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Competing exchange interactions in Li_2CuO_2

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PACS. 75.25+z – Spin arrangements in magnetically ordered materials (including neutron and spin-polarized electron studies, synchrotron-source X-ray scattering, etc.).
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Abstract. – The dispersion of the spin-waves in single crystals of Li_2CuO_2 has been investigated by means of inelastic neutron scattering. The results yield a single spin-wave branch characterized by a large gap $\Delta = 1.4$ meV at the zone centre due to easy-axis uniaxial anisotropy. Linear spin-wave theory is used to obtain the exchange integrals in this material. It turns out that the nearest-neighbor exchange interactions in the basal plane are antiferromagnetic leading to frustration between the magnetic moments. Our results show that Li_2CuO_2 is an $S = 1/2$ antiferromagnetic insulator with competing interactions.

For 1-dimensional compounds with half-integer ($S = 1/2$) spins and strong antiferromagnetic interactions, theory predicts that for a vanishing small ratio of intra (J) to interchain (J') coupling, Néel order is favored over singlet ground state [1]. Recent elastic neutron diffraction and muon spin relaxation measurements revealed low Néel ordering temperatures and strongly reduced magnetic moments in the prototype quantum 1-dimensional antiferromagnets Sr_2CuO_3 and Ca_2CuO_3 [2]. These results are in agreement with the predictions of the chain mean-field theory [3] that the size of the staggered magnetisation scales with the coupling ratio J'/J. Competitive exchange interactions can also lead to a drastic reduction of the ordering temperature and of the magnetic moment as recentely observed in the zig-zag chain compound $SrCuO_2$ [4]. In that context, Li_2CuO_2 represents an interesting case as it has $S = 1/2$ spins arranged in chains while the magnetic moment at saturation is close to the value of the free Cu^{2+} ion $\mu = 1\ \mu_B$ [5].

The chemical structure of Li_2CuO_2, as previously investigated with X-ray [6] and neutron diffraction [5] techniques, consists of square planar CuO_4 structural units that share common

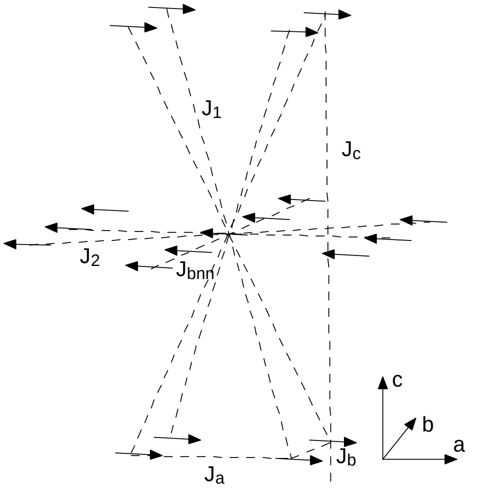

Fig. 1

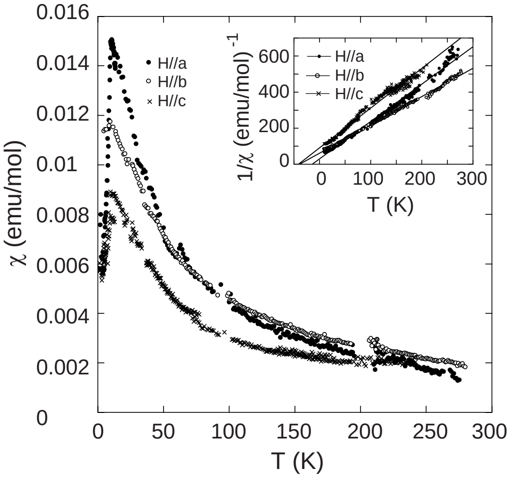

Fig. 2

Fig. 1. – The magnetic structure of Li_2CuO_2. The arrows indicate the direction of the magnetic moments on the Cu^{2+} ions.

Fig. 2. – Susceptibility measurements of Li_2CuO_2 showing the transition to 3-dimensional antiferromagnetic ordering at $T_N \approx 9$ K. Fitting to the inverse susceptibility as shown in the insert gives values of $\theta_N = -15 \pm 3$ K, $\theta_N = -39 \pm 4$ K and $\theta_N = -41 \pm 3$ K along a, b and c, respectively, while μ_{eff} has the values $2.0 \pm 0.1\,\mu_B$, $2.3 \pm 0.1\,\mu_B$, and $1.9 \pm 0.1\,\mu_B$ along the respective axes.

edges to form chains of Cu^{2+} ions along the b-axis, separated by Li-O groups along the c-axis. The accepted picture of the magnetic structure of Li_2CuO_2 is shown by arrows on the Cu^{2+} ions in fig. 1 together with the exchange interactions used for the model calculation. Ferromagnetic sheets of Cu^{2+} ions in the (a,b)-plane with spins directed parallel to the a-axis are layered antiferromagnetically along the c-axis [5]. As the superexchange pathways along the b-axis are mediated by a 94° Cu-O-Cu bond, a first assumption was that Li_2CuO_2 should be an ideal candidate to exhibit 1D ferromagnetic properties in the paramagnetic phase. From an analysis of the high-temperature specific heat Okuda *et al.* [7] obtained an intrachain exchange interaction $J/k = 15$–30 K which supported the above argument. On the other hand, magnetic-susceptibility results [8] (see fig. 2) show a large Curie-Weiss constant $\Theta \approx -40$ K indicating that the magnetic interactions are predominantly antiferromagnetic. Antiferromagnetic resonance experiments [9] performed below the Néel temperature $T_N \approx 9.5$ K have shown that the largest exchange interaction in Li_2CuO_2 is antiferromagnetic and couples the spins along the body diagonal.

The single crystals studied here were grown via the floating-zone technique associated with an infrared image furnace. Seed crystals were used for oriented growth at a controlled rate of 3 mm/h in 1 atm of flowing oxygen. The susceptibility results in fig. 2 characterise the Néel transition $T_N = 9.4$ K. The main goal of the experiments reported here was the measurements of spin-wave excitations in Li_2CuO_2 below T_N via inelastic neutron scattering. The measurements were performed at the IN3 thermal neutron triple-axis spectrometer at the Institut Laue-Langevin, France. The experimental configuration consisted of a vertically focusing PG002 monochromator and a horizontally focusing PG002 analyser with fixed final energy $E_F = 13.7$ meV (FWHM resolution = 0.75 meV). In a separate experiment on the same crystal, measurements were recorded with the energy of the analyzer kept fixed at 5 meV

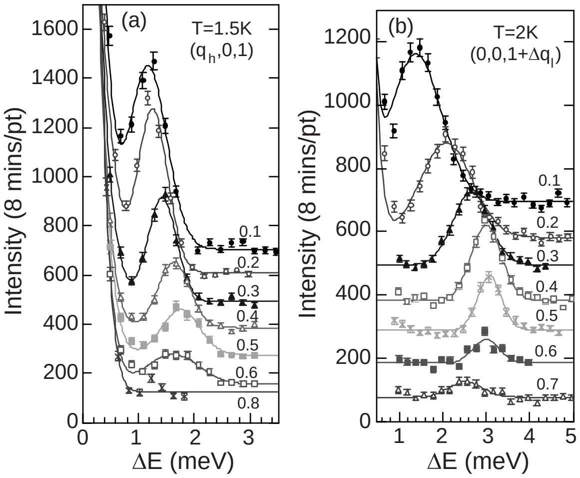

Fig. 3

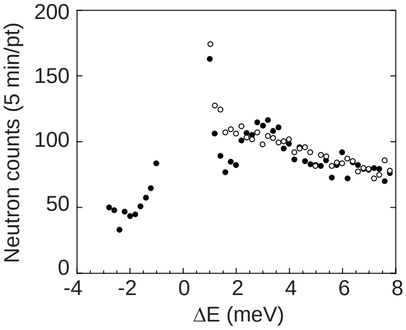

Fig. 4

Fig. 3. – spin-waves measured in Li_2CuO_2 along three symmetry directions (a) [100], (b) [001] from the magnetic zone centre $\mathbf{Q} = (0, 0, 1)$. The lines are Gaussian fits to the data.

Fig. 4. – A typical scan along the b-direction in Li_2CuO_2. This measurement at $\mathbf{Q} = (0, 0.85, 2)$ and $T = 1.5$ K, shows a broad, heavily damped excitation. Above T_N this excitation diminishes slightly and moves closer to the peak at $\Delta E = 0$. ● 1.5 K, ○ 10 K.

yielding a vanadium width of 0.25 meV. In that configuration a berillyum filter was used to suppress the $\lambda/2$ contamination. All the scans were recorded in the constant Q-mode. In contrast to measurements along the [1,0,0], [0,0,1] and [1,0,1], where the excitations are resolution-limited (see fig. 3), the spin waves in the [010] direction are heavily damped, as can be seen from the typical scan shown in fig. 4.

Figure 5 summarises the spin-wave dispersion curves that have been measured in Li_2CuO_2 at $T = 1.5$ K. A feature of the data is that while the dispersion along the c-axis is the steepest as a consequence of strong interchain coupling, the dispersion along the chain direction is weak. Moreover, the latter exhibits a minimum not only at the magnetic zone centre but also

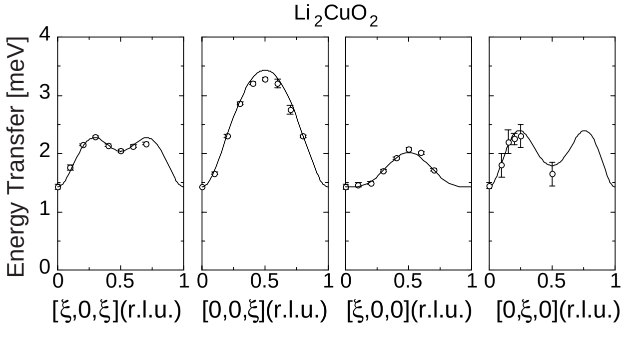

Fig. 5. – Dispersion of the spin-waves in Li_2CuO_2 at $T = 1.5$ K. The symbols indicate the measured data while the line corresponds to the calculation, as explained in the text.

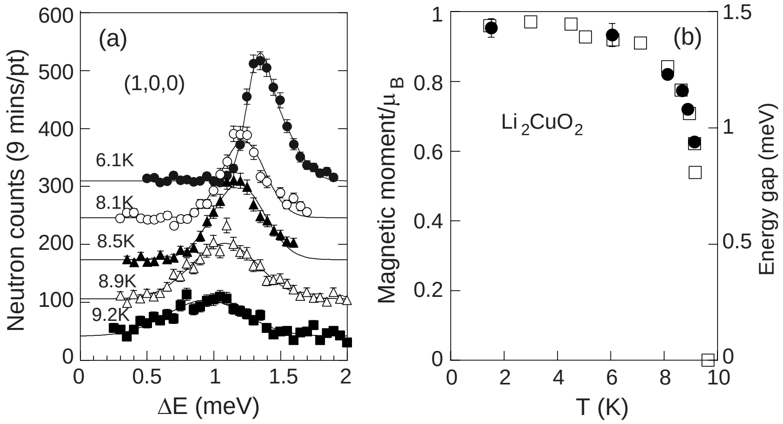

Fig. 6. – Temperature dependence of the spin-wave gap at $\mathbf{Q} = (1, 0, 0)$ in Li_2CuO_2. Constant-$\mathbf{Q}$ scans measured with $E_F = 5$ meV are shown in (a) from 6 to 9.2 K, while (b) contrasts the evolution of the spin-gap position (filled circles, right vertical axis) with the sublattice magnetisation (open circles, left vertical axis). The magnetistation has been measured by recording the intensity of the (0,0,1) Bragg reflection as a function of the temperature.

at $\mathbf{Q} = (0, 0.5, 0)$, indicating that the magnetic structure of Li_2CuO_2 is close to instability. The spectrum of the magnetic excitations of Li_2CuO_2 is characterised by the appearance of a large gap of $\Delta = 1.4 \pm 0.1$ meV at the zone centre that diminishes rapidly as T approaches T_N from below, as shown in fig. 6(a). The temperature dependence of the energy gap follows the sublattice magnetisation, as shown in fig. 6(b).

As for $S = 1/2$ spins, dipolar interactions are weak, the data were interpreted using a Hamiltonian operator that includes uniaxial anisotropy along the spin direction,

$$H = \sum_{i,j} J_{i,j} \vec{S}_i \cdot \vec{S}_j + \sum_{i,j} J''_{i,j} S^z_j S^z_j \, . \tag{1}$$

Within linear spin-wave theory, the dispersion of the magnetic excitations is given by

$$h\omega(\vec{q}) = S\sqrt{(I(\vec{q}) + J(0) - I(0) + D)^2 - J^2(\vec{q})} \, , \tag{2}$$

where $S = 1/2$, $J(q)$ and $I(q)$ are the Fourier transforms of the inter- and intra-sublattice exchange integrals, respectively, and $D = J''(0) - I''(0)$ is the effective staggered field that acts as a uniaxial anisotropy. Using eq. (2), the exchange constants in Li_2CuO_2 were obtained with a Monte Carlo fit procedure. In a first calculation, we introduced nearest-neighbour exchange interactions, J_a, J_b, J_c, along the main symmetry directions, J_1 along the body diagonal, and J_2 along the (1/2, 1/2, 0)-direction (see fig. 1). It turned out that ferromagnetic next–nearest-neighbour interactions, $J_{b\mathrm{nn}}$ along the chain direction had to be included also to obtain good agreement between the data and the model. These final parameters are listed in table I.

The nearest-neighbour exchange interactions are all antiferromagnetic in Li_2CuO_2. In particular, the antiferromagnetic interaction, J_b, contradicts the assumption that a 94° Cu-O-Cu bond is *a priori* ferromagnetic. Li_2CuO_2 joins the growing number of exceptions to this rule which consist mainly of a number of copper chloride salts for which the bridging angle is only slightly larger than 90° [10]. On the other hand, the intersublattice interaction J_1 is the largest and the value obtained in the present work compares well with $J_1 = 3.9\ \mathrm{cm}^{-1}$

TABLE I. – *Exchange integrals in* Li_2CuO_2.

J_1 (meV)	J_2 (meV)	J_a (meV)	J_b (meV)	J_c (meV)	J_{bnn} (meV)	D (meV)
−0.39	−0.08	−0.18	−0.24	0.0	0.16	−0.31
±0.01	±0.02	±0.01	±0.01	±0.02	±0.04	±0.01

that has been previously measured by antiferromagnetic resonance [9]. A source of frustration arises in Li_2CuO_2 from competition between the antiferromagnetic J_2 interaction and the nearest-neighbour exchanges J_a and J_b which tend to align the spins antiferromagnetically along the a- and b-axes, respectively. However, the antiferromagnetic interaction J_2 is sufficiently important to force the spins into a ferromagnetic arrangement in the (a, b)-plane. Only then, can the stability conditions for the magnetic structure of Li_2CuO_2 with the propagation vector $\mathbf{K} = [0, 0, 1]$ be fulfilled ($J_c = 0$)

$$\begin{aligned} &J_1 < 0\,, \\ &J_a + 2J_2 - J_1 > 0\,, \\ &J_b + 4J_{\text{bnn}} + 2J_2 - J_1 > 0\,. \end{aligned}$$

The large anisotropy ($D = -0.3$ meV) in Li_2CuO_2 is mainly due to anisotropy between the tensor components of the exchange interactions along the spin direction $J^{xx}_{i,j} = J^{yy}_{i,j} \neq J^{zz}_{i,j}$ which acts as an effective field and tends to align the spins along the a-axis. Within spin-wave theory, orthorhombic anisotropy ($J^{xx}_{i,j} \neq J^{yy}_{i,j} \neq J^{zz}_{i,j}$) would lift the twofold degeneracy of the spin-wave branches as well as producing a gap at the zone centre in the spectrum of the magnetic excitations. As neutrons are scattered by magnetic fluctuations that are perpendicular to the scattering vector $\mathbf{Q}$, the scans shown in fig. 7 probe spin fluctuations parallel to both the b- and c-axes when $\mathbf{Q} = (1, 0, 0)$, while only fluctuations parallel to the c-axis are observed at $\mathbf{Q} = (0, 0, 1)$. As can be seen from the figure, the splitting of the two branches is less than 0.2 meV. Within the resolution of the present experiment, this corresponds to a vanishing

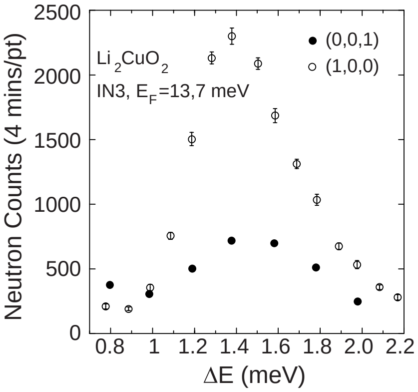

Fig. 7. – Comparison of neutrons scattered at the zone centre $\mathbf{Q} = (1, 0, 0)$ which probe spin fluctuations parallel to both the b- and c-axis with spin waves measured at $\mathbf{Q} = (0, 0, 1)$. At this momentum transfer only fluctuations along the b-axis appear in the neutron cross-section.

anisotropy between the (x, x) and (y, y)-components of the exchange interactions.

In conclusion, the values of the nearest-neighbour exchange constants are found to be antiferromagnetic in Li_2CuO_2. These results show that Li_2CuO_2 is a model $S = 1/2$ antiferromagnetic insulator with competing interactions. The easy-axis anisotropy produces a large gap in the energy spectrum of the magnetic excitations in Li_2CuO_2 and is therefore responsible for the small reduction of the magnetic moment in Li_2CuO_2 at saturation from the value of the free $S = 1/2$ Cu^{2+} ion.

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