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Incommensurate antiferromagnetic order in the $S = \frac{1}{2}$ quantum chain compound $LiCuVO_4$

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Abstract

The linear spin chain ($S = \frac{1}{2}$) compound $LiCuVO_4$ was investigated by elastic neutron diffraction, susceptibility and heat-capacity measurements on single crystals. Long-range incommensurate magnetic ordering with a propagation vector $k = (0,0.532,0)$ is observed below 2.1(1) K by elastic neutron diffraction. The refinement of the magnetic structure indicates that the Cu^{2+} moments lie within the *ab*-plane, to enclose an angle of $\sim 90^\circ$ to each other along the chain, and have a magnitude of $0.31(1)\mu_B$. These findings are attributed to the competition of nearest- and next-nearest-neighbour exchange coupling in the edge-sharing CuO_2 chains.

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Keywords: Incommensurate afm order; Quantum chain compound; Neutron diffraction; Heat capacity

1. Introduction

Stimulated by the vivid search for a theoretical understanding of high-T_C superconductivity, the magnetic properties of low-dimensional quantum antiferromagnetic (afm) systems that contain $S = \frac{1}{2}$ moments on Cu^{2+}, V^{4+} or Ti^{3+} ions have attracted increasing attention in the last 10 years. Unusual ground-state properties have been seen to evolve due to the proximity of such systems to quantum criticality via mainly a considerable sensitivity to higher-order effects in the exchange coupling and also to coupling to lattice or charge degrees of freedom. For example, the spin-Peierls transition observed in the inorganic one-dimensional Heisenberg antiferromagnet $CuGeO_3$ generates a non-magnetic singlet ground-state below ≈ 14 K, which was suggested to arise from the interplay of the nearest-neighbour (NN) and the next-nearest-neighbour (NNN) Cu–Cu superexchange and magnetoelastic coupling [1,2].

$LiCuVO_4$ ($\equiv V[LiCu]O_4$) in the standard spinel notation) crystallizes in an orthorhombically distorted inverse spinel structure (Fig. 1), with the non-magnetic V^{5+} ions at the tetrahedrally coordinated sites and Li^+ and Cu^{2+} ($3d^9$ configuration, $S = \frac{1}{2}$) occupying an ordered way in octahedrally coordinated sites [3]. The Jahn–Teller distorted CuO_6 octahedra connect via *trans* edges to form infinite Cu^{2+} chains along the *b*-axis

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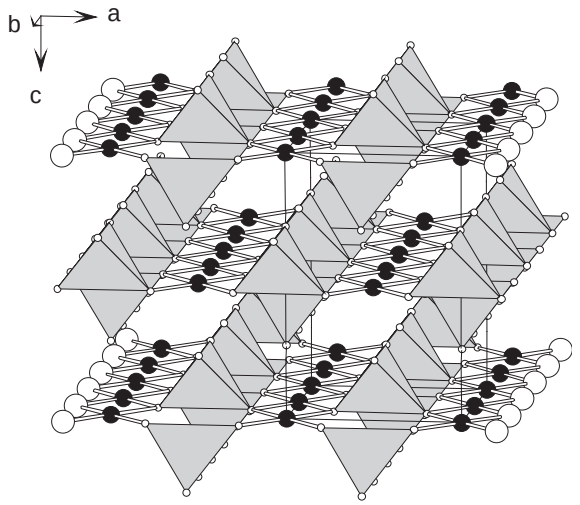

Fig. 1. Crystal structure of $LiCuVO_4$ according to [3]. VO_4 tetrahedra light grey, Cu (●), O (○). Li atoms not shown.

leaving two nearly rectangular ($\approx 95^\circ$) Cu–O–Cu super-exchange paths between NN Cu ions. The resulting CuO_2 ribbons are connected by VO_4 tetrahedra that alternate up and down along the chain direction. The topology of the CuO_2 ribbons is identical to that found in $CuGeO_3$; however, somewhat different bonding distances and angles are observed. There is a growing body of experimental and theoretical evidence that $LiCuVO_4$ behaves as a quasi one-dimensional $S = \frac{1}{2}$ Heisenberg afm although details of NNN, anisotropic and antisymmetry exchange components remain to be clarified [4–9]. In contrast to $CuGeO_3$, $LiCuVO_4$ shows no evidence of a diamagnetic ground state but rather anomalies in the heat capacity and the susceptibility suggest the onset of long-range afm ordering. Here we report an investigation of the ordered magnetic structure by means of elastic neutron diffraction on single crystals.

2. Experimental

Single crystals of $LiCuVO_4$ were grown from solutions of $LiCuVO_4$ in a $LiVO_3$ or $LiVO_3$–LiCl melt according to the procedures described in detail in Ref. [10]. Elastic neutron-diffraction measurements were performed on a large coffin-shaped single crystal ($\approx 125\,mm^3$) using the D10 diffractometer at the ILL, Grenoble which was set up in the standard four-circle mode ($\lambda = 2.354(2)$ Å) and equipped with a unique four-circle dilution refrigerator [11] to access temperatures down to ≈ 0.15 K. Crystal and magnetic structure refinements were performed using standard routines of the Cambridge Crystallographic Subroutine Library [12]. The magnetic susceptibilities of single crystals were measured in a MPMS7 SQUID magnetometer. The heat capacity was determined in a Quantum Design PPMS system.

3. Results

As observed previously for powders and single crystals [4–9] the magnetic susceptibility of our single crystals shows a broad maximum centred around 27 K due to afm short-range ordering, and similar kinks along all crystal axes at ≈ 2.5 K indicate the onset of long-range afm ordering. In agreement with a study on a powder sample, long-range ordering near this temperature is also evidenced by an anomaly in the heat capacity of a sample ($m \approx 13$ mg) cut from the crystal used for our neutron study (Fig. 2).

For the neutron-diffraction experiment, a large single crystal of $LiCuVO_4$ was oriented at an ambient temperature. The sample was then quickly

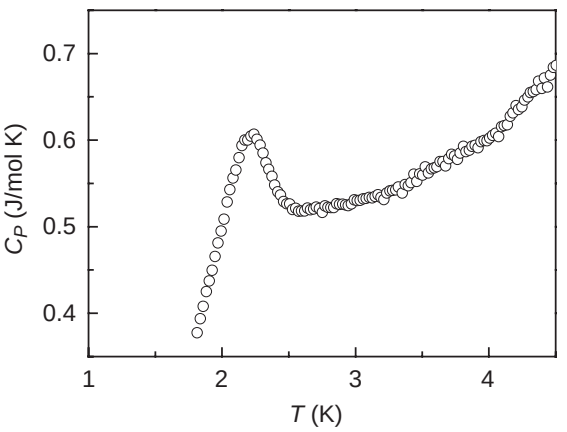

Fig. 2. Heat capacity of an end-piece cut from the crystal of $LiCuVO_4$ used for the neutron-diffraction study.

cooled to 1.6 K and the intensities of about 200 independent nuclear reflections were collected. A full refinement of the nuclear structure was carried out in the distorted orthorhombic spinel structure [3] and the results were in very good agreement with previous X-ray structure determinations with a slight temperature-induced lattice contraction. Scans through reciprocal space were performed at 1.6 K to search for additional reflections arising from the Cu^{2+} moment ordering. We first found a weak peak at the approximate position, $(1,\frac{1}{2},0)$. The peak disappeared upon heating at 2.5 K. We then checked for further peaks at $(h,\frac{1}{2},1)$ positions and observed a family of magnetic reflections which satisfied the general condition, $h+l=2n+1$.

Closer inspection of the magnetic reflections revealed an incommensurate magnetic structure that can be described by the propagation vector $k=(0,0.532,0)$ about the fundamental body-centred nuclear reflections. Subsequently, the temperature dependence of the intensity of the reflection '$(1,\frac{1}{2},0)$' was measured, from which we determined the Néel temperature to be $T_N=2.1(1)$ K. Detailed scans were made of various allowed magnetic reflections at 0.2 and 1.2 K (the ordering is nearly complete at 1.2 K—see Fig. 3), and the considerable background removed fitting the profile to a Gaussian. A magnetic structure of $LiCuVO_4$ compatible with the underlying crystal symmetry (i.e. that satisfies $h+l=2n$) can be generated by symmetry operations based on space group Imma, with the centring removed. Using this magnetic symmetry the refinement based on 14 unique allowed magnetic reflections at 0.2 and 1.2 K with 2 variables converged to $R_w(F^2)=6.2\%$ with spins in the *ab*-plane enclosing a polar angle of $\phi=44(5)^\circ$ with the *a*-axis. The average Cu^{2+} magnetic moment is $0.31(1)\mu_B$ (Fig. 4). Neighbouring moments along the chains along *b* enclose an angle of $\sim 90^\circ$.

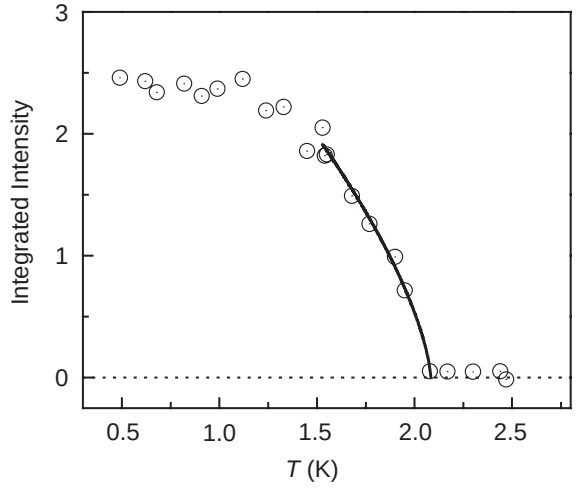

Fig. 3. Integrated intensity of the magnetic reflection '$(1,\frac{1}{2},0)$'. The full line represents a fit to a power-law with critical exponent $\beta\approx 0.3$.

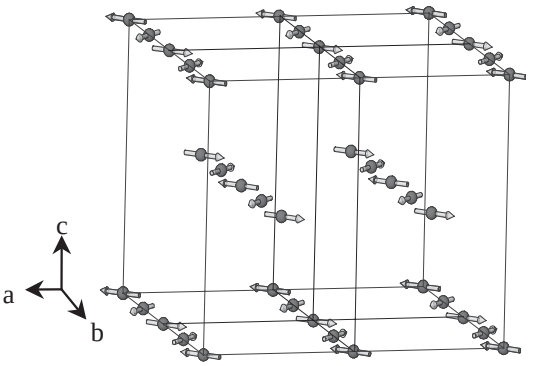

Fig. 4. Magnetic structure of $LiCuVO_4$, only Cu atoms shown. The moments are confined to the *ab*-plane.

4. Discussion

As indicated by the characteristic maximum in the susceptibility and the broad Schottky-like anomaly in the magnetic part of the heat capacity [6], $LiCuVO_4$ shows features typical of a one-dimensional afm system with predominant exchange coupling along the Cu chains. From the temperature of the maximum in the magnetic susceptibility T^{max} and by assuming a Heisenberg $S=\frac{1}{2}$ chain with uniform NN coupling implying the relation $T^{max}\approx 0.64\ J/k_B$ [13], we arrive at an intrachain exchange constant J^{intra} of ≈ 42 K (in the convention of Ref. [13]).

Long-range ordering of the short-range correlated chains had been concluded from the kink in the magnetic susceptibility and the anomaly in the heat capacity. This is conclusively confirmed by

our neutron-diffraction study. Long-range correlation between the chains is due to weaker interchain coupling. J^{inter} can be estimated from T_N and the intrachain coupling to be about 1 K [7]. The surprising result of the present refinement of the magnetic structure $LiCuVO_4$ is the observation of the unusual ordering scheme in the Cu chains. NN moments enclose an angle of $\approx 90^\circ$ to minimize the exchange energy between the NN moments. Our finding suggests that NNN exchange coupling via a Cu–O–O–Cu path is afm and dominates NN coupling. Irrespective of the sign of NN exchange the latter is frustrated and, in order to minimize the exchange energy, the moments assume a non-collinear arrangement. NNN coupling arises from hybridization of NN $O2p_x$ orbitals resulting in a sizable p_x–p_x hopping parameter between O atoms along the chain [14].

For a certain ratios J_2/J_1 (and $T = 0$), where J_1 and J_2 represent the NN and NNN intrachain exchange parameters, respectively, Hamiltonian (1) for a chain with NN and NNN exchange has been found to describe magnetic phases with incommensurate spiral correlations along the chain [15]. Magnetic frustration due to NNN coupling is suggested as the origin for the experimentally observed incommensurability of the moment order along the Cu chains. This explanation takes into consideration

$$H = \sum_i (J_1 \mathbf{S}_i \mathbf{S}_{i+1} + J_2 \mathbf{S}_i \mathbf{S}_{i+2}). \quad (1)$$

Heisenberg-type intra-chain exchange interaction only. Antisymmetrical spin coupling as another possible source of spin canting vanishes due to symmetry reasons in the given spin structure. Inelastic neutron scattering investigations are underway and first results are consistent with the proposed frustration scenario [16].

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