

Low-Dimensional Spin $S = 1/2$ System at the Quantum Critical Limit: $\text{Na}_2\text{V}_3\text{O}_7$

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We report the results of measurements of the dc susceptibility and the ^{23}Na -NMR response of $\text{Na}_2\text{V}_3\text{O}_7$, a recently synthesized, nonmetallic low dimensional spin system. Our results indicate that, upon reducing the temperature to below 100 K, the V^{4+} moments are gradually quenched, leaving only one moment out of nine active. The NMR data reveal a phase transition at very low temperatures. With decreasing applied field H , the critical temperature shifts towards $T = 0$ K, suggesting that $\text{Na}_2\text{V}_3\text{O}_7$ may be regarded as an insulator reaching a quantum critical point at $H = 0$.

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Low dimensional spin systems have recently been the subject of interest in a large number of research projects. The interest in these systems is manifest in many theoretical studies and much progress has been made in the synthesis of new compounds, which may be considered to be physical realizations of systems with one- and two-dimensional arrays of spins in the form of spin chains and ladders [1]. Prominent examples include cuprates and ternary vanadium oxides [2,3]. The physical properties of ladder compounds are largely determined by the number of legs of the individual ladders. Less clear is the influence of the topology of a system on its physical properties. It has been suggested [4,5] that the topology, specifically the periodic boundary conditions in the rung direction, is essential for the low temperature properties of some ladder compounds.

In this respect, new opportunities emerged from recognizing that variations in the composition of some two-dimensional layered compounds result in microscopic tubular structures [6–8]. In 1999, Millet and co-workers [9] reported the synthesis of $\text{Na}_2\text{V}_3\text{O}_7$, a material whose structure may be considered as composed by nanotubes oriented along the c axis of the crystal lattice (space group $P31c$). The individual nanotubes, with an inner diameter of approximately 5 Å, are formed by VO_5 square pyramids, joined at their edges and corners. The Na ions, occupying different sites inside and around individual nanotubes, are bonded to the O ions of up to three nanotubes. From our experimental data we infer that, upon reducing the temperature from 100 to 10 K, the effective moment of the V^{4+} ions in $\text{Na}_2\text{V}_3\text{O}_7$ is reduced by 1 order of magnitude. Below 20 K our data reveal that for $H = 0$, this material is close to a phase transition at $T = 0$ K.

Our $\text{Na}_2\text{V}_3\text{O}_7$ samples consisted of ensembles of randomly oriented small crystals, with typical dimensions of $10\ \mu\text{m} \times 10\ \mu\text{m} \times 1\ \text{mm}$. The material was grown under vacuum from melts with a starting composition of $\text{Na}_{1.9}\text{V}_3\text{O}_7$ [9]. The susceptibility was measured using a commercial SQUID magnetometer and the NMR mea-

surements employed standard spin-echo techniques. In Fig. 1 we display the temperature dependence of the molar magnetic susceptibility $\chi(T)$ of $\text{Na}_2\text{V}_3\text{O}_7$, at temperatures between 1.9 and 315 K. Curie-Weiss type features of $\chi(T)$ of the form

$$\chi(T) = \chi_{\text{dia}} + \frac{C}{(T - \Theta)} \quad (1)$$

are discernible in two different temperature regimes. The background χ_{dia} was extracted from the high-temperature data. Above 100 K, the best fit to the data, represented by the broken line in Fig. 1, yields $C \approx 1.4$ emu K/mol and $\Theta = -200 \pm 30$ K. These values imply an effective magnetic moment of $1.9\mu_B$ per V ion, close to the expected value for V ions in their tetravalent configuration,

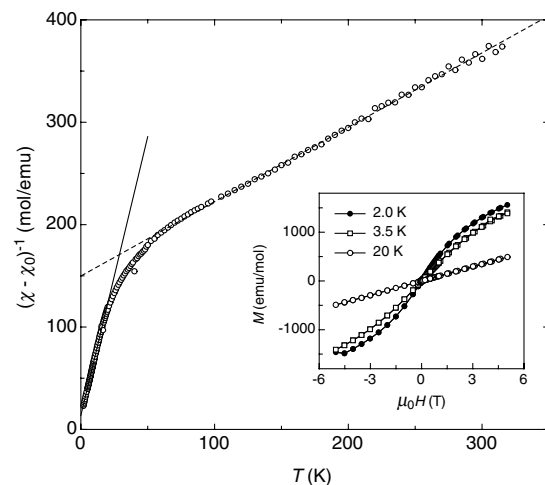


FIG. 1. Temperature dependence of the inverse magnetic susceptibility measured at 0.1 T. Below 20 K, data also measured in an applied field of 1 T are included (the two data sets cannot be distinguished). The broken and solid lines represent the best fits to a Curie-Weiss type behavior at high and low temperature, respectively. Inset: Magnetization $M(H)$ curves at three different temperatures.

and substantial antiferromagnetic interactions between them. Below approximately 100 K, $\chi(T)$ changes gradually. The straight solid line in Fig. 1, fitting the data between 20 and 1.9 K, implies that now $C = 0.178$ emu K/mol and $\Theta = -2.2$ K. With respect to the high-temperature values, C and Θ are thus reduced by approximately 1 and 2 orders of magnitude, respectively. These results confirm those obtained previously in higher external fields [10]. Considering these data and magnetization curves $M(H)$ displayed in the inset of Fig. 1, $\text{Na}_2\text{V}_3\text{O}_7$ exhibits neither a phase transition to a magnetically ordered state nor spin-freezing phenomena at temperatures above 2 K. The reduction of the effective magnetic moment is most likely due to a gradual process of moment compensation via the formation of singlet spin configurations with most but not all of the ions taking part in the process. This may be the result of antiferromagnetic interactions and geometrical frustration. We conjecture the compensation of eight out of the nine V spins along the ‘‘circumference’’ of the individual nanotubes of $\text{Na}_2\text{V}_3\text{O}_7$. This is natural if the dominant interactions are between edge-sharing VO_5 pyramids, but more difficult to understand if the dominant interactions are between corner-sharing pyramids, as suggested in Ref. [11].

The ^{23}Na -NMR response of $\text{Na}_2\text{V}_3\text{O}_7$ was measured in different external magnetic fields. An example of the ^{23}Na -NMR spectra is displayed in the inset of Fig. 2, measured at a fixed Larmor frequency of 31.728 MHz. No quadrupolar wings appear in our data because their intensity is distributed over a broad frequency range [12]. In the inset of Fig. 2, only the unresolved signals of the Zeeman central transitions ($+1/2 \leftrightarrow -1/2$) from the four Na sites are observed near 2.825 T, suggesting rather

modest differences, if any, in the hyperfine fields at the different Na sites. This is consistent with a direct dipolar coupling between the V^{4+} moments and the Na nuclei (see below).

In the main frame of Fig. 2, we display the temperature evolution of the ^{23}Na -NMR linewidth (FWHM), measured at a fixed frequency of 31.728 MHz. Between 50 to 150 K the NMR linewidth increases gradually with decreasing temperature by approximately a factor of 2. A more dramatic change occurs at lower temperatures where an increase of more than 1 order of magnitude is observed as the temperature is reduced to below 1 K. This type of behavior usually reflects magnetic ordering or spin-freezing phenomena. In our case, the temperature-independent linewidth at low temperatures increases with increasing applied field (data not shown), not consistent with either a simple ferro- or antiferromagnetic order.

In Fig. 3 we display the full ^{23}Na NMR linewidth at half maximum (FWHM) as a function of the molar magnetization M for temperatures above 3.5 K. Note the linear relation $\text{FWHM} = (-16 + 0.308M)$ Gauss. The NMR linewidth is caused by a distribution of internal static fields at the four inequivalent Na sites in randomly oriented grains. These fields arise from the polarization of the V moments in an external field, and, therefore, we assume $\text{FWHM} \approx \Delta A_{\text{hf}}(M/\mu_B N_A)$, where M is the molar magnetization, ΔA_{hf} is the width of the distribution of hyperfine field couplings, and μ_B and N_A are the Bohr magneton and Avogadro’s number, respectively. From the slope of the straight solid line in Fig. 3 we infer that $\Delta A_{\text{hf}} = 1.7$ kOe per μ_B of V moment [14].

In order to gain a numerical estimate, we have calculated the dipolar fields at the four Na sites generated by

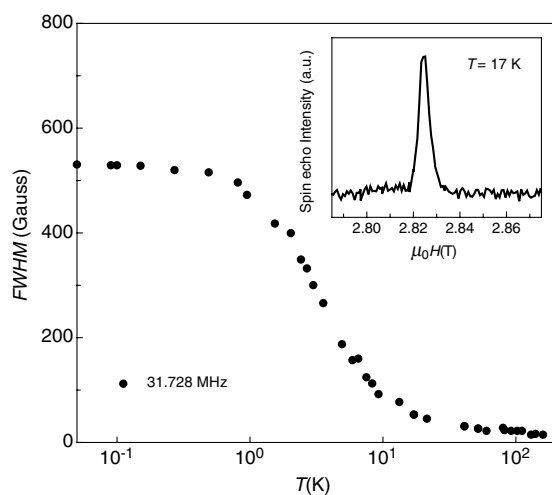


FIG. 2. ^{23}Na -NMR linewidth (FWHM) as a function of temperature measured at 31.728 MHz. A rather large (and field dependent) increase of the linewidth is observed below 30 K. Inset: ^{23}Na -NMR spectrum measured at 17 K.

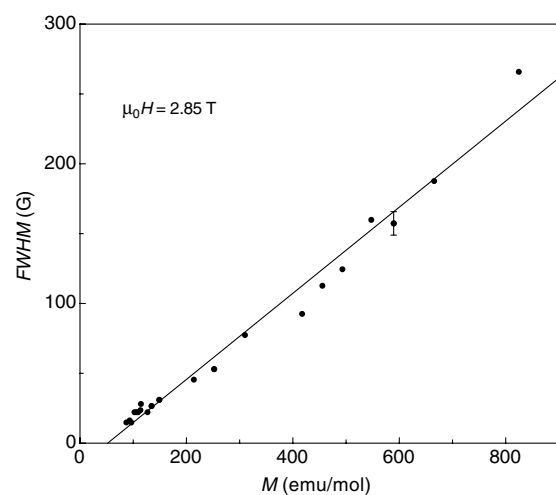


FIG. 3. FWHM as a function of the molar magnetization M , at the chosen field and at different temperatures. The linear relation between FWHM and M indicates that the increase of the linewidth is of magnetic origin.

equally polarized V moments of $1\mu_B$, with the polarization along several directions. The results [15] suggest that, for a randomly oriented powdered sample, the total width of the ^{23}Na -NMR signal ought be of the order of 2.5 kOe. The experimental value $\Delta A_{\text{hf}} = 1.7$ kOe per μ_B of V moment is thus consistent with a direct dipolar hyperfine coupling between the V moments and the Na nuclei. The quoted result still applies, if the formation of singlet states occurs for most of the V moments in clusters of ions, as long as the uncompensated spins are mobile in these clusters. The characteristic frequencies of this motion need to exceed the NMR Larmor frequencies. If, however, after the singlet formation the arrangements of spins are static, the dipolar fields are expected to vary depending on the details of the arrangement. Preliminary estimates indicate that, although the fields at individual Na sites change substantially, the spread of their values is of the same order of magnitude as mentioned above. We do not observe any specific structure in the NMR line at low temperatures. The corresponding analysis of the NMR line shape is complicated by the many possible spin arrangements and is the subject of ongoing work.

We now turn to the results of measurements of the spin-lattice relaxation rate T_1^{-1} as a function of temperature in various external fields. The values of T_1^{-1} were extracted from fits to nuclear magnetization recovery curves $m(t)$, obtained as follows. First the populations of the central ^{23}Na nuclear Zeeman levels ($I = +1/2, -1/2$) were equalized by applying a long comb of rf pulses. After a variable delay t , a $\pi/2 - \pi$ spin-echo sequence was applied and the corresponding spin-echo intensity, $m(t)$, was recorded and well fitted by a standard expression, appropriate for magnetic relaxation where spin diffusion is negligible [16].

In the main frame of Fig. 4 we display $T_1^{-1}(T)$ measured in a magnetic field of 68.13 kOe below 40 K. The complete data set, covering temperatures up to 300 K, gives no indication of a gap in the spin excitation spectrum at temperatures above the liquid He temperature range. Besides the peak at $T_a = 2.3$ K (see Fig. 4), two additional significant anomalies in $T_1^{-1}(T)$ appear at $T_b = 1$ K (left inset) and at $T_c = 0.43$ K (right inset). Below T_b , $T_1^{-1}(T) \propto \exp(-\Delta/k_B T)$ with values Δ/k_B of 3.8 and 0.28 K above and below T_c , respectively. The evolution of these features with magnetic field below 10 K is depicted in Fig. 5. This suggests a small gap in the spin excitation spectrum at these temperatures. The anomalies in $T_1^{-1}(T)$ are indicated by arrows at T_a and by the two dotted lines for T_b and T_c . Substantial field-induced changes in $T_1^{-1}(T)$ are observed at low temperatures, confirming that the state below T_a involves spin degrees of freedom. As is shown in the inset of Fig. 5, the transition temperature T_a , the onset of the spin gap at T_b , and the feature at T_c are all smoothly shifting to zero upon reducing the external field to zero. This indicates that $\text{Na}_2\text{V}_3\text{O}_7$, an insulator, may be considered as being

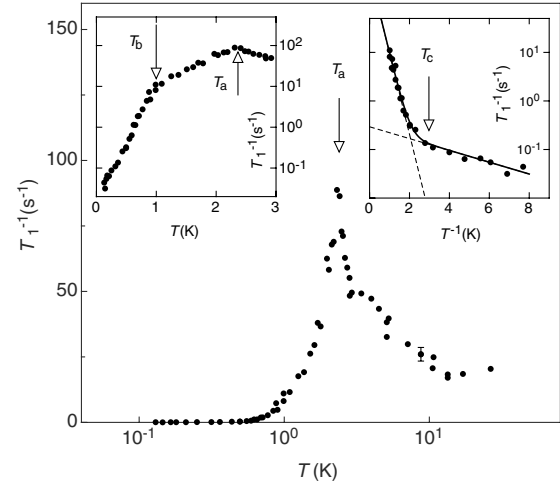


FIG. 4. Main frame: $T_1^{-1}(T)$ measured at 76.5 MHz below 40 K. A peak is observed at $T_a = 2.35$ K. Inset left: A slope change in $T_1^{-1}(T)$ is revealed at $T_b = 1$ K. Inset right: A third anomaly in $T_1^{-1}(T)$ appears at $T_c = 0.43$ K. The solid line represents the sum of two exponential functions.

close to or at a quantum critical point at $H = 0$. Preliminary results of measurements of the specific heat $C_p(T, H)$ of this compound show anomalous temperature and field dependences of C_p which are consistent with our claims. These results will be presented elsewhere.

Features of $T_1^{-1}(T)$ as those shown in the main frame of Fig. 4 are usually associated with a cooperative phase transition which, in magnetic systems, involves spin (and in some cases, lattice) degrees of freedom. Although the observed features in $T_1^{-1}(T)$ are not all very pronounced, they are easily recognizable anomalies, marking a change of behavior of the nuclear relaxation. It should be kept in

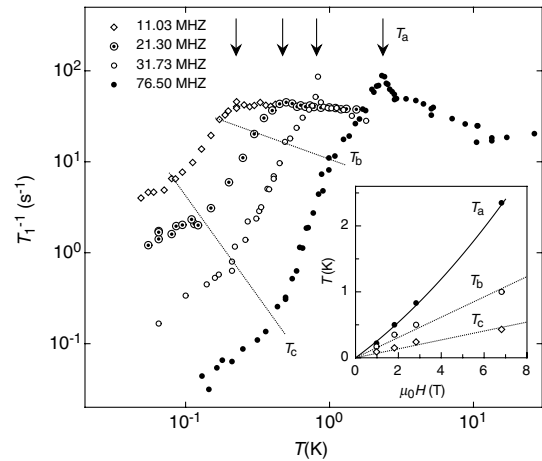


FIG. 5. $T_1^{-1}(T)$ for external fields of 9.8, 18.1, 28.25, and 68.13 kOe, corresponding to Larmor frequencies of 11.03, 21.30, 31.728, and 76.5 MHz, respectively. Anomalies in $T_1^{-1}(T)$ are emphasized by arrows at T_a and by two broken lines indicating T_b and T_c . Inset: Magnetic field dependence of T_a , T_b , and T_c . The different lines are to guide the eye.

mind that in some instances the expected peak in $T_1^{-1}(T)$ at the critical temperature of a magnetic phase transition can be very weak and even absent [17]. At this point, we assume that a cooperative phase transition occurs at T_a . From $\chi(T)$ at temperatures between 2 and 20 K, the related paramagnetic Curie temperature for $\text{Na}_2\text{V}_3\text{O}_7$ is $\Theta = -2.2$ K. Hence, it is tempting to conclude that a transition to an antiferromagnetic state occurs at T_a . However, as stated above, the behavior of the linewidth is not consistent with antiferromagnetic ordering. Besides, the temperature dependence of T_1^{-1} below T_a is not consistent with expectations for a common magnetically ordered system. In particular, the change of slope in $T_1^{-1}(T)$ at T_b suggests that the formation of a gap in the spin excitation spectrum of the ordered state does not occur at the transition T_a , but only at the lower temperature T_b . This clearly does not match with $T_1^{-1}(T)$ of ordinary varieties of ferro- or antiferromagnetically ordered systems.

These and previous arguments lead to the conclusion that in the observed phase transition degrees of freedom other than those of the spin system are involved. The coupling of spins to lattice distortions often leads to complications. A recent example is $\text{Cu}_2(\text{C}_5\text{H}_{12}\text{N}_2)_2\text{Cl}_4$, a spin ladder system [18] where magnetoelastic effects are believed to influence a rather rich $[H, T]$ phase diagram at low temperatures [19,20]. In this case, two quantum critical points at two different external magnetic fields H_{c1} and H_{c2} have been identified [20]. Since our data suggest a quantum critical point at or very close to $H = 0$, any intrinsic gap in the V spin excitation spectrum of the paramagnetic phase ought to be tiny. This is compatible with the topology of the spin arrangement in $\text{Na}_2\text{V}_3\text{O}_7$ and the observed reduction to one effective spin 1/2 per turn around the tubes at low temperatures. This type of spin tube is generically expected to have a much smaller gap than even-leg ladders. This is particularly clear in the limit where the rung coupling J_\perp is much larger than the leg coupling J_\parallel , presumably the relevant one for both systems: In two-leg ladders, the gap opens on each rung and scales with J_\perp [1], while in odd-leg ladders with periodic boundary conditions, the gap opens due to a dimerization along the tube and scales with J_\parallel [4,5].

In summary, from the results of our dc susceptibility and ^{23}Na -NMR measurements on $\text{Na}_2\text{V}_3\text{O}_7$, we conclude that at high temperatures, all the V ions are in a tetravalent state and all related moments contribute to the magnetic susceptibility. This situation changes gradually below 100 K. Below 20 K a different paramagnetic state is established with only one out of nine of the V magnetic moments contributing to the susceptibility. At much lower temperatures and in the presence of modest external magnetic fields, a phase transition occurs at a field-dependent transition temperature T_a . In the ordered phase, a gap Δ forms at temperatures distinctly below

T_a . All energy scales characterizing this ordered state, i.e., T_a , T_b , and T_c , shift towards $T = 0$ K with decreasing external field H . We therefore conclude that $\text{Na}_2\text{V}_3\text{O}_7$ may be considered as being very close to or at a quantum critical point at $H = 0$. It is conceivable that this quantum critical point is analogous to the one that appears in gapped systems when the field is large enough to close the gap.

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- [1] E. Dagotto and T. M. Rice, *Science* **271**, 618 (1996), and references cited therein.
 - [2] Y. Ueda, *Chem. Mater.* **10**, 2653 (1998).
 - [3] P. Millet, C. Satto, J. Bonvoisin, B. Normand, K. Penc, M. Albrecht, and F. Mila, *Phys. Rev. B* **57**, 5005 (1998).
 - [4] H. J. Schulz, in *Correlated Fermions and Transport in Mesoscopic Systems*, edited by T. Martin, G. Montambaux, and J. Tran Than Van (Editions Frontiers, Gif-sur-Yvette, 1996), p. 81.
 - [5] K. Kawano and M. Takahashi, *J. Phys. Soc. Jpn.* **66**, 4001 (1997).
 - [6] R. Tenne, L. Margulis, M. Genut, and G. Hodes, *Nature (London)* **360**, 444 (1992).
 - [7] G. L. Frey, S. Elani, M. Homyonfer, Y. Feldman, and R. Tenne, *Phys. Rev. B* **57**, 6666 (1998).
 - [8] G. Seifert, T. Frauenheim, T. Koehler, and H. M. Urbassek, *Phys. Status Solidi B* **225**, 393 (2001).
 - [9] P. Millet, J. Y. Henry, F. Mila, and J. Galy, *J. Solid State Chem.* **147**, 676 (1999).
 - [10] J. L. Gavilano, D. Rau, Sh. Mushkolaj, H. R. Ott, P. Millet, and F. Mila, *Physica (Amsterdam)* **312–313B**, 622 (2002).
 - [11] M.-H. Whangbo and H. J. Koo, *Solid State Commun.* **115**, 675 (2000).
 - [12] To estimate the field gradient, we have used a point charge model with ionic charges appropriate for Na^{+1} , V^{+4} , and O^{-2} and an antishielding Sternheimer factor of $\gamma_\infty = -5.3$ [13].
 - [13] G. Klösters and M. Jansen, *Solid State Nucl. Magn. Reson.* **16**, 279 (2000).
 - [14] This analysis cannot be easily performed with the line shift because the large NMR linewidth at low temperatures results in large error bars for the relatively small NMR line shift.
 - [15] For the considered site configurations, the extremal values of the dipolar magnetic fields are 1630 and -770 Oe, respectively.
 - [16] W. W. Simmons, W. J. O'Sullivan, and W. A. Robinson, *Phys. Rev.* **127**, 1168 (1962).
 - [17] D. E. MacLaughlin, O. Pena, and M. Lysak, *Phys. Rev. B* **23**, 1039 (1981).
 - [18] G. Chaboussant *et al.*, *Phys. Rev. B* **55**, 3046 (1997); see also P. R. Hammar and D. H. Reich, *J. Appl. Phys.* **79**, 5392 (1996).
 - [19] M. B. Stone *et al.*, *Phys. Rev. B* **65**, 064423 (2002).
 - [20] H. Mayaffre *et al.*, *Phys. Rev. Lett.* **85**, 4795 (2000).