Micro-Raman study of orbiton–phonon coupling in YbVO₃

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First-order and multiphonon Raman active excitations are studied in YbVO₃ as a function of temperature in the orthorhombic and monoclinic phases. Below T ∼ 170 K, a G-type orbital ordering with a concomitant monoclinic transition occurs. They enhance the phonon polarizabilities, allowing the resolution of room-temperature bands, and activate new excitations around 700 cm⁻¹. Below T ∼ 65 K, the 700 cm⁻¹ excitations disappear, indicating a C-type orbital ordering and a return to the orthorhombic structure. The observed phonon combinations around 1400 cm⁻¹ with a dominant Jahn-Teller vibration at ∼690 cm⁻¹ reflect a possible orbiton-phonon coupling. Copyright © 2011 John Wiley & Sons, Ltd.

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Introduction

Owing to their strong electron correlation, transition-metal oxides with perovskite-related structures display a variety of interesting properties such as Mott transition, high-Tc superconductivity and colossal magnetoresistance. They are prototypes for the interplay among the charge, orbital, spin and lattice excitations. Usually for cations with orbital degeneracy such as Mn³⁺, Ti³⁺ and V³⁺, long-range orderings of the occupied d orbitals accompanied by a Jahn–Teller distortion are expected at low temperatures. [1]

Orbitons or low-energy multipolar charge excitations are associated with the modulations of the electronic cloud shapes in transition-metal oxides ordered states. [2] They represent a dynamical response that propagates between the transition-metal ion orbitals and are considered as potential candidate for ultrafast switching. The Raman scattering study of LaMnO₃ that claimed orbiton detection [3] has been thoroughly contested [4–7]. In the case of YVO₃, while Sugai and Hirota [8] identified the 679 cm⁻¹ Raman active excitation as orbiton and the 489 cm⁻¹ excitation as phonon, Miyasaka et al. [9] reversed their identifications as phonon and orbiton, respectively. In a preliminary study, Jandl et al. [10] have shown that Raman excitations observed in YbVO₃ and YVO₃ were of phonon origin.

In their study of the RMnO₃ (R = rare earth) manganites, and based on polarization properties, lattice-dynamics calculation and oxygen isotope substitution, Iliev et al. [11] have shown that all the excitations attributed to orbitons by Saitoh et al. [12] are rather of phonon nature. Also, the Raman study of RMnO₃ multiphonons by Lavédière et al. [13] indicated a possible coupling of orbiton to the lattice with an intermediate electron–phonon strength. [11]

At room temperature, the RVO₃ crystallographic structure is orthorhombic with typical Pnma space group parameters a ≃ c ≃ √2a and b ≃ 2a, where a is the lattice parameter of the ideal cubic perovskite. The V³⁺ ions have two t₂g d electrons with coupled parallel spins (S = 1) according to Hund’s rule. One electron occupies the ac orbital whose energy is lowered because of the orthorhombic distortion which reduces the crystal-field symmetry. The other electron occupies either the ab or the bc orbital. [12] The two electron spins align ferromagnetically along the b-axis and antiferromagnetically in the ac plane (C-type spin), while the d_ab and d_bc orbitals, respectively, alternate (G-type orbit). [13,14] The C-type spin and G-type orbit transition temperatures depend on the ionic radius of the R ion. The Jahn–Teller distortion increases for the small R ionic radius, whereas the V–O–V bond angle deviates from 180° and the transfer interaction as well as the spin and orbital interactions decrease between the V³⁺ nearest neighbors. In the case of large Jahn–Teller distortions, a second transition characterized by a magnetization reversal occurs at a lower temperature (e.g. in YVO₃). The spins align this time antiferromagnetically along the b-axis (G-type spin) with identical orbits (either d_ab or d_bc) along the b-axis alternation in the ac plane (C-type orbit). According to Ulrich et al. [15] the spin exchange interaction parameters J_ac and J_bc are of the order of 5.7 ± 3 meV in the G-type spin-ordered state in YVO₃. This translates in two magnon excitations of the order of 60 meV. [16]

Polycrystalline samples of YbVO₃ have been studied by neutron powder diffraction, specific heat and magnetization measurements. [17] At room temperature, the crystal structure is orthorhombic (a = 5.5662(2) Å, b = 7.5446(2) Å, c = 5.2320(1) Å). An orbital ordering effect is observed around 170 K, coinciding with an anomaly in the specific heat, concomitant with a change in the thermal variations of the a and b parameters and the V–O distances. Below T₉ = 104 K, YbVO₃ becomes magnetically ordered with the magnetic moments antiferromagnetically coupled in the ac plane. [17]

In this study of the first-order and multiphonon Raman active excitations in YbVO₃, we report their evolutions as a function of

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Experimental

The Raman spectra at 0.5 cm\(^{-1}\) resolution were measured in the backscattering configuration using a Labram-800 Raman microscope equipped with a 50 × (∼0.35 mW μm\(^{-2}\); 3 μm laser spot) magnification objective, and a nitrogen-cooled charge coupled device (CCD) detector. A He–Ne (λ = 632.8 Å (1.96 eV)) laser, whose power was kept below 2 mW, and an appropriate notch filter were used with the samples mounted on the cold finger of a micro-Helium Janis cryostat. Polycrystalline samples of YbVO\(_3\) were prepared by the chemical reduction of YbVO\(_4\) powder obtained by high-temperature solid-state reaction microprobe spectrometer equipped with a 50 μm laser spot) magnification objective, and a nitrogen-cooled charge coupled device (CCD) detector. A He–Ne (λ = 632.8 Å (1.96 eV)) laser, whose power was kept below 2 mW, and an appropriate notch filter were used with the samples mounted on the cold finger of a micro-Helium Janis cryostat. Polycrystalline samples of YbVO\(_3\) were prepared by the chemical reduction of YbVO\(_4\) powder obtained by high-temperature solid-state reaction.

Results and Discussion

The orthorhombic YbVO\(_3\) primitive cell contains four molecular units resulting in 7\(A_g\) + 5\(B_{1g}\) + 7\(B_{2g}\) + 5\(B_{3g}\) Raman active modes.\(^{[9]}\) The \(A_g\) modes are observed in the (aa), (bb) and (cc) configurations for the incident and scattered light polarizations as given in parenthesis, and the \(B_{1g}\), \(B_{2g}\), \(B_{3g}\) in the (ab), (ac), (bc) configurations, respectively. When the \(Pnma\) orthorhombic lattice symmetry is lowered to the monoclinic symmetry, the \(A_g\) and \(B_{2g}\) modes become \(A_g\) and the \(B_{1g}\) and \(B_{3g}\) modes become \(B_{g}\) modes, respectively.

At 300 K, the apical V–O distance along the b direction and the short V–O distance in the ac plane are almost identical (∼1.98 Å). They diverge (∼1.980 and 1.990 Å, respectively) below 170 K, resulting in orbital ordering and octahedral tilting.\(^{[17]}\)

In the wide temperature range of 170–65 K, a cooperative Jahn–Teller distortion provokes a magnetostriective crystallographic transition. It corresponds to an abrupt decrease of the \(a\)-lattice parameter magnitude, leading to a contraction of the unit cell volume. Simultaneously with the transition, a magnetic ordering that couples the magnetic moments antiferromagnetically in the ac plane and also along the b-axis occurs.\(^{[17]}\)

In Fig. 1, Raman active excitations of YbVO\(_3\) are shown as a function of temperature in the (ac) configuration allowing the \(B_{2g}\) symmetry phonons to be observed. At \(T = 300\) K, two excitations are observed around 440 and 500 cm\(^{-1}\) and two broad bands around 325 and 680 cm\(^{-1}\). The orbital ordering below 170 K enhances the phonon polarizabilities, allowing the resolution of the broad bands in four excitations: 325, 350, 680 and 700 cm\(^{-1}\). The 350 cm\(^{-1}\) excitation corresponds to a leakage of the strongest \(A_g\) symmetry phonon and the 700 cm\(^{-1}\) to phonon density activated by orbital ordering as discussed below. Below \(T_{N1} = 104\) K and down to 65 K, the phonon bandwidths become narrower and the following \(B_{2g}\) phonons are better resolved: 327 cm\(^{-1}\) (out-of-phase c-rotation), 445 cm\(^{-1}\) (oxygen vibration along c-axis), 507 cm\(^{-1}\) (out-of-plane bending), 545 cm\(^{-1}\) (in-phase bending) and 681 cm\(^{-1}\) (in-phase oxygen stretching vibration) as described in analogy with RMnO\(_3\) phonon

Figure 1. \(B_{2g}\) Raman active phonons in YbVO\(_3\) as a function of temperature in the orthorhombic and monoclinic phases. Inset: frequency of the 350 cm\(^{-1}\) phonon as a function of temperature. \(^{[17]}\) indicates plasma lines.

Figure 2. \(A_g\) Raman active phonons in YbVO\(_3\) as a function of temperature in the orthorhombic and monoclinic phases. Inset: frequency of the 350 cm\(^{-1}\) phonon as a function of temperature. \(^{[17]}\) indicates plasma lines.

and their corresponding lattice dynamical calculations.\(^{[18]}\) Below \(T ∼ 65\) K, following the complete alignment of the spins, a new two-magnon broad excitation around 475 cm\(^{-1}\) is observed, which is in agreement with the predictions of Ref. [16], while the 700 cm\(^{-1}\) excitation disappears.

In Fig. 2, Raman active excitations of YbVO\(_3\) are shown as a function of temperature in the (bb) configuration allowing the \(A_g\) symmetry phonons to be observed. At \(T = 180\) K, two excitations are observed at 267 cm\(^{-1}\) (VO\(_6\) octahedra rotation) and 342 cm\(^{-1}\) (bending of the VO\(_6\) octahedra) with broad bands around 450 and 700 cm\(^{-1}\). Similar to the \(B_{2g}\) symmetry phonons, the orbital ordering below 170 K, with monoclinic lattice distortions, enhances the phonon polarizabilities and allow the observation of additional \(A_g\) modes at ∼170 (Yb vibration along the c-axis), ∼240, ∼470 cm\(^{-1}\) (anti-stretching vibrations of oxygens in the ac plane) as well as some of the \(B_{2g}\) phonons (∼440 and ∼500 cm\(^{-1}\)) which are allowed now in the \(A_g\) symmetry. The broad band around 700 cm\(^{-1}\) is also resolved in two excitations around 666
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and 690 cm⁻¹. Sensitivity of these modes to the phase transitions and crystal symmetry, with normal bandwidth broadenings at low temperatures, prompts us to rule out defects associated with oxygen non-stoichiometry and their corresponding unusual broad band Raman excitations as encountered in similar compounds.[18] At lower temperatures down to 65 K, the phonon bandwidths become narrower. Below T ≅ 65 K the A_g phonons (170, 244, 269, 350 and 394 cm⁻¹) are better resolved and the 439 and 500 cm⁻¹ B_{2g} phonons as well as the 666 cm⁻¹ excitation intensities drop, indicating a return to the orthorhombic symmetry and a change in the orbital ordering and resulting polarizabilities as observed in the evolution of the V–O distances between 104 and 65 K (2.020–1.985 Å for the long V–O distance in the ac plane and 2.000–2.025 Å for the short V–O distance in the ac plane[17]).

Various orderings below 170 and 65 K are observed in the strongest A_g mode (~350 cm⁻¹) wavenumber shifts as a function of temperature (Fig. 2, inset).

The first-order Raman active phonon temperature evolutions indicate a strong similarity with YVO₃ structural and orbital orderings as a function of temperature. Actually, the YVO₃ structure changes successively from orthorhombic Pnma space group at room temperature to monoclinic P2₁/c space group at T = 200 K and back to Pnma space group at T = 77 K.[1,12] The increased tilting of the octahedra orders the orbitals in the G-type configuration below 200 K and in the C-type configuration below 77 K.[13,14]

Using a Hamiltonian that incorporates both superexchange and intermediate strength electron–phonon interaction that couples electrons to Jahn–Teller modes, Van den Brink[11] has shown that excitations of mixed orbiton–phonon character can arise. In the YVO₃ monoclinic phase and G-type configuration orbital, between 200 and 77 K, Sugai and Hirota[8] have associated the 675 cm⁻¹ excitation to two-orbiton wave. Even if this identification cannot be definitely ruled out, we associate the 666 and 690 cm⁻¹ (A_g symmetry excitations) and 700 cm⁻¹ (B_{2g} symmetry excitation), which appear in the monoclinic phase, to phonon modes activated by orbital ordering as reported in YVO₃ for the 664 and 688 cm⁻¹ excitations by Miyasaka et al.[9] and in RMnO₃ (R = Pr, Sm, Eu, Tb, Y) for the modes around 650 cm⁻¹ by Lavédière et al.[5] It is noteworthy that in the case of DyMnO₃, the ~650 cm⁻¹ excitation was also identified as of phonon origin based on polarization properties and in close comparison with the results of lattice-dynamics calculations.[7]

Figure 3(a) and (b) shows, in addition to the A_g and the B_{2g} phonons, Raman excitations up to 1600 cm⁻¹ as a function of temperature. Multiphonons are observed as a broad band around 1380 cm⁻¹ at 300 K in both symmetries. At lower temperatures, the band intensities are enhanced down to ~65 K, and then they decrease down to 20 K.

In addition to the excitations of mixed orbiton–phonon character, Van den Brink[11] has predicted a phonon pattern that repeats at the wavenumber interval (~650 cm⁻¹) of the on-site Jahn–Teller vibration (oxygen octahedron elongation along the b-axis and contraction in the ac-plane). Also, multiphonons are expected in the higher energy range with lower intensities than in the strong coupling regime. Similar to the study of RMnO₃ (R = Pr, Sm, Eu, Tb, Y), where multiphonons are separated by the Jahn–Teller mode wavenumber,[5] we associate the ~1380 cm⁻¹ band with the phonon wavenumber combinations (666 + 690), (690 + 690) and (700 + 690) cm⁻¹. Also, the 690 cm⁻¹ mode and the multiphonon intensities are correlated as a function of temperature and the 690 cm⁻¹ mode predominates in the phonon combinations as expected by the Jahn–Teller mode.[11] By comparing the intensities of the 666, 690 and 700 cm⁻¹ excitations, the phonon combination intensities increase remarkably between first- and second-order processes and then decrease rapidly with their increasing order (inset, Fig. 3(a)) as previously observed in the manganites.[5,20] This indicates that the electron–phonon coupling constant g is of intermediate strength, as considered in Ref. [11], and not as strong as supposed in the localized limit with Franck–Condon processes[21] where intensities of the combination order n follow the power law gn.

Conclusion

The A_g and B_{2g} Raman active phonons of YbVO₃ have been studied as a function of temperature retracing the various phase transitions observed by neutron powder diffraction, specific heat and magnetization measurements.[17] Hence, below 170 K a G-type orbital ordering is formed and new phonon density excitations around 700 cm⁻¹ are activated in both A_g and B_{2g} symmetries associated with a transition from orthorhombic to monoclinic structure. Such excitations are particularly enhanced between
$T_N \sim 104$ K (C-type spin) and $T \sim 65$ K and vanish at lower temperatures. Similar to previous observations in YVO$_3$, a possible change to C-type orbital and G-type spin orders occurs.

High-energy phonon combinations are also observed, which reflect an intermediate strength electron–phonon coupling as described by Van den Brink within an orbiton–phonon coupling scheme Ref. [11].

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