

NMR studies of incommensurate quantum antiferromagnetic state of LiCuVO_4

R. Smith^a, A.P. Reyes^a, R. Ashey^a, T. Caldwell^b, A. Prokofiev^c,
W. Assmus^c, G. Teitel'baum^{d,*}

^aNHMFL, Florida State University, 1800 E P. Dirac Dr., Tallahassee FL 32310, USA

^bNHMFL, Los Alamos, NM 87545, USA

^cGoethe University, 60054 Frankfurt, Germany

^dE.K. Zavoiskii Institute for Technical Physics of the RAS, Sibirskii Trakt 10/7, Kazan 420029, Russia

Abstract

Our ^{51}V NMR measurements in the LiCuVO_4 single crystal reveal that the classical quadrupole split signal transforms upon lowering temperature to the single line with the shape typical for the systems undergoing the phase transition to the incommensurate magnetic state. The angular dependence of such a lineshape together with the anomalies of the ^{51}V nuclear spin relaxation rates make it possible to conclude that the low-temperature magnetic order corresponds to the antiferromagnetic state with the incommensurate modulation along the b -axis of the crystal.

© 2006 Elsevier B.V. All rights reserved.

PACS: 75.10.Pq; 75.50.Ee; 76.60.-k

Keywords: Low-dimensional systems; Magnetic ordering; NMR

One-dimensional spin systems attract much attention due to the large quantum fluctuations existing at low temperatures. The special place belongs here to the frustrated spin systems, where in addition to the nearest neighbours coupling the interaction of more distant spins may be crucial. The low-temperature magnetic state being a result of subtle interplay of these couplings, is highly dependent on the interchain interactions, anisotropy effects, temperature and quantum fluctuations. One of the potential candidates for such a behaviour is the quasi-one-dimensional magnet LiCuVO_4 .

We report an investigation of the ordered magnetic structure of spin-chain compound LiCuVO_4 single crystals using NMR. The structure of LiCuVO_4 [1,2] is characterized by chains of edge-coupled LiO_6 and CuO_6 octahedra running along the a - and b - crystal axes, respectively, and thus consists of alternating packed layers containing arrays of Li^+ or Cu^{2+} chains. Within the planes, neighbouring

Cu chains are connected with each other by VO_4 tetrahedra that alternate up and down along the chain direction and form Cu-O-V-O-Cu superexchange bonds. The Cu^{2+} ions in this compound carry magnetic moments which are connected by the various exchange couplings. There is a growing evidence about a dimensional crossover in the magnetic correlations from 1D to higher dimensionality (2D or 3D) upon lowering temperature [3]. Nevertheless the ordered magnetic structure of LiCuVO_4 needs further refinement. Therefore, the application of the local methods such as NMR enables one to obtain the crucial information for solving this problem. ^{51}V NMR and spin-lattice relaxation measurements were carried out in the wide temperature range. At high temperatures ^{51}V spectra exhibit a classic quadrupole-split line expected for $I = 7/2$.

Nuclei with the quadrupole coupling $\nu_Q \approx 68$ kHz (Fig. 1). Due to the slowing down of the 1D magnetic fluctuations the splitting becomes smeared upon cooling and disappears completely below ~ 50 K. At further cooling linewidth anomalies correlated with characteristic

*Corresponding author. Tel.: +7 843 272 1154; fax: +7 843 272 1154.

E-mail address: grteit@kfti.knc.ru (G. Teitel'baum).

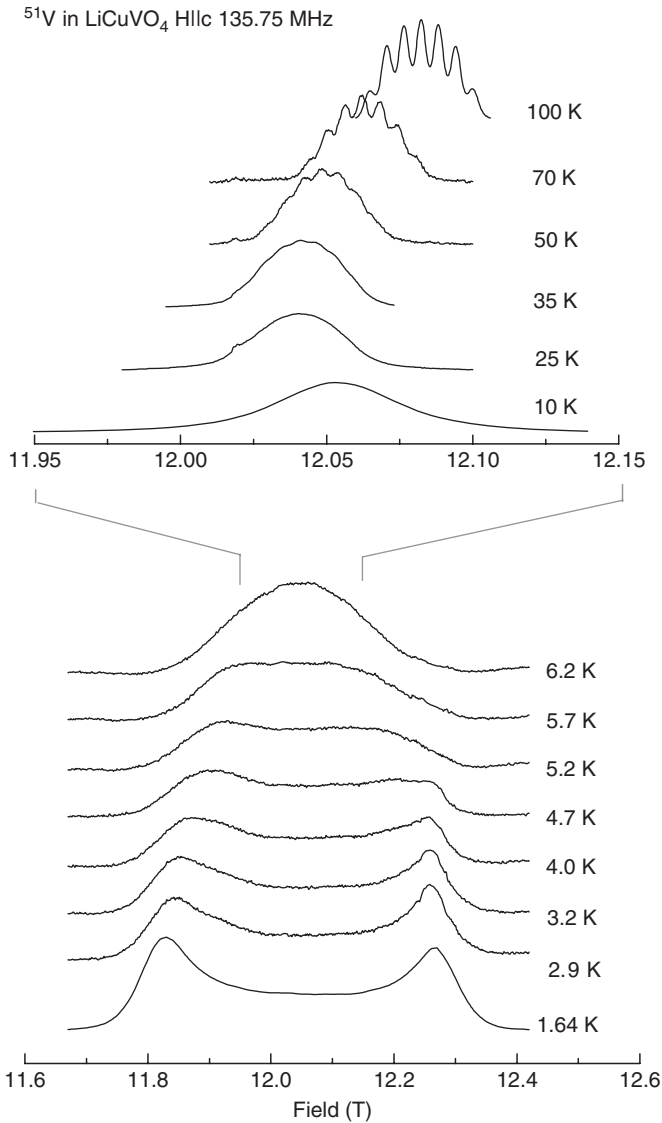


Fig. 1. Temperature evolution of ^{51}V NMR spectrum at a fixed frequency of 135.75 MHz. Note the change in scale.

features of the resonance shift were observed near 25, 6 and 2 K. This is attributed to increased spin correlations leading to 3D antiferromagnetic order at low temperatures. The Knight shift tracks susceptibility giving a hyperfine field of $A_{\text{hf}} = 6.5 \text{ kOe}/\mu_{\text{B}}$ transferred on the ^{51}V nuclei from Cu magnetic moments. Below 5 K for a field parallel to crystal c -axis the spectra exhibit a broad two-peak feature (see bottom of Fig. 1) which is unresolved for field along the b -axis. The moments orientation determined from the spectra suggests an incommensurate (IC) antiferromagnetic (AF) modulation along the b -axis at temperatures below 4 K. Accordingly the double-horn NMR lineshape is due to the harmonic space variation of the resonant field (frequency) around the Zeeman value H_0

resulting in the spectral density

$$\rho(H) \propto \left(1 - [2(H - H_0)/H_s]^2\right)^{-1/2} \quad (1)$$

with H_s as the transferred hyperfine field.

Eq. (1) enables us to obtain a good fit of the spectra at the bottom of Fig. 1 with the temperature dependence of the modulation amplitude (the splitting between peaks, H_s) given by the power law $(T_m - T)^{0.29}$. Here $T_m = 5.9 \text{ K}$ is the magnetic field-dependent modulation onset temperature.

To elucidate the origin of such IC spin ordering we refer to the recent neutron scattering data for LiCuVO_4 [4,5]. The analysis of the magnetic neutron reflections revealed an IC AF structure with the helical ordering that can be described by the propagation vector \mathbf{k} (0,0.532,0) about the fundamental bodycentred nuclear reflections. The temperature dependence of the integrated intensity of the corresponding additional reflections is described by a power law with a critical exponent $\beta = 0.31$ which is fairly close to our NMR data. According to neutron data the nearest neighbours (NN) moments along the chains enclose an angle slightly smaller than 90 degrees to minimize the exchange energy between the NN moments. The reason of such orientation is that the next nearest neighbours (NNN) exchange coupling via a Cu–O–O–Cu path is AF and dominates NN coupling. Therefore, irrespective of the sign of NN exchange the latter is frustrated and, in order to minimize the exchange energy, the moments acquire a non-collinear arrangement. NNN coupling arises from hybridization of NN $\text{O}2p_x$ orbitals resulting in a sizable p_x – p_y hopping parameter between O atoms along the chain.

It is interesting that the longitudinal spin relaxation rate divided by T is proportional to the spin susceptibility for $T > 25 \text{ K}$, whereas below this temperature it acquires the thermally activated character. The extremely low activation energy ($\sim 1 \text{ K}$) gives indication in favour of sliding magnetic excitations of IC magnetic state, which are responsible for magnetic relaxation in LiCuVO_4 at low temperatures. In conclusion we note that the transition temperature to the incommensurate AF state as well as the relaxation rate reveal the hysteretic features giving evidence about the importance of the pinning phenomena.

We acknowledge useful discussions with W.G. Moulton, V.E. Kataev, P.L. Kuhns, and M.J.R. Hoch. Work supported by NHMFL In-House Research Program. G.B.T. is supported by the RFBR Grant no. 04-02-17137.

References

- [1] H. Saji, J. Phys. Soc. Japan. 33 (1972) 671.
- [2] M.A. Lafontaine, et al., Acta Crystallogr. Sect. C. 45 (1989) 1205.
- [3] A.N. Vasil'ev, JETP Lett. 69 (1999) 876.
- [4] B.J. Gibson, et al., Physica B 350 (Suppl. 1–3) (2004) e253–e256 and references therein.
- [5] M. Enderle, et al., Europhys. Lett. 70 (2005) 237.