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Raman scattering study of η-Na$_{1.3}$V$_2$O$_5$ in the charge disordered and ordered phases

Z.V. Popović [a,*], V.V. Moshchalkov [b], M. Isobe [c], Y. Ueda [c]

[a] *Center for Solid State Physics and New Materials, Institute of Physics, Pregrevica 118, 11080 Belgrade, Serbia*
[b] *The Laboratory of Solid State Physics and Magnetism, Catholic University of Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium*
[c] *Materials Design and Characterization Laboratory, Institute for Solid State Physics, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan*

Abstract

Polarized Raman spectra of sodium vanadium oxide η-Na$_{1.3}$V$_2$O$_5$ single crystals were measured over wide temperature and frequency ranges. In total 27 first-order Raman modes, as well as overtones and combinational lines, are observed. For the charge ordered phase no appearances of new phonon- or spin-related Raman modes are registered on lowering the temperature to 10 K. The phase transition at about 100 K is manifested through an abrupt change of the phonon mode frequencies and dampings.
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1. Introduction

In the sodium–vanadium oxide system Na$_x$V$_2$O$_5$, there exist seven phases denoted as α-, β-, δ-, τ-, α'-, η-, and κ-phases in ascending order of x. They are mixed-valence compounds of V^{4+} (d^1, S = 1/2) and V^{5+} (d^0, S = 0) ions, among which α'-Na$_x$V$_2$O$_5$ ($x = 1.0$) has been studied most intensively because of its anomalous phase transition like a spin–Peierls transition [1,2]. Recently, Isobe and Ueda [3] have reported that the η-phase Na$_x$V$_2$O$_5$ ($x \sim 1.3$) exhibits low dimensional behavior of the magnetic susceptibility. They also suggested a spin-singlet state since the magnetic susceptibility became very low at low temperatures. A tentative explanation for this spin-gap behavior can be found in Ref. [4].

The η-phase, which can also be denoted by the stoichiometric formula Na$_9$V$_{14}$O$_{35}$, crystallizes at room temperature in the monoclinic system (space group $P2/c$) with an original structure built up of layers consisting of VO$_5$ square pyramids sharing edges and corners, with their apical oxygens pointing up

and down alternately to form double zigzag chains in the [100] direction; Fig. 1(a). These double chains, structurally similar to that of V$_2$O$_5$ layers of α'-NaV$_2$O$_5$, are bridged by VO$_4$ tetrahedra to form the V$_2$O$_5$ layers. A peculiarity of the Na$_9$V$_{14}$O$_{35}$ crystal structure is sharing of VO$_5$ chains every five VO$_5$–VO$_5$ units, as illustrated in Fig. 1(b). The Na atoms are located between the layers; Fig. 1(c). The V$_2$O$_5$ layers contain V^{4+}, V$^{4.5+}$, and V^{5+} ions. Each V(i)O$_4$ ($i = 4, 7$) tetrahedron has a V^{5+} ion (d^0), each V(i)O$_5$ ($i = 1, 2, 3, 6$) square pyramid has a V^{4+} (d^1) ion, and each V(5)O$_5$ square pyramid has a V$^{4.5+}$ ion; see Fig. 1(b).

Many of the physical properties of Na$_9$V$_{14}$O$_{35}$, including the lattice dynamics, are unknown. Very recently, low temperature structural measurements [5] have revealed the existence of a structural second-order phase transition in this oxide, around 100 K, associated with a concomitant charge ordering. The low temperature structure remains centrosymmetric with space group $P2/c$ but with a doubled b lattice parameter in comparison with that at high temperature, and the two vanadium sites which host V$^{4.5+}$ ions at room temperature become stabilized as one V^{4+} and one V^{5+} at low temperature. The dimerization along the b-axis observed below 100 K means

* Corresponding author. Tel.: +381 11 3161385; fax: +381 11 3162190.
E-mail address: Zoran.Popovic@phy.bg.ac.yu (Z.V. Popović).
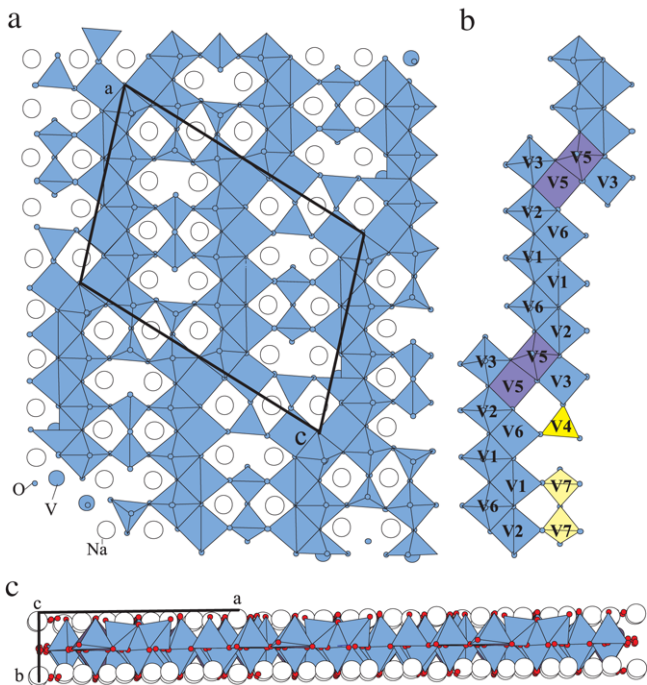
Fig. 1. (a) Crystal structure of η-Na$_{1.3}$V$_2$O$_5$ projected on the (ac) plane. (b) The VO$_5$ chains running parallel to the a-axis. (c) Schematic representation of the η-Na$_{1.3}$V$_2$O$_5$ crystal structure projected on the (ab) plane.

that each magnetic unit contains, at low temperature, 2×9 S = 1/2 spins. The origin of the spin gap can hence be related to the formation of this superstructure below 100 K in the system. The X-band electron spin resonance [6] and complementary magnetic susceptibility data [5] give additional evidence for the transition around 100 K and confirm the existence of the spin gap, which is estimated to be of the order of 35 K.

Raman scattering offers several unique features in the investigation of charge ordered systems [7–9]. For example, by providing energy, symmetry, and lifetime information concerning lattice, spin, as well as charge excitations, Raman scattering affords unique insight into the interplay among these coupled excitations in various phases. Here we report the Raman scattering measurements made on the η-Na$_{1.3}$V$_2$O$_5$ single crystals at different temperatures. We have observed 27 first-order Raman active modes, their overtones and combinational lines. The appearance of new phonon- or spin-related modes is not registered in the low temperature phase. The temperature dependence of the phonon frequency and damping shows that the phase transition has a rather strong influence on the phonon dynamics of η-Na$_{1.3}$V$_2$O$_5$.

2. Experiment

The present work was performed on single-crystal plates of Na$_{1.285}$V$_2$O$_5$ with dimensions typically about $1.5 \times 2.5 \times 0.3$ mm^3. The details of the sample preparation were published elsewhere [10]. The Raman spectra were measured in the backscattering configuration using a micro-Raman system with a DILOR triple spectrometer including a liquid nitrogen cooled charge-coupled-device detector. The 514.5 and 532 nm lines of

an Ar-ion laser and an Nd-YAG laser were used as excitation sources. Low temperature measurements were carried out in an Oxford continuous flow microscope cryostat with a 0.5 mm thick window. The laser beam was focused by a long working distance ($\sim$10 mm focal length) microscope objective (magnification 50$\times$). Overheating of the samples was observed with the laser power levels as low as 40 mW (2.5 mW at the sample). We found that a laser power level of 0.25 mW on the sample is sufficient to obtain a Raman signal and, except as regards the signal-to-noise ratio, no changes of the spectra were observed as a consequence of laser heating on further lowering the laser power. The corresponding excitation power density was less than 1.25 kW/cm^2.

3. Results and discussion

Na$_9$V$_{14}$O$_{35}$ has a P-centered monoclinic unit cell [3] with parameters $a = 1.5209$ nm, $b = 0.5036$ nm, $c = 2.0786$ nm and space group $P2/c$ (C_{2h}^4). The unit cell consists of two formula units ($Z = 2$) comprising 116 atoms in all. Since there are a large number of atoms in the unit cell, we can expect a large number of optically active modes. The site symmetries of the V(1),... V(7), Na(1),... Na(4), O(1),... O(8), and O(10),... O(18) atoms in the (C_{2h}^4) space group are C_1 (4g). The Na(5) and O(9) atoms have (2e) and (2f) site symmetry (C_2), respectively. The factor-group analysis (FGA) yields

$$(C_1) : \Gamma = 3A_g + 3B_g + 3A_u + 3B_u,$$
$$(C_2) : \Gamma = A_g + A_u + 2B_g + 2B_u.$$

Summarizing these representations and subtracting the acoustic ($A_u + 2B_u$) modes, we obtained the following irreducible representations of Na$_9$V$_{14}$O$_{35}$ vibrational modes of the $P2/c$ space group:

$$\Gamma^{\text{opt.}}_{\text{Na}_9\text{V}_{14}\text{O}_{35}} = 86A_g(xx, yy, zz, xz) + 88B_g(xy, yz)$$
$$+ 85A_u(\mathbf{E} \parallel \mathbf{y}) + 86B_u(\mathbf{E} \perp \mathbf{y}).$$

According to this representation one can expect 345 modes from which 174 are Raman active. At first glance, in the room temperature Raman spectra of η-Na$_{1.3}$V$_2$O$_5$ (Fig. 2) we found that the number of observed modes is much less than the FGA predicted. Namely, for parallel polarizations (A_g symmetry modes) in total 23 modes at about 162, 213, 232, 250, 321, 333, 355, 377, 439, 466, 484, 514, 527, 565, 648, 811, 823, 849, 900, 931, 943, 964, and 990 cm^{-1} are clearly seen for the (aa) polarization and three additional modes at 309, 400, and 948 cm^{-1} for the (cc) polarization. For the crossed (ac) polarization only one Raman active B_g symmetry mode at 817 cm^{-1} is observed. Further, almost all of observed modes with energies lower than 850 cm^{-1} have a large width. This strong broadening is due to a strong electron–phonon coupling and/or near degeneracy of many modes with nearly the same energies. Finally, we found that these spectra are similar to the AV$_2$O$_5$ (A = Na, Cs) Raman spectra [11], due to the structural similarities (VO$_5$ pyramids and VO$_4$ tetrahedra in Na and Cs vanadates, respectively) and similarities in the normal coordinates of their vibrational modes.