Ferromagnetically coupled Shastry-Sutherland quantum spin singlets in \((\text{CuCl})\text{LaNb}_2\text{O}_7\)

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Using inelastic neutron scattering, x-ray, neutron diffraction, and the first-principle calculation techniques, we show that the crystal structure of the two-dimensional quantum spin system \((\text{CuCl})\text{LaNb}_2\text{O}_7\) is orthorhombic with \(Pbam\) symmetry in which \text{CuCl}_2\text{O}_2 octahedra are tilted from their high symmetry positions and the \text{Cu}^{2+} (s = 1/2) ions form a distorted square lattice. The dominant magnetic interactions are the fourth nearest neighbor antiferromagnetic interactions with a \text{Cu}-\text{Cl}–\text{Cl}–\text{Cu} exchange path, which lead to the formation of spin singlets. The two strongest interactions between the singlets are ferromagnetic, which makes \((\text{CuCl})\text{LaNb}_2\text{O}_7\) the first system of ferromagnetically coupled Shastry-Sutherland quantum spin singlets.

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Quantum magnets continue to attract interest due to the wide range of exotic ground states and excitations that they display.\(^1\) Such magnets usually have magnetic ions with low spin values (typically spin-1/2 or 1) which are coupled by low-dimensional and/or frustrated magnetic interactions. A quantum magnet that has attracted a lot of theoretical interest is the square lattice. Here the magnetic \text{Cu}^{2+} ions which possess spin moment \(S=1/2\) are octahedrally co-ordinated and form \text{CuCl} planes well separated by \text{LaNb}_2\text{O}_7 layers. The crystal symmetry was originally found to be tetragonal with space group \(P4/mmm\) and one copper ion per unit cell (\(a = b = 3.88\) Å) forming an ideal undistorted square lattice of \(S = 1/2\) ions with uniform \(J_1\) and \(J_2\).\(^2\) Theory suggests that \((\text{CuCl})\text{LaNb}_2\text{O}_7\) would have long-range magnetic order which is ferromagnetic or antiferromagnetic depending on the ratio of the two exchange constants.\(^3\) Gapped excitations are not expected except for a very limited region of the phase diagram when the ratio of interactions along the diagonal to those along the square are \(\approx 0.5\) while a gapless spin disordered phase is predicted when this ratio is \(\approx -0.5\).\(^4\) However the experimental data appears to contradict the theory, heat capacity and magnetization measurements suggested that the ground state is in fact a singlet and that the excitations are gapped.\(^5\) Neutron scattering also revealed the absence of long range magnetic order and showed that the excitations are gapped and centered at 2.3 meV.\(^6\) Such behavior is typical of a dimerised magnet where a dominant antiferromagnetic exchange interaction couples the spins into dimer pairs with no net moment and a finite energy is required to break up the dimers and create a triplet \((S = 1)\) excitation. However such dimerization is incompatible with the high crystal symmetry where \(J_1\) and \(J_2\) are uniform and the spins cannot be paired.

This paper describes a reinvestigation of the crystal structure and shows that the space group is in fact orthorhombic \((Pbam)\) with a unit cell that is doubled along both directions within the \(ab\)-plane compared to the original tetragonal symmetry, thus allowing for dimerisation. The \text{Cu}-\text{Cl} bonds are considerably distorted and band structure calculations reveal highly spatially anisotropic exchange interactions and predict dimerisation between fourth neighbour ions, in agreement with our inelastic neutron scattering data. The resulting magnetic structure is best described as antiferromagnetic dimers which...
are coupled together by frustrated ferromagnetic interactions in a Shastry-Sutherland type arrangement.

A 15 g powder sample of (CuCl)LaNb$_2$O$_7$ was synthesized by an ion-exchange reaction using a powder mixture of RbLaNb$_2$O$_7$ and CuCl$_2$ with a molar ratio of 1:2 heated at 335 °C for one week, as described previously.[3] Concerning single-crystal samples, precursor CsLaNb$_2$O$_7$ single crystals (see Ref. [10]) with typical size of 0.5 × 0.5 × 0.1 mm$^3$ were embedded in a molar excess of CuCl$_2$ powder (99.99%) sealed in an evacuated tube and reacted at 340 °C for one week. The mixture was then washed with distilled water to remove the byproducts and unreacted CuCl$_2$. The square, plate-like dark green crystals of (CuCl)LaNb$_2$O$_7$ were then dried overnight at 120 °C. The Energy Dispersive Spectroscopy (EDS) study revealed the absence of the Cs atoms, indicating that the ion exchange reaction occurs completely even for the single crystal.

A CCD and a 4-circle diffractometers were used for the single-crystal data collection at 293 and 14 K, respectively. Diffraction patterns of the powder were measured at room and low temperature using synchrotron light with $\lambda = 0.77749$ Å at BL02B2 beamline at SPring-8 as well as neutron beam with $\lambda = 1.9085$ Å at D1A at ILL. Powder inelastic neutron scattering measurements were done with $\lambda = 3.8$ Å at the Disk-Chopper-Spectrometer (DCS) at NCNR, NIST under an external magnetic field. The crystal structure was solved by direct methods against single crystal data and further refined by taking into account the twinning due to the pseudo-symmetry. The structural parameters were optimized by a Rietveld refinement against neutron diffraction data, more sensitive for O and Cl atoms. All the refinements were carried out by the means of the JANA2000 refinement program [11].

Fig. 1 (a) shows the inelastic neutron scattering data as a function of energy transfer, $h\omega$. In the absence of an external magnetic field, $B = 0$ T, a single peak is observed centered at $h\omega = 2.22(1)$ meV in agreement with previous work.[3] An external magnetic field of $B = 11.5$ T splits this peak into three peaks at $h\omega = 1.19(1)$, 2.45(3), and 3.95(11) meV. The energies are consistent with the Zeeman splitting expected for a magnon excitation with spin $S = 1 (g\mu_B S, B)$ thus confirming that the excitations are due to a transition from a singlet ground state to a triplet excited state and implying that the spins in (CuCl)LaNb$_2$O$_7$ are paired into dimers where the dimer exchange constant is $\approx 2.22$ meV. In zero field the excitation extends in energy from $\sim 1.2$ meV to $\sim 3.0$ meV and is thus much broader than the resolution (0.16 meV) implying that it is dispersive due to interactions between dimers. Indeed the lower edge of the excitation is consistent with the critical field of $B_{c1} = 10.3$ T from magnetization measurements, for condensation of magnons into the ground state.[8]

The nature of the spin dimers in (CuCl)LaNb$_2$O$_7$ can be obtained from the wavevector-dependence of the triplet excitations, $I(Q)$. As shown in Fig. 1 (b), the $Q$-dependence exhibits a prominent peak centered at $Q_c \approx 0.5$ Å$^{-1}$. If we assume the dimers are non-interacting, the $Q$-dependence of their excitation goes as $1 - \sin(Qd)/Qd$ where $d$ is the intradimer distance. The best fit of the data to the isolated spin dimer model was obtained with $d = 8.4(2)$ Å (black line in Fig. 1 (b)) in agreement with previous work.[4] The model reproduces the observed peak position of $Q_c \sim 0.5$ Å$^{-1}$ well. This reveals that the dominant magnetic interactions are between the Cu$^{2+}$ ions that are separated much further than the nearest neighbor distance of 3.88 Å, a result that is inconsistent with the currently accepted structure of (CuCl)LaNb$_2$O$_7$.

To understand this unusual $Q$-dependence, we have reinvestigated the crystal structure in great detail. Fig. 2 (a) shows the CCD image of the diffraction data taken for

![FIG. 1: Inelastic neutron scattering data obtained at 70 mK from the powder sample. (a) Energy dependence of the triplet excitations for $B = 0$ T (blue) and $B = 11.5$ T (red). (b) $Q$-dependence for $B = 0$ T. Lines are described in the text.](image-url)
indicating that the real unit cell is 2
structure, half-integer superlattice spots are also found,
the allowed integer peaks for the
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FIG. 2: Single crystal laboratory X-ray and powder neutron
diffraction data of (CuCl)LaNb2O7. (a) the X-ray CCD im-
age of the ab-plane at 14 K. The single crystal was twinned,
thus a- and b-axes are interchangeable. The spots with green
circles are the allowed integer Bragg reflections for the ori-
ginal tetragonal structure, the other spots are the half-integer
reflections. (b) Neutron diffraction pattern at 2 K. Dots are
the data, solid line is the fit to the orthorhombic structure,
and the line on the bottom panel is the difference between
the data and the model. The indices of the reflections in the
inset are in the tetragonal notation.

the (h00) plane at 14 K. Note that the crystal is twinned
and thus h and k are interchangeable. In addition to
the allowed integer peaks for the P4/mmm tetragonal
structure, half-integer superlattice spots are also found,
indicating that the real unit cell is 2a \times 2b \times c
compared to the tetragonal unit cell. Similar superreflections
are also observed in the powder synchrotron x-ray and
neutron diffraction (see Fig. 2 (b)). Furthermore, the
CCD image shows that the superlattice peaks (odd h,0,0)
and (0,odd k,0) are absent in the orthorhombic notation
(red arrows). This extinction condition tells us that the
crystal structure is orthorhombic with either Pbam or
Pbca space group. The best fit to the x-ray and neutron
diffraction data was obtained with the Pbam structure.
Table I lists the optimal structural parameters from the
neutron diffraction data that are more sensitive to the
Cl and O atoms than the x-ray data. The validity of
the structural analysis is further supported by the bond
valence sum calculation for copper yielding +2.02. A
comparison of diffraction patterns at different tempera-
tures revealed that no structural phase transition occurs
below 293 K.

The refined orthorhombic crystal structure differs
markedly from the tetragonal structure previously re-
ported. While the NbO6 octahedra align with the axes in
the tetragonal structure they are strongly tilted in the
orthorhombic structure particularly around the a-axis in
a staggered manner. Furthermore, the Nb ions are shifted
along the c-axis from the center of the octahedron. The
tilting pattern of the NbO6 strongly influences the po-

the (a) Magnetic exchange interactions in the ab-plane of
(CuCl)LaNb2O7. The blue, green, and red spheres rep-
sitions of both the copper and chlorine atoms. In particular, the chlorine atoms move significantly along the b-direction and slightly along the a-direction from their tetragonal position, probably to reduce Coulomb repulsion between chlorine and apical oxygen atoms. The Cu ions occupy the 4h sites. Along the a-direction, they are mostly transversally displaced, i.e., along the b-axis, yielding the distance between the nearest neighbor Cu-Cu ions to be 3.626 Å and 4.129 Å along the b-axis and 3.885 Å along the a-axis. The copper ion is coordinated octahedrally by two oxygen ligands with a distance of 1.865 Å as well as four chlorine ligands with two shorter bonds (2.386 Å, 2.389 Å) and two longer bonds (3.136 Å, 3.188 Å). When the local z- and x-axes for each Cu$^{2+}$ ion are taken along the Cu-O and the short Cu-Cl bonds, respectively, the overall symmetry of the magnetic orbital including the ligand p-orbitals has the $z^2 - x^2$ character. As a result, the spin exchange interactions in the CuCl layer become highly anisotropic.

As for the spin exchanges of (CuCl)LaNb$_2$O$_7$, we consider Cu-Cu-Cu and Cu-Cl-Cu superexchanges. In general, one expects that the Cu-Cu-Cu exchange is ferromagnetic if the bond angle is close to 90°, and antiferromagnetic if it deviates from 90°. However, when a Cu-Cu-Cu exchange path contains a long Cu-Cu bond (represented by Cl-Cu-Cl in Table II), the exchange becomes ferromagnetic even if the Cl-Cu–Cl angle deviates considerably from 90° because the magnetic orbital is not contained in the long Cu-Cu bond. The Cu-Cl-Cu spin exchange should become more strongly antiferromagnetic with increasing Cu-Cl-Cu angle and shortening Cl-Cl contact distance so that the overlap between the Cl 3p orbitals in the Cl-Cl contact becomes large. The six exchanges considered in our study are listed in Table II and described in Fig. 4 (a). To evaluate these exchanges, we determine the relative energies of seven possible ordered spin states of (CuCl)LaNb$_2$O$_7$ (see Fig. 4 (b)) on the basis of density functional calculations employing the frozen-core projector augmented wave method [13][14] encoded in the VASP [17] with the generalized-gradient approximation (GGA) for the exchange-correlation functional [15]. The GGA plus on-site repulsion U (GGA+U) method [11] with effective U = 4 eV was used to properly describe the strong electron correlation of the Cu 3d states. By mapping the relative energies of the seven states determined from the GGA+U calculations onto the corresponding energies determined from the spin Hamiltonian defined in terms of the six exchanges, we obtain their values listed in Table II. The fourth nearest neighbor (NN) interaction, $J_4$, of the Cu-Cl-Cu exchange type is the strongest and antiferromagnetic. The other fourth NN coupling $J_3$ is also antiferromagnetic, but is much weaker than $J_4$: $J_4/J_3 = 0.18$. This is because $J_4$ has a larger Cu-Cl-Cu angle and a shorter Cl-Cl distance than $J_3$: 164.9° and 3.835 Å for $J_4$ vs. 156.0° and 4.231 Å for $J_3$. All other $J$s are ferromagnetic. The strengths of the six exchanges decrease in the order, $J_4 > J_1a > J_2a > J_3 > J_{2b} > J_{1b}$.

The fact that $J_4$ is both the strongest interaction and is antiferromagnetic explains the long standing mystery of the spin singlet formation in (CuCl)LaNb$_2$O$_7$: the distance between the Cu ions connected by $J_4$ is indeed $r = 8.533$ Å, consistent with the intradimer distance obtained by the isolated spin dimer model. To improve the model we considered the exchange paths $J_{1a}$ and $J_{2a}$ in addition to $J_4$ and fitted the inelastic neutron scattering data to the first moment sum rule for powder data [20].

$$\langle E(Q) \rangle = \frac{\hbar^2}{2m} \int d\omega \int d\Omega \omega S(\omega, \omega) d\omega d\Omega \propto - \sum_{s} \langle S_0 \cdot S_{d_s} \rangle |J_{Cu^{2+}}(Q)|^2 \left( 1 - \frac{\sin(Qd_s)}{Qd_s} \right).$$

In this equation the integration is over solid angle and energy, $J_s$ is the exchange constant coupling the $s^{th}$ nearest neighbor spins, $d_s$ is their separation and $\langle S_0 \cdot S_{d_s} \rangle$ is the two spin correlation function for this pair. From this expression it is clear that each coupling constant $J_s$ produces a modulation in the first moment with a periodicity depending on the separation $d_s$ of the spins. Therefore the dominant exchange interactions can be deduced but the magnitude of the exchange constant cannot be determined because the fitted quantity is the product of the exchange constant and the spin correlation function. The best fit was obtained with $J_4 \langle S_0 \cdot S_{d_4} \rangle = 0.027(2)$, $J_1a \langle S_0 \cdot S_{d_1a} \rangle = 0.011(2)$ and $J_2a \langle S_0 \cdot S_{d_2a} \rangle = 0.005(2)$. Note that the ground state obtained by the first principle calculations is the AF3 state shown in Fig. 4 (b), and thus a positive value of $J_s \langle S_0 \cdot S_{d_s} \rangle$ indicates that the spin correlation agrees with the sign of the exchange constant, i.e., the spins are parallel for a ferromagnetic interaction and antiparallel for an antiferromagnetic interaction. The fit is much better than that of the simple dimer model, and the fitted parameters are consistent with our first principle calculation results. This indicates that in (CuCl)LaNb$_2$O$_7$ the fourth nearest neighbor Cu$^{2+}$ ions form spin singlets, which are arranged orthogonally in the ab-plane, while the coupling between them is primarily ferromagnetic. Thus, the spin lattice of (CuCl)LaNb$_2$O$_7$ is best described as ferromagnetically coupled Shastry-Sutherland quantum spin singlets.

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