A comparative Raman study between YbVO$_3$ and YVO$_3$

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Abstract. An orbital ordering effect is observed in YbVO$_3$ around 170 K while the crystal structure is orthorhombic (space group $\textit{pnma}$). A monoclinic transition has been reported below $T_N = 104$ K, while according to recent specific heat measurements, it occurs at 170 K. The crystal structure of YVO$_3$ at 300 K is also orthorhombic. It becomes monoclinic at $T_c = 200$ K and back orthorhombic at $T = 77$ K. Spins order into the C-type antiferromagnetic structure below $T_{N1} = 116$ K and the order changes into the G-type antiferromagnetic structure below $T_{N2} = 77$ K. Controversial interpretations of YVO$_3$ Raman active excitations have been reported. For instance the 489 and 679 cm$^{-1}$ excitations have been assigned either to phonons or orbitons in two recent studies. In this communication we present a micro-Raman study of YbVO$_3$ and YVO$_3$ Raman active excitations as a function of temperature in order to trace the multiple phase transitions. Also by comparing the two single crystals spectra and previous studies in rare-earth manganites, high energy Raman active excitations are tentatively assigned.

1. Introduction
Recently, the experimental confirmation of a new kind of predicted elementary orbital wave excitations or orbitons [1] has represented a challenge for the condensed matter experimentalists. In transition metal oxides which are electron correlated Mott insulators, modulations in the relative shape of the electronic clouds in an orbitally ordered state could give rise to orbitons [2]. The orbitons represent a dynamical response that propagates between the lattice transition metal ion orbitals. They are considered as potential candidate for ultrafast switching using light electromagnetic field. First claim of orbiton detection was reported in a Raman scattering study of LaMnO$_3$ involving the exchange of O-2$p$ and Mn-c$g$ electrons [3]. Nevertheless, the assignment of these excitations to orbitons have been questioned [4-7]. Orbiton waves have also been investigated by infrared [8] and Raman scattering in YVO$_3$ a perovskye-type vanadium oxide; again controversial interpretations of the Raman active excitations have been reported [9, 10]. While Sugai and Hirota identified the 679 cm$^{-1}$ excitation as orbiton and the 489 cm$^{-1}$ excitation as phonon [9], Miyasaka et al. [10] reversed their identifications as phonon and orbiton respectively. In the case of the RMnO$_3$ (R= Pr, Eu, Dy, Ho, Y) manganites, and based on polarization properties, lattice-dynamics calculation, and oxygen isotope substitution, Iliev et al. [7] have shown that all the
excitations attributed to orbitons by Saitoh et al. [3] are pure phonons. In this communication we argue that the same situation prevails in high quality vanadates YVO$_3$ and YbVO$_3$.

2. Experiment

0.5 cm$^{-1}$ resolution Raman spectra were measured in the back-scattering configuration using a Labram-800 Raman microscope spectrometer equipped with a 50X (~0.35 mW/(µm)$^2$; 3 µm laser spot) magnification objective, and a nitrogen cooled CCD detector. He:Ne (λ = 6328 Å (1.96 eV)) laser, whose power was kept below 2 mW, and appropriate notch filter were used with the samples mounted on the cold finger of a micro-Helium Janis cryostat. Polycrystalline samples of Y(Yb)VO$_3$ were prepared by the chemical reduction of Y(Yb)VO$_4$ powder obtained by high-temperature solid-state reaction of stoichiometric mixtures of predried Y(Yb)$_2$O$_3$ and V$_2$O$_5$. Y(Yb)VO$_4$ was reduced by annealing the powder in a flow of pure H$_2$ at 1000 °C. A single-crystalline boule of approximately 6mm in diameter and 60-70 mm in length was grown by traveling solvent floating zone method. The crystallinity of the boule was checked by X-ray and the composition by electron probe microanalysis.

3. Results and Discussion

The room temperature YVO$_3$ crystallographic structure is orthorhombic with Pnma space group (a = 5.61 Å, b = 7.55 Å and c = 5.61 Å). It becomes monoclinic (P2$_1$/a) at T = 200 K and undergoes two magnetic transitions at T$_{N1}$ = 116 K and T$_{N2}$ = 77 K [11]. The primitive cell contains four molecular units resulting in 7A$_g$ + 5B$_{1g}$ + 7B$_{2g}$ + 5B$_{3g}$ Raman active modes.

A$_g$ symmetry YVO$_3$ Raman active excitations as observed at 300 K (~266, 278, 337, 427, 475, 495 cm$^{-1}$) are shown in Fig. 1 as well as their temperature evolutions (~268, 279, 338, 429, 475, 500 cm$^{-1}$) at 80 K. A broad band (650-750 cm$^{-1}$), not predicted by group analysis, is observed at 300K and is better resolved at 80 K (~650, 685, 705, 722 cm$^{-1}$).

![Figure 1. YVO$_3$ Raman active excitations as a function of temperature in the a(bb)a experimental configuration. Arrows indicate the excitations previously assigned to orbitons.](image-url)

YbVO$_3$ vanadate is also orthorhombic, as YVO$_3$, at room temperature and becomes magnetically ordered and monoclinic below T$_{N}$ = 104 K [12] (however, recent unpublished specific heat measurements indicate that the monoclinic transition occurs at T = 170 K). Its Raman active excitation frequencies are close to the ones of YVO$_3$ and have the same temperature evolutions as...
shown in Fig. 2. (~ 253, 272, 544, 441, 486, 503 cm$^{-1}$) at 300 K and (~254, 272, 345, 442, 482, 516 cm$^{-1}$) at 80 K. Also similarly to YVO$_3$, a broad band (~ 640-800 cm$^{-1}$) is observed at 300 K and resolved at 80 K (~ 653, 673, 694 cm$^{-1}$).

Figure 2. YbVO$_3$ Raman active excitations as a function of temperature in the a(bb)a experimental configuration. Arrows indicate the excitations previously assigned to orbitons.

In YVO$_3$ and YbVO$_3$, the V$^{3+}$ ion has two $t_{2g}$ d electrons. One electron occupies the lower energy $xy$ orbital and the other electron occupies either the $yz$ or the $xz$ orbital. While in YVO$_3$ the $yz$ and $xz$ orbitals order in the G-type below 200 K, and in the C-type below 77 K [11], in YbVO$_3$ important changes in the V-O distances are accompanied by reinforced orbital ordering below the magnetic transition at $T_N = 104$ K [12]. Interestingly, the excitations that have been designated in YVO$_3$ as orbitons around 700 cm$^{-1}$ by one group [9] and 500 cm$^{-1}$ by another group [10], are actually observed at room temperature in both YVO$_3$ and YbVO$_3$ vanadates at a temperature well above the orbital ordering temperatures for both compounds. Thus the 500 and 700 cm$^{-1}$ excitations have phononic character. Nevertheless, as attested by their relative intensities with the $A_g$ symmetry phonon 338 cm$^{-1}$ (in YVO$_3$) or 345 cm$^{-1}$ (in YbVO$_3$), their polarizabilities are affected by the various magnetic transitions and orbital orderings [13].

The detected excitations around 700 cm$^{-1}$ outnumber the $\Gamma$ point predicted phonons in the $A_g$ symmetry. Moreover, they are not only observed in the $A_g$ configuration but also in the b(ac)b configuration that corresponds to $B_{1g}$ symmetry as shown in Fig. 3.
Figure 3. YbVO₃ Raman active excitations in the b(ac)b configuration at T = 80 K. Similarly to the manganites which have the same structure and close frequency phonon excitations as vanadates, the excitations (~ 650, 685, 705, 722 cm⁻¹) in YVO₃ and (~ 653, 673, 694 cm⁻¹) in YbVO₃ could rather be of phonon density-of-states origin related to apex oxygens and plane oxygens as predicted by lattice dynamical calculations using a shell model [14]. Nature of these vibrations is further confirmed in the manganites by oxygen isotope substitution (O¹⁶/O¹⁸) that results in frequency-shifts proportional to the square root of the isotope mass [7]. Such result is consistent with phononic character and excludes orbiton character whose excitation frequency is not affected by oxygen substitution.

4. Conclusion
In this comparative Raman study of the YVO₃ and YbVO₃ single crystals, it is shown that all the Raman active excitations are of phonon origin solving an earlier controversy about their identifications. Their relative intensities are influenced by the various magnetic and orbital orderings that affect their polarizabilities as temperature is lowered. Similarly to the manganites, the excitations that are observed around 700 cm⁻¹ at room temperature are associated with apex and plane oxygens [14] and assigned to some disorder induced phonon density-of-states.

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References