Lattice vibrations in CaV$_2$O$_5$ and their manifestations: a theoretical study based on density functional theory

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Abstract. We present a comprehensive ab initio study of all non fully symmetric Γ point lattice vibrations in CaV$_2$O$_5$. The characteristics of CaV$_2$O$_5$ are a half-filled upper electron band and a ladder-like crystal structure. Adopting the frozen-phonon approach we calculate and analyze in detail the phonon eigenfrequencies and eigenvectors. The corresponding spectra of inelastic light scattering are computed for all Raman-active modes, including their resonance behavior as a function of incoming light. Our results allow for a qualitative and quantitative understanding of the phonon-related features in experimental optical excitation spectra. The theoretical data are employed to discuss available measurements and provide an improved assignment of the observed modes with respect to symmetry and displacement patterns. Electron hopping parameters and spin–spin exchange matrix elements are evaluated from the electronic bands. The changes in these parameters upon atomic displacements along the phonon eigenvectors are analyzed semiquantitatively, yielding the effect of

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lattice vibrations on charge and spin degrees of freedom. It is discussed how all the obtained results differ from the ones in the quarter-filled NaV$_2$O$_5$ compound due to differences in the electron band structure and in the chemistry.

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1. Introduction

Fascinating physical properties of ladder compounds have been stimulating very active studies in this field over the last 15 years [1], (and references there in [2]). The common feature of these crystals are the pairs of metal ions linked by an oxygen, which form the rungs of the ladder. These rungs are arranged in one dimension in the direction of the ladders’ legs. The main electron–electron interactions and electron motion occur within one ladder, while the interactions between neighboring ladders in the same plane are considerably weaker, and ladders in different planes are hardly coupled. In this situation, the coupling of the charge, spin and lattice degrees of freedom causes a rich variety of physical phenomena.

The most intensively studied examples of ladder compounds are formed by copper ions with spin 1/2 per magnetically active site and have half-filled upper bands, such as SrCu$_2$O$_3$ or (Sr, Ca)$_{14}$Cu$_{24}$O$_{41}$. However, there exist also two half-filled V-based ladder compounds, namely CaV$_2$O$_5$ and MgV$_2$O$_5$. In spite of the fact that Ca and Mg have the same valence configuration and both compounds are very similar in their V subsystem, they form crystals with different space groups: Cmnm and Pmmm for MgV$_2$O$_5$ and CaV$_2$O$_5$, respectively. The structural differences have a strong impact on the magnetic properties [3, 4]. While CaV$_2$O$_5$ is best described as a collection of well-isolated single two-leg spin ladders [5, 6], MgV$_2$O$_5$ exhibits an additional strongly frustrated interladder coupling [7, 8]. This leads to a very large gap of 500 K for the triplet excitations in the former compound [5], while in the latter a small gap of only 15 K is observed experimentally [7].

In addition to half-filled systems, V-based ladders show the unique realization of quarter-filling in NaV$_2$O$_5$ [10], which emphasizes the crucial importance of the chemical composition. Since a spin-Peierls transition in this compound was discovered NaV$_2$O$_5$ has become the most intensively investigated vanadium ladder system. It is especially interesting in the context of a
comparison with CaV$_2$O$_5$ since both compounds crystallize in the same $Pmmn$ structure with two formula units per unit cell (figure 1) at room temperature.

Since the properties of the ladder compounds are expected to be strongly influenced by the interplay of the electron motion, the lattice and the magnetic degrees of freedom, quantitative information about spin–lattice and charge–lattice coupling is strongly desirable, however, so far still lacking. To fill this gap and to gain an understanding of the physics of these compounds, we perform, to the best of our knowledge, the first ab initio investigation of the lattice dynamics of all non fully symmetric phonons in a half-filled ladder system using the example of CaV$_2$O$_5$. We report the theoretical phonon frequencies and eigenvectors for the $B_{1g}$, $B_{2g}$ and $B_{3g}$ modes, which are visible in Raman measurements, as well as all infrared-active vibrations, seen in light absorption and reflection experiments. A detailed comparison of the theoretical results, including the calculated Raman spectra, to experiment is presented and allows for a better understanding of the inelastic light scattering in this compound. In addition, we study electron– and spin–phonon coupling by mapping the ab initio results on a model band structure and identify the modes showing strong coupling to the electron subsystem. We relate the properties of CaV$_2$O$_5$ to those of NaV$_2$O$_5$ to understand the role of the electron occupancy at the vanadium site, which determines the filling of the upper electron band.

2. Computational methods

All total-energy and band-structure calculations are performed within density functional theory (DFT) using the full-potential augmented plane waves + local orbitals (FP-APW + lo) [11] formalism implemented in the WIEN2k code [12]. Exchange and correlation terms are described within the generalized gradient approximation (GGA) [13]. The atomic sphere radii are chosen as 1.6 au for V, 1.8 au for Ca and 1.4 au for the O atoms. A $K_{\text{max}}$ value of 4.64 is used in all calculations, corresponding to $R_{\text{MT}} \times K_{\text{max}}$ values of 6.5 for O, 7.43 for V and 8.36 for Ca.

The number of $k$ points in the full Brillouin zone (BZ) for the self-consistent field cycles is typically about 600. For the calculation of the dielectric function, which serves as input for the Raman spectra, a number of 3800 $k$ points in the full BZ is used. The $G_{\text{max}}$ used for charge density and potential is 14. The internal geometry is fully relaxed, taking the experimental atomic positions reported in [14] as starting point. Details about the relaxation can be found in [15].

$^6$ Crystal structures are produced with XCrySDen [9].
The phonon eigenfrequencies and eigenvectors are determined in the frozen-phonon approximation, where for each degree of freedom corresponding to the symmetry coordinates four displacements, two in positive and two in negative direction, are considered. The symmetry coordinates for each irreducible representation can be inferred from the degrees of freedom appearing in the corresponding table and figure, respectively.

3. Phonon modes

A factor group analysis yields, after subtraction of three acoustic ($B_{1u} + B_{2u} + B_{3u}$) and three silent $A_{1u}$ modes,

$$\Gamma = 8A_g(xx, yy, zz) + 3B_{1g}(xy) + 8B_{2g}(xz) + 5B_{3g}(yz)$$

$$+ 7B_{1u}(E \parallel \hat{z}) + 4B_{2u}(E \parallel \hat{y}) + 7B_{3u}(E \parallel \hat{x}),$$

where the letters in parenthesis indicate the polarization of the incoming and outgoing light, respectively. Hence, there are 24 Raman-active $A_g$ and $B_{ng}$ modes and 18 infrared-active $B_{nu}$ modes ($n \in \{1, 2, 3\}$). The eigenvectors and frequencies of the Raman-active $B_{1g}$, $B_{2g}$ and $B_{3g}$, and all infrared-active phonon modes are presented in Table 1, while the fully symmetric $\Gamma$ point phonons have already been published in [15]. The eigenvectors $e_\alpha^\zeta$ (where $\alpha$ denotes the atom and $\zeta$ indicates the phonon mode) are normalized with respect to the whole unit cell including two formula units of $CaV_2O_5$. For each set of equivalent atoms only the components corresponding to one atom are reported, where this reference atom is highlighted in the respective figures using bold italic characters.

3.1. Eigenvectors

Due to the structural similarity to $NaV_2O_5$ most of the phonon modes of both compounds are close in frequency [16], and the eigenvectors differ only very little. Figure 2 shows a selection of phonon modes which most strongly differ from their $NaV_2O_5$ counterparts.

As in the case of $NaV_2O_5$ the eigenvectors of the $B_{1g}$ modes represent a $V$–$O_2$ stretching, an $O_3$–$V$–$O_2$ bending, and a vibration where the two legs of one ladder are shifted antiparallelly along $\hat{y}$, respectively. The same situation is found for the $B_{2g}$ modes, where the features of the atomic displacements are the same as in the Na compound.

Within the $B_{3g}$ vibrations, two $CaV_2O_5$ modes exhibit a particular behavior. The $O_1$–$V$–$O_2$ $B_{3g}$ mode with 392 cm$^{-1}$ has some contribution from the Ca atom moving in the $\hat{y}$-direction, in contrast to Na which hardly participates in the corresponding $NaV_2O_5$ mode. For the 195 cm$^{-1}$ vibration with the same symmetry, where Ca moves out of phase with respect to the ladder and parallel to the $\hat{y}$-axis, the Ca eigenvector component is twice as large as the corresponding Na component in $NaV_2O_5$. Moreover, in $CaV_2O_4$ also the in-rung oxygen $O1$ takes part. Also two of the $B_{1u}$ phonon modes differ from their counterparts in $NaV_2O_5$: in $CaV_2O_5$, the $V$–$O_2$–$V$ bending mode (559 cm$^{-1}$) does not involve a shift of the in-rung oxygen $O1$, which is present in $NaV_2O_5$, and the apex oxygen $O3$ has a considerable $z$-component. In the $483$ cm$^{-1}$ $B_{1u}$ mode the $O3$ atom has a larger $x$-component, while the $x$-component of the in-leg oxygen $O2$ is quite small compared to the $NaV_2O_5$ mode. Among the phonons with $B_{3u}$ symmetry, the 401 cm$^{-1}$ vibration shows a noticeable Ca contribution, which makes it differ from the $O1$–$V$–$O3$ bending mode of $NaV_2O_5$. The $B_{3u}$ vibration exhibiting the clearest deviation from...
Table 1. Calculated eigenfrequencies in cm$^{-1}$ and eigenvectors of $\Gamma$ point phonon modes of CaV$_2$O$_5$. An assignment of the modes in terms of the actual displacement patterns is given in tables 2 and 3, respectively.

| $\omega$ (cm$^{-1}$) | $V_x$ | $V_y$ | $V_z$ | $C_{ax}$ | $C_{ay}$ | $C_{az}$ | $O_{1x}$ | $O_{1y}$ | $O_{1z}$ | $O_{2x}$ | $O_{2y}$ | $O_{2z}$ |
|---------------------|--------|--------|--------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| $B_{1\gamma}$       | 593    | -0.17  | -       | -        | -        | -        | -0.47    | -        | -0.11    | -        | -        | 0.14     | 0.30     |
|                     | 253    | -0.28  | -       | -        | -        | -        | -        | -        | -0.11    | -        | -        | 0.40     | -        |
|                     | 136    | 0.38   | -       | -        | -        | -        | -        | -        | -0.11    | -        | -        | 0.30     | -        |
| $B_{2\chi}$         | 842    | 0.04   | -0.25   | -0.02    | -        | 0.03     | -0.03    | -0.01    | -0.05    | -        | -0.04    | 0.43     | -        |
|                     | 652    | -0.21  | -0.02   | -0.01    | -        | 0.62     | -0.07    | -0.07    | -0.02    | -        | -0.04    | -        | -        |
|                     | 499    | -0.01  | 0.03    | 0.02     | -        | -0.04    | -0.48    | 0.12     | -0.01    | -        | -0.02    | -        | -        |
|                     | 342    | -0.33  | 0.18    | -0.04    | -        | -0.12    | -0.03    | -0.21    | 0.18     | -        | 0.15     | -        | -        |
|                     | 259    | -0.19  | -0.23   | -0.05    | -        | -0.03    | 0.06     | 0.29     | 0.25     | -        | -0.07    | -        | -        |
|                     | 219    | 0.28   | -0.02   | -0.14    | -        | 0.07     | -0.07    | -0.16    | 0.36     | -        | -0.02    | -        | -        |
|                     | 190    | -0.04  | -0.28   | 0.39     | -        | -0.06    | -0.06    | -0.26    | 0.05     | -        | -0.15    | -        | -        |
|                     | 135    | -0.10  | -0.24   | -0.38    | -        | -0.09    | -0.05    | -0.20    | -0.18    | -        | -0.17    | -        | -        |
| $B_{3\delta}$       | 605    | -0.18  | -        | -0.00    | -        | -0.01    | 0.46     | -        | 0.02     | -        | -        | -        | -        |
|                     | 392    | -0.16  | -        | -0.11    | -        | 0.59     | -0.06    | -        | 0.19     | -        | -        | -        | -        |
|                     | 254    | -0.27  | -        | 0.06     | -        | -0.20    | -0.12    | -        | 0.38     | -        | -        | -        | -        |
|                     | 195    | 0.24   | -        | -0.51    | -        | -0.10    | 0.08     | -        | 0.22     | -        | -        | -        | -        |
|                     | 113    | -0.34  | -        | -0.28    | -        | -0.07    | -0.13    | -        | -0.27    | -        | -        | -        | -        |
| $B_{1\omega}$       | 903    | -0.09  | 0.23    | -        | -0.01    | -        | 0.03     | 0.05     | -0.01    | 0.10     | -        | -0.42    | -        |
|                     | 559    | -0.30  | -0.02   | -        | 0.02     | -        | -0.00    | 0.37     | -0.10    | 0.05     | -        | 0.11     | -        |
|                     | 483    | -0.15  | -0.25   | -        | 0.00     | -        | 0.39     | -0.05    | 0.28     | 0.06     | -        | -0.07    | -        |
|                     | 348    | 0.11   | -0.11   | -        | -0.06    | -        | 0.34     | 0.07     | -0.25    | -0.31    | -        | -0.00    | -        |
|                     | 282    | 0.17   | -0.08   | -        | 0.04     | -        | -0.12    | 0.27     | 0.25     | -0.24    | -        | -1.12    | -        |
|                     | 235    | -0.30  | -0.05   | -        | 0.13     | -        | -0.13    | -0.19    | -0.02    | -0.32    | -        | -0.07    | -        |
|                     | 195    | -0.14  | 0.14    | -0.56    | -        | -0.06    | -0.04    | 0.18     | -0.11    | -        | 0.09     | -        | -        |
| $B_{2\omega}$       | 550    | 0.26   | -        | 0.01     | -        | -0.01    | -0.43    | -        | -0.04    | -        | -        | -        | -        |
|                     | 401    | -0.16  | -        | -0.10    | -        | 0.58     | -0.13    | -        | 0.19     | -        | -        | -        | -        |
|                     | 229    | -0.16  | -        | 0.06     | -        | -0.21    | -0.13    | -        | 0.43     | -        | -        | -        | -        |
|                     | 196    | 0.23   | -        | -0.56    | -        | -0.06    | 0.11     | -        | 0.16     | -        | -        | -        | -        |
| $B_{3\varepsilon}$  | 845    | -0.05  | 0.24    | 0.02     | -        | -0.01    | -0.01    | -0.00    | 0.06     | -        | -0.43    | -        | -        |
|                     | 658    | -0.18  | -0.07   | -0.01    | -        | 0.63     | -0.10    | 0.01     | -0.01    | -        | -0.03    | -        | -        |
|                     | 479    | -0.24  | 0.03    | 0.01     | -        | 0.00     | -0.41    | -0.14    | -0.02    | -        | 0.05     | -        | -        |
|                     | 367    | 0.12   | -0.24   | -0.03    | -        | 0.06     | -0.09    | -0.38    | -0.10    | -        | 0.11     | -        | -        |
|                     | 229    | -0.13  | 0.08    | -0.09    | -        | -0.03    | -0.09    | -0.04    | 0.44     | -        | 0.12     | -        | -        |
|                     | 174    | 0.20   | -0.02   | -0.58    | -        | 0.07     | -0.17    | 0.06     | 0.00     | -        | -0.05    | -        | -        |
|                     | 114    | -0.07  | -0.34   | -0.06    | -        | -0.07    | -0.09    | -0.28    | 0.03     | -        | -0.18    | -        | -        |
3.2. Frequencies

Given the close relation between the two compounds in terms of their eigenvectors, it is of special interest to compare the frequencies in CaV$_2$O$_5$ and NaV$_2$O$_5$ (presented in [16]) since they can give a direct information on the bonding and the interaction between the atoms in the two materials. It turns out that the phonon modes can be divided into several groups showing different tendencies in terms of the phonon frequency.

The first group is formed by the V–O$_3$ stretching modes and exhibits a strong frequency decrease compared to NaV$_2$O$_5$. In detail, the changes are $-14\%$ for the mode with $B_{2g}$ symmetry (842 cm$^{-1}$), $-7\%$ for the one with $B_{1u}$ symmetry (903 cm$^{-1}$) and $-10\%$ for the $B_{3g}$ V–O$_3$ stretching mode (845 cm$^{-1}$). A very similar tendency is found for the V–O$_2$ stretching modes, where the frequencies are lowered by 10 and 15% in case of the $B_{1g}$ (593 cm$^{-1}$) and the $B_{3g}$ vibration (605 cm$^{-1}$), respectively. In this context the V–O$_2$ stretching mode of the $B_{2u}$ species (550 cm$^{-1}$) represents an exception, since its frequency is only slightly decreased with respect to NaV$_2$O$_5$. The main reason for the lower energy of the V–O stretching in CaV$_2$O$_5$ is found in the chemical difference between Na and Ca. While Na contributes only one $s$ electron to the system, thus yielding V$^{4+5+}$ ions, the extra valence electron in Ca reduces the formal V charge to 4. Correspondingly, a Coulomb picture would imply a frequency decrease by a factor of $\sqrt{4/4.5}$, i.e. approximately 6%.
A trend to lower frequencies is also found for the group of V–O2–V bending modes with components perpendicular to the x–y plane. These vibrations also change the length of the V–O3 bond, such that the same argument as for the stretching modes applies. In case of the \( B_{2g} \) vibration with 259 cm\(^{-1} \) and the \( B_{3u} \) vibration with 367 cm\(^{-1} \) the decrease is about 10%, while it is more moderate for the 342 cm\(^{-1} \) \( B_{2g} \) mode with 5%. The \( B_{1u} \) 483 cm\(^{-1} \) and the \( B_{1u} \) 348 cm\(^{-1} \) vibrations have very similar frequencies in both CaV\(_2\)O\(_3\) and the NaV\(_2\)O\(_5\).

The situation is different for the V–O2–V bending modes parallel to the x–y plane. Here the vibrations in the Ca compound rather exhibit a frequency increase, which is only 1% for the \( B_{1u} \) mode with 559 cm\(^{-1} \), but 6% for the 499 cm\(^{-1} \) \( B_{2g} \) mode and even 8% for the \( B_{3u} \) mode with 479 cm\(^{-1} \). This tendency can be related to the stronger ladder–ladder interaction, which shows up in the slightly smaller inter-ladder distance in CaV\(_2\)O\(_3\) (1.98 Å, compared to 2.01 Å in NaV\(_2\)O\(_5\)) and in a much larger inter-ladder hopping parameter \( t_i \) [15]. The latter can be explained by a stronger overlap of orbitals of the V and O\(_2\) atoms in neighboring ladders, a consequence of the fact that the \( z \) coordinates of these two atoms differ by 0.06 Å less in CaV\(_2\)O\(_3\) (\( \Delta z_{V,O2} = 0.42 \) Å) compared to NaV\(_2\)O\(_5\) (\( \Delta z_{V,O2} = 0.48 \) Å).

The last group is represented by low-energy modes involving Ca. These modes show much higher frequencies compared with their counterparts in NaV\(_2\)O\(_5\). In detail, the increase is 21% in the \( B_{2g} \) mode with 190 cm\(^{-1} \), 4% in the \( B_{3g} \) mode with 195 cm\(^{-1} \), 24% in the 235 cm\(^{-1} \) \( B_{1u} \) mode, 27% in the \( B_{1u} \) vibration with 195 cm\(^{-1} \), 13% for the \( B_{2g} \) mode with 196 cm\(^{-1} \) and 20% in the 174 cm\(^{-1} \) \( B_{3u} \) vibration. A straightforward explanation of this tendency is delivered by the larger ionicity of Ca\(^{2+}\) than Na\(^+\) ions. This effect alone would imply even larger frequency increases, but it is partly compensated by the larger mass of Ca (40.08 au) compared with Na (22.99 au).

4. Comparison with experiment

4.1. Raman spectra

In order to compute the Raman intensities the atoms are displaced according to the calculated eigenvectors, and the dielectric function for the distorted crystal is calculated. The changes of the dielectric function with respect to such displacements along an eigenvector of mode \( \zeta \) allow the determination of the corresponding Raman intensity \( I_{ij} \). To this end we first define the operator \( \hat{Q} \) corresponding to the phonon coordinate via the following relation with the actual displacement coordinate \( u_{\zeta}^x \):

\[
\hat{Q} \sqrt{\frac{\hbar}{M_{\alpha}\omega_{\zeta}}} e_{\alpha \zeta} = u_{\zeta}^x.
\]

(1)

Here, \( M_{\alpha} \) is the mass of ion \( \alpha \) and \( \omega_{\zeta} \) defines the corresponding frequency. Then, \( I_{ij} \) is given by

\[
I_{ij}(\omega_R) = \sum_{\zeta} [n_B(\omega_{\zeta}) + 1] \left| \langle 1 | \frac{\partial \epsilon_{ij}}{\partial \hat{Q}} \hat{Q} | 0 \rangle \right|^2 L(\omega_R, \omega_{\zeta}, \Gamma).
\]

(2)

where \( \omega_R \) is the Raman shift, the Cartesian indices \( ij \) correspond to the polarizations of incident and scattered light, respectively, \( |1\rangle \) and \( |0\rangle \) denote the one-phonon and the phonon-less states, respectively, \( n_B(\omega_{\zeta}) = 1/\exp(\hbar \omega_{\zeta}/T) - 1 \) is the phonon Bose distribution function, \( \omega_l \) is the frequency of the incoming light, and \( L(\omega_R, \omega_{\zeta}, \Gamma) \) is the Lorentzian shape of the phonon line.
Table 2. Comparison of theoretical frequencies with experimental results from literature for the Raman-active phonon modes of CaV$_2$O$_5$. Columns marked with * represent an assignment of experimental spectra based on theoretical frequencies and Raman intensities.

| Experiment | Theory | Assignment |
|------------|--------|------------|
| $B_{1g}$  | 638    | 638 636 636 636 593 | 636 | V–O2 stretching |
|           | 292    | – 292 – | 253 | O3–V–O2 bending |
|           | 212    | 137 182 138.6 | 136 | antiparallel leg-shift |
| $B_{2g}$  | – 842  | V–O3 stretching |
|           | – 652  | V–O1 stretching |
|           | – 292  | 310 334 311 | 342 | O2–V–O3 bending |
|           | – 212  | 211 213 213 | 259 | O2–V–O3 bending |
|           | – 137  | 182 138.6 | 190 | Ca $\parallel \hat{x}$ + chain rotation |
|           | – 136  | 135 | chain rotation |
| $B_{3g}$  | – 605  | V–O2 stretching |
|           | – 369  | 366 366 | 392 | O1–V–O3 bending |
|           | – 212  | 212 280 213 | 254 | rung versus O3 shear |
|           | – 112  | 112 | antiparallel ladder shift |

with a broadening $\Gamma$, which is chosen to be 15 cm$^{-1}$ for all modes. Further information on the applied method can be found in [17].

The results for the $B_{1g}$, $B_{2g}$ and $B_{3g}$ modes are presented in figure 3. The highest peaks are found at 593 cm$^{-1}$ for $xy$ polarization, at 135, 259 and 652 cm$^{-1}$ for $xz$ polarization, and at 254 cm$^{-1}$ for $yz$ polarization. A specially subtle feature is found for the 219 cm$^{-1}$ $B_{2g}$ peak, which is surrounded by much higher neighbors. The signal of the $B_{3g}$ mode at 195 cm$^{-1}$ is completely covered by the strongly dominating 254 cm$^{-1}$ peak.

Figure 4 shows the change of the dielectric function for atomic displacements along the respective eigenvector, i.e. $|\partial \varepsilon_{ij}/\partial Q|^2$, for selected $B_{1g}$, $B_{2g}$ and $B_{3g}$ modes, where modes with maximum changes smaller than 0.01 have been omitted. Large values of $|\partial \varepsilon_{ij}/\partial Q|^2$ at a certain photon energy imply resonances observed with the corresponding laser frequency. Figure 4 shows that some of the modes exhibit a strong dependence on the applied photon energy, among them the $B_{2g}$ mode with 253 cm$^{-1}$, the $B_{2g}$ mode with 652 cm$^{-1}$ and the $B_{3g}$ mode with 254 cm$^{-1}$. Moreover, it is found that the experimentally used 514.5 nm (2.41 eV) line of an Ar$^+$ ion laser [18]–[20] leads to a very small response of the system for all but the 254 cm$^{-1}$ $B_{3g}$ mode. Instead, all modes exhibit resonances for photon energies below 2.0 eV, and many of the modes at photon energies between 2.5 and 3.0 eV.

In literature one polarized Raman measurement using a polycrystalline sample [18] and two unpolarized ones [19, 20] are reported, but there are no spectra obtained from CaV$_2$O$_5$ single crystals. For this reason no unambiguous experimental evidence for the symmetry of the peaks is found. Table 2 shows a comparison of the measured results with theoretical frequencies.
Figure 3. Theoretical Raman spectra for the $B_{1g}$ (upper panel), the $B_{2g}$ (central panel) and the $B_{3g}$ modes (lower panel) of CaV$_2$O$_5$, with the polarization of the incoming and outgoing light in parenthesis. All spectra are calculated for an incoming photon energy of 2.54 eV (514 nm).

Figure 4. Change of the dielectric function with respect to displacements along the eigenvector as a function of the photon energy $\omega$ for selected phonon modes. Left panel: $|\partial \varepsilon_{xy}/\partial Q|^2$ for the $B_{1g}$ modes; upper right panel: $|\partial \varepsilon_{xz}/\partial Q|^2$ for the $B_{2g}$ modes; lower right panel: $|\partial \varepsilon_{yz}/\partial Q|^2$ for the $B_{3g}$ modes.

Theory reveals that the experimental feature at 638 cm$^{-1}$ goes back to the highest-frequency $B_{1g}$ mode, which shows up as a very pronounced peak in the theoretical Raman spectra. A $B_{2g}$ mode at almost the same energy is probably covered by the $B_{1g}$ signal in experiment. A measured feature at 138 cm$^{-1}$, which was interpreted as $A_g$ mode in [19], and not assigned any symmetry in [18], can neatly be traced back to a superposition of the $B_{1g}$ and the $B_{2g}$ peak lowest in energy. A peak measured at about 370 cm$^{-1}$ is explicitly addressed in [19] and also clearly visible in the crossed-polarized spectra of [18]. This peak is in reasonable
agreement with the low theoretical $B_{3g}$ peak at 392 cm\(^{-1}\). The situation is comparable for the modest $B_{2g}$ feature at 342 cm\(^{-1}\), which is resolved in the unpolarized measurements [19, 20] at a slightly lower energy of 311 cm\(^{-1}\). Very good agreement is found for the theoretical $B_{2g}$ peak at 190 cm\(^{-1}\) and the experimental peak at 182 cm\(^{-1}\). A $B_{3g}$ feature at virtually the same energy has very low intensity and is therefore either not visible in experiment or integrated in the stronger $B_{2g}$ peak. Another $B_{3g}$ feature, which is not explicitly addressed in the experiment, but still distinguishable, is found at 113 cm\(^{-1}\), where the position of the experimental and the theoretical peak agree perfectly.

The comparison of ab initio results and measurements is more intriguing for the frequency range between 200 and 300 cm\(^{-1}\): while experiments show two pronounced peaks at 212 and 292 cm\(^{-1}\), theory yields high-intensity peaks at 259 cm\(^{-1}\) in the $B_{2g}$ spectra and at 254 cm\(^{-1}\) in the $B_{3g}$ spectra. Since the peak belonging to the latter is by far the highest, it most probably can be related to the measured feature at 212 cm\(^{-1}\), while the intensity of the former mode is in good qualitative agreement with the experimental peak at 292 cm\(^{-1}\). A third phonon mode with almost the same theoretical frequency is found among the $B_{1g}$ vibrations. However, the intensity of this mode is much smaller, which implies that in the experimental spectra it is probably masked by the $A_g$ peak at 238 cm\(^{-1}\). The tiny calculated $B_{2g}$ peak appearing at 212 cm\(^{-1}\) is most probably integrated in the large experimental feature at 219 cm\(^{-1}\).

For the rest of the Raman peaks no experimental counterpart is found, in perfect accordance with theory yielding very low scattering intensities.

### 4.2. Infrared active modes

In table 3, the theoretical frequencies for the infrared-active phonon modes are compared to experiment. To the best of our knowledge up to now only one, unpolarized measurement is found in literature [19], where a symmetry assignment was only done by comparison with polarized results for NaV\(_2\)O\(_5\). Thus theory can substantially contribute to a proper symmetry assignment of the peaks. The root mean square deviation between measured and calculated frequencies is less than 5%, with the largest difference (\(-9\) cm\(^{-1}\) = \(-7.3\%\)) found for the $B_{3u}$ chain-rotation mode with a theoretical frequency of 123 cm\(^{-1}\). As in [16] we have estimated the theoretical intensities of the infrared spectra. To do so, we have calculated the dipole moment $\mathbf{P}$ induced by a phonon distortion using a simple model with fixed ion charges (V\(^{4.5+}\), Ca\(^{2+}\), O\(^{2-}\)), but taking into account the real displacements according to the eigenvectors.

In the experimental infrared spectra, we identify five features as stemming from $B_{1u}$ phonons: in addition to the ones at 957, 282 and 198 cm\(^{-1}\), already identified in [19], the theoretical results show that also the 579 cm\(^{-1}\) and the peak at 198 cm\(^{-1}\) are related to a $B_{1u}$ vibration. In case of the former not only the theoretical frequency but also the rather small induced dipole moment imply that this small experimental peak is associated with the calculated mode at 559 cm\(^{-1}\). The latter turns out to represent a superposition with a $B_{2u}$ mode at the same frequency.

Other $B_{2u}$ modes that can be distinguished in experiment are found at 515 cm\(^{-1}\), where the large phonon-induced dipole moment obtained by theory agrees nicely with experiment, and the feature at 408 cm\(^{-1}\), which just perfectly corresponds to the calculated phonon energy. This is in contrast to the assignment obtained by comparison with NaV\(_2\)O\(_5\), which related these two peaks to $B_{3u}$ modes [19].
### Table 3. Comparison of theoretical frequencies with experimental results from literature for the infrared-active phonon modes of CaV$_2$O$_5$. The column marked with * represents an assignment of experimental spectra based on theoretical frequencies.

| Experiment | Theory | Assignment |
|------------|--------|-------------|
| $B_{1u}$   | 957    | 903 V–O3 stretching |
| –          | 579    | 559 V–O2 stretching |
| –          | –      | 483 O1–V–O2 bending |
| –          | –      | 348 O1–V–O2 bending + O3$_x$ |
| 264        | 264    | 282 rung stretching |
| –          | 244    | 235 O1–V–O3 bending + Ca || \hat{z} |
| 198        | 198    | 195 Ca || \hat{z} |
| $B_{2u}$   | 579    | 550 V–O2 stretching |
| 369        | 408    | 401 O1–V–O3 bending |
| –          | –      | 229 O3 versus ladder shear |
| 123        | 198    | 196 Ca || \hat{y} |
| $B_{3u}$   | 892    | 845 V–O3 stretching |
| 515        | –      | 658 O1 || \hat{x} |
| 408        | –      | 479 O2–V–O1 bending || \hat{x} |
| –          | 369    | 367 V–O2 bending || \hat{z} |
| 244        | –      | 229 V–O3 bending |
| –          | –      | 174 Ca || \hat{x} |
| –          | 123    | 114 chain rotation |

The peak at 892 cm$^{-1}$, which is the second highest in frequency in the infrared spectra, is readily identified as belonging to the $B_{3u}$ species. While the two phonon modes next lower in frequency are not found in the measurement, the peak at 369 cm$^{-1}$ fits perfectly to the theoretical result of 367 cm$^{-1}$. The feature with the lowest energy in the measurement, i.e. the one at 123 cm$^{-1}$, clearly belongs to the $B_{3u}$ species, which means that the assignment based on the comparison with NaV$_2$O$_5$ fails in this case.

### 5. Model parameters

In order to extract effective model parameters from the Kohn–Sham band structure six bands where mapped onto a tight-binding model, namely the bonding and anti-bonding pair of the V 3d$_{xy}$ bands at the Fermi level and the two highest lying O 2p bands. We restrict ourselves to the direction $\mathbf{k} || \hat{y}$ and take into account the hopping along the ladder $t_\parallel$, the in-rung hopping $t_\perp$, and the inter-ladder transfer $t_i$. Since the overall features of the electronic structure, except for the Fermi energy, are very similar to the ones in NaV$_2$O$_5$, the same mapping procedure as described [16] is applicable.

The values of the hopping parameters in the undistorted structure, $t_\parallel = 0.143$, $t_\perp = 0.321$ and $t_i = 0.244$ eV, as well as the vanadium Hubbard parameter $U = 2.45$ eV have been presented in [15]. With the knowledge of these parameters, one can calculate the spin–spin...
Table 4. Parameters of electron–phonon (eV) and spin–phonon coupling for selected phonon modes of CaV$_2$O$_5$ (frequency $\omega_c$ in cm$^{-1}$) as obtained from theory. The model parameters for the undistorted system [15] are $t_\parallel = 0.143$ eV and $t_\perp = 0.321$ eV, respectively.

| Symmetry | $\omega_c$ | Assignment | $\delta t_\parallel/\delta Q$ | $\delta J_\parallel/\delta Q$ |
|----------|------------|------------|-----------------------------|-----------------------------|
| $B_{1g}$ | 593        | V–O2 stretching | 0.040                       | 0.601                       |
| $B_{3g}$ | 605        | V–O2 stretching | 0.016                       | 0.210                       |
| $B_{3g}$ | 254        | rung versus O3 shear | 0.009                       | 0.139                       |
| $B_{3g}$ | 113        | antipar. ladder shift | 0.008                       | 0.134                       |
| $B_{1u}$ | 903        | V–O3 stretch. | 0.008                       | 0.104                       |
| $B_{1u}$ | 559        | V–O2 stretch. | 0.013                       | 0.155                       |
| $B_{1u}$ | 483        | O1–V–O2 bend. | 0.008                       | 0.106                       |

Figure 5. Two phonon modes with strong electron phonon coupling.

exchange. Below we consider exchange along the ladder $J_\parallel$, using the expression $J_\parallel = t_\parallel^2 / E_g$, where $E_g$ is the charge transfer gap between V and O [21]. In order to compare the electron– and spin–phonon coupling parameters for the different phonon modes with each other, the displacements are normalized with respect to the dimensionless phonon coordinate $Q$ defined in equation (1). Since the contribution to $E_g$, which is linear in $Q$ vanishes for all but the fully symmetric phonons, we consider below only the effect of the lattice vibrations on the hopping and spin–spin exchange.

The largest parameters of electron–phonon and spin–phonon coupling for the Raman active $B_{1g}$, $B_{2g}$ and $B_{3g}$ vibrations and all infrared active phonon modes of CaV$_2$O$_5$ ($\delta t_\parallel/\delta Q \geq 0.008$ eV), are presented in table 4. Comparing the coupling of $t_\parallel$ to lattice distortions corresponding to the $\Gamma$ point vibrations, similarly to NaV$_2$O$_5$, the strongest effect is related to the V–O2 stretching modes. Again, the largest value ($\delta t_\parallel/\delta Q = 0.040$ eV) is found for the $B_{1g}$ mode highest in frequency. This vibration is followed by the $B_{1g}$ V–O2 stretching with 605 cm$^{-1}$ (figure 5), with a $\delta t_\parallel/\delta Q$ of 0.016 eV, where the corresponding parameter is much less significant in the respective mode of NaV$_2$O$_5$. The phonon mode with the next smaller change of $t_\parallel$ coincides with its counterpart in NaV$_2$O$_5$ again, i.e. it is the $B_{1u}$ mode second highest in energy.

The $t_\perp$ show very weak coupling to phonon-distortions for all phonon modes considered here, with all values of $\delta t_\perp/\delta Q$ less than 0.007 eV, and are therefore not presented in the table.
This means that the $A_g$ vibrations [15] have by far the strongest effect on the hopping matrix element along the rung.

The spin–phonon coupling parameters expressed in terms of relative changes of $J_\parallel$ as induced by phonon distortions are presented in the last column of table 4. In CaV$_2$O$_5$, the highest values for $\delta J_\parallel/(J_\parallel \delta Q)$ are found for the V–O2 stretching modes with $B_{1g}$ symmetry (0.601), $B_{3g}$ symmetry (0.210), $A_g$ symmetry (0.186) and $B_{1u}$ symmetry (0.155). In fact, the mentioned vibrations are also the ones dominating the electron–phonon coupling of hoppings along the ladder, which seems reasonable due to the interrelation of both quantities. Besides, also in NaV$_2$O$_5$ the V–O2 stretching modes turn out to give the largest respective parameters. All other phonon modes lead to changes of $\delta J_\parallel/J_\parallel$ per $\delta Q$ smaller than 0.15. Since $t_\perp$ changes very little, all phonon-induced changes of $J_\perp$ for the considered phonon modes are very small, too.

6. Conclusions

We have determined the frequencies and eigenvectors of all Raman- and infrared-active low-symmetry $\Gamma$ point phonons of CaV$_2$O$_5$, a representative example of a half-filled compound with a ladder-like crystal structure. Our results provide detailed information on the lattice dynamics, which is desirable for both, the understanding of experimental data and the development of better models to describe such compounds. Our results provide the first direct symmetry assignment of the phonon modes, thus complementing former assignments based on a mere frequency-based comparison with polarized Raman experiments for NaV$_2$O$_5$ single crystals [19].

We have compared the phonon eigenvectors to the ones of the isostructural NaV$_2$O$_5$, and we have found that, in contrast to the latter, not only the low-frequency vibrations but also the O2–O1–O2 bending modes with $B_{3g}$ symmetry (392 cm$^{-1}$) and $B_{2u}$ symmetry (401 cm$^{-1}$) mode exhibit a significant Ca contribution. This shows that the interaction between the in-leg oxygen O1 and the interstitial ion is significantly larger than in NaV$_2$O$_5$, which is also reflected in the smaller distance between them (2.31 Å in CaV$_2$O$_5$, compared with 2.43 Å in NaV$_2$O$_5$).

In terms of frequencies we have distinguished four different groups of vibrations: the first two of them, i.e. the V–O3 stretching modes and the V–O2–V bending modes out of the $x$–$y$ plane, show significantly lower frequencies compared to their NaV$_2$O$_5$ counterparts, which is due to the different chemical situation where Ca provides one more valence electron to the two V sites of one rung, thus increasing its own ionicity and lowering the positive charge on the V sites. In contrast, V–O2–V bending modes within the $x$–$y$ plane show rather higher frequencies compared to NaV$_2$O$_5$, which is due to the stronger overlap of orbitals of the V and O2 atoms in neighboring ladders, a consequence of the fact that the $z$-coordinates of these atoms differ less in CaV$_2$O$_5$ compared with NaV$_2$O$_5$. The group of low-frequency vibrations involving Ca$^{2+}$, finally, exhibits strongly increased phonon frequencies due to the much stronger ionicity compared to Na$^+$ in the sodium ladder compound.

We have calculated the spectra of all Raman active $\Gamma$ point phonons from first principles, thus providing a sound basis for the analysis of the experimental spectra. This way we can make a direct assignment of the experimental peaks in terms of their symmetry. We have shown that, for example, the experimental peak at 139 cm$^{-1}$ goes back to a superposition of a $B_{1g}$ and a $B_{2g}$ mode, and that a small feature at 113 cm$^{-1}$, which is clearly visible but not explicitly addressed in the experimental works, is related to the anti-parallel ladder shift with $B_{3g}$ symmetry.

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In addition to the Raman spectra, we have determined the dependence of the Raman intensities on the energy of the exciting photons. It turns out that for the photon energy applied in the available experiments the response of the system is rather weak, while strong resonances for all modes are found at energies below 2 eV, and for many phonon modes at the energies between 2.5 and 3.0 eV. Hence, we propose to perform Raman experiments with corresponding laser frequencies, which would allow us to see phonon modes not observed before.

The theoretical eigenmodes of the infrared active phonons, together with an estimate of their induced dipole moment, elucidate experiments as well. We have improved the interpretation of the measured spectra, and shown, e.g. that the experimental feature at 579 cm$^{-1}$ stems from a $B_{1u}$ mode, while the peak at 198 cm$^{-1}$ represents a superposition of a $B_{1u}$ and a $B_{3u}$ peak. The measured peak at 123 cm$^{-1}$, in turn, can be assigned to a $B_{3u}$ vibration.

Finally, we have determined the electron–phonon and spin–phonon coupling parameters by mapping the ab initio eigenvalues for phonon-distorted structures on a 6-band Hamiltonian. We have found that $t_{\parallel}$, and consequently also $J_{\parallel}$, are little affected by the non fully symmetric $\Gamma$ point phonons. Regarding the hopping along the legs $t_{\perp}$, and the corresponding exchange coupling $J_{\perp}$, the V–O2 stretching modes show the largest changes, where the $B_{1g}$ 593 cm$^{-1}$ mode reveals the strongest electron- and spin–phonon coupling of all $\Gamma$ point phonons. In summary, a quantitative description of the interactions that can strongly influence the electron subsystem has been achieved, yielding a profound understanding of this representative half-filled ladder compound.

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References

[1] Dagotto E and Rice T M 1996 Surprises on the way from one- to two-dimensional quantum magnets: the ladder materials Science 271 618
[2] Lemmens P, Güntherodt G and Gros C 2003 Magnetic light scattering in low-dimensional quantum spin systems Phys. Rep. 375 1–103
[3] Korotin M A, Elfimov I S, Anisimov V I, Troyer M and Khomskii D I 1999 Exchange interactions and magnetic properties of the layered vanadates CaV$_2$O$_5$, MgV$_2$O$_5$, CaV3O7 and CaV4O9 Phys. Rev. Lett. 83 1387
[4] Korotin M A, Anisimov V I, Saha-Dasgupta T and Dasgupta I 2000 Electronic structure and exchange interactions of the ladder vanadates CaV$_2$O$_5$ and MgV$_2$O$_5$ J. Phys.: Condens. Matter 12 113
[5] Iwase H, Isobe M, Ueda Y and Yasuoka H 1996 Observation of Spin Gap in CaV$_2$O$_5$ by NMR J. Phys. Soc. Japan 65 2397
[6] Isobe M and Ueda Y 1998 Doping effects in AV$_2$O$_5$ (A = Li, Na and Ca) J. Magn. Magn. Mater. 177–81 671–2
[7] Isobe M, Ueda Y, Takizawa K and Goto T 1998 Observation of a Spin Gap in MgV2O5 from high field magnetization measurements J. Phys. Soc. Japan 67 755
[8] Millet P, Satto C, Bonvoisin J, Normand B, Penc K, Albrecht M and Mila F 1998 Magnetic properties of the coupled ladder system MgV2O5 Phys. Rev. B 57 5005
[9] Kokalj A 2003 Comput. Mater. Sci. 28 155 (http://www.xcrysden.org/)
[10] Smolinski H, Gros C, Weber W, Peuchert U, Roth G, Weiden M and Geibel C 1998 NaV$_2$O$_5$ as a quarter filled ladder compound Phys. Rev. Lett. 80 5164
[11] Sjöstedt E, Nordström L and Singh D J 2000 An alternative way of linearizing the augmented plane-wave method Solid State Commun. 114 15
[12] Blaha P, Schwarz K and Luitz J 1997 WIEN2k (Release 97.8) (Improved and updated Unix version of the original copyright WIEN code, which was published in Blaha P, Schwarz K, Sorantin P and Trickey S B 1990 Comput. Phys. Commun. 59 399)
[13] Perdew J P, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple Phys. Rev. Lett. 77 3865–68
[14] Onoda M and Nishiguchi N 1996 Crystal structure and Spin Gap state of CaV$_2$O$_5$. J. Solid State Chem. 127 359
[15] Spitaler J, Sherman E Ya, Evertz H G and Ambrosch-Draxl C 2004 Optical properties, electron–phonon coupling, and Raman scattering of vanadium ladder compounds Phys. Rev. B 70 125107
[16] Spitaler J, Sherman E Ya and Ambrosch-Draxl C 2007 Zone-center phonons in NaV2O5: a comprehensive ab initio study including Raman spectra and electron–phonon interaction Phys. Rev. B 75 014302
[17] Ambrosch-Draxl C, Auer H, Kouba R, Sherman E Ya, Knoll P and Mayer M 2002 Raman scattering in YBa$_2$Cu$_3$O$_7$: a comprehensive theoretical study in comparison with experiments Phys. Rev. B 65 064501
[18] Konstantinović M J, Popović Z V, Isobe M and Ueda Y 2000 Raman scattering from magnetic excitations in the spin–ladder compounds CaV$_2$O$_5$ and MgV$_2$O$_5$ Phys. Rev. B 61 15185
[19] Popović Z V, Konstantinović M J, Gajić R, Popov V N, Isobe M, Ueda Y and Moshchalkov V V 2002 Phonon dynamics in AV$_2$O$_5$ (A=Na, Ca, Mg, Cs) oxides Phys. Rev. B 65 184303
[20] Popović Z V, Stergiou V, Raptis Y S, Konstantinović M J, Isobe M, Ueda Y and Moshchalkov V V 2002 High pressure Raman study of CaV$_2$O$_5$. J. Phys.: Condens. Matter 14 L583
[21] Sherman E Ya, Fischer M, Lemmens P, van Loosdrecht P H M and Güntherodt G 1999 Electron–phonon and spin–phonon coupling in NaV$_2$O$_5$: charge fluctuation effects Europhys. Lett. 48 648