Available online at www.sciencedirect.com
SCIENCE DIRECT®
Physica B 329–333 (2003) 703–704
PHYSICA B
www.elsevier.com/locate/physb

Low-temperature NMR studies of $Na_2V_3O_7$

J.L. Gavilano[a,*], D. Rau[a], Sh. Mushkolaj[a], H.R. Ott[a], F. Mila[b], P. Millet[c]

[a] *Laboratorium für Festkörperphysik, ETH-Hönggerberg, Zürich CH-8093, Switzerland*
[b] *Institut de Physique Théorique, Université de Lausanne, Lausanne CH-1015, Switzerland*
[c] *Centre d'Elaboration des Matériaux et d'Etudes Structurales, Toulouse 31055 Cedex, France*

Abstract

We report low-temperature ^{23}Na-NMR measurements on the quasi-one-dimensional spin $\frac{1}{2}$ system $Na_2V_3O_7$. The temperature dependence of the spin-lattice relaxation rate $T_1^{-1}(T)$, measured at a frequency of 76.5 MHz, exhibits a narrow peak near 2.5 K, indicating the onset of a cooperative phase transition to a state with a small gap in the spectrum of V spin excitations. Considering the results of the NMR spectra at low temperatures and of the magnetic susceptibility at higher temperatures, it seems unlikely that this transition reflects the onset of either ferromagnetic or antiferromagnetic order. The nature of the transition needs to be investigated in more detail.

Keywords: NMR; Magnetism; Low-dimensional systems

1. Introduction

In 1999 Millet and co-workers [1] reported the first synthesis of $Na_2V_3O_7$. This material has a remarkable crystal structure. Each V ion is enclosed in a O_5 square pyramid. These pyramids share common edges, forming an array of parallel and well separated quasicircular nanotubes, of approximately 5 Å in diameter. The circumference of the individual nanotubes may be viewed as being formed by three structural subunits, and each subunit contains three O_5 square pyramids. The Na ions are distributed on four inequivalent sites inside and around the nanotubes and serve to stabilize the structure. Since only the V ions in $Na_2V_3O_7$ carry a magnetic moment, it is clear that the magnetic system formed in this material is very unusual, with the magnetic moments sitting on the walls of nanotubes. This is particularly interesting, because it has been established [2] that the electronic structure of $Na_2V_3O_7$ is very similar to those adopted in some layered (non-tubular) Vanadates.

The results of the magnetic susceptibility above 150 K confirm that the V ions in $Na_2V_3O_7$ have indeed a spin $S = \frac{1}{2}$ [3]. Therefore, taking into account the peculiar crystalline structure of this material, it seems reasonable to regard $Na_2V_3O_7$ as containing three-legged ladder structural elements [1]. It has also been suggested [4] that $Na_2V_3O_7$ may be described as a system of six mutually intersecting helical chains. Neither of these models, however, seems to account for the experimental results concerning the magnetic properties of this compound [3]. Using standard spin-echo techniques, we made ^{23}Na-NMR measurements on a sample consisting of 13 mg of randomly oriented fibers. The sample preparation was described elsewhere [1].

2. Experimental results and discussion

In the inset of Fig. 1 we display one example of the ^{23}Na-NMR spectrum for $Na_2V_3O_7$ measured at a resonance frequency of 76.5 MHz and at a temperature of 2.1 K. The spectrum reveals a single broad line of a width FWHM of 590 G. With decreasing temperatures the width of the spectrum gradually increases for temperatures below 15 K as seen in Fig. 1. The signals originating from different Na sites can be resolved here, but this is not surprising if we keep in mind that in this

*Corresponding author. Tel.: +41-1-633-2245; fax: +41-1-633-1077.
E-mail address: gavilano@solid.phys.ethz.ch (J.L. Gavilano).

0921-4526/03/$ - see front matter
doi:10.1016/S0921-4526(02)02013-6

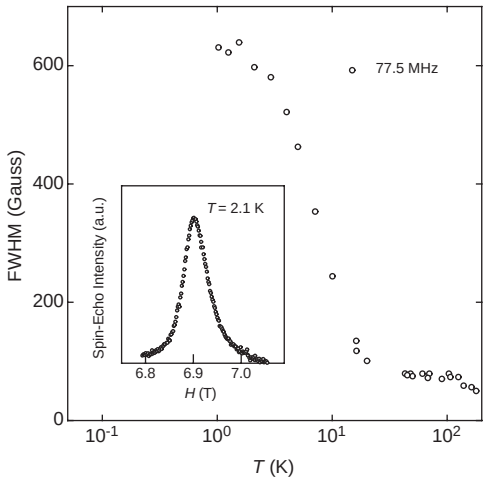

Fig. 1. ^{23}Na-NMR spectrum of $Na_2V_3O_7$ measured at the fixed frequency of 77.5 MHz and at a temperature of 2.1 K.

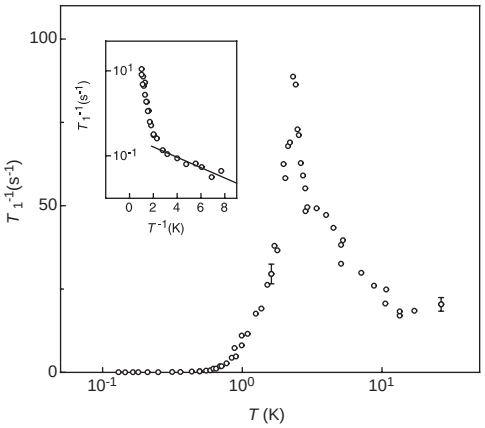

Fig. 2. Spin-lattice relaxation rate T_1^{-1} as a function of temperature of $Na_2V_3O_7$. A sharp peak near 2.5 K signals the onset of a cooperative phase transition of unknown origin. The inset displays $T_1^{-1}(T^{-1})$ at low temperatures.

structure the V and Na sites are fairly well separated. The weak hyperfine coupling between the V magnetic moments and the Na nuclei is presumably of magnetic dipolar type.

As an additional characterization of the NMR response of $Na_2V_3O_7$ we have also measured the spin-lattice relaxation rate T_1^{-1} at various temperatures. This was achieved by applying a long comb of RF pulses, to destroy the nuclear magnetization, followed by a variable delay and a $\pi/2-\pi$ spin-echo sequence. The T_1's were obtained from fits to the nuclear magnetization recovery curves (for details see Ref. [5]). At low temperatures the spectrum broadens and the quality of the fits deteriorates. However, we have repeated the measurements at different irradiation conditions and we found the same results for T_1.

In Fig. 2 we display the temperature dependence of the ^{23}Na spin-lattice relaxation rate measured at the resonance frequency of 76.5 MHz. One clearly observes a sharp peak at a temperature near $T_0 = 2.5$ K, which marks the onset of a phase transition of unknown origin, and is preceded by a significant increase of the spin-lattice relaxation rate with decreasing temperatures. The latter is interpreted as a precursor of the transition, i.e., the onset of short range correlations among the V spins. Below T_0 the spin-lattice relaxation rate decreases abruptly and at very low temperatures $T_1^{-1}(T)$ is well represented by

$$T_1^{-1}(T) \propto \exp(-T_G/T), \quad (1)$$

where $T_G = 0.3$ K (solid line in the inset of Fig. 2). This observation suggests the existence of a very small gap in the spectrum of the V spin excitations. The Zeeman energy pro V-moment due to the applied magnetic field is much larger than either $k_B T_0$ or $k_B T_G$ and therefore, the applied field may have a large impact on the observed NMR response of $Na_2V_3O_7$.

The temperature evolution of the ^{23}Na-NMR spectra does not really seem to be consistent with a simple antiferromagnetic type of ordering below T_0. As mentioned above, the width of the NMR spectrum starting at temperatures much higher than T_0 simply increases with decreasing temperatures with no anomalies at, or near, T_0. Only in very special situations, where for symmetry reasons the static fields cancel out at the nuclear sites probed by NMR, the onset of an antiferromagnetic ordering may have little impact on the NMR spectra. However, this scenario seems rather unlikely in our case because in the structure of $Na_2V_3O_7$ there are four rather different Na sites. Therefore, most probably the observed transition is not of antiferromagnetic type. A ferromagnetic type of order below T_0, seems equally unlikely because the temperature dependence of the magnetic susceptibility shows that the interactions between the V moments are predominantly antiferromagnetic. We therefore conclude that the magnetically ordered state of $Na_2V_3O_7$ below T_0 has not yet been identified.

References

[1] P. Millet, J.Y. Henry, F. Mila, J. Galy, J. Solid State Chem. 147 (1999) 676.
[2] J. Choi, J.L. Musfeldt, Y.J. Wang, H.J. Koo, M.H. Whangbo, J. Galy, P. Millet, Chem. Mater 14 (2002) 924.
[3] J.L. Gavilano, D. Rau, Sh. Mushkolaj, H.R. Ott, P. Millet, F. Mila, Physica B 312–313 (2002) 622.
[4] M.H. Whangbo, H.J. Koo, Solid State Commun. 115 (2000) 675.
[5] J.L. Gavilano, D. Rau, Sh. Mushkolaj, H.R. Ott, P. Millet, Mila, cond-mat/0210541, 2002.