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Raman and infrared study of 4f electron–phonon coupling in HoVO_3

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Abstract

First-order Raman scattering and multiphonons are studied in RVO_3 ($\text{R} = \text{Ho}$ and Y) as a function of temperature in the orthorhombic and monoclinic phases. Raman spectra of HoVO_3 and YVO_3 unveil similar features since both compounds have nearly identical R-radii. However, the most important difference lies in the transition temperature involving the V^{3+} orbitals, the V^{3+} magnetic moments as well as the crystallographic structure. Particularly, the magnetic and orbital reorientations occur at $T_{N2} = 40$ K for HoVO_3 instead $T_{N2} = 77$ K in the case of YVO_3 . For both systems, anomalous phonon shifts which are related to spin-phonon coupling are observed below the V^{3+} magnetic ordering temperature ($T_{N1} \approx 110$ K) while additional phonon anomalies are exclusively observed in HoVO_3 around $T^* \approx 15$ K. On the other hand, infrared (IR) transmittance measurements as a function of temperature reveal $\text{Ho}^{3+} {}^5\text{I}_8 \rightarrow {}^5\text{I}_7$ excitations and additional excitations assigned as vibronics. These latter combined with drastic changes in $\text{Ho}^{3+} {}^5\text{I}_8 \rightarrow {}^5\text{I}_7$ excitations at T_{N2} , are indicative of a strong coupling between the Ho^{3+} ions and the ligand field. This could explain the large magnetocaloric capacity shown by HoVO_3 .

Keywords: HoVO_3 , Raman spectroscopy, infrared spectroscopy, spin-phonon coupling

(Some figures may appear in colour only in the online journal)

1. Introduction

Due to their strong electron correlations, transition-metal oxides with perovskite or related structure are prototypes of the interplay among the charge, orbital, spin and lattice excitations. Usually for cations with orbital degeneracy such as Mn^{3+} , Ni^{3+} , Ti^{3+} and V^{3+} , long-range orderings of the occupied d orbitals accompanied by a Jahn–Teller (JT) distortion are expected at low temperatures with dramatic effects on magnetic, electronic and structural properties. Complex interplay between multiple interactions generates interesting macroscopic properties such as multiferroicity and colossal magnetoresistance [1–3]. Recent works have

also shown the strong potential of transition-metal oxides in developing memory devices and magnetic refrigeration systems [1, 4].

Particularly, the RVO_3 vanadates, characterized by two distinct orbital ordered states have recently attracted an increasing interest due to their fascinating physical properties [5–7]. In these systems, the orbital-active t_{2g} electrons are very sensitive to the ionic radius R^{3+} , the temperature and the external stimuli [8–11]. One of the orbital ordered states is driven by the superexchange interaction leading to strong orbital fluctuations [8, 9, 12–14]. This orbital state competes with another one resulting from JT coupling that tends to suppress the orbital fluctuations [15, 16].

Figure 1. HoVO₃ temperature dependent Raman spectra in a(bb)a configuration. α and β are characteristic excitations associated with the G-OO/C-SO and the C-OO/G-SO phases respectively.

The RVO₃ compounds adopt a distorted perovskite structure with the Pbnm orthorhombic space group at room temperature. According to Hund's rule the two t_{2g} electrons of the V^{3+} ion have parallel aligned spins ($S = 1$). Long and short V–O distances alternate in the ab plane, causing a lifting of degeneracy of the V^{3+} t_{2g} orbitals into a doublet of low energy and a singlet of high energy. While one electron occupies the d_{xy} orbital, the other one occupies either the d_{xz} or the d_{yz} orbitals. At lower temperatures, the spins couple ferromagnetically along the c -axis and antiferromagnetically in the ab plane (C-type spin), while, concomitantly, the d_{xz} and d_{yz} orbitals respectively alternate (G-type orbit) in the x , y , z , orthogonal directions [5, 6]. For small R^{3+} ionic radius, the V–O–V bond angle deviates from 180° reducing spin, exchange and orbital nearest neighbour interactions. Also a second transition characterized by a spin (C–SO to G–SO with spins alternating along x , y and z) and an orbital (G–OO to C–OO with d_{xz} and d_{yz} orbitals alternating only along x and y) rearrangements occurs at a lower temperature [5, 6].

In HoVO₃, neutron diffraction, synchrotron x-ray diffraction and magnetic susceptibility measurements have evidenced at $T_{OO} = 188$ K a structural phase transition from orthorhombic Pbnm to monoclinic P2₁/a with the t_{2g} orbitals adopting a G-type order [17]. The V^{3+} spins align in the C-type antiferromagnetic fashion below $T_{N1} = 114$ K [17]. At $T_{N2} = 33$ K, a reorientation of the ordered spins and a first order structural phase transition involving a sudden change in the unit-cell volume takes place. With the increased tilting of the octahedra, the crystal symmetry changes back to orthorhombic, the orbital order becomes C-type and the spin order changes to G-type [17]. In the orthorhombic lattice, there is only one single C_s symmetry position for Ho^{3+} . In contrast, there are two unequivalent C_i symmetry positions for Ho^{3+} in the monoclinic phase [17]. Three different T_{N2} where important magnetic, structural and orbital changes occur have

been reported (33 K [17], 27 K [18] and 15 K [10]) as well as two different temperatures for Ho^{3+} at $T^* = 11$ K and $T = 4$ K assigned respectively to paramagnetic–ferromagnetic and ferromagnetic–antiferromagnetic transitions [7, 18, 19].

It is worth noting that several studies have underlined the impact of rare earth 4f electrons on the HoVO₃ macroscopic physical properties [7, 10, 18]. In this context, a large magnetocaloric effect (MCE) combined with a giant refrigerant capacity (RC) have been observed in this compound [7]. However, the physics behind the observed magnetocaloric properties is not well elucidated. Furthermore, only few data on the role of Ho^{3+} 4f electrons in controlling the HoVO₃ physical properties are reported in the literature. Also, the contrast between the reported values for T_{N2} makes the identification of the microscopic mechanisms behind the Ho^{3+} magnetic moments and the VO₃ matrix interactions more challenging [7, 10, 17, 18]. In the present work we demonstrate that Ho^{3+} magnetic moments interact with both the atomic lattice via electron–phonon coupling as well as with the V^{3+} spins via superexchange interactions. Such couplings decrease significantly the T_{N2} transition temperature and change dramatically the Ho^{3+} spins temperature behavior, enhancing remarkably the RC of HoVO₃ as reported by Balli *et al* [7].

In this study of the first-order Raman active excitations in HoVO₃, we report their evolutions as a function of temperature, correlate them with the expected orbital and magnetic orders and compare them with those observed in YVO₃. We accurately identify the T_{N2} transition temperature and compare it with the T_{N2} transition temperature reported in the literature. Phonon softening is observed below T_{N1} and phonon anomalies related to Ho^{3+} magnetic ordering are reported at T^* . Ho^{3+} ion $^5I_8 \rightarrow ^5I_7$ transitions are also observed as a function of temperature in the IR transmittance measurements with some features related to the 4f-phonons and the 3d–4f superexchange interactions.

Figure 2. Comparison of YVO₃ and HoVO₃ Raman spectra in both orthorhombic and monoclinic phases.

2. Experimental

Single crystal samples of RVO₃ (R = Ho and Y) were prepared starting by the chemical reduction of RVO₄ powder obtained by high-temperature solid-state reaction of stoichiometric mixtures of pre-dried Ho₂O₃ and V₂O₅. HoVO₄ was then reduced by annealing the powder in a flow of pure H₂ at 1000 °C. A single-crystalline boule of 6 mm in diameter and a 60–70 mm in length was then grown by the traveling solvent floating zone method. The crystallinity of the boule was checked by x-ray analysis and the composition by the electron probe microanalysis [5]. Raman spectra at 0.5 cm⁻¹ resolution (400 μm slit width) were measured in the backscattering configuration using a Labram-800 Raman microscope spectrometer equipped with a 50X (≈0.35 mW μm²; 3 μm laser spot) magnification objective, and a nitrogen-cooled charge coupled device (CCD) detector. A He–Ne (λ = 6328 nm (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. Magnetization measurements as a function of temperature and magnetic field were realized using a commercial superconducting quantum interference device (SQUID) from Quantum Design, model MPMS XL. The infrared transmission measurements as a function of temperature were obtained in the 2000–5000 cm⁻¹ range with a Fourier transform interferometer BOMEM DA3.002 equipped with an InSb detector, a quartz-halogen source and a CaF₂ beamsplitter.

3. Results and discussion

The orthorhombic HoVO₃ primitive cell contains four molecular units resulting in 7 A_g + 7 B_{1g} + 5 B_{2g} + 5 B_{3g} Raman active modes [20]. The A_g modes are observed in the (aa), (bb) and (cc) configurations of the incident and scattered light polarizations, and the B_{1g}, B_{2g}, B_{3g} in the (ab), (ac), (bc) configurations respectively. When the orthorhombic lattice

Table 1. Comparison between phonon frequencies and linewidth of HoVO₃ and YVO₃ in the orthorhombic and monoclinic phases.

Phonon assignment	Orthorhombic phase (20 K)		Monoclinic phase (80 K)	
	HoVO ₃ ω/γ (cm ⁻¹)	YVO ₃ ω/γ (cm ⁻¹)	HoVO ₃ ω/γ (cm ⁻¹)	YVO ₃ ω/γ (cm ⁻¹)
A _g (2)	274.1/6	278.8/5	274.7/10	278.3/10
A _g (O)	345.5/3.6	343.7/3.9	335.4/6.0	337.5/4.5
α			365.5/12	369.0/16
β	398/14	405/17		
A _g (4)	433/10	425/17	425/6	N.A.
A _g (3)	458/21	469/19	471.0/10.1	471.1/14
B _{1g} (2)			508/18	509/18
B _{1g} (1)			670/24	683/29
PDS			697/ 21	706/22

symmetry is changed to monoclinic, the A_g and B_{1g} modes become A_g while the B_{2g} and B_{3g} modes become B_g modes, respectively.

In figure 1, Raman active excitations of HoVO₃ with incident light perpendicular to the *bc* plane are shown as a function of temperature. The phonons are compared with the YMnO₃ orthorhombic modes [21] and their symmetries are assigned using an analyzer. The 275 cm⁻¹, 345 cm⁻¹, 431 cm⁻¹ and 458 cm⁻¹ excitations are four A_g modes. The 509 cm⁻¹, 670 cm⁻¹ and 694 cm⁻¹ excitations are respectively B_{1g}(2) mode, B_{1g}(1) phonon and phonon density of state (PDS) reported in YbVO₃ [22]. Raman excitation polarizabilities and their associated intensities are greatly affected by the orbital and magnetic ordering. Below *T*_{OO}, the Raman intensity increases slowly as we decrease temperature until *T*_{N1}. At *T* < *T*_{N1}, intensities of all excitations are greatly enhanced with decreasing temperature down to *T*_{N2}. Following the first order phase transition at *T*_{N2}, the intensity of all excitations, except the β excitation, decreases significantly. The α excitation around 365 cm⁻¹ has been previously assigned to an orbiton [20, 23]. However, some controversy still persists in

Figure 3. Magnetization measurement of HoVO_3 done under 1 T magnetic field oriented along the c axis. The right and left insets are Raman spectra in $a(cc)a$ configuration as a function of temperature around T_{N2} -warming and T_{N2} -cooling respectively.

the assignment of the β excitation at 399 cm^{-1} . While Sugai *et al* assigned it to an orbiton, Miyasaka *et al* identified it as a magnon [20, 23]. Finally, in the insert, we observe excitations around 1400 cm^{-1} enhanced by the G–OO orbital ordering via orbiton-phonon coupling [24] and assigned to multiphonons as in YVO_3 , YbVO_3 and LaVO_3 [20, 22, 23].

Due to Ho^{3+} and Y^{3+} nearly identical radii between HoVO_3 and YVO_3 Raman spectra are very similar in both phases (figure 2). However, we observe an important difference of 8 cm^{-1} between the $A_g(2)$ frequency of the two compounds which is not observed in the $A_g(O)$, $A_g(4)$ and $A_g(3)$ peaks. This observation point out the impact of the 4f electron states on the lattice and on the 3d electrons. Table 1 compares phonon frequencies and linewidth observed in YVO_3 and HoVO_3 in both monoclinic ($T = 80\text{ K}$) and orthorhombic ($T = 20\text{ K}$) phases. In the monoclinic phase, low energy modes of HoVO_3 and YVO_3 are close ($<5\text{ cm}^{-1}$) and only the $B_{1g}(1)$ and PDS differ significantly ($11 \pm 1\text{ cm}^{-1}$ and $7 \pm 1\text{ cm}^{-1}$ respectively). More differences are observed in the phonon linewidth. More precisely, the α , the $A_g(3)$ and $B_{1g}(1)$ excitation linewidth are larger in YVO_3 while $A_g(O)$ is slightly larger in HoVO_3 . The Ho^{3+} magnetic moments manifest at low temperature and influence the HoVO_3 modes. We notice that following the first order structural transition associated with the orbital and magnetic rearrangements, the $A_g(2)$ phonon frequency hardens in YVO_3 while it softens in HoVO_3 . Also, the $A_g(O)$ phonon in HoVO_3 is found to harden more than in YVO_3 and the $A_g(3)$ phonon softens significantly in HoVO_3 ($13 \pm 1\text{ cm}^{-1}$) as compared to YVO_3 ($2 \pm 1\text{ cm}^{-1}$). The most important difference between YVO_3 and HoVO_3 is T_{N2} which is observed around 40 K in HoVO_3 and at 77 K in YVO_3 . The similarities of phonon energies and lineshapes suggests that the small difference between Y^{3+} and Ho^{3+} radii can't explain the disparity in T_{N2} . Therefore, electron–phonon coupling of 4f electronic states must be considered to explain the phase diagram of HoVO_3 .

Hysteresis in the magnetization measurements of HoVO_3 (1 T magnetic field oriented along the c axis) around T_{N2} is observed in figure 3 with T_{N2} -warming $\approx 44\text{ K}$ and T_{N2} -cooling $\approx 31\text{ K}$. The left and right insets (Raman spectra in the $a(cc)a$ configuration) correspond to T_{N2} -warming = $42 \pm 2\text{ K}$ and T_{N2} -cooling = $32 \pm 2\text{ K}$. Hence the structural and magnetic transitions occur at the same critical temperature and thus, evidence a coupling between the lattice and the V^{3+} spins. Previous studies of HoVO_3 have identified T_{N2} at three different temperatures. While Blake *et al* [17] is in agreement with our results with T_{N2} -warming reported around 40 K, other works have reported T_{N2} at lower temperatures. Reehuis *et al* [18] have identified T_{N2} -cooling at 23 K and T_{N2} -warming at 35.5 K with a Ho^{3+} total moment ($\approx 6.9\text{ }\mu_B$) smaller than reported previously ($\approx 9.4\text{ }\mu_B$) [7, 19]. Fujioka *et al* assigned two magnetic and dielectric anomalies at 11 K (T_{N2} -cooling) and 36 K (T_{N2} -warming) [10]. The impact of inhomogeneities in RVO_3 magnetic properties has been studied by Tung *et al* [25] They suggested that such inhomogeneities caused by defects in a quasi-1D orbital system could account for the unusual magnetization reversal of V^{3+} and its staircase like and glassy behaviour [25]. Previous works have suggested that those defects can impact the phase diagram of RVO_3 by freezing locally the monoclinic phase below T_{N2} [25–28]. Phase coexistence was observed in HoVO_3 below T_{N2} in some sample's regions, but disappeared gradually with decreasing temperature down to 6 K. This observation contrasts with what has been observed in YVO_3 where the monoclinic phase existing below T_{N2} remains robust at low temperature [28]. Such phase coexistence impacts the physical properties and explains the discrepancies between the critical temperatures reported by Fujioka *et al* and the other studies [7, 10, 17, 18].

Frequencies of $A_g(2)$, $A_g(O)$ and $A_g(4)$ excitations as a function of temperature in YVO_3 and HoVO_3 are shown in figure 4. According to previous lattice dynamical calculations [21], the $A_g(O)$ mode involves apical oxygen oscillations in

Figure 4. HoVO₃ and YVO₃ phonon frequency variations as a function of temperature above $T_{N2} = 40$ K. Anharmonic model fits with HoVO₃ data are illustrated with black lines.

the *ab* plane while the $A_g(2)$ mode is related to basal oxygen movements in the same plane. The $A_g(O)$ and $A_g(2)$ frequencies follow above T_{OO} the anharmonic model introduced by Balkanski *et al* [29] with:

$$\omega(T) = \omega_0 - C \left[1 + \frac{2}{(e^{\omega_0/2k_B T} - 1)} \right]$$

C and ω_0 being fitting parameters in cm^{-1} . Anharmonic behaviours in HoVO₃ are represented in figure 4 by black lines. In a typical anharmonic trend, the frequencies follow a plateau at very low temperatures and decrease linearly at high temperature. The fitting values obtained for the $A_g(O)$ and $A_g(2)$ phonons are $\omega_0 = 339$, $C = 2.20$ and $\omega_0 = 274$, $C = 1.60$ respectively. The ω_0 value is in agreement with the scenario proposed by Balkanski *et al* [29] where the optical phonon decays into two acoustic phonons with opposite wavevector and half the energy of the optical phonon. A slight divergence from the anharmonic model is detected below T_{OO} and is correlated with the structural and orbital transition. Also, a softening is observed at lower temperature. It corresponds roughly to the emerging V^{3+} magnetic order at T_{N1} . In anti-ferromagnetic systems, such softening is attributed to significant spin-phonon coupling [30]. The $A_g(4)$ phonon frequency behaviour differs from the $A_g(2)$ and the $A_g(O)$ phonons at low temperatures. An important softening is observed below 150 K down to 90 K then, it starts to increase slowly down to 40 K. This behaviour reflects subtle changes in the balance between the JT coupling and the superexchange interactions. A comparison between YVO₃ and HoVO₃ phonons reveals no important differences above 40 K, as expected for two compounds with nearly identical R-radii.

Figure 5. (a) Comparison of YVO₃ and HoVO₃ $A_g(2)$ phonon frequencies as a function of temperature and (b) $A_g(2)$ phonon linewidths as a function of temperature below T_{N2} .

Following the structural, magnetic and orbital rearrangements below T_{N2} , phonon characteristics change drastically, the α excitation disappears and the β excitation becomes

Figure 6. $\text{Ho}^{3+5}\text{I}_8 \rightarrow {}^5\text{I}_7$ CF transitions in both orthorhombic (16 K) and monoclinic (45 K) phases. The depolarized light wavevector was perpendicular to the ab plane.

active. The $A_g(\text{O})$ frequency hardens by 10 cm^{-1} while its linewidth is reduced (from 6 cm^{-1} to 3 cm^{-1}). The $A_g(2)$ frequency is unchanged ($<1\text{ cm}^{-1}$) but its linewidth is reduced. As the temperature is decreased, the $A_g(\text{O})$ frequency and linewidth follow the anharmonic trend. Anomalous phonon behaviour is observed for the $A_g(2)$ phonon at low temperatures (see figure 5). From $274.0 \pm 0.1\text{ cm}^{-1}$, it increases and reaches a maximum at $274.6 \pm 0.1\text{ cm}^{-1}$ with decreasing temperature. Its linewidth ($5.8 \pm 0.5\text{ cm}^{-1}$ at 40 K) reaches a maximum ($7.2 \pm 0.5\text{ cm}^{-1}$) at 11 K. This anomaly is related to the 4f electronic states in HoVO_3 . Balli *et al* have reported a characteristic temperature at $T^* \approx 15\text{ K}$ where the Ho^{3+} spins previously paramagnetic become ferromagnetic [7]. Assuming that the incident laser heats by 2 K the sample, we correlate this anomaly with the magnetic ordering of the Ho^{3+} spins.

The lattice effects on the 4f electronic states are also visible in $\text{Ho}^{3+5}\text{I}_8 \rightarrow {}^5\text{I}_7$ CF transitions. The $\text{Ho}^{3+5}\text{I}_8$ ground state are typically described by the CF Hamiltonian:

$$H_{\text{CF}} = \sum_{kq} B_{k,q} [C_q^k + C_{-q}^k]$$

where the functions C_q^k transform as tensor operators under simultaneous rotation of the coordinates of all the f electrons and $B_{k,q}$ are the so-called CF parameters. In figure 6 and table 2, we compare those transitions in both orthorhombic and monoclinic phases. While some CF excitations are not affected by the structural, orbital and magnetic transitions at T_{N2} , others (peaks 1, 2, 12 and 15) vary by 10 cm^{-1} . These variations are due to the structural transition which changes the CF parameters. However, the CF analysis fails to explain the splitting of peak 10 into two new excitations (peak 9 and 11) following the monoclinic to orthorhombic phase transition since the Ho^{3+} point symmetry is higher in the orthorhombic phase (one site Cs) than in the monoclinic phase (two non-equivalent sites Ci). Furthermore, peak 10 is still visible in the

Table 2. $\text{Ho}^{3+5}\text{I}_8 \rightarrow {}^5\text{I}_7$ CF excitations frequency and linewidth in orthorhombic (16 K) and monoclinic (45 K) phases.

CF excitation	Orthorhombic phase (16 K)		Monoclinic phase (45 K)	
	Frequency (cm^{-1})	Linewidth (cm^{-1})	Frequency (cm^{-1})	Linewidth (cm^{-1})
1	5083.9	2.8	5094.3	7.0
2	5090.4	7.6	5102.0	7.9
3	5106.9	3.8	5111.1	6.9
4	5116.0	5.6	5121.3	8.8
5	5174.0	3.8	5172.6	4.4
6	5178.9	4.9	5178.6	8.4
7	5203.6	24.3		
8	5218.6	5.8		
9	5225.8	7.2		
10	5241.3	7.8	5242.0	13.1
11	5257.2	9.4		
12	5275.0	6.9	5285.9	5.9
13	5290.0	11.3	5290.0	4.6
14	5302.7	6.9	5295.5	7.5
15	5311.8	7.0	5302.2	7.3
16	5325.9	8.9	5319.8	16.4
17	5385.1	17.8		
X1	4961.5	11.7	4963.1	10.6
X2	4984.7	13.9	4986.9	15.9
X3	5041.2	15.1	5044.7	15.6

high temperature orthorhombic regime which confirms that the splitting is not related to the CF symmetry changes but rather to the hybridization of Ho^{3+} 4f and V^{3+} 3d orbitals. Such hybridization between 4f states of Ho^{3+} and 3d states of V^{3+} can result in a $\text{Ho}^{3+}\text{--V}^{3+}$ superexchange field that lifts the degeneracy of 4f ground state levels. The hybridization itself breaks the parity of the 4f–4f transitions and allows their observation by IR absorbance. The superexchange field splitting does not reduce significantly the Ho^{3+} total magnetic moment as suggested by several studies [7, 19], but it tends to align the Ho^{3+} moment into a specific direction and

Figure 7. Temperature evolution of $\text{Ho}^{3+}\text{I}_8 \rightarrow ^5\text{I}_7$ CF transitions in HoVO_3 as determined by infrared absorption. The depolarized light wavevector was perpendicular to the ab plane.

Figure 8. HoVO_3 infrared absorption spectrum at $T = 130$ K. Vibronic transitions involving the $\text{A}_g(2)$ and $\text{A}_g(\text{O})$ phonons are shown.

thus, results in the unusually high spin polarization below T_{N2} as reported in references [7, 18]. Therefore, Ho^{3+} and most likely all R^{3+} in RVO_3 , with non-empty 4f shell cannot be described purely by the CF scheme where the 4f electrons are shielded from the external environment, but by ligand field theory where non negligible covalent bonding exists between the R^{3+} and the V^{3+} .

The intensity of the excitation assigned as X1, X2, X3 in figure 6 are found to increase with temperature as shown in figure 7. These excitations are CF transitions involving thermally populated $^5\text{I}_8 \rightarrow ^5\text{I}_7$ electronic excitations [31, 32]. Several neutron-scattering studies of related transition metal oxides such as HoMnO_3 and HoVO_4 estimated the energy range of the ground state $^5\text{I}_8$ CF excitations between 12 and 300cm^{-1} [33, 34]. Therefore, the difference of energy between the lowest absorption band (4740cm^{-1}) and the lowest CF transitions ($\approx 5100\text{cm}^{-1}$) is too large to share the

same origin as X1, X2 and X3. Figure 8 shows the absorption bands at $T = 130$ K. A careful examination of the band positions reveals that some are separated roughly by 270cm^{-1} and 330cm^{-1} from typical CF transitions observed in figure 6. These values correspond to the $\text{A}_g(2)$ and $\text{A}_g(\text{O})$ phonon frequency and, thus, we conclude that some of the lowest energy bands are vibronic transitions resulting from the combination of Raman active phonons with CF excitations.

IR Transmittance measurements reveal the presence of excitations resulting from 4f-phonon coupling but also a splitting indicative of superexchange coupling between the V^{3+} and Ho^{3+} spin. Therefore, both interactions must be taken into account in order to explain the impact of the rare earth magnetism on the RVO_3 physical properties. The role of the oxygen in these interactions is underlined by the presence of vibronic transitions involving the oxygen modes $\text{A}_g(2)$ and $\text{A}_g(\text{O})$. The observation of the anomalous behavior of $\text{A}_g(2)$ phonon

supports this scenario and also suggests that the Ho^{3+} spins interact more with the basal oxygen than the apical one. RVO_3 with intermediate R-radii are characterized by the existence of two possible orbital configurations close energetically. In this regime, small variations of the V–O–V bond angle caused by magnetostrictive effects impact significantly the V^{3+} electronic states and the resulting orbital configuration [26, 27]. Rare earth magnetostrictive effects can play a similar role and favor a specific V^{3+} orbital and spin order. Hence, dramatic effects were observed in DyVO_3 where the 4f magnetic moments ordering partially restores the C–OO configuration in the G–OO phase [11]. Inversely, the VO_3 matrix interaction with the Ho^{3+} spin explains the unusually high polarization of the Ho^{3+} spins above T^* and the Ho^{3+} spin polarization anomaly at T_{N2} [7, 18]. Consequently, the Ho^{3+} spins are able to be completely aligned which enlarges the entropy variation and, in contrast to other RMnO_3 manganites [35–38], they become significantly polarized above T^* . This contributes to the broadening of the entropy variation curve which enhances considerably the refrigerant capacity of HoVO_3 .

4. Conclusion

Comparative Raman study of HoVO_3 and YVO_3 confirms that both compounds share similar lattices. Structural transition temperature is accurately identified in HoVO_3 at T_{N2} -warming = 43 ± 2 K and T_{N2} -cooling = 32 ± 2 K and coincides with the magnetic transition temperature reported by Balli *et al* [7] and Blake *et al* [17]. Phonons are sensitive to V^{3+} antiferromagnetic state below T_{N1} and Ho^{3+} magnetic state at T^* . Reciprocally, 4f CF transitions display characteristics indicative of 4f-phonon and 4f–3d couplings. Therefore, both Ho^{3+} magnetostrictive effects and 4f–3d superexchange interactions must be taken into account in order to describe accurately the physics of HoVO_3 . These interactions also enhance considerably the magnetocaloric properties of HoVO_3 and should be actively considered in the quest for new magnetocaloric materials.

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