Proc. 2nd Int. Symp. Science at J-PARC — Unlocking the Mysteries of Life, Matter and the Universe —
JPS Conf. Proc. **8**, 034012 (2015)
http://dx.doi.org/10.7566/JPSCP.8.034012

Neutron Diffraction Study of 1D Quantum Spin System Li_2ZrCuO_4 with Incommensurate Magnetic Structure

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(Received October 13, 2014)

Neutron diffraction, magnetic susceptibility, and specific heat have been measured for polycrystalline samples of Li_2ZrCuO_4, in which quasi-one-dimensional quantum spin chains are formed from edge-sharing CuO_4 square planes called CuO_2 ribbon chains. Using neutron powder diffraction, an antiferromagnetic transition with incommensurate magnetic ordering has been found at T_N ~ 7 K. Below T_N, super-lattice magnetic reflections $h\ k\ l{\pm}\delta$ (h, k and l = even) with incommensurate modulation δ ~ 0.487 have been observed. This value for incommensurate modulation δ implies α (= $-J_2/J_1$) = 6.2 on the basis of theoretical results from a J_1– J_2 classical spin model. This α-value contradicts α = 0.3 value reported by Drechsler *et al.* [Phys. Rev. Lett. 98, 077202 (2007)], which is close to the critical value α_c = 1/4 for Li_2ZrCuO_4 estimated from magnetic susceptibility data. The indices of magnetic reflection $h\ k\ l{\pm}\delta$ (h, k, and l =even) for Li_2ZrCuO_4 indicate that the relation between nearest neighbor spin chains is “in-phase.” It also indicates that inter-chain coupling is ferromagnetic, which differs from that for $LiVCuO_4$. On the basis of the obtained results, characteristics of the magnetic structure are discussed.

KEYWORDS: quantum spin, Li_2ZrCuO_4, incommensurate magnetic structure

1. Introduction

Frustrated quantum spin systems caused by geometrical arrangements or competing magnetic interactions are attracting much attention because emergent phenomena often arise from a fine balance between exchange interactions and spin fluctuation. One class of systems that may have these characteristics is the spin system having quasi-one-dimensional Cu^{2+} spin 1/2 chains of edge-sharing CuO_4 square planes; these are called CuO_2 ribbon chains. In CuO_2 ribbon chain systems, the next-nearest-neighbor exchange interaction J_2 through Cu– O– O– Cu exchange paths is antiferromagnetic (J_2 > 0), while the nearest-neighbor exchange interaction J_1 through Cu– O– Cu paths is ferromagnetic (J_1 < 0) because the Cu– O– Cu angle is close to 90°. For CuO_2 ribbon chain systems, the competition between J_1 and J_2 causes magnetic frustration, which induces a nontrivial magnetic structure in the magnetically ordered phase. Theoretically, a helical magnetic structure is expected for α (= $-J_2/J_1$) > 1/4 (= α_c) within classical and quasi-quantum spin models [1]. Actually, $LiVCuO_4$ [2,3], $LiCu_2O_2$ [4], and $PbCuSO_4(OH)_2$ [5,6] with CuO_2 ribbon chains have helical magnetic order.

Li_2ZrCuO_4 is another system having CuO_2 ribbon chains. Figure 1 shows the crystal structure schematically. The structure is orthorhombic (space group *Cccm*), and the CuO_2 ribbons along the *c*-direction are separated by Li^+ ions and ZrO_6 octahedra [7]. In a unit cell, there are two CuO_2 ribbon chains represented by Cu chain-A and chain-B, as shown in Fig. 1.

Drechsler *et al.* reported that the value of α (= – J_2/J_1) estimated from the analysis of a plot of magnetic susceptibility (χ) vs temperature (T) for Li_2ZrCuO_4 is ~ 0.3, which is close to the critical value α_c = 1/4 [8,9]. From ^{7}Li-NMR results for Li_2ZrCuO_4, Tarui *et al*. proposed that some possible magnetic structures with phase differences between neighboring spins $\Delta\varphi$ = 33 ± 2° reproduced the ^{7}Li-NMR spectra [10]. This $\Delta\varphi$-value corresponds to α = 0.33 and is close to the critical value α_c.

In this work, we have investigated the magnetic structure by measuring magnetic susceptibility, specific heat, and neutron diffraction of polycrystalline samples of Li_2ZrCuO_4. On the basis of the observed $h\ k\ l{\pm}\delta$ (h, k, and l = even, and δ ~ 0.487) magnetic reflections, the magnetic structure and α value for Li_2ZrCuO_4 are discussed.

2. Experiments

Polycrystalline samples of Li_2ZrCuO_4 were prepared through a standard solid-state reaction: Li_2CO_3, ZrO_2, and CuO were mixed in a proper molar ratio, then the mixtures were pressed into pellets and heated for a few hours at 700 °C in flowing O_2 gas. The obtained samples were reground and pressed into pellets and heated at 1050 °C for 24 h in flowing O_2 gas. Because the ^{6}Li isotope included in natural Li atoms has a large neutron absorption, we used the ^{7}Li isotope to prepare samples for neutron diffraction. The magnetic susceptibility χ was measured in a magnetic field of H = 0.1 T using a SQUID magnetometer (Quantum Design) in the temperature range from 2 to 300 K. The specific heat C was measured by the thermal relaxation method using a Quantum Design PPMS (Quantum Design). Powder neutron diffraction measurements were carried out using the high-resolution powder diffractometer (HRPD) installed at JRR-3 of JAEA in Tokai. The 331 reflection of a Ge monochromator was used. The horizontal collimations were open(36´)-20´-6´ and the neutron wavelength was 1.8237 Å. The sample was packed in a vanadium cylinder (10 mmϕ), and the cylinder was set in an Al can filled with exchange gas. A displex-type refrigerator was used to cool the sample. The diffraction intensities were measured in the 2θ-range from 2.5° to 165° with a step of 0.05°.

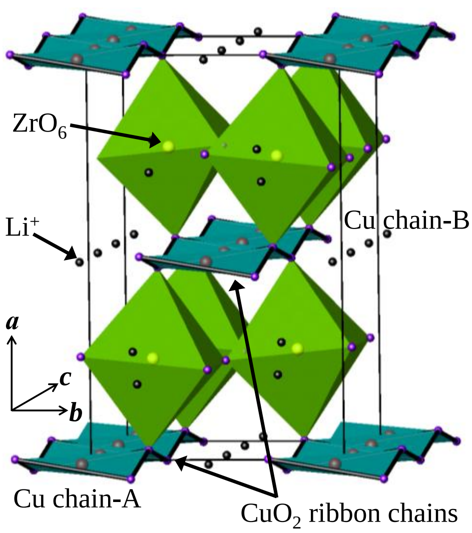

Fig. 1. Crystal structure of Li_2ZrCuO_4. Edge-sharing chains of CuO_4 square planes (called CuO_2 ribbon chains) are separated by Li^+ ions and ZrO_6 octahedra. In a unit cell, there are two CuO_2 ribbon chains: Cu chain-A and chain-B.

3. Experimental Results and Discussion

Figure 2 and the inset in Fig. 2 show the T-dependence of the magnetic susceptibilities

χ of Li_2ZrCuO_4 measured under the condition of zero field cooling (ZFC) for the applied field H = 0.1 T. The broad peak of χ around 9 K is attributed to growth of short-range spin correlation with decreasing T. With further decrease in T, χ exhibits a sharp decrease at T_N = 7 K, which is consistent with data in [8] and [10]. The temperature derivative of the magnetic susceptibility, $d\chi/dT$, for Li_2ZrCuO_4 at H = 0.1 T is shown in the inset of the figure. The peak temperature of the $d\chi/dT$– T curve corresponds to the antiferromagnetic transition temperature T_N = 7 K.

The T-dependences of the specific heat divided by T, C/T, for Li_2ZrCuO_4 under magnetic fields of 0, 3, and 7 T are shown in Fig. 3; the figure clearly shows the peak structure of the C/T– T curve at the antiferromagnetic transition temperature [8]. The antiferromagnetic transition temperature decreases with increasing H, which is the usual behavior for antiferromagnets. We have carried out analyses of the C/T– T curve at H = 0. Considering a phonon component of specific heat C_{ph}, the specific heat C is naturally described by $C = C_{spin} + C_{ph} = C_{spin} + \beta T^3$, where C_{spin} and β are the spin component of the specific heat and lattice specific heat coefficient, respectively. We have chosen the C_{ph}/T values represented by the dotted curve in Fig. 3. Magnetic entropies S deduced by T-integration of C_{spin}/T are shown as a function of T in the inset of Fig. 3. In the

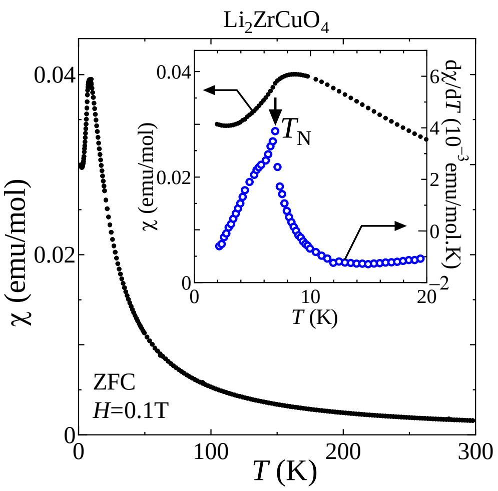

Fig. 2. Temperature dependence of the magnetic susceptibility χ of Li_2ZrCuO_4 measured under zero field cooling (ZFC) for a magnetic field of 0.1 T. Inset shows the T-dependences of χ and $d\chi/dT$ of Li_2ZrCuO_4 and reveals the existence of an antiferromagnetic transition at T_N=7 K (thick arrow).

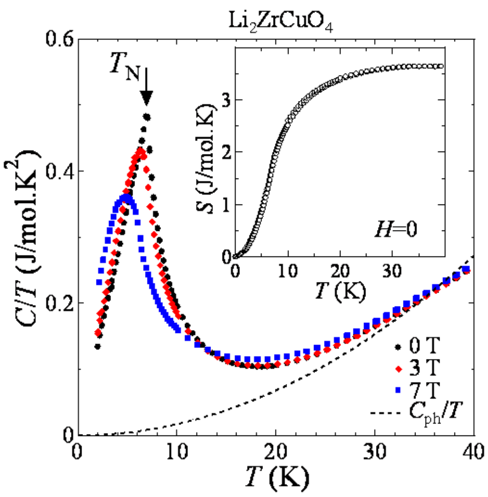

Fig. 3. Specific heat divided by T, C/T, for Li_2ZrCuO_4 as a function of T under magnetic fields of 0, 3, and 7 T. Dotted curve is the phonon component C_{ph} divided by T, C_{ph}/T. Inset shows T-dependence of the magnetic entropy S deduced from T-integration of the spin component C_{spin} divided by T, C_{spin}/T (= C/T – C_{ph}/T) for H = 0.

integration, C_{spin}/T below 2K was evaluated by extrapolating the data from the T-region 2 K < T < 5 K. The value of the magnetic entropy S(35 K) = 3.6 J/(mol·K) corresponds to ~ 62 % of Rln2 expected for spin 1/2 systems; here, R is the gas constant. Interestingly, the evaluated entropy is relatively small. Possible origins for the discrepancy are effects of quantum fluctuations and low dimensionality of the spin system. A further experiment is needed to test these possibilities.

To investigate the magnetic structure of $^7Li_2ZrCuO_4$, powder neutron diffraction studies were carried out at 3 K (< T_N) and 40 K (> T_N). The resulting neutron powder patterns are shown in Fig. 4. All observed peaks at 40 K correspond to nuclear Bragg reflections of $^7Li_2ZrCuO_4$ and T-independent peaks of an unknown impurity phase. In Fig.4, the former peaks are marked with integer indices, while the latter peaks are indicated by asterisks. At 3 K, in addition to the observed peaks at 40 K, super-lattice peaks derived from magnetic ordering appear in the low-angle region 2θ < 50° in Fig. 4. All observed magnetic reflections can be assigned $h\ k\ l\pm\delta$ indices (h, k, and l = even, and δ ~ 0.487). In Fig. 4, the thick arrows indicate 2θ-positions for magnetic reflections of $^7Li_2ZrCuO_4$ with a displayed index. Determination of the magnetic structure of the present system is difficult using only the present neutron diffraction data because the number of observed magnetic reflections is insufficient to determine the numerous parameters of the incommensurate modulated magnetic structure. Therefore, on the basis of the obtained results, we discuss characteristics of the magnetic structure of Li_2ZrCuO_4 by comparing with that for $LiVCuO_4$.

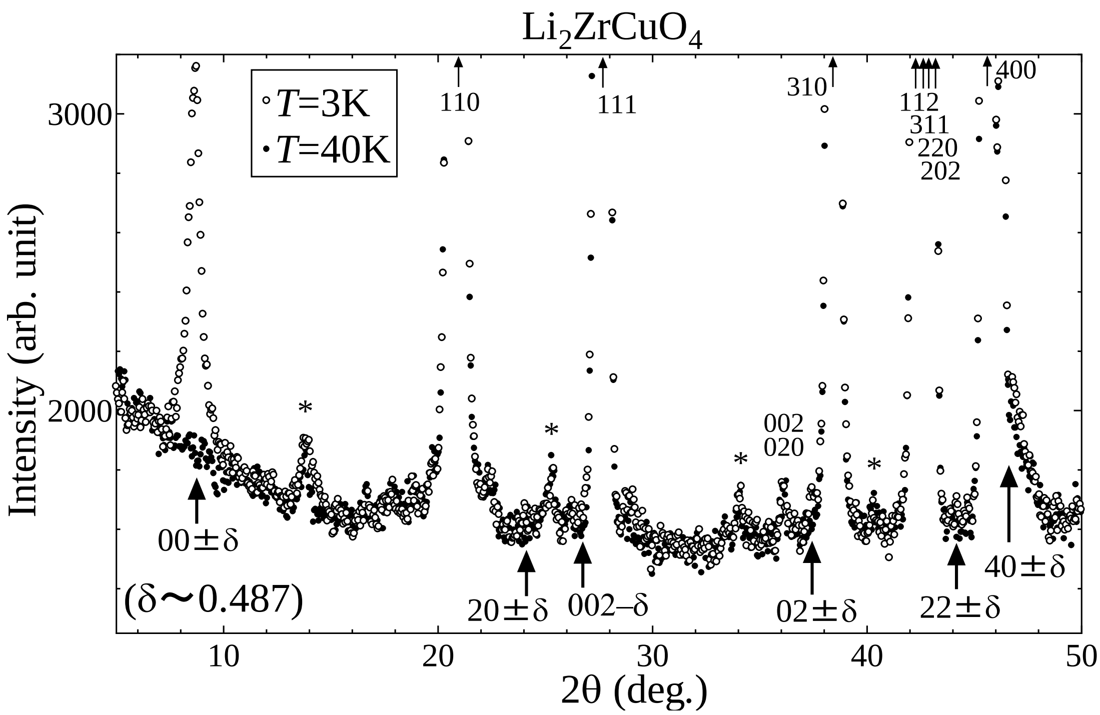

Fig. 4. Neutron powder diffraction patterns of $^7Li_2ZrCuO_4$ taken at T = 3 K and 40 K. Peaks marked with integer indices correspond to nuclear Bragg reflections. Thick arrows indicate the 2θ-positions of magnetic reflection peaks at T = 3 K. Indices of the observed magnetic reflections of $^7Li_2ZrCuO_4$ are found to be $h\ k\ l\pm\delta$ (h, k, and l =even, and δ ~ 0.487). Asterisks (*) mark T-independent peaks of an unknown impurity phase.

Figures 5(a) and 5(b) show schematic crystal structures of Cu atoms of Li_2ZrCuO_4 and $LiVCuO_4$, respectively. For Li_2ZrCuO_4, the observed magnetic reflections $h\ k\ l{\pm}\delta$ (h, k, and l = even, and $\delta \sim 0.487$) indicate the incommensurate spin modulation vector $\boldsymbol{q}$ = (0, 0, 0.487) along the CuO_2 ribbon direction and a phase difference between neighboring Cu spins $\Delta\varphi \sim 87.7°$, as shown in Fig. 5(a). For $LiVCuO_4$, the magnetic reflections $h\ k{\pm}\delta'\ l$ (h and l = odd, k = even, and $\delta' \sim 0.466$) are reported in [2] and [3], indicating the incommensurate spin modulation vector $\boldsymbol{q}'$ = (0, 0.466, 0) and the phase difference $\Delta\varphi' \sim 83.9°$, as shown in Fig. 5(b). Note that the CuO_2 ribbon directions of Li_2ZrCuO_4 and $LiVCuO_4$ are the c-axis and b-axis, respectively. Because the spin modulation and phase difference between Li_2ZrCuO_4 and $LiVCuO_4$ have similar values, the α value of Li_2ZrCuO_4 is expected to be almost the same as that of $LiVCuO_4$. For Li_2ZrCuO_4, the value of $\Delta\varphi$ (~ 87.7°) implies $\alpha = 6.2$ by using the theoretical equation for a $J_1 - J_2$ classical spin system, where $\alpha = 1/(4\cos(\Delta\varphi))$. Moreover, the value of α for Li_2ZrCuO_4 is found to be large ($\alpha > 6.2$) from theoretical results of the $J_1 - J_2$ quasi quantum spin system reported in [1]. This result for the α value of Li_2ZrCuO_4 contradicts the value $\alpha = 0.3$ reported by Drechsler *et al.* [8,9] and does not approximate the critical value $\alpha_c = 1/4$.

The indices of the magnetic reflections of Li_2ZrCuO_4 are found to be $h\ k\ l{\pm}\delta$ (h and k = even), indicating that the relation between the spins of Cu chain-A and chain-B is "in-phase," as shown in Fig. 5(a). This result indicates that inter-chain interactions J_{inter}

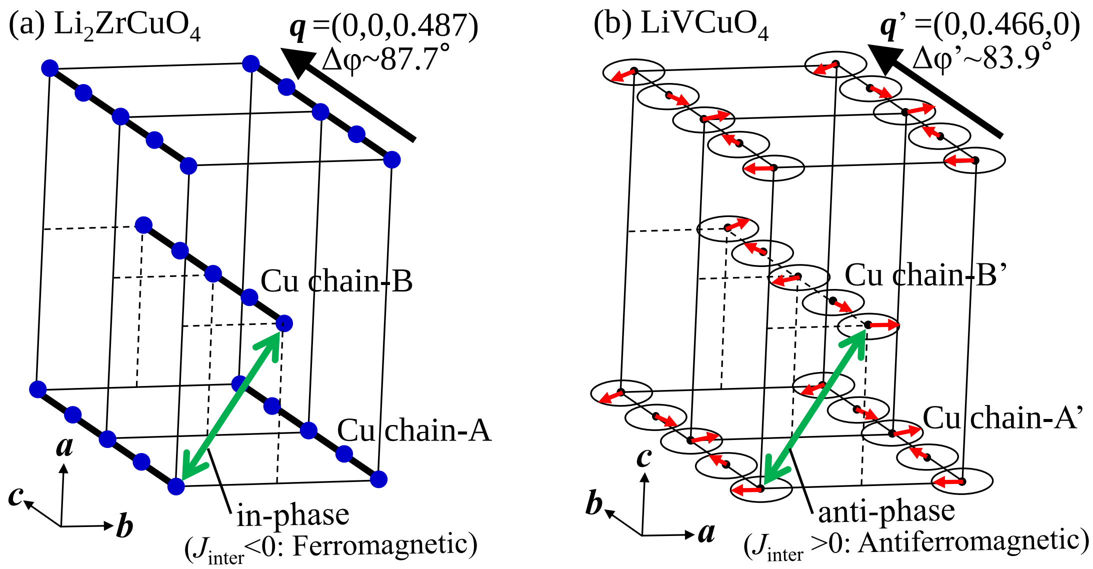

Fig. 5. Schematic distributions of Cu atoms in (a) Li_2ZrCuO_4 and (b) $LiVCuO_4$. For Li_2ZrCuO_4, the observed magnetic reflections $h\ k\ l{\pm}\delta$ (h, k, and l = even, and $\delta \sim 0.487$) indicate the spin modulation vector $\boldsymbol{q}$ = (0, 0, δ) and phase difference $\Delta\varphi \sim 87.7°$. The relation between spins of Cu chain-A and chain-B is "in-phase," indicating an inter chain interaction $J_{inter} < 0$ (ferromagnetic). However, for $LiVCuO_4$, the magnetic reflections $h\ k{\pm}\delta'\ l$ (h and l = odd, k = even, and $\delta' \sim 0.466$) indicate $\boldsymbol{q}'$ = (0, δ', 0) and $\Delta\varphi' \sim 83.9°$ [2,3]. The relation between the spins of Cu chain-A' and chain–B' is "anti-phase," indicating $J_{inter} > 0$ (antiferromagnetic interaction). Although the magnetic structure of $LiVCuO_4$ is an *ab*-helical structure [2,3], the magnetic structure of Li_2ZrCuO_4 cannot be determined solely from the present studies only.

are ferromagnetic (J_{inter}<0). However, indices of the magnetic reflections of $LiVCuO_4$ are *h k*±δ' *l* (*h* and *l* = odd), indicating that the relation between spins of Cu chain-A' and chain–B' is "anti-phase," as shown in Fig. 5(b) [2,3]. This corresponds to J_{inter} > 0 (antiferromagnetic interaction). Note that the *ab*-helical structure was reported for $LiVCuO_4$, as shown in Fig. 5(b). On the basis of the ^{7}Li-NMR spectra of Li_2ZrCuO_4, Tarui *et al*. reported several candidate magnetic structures and Δφ = 33 ± 2°, assuming that the relation between the inter-chain spins is "anti-phase" [10]. However, the ^{7}Li-NMR spectra should be reanalyzed because the relation between the spins of the Cu chain-A and chain-B for Li_2ZrCuO_4 is found to be "in-phase" in the present work.

4. Conclusions

We have shown experimental results for neutron magnetic reflection, magnetic susceptibility, and specific heat for polycrystalline samples of Li_2ZrCuO_4. We have observed magnetic reflections *h k l*±δ (*h*, *k*, and *l* = even) with incommensurate modulation δ ~ 0.488 below the antiferromagnetic transition temperature T_N ~ 7 K. The incommensurate modulation value δ implies α (= – J_2/J_1) = 6.2 on the basis of theoretical results from the J_1– J_2 classical spin model. This value for α contradicts α = 0.3 reported by Drechsler *et al.*[8,9] and does not approximate the critical value α_c = 1/4. The indices of magnetic reflection *h k l*±δ (*h* and *k* = even) for Li_2ZrCuO_4 indicate that the relation between inter-chain spins is "in-phase." These results indicate that the inter-chain interactions of Li_2ZrCuO_4 are ferromagnetic, which differs from that for $LiVCuO_4$.

Acknowledgment

Powder neutron scattering at JRR-3 was performed within the frame of JAEA Collaborative Research Program.

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