Raman scattering of magnetic excitations of independent antiferromagnetic spin chains in $(VO)_2P_2O_7$

U. Kuhlmann and C. Thomsen
Institut für Festkörperphysik, Technische Universität Berlin, Hardenbergstrasse 36, D-10623 Berlin, Germany

A. V. Prokofiev, F. Büllesfeld, E. Uhrig, and W. Assmus
Physikalisches Institut, Universität Frankfurt, D-60054 Frankfurt, Germany

(Received 28 July 2000)

Raman scattering experiments on $(VO)_2P_2O_7$ single crystals revealed a shoulder at ≈ 90 cm^{-1} due to magnetic light scattering on different spin chains in addition to the one known at ≈ 45 cm^{-1}. Our experimental data correspond to spin gaps of ≈ 64.7 and 32.4 K, respectively, in good correspondence with the results obtained by neutron scattering experiments giving independent evidence for the coexistence of double antiferromagnetic (AF) alternating Heisenberg chains in $(VO)_2P_2O_7$. Our results resolve a discrepancy in the literature between light scattering on the one hand and neutron scattering, susceptibility and NMR experiments on the other hand.

The spin system of the catalyst vanadium pyrophosphate $(VO)_2P_2O_7$ has now been examined for more than a decade, in which several models have been proposed to explain its magnetic properties. Based on crystallographic considerations it was initially viewed as the realization of a spin ladder system. The lattice structure of $(VO)_2P_2O_7$ depicted in Fig. 1, was determined by Gorbunova *et al.* in 1979,[1] who found an acentric orthorhombic $Pca2_1$ structure. This was confirmed repeatedly in other studies[2,3] and is now widely accepted. Refinements which came to other results such as the study of Nguyen *et al.*[4] differ only in detail and reflect most likely different preparation conditions. $(VO)_2P_2O_7$ is composed of vanadyl $(V{=}O)^{2+}$ cations and pyrophosphate $(P_2O_7)^{2-}$ groups. The vanadium atoms, which are surrounded by five oxygen atoms in pyramidal coordination, are in the 4+ oxidation state and possess an unpaired electron with spin-$\frac{1}{2}$ responsible for the magnetic properties. From the vanadium-oxygen coordination it seemed obvious that the spins of the V atoms were coupled by superexchange along the crystallographic *b* axis by oxygen atoms on the corners of the pyramids (bond angle $\approx 90°$, rungs) with exchange constant $J(\equiv J_2)$ as well as parallel to the *a* axis by the apical oxygen atoms (bond angle $\approx 180°$, legs) with exchange constant $J_\perp$, thus building up a one-dimensional two-leg spin ladder. For such a spin-ladder system the existence of a spin gap was predicted for $\alpha \neq 1$, $\alpha = J_1/J_\perp$.[5]

In their initial work Johnston *et al.*[6] measured the magnetic susceptibility of $(VO)_2P_2O_7$ and fitted their results with an AF alternating Heisenberg model which exhibits a spin gap, too, since a theoretical prediction for $\chi(T)$ in ladder compounds was lacking at that time. They found that the spin-chain model could accurately describe the experimental data and raised the question, whether the magnetic interactions in $(VO)_2P_2O_7$ were actually best described by the concept of spin ladders. Later on Barnes *et al.*[7] were able to compare numerically a spin ladder model with a spin dimer-chain model and concluded in favor of the ladder model, with a prediction of 3.9 meV for the spin gap energy. However, the measurement of the dispersion relations of the magnetic excitations by inelastic neutron scattering[8,9] (INS) on an array of small single crystals then unequivocally proved that in $(VO)_2P_2O_7$ the strongest antiferomagnetic interactions occur along the *b* axis, whereas the exchange along the ladder direction (P-O-P pathway along the apical oxygen) was found to be weakly ferromagnetic. Different from the spin ladder model the authors proposed a second exchange path V-O-P-O-V over the phosphate group with coupling constant J_1 (see Fig. 1). An unexpected finding was that this rather complicated exchange path possesses the larger exchange constant.[9]

Whereas the concept of $(VO)_2P_2O_7$ being a spin-chain rather than a spin-ladder compound became widely accepted, difficulties remained for the explanation of all magnetic excitations observed in $(VO)_2P_2O_7$ with the AF alternating spin-chain model. A second spin excitation observed by Garrett *et al.* with INS at ≈ 6.0 meV was supposed to be a two-magnon bound state, inferred from predictions of Uhrig *et al.*[10] Later, Uhrig *et al.* proposed a more elaborate AF alternating chain model for the explanation of the magnetic properties of $(VO)_2P_2O_7$ including two dimensional spin frustration for which they could show that it promotes two-magnon bound states as an explanation for the second excitation.[11]

An alternative model for the second excitation was then proposed by Kikuchi *et al.* in 1999.[12,13] From the analysis of the temperature dependence of the ^{31}P nuclear magnetic resonance (NMR) signal in $(VO)_2P_2O_7$ the authors concluded the existence of two independent alternating spin chains occupying inequivalent crystal sites and hence possessing different spin gaps. This model evaded the complications of those models which take frustration into account and was supported by most, but not all observations so far. Grove *et al.* searched for the spin gap with polarized Raman scattering on $(VO)_2P_2O_7$.[14] They observed a shoulder in the excitation spectra at 47 cm^{-1} (5.8 meV) and assigned it to a singlet bound state lying closely beneath $2\Delta_{gap}$ in the exci-

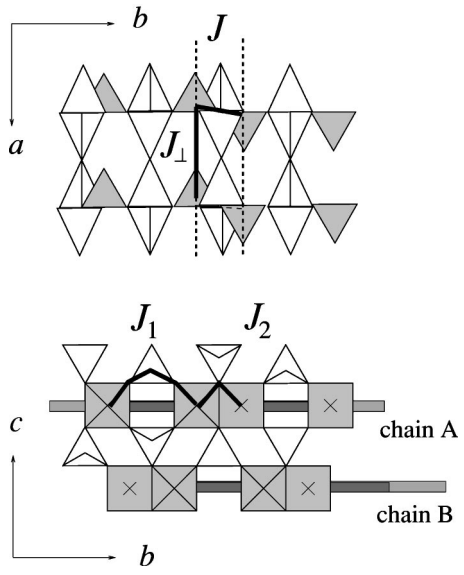

FIG. 1. Schematic depiction of the crystal structure of $(VO)_2P_2O_7$. The $V^{4+}O_5$ pyramids and the PO_4 tetraheder are depicted in gray and white, respectively. In the previously suggested spin ladder model the dominant magnetic interactions were supposed to occur along the *a* axis and the *b* axis with coupling constants $J_\perp$ (legs) and J (rungs). The alternating AF spin chain model supposes different coupling constants J_1 and $J_2(\equiv J)$ along the crystallographic *b* axis. The chains *A* and *B* are crystallographically not equivalent so that both chains may possess different alternation parameters $\alpha = J_1/J_2$.

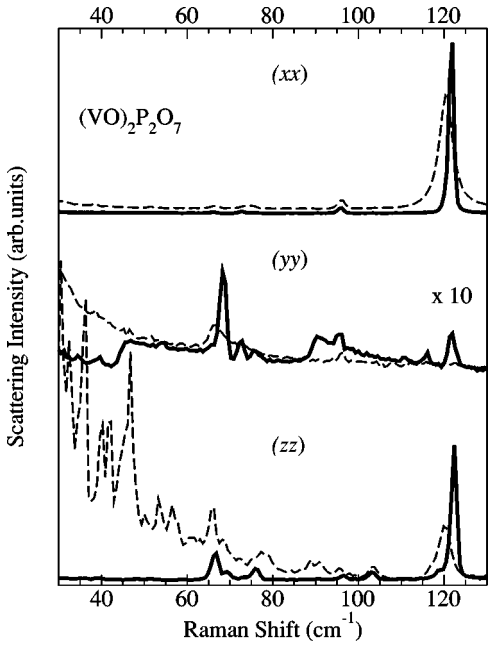

FIG. 2. Low-energy Raman spectra of $(VO)_2P_2O_7$ in parallel scattering geometries. Spectra at temperatures below 5 K (solid line) and above 100 K (dashed line) are depicted.

tation spectrum of an AF alternating spin chain. The absence of a similar signal around 90 cm^{-1}, which would be expected in the case of a second spin chain, caused them to reject the model of two independent spin chains. In a recent work of Johnston *et al.*[15] the authors report on modeling the magnetic susceptibilities of the ambient pressure phase (AP) and a high pressure (HP) phase of $(VO)_2P_2O_7$. HP-$(VO)_2P_2O_7$, which was reported recently by Azuma *et al.*, possesses a unit cell of half the size of that of the AP phase and a *unique* AF alternating spin-chain with a spin gap around 25 K.[16] Johnston *et al.* used an expression for $\chi(t)$ in their work which they had derived earlier (see Ref. 15) and demonstrated the consistency of the model with two distinct types of alternating-exchange chains in the AP phase as well as the consistency of the model with a single type chain in the HP phase. Their work also gives a review of the experiments on the magnetic properties of $(VO)_2P_2O_7$. The results of the Raman experiments had thus left the most serious doubt on the concept of two different spin chains in $(VO)_2P_2O_7$. In this paper we now provide further independent proof from the Raman scattering experiments for the coexistence of two alternating AF spin chains in $(VO)_2P_2O_7$.

The experiments were performed on $(VO)_2P_2O_7$ single crystals, which were prepared as described by Prokofiev *et al.*[17] X-ray diffraction on the sample material confirmed the above discussed crystal structure.[3] The spectra were recorded with a DILOR XY 800 triple spectrometer in combination with a liquid nitrogen cooled CCD. The spectral resolution was 1.3 cm^{-1}, as excitation we used the 5145 Å line of an Ar^+ laser. The sample was mounted in a liquid helium bath cryostate with a low-temperature limit of ≈1.4 K.

In Fig. 2 the low frequency portion of the Raman spectra in parallel scattering geometries is depicted. Some of the features were already described in an earlier Raman study.[14] In (*xx*) and (*zz*) polarizations one observes a strongly anharmonic phonon mode (symmetry A_{1g}) at 123 cm^{-1}. It softens by 6% when warming up the sample from 5 to 250 K and broadens by a factor of 6 as already reported by Grove et al. In the (*yy*) spectra a similar but much weaker mode appears at 70 cm^{-1}. Grove *et al.* attributed the anharmonicity of both modes to spin-phonon coupling. With rising temperature a quasielastic scattering background in (*yy*) polarization increases in intensity and was assigned to fluctuations of the energy density of the spin system. The scattering background observable in the high temperature spectra in (*zz*) geometry does not behave uniformly with changing temperature, and we believe it is due to Raleigh scattering on the poor sample surface. Upon cooling the sample below ≈40 K two shoulders appear in the (*yy*) spectra at 45 and 90 cm^{-1}, i.e., with polarization parallel to the spin chains. Since we do not observe them in the other scattering geometries, we consider this as a clear manifestation of the spin system. Both shoulders reveal nearly identical shapes, which is displayed in an expanded view in Fig. 3. Together with the uniform temperature dependence of the shoulder heights, shown in Fig. 4 this indicates a common origin of both shoulders. The energies of the shoulders, 32.4 and 64.7 K are in good correspondence with other measurements of the magnetic excitations in $(VO)_2P_2O_7$, illustrated in Fig. 5 where a compilation of the results in the determination of the spin gap by various methods is given. The two shoulders can thus safely identify with magnetic light scattering on two unequal but similar spin chains as suggested by experiments, resolving the discrepancy between Raman and neutron measurements.

In Ref. 14 a linear decrease of the shoulder height with rising temperature was reported. This could not be reproduced by our measurements. Instead we observe a saturation

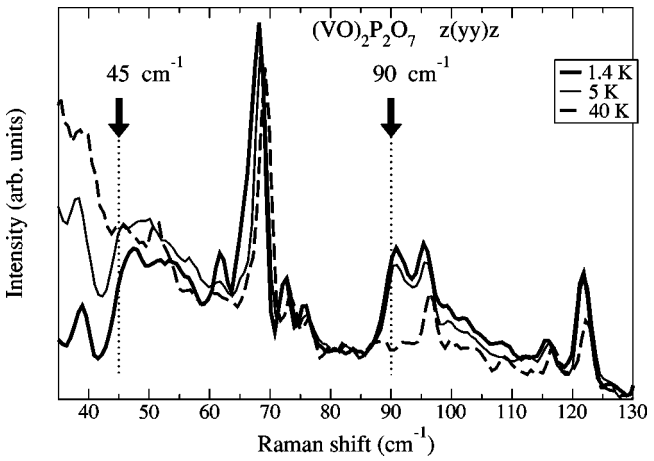

FIG. 3. Spin gap induced Raman scattering at selected temperatures. The spectrum at 1.4 K is depicted by the thick solid line, spectra at 5 and 40 K are depicted by a thin solid line and a dashed line, respectively. Apart from superimposed phonons at 69 and 95 cm^{-1}, both gaps (marked by arrows) reveal similar shapes which indicates their common origin.

of the scattering intensity below ≈20 K (Fig. 4). This observation is important for the correct interpretation of these shoulders. Since the energy of the shoulder at 45 cm^{-1} is slightly below the values given in most of the other studies of the magnetic properties of $(VO)_2P_2O_7$ (see Fig. 5), it had been assigned to a singlet bound state lying closely below the two-magnon continuum.[10,14] This assignment was strengthened by the absence of any magnetic field effect up to 6 T and by the stated temperature behavior. As it is pointed out in Ref. 14 and in Ref. 18, a linear temperature decrease of the scattering intensity can be considered as a ''fingerprint'' for magnon bound-states, since these modes are very sensitive to thermal fluctuations. Hence, based on our observations we tentatively assign the shoulders in the spectra of $(VO)_2P_2O_7$ to the two-magnon continuum of the magnon dispersion relations of the two spin chains rather than to magnon bound-states. Further experiments with higher magnetic fields applied are planned to clarify this point.

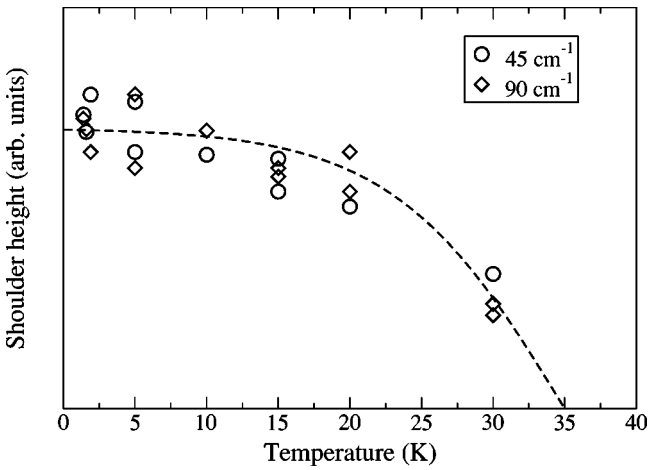

FIG. 4. Shoulder height of spin gap induced Raman scattering at 45 and 90 cm^{-1}. The shoulder height decreases rapidly at temperatures higher than ≈20 K and was not detectable at temperatures above 30 K. The dashed line is given as a guide for the eyes.

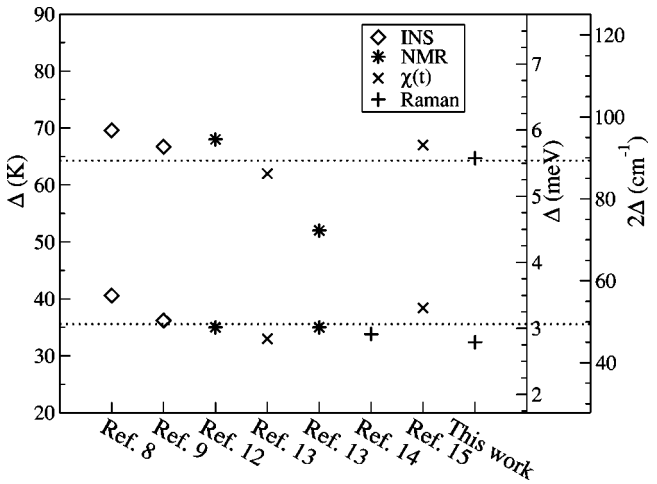

FIG. 5. Compilation of the results of various methods in the determination of the spin gap energies in $(VO)_2P_2O_7$, displayed with the commonly used energy scales Δ/k_B[K] to the left and Δ[meV] and 2Δ[cm^{-1}] to the right. The corresponding references are given on the abscissa. The mean of the depicted values is marked by dotted lines.

With the concept of two independent alternating AF spin chains, the magnetic properties of $(VO)_2P_2O_7$ are well described in general. However, some details of the experimental results are not yet fully understood and subject to further experimental and theoretical work. Grove *et al.* used the anharmonic A_{1g} mode at 123 cm^{-1} as evidence against the two-spin-chain model. It had been shown theoretically that phonons with an energy smaller than or close to the maximum energy of the triplet dispersion branch show anharmonic behavior due to damping by two-magnon processes. If different spin systems exist an additional effect should be observable but was not found and the damping of the A_{1g} mode at 123 cm^{-1} seemed to be related only to one triplet branch. However, in the triplet dispersion obtained by INS (Ref. 9) both triplet branches appear to converge towards $q = k_c c/\pi$, where only a single maximum with an energy of ≈15.5 meV (125 cm^{-1}) was observed. This would rule out the possibility of observing distinguishable effects on the phonons. Recent model calculations of triplet dispersion relations in Ref. 15 on basis of their accurate $\chi(t)$ fit revealed a crossing of the two triplet branches around $k_c c/\pi = 0.4$ and a gap at $q = k_c c/\pi$ of about 2 meV (16 cm^{-1}) in the triplet maximum energies. We did not observe any indications in that direction, but such small energy differences may have only small effects on the anharmonicity of phonons. Grove *et al.* referred to the monoclinic model of Nguyen *et al.*[4] where relative differences of the V-O-V and V-(PO_4)-V bond distances on different sites of less than 0.5% (0.02 Å) were found and questioned whether such small geometric differences between the two spin chains could produce a doubling of the spin gap energy. Recent structure determinations,[2] though, which confirmed the orthorhombic structure, revealed a relative difference of these bond distance of 2.5 and 1%, respectively which suggests a larger difference in the alternation of the chains.

In summary we performed temperature dependent polarized Raman scattering on $(VO)_2P_2O_7$ single crystals. In addition to the shoulder in scattering intensity at ≈45 cm^{-1}

which had already been published, we observe a similar structure at ≈ 90 cm^{-1} below a temperature of ≈ 40 K. We assign both structures to magnetic excitations of two inequal alternating spin chains as proposed in Ref. 12. The frequencies of 45 and 90 cm^{-1} correspond to spin gaps of 32.4 and 64.7 K, which is in excellent agreement with results obtained by other methods. Our results thus give independent evidence for $(VO)_2P_2O_7$ being best described as a two independent alternating spin-chain compound, resolving a previous discrepancy in the literature.

[1] Y. E. Gorbunova and S. A. Linde, Sov. Phys. Dokl. **24**, 138 (1979).

[2] Z. Hiroi, M. Azuma, Y. Fujishiro, T. Saito, M. Takano, F. Izumi, T. Kamiyama, and T. Ikeda, J. Solid State Chem. **146**, 369 (1999).

[3] S. Geupel (private communication).

[4] P. Nguyen, R. Hoffman, and A. Sleight, Mater. Res. Bull. **30**, 1055 (1995).

[5] T. Barnes, E. Dagotto, J. Riera, and E. S. Swanson, Phys. Rev. B **47**, 3196 (1993).

[6] D. C. Johnston, J. W. Johnson, D. P. Goshorn, and A. J. Jacobson, Phys. Rev. B **35**, 219 (1987).

[7] T. Barnes and J. Riera, Phys. Rev. B **50**, 6817 (1994).

[8] A. W. Garrett, S. E. Nagler, T. Barnes, and B. C. Sales, Phys. Rev. B **55**, 3631 (1997).

[9] A. W. Garrett, S. E. Nagler, D. A. Tennant, B. C. Sales, and T. Barnes, Phys. Rev. Lett. **79**, 745 (1997).

[10] G. S. Uhrig and H. J. Schulz, Phys. Rev. B **54**, 9624 (1996).

[11] G. S. Uhrig and B. Normand, Phys. Rev. B **58**, 14 705 (1998).

[12] J. Kikuchi, K. Motoya, T. Yamauchi, and Y. Ueda, Phys. Rev. B **60**, 6731 (1999).

[13] T. Yamauchi, Y. Narumi, J. Kikuchi, Y. Ueda, K. Tatani, T. C. Kobayashi, K. Kindo, and K. Motoya, Phys. Rev. Lett. **83**, 3729 (1999).

[14] M. Grove, P. Lemmens, G. Güntherodt, B. C. Sales, F. Büllesfeld, and W. Assmus, Phys. Rev. B **61**, 6126 (2000).

[15] D. Johnston, T. Saito, M. Azuma, M. Tanako, T. Yamauchi, and Y. Ueda, cond-mat/0003065 (unpublished).

[16] M. Azuma, T. Saito, Y. Fujishiro, Z. Hiroi, M. Takano, F. Izumi, T. Kamiyama, T. Ikeda, Y. Narumi, and K. Kindo, Phys. Rev. B **60**, 10 145 (1999).

[17] A. V. Prokofiev, F. Büllesfeld, and W. Assmus, Cryst. Res. Technol. **33**, 157 (1998).

[18] M. J. Konstantinović, Z. V. Popović, M. Isobe, and Y. Ueda, Phys. Rev. B **61**, 15 185 (2000).