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Symmetry of the Optical Phonons in LuVO₄: A Raman Study

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Abstract: A thorough analysis of the first-order vibrational spectrum of LuVO₄ is presented by using polarized micro-Raman spectroscopy with special focus on the phonon modes with the weakest intensity and occasional controversial assignment. Group-theory analysis is carried out to demonstrate the determination of numbers and symmetries of the Raman active modes. Crystal- and correlation-field splitting effects in the vibrational spectrum of LuVO₄ are discussed. Under conditions adjusted to minimize the birefringence effects we recorded, in each main scattering configuration, a series of Raman spectra in different sample orientations achieved by rotating the sample around the incident laser beam. The dependence of the Raman intensity on the rotational angle allowed us to identify the correct symmetry of the phonons with exceptionally weak scattering cross-section. A complete assignment of all twelve first-order Raman active phonons of LuVO₄ is thus obtained.

Keywords: rare-earth orthovanadates; single crystal; LuVO₄; Raman spectroscopy; optical phonons

1. Introduction

Rare-earth orthovanadates (RVO₄, with R being a lanthanide element) are intensively studied because of their interesting magnetic, optical, and electronic properties. These compounds show prospects for applications in a wide range of research fields, such as laser host crystals [1,2], scintillators [3], sensors [4], phosphor materials [5], and catalysts [6]. Due to their exceptional optical properties, such as wide optical transparency and large birefringence [7], the RVO₄ materials are suitable for various components for polarizing optics. Besides the technological importance, these compounds attract considerable theoretical interest due to the presence of 4f electrons.

Among them, LuVO₄ single crystals are of particular interest as laser host material due to the broad bandwidth, larger absorption cross-section near 800 nm, and larger emission cross section at 1.064 μm in comparison to those of other vanadate crystals [2]. These features are highly desirable for diode pumped solid-state lasers, as they make it feasible to achieve highly efficient pumping and to realize low threshold laser operation with high optical-to-optical efficiency. Recently, the vanadates GdVO₄ and LuVO₄ doped with several trivalent lanthanide ions showed promising results in diode pumped lasers [8]. Subsequent works demonstrated different χ(3)-nonlinear generation effects in tetragonal LuVO₄ vanadate under picosecond pumping [9]. LuVO₄ thus turned out to be a promising material for utilization of the high-gain stimulated Raman scattering (SRS), especially in the development of

novel Raman converters such as self-Raman lasers with lanthanide dopants. Four of the fundamental vibrational modes of LuVO_4 were identified as $\chi(3)$ -promoting modes (113 , 261 , 826 , and 900 cm^{-1}) [10]. Furthermore, cross-cascaded ($\chi(3) \leftrightarrow \chi(3)$) nonlinear lasing effects were observed with the participation of two pairs of SRS-active LuVO_4 vibrations (900 cm^{-1} together with 826 cm^{-1} and 900 cm^{-1} together with 261 cm^{-1}) in LuVO_4 [10]. These properties were detected in almost all known SRS-active tetragonal RVO_4 vanadates based on the same phonons and with similar Raman gain coefficients. The octave-spanning Stokes and anti-Stokes lasing combs generation was also demonstrated [10].

Given the large number of LuVO_4 normal modes participating in the SRS-effect, precise knowledge of the LuVO_4 vibrational spectrum is of vital importance for better understanding of its lasing properties. An impressive deal of Raman work has been performed in recent decades to explore the vibrational spectra of LuVO_4 and other orthovanadates. Nevertheless, some contradictions in the assignment of the Raman active modes still persist, most probably due to the large birefringence of the material and the vast difference in the Raman intensity of the distinct normal modes. In this paper, we present a Raman investigation of LuVO_4 with full utilization of the symmetry properties of the different modes. This allows us to detect modes with exceptionally low Raman intensity and to assign all 12 Raman active vibrations.

2. Materials and Methods

LuVO_4 single crystals were grown by the high-temperature solution growth method. As a first step, polycrystalline LuVO_4 seed was synthesized by solid state reaction and subsequently enriched with V_2O_5 . The mixture was further melted and annealed at $1100\text{ }^\circ\text{C}$ in a platinum crucible. Single crystals were obtained by slow cooling of the solution from 1100 to $700\text{ }^\circ\text{C}$. Details of the growth procedure are given in [7]. The obtained crystals with tetragonal rectangular shape and typical size of $8 \times 10 \times 1\text{ mm}^3$ were collected from the bottom and the walls of the crucible.

A single crystal specimen of LuVO_4 was used for the X-ray crystallographic analysis. X-ray intensity data were obtained at room temperature on Bruker-AXS Smart Apex three-circle diffractometer equipped with a CCD detector. Data collection was carried out with operating parameters of 50 kV and 30 mA and graphite monochromatic $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). Details of the X-ray crystallographic analysis are given in [7]. Additionally, X-ray Powder Diffraction for phase analysis was performed on LuVO_4 powder prepared from the single crystal sample at a D8 Bruker powder diffractometer [11].

For the spectroscopic measurements, single crystals with elongated shapes along the c -axis with naturally grown $\{100\}$ and $\{001\}$ surfaces were selected. The Raman spectra were measured in backscattering geometry in the range of 80 – 1000 cm^{-1} on a HORIBA Jobin Yvon Labram HR visible spectrometer equipped with a Peltier-cooled CCD detector. The 632.8 nm line of a He-Ne laser (power 5 mW) as well as the 514.5 nm line of an Ar^+ laser (power 8 mW) was used for excitation. Both diffraction gratings of the instrument were used: with 600 grooves/mm and 1800 grooves/mm, the latter giving an absolute accuracy of 0.3 cm^{-1} for $\lambda = 632.8\text{ nm}$ and 0.55 cm^{-1} for $\lambda = 514.5\text{ nm}$.

3. Results and Discussion

3.1. Characterization of the Vibrational Properties and Vibrational Splitting in LuVO_4 Crystals

According to X-ray powder diffraction analysis [11], the as-grown crystals had a single-phase zircon structure. All of the diffraction peaks were identified to result from LuVO_4 and no peaks of a second phase were found. The lattice structure of this crystal is depicted in Figure 1. It can be considered as made up of chains formed by alternating LuO_8 polyhedra (bisdisphenoid) and VO_4 tetrahedra along the c -axis. These chains are joined together by sharing other edges of the LuO_8 polyhedra along the a - and b -directions to form a three-dimensional lattice with centrosymmetric tetragonal structure with the point group symmetry D_{4h} and space group $I4_1/amd$ (D_{4h}^{19}). Despite the different coordination environment, both Lu^{3+} and V^{5+} ions occupy sites of D_{2d} symmetry [12].

The unit cell contains 4 formula units (2 formula units per primitive cell) with lattice parameters of $a = b = 7.0236\text{\AA}$ and $c = 6.2293\text{\AA}$ [11]. Consequently, 12 atoms per primitive cell with 36 degrees of freedom should be taken into account.

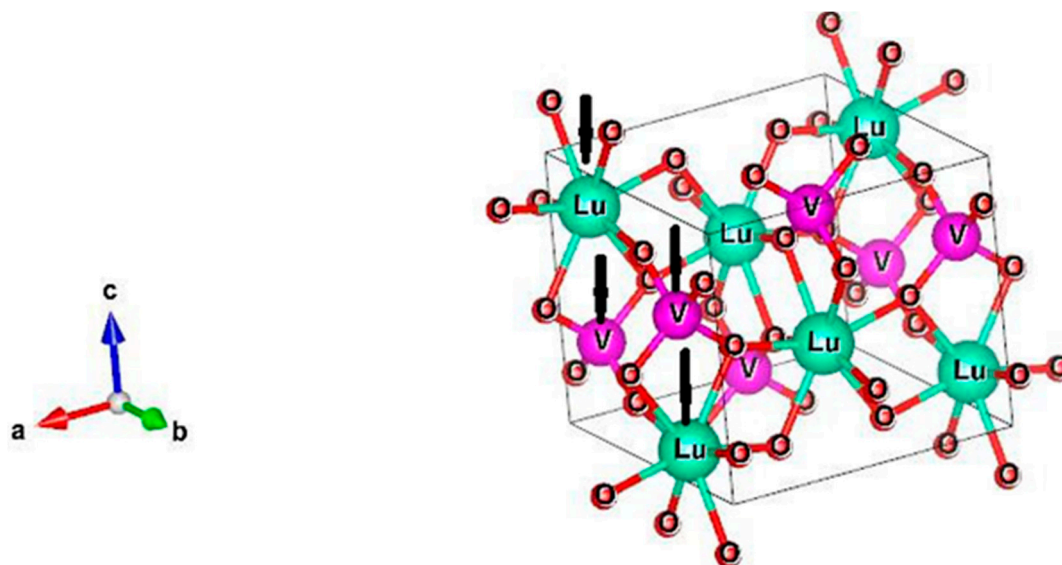


Figure 1. Structure of the zircon-type crystal lattice of LuVO_4 . The two Lu atoms and the two VO_4 tetrahedra in the primitive cell are marked by vertical black arrows [13].

According to the determined crystal structure [7,11,12] and the data available in the International Tables for Crystallography for the space group D_{4h}^{19} , the occupied Wyckoff positions are as follows: 4a (Lu^{3+} ions), 4b (vanadium) and 16h (oxygen). As the mirror plane σ_v is the common symmetry element of the point group of the crystal D_{4h} and the site symmetry group C_s , $C_s(\sigma_v)$ is identified as the correct site symmetry for the oxygen atoms, thus removing the ambiguity in the 16h positions for this structure. By carrying out the nuclear site group analysis [14], shown in detail in Table 1, one ultimately obtains the representation of the Raman active modes as follows:

$$\Gamma_{\text{Raman}} = 2A_{1g} + 4B_{1g} + B_{2g} + 5E_g, \quad (1)$$

Table 1. Occupied Wyckoff positions and resulting phonon modes.

Atomic Species	Wyckoff Position and Site Symmetry	Irreducible Representations (Symmetries of Phonon Modes) Resulting for These Species' Vibrations)
Lu^{3+}	4a (D_{2d})	$A_{2u} + B_{1g} + E_g + E_u$
V^{5+}	4b (D_{2d})	$A_{2u} + B_{1g} + E_g + E_u$
O^{2-}	16 h ($C_s(\sigma_v)$)	$2A_{1g} + A_{1u} + A_{2g} + 2A_{2u} + 2B_{1g} + B_{1u} + B_{2g} + 2B_{2u} + 3E_g + 3E_u$

It is also instructive to classify the vibrational modes with the molecular site group analysis, which is suitable for treating isolated ionic or molecular species within a crystal matrix [14,15]. The orthovanadate structure consists of heavy rare-earth ions and VO_4^{3-} tetrahedra that can be approximately regarded as separate units due to the strong internal bonds within each tetrahedron. Therefore, the lowest-frequency vibrations of LuVO_4 should comprise of translations and librations of the VO_4^{3-} tetrahedra as rigid units against the rare-earth ions, while the higher-frequency phonons should be almost entirely due to internal vibrations of the tetrahedra [16]. The isolated VO_4^{3-} complex

has the relatively high symmetry T_d and its degrees of freedom can be classified in terms of irreducible representations of the T_d group as follows:

$$\Gamma_{XY4} = A_1(\nu_1) + E(\nu_2) + F_1(\text{pure rotation}) + F_2(\text{pure translation}) + F_2(\nu_3) + F_2(\nu_4), \quad (2)$$

The pure rotation and translation comprise zero-frequency motions of the complex as rigid structure that transform into librations and external translational modes, respectively, in the LuVO_4 crystal structure [16]. The remaining four terms represent the four fundamental internal vibrations of the VO_4^{3-} tetrahedron. The first publications analyzing the Raman phonons in zircon-type structure and dividing them into external and internal modes according to the vibrating species were made by Miller et al. in 1968 [16] and Elliot et al. in 1972 [17]. Since then, these modes have been extensively studied by many authors for a number of orthovanadates. On lattice sites with D_{2d} symmetry (see Table 1), the vibrational states undergo partial (crystal-field-induced) splitting according to the T_d/D_{2d} group-subgroup correlation rules. Then one should take into account the interaction between the two formula units in the primitive cell, which is equivalent to induction from the representations of the D_{2d} group to those of the D_{4h} group. In this way, a doubling of the vibrational states to the real number of degrees of freedom per primitive cell takes place and this doubling indicates the Davidov or correlation-field splitting, which is a measure of the interaction between non-equivalent tetrahedra in the primitive cell and also of the magnitude of the phonon dispersion in the Brillouin zone [15].

From this analysis, the same total representation of the Raman active modes (Equation (1)) can be constructed with the valuable additional information that there will be $2A_{1g} + 2B_{1g} + B_{2g} + 2E_g$ internal (higher-frequency) VO_4^{3-} modes; $2B_{1g} + 2E_g$ external (translational) VO_4^{3-} modes and a librational E_g mode of the VO_4^{3-} tetrahedron [16]. The infrared active vibrations are: $A_{2u} + E_u$ translational, an E_u librational and $2A_{2u} + 2E_u$ internal VO_4^{3-} modes. The distribution of the optically active internal modes shall be as follows: $A_1(\nu_1) \rightarrow A_{1g}$; $E(\nu_2) \rightarrow A_{1g} + B_{2g}$ and for both ν_3 and ν_4 from Equation (2): $F_2(\nu_i) \rightarrow B_{1g} + E_g + A_{2u} + E_u$. This picture is of course an approximation of the real situation, where there are no purely internal or external modes, but still very helpful for the Raman mode assignment [16,17]. It also becomes clear that no Davidov splitting can be established from Raman measurements because the Davidov counterpart of each Raman mode is an odd-parity one. Combined Raman and IR measurements can detect the Davidov doublet $E_g + E_u$ of the librational mode and the doublets $A_{2u} + B_{1g}$ and $E_g + E_u$ resulting from the $F_2(\nu_3)$ and $F_2(\nu_4)$ internal vibrations of the VO_4^{3-} tetrahedron.

The pertinent Raman tensors for the D_{4h} point group are the following [15]:

$$A_{1g}: \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix}; \quad B_{1g}: \begin{bmatrix} c & 0 & 0 \\ 0 & -c & 0 \\ 0 & 0 & 0 \end{bmatrix}; \quad B_{2g}: \begin{bmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}; \quad \text{and} \quad E_{g,1}: \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & e \\ 0 & e & 0 \end{bmatrix}; \quad E_{g,2}: \begin{bmatrix} 0 & 0 & -e \\ 0 & 0 & 0 \\ -e & 0 & 0 \end{bmatrix}.$$

The scattering intensity of a particular mode with Raman tensor α is given by:

$$I \sim |\mathbf{e}_i \cdot \alpha \cdot \mathbf{e}_s|^2 \quad (3)$$

where the unit vectors $\mathbf{e}_i$ and $\mathbf{e}_s$ denote the polarization of the incident and scattered light, respectively. For the polarized Raman measurements, we use the notations $X(100)$, $Y(010)$ and $Z(001)$ for the main crystal axes, and $X'(110)$ and $Y'(-110)$ for diagonal directions in the XY plane. The applied scattering configurations are labelled by Porto notations. Raman selection rules may suffer from depolarisation effects caused by the extremely strong birefringence of the LuVO_4 crystal. These effects lead to partial mixing of allowed and forbidden intensity between different Raman modes, which, nevertheless, can be minimized by using focusing/collecting optics with small numerical aperture (N.A.), while keeping the beam path within the sample short [18]. The above two requirements were satisfactorily met by

using a 20× microscope objective with N.A. = 0.4. Special care was also taken to achieve as perfect as possible back-scattering conditions on samples with smooth and optically defect-free surfaces. The main crystallographic planes of our samples were identified by X-ray diffractometry [11].

The spectra also contain features that do not obey the Raman selection rules and obviously do not pertain to the first-order vibrational spectrum of the LuVO₄ crystal. Their intensity turns out to be dependent on the investigated sample spot and the excitation wavelength λ with strongest intensity appearing upon red ($\lambda = 632.8$ nm) excitation. Our earlier experience with similar polarized Raman measurements on LuVO₄ at 632.8 nm excitation [11] shows that these features also display various polarization behaviour. As no significant impurities or second-phase inclusions were detected by XRD, we attribute these features to photoluminescence lines from electronic transitions of other rare-earth ions that are unavoidably present as substitutional defects in LuVO₄. In the spectra excited at 514.5 nm photoluminescence features are largely suppressed and upon blue excitation (488 nm) they are virtually missing. Besides, the birefringence of LuVO₄ is minimal in the blue spectral region [7]. The 488 nm laser thus appears to be the obvious choice of excitation wavelength. We, nevertheless, used the 514.5 nm laser line in the present study because of indications that the generally missing Raman active E_g(4) mode might be resonantly enhanced in the green spectral region, and carefully selected sample regions with minimum and non-variable intensity of impurity features. For some spectra when the luminescence lines lie far from the studied Raman modes, the He-Ne laser excitation (632.8 nm) was used.

The measured Raman spectra are presented in Figure 2. Although Raman selection rules are clearly discernible, in view of the known birefringence, the question may arise if the mode intensities in different scattering configurations are directly comparable. To address this question, we recall that besides the scattering cross section (given by the magnitude of the tensor elements), the Raman signal is influenced by the reflectivity R at the sample surface, the possible absorption within the sample, and the size of the volume, in which the detected Raman scattering effectively occurs (scattering volume). The latter is determined by the focus spot depending entirely on the focusing optics and the depth of focus. The correction factor resulting from reflection losses has the form $(1 - R)^2$ because both the incident and the scattered radiation undergo reflection. By means of the Fresnel equation for normal-incidence reflectivity, we obtain $(1 - R)^2 = 16n^2/(n + 1)^4$. We shall inspect that factor for the spectra labelled X(YY) $\bar{X}$ and X(ZZ) $\bar{X}$ representing the two limiting cases: ordinary wave ($n = n_o = 2.1$) and extraordinary wave ($n = n_e = 2.3$), respectively. Using the results for the refraction index n from [7], we obtain a value of 0.764 for spectrum X(YY) $\bar{X}$ and for spectrum X(ZZ) $\bar{X}$ $(1 - R)^2 = 0.714$. According to Gaussian beam theory [19], the depth of focus is of the order $\lambda/(N.A.)^2$ but it also linearly depends on n . Thus, the larger value of n_e effectively increases the scattering volume by about 10%, entirely compensating the higher reflection losses. Even if we neglect one of these counter-acting effects and consider only the other, the expected change in Raman signal does not exceed 10%. The depth of focus is of the order 10 μ m and the crystal exhibits high transparency above 500 nm [11]; therefore, possible absorption losses should be negligible. Consequently, the different spectra in Figure 2 are perfectly comparable for the purpose of Raman mode assignment and even for establishing relations between the Raman tensor elements a and b for the A_{1g} modes. The relative peak intensity of the A_{1g}(2) line in spectra X(YY) $\bar{X}$ and X(ZZ) $\bar{X}$ is ≈ 17000 and ≈ 19900 (arb. u.), respectively. This implies $|a| \approx |b|$ for the A_{1g}(2) mode. However, the intensity of the A_{1g}(1) line in spectrum X(YY) $\bar{X}$ is about four times smaller than in spectrum X(ZZ) $\bar{X}$. The A_{1g}(1) mode thus has a strongly anisotropic Raman tensor ($|b| \approx 2|a|$).

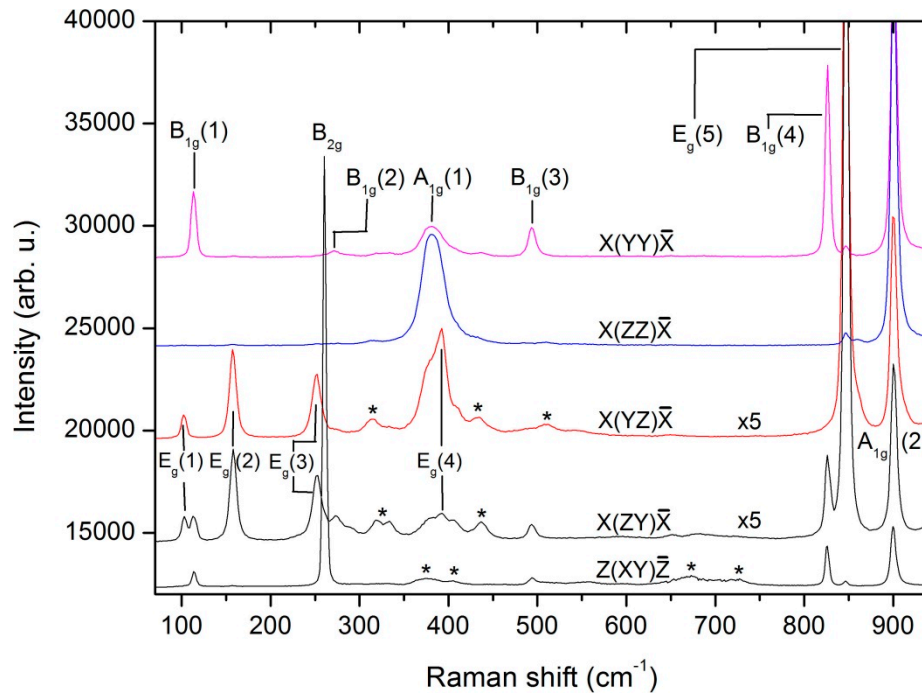


Figure 2. Raman spectra with mode assignment of LuVO₄ single crystal in different polarization configurations given in Porto notations. The laser excitation wavelength is 514.5 nm. The asterisks mark photoluminescence features (see text).

Concerning the depolarization effect addressed in [18], we point out that the allowed $A_{1g}(2)$ intensity in spectrum $X(YY)\bar{X}$ is more than 10 times higher than the corresponding forbidden intensity in spectrum $X(ZY)\bar{X}$. Similar relations are valid for all higher-intensity lines in Figure 2, i.e., their assignment is not threatened by birefringence effects.

Based on the polarization behavior of the different spectral lines, most of them could be unambiguously assigned to predicted Raman active phonon modes of the LuVO₄ crystal. Besides phonon lines, there are several photoluminescence lines within the spectral region of 300–450 cm^{−1}. The mode assignment, along with some new results on problematic modes that will be outlined in detail in Section 3.2, is given in Table 2 with juxtaposition with the vibrational species of the isolated VO₄^{3−} tetrahedron [20,21]. We also included in Table 2 the peak-intensities and the linewidths in order to highlight the SRS-promoting phonons by means of their two most important properties: high Raman efficiency and long lifetime. As noted in [22], the steady-state Raman gain coefficient of a certain phonon mode in SRS depends linearly on the ratio of its scattering cross-section (integral intensity) and its linewidth in spontaneous Raman scattering. This ratio is proportional to the peak intensity [22]. Indeed, for phonons that were identified as SRS-promoters [10], the peak intensity (given in bold font in Table 2) is many times higher than for most of the other normal vibrations in LuVO₄, and the linewidth is small.

Table 2. Frequencies and assignment of the Raman active phonons of LuVO₄. Additionally, for the librational E_g and the internal B_{1g} and E_g modes, in the first column, the symmetries and frequencies of their IR active Davidov counterparts are given in brackets, as taken from [23]. In those doublets, both VO₄^{3−} complexes in the primitive cell execute the same vibration: *u*-modes in phase and *g*-modes – out of phase. The data for the problematic modes discussed in Section 3.2 are given in red bold font.

Symmetry Species (D _{4h}), Frequency and Origin in Isolated VO ₄ ^{3−} (T _d)	Vibrational Pattern	Peak Intensity (arb. u.); Linewidth (cm ^{−1})	Frequencies (cm ^{−1}) from Available References		
			[24]	[25]	[26]
E_g(1): 103 cm^{−1} pure translation	Lu ³⁺ /VO ₄ ^{3−} translation	220; 8	—	—	—
B _{1g} (1): 113 cm ^{−1} pure translation	Lu ³⁺ /VO ₄ ^{3−} in-phase translation	3120; 6	114	112	113
E _g (2): 157.5 cm ^{−1} pure translation	Lu ³⁺ /VO ₄ ^{3−} translation	800; 9	158	157	250
E _g (3): 252 cm ^{−1} (E _u at 248 cm ^{−1}) pure rotation	VO ₄ ^{3−} libration	580; 12	251	259	158
B _{2g} (2): 261.5 cm ^{−1} E(<i>v</i> ₂)	<i>v</i> ₂ , O–V–O asymmetric bending	19800; 4.5	—	259 826	—
B_{1g}(2): 269 cm^{−1} pure translation	Lu ³⁺ / VO ₄ ^{3−} out-of-phase translation	200; 12	261	—	262
A _{1g} (1): 380 cm ^{−1} E(<i>v</i> ₂)	<i>v</i> ₂ , O–V–O symmetric bending	4900; 27	382	381	379
E_g(4): 393 cm^{−1} (E _u still missing) F ₂ (<i>v</i> ₄)	<i>v</i> ₄ , VO ₄ ^{3−} asymmetric bending/stretching	120; 11	—	—	—
B _{1g} (3): 493 cm ^{−1} (A _{2u} at 451 cm ^{−1}) F ₂ (<i>v</i> ₄)	<i>v</i> ₄ , VO ₄ ^{3−} asymmetric bending/stretching	1460; 10	493	492	495
B _{1g} (4): 826 cm ^{−1} (A _{2u} at 819 cm ^{−1}) F ₂ (<i>v</i> ₃)	<i>v</i> ₃ , VO ₄ ^{3−} asymmetric stretching (synchronic parallel Z-motion of all 4 oxygens against the V ⁵⁺ ion)	9300; 6	826	824	826
E _g (5): 846 cm ^{−1} (E _u at 790 cm ^{−1}) F ₂ (<i>v</i> ₃)	<i>v</i> ₃ , VO ₄ ^{3−} asymmetric stretching (synchronic parallel X- and Y-motion of all 4 oxygens against the V ⁵⁺ ion)	7000; 6.5	847	846 900	847
A _{1g} (2): 900 cm ^{−1} A ₁ (<i>v</i> ₁)	<i>v</i> ₁ , VO ₄ ^{3−} symmetric stretching (breathing of the tetrahedron)	19900; 7.5	901	900	901

Table 2 contains some new results on the LuVO_4 Raman mode assignment, which will be discussed in detail in the next subsection. Here, we will briefly review the crystal-field splitting $\Delta\omega_{\text{CF}}$ and Davidov splitting $\Delta\omega_{\text{D}}$ within the manifolds arising from the fundamentals ν_3 and ν_4 , all components of which are optically active. Within those manifolds, the frequency difference between the $E_g(E_u)$ and the $B_{1g}(A_{2u})$ mode provides an estimate for the crystal-field splitting while the separation in the E_g/E_u or B_{1g}/A_{2u} doublet serves as a measure for the Davidov splitting. Although IR measurements on LuVO_4 [6,23] are scarce, its IR active modes are long known [23], except for the E_u in the ν_4 manifold. Nevertheless, this mode can be credibly assumed to lie between 300 and 350 cm^{-1} by analogy to the well-studied internal vibrations of YVO_4 [16,27,28]. Additionally, only $\Delta\omega_{\text{CF}}$ can be estimated for ν_2 by the separation $A_{1g}(1)-B_{2g}$ for their odd-parity counterparts A_{1u} and B_{2u} are not optically active.

Table 3 represents the estimated splitting using the first column of Table 2. Three observations can be made from Table 3, which should be more or less valid for all members of the orthovanadate family: (i) $\Delta\omega_{\text{CF}}$ decreases monotonically in going from bond-bending to bond-stretching vibrations. (ii) For the mixed bending/stretching vibrations of the ν_4 manifold, $\Delta\omega_{\text{CF}}$ and $\Delta\omega_{\text{D}}$ are comparable with slight prevalence of $\Delta\omega_{\text{CF}}$. (iii) In the ν_3 manifold, $\Delta\omega_{\text{D}}$ for the E-modes dominates over $\Delta\omega_{\text{CF}}$ and is eight times stronger than $\Delta\omega_{\text{D}}$ for the $B_{1g}(4)/A_{2u}$ doublet. The fundamental frequency $\nu_3 = 825 \text{ cm}^{-1}$ of isolated VO_4^{3-} [21] appears like a “common center of gravity” of both doublets. For this effect, we propose a simple qualitative explanation. In crystals of complex ions as VO_4^{3-} , the interaction causing Davidov splitting is mainly governed by short-range repulsion forces [15]. Therefore, $\Delta\omega_{\text{D}}$ should primarily depend on the relative motion of the vibrating ions for the modes of a particular doublet. In the rectangular unit cell, the difference in the Z-coordinates of the two non-equivalent tetrahedra of the primitive cell is more than twice smaller than their horizontal distance [17] (see also Figure 1). The $E_g(5)$ mode has equally charged ions of the two tetrahedra vibrating horizontally against each other, while the corresponding E_u mode has these ions executing the same vibration in phase. Due to the proximity of their Z-coordinates, a considerable additional repulsive force should arise between the two tetrahedra during the $E_g(5)$ vibration, unlike the corresponding E_u motion, which completely lacks such a force. In the analogous case with the $B_{1g}(4)$ mode and its Davidov counterpart A_{2u} , the vibrational motion takes place along the vertical Z-axis. Due to the larger horizontal distance between the two non-equivalent tetrahedral, the mutual influence between motions of equally charged ions during the $B_{1g}(4)$ vibration should be much weaker, which might explain the small $\Delta\omega_{\text{D}}$ of only 7 cm^{-1} in the $B_{1g}(4)/A_{2u}$ doublet. This splitting resembles only a slight perturbation of the fundamental $F_2(\nu_3)$.

Table 3. Estimated crystal field $\Delta\omega_{\text{CF}}$ and Davidov splitting $\Delta\omega_{\text{D}}$ of the internal vibrational modes of the VO_4^{3-} ion in LuVO_4 .

VO_4^{3-} Fundamental		$\Delta\omega_{\text{CF}} \text{ (cm}^{-1}\text{)}$	$\Delta\omega_{\text{D}} \text{ (cm}^{-1}\text{)}$	
ν_2	$A_{1g}-B_{2g}$	120	—	—
ν_4	E_g-B_{1g}	100	E_g-E_u	50–100
	E_u-A_{2u}	≈ 100	$B_{1g}-A_{2u}$	≈ 50
ν_3	E_g-B_{1g}	20	E_g-E_u	≈ 55
	E_u-A_{2u}	≈ 30	$B_{1g}-A_{2u}$	≈ 7

3.2. Assignment of Problematic Raman Active Modes Using Their Rotational Transformation Properties

Thanks to several detailed group-theoretical and spectroscopic investigations of orthovanadate crystals, the symmetry properties of the stronger lines in their Raman spectra are well-established and their assignment has been known for decades [16–18,24,29]. However, the modes $E_g(1)$, $B_{1g}(2)$ and $E_g(4)$ are known to have exceptionally weak scattering intensity in almost all orthovanadates of the zircon-family [28]. Due to their low intensity and complications from birefringence effects, these

modes are frequently missing [24] or wrongly assigned [10,25,26] in some recent Raman studies of orthovanadates. Therefore, to complete the mode assignment for the LuVO_4 crystal, i.e., to obtain the results shown in Table 2, we measured Raman spectra as a function of the rotation angle φ by rotating the sample around the exciting beam in its polarization plane. This approach utilizing the differences in the transformation properties of phonons of different symmetry has proved to be helpful in many instances. Beside its conventional use for checking phonon symmetry, it has also been applied for determination of crystal structure [30] and detection of lattice defects [31].

For the present experiments, φ is defined as the angle between the X-axis and the actual polarization direction of the exciting laser beam. For rotating scattering configurations in perpendicular polarization $x_\varphi y_\varphi$ and $x_\varphi z_\varphi$ are orthogonal φ -dependent directions in the XY and the XZ plane, respectively. For rotation in parallel polarization, the transition from the initial to the final polarization is denoted. For instance, $Y(XX \rightarrow ZZ)\bar{Y}$ means gradual transition from $Y(XX)\bar{Y}$ to $Y(ZZ)\bar{Y}$ through rotation about the Y axis. Vertically stacked rotation-angle dependent spectra are shown in Figures 3–6 for various frequency regions and scattering configurations. The theoretically predicted dependence of the Raman intensity (Equation (3)) on the angle φ for the examined configurations is given in Table 4. The angular dependences of the measured mode intensities normalized to the maximum intensity for each line of interest are plotted in Figure 7. Theoretical curves of the corresponding functions in Table 4 are also plotted in Figure 7 for comparison.

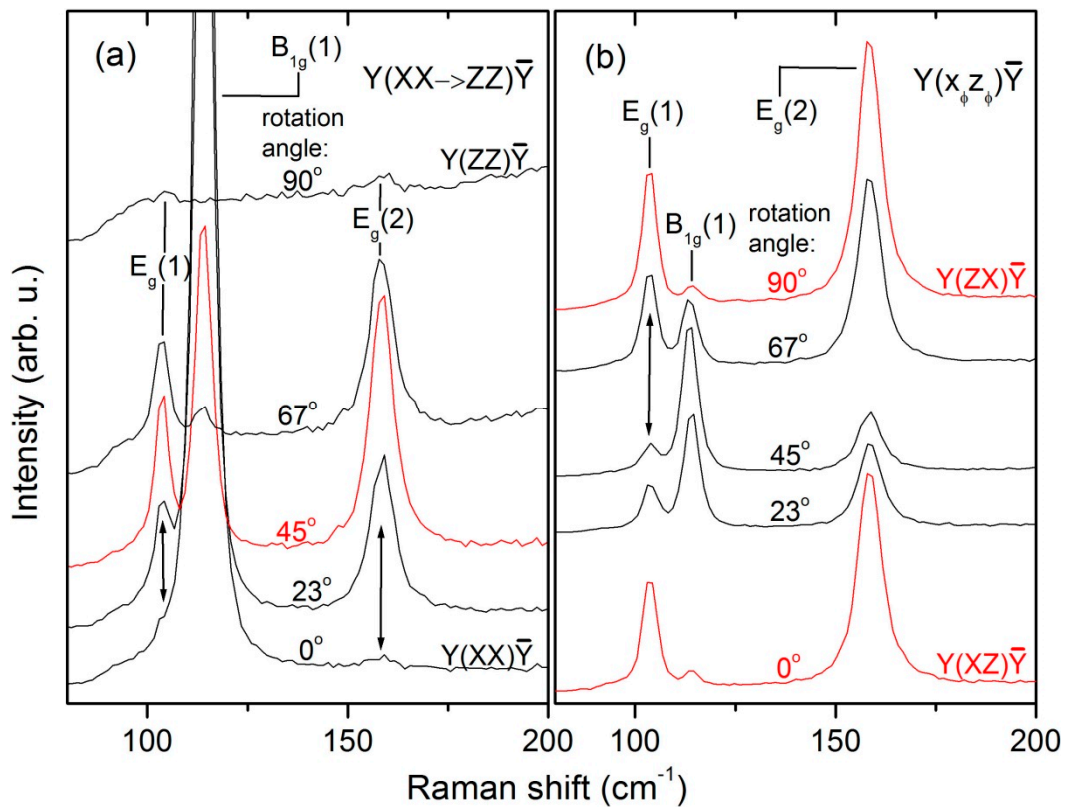


Figure 3. Rotation-angle dependent Raman spectra of the $E_g(1)$ mode of the LuVO_4 crystal in parallel (a) and perpendicular (b) polarization. The spectra with the highest $E_g(1)$ intensity are plotted in red. The laser excitation wavelength is 632.8 nm.

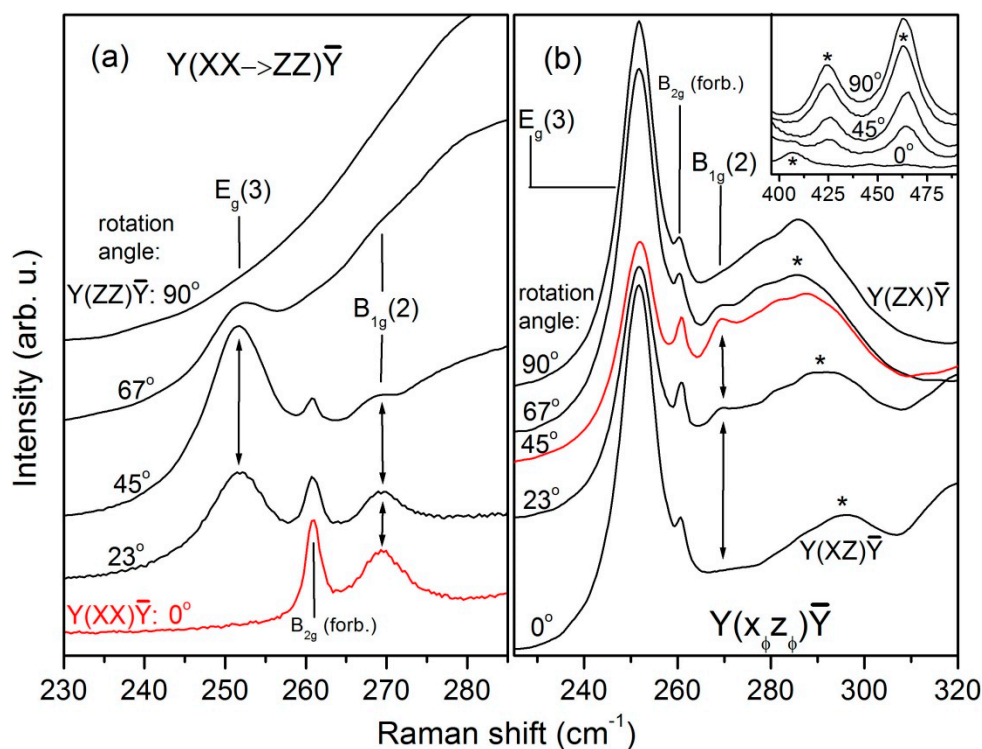


Figure 4. Rotation-angle dependent Raman spectra of the $B_{1g}(2)$ mode of the LuVO_4 crystal in parallel (a) and perpendicular (b) polarization in the XZ plane. The spectra with the highest $B_{1g}(2)$ intensity are plotted in red. The laser excitation wavelength is 632.8 nm. Due to interference-fringe effects, the spectra are smoothed out by means of FFT filtering. The asterisks mark luminescence features. Inset: Rotation-angle dependent spectra of the luminescence lines found in the spectra of panel (b) around 450 cm^{-1} .

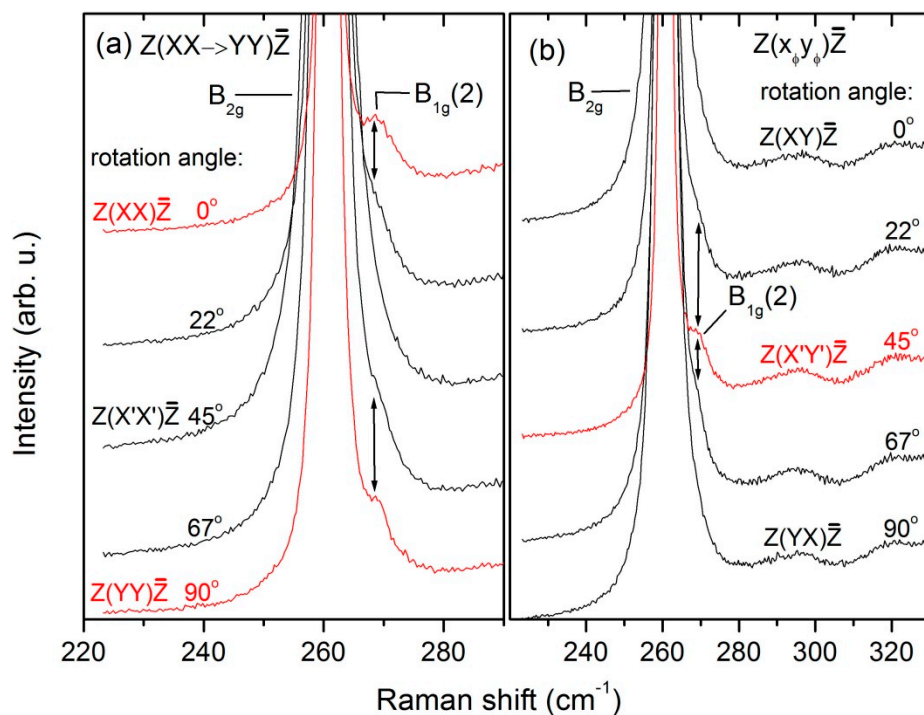


Figure 5. Rotation-angle dependent Raman spectra of the $B_{1g}(2)$ mode of the LuVO_4 crystal in parallel (a) and perpendicular (b) polarization in the XY plane. The spectra with the highest $B_{1g}(2)$ intensity are plotted in red. The laser excitation wavelength is 632.8 nm.

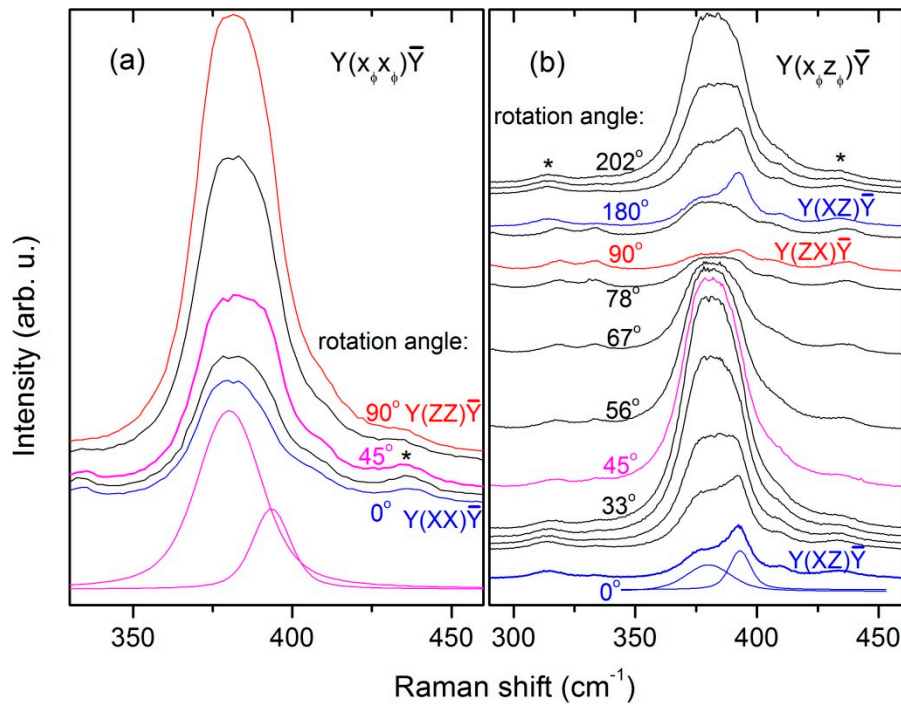


Figure 6. Rotation-angle dependent Raman spectra of the $E_g(4)$ mode of the LuVO_4 crystal in parallel (a) and perpendicular (b) polarization in the XZ plane. The laser excitation wavelength is 514.5 nm. The lowest two traces are model Lorentzians for the modes $A_{1g}(1)$ and $E_g(4)$ used to fit the spectrum at 45° (a) and at 0° (b). The asterisks mark luminescence features.

Table 4. Theoretical dependence of the Raman intensities of LuVO_4 phonons on the rotational angle φ .

ModeSymmetry	$Z(x_\varphi x_\varphi)\bar{Z}$ (XX→YY)	$Z(x_\varphi y_\varphi)\bar{Z}$ (XY→YX)	$Y(x_\varphi x_\varphi)\bar{Y}$ (XX→ZZ)	$Y(x_\varphi z_\varphi)\bar{Y}$ (XZ→ZX)
A_{1g}	$ a ^2$	0	$ a \cdot \cos^2 \varphi + b \cdot \sin^2 \varphi ^2$	$(a - b ^2/4) \cdot \sin^2 2\varphi$
B_{1g}	$ c ^2 \cdot \cos^2 2\varphi$	$ c ^2 \cdot \sin^2 2\varphi$	$ c ^2 \cdot \cos^4 \varphi$	$(c ^2/4) \cdot \sin^2 2\varphi$
B_{2g}	$ d ^2 \cdot \sin^2 2\varphi$	$ d ^2 \cdot \cos^2 2\varphi$	0	0
E_g	0	0	$ e ^2 \cdot \sin^2 2\varphi$	$ e ^2 \cdot \cos^2 2\varphi$

The rotation-angle dependent spectra of the lowest-energy translational modes of the LuVO_4 crystal are displayed in Figure 3. From Figure 7c and the observed behavior of the line at 103 cm^{-1} , it is evident that its φ -dependent intensity oscillation is in excellent agreement with the formulae listed in the last row of Table 4. Consequently, we can unambiguously assign the $E_g(1)$ mode to the line at 103 cm^{-1} .

To confirm the assignment of the $B_{1g}(2)$ mode, which has extremely weak intensity, we performed thorough investigations by rotating in two perpendicular planes: XZ (excitation along Y) and XY (excitation along Z) using the high-resolution diffraction grating (1800 gr./mm). The corresponding sets of Raman spectra are shown in Figures 4 and 5, respectively. Because of interference fringes, the spectra in Figure 4 were smoothed out by means of fast Fourier Transform (FFT) filtering. The first impression from Figure 4 is that both 261.5 cm^{-1} and 269 cm^{-1} lines satisfy the theoretical φ -dependence of the intensity of the B_{1g} mode. Thus, if only the polarizations used in Figure 4 are considered, one can easily declare that the stronger 261.5 cm^{-1} line is associated with the $B_{1g}(2)$ mode. However, due to its high intensity in XY polarization (Figure 2) and its φ -dependent behavior (Figure 5), the 261.5 cm^{-1} line is undoubtedly recognized as the only B_{2g} mode of the LuVO_4 crystal. In Figure 7a,b, the φ -dependence

of the 269 cm^{-1} line intensity is presented together with theoretical curves according to the formulae listed in the second row of Table 4.

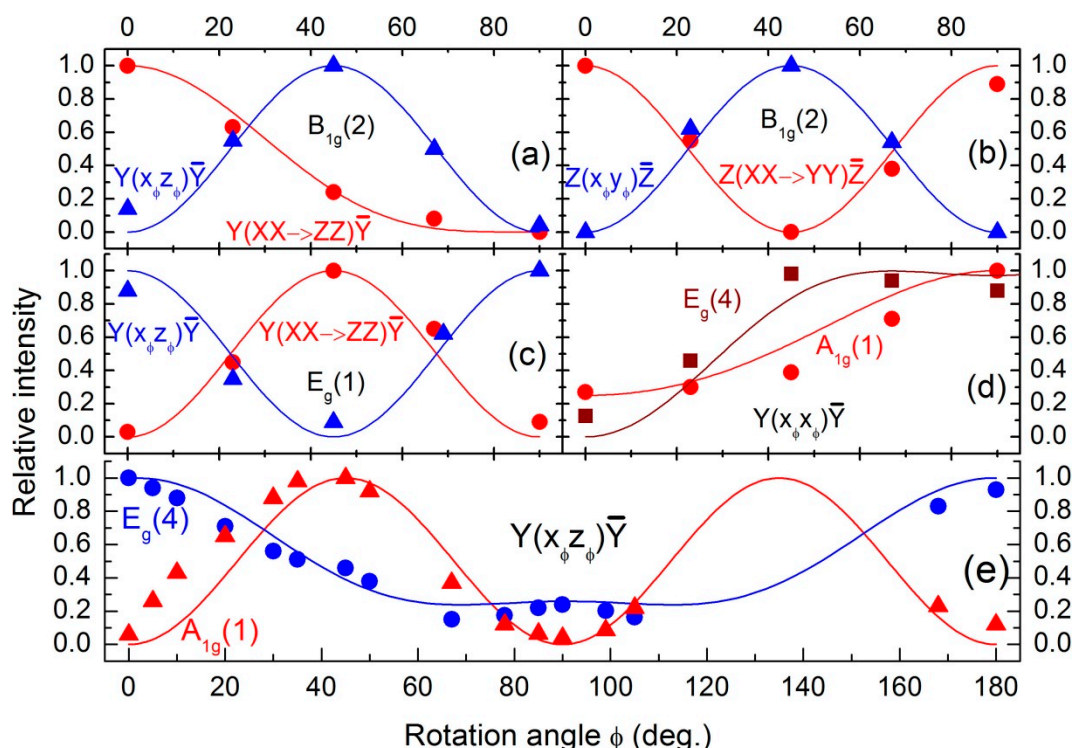


Figure 7. Angular dependence of the relative intensity of Raman lines (see the text and Table 2). The polarization configurations are indicated in the plots. Panels (a) and (b): $B_{1g}(2)$ mode at 269 cm^{-1} . Panel (c): $E_g(1)$ mode at 103 cm^{-1} . Panel (d): The $E_g(4)$ mode at 393 cm^{-1} and the $A_{1g}(1)$ mode at 381 cm^{-1} in parallel polarization. Panel (e): The $E_g(4)$ mode at 393 cm^{-1} and the $A_{1g}(1)$ mode at 381 cm^{-1} in perpendicular polarization. The solid lines are graphs of the theoretically predicted functional dependencies.

The excellent agreement between theory and experiment manifested in Figure 7a,b confirms the assignment of the 269 cm^{-1} line to the $B_{1g}(2)$ mode. This assignment is further corroborated by Figure B1 of [32], where the lines $E_g(3)$, B_{2g} and $B_{1g}(2)$ of LuVO_4 are detected in the same sequence and at nearly the same frequencies. From that figure it is seen that the $B_{1g}(2)$ mode crosses over the B_{2g} mode in going from NdVO_4 to LuVO_4 , while the B_{2g} frequency remains nearly constant at $260\text{--}261\text{ cm}^{-1}$. The same behaviour may be deduced from Table 1 of [24], if the labels $B_{2g}(\nu_2)$ and $B_{1g}(2)$ are interchanged. We therefore argue that it is the B_{2g} mode that remains relatively unchanged for all rare-earth vanadates while the $B_{1g}(2)$ mode undergoes a slight hardening over the rare-earth vanadate series from NdVO_4 to LuVO_4 . This is, however, contradictory to the mass-dependent frequency behavior $\omega \sim (\mu)^{-1/2}$ (here μ is the reduced mass of the rare-earth and the VO_4^{3-} ions) for its vibrational pattern (out-of-phase translation) expected from the simple model adopted in [24]. This seemingly contradictory behavior is supposed to be due to the mixing of the three close-by lying modes $E_g(3)$, B_{2g} and $B_{1g}(2)$ of totally different character. B_{2g} as internal tetrahedral mode should be least susceptible to such mixing which supports the assumption for its nearly constant frequency. Additionally, the B_{2g} vibrational pattern having all 4 oxygens move perpendicular to the V-O bonds should also keep this phonon insensitive to a change in the rare earth ion radius. On the other hand, the mass-dependent frequency behavior of the in-phase translational $B_{1g}(2)$ mode (113 cm^{-1} for LuVO_4) agrees qualitatively with the analogue model expected for its vibrational pattern, namely, $\omega \sim (m)^{-1/2}$ with m being the total mass of the rare-earth and the VO_4^{3-} ions [24].

The $E_g(4)$ mode is expected to lie in the vicinity of the $A_{1g}(1)$ mode at 381 cm^{-1} for all members of the orthovanadate family with a frequency nearly independent of the mass of rare-earth ion [28]. It is the second lowest in energy of the internal Raman modes of the VO_4^{3-} complex and seems to have exceptionally low scattering intensity. The experimental detection of the $E_g(4)$ mode in orthovanadates has almost never been reported, except for the study of Sanson et al. [28] on YVO_4 , where the $E_g(4)$ mode was found at 387 cm^{-1} . Interestingly, in the present study, we find in the spectra excited at 514.5 nm a line at 393 cm^{-1} with promising polarization behaviour (see Figures 2 and 6a). In parallel polarization, the relative intensity of this line resembles more or less the φ -dependence for an E_g mode, as depicted in Figure 7d. However, its intensity drops significantly when going from $Y(XZ)\bar{Y}$ to $Y(ZX)\bar{Y}$ scattering configuration (see Figure 2), which is extremely unusual for a phonon mode. We therefore scanned its angular dependence in perpendicular polarisation in the full range from $\varphi = 0^\circ$ to 180° using the high-resolution diffraction grating (1800 gr./mm). The obtained spectra are shown in Figure 6b and the resulting φ -dependences are plotted in Figure 7e. It is seen that, despite the intensity drop towards 90° , the relative intensity of this line tends to form a local minimum at about 45° and has a weak local maximum at 90° . It thus appears that there is an accidental coincidence of two lines: a weak one with a period of 90° and a stronger one with a period of 180° in the angular dependence of their intensities. The former one has the right angular dependence for an E_g mode, while the latter one has the right angular dependence for a polarized luminescence line. Although luminescence features normally appear in optical spectra in form of wider bands, rare-earth compounds are an exception. Sharp phonon-like luminescence lines are typical for rare-earth ions due to the radial confinement of their f-electrons [33]. Radiative discharge of some excited states in RE ions via dipole-allowed transitions was shown to produce polarized spectra [34] having $\cos^2\varphi$ -like angular dependence (hence period of 180°), which is typical for radiation of an oscillating dipole with fixed orientation. We also established a $\cos^2\varphi$ -like angular dependence for the intensity of some luminescence features around 400 cm^{-1} in the spectra from Figure 4b, which we have depicted in the inset of Figure 4b. Therefore, to provide theoretical curves for panels (d) and (e) of Figure 7, we modelled the intensity behaviour of the 393 cm^{-1} line with functions proportional to $(\sin^2\varphi + A \sin^2 2\varphi)$ for parallel and $(\cos^2\varphi + A \cos^2 2\varphi)$ for perpendicular polarization, respectively. The constant A was estimated to be $\approx 1/3$ from comparison of the line's intensity in crossed polarization at 0° where both components should be at maximum and 90° where the Raman line is again at maximum while the luminescence vanishes. The model shows satisfactory agreement with the measured data in both polarizations, especially in view of the fact that the region $300\text{--}450\text{ cm}^{-1}$ is rich in luminescence lines and there might be more than one of them interfering with the Raman modes $A_{1g}(1)$ and $E_g(4)$. For instance, in [35] luminescence spectra of rare-earth-doped LuVO_4 nanoleaves were reported containing lines around 526 nm , which corresponds to a Raman shift of $\approx 400\text{ cm}^{-1}$ in a spectrum excited at 514.5 nm . We consider the presented arguments sufficient to assign the 393 cm^{-1} line to the so far missing $E_g(4)$ mode. This assignment is corroborated by the presence of a weak line in an E_g Raman spectrum of LuVO_4 at the same frequency in Figure B3 of [32] for 514.5 nm excitation and at 386 cm^{-1} in Figure 5 of [25] for 532 nm excitation. In both publications, these faint features were not discussed probably due to their weak intensity. We should also mention the work of Voron'ko et al. [36] who reported to have found the $E_g(4)$ mode around 440 cm^{-1} in $X(ZY)\bar{X}$ Raman spectra of YVO_4 and GdVO_4 . In their temperature-dependent Raman study, these authors observed a double-peak structure for the $A_{1g}(1)$ line, which they explained by thermally-activated population of higher local minima in the lattice potential through rotation of some VO_4^{3-} tetrahedra. The higher-energy component, whose A_{1g} character was reportedly confirmed by polarization studies [36], nearly coincides in frequency with the line identified by us as the $E_g(4)$ mode. Although we do not rule out a possible inhomogeneous broadening of the A_{1g} line in our LuVO_4 crystal due to VO_4^{3-} to rotation at higher temperatures, we emphasize that we do not detect any splitting in its lineshape despite the large linewidth. We also have confirmed the symmetry of the $E_g(4)$ mode at 393 cm^{-1} in the relevant polarization configurations, and additionally by demonstrating its rotational transformation properties. Furthermore, the $E_g(4)$ mode is expected at a nearly constant

position between 370 and 410 cm^{-1} for all orthovanadates and has already been detected at 387 cm^{-1} for YVO_4 in full agreement with theoretical model calculations [28].

It should be pointed out, however, that no Raman feature at 393 cm^{-1} is detectable upon blue excitation at 488 nm where the spectrum is almost free of luminescence lines. This implies a possible resonance character of the $E_g(4)$ mode. A strong dependence of another E_g mode intensity on the excitation energy has already been established for YVO_4 [28]. Unfortunately, no complete resonance excitation profile can be constructed for this mode because upon red excitation (633 nm) the region 350–500 cm^{-1} is overshadowed by intense luminescence features stronger than the phonon lines. Still, measurements at other excitation wavelengths in the green region and, possibly at low temperatures, could provide ultimate confirmation of our $E_g(4)$ mode assignment.

4. Conclusions

Large single crystals of lutetium vanadate (LuVO_4) have been successfully grown by the high-temperature solution method. Group-theoretical analysis is performed and the determination of the various types of Raman active modes is demonstrated. An assignment of three controversial Raman lines of LuVO_4 with exceptionally low scattering intensity was achieved by investigation of polarized rotational-angle dependent Raman spectra. Thus, the correct assignment of all twelve first-order Raman active phonons of LuVO_4 is completed. We also show how details of the crystal structure of LuVO_4 are related to crystal- and correlation-field splitting effects in its vibrational spectrum.

Author Contributions: This article was coordinated by J.-Y.J., most of the text was written by P.R., who also performed the Raman measurements, with all authors giving input throughout. In particular, D.D. wrote most of the Introduction and Materials and Method, and provided the crystal samples, Y.-F.C. and C.-S.L. performed XRD measurements and their data interpretation. All authors have read and agreed to the published version of the manuscript.

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