl_3 ($H//b$). The three groups of peaks from $^{63/65}$Cu, ^{35}Cl and ^{14}N are separately seen. Vertical dashed arrows show the zero-shift position of each nuclear species.

Single crystals of NH_4CuCl_3 were synthesized by evaporation of the saturated solution of NH_4Cl and $CuCl_2$ in ethanol. Sample shape is a distorted hexagonal prism, the long column of which corresponds to the crystallographic *a*-axis. NMR spectra were measured by the conventional spin-echo method. The measurement up to 30T was realized by the hybrid magnet HM-1a at High Field Laboratory for Superconducting Materials at IMR. In order to separate the magnetic Knight shift and electric quadrupolar shift, angular de-

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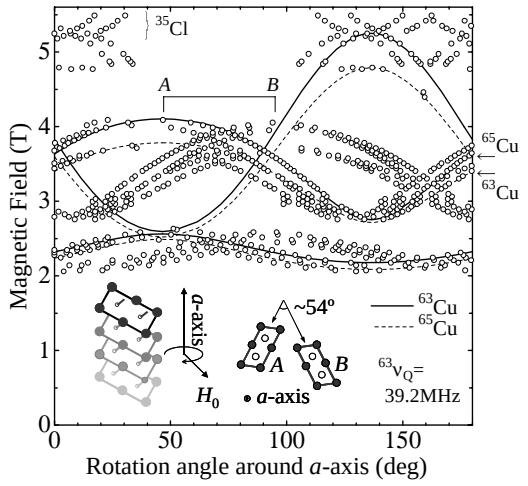

Fig. 2. $^{63/65}$Cu-NMR peak position versus angle between the applied field and the crystallographic axis. The sample is rotated around a-axis, the stacking direction of Cu_2Cl_6 plane. Calculated curves for one of the two ladders in the unit cell are shown by solid and dashed curves. Arrows at the right side show the zero-shift resonance position of $^{63/65}$Cu. Inset shows the configuration of applied field and the crystallographic axis. The narrowly-separated two peaks for each transitions come from the domains in the sample.

pendence of the peak position was measured and fitted to the theoretical curve obtained by the numerical diagonalization of nuclear spin hamiltonian[4].

Fig. 1 shows NMR spectra in the magnetic field up to 30T. By the investigation of spectra taken with several different resonance frequencies, three groups of peaks are assigned to $^{63/65}$Cu, $^{35/37}$Cl and ^{14}N. Fig. 2 shows the rotation-angle dependence of the peak position of $^{63/65}$Cu. Observed twelve peaks are explained in terms of rather a large eqq-interaction $^{63}\nu_{\rm Q}$ =39.2MHz with nearly zero magnetic shift below one percent. This means that the observed Cu-signal comes only from the singlet site. The signal from the triplet site is not detected in the surveyed range of magnetic field up to 30T. The hyperfine field at Cu site is roughly estimated, from the spin-echo oscillation frequency for the iso-structure compound $KCuCl_3$ to be around $-18T$ [4]. This value is much smaller than the upper limit of the field, if considering the estimation ambiguity. Therefore, the reason why the signal from triplet sites is invisible may be the strong spin fluctuation of on-site $3d$ spins. The signal intensity from singlet sites become weak rapidly as increasing the measurement field, reflecting the fact that the number of singlet sites decreases at high field.

Under the finite applied field, there exist a finite number of triplet sites around the singlet site. The effect of the transferred hyperfine field from those neighboring triplets is very small, and is hidden in the resonance line width of a few hundreds Oe, causing no splitting in resonance peaks. This is because all the exchange paths between $3d$ spins are nearly right-angled in this system.

The fact that the distinct resonance peaks were observed at nearly zero magnetic shift indicates that Cu sites in NH_4CuCl_3 are well separated into non-magnetic singlet sites and magnetic triplet sites, rather than a paramagnetic-like state. This holds irrelevant of the applied magnetic field being in or outside of the plateau region.

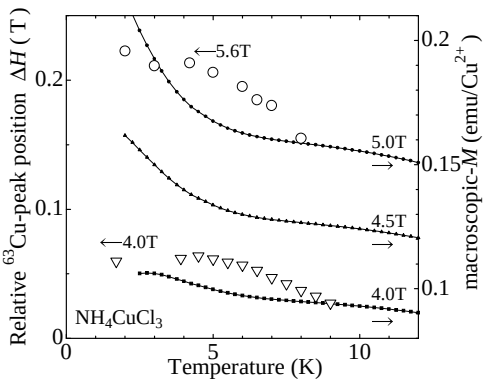

Fig. 3. Temperature dependence of relative peak position for ^{63}Cu-NMR and of macroscopic magnetization taken under several applied fields. Note that the two quantities does not scale each other below 6K.

Next, we discuss the *mobility* of the excited triplet sites, the number of which is proportional to the macroscopic magnetization. In the gapped ground state of $KCuCl_3$, thermally excited triplet sites move around along the exchange path to produce a averaged field in the system[4]. Consequently, the local magnetization of the singlet site probed by Cu-NMR and the macroscopic magnetization show the same temperature dependence, reflecting the energy gap. On the contrary, as shown in Fig. 3, the result in NH_4-system makes a clear contrast to K-system. The NMR shift saturates below 6K, while the macroscopic magnetization increases. This difference is also observed under the magnetic field on the plateau. This means that the field-induced triplets in NH_4-system have a tendency to be immobile at low temperatures, both in and outside of the magnetization plateau.

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