ToF inelastic neutron scattering studies on quantum spin systems (CuCl)LaB$_2$O$_7$ ($B = $ Nb, Ta)

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Abstract. Magnetic excitations in quantum spin system (CuCl)LaB$_2$O$_7$ ($B = $ Nb, Ta) have been studied by the time-of-flight (ToF) inelastic neutron scattering technique. (CuCl)LaNb$_2$O$_7$ exhibits a spin-singlet ground state with an excitation gap of $\Delta E \sim 2.3$ meV, while (CuCl)LaTa$_2$O$_7$ exhibits an antiferromagnetic (AFM) ordering below $T_N = 7$ K. In (CuCl)LaNb$_2$O$_7$, a band-like excitation with an energy width of $\sim 1$ meV was observed at $\Delta E \sim 2$ meV. The magnitude of scattering vector $Q$ dependence of the integrated intensity of the magnetic excitation around $\Delta E \sim 2$ meV for this system well reproduces that observed by a triple-axis spectrometer, indicating a spin-singlet feature. The excitation spectra show modulations for both the intensity of excitation and the peak position in $\Delta E$ along the $Q$ direction, which indicates that spin pairs forming a singlet state are not simply isolated but have some interaction. Using the isolated dimer model as well as the previous study, the modulation is characterized by a length $\sim 8.7$ Å, which corresponds to the fourth-neighbor distance. (CuCl)LaTa$_2$O$_7$ in the AFM state also shows modulating behaviour in the excitation spectra. However, the integrated intensity exhibits a different $Q$ dependence, reflecting a different ground state.

1. Introduction

Low-dimensional magnetic systems where quantum fluctuations play an important role for their magnetic properties have been of great interest in recent years. In particular, spin frustration often brings about some exotic ground state. While some quantum phenomena have been reported for geometrically frustrated systems such as triangular lattice and Kagomé lattice, two-dimensional (2D) square lattice can also exhibit interesting quantum spin behavior by competing magnetic interactions. A series of compounds (CuCl)LaB$_2$O$_7$ ($B = $ Nb or Ta) have the CuCl and LaB$_2$O$_7$ alternative layers, and these systems are candidates of such novel frustrated 2D spin systems [1-3]. The magnetic Cu ions form a square lattice within the layer. It has been expected that the system is described by $J_1$-$J_2$ model [4-6], namely, the nearest and next-nearest exchange interactions, $J_1$ and $J_2$, compete within the CuCl layer. The magnetic ground state depends on the ratio of $J_1$ to $J_2$. The ground state of (CuCl)LaNb$_2$O$_7$ ($B = $ Nb) has been suggested to be a spin-singlet state [1]. A gap energy is estimated to be $\Delta E \sim 2.3$ meV ($\sim 27$ K) assuming an $S = 1/2$ isolated dimer model. A neutron scattering measurement on this
system by using a triple-axis spectrometer by Kageyama et al. showed magnetic excitation at 2.2 meV, where modulation of the intensity along the $Q$ direction was observed ($Q$ is the magnitude of the scattering vector). Furthermore, the results of the structure analysis on the single crystal by using x-ray and neutron diffraction measurements were recently reported by Tassel et al. [7]. There band structure calculations reveal that the magnetism of this system is described as antiferromagnetic (AFM) spin pairs between fourth neighbors coupled by frustrated ferromagnetic interactions in a Shastry-Sutherland-type arrangement. On the other hand, (CuCl)$_2$LaTa$_2$O$_7$ ($B = Ta$) exhibits an antiferromagnetically ordered state with collinear spin structure below $T_N = 7$ K [2,3].

The time-of-flight (ToF) inelastic neutron scattering technique using a chopper spectrometer is useful to investigate a whole aspect in magnetic excitation in such systems. Especially, new-generation chopper spectrometers installed recently at new neutron sources such as J-PARC can give detailed information for dynamics in a wide $Q$-$E$ range, on which measurements give us alternative opportunities to those on the conventional triple-axis spectrometers. We have performed ToF inelastic neutron scattering measurements on (CuCl)$_2$La$B_2$O$_7$ ($B = Nb$ and Ta) to investigate their magnetic excitation. We report here the characteristic magnetic excitation in these systems. A band-like excitation was observed at $\Delta E \sim 2$ meV in both systems. The $Q$ dependence for (CuCl)$_2$LaNb$_2$O$_7$ well reproduces that observed at a triple-axis spectrometer, which is indicative of a spin-singlet feature with a characteristic length $\sim 8.7 \text{Å}$ assuming the isolated dimer model. On the other hand, (CuCl)$_2$LaTa$_2$O$_7$ in the AFM state exhibits a different $Q$ dependence. In both systems, characteristic modulations for both the intensity of magnetic excitation and its peak position were observed along the $Q$ direction.

2. Experimental procedure

Powder samples of (CuCl)$_2$LaNb$_2$O$_7$ and (CuCl)$_2$LaTa$_2$O$_7$ were prepared by the method reported elsewhere [1,2]. About 10g of the (CuCl)$_2$LaNb$_2$O$_7$ sample and 17g of (CuCl)$_2$LaTa$_2$O$_7$ sample were respectively packed into an Al foil to shape a cylinder with 10mm of diameter and 50mm of height. The packed sample was mounted into an Al sample can with the He gas, and set to a closed-cycle refrigerator. The inelastic neutron scattering measurements were carried out using a cold-neutron disk-chopper spectrometer AMATERAS installed at BL14 in Materials and Life science Experimental Facility at J-PARC, Japan [8,9]. We chose a chopper condition in which neutrons with the incident energies $E_i = 41.9$, 15.1, 7.7, 4.7 and 3.1 meV were extracted simultaneously. All the obtained data were analyzed with the software suite Utsusemi [10].

![Figure 1](image-url)  
*Figure 1.* Excitation spectra in $Q$-$E$ maps for (CuCl)$_2$LaNb$_2$O$_7$ with $E_i = 7.7$ meV obtained at (a) 4.5 K, (b) 7 K, (c) 9 K, (d) 30 K and (e) 50 K.
3. Results and discussion

Figure 1 shows the excitation spectra observed in Q-E maps for (CuCl)LaNb$_2$O$_7$ with $E_i = 7.7$ meV at various temperatures. The neutron count is normalized by proton beam current. A band-like excitation with an energy width of $\sim 1$ meV is clearly observed at around $\Delta E \sim 2$ meV, indicating a singlet-triplet excitation. This excitation signal becomes ambiguous with increasing temperature, but survives even at 50 K. The peak position for the excitation along the $\Delta E$ direction does not change with temperature. The $Q$ dependence of the integrated intensity of the magnetic excitation, which is obtained from a $Q$-scan at $\Delta E = 2.1 \pm 1.2$ meV, is displayed in figure 2. A clear oscillation of the intensity is observed here, and its amplitude decreases as temperature increases. However, the $Q$ dependence does not change up to 50 K. Four peaks are seen at a glance. Its $Q$ dependence well reproduces that obtained from the neutron scattering study by a triple-axis spectrometer, indicating the spin-singlet feature [1].

We introduce the isolated dimer model to analyze the present data as well as the previous neutron scattering study. In this model, the intensity as a function of $Q$ can be described by the product of the squared form factor $f^2(Q)$ [11] and the interference term $(1 - \sin QR / QR)$ parameterized by the intradimer separation distance $R$ [12,13]. Using this model, $R$ is estimated to be $\sim 8.7$ Å. This value corresponds to the distance for fourth neighbors, 8.67 Å. In figure 2, the obtained $R$ value seems to reasonably fit the observed oscillation frequency, which clearly indicates the fourth-neighbor interaction is dominant.

Looking at the $Q$-$E$ maps carefully, we notice remarkable behavior: not only the intensity but the $\Delta E$ value of the peak position slightly modulates along the $Q$ direction. This fact implies that the singlet spin pairs are not simply isolated ones but have some interaction. The spin-singlet state in this system neighbors long-range AFM states appearing for the Ta-for-Nb or Cl-for-Br substitution and application of magnetic field [4,5]. Therefore, it is likely that such correlation exists between the coupled spin pairs. We also note that the recent report shows that this system is described as a ferromagnetically coupled Shastry-Sutherland quantum spin system with the spin pairs between fourth neighbors [7]. The observed structure might be a precursor to induce the long-range ordering. In a constant-$Q$ scan at $Q = 0.8 \pm 0.1$ Å$^{-1}$ with $E_i = 15.1$ meV, another excitation was observed at around 5 meV (not shown), showing consistency with the result obtained by a triple-axis spectrometer [1].

$Q$-$E$ maps for (CuCl)LaTa$_2$O$_7$ with $E_i = 7.7$ meV are shown in figure 3. The neutron count is normalized by proton beam current as well as in (CuCl)LaNb$_2$O$_7$. The collinear AFM ordering in this system is characterized by a propagation vector $\mathbf{q} = (1/2, 0, 1/2)$, which corresponds to $Q = 0.84$ Å$^{-1}$[2]. Clear dispersive behavior is not seen there. Instead, at 4.5 K, a band-like magnetic excitation was observed similarly to that in (CuCl)LaNb$_2$O$_7$ at $\Delta E \sim 2$ meV. The excitation spectra in (CuCl)LaTa$_2$O$_7$ also exhibits modulations for both the intensity and the peak position in $\Delta E$ along the $Q$ direction.
However, the modulation pattern is different from (CuCl)LaNb$_2$O$_7$. This difference in dispersion is presumably attributed to spin dynamics in this three-dimensionally ordered system being different from those in (CuCl)LaNb$_2$O$_7$. In contrast to (CuCl)LaNb$_2$O$_7$, the excitation energy decreases with increasing temperature. Its intensity also decreases and then the signal disappears at 30 K.

![Figure 3](image1.png)

**Figure 3.** Excitation spectra in $Q$-$E$ maps for (CuCl)LaTa$_2$O$_7$ with $E_i$ = 7.7 meV obtained at (a) 4.5 K, (b) 5.5 K, (c) 9 K and (d) 30 K.

![Figure 4](image2.png)

**Figure 4.** $Q$ dependence of the integrated intensity of the magnetic excitation in (CuCl)LaTa$_2$O$_7$, obtained from a $Q$-scan at $\Delta E = 2.1 \pm 1.2$ meV.

The $Q$ dependence of the integrated intensity of magnetic excitation, obtained from a $Q$-scan at $\Delta E = 2.1 \pm 1.2$ meV, is shown in figure 4. This system also shows oscillating behavior. However, the $Q$ dependence at 4.5 K is different from that in (CuCl)LaNb$_2$O$_7$, reflecting the different ground state. Below $T_N$, peaks are seen at around 0.5, 0.85, 1.4 and 1.9 Å$^{-1}$. The second peak appears approximately at a position for $q = (1/2, 0, 1/2)$. Above $T_N$, the second peak is ambiguous and the third peak appears to be slightly shifted to the lower $Q$ side. The $Q$ dependence at 9 K resembles that in (CuCl)LaNb$_2$O$_7$,
rather than (CuCl)LaTa$_2$O$_7$ below $T_N$. The correlating coupled-spin feature lying in (CuCl)LaNb$_2$O$_7$ may remain even in (CuCl)LaTa$_2$O$_7$. Comparing the results in both systems to each other, it may be a common feature that a band-like excitation exists around 2 meV. Though the excitation observed in (CuCl)LaTa$_2$O$_7$ cannot be explained at the present stage, the obtained $Q$ dependence of the intensity will give an important hint to understand the magnetic excitation. We need some model to describe the $Q$ dependence of the intensity of the magnetic excitation in (CuCl)LaTa$_2$O$_7$.

4. Summary
ToF inelastic neutron scattering measurements using a chopper spectrometer were performed on (CuCl)LaB$_2$O$_7$ ($B = Nb$ and Ta) to study their magnetic excitation. In a spin-singlet system (CuCl)LaNb$_2$O$_7$, a band-like excitation with an energy width of $\sim 1$ meV was observed at $\Delta E \sim 2$ meV. The $Q$ dependence of the integrated intensity of magnetic excitation for this system shows good agreement with the previous result obtained by using a triple-axis spectrometer, indicating the characteristics of a singlet-triplet excitation. The excitation spectra further shows modulations for not only its intensity but the peak position in $\Delta E$ along the $Q$ direction. This implies that the singlet spin pairs are not simply isolated ones but have some interaction. (CuCl)LaTa$_2$O$_7$ in the antiferromagnetically ordered state exhibits similar excitation spectra with a band-like excitation at $\Delta E \sim 2$ meV and peculiar modulations. However, the $Q$ dependence of its intensity differs from that for (CuCl)LaNb$_2$O$_7$, reflecting the different ground state.

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References
[1] Kageyama H, Kitano T, Oba N, Nishi M, Nagai S, Hirota K, Viciu L, Wiley J B, Yasuda J, Baba Y, Ajiro Y and Yoshimura K 2005 J. Phys. Soc. Jpn. 74 1702
[2] Kitada A, Tsujimoto Y, Kageyama H, Ajiro Y, Nishi M, Narumi Y, Kindo K, Ichihara M, Ueda Y, Uemura Y J and Yoshimura K 2009 Phys. Rev. B 80 174409
[3] Uemura Y J, Aczel A A, Ajiro Y, Cario J P, Goko T, Goldfeld D A, Kitada A, Luke G M, MacDougall G J, Mihailescua J G, Rodriguez J A, Russo P L, Tsujimoto Y, Wiebe C R, Williams T J, Tamamoto Y, Yoshimura K and Kageyama H 2009 Phys. Rev. B 80 174408
[4] Read N and Sachdev S 1989 Phys. Rev. Lett. 62 1694
[5] Gelfand M P et al. 1989 Phys. Rev. B 40 10801
[6] Becca F and Mila F 2002 Phys. Rev. Lett. 89 037204
[7] Tassel C, Kang J, Lee C, Hernandez O, Quy P, Paulus W, Collet E, Lake B, Guidi T, Whangbo M-H, Ritter C, Kageyama H and Lee S -H 2010 Phys. Rev. Lett. 105 167205
[8] Nakajima K, Nakamura M, Kajimoto R, Osaka K, Kayutani K, Matsu S, Metoki N, Wakimoto S, Sato T J, Itoh S, Arai M, Yoshi K and Nitta K 2007 J. Neutron Res. 15 13–21
[9] Nakajima K and Ohira-Kawamura S 2010 Hamon 20 49–53 (in Japanese)
[10] Iwamura Y, Nakajima K, Kajimoto R, Takatani N, Arai M, Otomo T, Suzuki J, So J Y and Park J G Proc. 19th meeting on Collaboration of Advanced Neutron Sources, to be published
[11] International Tables for Crystallography, ed. A. J. C. Wilson, Vol. C.
[12] Furrer A and Güdel H U 1977 Phys. Rev. Lett. 39 657
[13] Güdel H U et al. 1979 Inorg. Chem. 18 1021