Spin waves and magnetic interactions in LiCu$_2$O$_2$.

T. Masuda,$^{1}$ A. Zheludev,$^{1}$ B. Roessli,$^{2}$ A. Bush,$^{3}$ M. Markina,$^{4}$ and A. Vasiliev$^{4}$

$^1$Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6393, USA.
$^2$Laboratory for Neutron Scattering, ETH Zurich and Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland.
$^3$Moscow Institute of Radiotechnics, Electronics and Automation, Moscow 11744, Russia.
$^4$Low Temperature Physics Department, Moscow State University, Moscow 119992, Russia.

(Dated: August 31, 2021)

The quasi-one-dimensional helimagnet LiCu$_2$O$_2$ was studied by single crystal inelastic neutron scattering. The dispersion relation of spin wave excitations was measured in the vicinity of the principal magnetic Bragg reflection. A spin wave theoretical analysis of the data yields an estimate of the relevant exchange constants and explains the mechanism of geometric frustration that leads to helimagnetism. It is found that the simple antiferromagnetic $J_1-J_2$ model that was previously proposed is inadequate for LiCu$_2$O$_2$. The experimental findings are generally in qualitative agreement with first principal calculations of [A. A. Gippius et al., Phys. Rev. B 70, 020406 (2004)], though certain important discrepancies remain to be explained.

PACS numbers:

I. INTRODUCTION

LiCu$_2$O$_2$ is a quasi-one-dimensional magnetic material that has recently attracted a great deal of attention. Muon spin resonance, neutron scattering experiments, and NMR studies clearly demonstrated that this $S = 1/2$ system has an incommensurate helimagnetic ground state. In our previous work we postulated a simple model of magnetic interactions that seemed to account well for the observed properties. It was proposed that LiCu$_2$O$_2$ features weakly coupled zig-zag $S = 1/2$ chain with competing nearest-neighbor $J_1$ and next-nearest-neighbor $J_2$ antiferromagnetic interactions. Due to geometric frustration this model exhibits an unusual competition between a quantum-disordered gapped ground state with commensurate spin correlations and semi-classical helimagnetic incommensurate state. However, independent first-principle numerical studies suggested a totally different model for the geometric frustration in LiCu$_2$O$_2$. According to that work, the nearest-neighbor $J_1$ interactions are actually ferromagnetic, and it is the unusually large fourth-nearest neighbor antiferromagnetic coupling constant $J_4$ that causes geometric frustration and favors helimagnetism. A similar scenario was recently proposed for a very similar isostructural helimagnet NaCu$_2$O$_2$.

Bulk magnetic susceptibility data for LiCu$_2$O$_2$ seem to be compatible with both models and are thus inconclusive. The only direct way to determine (effective) exchange constants is by means of single crystal inelastic neutron spectroscopy. This technique can probe the dispersion relation of spin wave excitations in the system. In the present paper we describe the results of such a study. We find that the actual topology of magnetic coupling is indeed more complex than originally envisioned.

A. Structural considerations

LiCu$_2$O$_2$ has a layered charge-ordered orthorhombic crystal structure (space group Pnma, $a = 5.730(1)$Å, $b = 2.8606(4)$Å, and $c = 12.417(2)$Å), as described in detail in Refs. 6,7. The magnetism is due to double chains of Cu$^{2+}$ ions that run along the crystallographic $b$ axis. The period of each “leg” of the double spin chains is equal to $b$. The two legs are offset by $b/2$ relative to each other and thus form a “triangular ladder”, as illustrated in Fig. 1. These double chains are arranged in layers parallel to the $(a, b)$ plane and are effectively separated along the $c$ direction by planes of non-magnetic Cu$^+$ ions.

The approximate magnetic structure was determined in Ref. 4 and is illustrated in Fig. 1 of that paper. The ordering temperature is $T_c = 24$ K. Each double spin chain carries a planar helix of spins. The magnetic propagation vector is $q_0 = (0.5, \zeta, 0)$ with $\zeta \approx 0.827$. Consecutive spins on each rung are almost parallel, being rotated relative to each other by an angle $\phi = 2\pi\zeta$. Within each double chain any nearest-neighbor spins from opposite legs are almost antiparallel and form an angle $\phi/2 = \pi\zeta$. Preliminary neutron diffraction experiments were consistent with $(a, b)$ being the spin rotation plane, but independent NMR studies clearly show an out-of-plane component. This suggests that the spin rotation planes are, in fact, tilted relative to a high-symmetry orientation. The issue deserves further investigation, perhaps involving more accurate diffraction measurements. However, if magnetic anisotropy effects are negligible compared to Heisenberg exchange interactions (a reasonable assumption for Cu$^{2+}$ ions), the actual arrangement of spin rotation planes should not affect spin wave dispersion relations that are the focus of the present study.

The main goal of the inelastic neutron scattering experiments described below is to establish the hierarchy of exchange interactions. The corresponding coupling constants are schematically shown in Fig. 1., and define a...
In the present study we employed a 5 g single-crystal sample of LiCu$_2$O$_2$. Crystal mosaic was not particularly good: irregular, with as much as 4° FWHM spread. This circumstance imposed certain constraints as will be discussed below. The measurements were carried out in two separate series of experiments. Neutrons with a fixed final energy of $E_f = 13.5$ meV were used at the HB-1 thermal 3-axis spectrometer at the High Flux Isotope Reactor at ORNL (Setup 1). Pyrolitic graphite PG (002) reflections were used for monochromator and analyzer. A PG filter was installed after the sample to eliminate higher-order beam contamination. The setup employed $48'-80' - 80' - 240$ collimators. Alternatively, we utilized cold neutrons with a final energy fixed at $E_f = 5$ meV at the TASP 3-axis instrument installed at the SINQ spallation source, Villigen PSI, Switzerland (Setup 2). PG monochromator and analyzer were used with no additional collimation and a cold Be filter positioned after the sample. In all cases the sample was mounted with the $(a, b)$ plane coinciding with the horizontal scattering plane of the instrument. Sample environment was a standard “Orange”-type flow cryostat. Most of the data were taken at $T = 1.5$ K.

Data collection procedures were aimed at minimizing the adverse effects of the broad mosaic spread of the sample. A large mosaic translated to a poor wave vector resolution perpendicular to the momentum transfer $\mathbf{q}$. Since the spin wave dispersion is steepest along $b^*$, the best focusing conditions are obtained for $\mathbf{q}$ pointing close to that direction. Considering the intensity reduction due to the effect of magnetic form factors at large $|q|$, an optimal “window” for low-energy spin wave measurements was identified in the vicinity of the $(0.5, 0.827, 0)$ and $(0.5, 1.173, 0)$ magnetic Bragg peaks. Another advantage of this reciprocal-space region is that it is relatively clear of spurious scattering and phonons, that were carefully checked for. Most scans were repeated at $T = 75$ K, i.e., well above $T_c$, to verify that the signal observed at low temperature is indeed of magnetic origin. In some cases smoothed high-temperature scans were used as background for point-by-point subtraction from the corresponding low-temperature data sets.

Another important technical problem that had to be dealt with is crystal twining. In LiCu$_2$O$_2$ twinning occurs at a microscopic level. The $a$ axis of one type of domains coincides with the $b$ axis of the other domain type, since $a \approx 2b$. The immediate consequence is that neutron diffraction and inelastic scattering necessarily detect a joint signal originating from both domain types. As will be discussed in detail below, the contributions from different domains and different spin wave branches within each domain could be reliably separated only in the direct proximity of the $(0.5, 0.827, 0)$ and $(0.5, 1.173, 0)$ peaks. Even so, twinning reduces the effective sample volume by a factor of two. To avoid any confusion we will use the indexes $h$, $k$ and $l$ to label wave vector components in the coordinate system defined by the reciprocal lattice of one particular domain type (type-A). Indexes $h_B = 2k$, $k_B = h/2$ and $l_B = l$ will refer to the other crystallographic domain (type-B).

II. EXPERIMENTAL

In the present study we employed a 5 g single-crystal sample of LiCu$_2$O$_2$. Crystal mosaic was not particularly good: irregular, with as much as 4° FWHM spread. This circumstance imposed certain constraints as will be discussed below. The measurements were carried out in two separate series of experiments. Neutrons with a fixed final energy of $E_f = 13.5$ meV were used at the HB-1 thermal 3-axis spectrometer at the High Flux Isotope Reactor at ORNL (Setup 1). Pyrolitic graphite PG (002) reflections were used for monochromator and analyzer. A PG filter was installed after the sample to eliminate higher-order beam contamination. The setup employed $48'-80' - 80' - 240$ collimators. Alternatively, we utilized cold neutrons with a final energy fixed at $E_f = 5$ meV at the TASP 3-axis instrument installed at the SINQ spallation source, Villigen PSI, Switzerland (Setup 2). PG monochromator and analyzer were used with no additional collimation and a cold Be filter positioned after the sample. In all cases the sample was mounted with the $(a, b)$ plane coinciding with the horizontal scattering plane of the instrument. Sample environment was a standard “Orange”-type flow cryostat. Most of the data were taken at $T = 1.5$ K.

Data collection procedures were aimed at minimizing the adverse effects of the broad mosaic spread of the sample. A large mosaic translated to a poor wave vector resolution perpendicular to the momentum transfer $\mathbf{q}$. Since the spin wave dispersion is steepest along $b^*$, the best focusing conditions are obtained for $\mathbf{q}$ pointing close to that direction. Considering the intensity reduction due to the effect of magnetic form factors at large $|q|$, an optimal “window” for low-energy spin wave measurements was identified in the vicinity of the $(0.5, 0.827, 0)$ and $(0.5, 1.173, 0)$ magnetic Bragg peaks. Another advantage of this reciprocal-space region is that it is relatively clear of spurious scattering and phonons, that were carefully checked for. Most scans were repeated at $T = 75$ K, i.e., well above $T_c$, to verify that the signal observed at low temperature is indeed of magnetic origin. In some cases smoothed high-temperature scans were used as background for point-by-point subtraction from the corresponding low-temperature data sets.

Another important technical problem that had to be dealt with is crystal twining. In LiCu$_2$O$_2$ twinning occurs at a microscopic level. The $a$ axis of one type of domains coincides with the $b$ axis of the other domain type, since $a \approx 2b$. The immediate consequence is that neutron diffraction and inelastic scattering necessarily detect a joint signal originating from both domain types. As will be discussed in detail below, the contributions from different domains and different spin wave branches within each domain could be reliably separated only in the direct proximity of the $(0.5, 0.827, 0)$ and $(0.5, 1.173, 0)$ peaks. Even so, twinning reduces the effective sample volume by a factor of two. To avoid any confusion we will use the indexes $h$, $k$ and $l$ to label wave vector components in the coordinate system defined by the reciprocal lattice of one particular domain type (type-A). Indexes $h_B = 2k$, $k_B = h/2$ and $l_B = l$ will refer to the other crystallographic domain (type-B).

III. RESULTS

A typical constant-energy scan collected using Setup 1 is shown in Fig. 3. The non-magnetic background for this scan (featureless and typically about 80 counts per 5
FIG. 2: A constant-$E$ scan along the $(−0.5, k, 0)$ reciprocal-space rod measured in LiCu$_2$O$_2$ at $T = 1.5$ K at an energy transfer of 5 meV (symbols) using Setup 1. The lines are a simulation based on the measured spin wave dispersion relation and the known resolution function of the instrument.

min.) was measured at $T = 75$ K. A linear fit to the measured background was subtracted from the data shown. The four prominent peaks seen in this scan can be attributed to an acoustic spin wave emanating from two magnetic Bragg peaks at $(0, 0.827, 0)$ and $(0.5, 1.173, 0)$. Representative constant-$q$ scans collected using the same setup are shown in Fig. 3 where a flat background has been subtracted from the data. All inelastic peaks observed for $0.75 \lesssim k \lesssim 1.25$ and $\hbar \omega \lesssim 8$ meV can be associated with a single branch of excitations. The corresponding dispersion relation along the crystallographic $b$ axis was extracted from the measured scans using Gaussian fits. The result is plotted in circles in Fig. 4a, where solid and open symbols indicate constant-$q$ and constant-$E$ measurements, respectively. Any attempts to follow the observed spin wave branch to higher energies were not successful. The mode’s intensity drops progressively, while the background increases and becomes structured. As will be explained below, part of this problem may be due to a multitude of additional spin wave branches from both types of domains. The situation was further aggravated by limited resolution, phonon scattering and instrument-related spurious peaks. For this reason, throughout this paper we shall limit the discussion to experimental data collected at low energies in direct proximity of the two above-mentioned magnetic Bragg peaks.

Additional measurements were performed using Setup 2 to determine the dispersion along the $a^*$ axis. Typical scans and the measured dispersion curve are shown in Figs. 4c and 4d, respectively. The important zone-boundary scan at $(0, 0.827, 0)$ was also measured using Setup 1 in the range 2–15 meV and found to be fully consistent with that shown in Fig. 4c.

FIG. 3: Typical constant-$q$ scans measured in LiCu$_2$O$_2$ (symbols) at $T = 1.5$ K. The lines are as in Fig. 2. The shaded area in the lower scan is an “accidental Bragg” spurious peak originating from $2k_i$ scattering in the monochromator, $(0, 2, 0)$ Bragg scattering in the sample and inelastic thermal-diffuse scattering in the analyzer. The spurious peak appears much narrower than the experimental resolution (about 2 meV FWHM).

Data analysis

In order to extract the relevant exchange constants from the measured dispersion curves the data were analyzed in the framework of semiclassical spin wave theory (SWT).

1. Equivalent Bravais lattice

At a first glance, calculating the dispersion relation is quite tedious, since we are dealing with a non-Bravais lattice of spins with four magnetic ions per unit cell. Within the approximation of the Hamiltonian (1), however, any interactions between the double-chain layers are ignored, and only two spins per unit cell remain. Moreover, the spin network can be made equivalent to one on a Bravais lattice by displacing the atoms as shown in Fig. 1b. The dynamic structure factor $S_0(q, \omega)$ of this “straight-
FIG. 4: Spin wave dispersion measured in LiCu$_2$O$_2$ at $T = 1.5$ K (symbols). Shaded and open circles are data points obtained from constant-$E$ and constant-$q$ scans, respectively. The lines are a fit to the data, as described in the text. Heavy solid, heavy dashed and thin dotted lines correspond to Models 1, 2 and 3, respectively. In both panels the ellipses represent the FWHM of the instrument resolution function in the appropriate projection (open ellipse) and section (shaded ellipse).

FIG. 5: Typical scans measured in LiCu$_2$O$_2$ using Setup 2 (symbols). The lines are as in Fig. 2.

particular properties of $S^{(0)}(q, \omega)$ and $S(q, \omega)$, and relies only on the definitions of these correlation functions.

2. SWT dynamic structure factor

A very useful recipe for calculating the SWT dynamic structure factor of a simple helimagnet on a Bravais lattice can be found in Ref. 13. The magnon dispersion relation is given by:

$$\omega_q^2 = A_q^2 - B_q^2,$$

$$A_q = 2S \left\{ J_1 + \frac{1}{4} [J_{q-q_0} + J_{q+q_0}] - J_{q_0} \right\},$$

$$B_q = 2S \left\{ J_1 - \frac{1}{4} [J_{q-q_0} + J_{q+q_0}] \right\},$$

where, for our model Hamiltonian,

$$J_{h,k,l} = J_1 \cos(\pi k) + J_2 \cos(2\pi k) + J_4 \cos(4\pi k) + J_\perp \cos(2\pi h).$$

The requirement that $q_0$ minimizes $J(q)$ fixes the relation between $J_1$, $J_2$, $J_4$ and $\zeta$:

$$J_1 + 4J_2 \cos(\pi \zeta) + 16J_4 \cos(3\pi \zeta) \cos(2\pi \zeta) = 0.$$
Conveniently, $J_\perp$ does not enter this expression. The single-magnon cross section has three contributions:

$$S_0^+(\mathbf{q}, \omega) = \frac{S}{2} \frac{A_\mathbf{q} + B_\mathbf{q}}{\omega_\mathbf{q}} \delta(\omega - \omega_\mathbf{q}),$$  \hspace{5cm} (6a)

$$S_0^-(\mathbf{q}, \omega) = \frac{S}{8} \frac{A_{\mathbf{q}-\mathbf{q}_0} - B_{\mathbf{q}-\mathbf{q}_0}}{\omega_{\mathbf{q}-\mathbf{q}_0}} \delta(\omega - \omega_{\mathbf{q}-\mathbf{q}_0}),$$  \hspace{5cm} (6b)

$$S_0^0(\mathbf{q}, \omega) = \frac{S}{8} \frac{A_{\mathbf{q}+\mathbf{q}_0} - B_{\mathbf{q}+\mathbf{q}_0}}{\omega_{\mathbf{q}+\mathbf{q}_0}} \delta(\omega - \omega_{\mathbf{q}+\mathbf{q}_0}).$$  \hspace{5cm} (6c)

Here $S_0^\pm(\mathbf{q}, \omega)$ represents fluctuations of the spin component perpendicular to the plane of the helix, while $S^-(\mathbf{q}, \omega)$ and $S^0(\mathbf{q}, \omega)$ are in-plane excitations. The total SWT cross section for LiCu$_2$O$_2$ is related to $S_0(\mathbf{q}, \omega)$ through Eq. 2.

It now becomes clear why measuring spin waves in LiCu$_2$O$_2$ is so technically challenging: there are six spin wave branches in each crystallographic domain. As a result, in any experiment one has to deal with a total of twelve spin wave branches, all of which are acoustic and therefore contribute to scattering at low energies. Also, compared to a simple antiferromagnet on a Bravais lattice, the scattering by each individual branch is typically much weaker, since intensity is effectively re-distributed between twelve modes. The existence of a suitable, albeit narrow, measurement window that was exploited in our experiments is a fortunate coincidence.

### Fits to experimental data

The energy of the spin wave branch observed in our experiments clearly goes to zero at the principal magnetic Bragg peaks of the A-type domain. It must therefore be associated with the $S^+(\mathbf{q}, \omega)$ mode and the first term in Eq. 2a. An analysis of the polarization of spin wave excitations is beyond the scope of this work. Nevertheless, we can point out that $(a, b)$ being the spin rotation plane is consistent with a strong $S^+(\mathbf{q}, \omega)$. Indeed, the corresponding polarization factor for unpolarized neutrons is a maximum for in-plane momentum transfers. As a first step in our analysis we ignored all other spin wave branches and used Eq. 1a to fit the experimental data. It is easy to show that there are exactly two sets of exchange parameters that exactly reproduce (i) the experimentally determined incommensurability parameter $\zeta$, (ii) the excitation energies at the zone boundaries $(0.5, 1, 0)$ and $(0.827, 0)$, and (iii) the spin wave velocity along the $b^*$ direction near the magnetic Bragg peaks. Using these two sets of parameters as initial points, we employed a least-squares algorithm to best-fit the data under the rigid constraint set by Eq. 3. The two resulting optimized sets of parameters are listed in Table I and will be referred to as Models 1 and 2, respectively. For a purpose that will be made clear in the next section, we also attempted a fit to the data taken only along the $b$-axis while fixing $J_1 = 0$. The measured $a$-axis dispersion was not included in this fit. The resulting set of exchange constants is also listed in Table I and will be referred to as Model 3. Dispersion relations for the out-of-plane branch and the first term in Eq. 1 calculated for type-A domains using Models 1 through 3 are plotted in lines in Fig. 4.

The next step is to understand why the other 11 spin wave branches were not observed in the studied wave vector and energy ranges. All twelve dispersion curves calculated using Model 1 are plotted in Fig. 6. The intensities of each branch were scaled by the energy transfer (to get rid of the $1/\omega$ factors in Eq. 4) and are plotted in Fig. 6b. The neutron polarization factor was not included in this calculation, and the maximum value (unity) was assumed for each branch. One readily sees that all branches originating from type-B domains and the 1st term in Eq. 2a are extremely weak in our area of interest. The same is true for all spin waves associated with type-A domains and the 2nd term in Eq. 2a. Contributions from type-B domains and the 2nd term in Eq. 2a are either weak or at very high energy. In the end, only the “principal” modes originating from type-B domains and the 1st term in Eq. 2a are relevant to our experiments. Of these three branches the two in-plane modes are almost entirely outside the studied energy range and do not affect any of the scans collected. As a result, only one out-of-plane mode is seen. Similar arguments can be made regarding the dispersion measured along the $a$-axis. The simulation also explains why we were unable to follow the “principal” out-of-plane mode to higher energies. At around 8 meV energy transfer any inelastic scans become crowded with a host of peaks associated with other spin wave branches that can not be reliably resolved due to

| Parameter | Model 1 | Model 2 | Model 3 | LDA$^a$ |
|-----------|---------|---------|---------|---------|
| $J_1$     | 6.4(0.95) meV | 105.5 (8.0) meV | 0 (fixed) | 0.4 meV |
| $J_2$     | -11.9 meV | 33.8 meV | -14.0 meV | -8.1 meV |
| $J_4$     | 7.4 (0.5) meV | -1.6 (0.2) meV | 7.5 (0.1) meV | 14.4 meV |
| $J_3$     | 1.8(0.2) meV | 0.23 (0.02) meV | 6.8 (0.4) meV | 5.7 meV |

$^a$From Ref. 7
$^b$Not refined: fixed by Eq. 5

---

**TABLE I: Sets of exchange constants obtained by fitting the calculated spin wave dispersion relation to the experimental curves in comparison with first-principle calculations.**

The next step is to understand why the other 11 spin wave branches were not observed in the studied wave vector and energy ranges. All twelve dispersion curves calculated using Model 1 are plotted in Fig. 6. The intensities of each branch were scaled by the energy transfer (to get rid of the $1/\omega$ factors in Eq. 4) and are plotted in Fig. 6b. The neutron polarization factor was not included in this calculation, and the maximum value (unity) was assumed for each branch. One readily sees that all branches originating from type-B domains and the 1st term in Eq. 2a are extremely weak in our area of interest. The same is true for all spin waves associated with type-A domains and the 2nd term in Eq. 2a. Contributions from type-B domains and the 2nd term in Eq. 2a are either weak or at very high energy. In the end, only the “principal” modes originating from type-B domains and the 1st term in Eq. 2a are relevant to our experiments. Of these three branches the two in-plane modes are almost entirely outside the studied energy range and do not affect any of the scans collected. As a result, only one out-of-plane mode is seen. Similar arguments can be made regarding the dispersion measured along the $a$-axis. The simulation also explains why we were unable to follow the “principal” out-of-plane mode to higher energies. At around 8 meV energy transfer any inelastic scans become crowded with a host of peaks associated with other spin wave branches that can not be reliably resolved due to
FIG. 6: (a) Dispersion of all twelve spin wave branches along the (0, 0.5, k, 0) reciprocal-space rod in twinned LiCu$_2$O$_2$ crystals calculated using Model 1. (b) The corresponding structure factors scaled by energy transfer. In both panels the out-of-plane modes are plotted in red. Modes shown in blue and green lines are polarized in the plane of spin rotation. Thick and thin lines of all types correspond to the first and second terms in Eq. 2a, respectively. Solid and dashed lines refer to type-A and type-B crystallographic domains. Symbols are as in the top panel of Fig. 4.

limited experimental resolution.

From Fig. 6 it is apparent that the studied energy and wave vector transfer range the dispersion relations produced by Model 2 are virtually identical to those resulting from Model 1. Both models fit the available experimental data rather well. The only small discrepancy is seen along the $a$-direction where the observed spin wave velocity near $\mathbf{q} = (-0.5, 0.827, 0)$ appears slightly larger than calculated, while the zone-boundary energy at $\mathbf{q} = (0, 0.827, 0)$ is slightly smaller. This discrepancy is easily explained if one assumes a small anisotropy-induced gap $\Delta$ in the spin wave spectrum at the magnetic Bragg peak position. From the existing scans it is possible to tentatively estimate $\Delta \approx 1.5$ meV, though more high-resolution data will be needed for a reliable determination. As far as only the $b$-axis dispersion is concerned, Model 3 seems to work just as well as the other two sets of parameters, and for the (0.5, k, 0) reciprocal-space rod produces almost identical curves. However, this good agreement under the constraint $J_1 = 0$ necessarily results in a very poor agreement with the $a$-axis dispersion relation. The corresponding bandwidth calculated using Model 3 (thin dotted line in Fig. 4b) is considerably larger than the observed value. In other words, assuming $J_1 = 0$ in Hamiltonian can not be made consistent with the bulk of the experimental data.

The resulting parameter values for Model 1 were used to simulate the measured inelastic neutron scans. For this purpose we utilized the magnetic dynamic structure factor as given by Eq. 6a. This model cross section was scaled by the magnetic form factor for Cu$^{2+}$ and numerically convoluted with the 4-dimensional spectrometer resolution function. The latter was calculated in Gaussian form using the Cooper-Nathans approximation. The evolution of the corresponding FWHM resolution ellipsoid in the surveyed areas of $(E, \mathbf{q})$ space is shown in Fig. 4. An overall scaling factor was chosen to best-fit the measured scans. The results of such simulations are shown in solid lines in Figs. 2–5. Overall, the experimental peak shapes are well explained by resolution effects alone.

IV. DISCUSSION

As mentioned in the introduction, the knowledge of spin wave dispersion in an ordered magnetic material can, in principle, provide comprehensive information on the exchange interactions. This requires measurements of dispersion curves across the entire Brillouin zone. In the particular case of LiCu$_2$O$_2$, twinning, less than perfect sample mosaic, and a complex spectrum limit us to only observing spin waves in the direct proximity of the principal magnetic Bragg reflections. For this reason the resulting sets of parameters can be regarded as unique only under the assumption of the validity of Hamiltonian and the SWT approximation.

The Hamiltonian has a solid justification in the crystal structure, and is well supported by first-principle calculations. However, a vital question is to what extent an analysis based on essentially classical spin wave theory can be valid in the case of a quasi-low-dimensional frustrated magnet such as LiCu$_2$O$_2$? At the very least, the exchange constants obtained from such an analysis will be renormalized compared to their actual values due to quantum corrections. Nevertheless, even for highly anisotropic or frustrated systems, acoustic modes can be associated with waves in the order parameter field. In this case a renormalized SWT with some effective set of exchange parameters typically works rather well. Just two examples are the weakly-coupled $S = 1/2$ chains compound KCuF$_3$ (Ref. 14) and the quasi-2D frustrated
helimagnet Cs$_2$CuCl$_4$. Deviations from classical behavior in LiCu$_2$O$_2$ do not appear particularly severe. The typical energy scale of exchange interactions computed by LDA exceeds the temperature of 3D long-range ordering by less than an order of magnitude. While the absolute value of the ordered moment has not been determined to date, that in the very similar helimagnet NaCu$_2$O$_2$ is quite large (0.64 $\mu_B$). We therefore have good reason to assume that renormalized SWT will work well for our system.

Turning now to the two solutions that we obtained we note that Model 2 almost exactly corresponds to the simple $J_1 - J_2$ model that we originally proposed. However, unless the renormalization of exchange parameters is severe and all actual in-chain exchange constants are much smaller than the effective SWT ones, the estimated parameters are not consistent with a previous analysis of magnetic susceptibility. We thus conclude that Model 1 is a much more likely to be an adequate description of LiCu$_2$O$_2$. It’s key features, namely a ferromagnetic $J_2$ bond and a substantial $J_4$ coupling constant, are similar to those of the LDA calculations of Ref. 1. Geometric frustration in LiCu$_2$O$_2$ is thus similar to that in NaCu$_2$O$_2$.

The main difference between the exchange parameters in Model 1 and those emerging from LDA calculations of Ref. 2 is in the magnitude of $J_1$. As illustrated by Model 3, assuming that $J_1$ is negligibly small makes the SWT calculation incompatible with the measurements. We conclude that either LDA severely underestimate $J_1$, or this exchange constant is renormalized by over an order of magnitude in the SWT. Of course, one can never entirely rule out the possibility that both the LDA calculations and our SWT analysis are missing some crucial terms in the Hamiltonian. Further experimental and theoretical insight will be required to fully resolve this remaining mystery.

V. CONCLUSION

In summary, based on inelastic neutron scattering measurements we can conclude that the simple $J_1 - J_2$ model that we originally proposed does not apply to LiCu$_2$O$_2$. The frustration mechanism is more complex and resembles that proposed in Refs. 5, 10. It involves a competition between a combination of antiferromagnetic $J_1$ and ferromagnetic $J_2$ interactions against an additional antiferromagnetic long-range $J_4$ coupling. We find the three corresponding exchange constants to be of comparable absolute strength. This discrepancy between an SWT-based interpretation of the experimental data and first-principle calculations remains to be explained.

Acknowledgments

One of the authors (AZ) would like to thank A. Drechsler for numerous insightful discussions on the subject and for his constructive comments on Ref. 6. This work was partially supported by the Civilian Research and Development Foundataion project RU-P1-2599-04. Work at ORNL was carried out under Contracts No. DE-AC05-00OR22725, US Department of Energy. Part of this work was done at the Swiss Neutron Spallation Source SINQ, Switzerland.

1. A. M. Vorotynov et al., JETP 86, 064424 (1998); J. Magn. magn. Mater. 188, 233 (1998).
2. F. Fritschij, H. Brom, and R. Berger, Solid State Commun. 107, 719 (1998).
3. S. Zvyagin et al., Phys. Rev. B 66, 064424, (2002).
4. A. A Zatsepin et al., Phys. Rev. B 57, 4377 (1998).
5. B. Roessli et al., Physica B 296, 306 (2001).
6. T. Masuda, A. Zheludev, A. Bush, M. Markina, and A. Vasiliev, Phys. Rev. Lett. 92, 177201 (2004).
7. A. A. Gippius, E. N. Morozova, A. S. Moskvin, A. V. Zalessky, A. A. Bush, M. Baenitz, H. Rosner, and S.-L. Drechsler, Phys. Rev. B 70, 020406 (2004).
8. C. K. Majumdar and D. K. Ghosh, J. Math. Phys. 10, 1388 (1969); B. S. Shastry and B. Sutherland, Phys. Rev. Lett. 47, 964 (1981); F. D. M. Haldane, Phys. Rev. B 25, 4925 (1982); S. R. White and I. Affleck, Phys. Rev. B 54, 9862 (1996); A. A. Aligia, C. D. Batista and F. H. L. Essler, Phys. Rev. B 62, 3259 (2000) and references therein.
9. T. Tonegawa and I. Harada, J. Phys. Soc. Jpn. 56, 2153 (1987); R. Chitra et al., Phys. Rev. B 52, 6581 (1995).
10. S.-L. Drechsler, J. Miek. J. Richter, A. S. Moskvin, A. A. Gippius, H. Rosner, H., cond-mat/0411753.
11. L. Capogna, M. Mayr, P. Horsch, M. Raichle, R. K. Kremer, M. Sofin, A. Maljuk, M. Jansen and B. Keimer, cond-mat/0411753.
12. See, for example, T. Nagamiya, Solid State Physics, Academic Press, New York, 1967, Vol. 20, p. 305.
13. R. Coldea D. A. Tennant, and Z. Tylczynski, Phys. Rev. B 68, 134424 (2003).
14. D. A. Tennant, S. Nagler, D. welz, G. Shirane, and K. Yamada, Phys. Rev. B 52, 13381 (1995).