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Micro-Raman study of the spin and orbital ordering in SmVO₃

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Abstract. The spin and orbital ordering have been examined for high-quality SmVO₃ polycrystalline compound using Raman spectroscopy. Measurements were obtained on individual microcrystallites in the approximate \( y(z)\bar{y} \) and \( y(xx)\bar{y} \) scattering configurations at low temperatures (down to 20K). Based on our experimental data we present evidence of a coexistence of the G and C-type OO phases that occur in SmVO₃ for temperatures below 100K. This phase coexistence of orbital orderings puts SmVO₃ in a different category from all the other RVO₃ compounds that have been studied yet.

1. Introduction

SmVO₃ is a perovskite-type vanadate of the form RVO₃ (R=rear earth or Y) with medium size R-cation. The up to now experimental investigations have not defined clearly its phase diagram [1, 2, 3]. The first structural phase transition of SmVO₃ occurs at \( T_{OO1}=200K \) [1, 4]. At this temperature the symmetry of the lattice changes from orthorhombic Pbnm to monoclinic P2₁/c accompanied concomitantly with the G-type orbital ordering (OO), as temperature is lowered. The second transition occurs at \( T_N\approx129K \) [1, 2, 4] where the system undergoes a magnetic transition from paramagnetic to C-type (SO) antiferromagnetic phase. According to Blake et al [1] SmVO₃ undergoes a third transition at \( T_{OO2}=115K \), which leads to the coexistence of the G and C-type OO phases.

Raman spectroscopy can be used for the investigation of OO because of the sensitivity of this technique to lattice distortions that in the particular case are caused by the Jahn-Teller effect. In this work the temperature dependence of the modes observed in SmVO₃ is investigated in order to clear out the situation with the phase transitions that occur in this system.

2. Experimental setup

Polycrystalline compound of high-quality SmVO₃ has been examined using Raman spectroscopy. The Raman spectra were obtained at nominal temperatures of 20K to RT with a T64000 Jobin-Yvon triple spectrometer equipped with a liquid nitrogen charged coupled device (CCD) and a microscope (magnification x100). The 514.5 nm line of an Ar⁺ laser was used for excitation. Low temperature measurements were achieved using an Oxford micro-He cryostat appropriately modified to allow the study of microcrystallites at various scattering geometries. The spectra
presented here have been acquired on individual microcrystals (typical size of a few µm) in the zz and xx/yy polarization. Accumulation time were of the order of 3-6 hours.

3. Results and Discussion

Figs.1 and 2 present Raman spectra in the \( y(zz) \bar{y} \) and \( y(xx) \bar{y} \) (or \( x(yy) \bar{x} \) ) scattering polarization respectively, at various temperatures for SmVO\(_3\). The \( y(zz) \bar{y} \) polarization spectra at RT are characterized by three modes that appear at \( \sim 226 \text{ cm}^{-1} \), \( \sim 308 \text{ cm}^{-1} \) and \( \sim 442 \text{ cm}^{-1} \). Miyasaka et al., investigated the Raman spectra of other pervoskite-type RVO\(_3\) (R=La, Nd, and Y) compounds and observed similar peaks, the energy of which decreases as the ionic radii increases from Y to La [4]. Considering the ionic radii of Sm the relative modes are expected to appear very close to those observed in our spectra (242, 313 and 452 cm\(^{-1}\), respectively). Therefore, these bands share the same origin with those observed for the other RVO\(_3\) compounds. Based on this assignment the band appearing at \( \sim 226 \text{ cm}^{-1} \) is the rotation of the VO\(_6\) octahedra, while the other two modes are assigned as oxygen bending and Jahn-Teller mode, respectively [4, 5]. However, according to the proposal of Iliev et al. for the isostructural RMnO\(_3\) compounds a different assignment is suggested for the last two modes [6]. The mode appearing at \( \sim 308 \text{ cm}^{-1} \) is related to the vibrations of the O1 atoms, while the one appearing at \( \sim 442 \text{ cm}^{-1} \) has been assigned to the out of phase bending \( A_g \) phonon. Furthermore, based on the assignment of Sugai et al. for YVO\(_3\), the mode at \( \sim 308 \text{ cm}^{-1} \) is related with R-O1 mixed vibrations [7]. However, this mode, as mentioned before, follows very well the dependence of the size of R cation and not the mass harmonic law. Therefore the above assignment is rather impossible.

At low temperatures two extra peaks appear in the Raman spectra at \( \sim 497 \text{ cm}^{-1} \) and \( \sim 670 \text{ cm}^{-1} \). The energy of both peaks remains almost unchanged until 80K while a decrease of \( \sim 5 \text{ cm}^{-1} \) and \( \sim 7 \text{ cm}^{-1} \), respectively is observed at \( T=100K \). For higher temperatures both of these modes disappear. The normalized intensity of the lower energy mode shows a maximum at 40K and then decreases with increasing temperature (Fig.3a). A systematic decrease of intensity is
also observed for the mode appearing at $\sim 670 \text{ cm}^{-1}$ (Fig.3b). The extrapolation of a second order polynomial fit of the intensity of the first peak indicates that the band disappears at nominal temperature of $\sim 120K$, very close to $T_N=129K$ (the difference from 129K is due to the local heating of the sample from the laser beam). This denotes that the peak at $\sim 497 \text{ cm}^{-1}$ is related to the magnetic transition from paramagnetic to C-type antiferromagnetic phase.

The peak at $\sim 497 \text{ cm}^{-1}$ also appears in the Raman spectra for other RVO$_3$ compounds, while its energy remains unchanged and independent of R [4]. According to the analysis of Miyasaka et al this mode is assigned as two orbiton excitations [4, 5]. However, Raman measurements on other perovskite-like compounds show a peak in the same energy region, being almost independent of R, which has been assigned as a Jahn-Teller phonon [7, 8].

**Figure 3.** Temperature dependence of the energy and intensity of the $\sim 497 \text{ cm}^{-1}$ (a) and $\sim 670 \text{ cm}^{-1}$ (b) modes.

**Figure 4.** Temperature dependence of the energy (a), intensity (b) and width (c) of the $\sim 704 \text{ cm}^{-1}$ mode.

In the $xx$ polarization spectra at RT there are two characteristic modes appearing at $\sim 368 \text{ cm}^{-1}$ and $\sim 449 \text{ cm}^{-1}$. The first one is observed only in the Raman spectra of SmVO$_3$ and NdVO$_3$ [4] and compared it with other perovskites it is possible to be related with oxygen bending vibrations. The peak at $\sim 449 \text{ cm}^{-1}$ has an asymmetric shape but the asymmetry is reduced with decreasing temperature and below 80K two peaks at $\sim 450 \text{ cm}^{-1}$ and $\sim 459 \text{ cm}^{-1}$ are clearly observed. Therefore we believe that there are two modes appearing in the $xx$ Raman spectra at this energy region but the lower frequency one progressively disappears with increasing temperature leading to the apparent asymmetric shape of the higher energy peak.

Additionally, two broad bands at $\sim 250 \text{ cm}^{-1}$ and $\sim 503 \text{ cm}^{-1}$ appear at all temperatures studied. The first peak has an asymmetric tail (Fano shape) and based on the assignment for the RMnO$_3$ compounds it can be related with the octahedral tilting angle. The second one is very weak and it is possible to be the second order Raman scattering of the band appearing at $\sim 250 \text{ cm}^{-1}$, since its energy is about twice the energy of the Fano shaped one.

For temperatures below 180K an additional peak at $\sim 704 \text{ cm}^{-1}$ is observed in the $xx$ polarization spectra. The intensity of this mode strongly increases with decreasing temperature, reaches a maximum at 100K and then decreases again, but it is still observed as a strong peak.
down to $T=20K$ (Fig.4). At $T=100K$ another extra peak appears in the $xx$ polarization Raman spectra at $\sim 670 \text{ cm}^{-1}$ and is still observed down to $T=20K$ with increasing intensity.

The peak at $\sim 704 \text{ cm}^{-1}$ has also been observed for other perovskite-like RVO$_3$ (R=rear earth or Y) compounds with increasing energy as the ionic radius increases from Y to La [4, 9]. In all cases this band starts appearing for temperatures below $T_{OO1}$ and therefore it has been connected with the orthorhombic to monoclinic transition accompanied concomitantly with the G-type OO [4, 5, 9]. The appearance of this mode for low temperatures (down to 20K), as shown in Figure 2, indicates that SmVO$_3$ remains monoclinic at least until this temperature.

For temperatures below 100K the $\sim 704 \text{ cm}^{-1}$ band is accompanied with another peak at $\sim 670 \text{ cm}^{-1}$, which is still observed down to $T=20K$. This new mode has also been observed in YVO$_3$ [4, 7] and $Y_{1-x}Ca_xVO_3$ [10] and assigned to an oxygen stretching mode. In both cases the mode at $\sim 670 \text{ cm}^{-1}$ appears for temperatures below $T_{OO2}$ where a second phase transition from monoclinic to orthorhombic symmetry occurs in the system, while no sign of it has been observed for compounds with monoclinic symmetry at low temperatures [4]. For that reason it is connected with the C-type OO and the orthorhombic phase. In such a case, the coexistence of this mode with the one related with the G-type OO phase for temperatures below 100K, is an evidence that even though at low temperatures the monoclinic phase and the G type OO dominate in SmVO$_3$, in the specific temperature region the orbital ordering is not clear and a coexistence of the G and C-type OO is observed. This is in agreement with the results of ref. [1] in which it was observed, based on high resolution x-ray powder diffraction experiments, a coexistence of phases below 115K with monoclinic and orthorhombic symmetries until 5K.

4. Conclusions

In this work the temperature dependence of the modes appearing in the $zz$ and $xx$ Raman spectra of SmVO$_3$ is investigated in order to examine the possible relation between them and the phase transitions that occur in the compound. We found out that at low temperatures three extra peaks at $\sim 497 \text{ cm}^{-1}$, $\sim 670 \text{ cm}^{-1}$ and $\sim 704 \text{ cm}^{-1}$ appear in the Raman spectra, related with the C-type SO, C-type OO and G-type OO, respectively. The modes at $\sim 497 \text{ cm}^{-1}$ and $\sim 704 \text{ cm}^{-1}$ increase in intensity with decreasing temperature indicating that below $T_N$ the G-type OO coexists with the C-type SO phase. Finally, the appearance of a peak for temperatures below 100K related with the C-type OO additionally with the one connected with the G-type OO denotes the coexistence of the G and C-type orbital ordered phases in SmVO$_3$.

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