

Phonon anomalies in the two phases of the low-dimensional spin compound $(\text{VO})_2\text{P}_2\text{O}_7$

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We studied the temperature and pressure dependence of the phonons of the two different phases of $(\text{VO})_2\text{P}_2\text{O}_7$, the ambient (AP) and the high-pressure (HP) phase, by polarized Raman spectroscopy. Most modes in the lower-symmetry AP phase are split compared to the higher-symmetry HP phase. The V-O vibrations around 920 cm^{-1} of both phases reveal an anomalous mode softening with decreasing temperature as well as under moderate hydrostatic pressure ($<3\text{ GPa}$). We show that this is due to the interlayer interaction of neighboring V and O atoms as supported by temperature-dependent lattice parameter determinations. We identify a spin-phonon mode at 141 cm^{-1} in the HP phase, the counterpart of the spin-phonon mode at 123 cm^{-1} in the AP phase. Several modes of the AP phase around 200 cm^{-1} reveal a strongly anharmonic behavior; their integrated intensity disappears as a function of temperature near 30 K. We discuss the origin of this behavior as possibly related to the spin rather than to the lattice structure.

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I. INTRODUCTION

The catalyst vanadyl pyrophosphate [$(\text{VO})_2\text{P}_2\text{O}_7$] in its ambient pressure (AP) phase was initially considered to be a realisation of a Heisenberg spin ladder compound.¹ Subsequent research revealed that the observed magnetic properties of the V^{4+} sublattice fit better to alternating antiferromagnetic (AF) spin chains perpendicular to the initially supposed ladders.² Recent observations, moreover, suggest a unique model of two different alternating spin chains with different spin gaps due to small inequalities of the V-atom positions and their surroundings on the spin chains.^{3,4} Besides the observation of spin gaps with Raman spectroscopy⁵ anharmonicities of particular modes of AP- $(\text{VO})_2\text{P}_2\text{O}_7$ were observed.^{6,7} Recently the production of a high-pressure (HP) phase of $(\text{VO})_2\text{P}_2\text{O}_7$ with a higher space group symmetry was described ($Pbcn$ instead of $Pca2_1$).⁸⁻¹⁰ The question arises as to what influence the increase in symmetry has on the magnetic or vibrational properties of $(\text{VO})_2\text{P}_2\text{O}_7$.

AP- $(\text{VO})_2\text{P}_2\text{O}_7$ crystallizes in the orthorhombic system $Pca2_1$ with eight formula units per crystallographic unit cell. The V atoms, responsible for the low-dimensional magnetic properties, occupy four inequivalent crystallographic sites resulting in two distinct spin chains. At 2 GPa and $700\text{ }^\circ\text{C}$, $(\text{VO})_2\text{P}_2\text{O}_7$ was found to undergo a structural phase transition into the HP phase with orthorhombic symmetry (standard setting) $Pbcn$. The unit cell has about half the volume of the AP-phase one; one essential difference is that the vanadium atoms now occupy one single-crystallographic orbit. They therefore couple to a single alternating AF spin chain. From susceptibility and high-field magnetization measurements on polycrystalline samples spin gap values of 27 and 23 K of the HP phase, respectively, have been determined.⁸ However, this value could not yet be confirmed by Raman scattering experiments.

In this paper we focus mainly on two topics. After an

overview over the experimental results we first discuss the strong anharmonicity of the V-O vibrations on the basis of our temperature and pressure-dependent experiments. The second topic will be the observed anomalous behavior of some phonons in the low-energy region of the AP phase, which are absent in the HP phase. Finally, we discuss their possible relation to the spin system.

II. EXPERIMENTAL SETUP

In our experiments we examined AP- $(\text{VO})_2\text{P}_2\text{O}_7$ single crystals which were prepared as described in Ref. 11. Our first Raman experiments on the high-pressure phase were performed with polycrystalline material prepared by the authors of Ref. 10 with a method comparable to the one described in Ref. 8. Tiny single crystals of HP- $(\text{VO})_2\text{P}_2\text{O}_7$, grown from the melt under high pressure by the same group with a technique similar to the one described in Ref. 9, were also used. These crystals with dimensions far below a millimeter could not be oriented and prevented a measurement with scattering geometry parallel to the interesting direction of the spin chains. Gross *et al.* developed an alternative method to prepare single crystals of HP- $(\text{VO})_2\text{P}_2\text{O}_7$ by pressure-induced transformation of preoriented AP- $(\text{VO})_2\text{P}_2\text{O}_7$ single crystals.¹⁰ We examined such a crystal and confirmed our earlier findings on the polycrystals as well as the tiny single crystals; the following discussion is based mainly on the latter results.

The Raman experiments were carried out using a DILOR XY-800 triple-grating spectrometer in combination with a liquid-nitrogen-cooled charge-coupled device (CCD). The experiments with high hydrostatic pressure, up to 8.5 GPa, were performed at room temperature using a diamond anvil cell (DAC) with a methanol/ethanol mixture as pressure medium. We used the ruby luminescence technique for pressure determination.

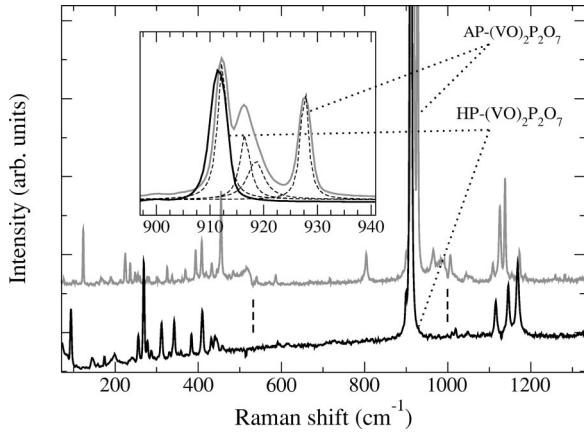


FIG. 1. Raman spectra of HP-(VO)₂P₂O₇ (black lines) together with AP-(VO)₂P₂O₇ (gray lines) for comparison. A spectrum of polycrystalline HP-(VO)₂P₂O₇ is displayed here and the modes appear irrespective of their symmetry. The higher crystallographic symmetry of the HP phase leads to a degeneracy of many of the modes (see inset for an example).

The experiments under high pressure required the preparation of crystallites smaller than 100 μm and the orientation of these samples in the pressure cell occurred accidentally. However, by comparison with the ambient pressure results we were able to approximately determine the scattering geometry for the AP-phase samples. Raman spectra of the HP phase were obtained on polycrystalline material.

III. EXPERIMENTAL RESULTS

A. Phonon spectra of HP-(VO)₂P₂O₇ compared with the AP phase

A full factor group analysis of HP-(VO)₂P₂O₇ was carried out but we will refrain from a lengthy presentation, as the results are similar to those of AP-(VO)₂P₂O₇.⁷ They can be summarized as follows. The main difference between the two crystallographic phases of (VO)₂P₂O₇ is that the unit cell in the HP phase has half the size of the AP phase, resulting in half of the total number of phonons in the HP phase. In contrast to the AP phase the HP phase possesses an inversion center so that only about one-quarter of the Raman-active modes of the AP phase remain. This result of the factor group analysis we found to be in full accordance with our experimental results.

The Raman spectrum of HP-(VO)₂P₂O₇, displayed in Fig. 1, has regions with peaks below 500 cm^{-1} , around 900 and above 1100 cm^{-1} similar to the AP phase which is shown for comparison. We base our mode assignment on the one described in Ref. 7 for the AP phase. In the high-energy region, above 1100 cm^{-1} , the asymmetric PO₃ stretching vibrations of the P₂O₇ polyhedra are expected. The correlation scheme of these modes predicts for HP-(VO)₂P₂O₇ two lines in each of the scattering geometries, whereas eight lines are predicted for AP-(VO)₂P₂O₇. These vibrations, which we observed as several lines in the AP phase, degenerate in the HP phase to two modes observed in $A_{1g}(zz), (yy)$ symmetry and two modes observed in B_{3g} symmetry. As in the AP phase

we found the strongest A_{1g} vibrations to be parallel to the spin-chain direction (z axis). The highest frequencies of the asymmetric stretching vibrations $\nu_{as}\text{PO}_3$ are somewhat lower than in AP-(VO)₂P₂O₇. As in the AP phase the symmetric PO₃ stretching vibrations at 1000 cm^{-1} are found to be comparatively weak. The strong VO vibrations which appeared in the AP phase as four lines around 920 cm^{-1} degenerate in HP-(VO)₂P₂O₇ to a single line, as expected since the vanadium atoms here occupy only one crystallographic orbit. The unusual anharmonicity of these vibrations, a shift to higher energy with rising temperature, is a common feature of both phases, and we will take up this point in the discussion. Below 500 cm^{-1} we find the bond bending vibrations of the P₂O₇ ions as well as the external vibrations of the P₂O₇ and VO groups. The degeneracy due to the higher symmetry of the unit cell reduces the number of observed modes in HP-(VO)₂P₂O₇ in this region, as well.

Besides the overall common appearance of the spectra we found remarkable differences in the temperature dependence of some of the low-energy modes. In Ref. 6 a strong anharmonicity of a mode at 123 cm^{-1} in the Raman spectra of AP-(VO)₂P₂O₇ was reported and related to a spin-phonon coupling. The mode was supposed to originate in a vibration of the P₂O₇ polyhedra since they mediate via a V-O-P-O-V link the stronger superexchange coupling of the alternating AF spin chains. This mode, although weakening more than the pure phonon modes with increasing temperature, still has considerable intensity even at room temperature. Based on its coupling and low energy we assign this mode to the external vibration of the P₂O₇ group. We observed further modes, depicted in Fig. 2, which drastically lose their intensity upon warming between 15 and 20 K. Such a remarkable behavior is usually observed near a structural phase transition which, however, has not been established for (VO)₂P₂O₇ so far. In contrast to these pronounced effects in the low-energy Raman spectra of AP-(VO)₂P₂O₇ we did not observe modes with a similar behavior in the Raman spectra of HP-(VO)₂P₂O₇. A mode at 92 cm^{-1} in the HP phase observed in (xx) and (zz) polarization—in relation to the direction of the spin chain these are the same polarizations as in AP-(VO)₂P₂O₇—could be the counterpart of the external P₂O₇ vibration at 123 cm^{-1} in the AP-phase. However, like all other modes in the HP phase, with the exception of the VO vibrations, this mode reveals only a small hardening with decreasing temperature and displays no obvious coupling to the spin system. As we shall show later, the pressure dependence of the spectra favors a different assignment.

In the AP-phase excitations into the two-magnon continuum appeared in the Raman spectra as two weak shoulders at low frequencies [45 and 90 cm^{-1} Ref. 5] with polarizations of incoming and scattered light parallel to the spin chains. We searched for these excitations in the HP phase where a value of $\approx 2.6 \text{ meV} \approx 42 \text{ cm}^{-1}$ was concluded for the spin-gap energy of the AF spin chain in HP-(VO)₂P₂O₇.^{8,12} However, in the Raman spectra we could not observe any such features around this energy; they are probably too weak to be detected.

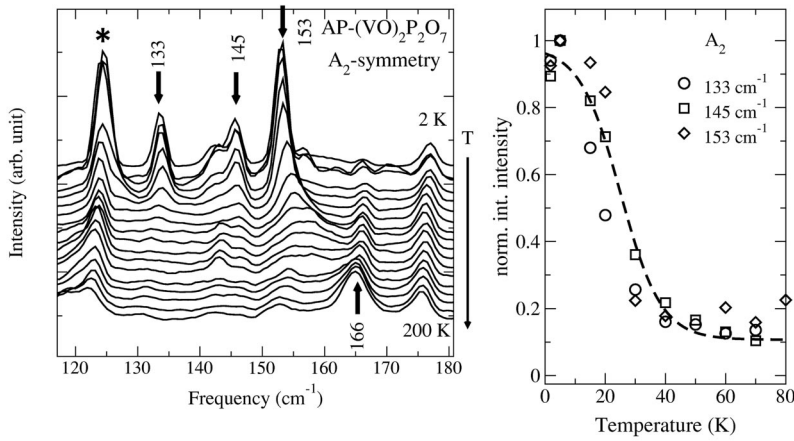


FIG. 2. (Left) Low-energy Raman spectra of $(VO)_2P_2O_7$ as a function of temperature in A_2 symmetry. Marked by arrows are three modes (133 , 145 , and 153 cm^{-1}) which disappear and a mode at 166 cm^{-1} which shows an increase in intensity with temperature. The spin-phonon mode with A_1 symmetry at 123 cm^{-1} (asterisk) appears here because of signal leakage. (Right) Normalized integrated intensity of the modes which disappear as a function of temperature. These modes decrease sharply in intensity around $20 \pm 3\text{ K}$, which was estimated by fitting a step-like function to the data (dashed line).

B. Raman scattering under high pressure

In order to investigate more the interaction between the polyhedral units we examined the Raman spectra under hydrostatic pressure. In Fig. 3 parts of the low-energy region

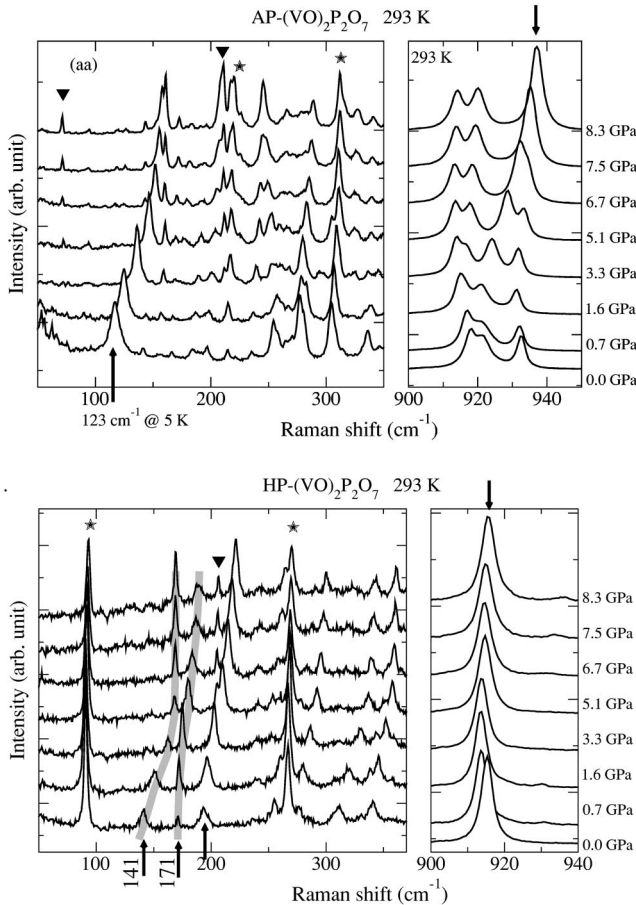


FIG. 3. Raman spectra of AP- $(VO)_2P_2O_7$ single-crystal (upper) and polycrystalline HP- $(VO)_2P_2O_7$ (lower) at different hydrostatic pressures, measured at room temperature. For a comparison of the relative intensities the spectra were normalized to a phonon in the high-energy range. In HP- $(VO)_2P_2O_7$ an anticrossing of two modes at 141 and 171 cm^{-1} (zero-pressures frequencies) occurs. An explanation for the other marks is given in the text.

and the region around the VO vibrations are displayed on an expanded scale. Pressure has roughly three types of effects: (i) a small shift to higher energies (peaks marked by an asterisk in Fig. 3), (ii) a large and nonlinear shift (arrows), and (iii) an activation of certain modes with rising pressure (triangles). In AP- $(VO)_2P_2O_7$ the three strong modes around 920 cm^{-1} [Fig. 3(a), right panel] exhibit a pronounced nonlinear behavior with rising temperature (not shown) and particularly with pressure. In Fig. 5, below, the peak positions of these modes versus hydrostatic pressure are displayed together with a third-degree fit. Under pressure the modes first soften and above 2.5 GPa and 5 GPa (lowest and other modes, respectively) shift to higher energies. An additional mode (arrow, Fig. 3) which seems to be hidden or degenerate at ambient pressure becomes apparent at around 3 GPa and shifts up in energy by more than 15 cm^{-1} at 8.3 GPa . In the HP phase a nonmonotonic shift of the V-O mode at 915 cm^{-1} is observed too; however, its variation is much smaller. To within 2 cm^{-1} its frequency is constant, with a slight tendency to larger frequency beyond $\sim 1\text{ GPa}$.

Figure 6, below, summarizes the energy shift in the low-energy region of selected modes in the AP and HP phases of $(VO)_2P_2O_7$. The AP- A_1 mode at 117 cm^{-1} , which shows spin-phonon coupling, shifts by more than 40 cm^{-1} in the investigated pressure range, which is more than 30% of its absolute value. The other modes remain at nearly the same frequency or even shift to lower energy, as the mode at 211 cm^{-1} which seems to split from a mode lying next to it. At 72 cm^{-1} a new mode appears. The question is whether it is induced by a structural phase transition or if the additional mode is activated by another mechanism. This point will be addressed in a further study, thus leaving the above question undecided for the moment. The spectra of the HP phase present a similar picture. Some weak modes show a strong shift (141 , 193 , 276) by more than 30 cm^{-1} whereas others almost keep their positions. Again, at higher pressures additional modes appear. However, since the strong mode at 915 cm^{-1} shows no trace of a splitting, it seems questionable that this is the result of a symmetry reduction. Instead they may appear because of a lifting of accidental degeneracies of some modes.

From the pressure effects on both phases of $(VO)_2P_2O_7$ described so far the following conclusion may be drawn. We

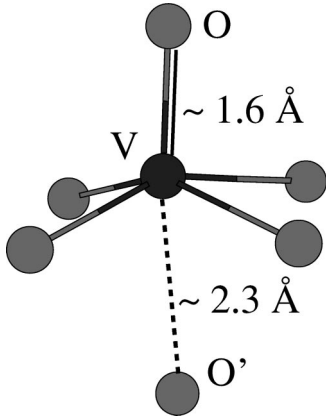


FIG. 4. The pyramidal oxygen coordination of vanadium in $(\text{VO})_2\text{P}_2\text{O}_7$. By including the apical oxygen atom O' from the next layer a distorted octahedral coordination is given with an additional weak V-O' bond.

assign those modes which show a strong positive shift, in particular the one at 117 cm^{-1} in the AP phase, to external vibrations of the P_2O_7 group. This raises the question as to why its supposed counterpart in the HP phase, the A_{1g} mode at 92 cm^{-1} based on its polarization selection rule, exhibits only little energy variation. Instead, this mode revealed a similar behavior to the mode at 915 cm^{-1} , i.e., a small shift to lower energy (less than one wave number) and a shift of about 3 cm^{-1} above approximately 2 GPa up to 8.3 GPa. On the other hand, the weak HP peak at 141 cm^{-1} , at least initially, shows a similarly large shift as the spin-phonon mode in AP- $(\text{VO})_2\text{P}_2\text{O}_7$, making it a better candidate for a spin-phonon coupled mode than the one at 92 cm^{-1} . We will take up this point in the discussion.

IV. DISCUSSION

A. Lattice anisotropy and V-O vibrations

In Ref. 7 we reported the observation of an anomalous temperature-dependent shift of the prominent V-O vibrations around 915 cm^{-1} and related it to an interaction of the vanadium atoms with oxygen atoms of adjacent layers, induced by a supposed pronounced anisotropy of the thermal expansion of the unit cell. We briefly summarize here the mechanism proposed in Ref. 7. The vanadium atoms (oxidation state $4+$) are pyramidally coordinated by five oxygen atoms, depicted in Fig. 4.

A peculiarity of the V^{4+} polyhedra is the presence of the vanadyl group of the central vanadium atom with the apical oxygen atom O1 , whose bond length is short compared to the other bonds.¹³ Because of the short length of the bond and the high frequency of the stretching vibration, the oxygen atom is considered doubly bonded. However, close inspection of the vanadium environment reveals that the distance to an apical oxygen $\text{O1}'$ from a neighboring layer ($2.25\text{--}2.37\text{ \AA}$) is short enough to give a distorted octahedral coordination¹³ so that the vanadium atoms are weakly bonded to the neighbor planes, too. The relatively large thermal expansion along the a axis will supposedly affect mainly

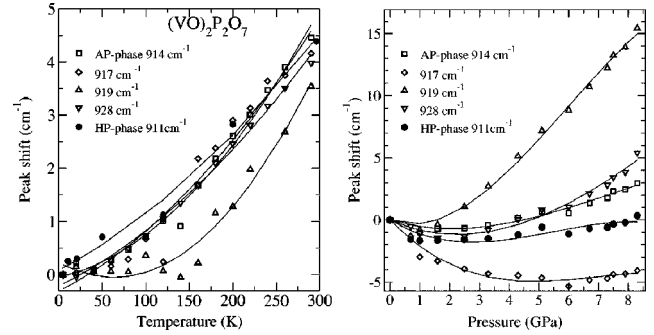


FIG. 5. Raman shift as a function of temperature (left) and hydrostatic pressure (right) of the V-O vibrations in AP- and HP- $(\text{VO})_2\text{P}_2\text{O}_7$. The curves of both graphs are third-order fits to the peak positions as a function of temperature and applied pressure, respectively. Up to a pressure of about 2.5 GPa (HP phase: 1 GPa) a softening of all modes is observed. The large dependence of the 919 cm^{-1} mode [AP- $(\text{VO})_2\text{P}_2\text{O}_7$] is discussed in the text.

the V— $\text{O1}'$ distance such that for low temperatures the distance is about 1% shorter than at room temperature. Hence through the decreasing layer distance the interlayer V— $\text{O1}'$ bond increasingly influences the intralayer V— O1 bond, which in effect lowers the V— O1 mode frequency. It would be desirable to prove this model by *ab initio* or force constant calculations of the lattice dynamics but AP- $(\text{VO})_2\text{P}_2\text{O}_7$ has a too complicated structure with 104 atoms in the unit cell [HP- $(\text{VO})_2\text{P}_2\text{O}_7$: 52 atoms] to make this a feasible task.

Because of the structural similarity of both phases with respect to the vanadium-oxygen coordination, we expect to observe a similar shift in the HP phase. Indeed, the V-O vibration in HP- $(\text{VO})_2\text{P}_2\text{O}_7$ was found to reveal the same temperature dependence as the corresponding modes in the AP phase, as displayed in Fig. 5. A temperature-dependent x-ray study of the lattice parameters of AP- $(\text{VO})_2\text{P}_2\text{O}_7$ down to 107 K (Ref. 14) revealed that the thermal expansion is anisotropic with a linear thermal expansion coefficient $\alpha_a = 2.3 \times 10^{-5}\text{ K}^{-1}$ in the direction of the V-O bond and $\alpha_{b,c} \approx 5 \times 10^{-6}\text{ K}^{-1}$ in the perpendicular directions. The value for the a -axis expansion coefficient fits well to the prediction in Ref. 7 ($\alpha_a = 3 \times 10^{-5}\text{ K}^{-1}$) based on a comparison to NaV_2O_5 .

If a cooling-induced contraction of the lattice is the origin of the observed line shift, then hydrostatic pressure should have a similar effect, at least in a first-order approach. The results of the pressure experiment are compiled in Fig. 5 (right panel). Up to a pressure of 2.5 GPa (1 GPa in the HP phase) this is indeed the case and the modes shift to lower energy. With higher pressures, however, the lattice distortion departs from the anomalous behavior, returning to the normal increase of the mode energies with pressure. A mode at 919 cm^{-1} in the AP phase deviates from the otherwise almost uniform pressure dependence. This sheds some doubt on the assignment of this mode to a V-O vibration since from a symmetry point of view none of the vibrations split by factor group should differ from the average frequency by more than a small amount. Furthermore, with increasing pressure this mode becomes much more intense than the others (see Fig. 3) so that it is likely to be a vibration of different origin, too

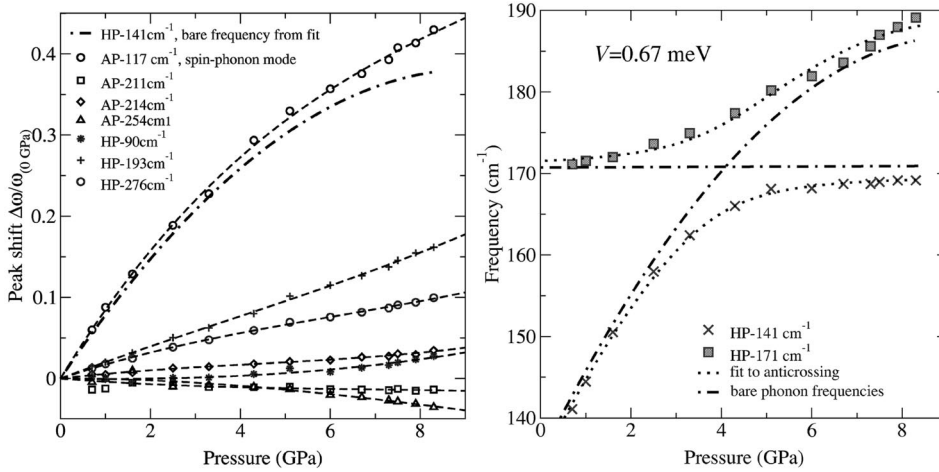


FIG. 6. (Left) Relative peak shift of various phonon frequencies with respect to the extrapolated values at 0 GPa; the dashed lines are third-order fits to guide the eye. (Right) The anticrossing behavior of the modes at 141 and 171 cm^{-1} is discussed in the text. The “bare” ($V=0$) pressure dependence of these two modes is shown as a dash-dotted line, and that of the 141 cm^{-1} mode is included in the left panel. It matches well the behavior of the spin-phonon mode in the AP phase.

weak and covered at ambient pressure. A possible candidate for such a vibration is the asymmetric ν_{as} POP vibration expected at this energy.⁷

For the HP phase temperature- or pressure-dependent x-ray data have not yet become available but from our results there is little doubt that HP- $(\text{VO})_2\text{P}_2\text{O}_7$ possesses a similar lattice thermal expansion anisotropy as the AP phase. Summarizing, the results of the Raman scattering of the V-O vibrations around 915 cm^{-1} in the AP and HP phases of $(\text{VO})_2\text{P}_2\text{O}_7$ as a function of temperature and pressure strongly support the explanation of the unusual peak shift of these modes by an interlayer interaction of adjacent vanadium and oxygen atoms together with a lattice expansion anisotropy.

B. Anomalies of low-energy modes

The reported strong anharmonicity of the spin-phonon mode at 123 cm^{-1} in the AP phase was suggested to originate from a coupling to the spin system. Our pressure experiments made it plausible that this mode is an external vibration of the P_2O_7 group. Only recently was the unusual temperature variation of this mode successfully modeled analytically below ~ 150 K by taking into account a strong spin phonon coupling.¹⁵ These calculations and the underlying spin phonon coupling even reproduced a small upshift of this mode with rising temperature at low temperatures. HP- $(\text{VO})_2\text{P}_2\text{O}_7$ has essentially the same arrangement of subgroups as the AP phase so that the external vibrational frequencies of the P_2O_7 group in the AP and HP phases are expected to be similar. More importantly, these modes should be coupled to spins in the same way as in the AP phase. Fits to the susceptibility data yielded similar values and ratio of the exchange coupling constants J_1 and J_2 in HP and AP- $(\text{VO})_2\text{P}_2\text{O}_7$.^{8,12} However, a mode with similar phenomenological temperature dependence could not be detected in the HP phase. There should be a Raman-active mode since the factor group analysis of both structures gives Raman-active external P_2O_7 vibrations.

The pressure experiments on HP- $(\text{VO})_2\text{P}_2\text{O}_7$, on the other hand, revealed a weak mode at 141 cm^{-1} [Fig. 3(b)]. Below ≈ 4 GPa the peak shift matches that of the spin-phonon

mode of the AP phase. At higher pressures there appears to be an anticrossing with another mode at 171 cm^{-1} with a lower-pressure coefficient. Modes, when the related eigenvectors have the same symmetry, may mix and lead to an anticrossing behavior if there is a finite interaction potential between the modes. We fitted the anticrossing and obtained a linear pressure slope of 0.23 $\text{cm}^{-1}/\text{GPa}$ for the 171 cm^{-1} and a quadratic dependence of $\omega(p) = 11.2(\text{cm}^{-1}/\text{GPa})p - 0.61(\text{cm}^{-1}/\text{GPa}^2)p^2$ for the 141 cm^{-1} mode, displayed in Fig. 6 (right panel). The interaction potential was 0.67 meV and kept constant as a function of pressure. In Fig. 6 (left panel) we included the so-obtained bare frequency of the 141 cm^{-1} mode as a dash-dotted line. It is seen to follow closely the corresponding mode of the AP phase and hence we are confident in assigning this mode to the spin-coupled P_2O_7 polyhedra in the HP phase.

In addition to the AP- A_1 spin-phonon coupled mode three weak peaks appear in A_2 scattering geometry below a temperature of about 30 K (Fig. 2). We compared their temperature dependences by fitting a steplike function to the integrated intensity and find them all to disappear at an estimated “transition” temperature of about 20 K. No other indications of a structural phase transition have been reported, and we thus find this an unlikely reason for the disappearance of these modes. We may, however, consider magnetic light scattering to be at the origin of this phenomenon. In Ref. 5 and 6 it had accordingly been reported that the intensity of the spin-gap-related scattering strongly increased below 25 K. We may therefore consider the modes of being either of magnetic origin or, more likely, as phonons coupled to the spin system. The scattering geometry in which we observe the modes excludes two-magnon scattering and favors one-magnon scattering, which, however, is Raman forbidden, ruling out purely magnetic excitations. The factor group analysis for $(\text{VO})_2\text{P}_2\text{O}_7$ predicts for every mode of the isolated molecular group at least one mode in each of the representations of the crystallographic space group. Therefore there likely exist vibrations with A_2 symmetry that affect the spin exchange interaction paths in a similar manner as the A_1 mode at 123 cm^{-1} . We thus tentatively assign the modes which disappear at 20 K to phonons coupled to and activated

by the spin chains. A detailed modeling of this spin-phonon coupling is, however, beyond the scope of this work.

V. SUMMARY AND CONCLUSIONS

We compared the ambient pressure phase of $(\text{VO})_2\text{P}_2\text{O}_7$ with the novel high-pressure phase by Raman scattering as a function of temperature and hydrostatic pressure. We found that, due to the higher symmetry, the modes split in the AP phase are degenerate in the HP phase. The V-O vibrations around 920 cm^{-1} in both phases show an unusual mode softening with decreasing temperature. We find this to be due to an increasing interlayer interaction which is supported (1) by our measurements under hydrostatic pressure and (2) by the results of a temperature-dependent x-ray study of the lattice parameters. From its pressure dependence we identified the counterpart of the spin-phonon mode in AP-

$(\text{VO})_2\text{P}_2\text{O}_7$ at 123 cm^{-1} at 141 cm^{-1} in the HP phase; an unusual temperature dependence of this mode as in the AP phase we did not observe in HP- $(\text{VO})_2\text{P}_2\text{O}_7$. We found three weak peaks of AP- $(\text{VO})_2\text{P}_2\text{O}_7$ in the low-energy region which show an anomalous rapid loss in intensity above $\sim 20\text{ K}$. We suggested that a coupling of these modes to the spin system is responsible for their loss in scattering intensity.

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