Charge Order driven Spin-Peierls Transition in $\alpha'$-Na$_5$V$_2$O$_5$

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(March 24, 2022)

We conclude from $^{23}$Na and $^{51}$V NMR measurements in $\alpha'$-Na$_5$V$_2$O$_5$ ($x=0.996$) a charge ordering transition starting at $T \lesssim 37$ K and preceding the lattice distortion and the formation of a spin gap $\Delta=106$ K at $T_c=34.7$ K. Above $T_c$, only a single Na site is observed in agreement with the $Pmmn$ space group of this first 1/4-filled ladder system. Below $T_c=34.7$ K, this line evolves into eight distinct $^{23}$Na quadrupolar split lines, which evidences a lattice distortion with, at least, a doubling of the unit cell in the $(a,b)$ plane. A model for this unique transition implying both charge density wave and spin-Peierls order is discussed.

PACS numbers: 76.60.-k, 74.25.Ha, 74.62.Dh

A large number of vanadium-oxides have recently been recognized as low-dimensional quantum spin systems with outstanding magnetic properties. In several cases, and at odd with the experience in copper-oxides, defining the parameters of the magnetic Hamiltonian has turned out to be more complicated, and more intriguing than originally anticipated, which has led to a number of surprises. The most striking example is $\alpha'$-Na$_5$V$_2$O$_5$. The $P2_1/mnm$ space group first proposed for its room-temperature crystal structure in 1975$^2$ allowed the discrimination between two distinct V sites in the unit cell, rationalizing the 1D magnetic properties: Namely, chains of V$^{4+}$ (3d$^1$) ions, antiferromagnetically (AF) coupled along the b-axis with an exchange constant $J=430-560$ K, are decoupled by spinless V$^{5+}$ (3d$^0$) chains$^3$. Three years ago, the discovery of a doubling of the lattice periodicity below $T_c=35$ K$^4$ associated with the opening of a gap $\Delta=9.8$ meV in the magnetic excitations$^5$, was first analyzed as the signature of a spin-Peierls (SP) transition, which would be the second case for inorganic solids, after CuGeO$_2$.$^6$

Nevertheless, several arguments can be raised against a simple SP-transition in this system: the strong BCS ratio 2$\Delta_0/k_B T_c=6$ $^7$ (compared to 3.5 in other SP systems), the weak field dependence of $T_c$ (5 times too small)$^8$ and the unusual distortion wave vector $k_c=(1/2,1/2,1/4)$ $^9$. In fact, recent X-ray investigations have revealed a centrosymmetric Pnmm space group (SG Pnmm) for the crystal structure with only one V site per unit cell $^{10,11}$. This has led to a redefinition of $\alpha'$-Na$_5$V$_2$O$_5$ as the first experimental realization of a 1/4-filled ladder system made of weakly coupled V$^{4.5+}$ chains, where a spin 1/2 is carried by the V-O-V orbitals on the rungs of the ladder (one d-electron per two equivalent V ions). This configuration leads to an effective S=1/2 1D Heisemberg AF spin Hamiltonian due to the strong AF coupling between the rungs $^{12,13,14}$. The most striking aspect of this new type of quantum spin chain is the strong interplay expected between lattice, spin and charge degrees of freedom, which should lead to peculiar instabilities $^{13,14}$. Below $T_c$, recent NMR results have proved the existence of two different V sites, attributed to V$^{4+}$ and V$^{5+}$.$^5$. This has motivated recent theoretical works taking into account a pure charge ordering (CO) instability$^{17,18}$ or CO coupled to SP-distortion$^{18,19}$. However, experimental proof in the vicinity of the transition is urgently required.

In this Letter, we present a $^{23}$Na ($I=3/2$) NMR study in a well-characterized single crystal of $\alpha'$-Na$_5$V$_2$O$_5$ $^{19}$. The strong quadrupolar interaction between $^{23}$Na nuclei and surrounding ions allows to monitor the structural transition occurring at $T_c=37$ K. Furthermore, by combining $^{23}$Na and $^{51}$V NMR, we infer a charge ordering of V$^{4.5+}$ into V$^{4+}$ and V$^{5+}$ ($\delta \ll 0.5$) for T$<37$ K, i.e. preceding the lattice distortion. This unconventional double transition implies the presence of both CO and SP ordering.

The three diagonal components of the quadrupolar tensor are given by $\nu_{\alpha\alpha} = eQV_{\alpha\alpha}/2h$ $^{22}$ with principal axes $\alpha,Z,Y,X$, $e$ the elementary charge, $Q$ the electric quadrupole moment, $h$ the Planck constant and $V_{\alpha\alpha}$ the principal values of the electric field gradient (EFG) tensor at the Na site. They can be readily extracted from the experimental data, free of the magnetic contribution, by measuring $|\nu_H|/|\nu_{H0}|$ (-1/2,-3/2) - $\nu_{H0}$ where $\nu_{H0}$ are the satellite lines for $H_0$||$\alpha$=X,Y,Z. Since the EFG tensor is traceless the two parameters, $\nu_{ZZ}$ and $\eta=(\nu_{XX}-\nu_{YY})/\nu_{ZZ}$ (asymmetry parameter) represent the EFG tensor fully. The $^{23}$Na NMR measurements were carried out by Fourier transforming the spin-echo signal recorded in a magnetic field $H_0=4.26$ Tesla. According to the local symmetry of the Na site in the SG Pnmm, the $a$, $b$ and $c$-axis are unambiguously identified as the principal axes and we deduced the parameters $\nu_{ZZ}=641$ kHz (-678 kHz), $\nu_{XX}=522$ kHz (581 kHz), $\nu_{YY}=118$ kHz (99 kHz) and $\eta=0.630$ (0.711) for $T=290$ K (resp. $T=50$ K) (see fig. 1) in agreement with earlier powder data at 50 K $^{23}$. 

1

19 Mar 2022
short distances due to covalency effects neglected in the model. The agreement is rather good but deviations are of course expected at large distances.

A) and vanadium (d\(5^+\)) site for \(T > T_0\) for \(T < T_c\) at 34.7 K. Inset 2: linear variation of \(\nu_0\) as function of \(1/T\) leading to a gap \(\Delta = 106\) K.

We note that the principal axes (XYZ) correspond to the crystal axes as (X=c, Y=a, Z=b). The EFG tensor can be expressed as \(V_{\text{total}} = [1 - \gamma_s]V_{\text{lattice}} + [1 - R_Q]V_{\text{ion}}\) with \(V_{\text{ion}}\) corresponding to the ion under investigation, and where \(\gamma_s\) and \(R_Q\) are empirical antishielding factors. \(V_{\text{lattice}}\) defines the pure lattice contribution and is given by

\[
V_{\text{lattice}} = V_{\alpha\beta} = \sum_j q_j [3X_{\alpha}^j X_{\beta}^j - \delta_{\alpha\beta} r_j^2]/r_j^2
\]

where \(q_j\) is the charge at site \(j\), \(X_{\alpha\beta}^j\) is the projection of the vector \(r_j^2\) from the nucleus under consideration to the charge \(q_j\). Applying an ionic point charge model by using the atomic positions of the SG Pnmn [2], and the average valencies Na\(^{+}\), O\(^{2-}\) and V\(^{4+}\) and \(V_{\text{ion}}=0\) (in the Na case) and by setting \(\gamma_{\infty}=0\), results in a lattice contribution of \(\nu_{bb} = -492\) kHz, \(\nu_{cc} = +469\) kHz and \(\nu_{aa} = +22\) kHz, which confirms our labeling of the axes. The main contribution to \(\nu_{\alpha\beta}\) comes from the oxygen (d\(\text{Na}-\text{O}=2.6\) Å) and vanadium (d\(\text{Na}-\text{V}=3.6\) Å) atoms. The agreement is rather good but deviations are of course expected at short distances due to covalency effects neglected in the ionic point charge approximation. Applying the same point charge model to the P2\(_1\)mn structure proposed in [2] leads to rotated principal axes in the a-c plane inconsistent with the experimental data. Thus, our observation of only one Na site at room temperature supports the SG Pnmn (on the NMR time scale [2]) in agreement with X-rays, Raman and \(^{51}\)V NMR data [10,11,9,15].

In order to check for modifications of \(V_{\text{lattice}}\) due to any change of the charge configuration, we have measured the T-dependence of \(\nu_{aa,bb,cc}\) between 8 and 300 K (fig. 1). We can divide the results into two different regimes. A high temperature regime for \(T \gg T_c = 34.7\) K (fig. 1), where an increase of \(\nu_{bb}\) and \(\nu_{cc}\) (a decrease of \(\nu_{aa}\)) was observed when decreasing \(T\). This is attributed to the decrease of the amplitude of lattice vibrations: The best fit (for \(H_0||a\)-axis) to the Bayer formula [2]

\[
\nu_{aa}(T) = \nu_{aa}(T=0)\left[\gamma + [\beta/(\exp(\Theta_D/T) - 1)]\right]
\]

with \(\gamma = 0.99\), \(\beta = 0.25\), \(\nu_{aa}(T=0) = 99.1\) kHz leads to a Debye temperature \(\Theta_D = 558\pm 13\) K in good agreement with reference [6]. Below \(T_c = 34.7\) K, a pronounced splitting of the Na satellite lines is observed for all magnetic field orientations (fig. 1), whereas no drastic change has been observed on the central line, thus ruling out any changes in magnetic interactions proving this to be a pure quadrupolar effect. Each satellite line is split into two sets of four lines of the same intensity (1/8) corresponding to 8 different quadrupolar Na sites in the low-T phase for \(H_0||a\) (fig. 1) and \(H_0||b\) (not shown here). In contrast only 3 lines are visible for \(H_0||c\) with half of the intensity for the central site and 1/4 for each of the two other sites. This is readily explained as a superposition of different sites for \(H_0||c\) when rotating the sample in the a-c plane (not shown here). For \(T < T_c\), \(\nu_{aa}(T)\) follows a critical behavior (for \(H_0||a,b\) or c-axis) corresponding to a second order transition connected with a continuous change of the atomic positions of vanadium and/or oxygen atoms as determined by X-rays [4]. Such a behavior is demonstrated...
here for one site for $H_0||c$ in the inset of fig. 1. We used a fit following the relation $\nu(T) = \nu(T_c) + \delta \nu [1 - T/T_c]^{\beta}$ resulting in the parameters $\nu(T = T_c) = 582.96$ kHz, $\delta \nu = 3.05 \pm 0.9$ kHz, $T_c = 34.66 \pm 0.04$ K and a critical exponent $\beta = 0.19 \pm 0.01$ in reasonable agreement with $\beta = 0.25$ and 0.20 as measured from the phonon anomaly [27] and by X-rays [28]. This critical exponent is far from the expected mean field value ($\beta = 0.5$) but also far from the one obtained in other SP compounds ($\beta = 0.32$) indicating clearly that this transition in $\alpha$-Na$_2$V$_2$O$_5$ is of a different type. According to the 8 distinct quadrupolar sites observed below $T_c$ in the a-b plane, the unit cell is at least doubled along the a and b-axis in agreement with the wave vector $k_c = (1/2, 1/2, 1/4)$ proposed in [2]. Considering the changes in $V_{lattice}$ ($\delta \nu_{ac}/\nu_{ac} = 4$ %, $\delta \nu_{bb}/\nu_{bb} = 8$ %, $\delta \nu_{aa}/\nu_{aa} = 85$ %) as derived from our measurements, the displacements occur unusually mainly along the a-axis. In addition, we found that applying only charge disproportionation at the V sites does not significantly affect the calculated EFG tensor at the Na site. We conclude that $^{23}$Na NMR probes a pure second order lattice distortion at $T_c = 34.7$ K.

In addition, we have performed $^{51}$V NMR in the same single crystal for $H_0||c$, in order to check on the change of the electronic state of the vanadium atoms when going through the transition. Only one V site (one set of 7 lines for a nuclear spin $I = 7/2$) was observed at $T = 100$ K, with the parameters $\nu_{cc} = 552$ kHz and $\eta = 0.24$, in agreement with Ref. [18]. The magnetic hyperfine shift $^{51}K_{cc}$ at this vanadium site (fig. 2) was extracted from the $T$-dependence of $^{51}\nu(-1/2, 1/2)$ between 5 and 300 K (inset 1, fig. 2). The shift measured for $H_0||c$ can be expressed as:

$$K_{aa}(T) = A_{aa} \chi_{aa}(T)/|B_N g_{aa}| + K_{orb} \eta$$

where $A_{aa}$ is the hyperfine coupling in Oe, $\chi_{aa}$ is the magnetic susceptibility in emu/mole, $B_N$ is the Bohr magneton in erg/Oe, $N_A$ the Avogadro number in mole$^{-1}$, $g_{aa}$ the corresponding g-tensor component and $K_{orb}$ is the orbital contribution. We first attribute the slow decrease of $^{51}K_{cc}$ above $T_c$ followed by a rapid drop around $T_c$ (inset 1, fig. 2) to the change of the magnetic susceptibility as is conceivable for a $S = 1/2$ Heisenberg AF chain approaching a singlet ground state through a SP-transition. In the $T = 0$ limit, $\chi$ vanishes, which allows us to determine $^{51}K_{orb} = 0.063 \%$. In order to determine $A_{cc}$ we have plotted $^{51}K_{cc}(T)$ as a function of $\chi(T)$ with $T$ as an implicit parameter (fig. 2). Usually, this leads to a unique linear relation in which the slope corresponds to the hyperfine coupling and the $T = 0$ limit is the orbital shift [29]. Suprisingly, we observe here a cross-over in the range 34.7 K < $T < 37$ K separating two distinct linear regimes. Two sets of parameters ($A_{cc} = -78.5$ kOe, $K_{orb} = 0.029 \%$ for $T > T_0 = 37$ K) and ($A_{cc} = -41.5$ kOe, $K_{orb} = 0.063 \%$ for $T < T_0 = 34.7$ K) are deduced, indicating a strong modification of the electronic state at the vanadium site in the vicinity of the transition. In the low-$T$ phase, we have detected two sets of $^{51}$V lines, but only the one with longer relaxation time and narrower linewidth is discussed here in detail, close to the transition [30]. The full spectrum has been recorded for this site at $T = 12$ K and we deduced $\nu_{cc} = 399$ kHz, $\eta = 0.5$ [31]. Referring to the parameters obtained previously for $T > T_c$ ($A_{cc} = -31$ kOe, $K_{orb} = 0.063 \%$, $\nu_{cc} = 399$ kHz, $\eta = 0.5$), we are now able to correlate this site with the one identified as the $V^{5+}$ site in Ref. [15]. This confirms charge ordering from only a single V site with valency $V^{5+}$ above $T_c$ to two different sites, a nominally $V^{4+}$ (shown here) and $V^{4+}$ site (not shown here) below $T_c$ (see discussion below). Applying the relation $T \chi^{spin}(T) \propto \exp(-\Delta/T)$ for a dimerized state [22], subtracting the orbital contribution, we deduce a spin gap with $\Delta = 106.3(1.3)$ K (inset 2, fig. 2) in good agreement with the values already derived from other data [22,4].

Noting that (i) $\nu_{ZZ} = 399$ kHz attributed to the nominal $V^{5+}$ site is larger than the one measured for the pure $V^{5+}$ site in V$_2$O$_5$ ($\nu_{ZZ} = 63$ kHz [23]), and (ii) we have measured a finite spin gap at this site. Thus this cannot be a pure $V^{5+}$ state but rather an hybridised $V^{4.5-\delta}$ site (resp. $V^{4.5-\delta}$ for the other one), with $\delta < 0.5$ varying slightly with temperature.

Fig. 3 summarizes the $T$-dependence of $^{51}K_{cc}$, reflecting the charge ordering at the V sites, of $^{23}$K$_{cc}$, reflecting the lattice distortion and of $^{23}$K$_{cc}$, which evidences the opening of the spin gap (scaling perfectly with $\chi(T)$). Here, we want to point out an important new observation not noticed before: It follows from fig. 3 that the charge ordering, evidenced by the rapid drop of $^{51}K_{cc}$ in the range $34.7 K < T_0 < 37 K$ precedes the lattice distortion and the opening of the spin gap, both occurring at $T_c = 34.7$ K. The linearity observed between $\chi(T)$ and $^{51}K_{cc}(T)$ (fig. 2), already holds at $T_c = 34.7$ K, and proves that this phase transition sets in only when the $V^{4.5-\delta}$ site is already in a new electronic configuration. In fact, this was proved directly by recording the low frequency
$^{23}$Na satellite line and the $^{51}$V$^{4.5+\delta}$ central line simultaneously (their resonance frequencies are very near to each other close to $T_c$): modifications of the $^{51}$V NMR spectrum between 37 and 34.7 K are not accompanied by any change of $^{23}\nu_{ce}$. We can also exclude the possibility of multiple transitions (as suspected in high resolution thermal expansion measurements [34]) by considering the sharp $C_p$ anomaly observed in crystals of the same batch $^{34}$ and by recalling that we probe, in the same sample, two different physical quantities on two different nuclei, both showing clearly distinct behaviors.

At this stage, we are ready to discuss (i) the nature of the transition and (ii) the corresponding low-$T$ structure. From our results, we can exclude a pure charge ordering as proposed in $^{19}$. This would lead to the simultaneous occurrence of lattice distortion and charge ordering in a single transition. On the other hand, the CO observed for $T_0 < 37 K$ excludes a pure SP ordering in agreement with the analysis of $^{33}$. The presence of CO as a precursor of the transition could be an explanation for the weak field dependence of $T_c$ $^{5}$ and the strong BCS ratio $^{6}$, as proposed in $^{16}$. Finally, recent numerical results point out the strong interplay between charge density wave instability and spin-Peierls order as intrinsic to this 1/4-filled ladder system and this should lead to a transition involving both lattice, spin and charge degrees of freedom $^{18}$. This is in good agreement with the double transition experimentally observed here. The simplest scenario consists in first a charge ordering restoring in part the magnetic decoupling between adjacent chains (for $34.7 K < T_0 < 37 K$), followed by a dimerisation at $T_c = 34.7 K$ with the formation of singlets along the b-axis. The low-$T$ structure should consist of dimerized chains of $V^{4.5+\delta}$ partially decoupled by inert chains of $V^{4.5+\delta}$ as proposed in $^{17}$. This simple ordering should however be energetically less favorable than a zig-zag arrangement between adjacent ladders $^{3,16,17,18}$.

Clearly, a better experimental characterization of the charge order is the key to understand the magnetism of $\alpha^-'Na_xV_2O_5$. Thus, a determination of the low-$T$ structure is definitively needed, which must be compatible with the NMR data, in order to unravel the configuration of the spin-singlets. The NMR results reported here, with eight inequivalent quadrupolar $^{23}$Na sites and two different Vanadium valencies, and where the lattice distortions occur predominantly along the a-axis provide a stringent test for the low-$T$ structure.

We would like to acknowledge X. Bourdon, S. Krämer, F. Mila and D. Poilblanc for helpful discussions and M.-H. Julien for his critical reading of the manuscript. Y.F.-R. was supported by a postdoctoral grant from the Alexander Von Humboldt Institut (AVH). M.M. would like to acknowledge support by the Fonds der Chemischen Industrie.

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