Low-energy excitations in NaV$_2$O$_5$.

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Abstract

In the (ab) polarized Raman scattering spectra of NaV$_2$O$_5$ single crystals, measured with 647.1 nm laser line at $T < T_c$, we found two modes at 86, and 126 cm$^{-1}$ not previously reported. These two modes, together with 66, and 106 cm$^{-1}$ modes, make an array of four low-energy equidistant modes below the energy onset of the continuum at about 132 cm$^{-1}$. All four modes are strongly suppressed by increasing Na deficiency, indicating their nonvibrational origin and the existence of a quantum phase transition at critical Na deficiency between 3 and 4%. These results question current understanding of NaV$_2$O$_5$ as quasi one-dimensional Heisenberg antiferromagnet.

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Sodium vanadate, NaV$_2$O$_5$, is a mixed valence compound ($V^{4+} : V^{5+} = 1 : 1$) with a structure consisting of vanadium-oxygen (VO$_5$) pyramids, that are connected via common edges and corners to form layers in the the ab plane. The structure can be described as an array of parallel ladders (running along the b axis) that are coupled to form a trellis lattice, see Fig. 1. Each rung is made of V-O-V bond, and contains one valence electron donated by the sodium atoms which are situated between layers as intercalants.

This compound exhibits a phase transition at $T_c = 34K$ [1] that is usually referred to in the literature as a charge-ordering (CO) phase transition. From the mixed-valence point of view its existence is not unusual, since a common consequence of the mixed valence is the appearance of charge-ordering, which is a class of metal-insulator transitions [2]. However, the phases on both sides of the transition in NaV$_2$O$_5$ are insulators, and a very interesting interplay between charge and spin dynamics results in the phase-transition discovered in this compound. Indeed, despite the fact that the vanadium ions have uniform valence of +4.5 at room temperature [3],[4] (indicating the quarter-filled structure of V-O-V rungs [4], and suggesting a metallic state!), the magnetic susceptibility of NaV$_2$O$_5$ is in excellent agreement with Bonner-Fisher curve for a one-dimensional antiferromagnet (AF) [1]. The one-dimensionality of the magnetic ordering is realized along the b axis which is perpendicular to the V-O-V rungs [1]. Furthermore, at low temperatures, the susceptibility decreases rapidly to zero in accord with a spin-liquid ground state, and suggesting the existence of a
spin-Peierls (SP) transition. However, since the physical properties (e.g. transition temperature) of NaV$_2$O$_5$ are insensitive to an applied magnetic field \[1,6\], the SP scenario can be ruled out.

Accordingly, several theoretical investigations of the role of electron correlations (intersite Coulomb interactions) in charge dynamics, and/or charge-ordering have been presented \[7–12\]. So far, almost all proposed charge configurations (“in-line”, ”zigzag”, or a ”ladder-like”) effectively lead to a 1D Heisenberg AF with a spin-excitation gap, and a spin-liquid ground state. In the spin-cluster model \[13\], which is different in that respect, the spin-gap arises from a finite number of spins of the isolated cluster. All concepts were tested by comparison with experimental data with some success, but no consistent picture has emerged yet. In fact, the central issue appears to be the energy scale of the CO in NaV$_2$O$_5$ and how it should manifest itself in optical \[14–18\], and neutron scattering spectra \[19,20\]. This concerns both the origin of optical transitions in the 0.8-5 eV energy range, as well as the origin of the low-frequency electronic excitations (observed in both IR and Raman spectra), and the modes associated with a spin dynamics.

In Raman spectra of NaV$_2$O$_5$, the phase transition manifests itself through the appearance of various new Raman active modes \[16–18\] below the phase transition temperature. The high-temperature phonon excitations in the Raman spectra \[18\] are well understood in terms of the crystal symmetry (space group Pmmm) and of the selection rules as determined from structural analysis \[4\]. The origin of the newly activated Raman modes is, however, still unclear mainly due to a lack of understanding of the low-temperature NaV$_2$O$_5$ crystal structure \[22\]. Of particular interest are the low-frequency modes at 66, 106, and 132 cm$^{-1}$ found in the Raman spectra of the low temperature phase \[16–18\]. These modes are of special interest because of their proximity to spin-gap energy ($\sim 65 – 85$ cm$^{-1} \[19,20\]$), and their potential magnetic origin. The 66 and 106 cm$^{-1}$ modes were previously assigned as magnetic bound states \[17\], mainly based on the slow increase (almost perfectly linear) of their intensities with decreasing temperature (similar behavior is found for the two-magnon bound state at 32 cm$^{-1}$ in CuGeO$_3$ \[23\]), and because of their insensitivity to the magnetic field. This assignation is supported by most of the theoretical models that predict a chain type effective magnetic ordering in NaV$_2$O$_5$. However, the energy of the 66 cm$^{-1}$ mode is very close to the spin gap. According to the recent neutron scattering study the spin-gap mode coincides in energy with 66 cm$^{-1}$ mode at ($Q_a = integer, Q_b = Q^{ZC}$), and at ($Q_a = half \! - \! integer, Q_b = Q^{AF}$). If this mode is truly a magnetic bound state of two spin-gap excitations, it is difficult to understand why its binding energy is close to (equal to), the spin-gap energy itself. Two questions naturally arise: Is the one-dimensional AF Heisenberg model relevant for the magnetic dynamics of NaV$_2$O$_5$, and are those low-frequency Raman-active modes really the magnetic bound states? Clearly, further experiments are necessary in order clarify present understanding of physical properties and Raman spectra of NaV$_2$O$_5$.

Here, we present the temperature dependent Raman spectra of Na$_x$V$_2$O$_5$, 1 $\geq x \geq$ 0.96. Four modes are found in the low-temperature, $T < T_c$, (ab) polarized Raman spectra of NaV$_2$O$_5$ that are separated by a common energy of 20 cm$^{-1}$. Two of them, at 66 and 86 cm$^{-1}$, are also detected in recent neutron scattering experiments \[20\]. Simultaneous activity of the modes in the Raman and neutron scattering spectra, suggest that, at least, the 66 cm$^{-1}$ mode is not the magnetic bound state. The equal energy separation of the low-frequency modes and a strong suppression of their energy and intensity by Na deficiency, question
current understanding of the low-temperature magnetism in NaV$_2$O$_5$ as being simple 1D alternating Heisenberg AF.

Polarized Raman experiments were performed on Na$_x$V$_2$O$_5$ single crystals (size $\sim 1 \times 3 \times 1$ mm$^3$ along a, b, and c) prepared as described in Refs. 1,21. As excitation source we used 647.1 nm line from Kr$^+$ ion laser. The beam, with an average power of 5 mW, was focused (spot diameter $\sim 80\mu$m) on (001) surfaces of the crystals. The spectra were measured in a quasi-backscattering geometry using a DILOR triple monochromator equipped with a LN$_2$ cooled CCD camera.

In Fig. 2 we present the typical Raman scattering spectra of nominally pure NaV$_2$O$_5$ in (aa) and (ab) polarized configurations, measured at T=6 K with 647.1 nm laser line. The modes in the (aa) spectra are in agreement with previous reported data but are more intense due to a resonance effect 24. However, in (ab) spectra the two new modes at 86 and 126 cm$^{-1}$ are found. These modes were not previously observed in the Raman spectra measured with 488 and 514.5 nm laser lines 16–18. Altogether, the modes at 66, 86, 106, and 126 cm$^{-1}$ make an array of four low-energy equidistant modes, separated by 20 cm$^{-1}$. Besides, all four modes have energies lower then the onset of the continuum that starts at about 132 cm$^{-1}$, which is twice the energy of the lowest mode, see Inset of Fig. 2. A four modes show strong temperature dependence. In fact, their intensities strongly reduce at the phase transition temperature, forming a broad band at higher temperatures, see Fig.3. Also, while all four modes have comparable intensities in the (ab) polarized configuration, the 86 and 126 cm$^{-1}$ modes are strongly suppressed in the (aa) and (bb) polarized geometries with respect to the 66 and 106 cm$^{-1}$ modes (Fig. 2). As we already mentioned, the simultaneous activity of the 66 cm$^{-1}$ mode as a magnetic bound state highly questionable, since singlet-singlet transitions cannot be observed with a neutron scattering. Possible interpretation of this mode as one-magnon excitation 14 seems also unlikely, since no change of either intensity or energy is found in the magnetic fields up to 12 T, which is in contrast to the expected linear splitting for a singlet-triplet transition. The next possibility is that 66 cm$^{-1}$ excitation is a vibrational mode; folded phonon for example. If so, the equidistant energy separation between modes in (ab) polarization would then be a simple coincidence, which we believe is not the case as discussed in the next paragraph.

In order to further examine the low-frequency dynamics of NaV$_2$O$_5$ we analyze the effects associated with sodium deficiency. Sodium deficiency strongly influences the properties of NaV$_2$O$_5$ 1,21. With increasing sodium deficiency, the CO phase transition temperature decreases and disappears with Na content around 0.97 (3% deficiency) 28. Fig. 3 shows the low-frequency Raman spectra of nominally pure NaV$_2$O$_5$ as a function of temperature (upper panel), and several Na-deficient Na$_x$V$_2$O$_5$ samples at T=6 K (lower panel) in the (aa) scattering geometry. For sodium deficiencies above 3% the modes associated with the CO phase completely vanish, in a good agreement with earlier data showing a full suppression of the phase transition at about this concentration 28. The modes also shift in energy as the Na concentration is reduced by about 6-7% in clear contrast to other (aa) low-temperature modes (shifts are $\sim 1\%$). In the (ab) scattering geometry these modes behave in a similar way, except that now the 86 and 106 cm$^{-1}$ modes cannot be observed for $[Na] \leq 0.99$, probably because of their relatively small intensity. Decreasing $[Na]$ introduces the holes in the V-O planes since it transforms the V$^{4+}$ (S=1/2) ions into V$^{5+}$ (S=0). This effect is
similar to nonmagnetic-magnetic substitution of ions. Similar mode suppression is observed in the Raman spectra of Zn-substituted CuGeO$_3$ [29], where the singlet mode (the magnetic bound state) shifts to lower energies with increasing Zn doping, demonstrating renormalization of the spin-gap (a suppression of the phase transition is observed by substitution of non-magnetic ions for Cu in the spin-Peierls compound CuGeO$_3$ [30]). In this case the effect is caused by the presence of unpaired spins, introduced by breaking of the spin-singlets upon substitution. Thus, although we question here the assignation of 66 and 106 cm$^{-1}$ modes as magnetic bound states, sodium deficient Raman spectra indicate that low-frequency modes in NaV$_2$O$_5$ are not vibrational modes, since phonon energies should not be so sensitive to small impurity concentrations.

From the neutron scattering spectra [20] it has been argued that the 66 and 86 cm$^{-1}$ modes have a common origin (two spin-gap modes from two unequal magnetic chains), but on the other hand, the Raman spectra indicate that 66 and 106 cm$^{-1}$ make pair. Therefore, having all this in mind, it is possible that all four modes have the same origin (note, that the weak structure around 106 cm$^{-1}$ seems to exist in the neutron scattering spectra [20]). If so, this question our present understanding of physical properties of NaV$_2$O$_5$ since, the equidistant mode separation is not inherent property of 1D Heisenberg AF model. The quasi-1D Heisenberg or spin-phonon model has been predicted to have a spectrum consisting of multiple soliton-antisoliton boundstates, with the number of boundstates increasing as the inter-chain coupling gets weaker. However, such a model does not naturally predict 4 equally spaced states [23].

Still, the presence of a strong singularity at 2$\Delta_s$ in the Raman spectra is the important indication of the low-dimensional magnetism. The features that represent the onset of a two-magnon continuum at 2$\Delta_s$ have been observed in the Raman spectra of CuGeO$_3$ [23], and CaV$_2$O$_5$ [20], in the form of strong asymmetric lines with a tail towards higher energies. The both compounds are quasy-1D magnetic systems with a spin-gap. CuGeO$_3$ is a 1D AF with a spin gap which opens due to alternation of exchange constants along the chain. CaV$_2$O$_5$ is a weakly coupled dimmer system, i.e a two-leg-ladder compound with much stronger exchange along the rungs than along the legs. In NaV$_2$O$_5$ a similar structure is found around 132 cm$^{-1}$ which could represent the onset of two-magnon continuum (see Inset Fig. 2). If so, the spin-gap in NaV$_2$O$_5$ should be 66 cm$^{-1}$, and there is a mode at this energy in both neutron and Raman spectra. The spin-gap mode is a singlet-triplet transition which should split in an applied magnetic field (which is not observed), unless the triplet ($S^z$) degeneracy is already somehow removed? On the other hand, its activity in (ab) polarized scattering configuration indicates that the magnetic order in NaV$_2$O$_5$ is not the chain-type like CuGeO$_3$, where two-magnon excitation is observed only with incident and scattered electromagnetic fields polarized parallel to the chain direction (note that in a ladder case the Fleury and Loudon exchange scattering mechanism [27], allows the two-magnon Raman scattering in a crossed configuration as well).

Finally, let us return to Fig. 3. The most remarkable effect is the similarity between the temperature dependent Raman spectra of pure NaV$_2$O$_5$, and Na deficient, T=6 K Raman spectra. If the behavior of any of these modes can be related to order parameter of the NaV$_2$O$_5$ phase transition, then the order parameter must have the same scaling for either T or x. At the moment, it is not clear what causes such an effect, but we believe that it indicates the influence of quantum criticality to the phase transition of NaV$_2$O$_5$. 
In conclusion, we find four low-frequency modes separated by a common energy of 20 cm$^{-1}$, that can be associated with the CO phase of NaV$_2$O$_5$. These modes are strongly suppressed with Na deficiency indicating their nonvibrational origin and the existence of a quantum phase transition at critical Na deficiency between 3 and 4%. The equal energy separation of the low-frequency modes and a strong suppression of their energy and intensity with Na deficiency, question current description of the low-temperature magnetism in NaV$_2$O$_5$ as being simple 1D alternating Heisenberg AF.

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FIGURES

FIG. 1. Schematic representation of the NaV$_2$O$_5$ crystal structure in the (001) and (010) planes. Effective representation of parallel ladders coupled in a trellis lattice is also shown.

FIG. 2. The low-frequency (aa) and (ab) polarized Raman scattering spectra of NaV$_2$O$_5$ at 6 K, measured using $\lambda =647.1$ nm laser line. Inset: The (ab) Raman spectra in extended frequency range at temperatures above and below CO phase transition.

FIG. 3. upper panel: The low-frequency (aa) polarized Raman scattering spectra at various temperatures between 10 K and 35 K. lower panel: The (aa) polarized Raman scattering spectra of samples with different Na content, measured at T=6 K. Inset: The Raman spectra of nominally pure NaV$_2$O$_5$ at various temperatures up to 100 K.
M.J. Konstantinovic et al. Fig. 1
Konstantinovic et al. Fig. 2

Intensity (arb. units) vs. Raman shift (cm\(^{-1}\))

- (aa) peak at 66 cm\(^{-1}\)
- (ab) peak at 89 cm\(^{-1}\) (high-T phonon)
- Neutrons peak near 126 cm\(^{-1}\)

Inset: Raman spectra for ab and neutrons at 6 K.

λ = 647.1 nm

T = 6 K
Konstantinovic et al. Fig. 3

$x=1$  $T=10$ K

$x=1$  $T=6$ K

$Na_xV_2O_5$

$\lambda=647.1$ nm

Raman shift (cm$^{-1}$)

Intensity (arb. units)