Neutron-scattering study of magnetic excitations in $(VO)_2P_2O_7$

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(Received 9 July 1996; revised manuscript received 3 October 1996)

We report results from inelastic neutron-scattering experiments on powder samples of vanadyl pyrophosphate, $(VO)_2P_2O_7$ (VOPO). We see evidence for three magnetic excitations, at 3.5, 6.0, and 14 meV. The 3.5 meV mode peaks at $Q=0.8$ Å^{-1} and is consistent with the one-magnon gap mode reported previously. The 6.0 meV mode is inconsistent with expectations for magnetic excitations in the usual spin-ladder model. Our results imply that VOPO must be described by a different magnetic Hamiltonian than the simple Heisenberg antiferromagnetic spin ladder. [S0163-1829(97)01705-0]

I. INTRODUCTION

The antiferromagnetic insulator $(VO)_2P_2O_7$ (Ref. 1) is widely considered to be the prototypical realization of a Heisenberg spin ladder. Heisenberg spin ladders are interesting theoretically[2] as intermediaries between one-dimensional (1D) Heisenberg antiferromagnets and 2D systems. Theoretical studies of this model have concluded that $S=1/2$ spin ladders have a gap if they have an even number of chains, but are gapless for an odd number of chains. This is reminiscent of the Haldane result that half-integer-spin chains are gapless but integer-spin chains have energy gaps. Studies of hole-doped two-chain ladders in the t-J model find that strong d-wave hole pairing takes place on equal-strength ladders, so analogues of the high-T_c superconductors might be found in hole-doped spin ladders. Additional examples of spin ladders are known, including a Sr-Cu-O series,[3] a La-Cu-O series,[4] and $Cu_2(C_5H_{12}N_2)_2Cl_4$.[5] The subject of spin ladders was reviewed recently by Dagotto and Rice.[6]

The magnetic properties of VOPO have been interpreted in terms of the two-chain Hamiltonian with isotropic exchange:

$$H=J_\parallel \sum_{\langle ij\rangle}^{\text{chains}} \vec{S}_i\cdot\vec{S}_j + J_\perp \sum_{\langle ij\rangle}^{\text{rungs}} \vec{S}_i\cdot\vec{S}_j . \quad (1)$$

This model gives an accurate fit to the VOPO magnetic susceptibility[7] with the parameters $J_\parallel=J_\perp = 7.8$ meV. Theoretical studies of this symmetric ($J_\parallel=J_\perp$), isotropic Heisenberg antiferromagnetic ladder (SHAL) model predict an energy gap of $E_{\text{gap}}=0.5037$ J,[8] hence the susceptibility results imply $E_{\text{gap}}=3.9$ meV. A pulsed neutron scattering experiment on VOPO powder[9] observed a gap of 3.7(2) meV, consistent with this expectation.

Many unanswered questions remain concerning the dispersion relations, spectral weight, and detailed band structure of magnetic excitations in VOPO. Despite the good agreement with the SHAL model susceptibility, it has not been demonstrated that magnetic interactions in VOPO actually are accurately described by the isotropic SHAL model; note for example that the susceptibility can also be fit by a dimer chain model,[1,7] and the gap in the excitation spectrum may be dominantly due to other magnetic interactions than the ladder terms. We have carried out triple-axis inelastic neutron scattering studies of VOPO to investigate these issues in more detail. In addition to confirming the existence of the gapped spin wave mode observed previously,[9] our results reveal an unexpected magnetic excitation.

Most of the theoretical work on the two-chain ladder has been concerned with the $S=1/2$ SHAL model. The spectrum of low-lying spin waves in this model has been discussed at length in the literature.[2,7,10] The one-magnon band can be approximately described by the function[7]

$$\omega(k)=[\omega(0)^2\cos^2(k/2)+\omega(\pi)^2\sin^2(k/2)+c_0^2\sin^2(k)]^{1/2}, \quad (2)$$

where k is the one-dimensional wave vector in units in which the intrachain ion separation is set to unity. This dispersion relation for the one-magnon band $\omega(k)$ in the SHAL model with $J=7.0$ meV (chosen to match the energy gap observed in the present work) is shown in Fig. 1, together with the lower edges of the two-magnon and three-magnon continua. [These are the lowest-energy sums $\omega(k_1)+\omega(k_2)$ and $\omega(k_1)+\omega(k_2)+\omega(k_3)$ with the constraint $\Sigma_i k_i=k$.] The parameters in (2) are $\omega(0)=1.72$ J, $\omega(\pi)=0.5037$ J, and $c_0=1.38$ J.

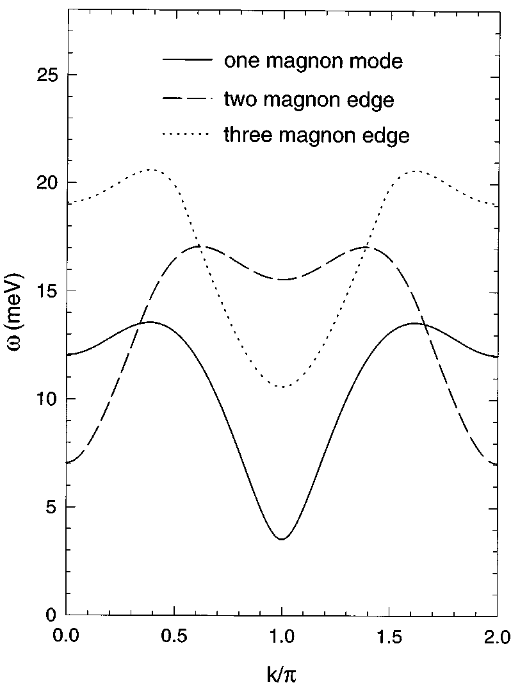

FIG. 1. Spin waves predicted in the SHAL model of $(VO)_2P_2O_7$ with $J_\perp = J_\| = 7.0$ meV. The one-magnon band (solid) and the onset of the two-magnon and three-magnon continua are shown.

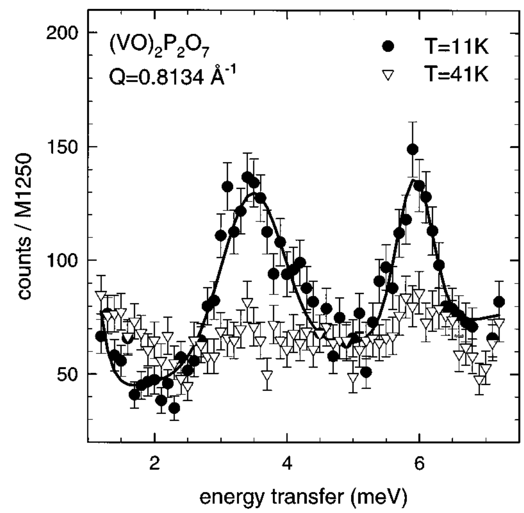

FIG. 2. Inelastic scattering from $(VO)_2P_2O_7$ at $Q = 0.813$ Å^{-1}, at temperatures of $T = 10.8$ K and 40.8 K, measured at HB1A with $E_i = 14.728$ meV and collimation $40'$-$20'$-$20'$-$70'$. The gap mode at 3.5 meV and the 6.0 meV mode are clearly visible in the 10.8K data. The neutron counts (see text) are normalized to counts observed in 1250 monitor units; each monitor unit corresponds to about 1 s of counting time.

The lowest-lying one-magnon excitation occurs at the one-dimensional antiferromagnetic point $k = \pi$, with an energy of $\omega(\pi) = E_{\rm gap}$. Exact calculations of the dynamical structure factor $S(k,\omega)$ on a 2×8 lattice[7,13] indicate that the spectral weight of the one-magnon band peaks strongly near $k = \pi$, so this should be the most prominent feature seen in neutron scattering. The next $k = \pi$ excitation expected in the SHAL model is the beginning of the three-magnon continuum, at $3\,E_{\rm gap}$.

II. EXPERIMENTAL DETAILS

To prepare $(VO)_2P_2O_7$, stochiometric amounts of V_2O_5 (44.1 grams, 99.99%) and $NH_4H_2PO_4$ (55.9 grams, 99.9%) powder were mixed and loaded into a platinum crucible. The mixed powders were heated to 500 °C at 1 °C/minute and held at 500 °C for 6 hours. This initial heating allowed the ammonia and water to escape from the crucible during the decomposition of $NH_4H_2PO_4$ to P_2O_5. The prereacted mixture was heated further to a temperature of 1100 °C and the resulting liquid was allowed to homogenize for several hours. The platinum crucible was removed from the furnace at 1100 °C and the liquid was ''cast'' into a cold, shallow platinum crucible measuring $10 \times 4 \times 2$ cm^3. The rapid cooling of the V_2O_5*P_2O_5 liquid resulted in the formation of a homogenous glass with a dark green to black color. The above steps were all performed in air.

The shallow platinum crucible containing the V_2O_5 *P_2O_5 glass was then placed in a tube furnace in which the oxygen partial pressure could be controlled. A mixture of 0.1% oxygen and 99.9% argon was passed through the furnace at 40 cc/minute, and this rate and oxygen partial pressure were maintained during the entire crystal growth procedure. An independent oxygen sensor was used to monitor the oxygen partial pressure in the furnace. The V_2O_5*P_2O_5 glass was heated to 1050 °C, maintained at that temperature for 6 h, and then cooled at 1 °C/h to 480 °C, after which the furnace was turned off. The resulting material consisted of several hundred mm sized single crystals of $(VO)_2P_2O_7$ embedded in a polycrystalline matrix of $(VO)_2P_2O_7$ and a small amount ($\approx 5-15$ %) of an additional phase, tentatively identified as $V(PO_3)_3$ by neutron powder diffraction.[11]

Inelastic neutron scattering measurements were carried out using the HB1A and HB3 triple-axis spectrometers at the High Flux Isotope Reactor at Oak Ridge National Laboratory.[14] The sample consisted of 18 grams of finely ground VOPO powder sealed in a 0.5 in. diameter thin-walled Al cylinder under a helium atmosphere. For the initial experiment on the HB1A spectrometer the sample was mounted in a standard He closed-cycle refrigerator with a temperature range of 10 to 300 K. A double-crystal PG(002) monochromator (M) was used to provide an incident neutron beam with a fixed energy of 14.7 meV. The incident beam intensity was monitored using a fission counter, and contamination of the beam by higher-order Bragg reflections was removed using the standard PG filter method. Neutrons scattered by the sample (S) were reflected by a PG(002) analyzer (A) into a ^{3}He detector (D). Effective beam collimations pre-M, M-S, S-A, and A-D of $40'$-$40'$-$40'$-$70'$ or $40'$-$20'$-$20'$-$70'$ were used.

A second experiment utilizing the HB3 spectrometer employed PG(002) monochromator and analyzer crystals with a fixed scattered neutron energy of 14.7 meV. The collimation was $40'$-$40'$-$40'$-$120'$, and the scattered beam was passed through a PG filter. For this experiment the sample was mounted in a pumped He cryostat capable of reaching 1.5 K.

VOPO has a slightly monoclinic unit cell with lattice parameters $a=7.728$ Å, $b=16.589$ Å, $c=9.580$ Å, and $\beta=89.98°$ at $T=296$ K.[12] The ladder consists of S=1/2 V^{4+} ions in -(VO)-(VO)- chains along the a axis and V $^{-O-}_{-O-}$ V rungs oriented along the b axis. The average V-V distance along the chain is approximately equal to $a/2$. Therefore in VOPO the one-dimensional antiferromagnetic points $k=n\pi$ (with n odd) occur in sheets with $Q_a=nQ_\pi$, where $Q_\pi=0.813$ Å^{-1}.

In scattering from *powder* the experimental momentum transfer to the sample $Q = |\vec{Q}|$ does not correspond to the one-dimensional momentum k of the excitations observed. Instead k is the projection of $\vec{Q}$ on the chain axis, and in the powder one averages over all orientations. Therefore for a given Q one can excite all 1D modes with the observed energy transfer and $k\leqslant Q$. In particular, one expects the gap mode, which has $k=\pi$, to appear first at $Q=Q_\pi$ as Q is increased, and to persist to higher Q due to the powder average. The scattering intensity observed at (Q,ω) involves the density of states as well as $S(k,\omega)$.

III. RESULTS

Figure 2 shows the results of constant-Q scans at $Q=Q_\pi$, taken at HB1A. The data have been scaled to a fixed monitor value. The data at 10.8 K clearly show two peaks in the scattering. The peak intensities are drastically reduced at higher temperatures, as illustrated by the data at 41 K, which provides strong evidence that they are both magnetic in origin. The lower peak at 3.48(3) meV is interpreted as the one-magnon gap mode previously reported at 3.7(2) meV by Eccleston *et al.*[9] Their slightly higher energy may arise from their broader Q acceptance. The neutron group observed in the present work has a FWHM significantly greater than the instrumental resolution limit of 0.7 meV.

The mode at $E=6.0$ meV has not been reported previously. It appears narrower in energy than the 3.5 meV mode, with a FWHM only slightly larger than the instrumental resolution; this suggests that the band is rather flat, corresponding to a relatively weakly coupled localized mode. Comparison with the theoretical magnon bands in Fig. 1 shows that this excitation is not predicted by the SHAL model (1).

Figure 3 shows the Q dependence of the intensities of the 3.5 meV and 6.0 meV modes. Both modes show very similar behavior, with an onset near 0.7 Å^{-1} and a peak near 0.8 Å^{-1}. These wave vectors are close to the value $Q_\pi=0.813$ Å^{-1} expected for the gap mode of antiferromagnetic spin waves propagating along the ladder, which was the interpretation Eccleston *et al.*[9] gave to the lower mode. It should be kept in mind that a definitive confirmation of this interpretation will require a single-crystal experiment, in which the dispersion of the modes along the various crystal axes can be isolated.

Both modes show a slight increase in intensity in the vicinity of $Q=1.6$ Å^{-1}, and a gradual falloff in intensity at higher Q. The scattering intensity from a powder sample is not easily interpreted beyond the first Brillouin zone, but the diminishing intensity with increasing momentum transfer is

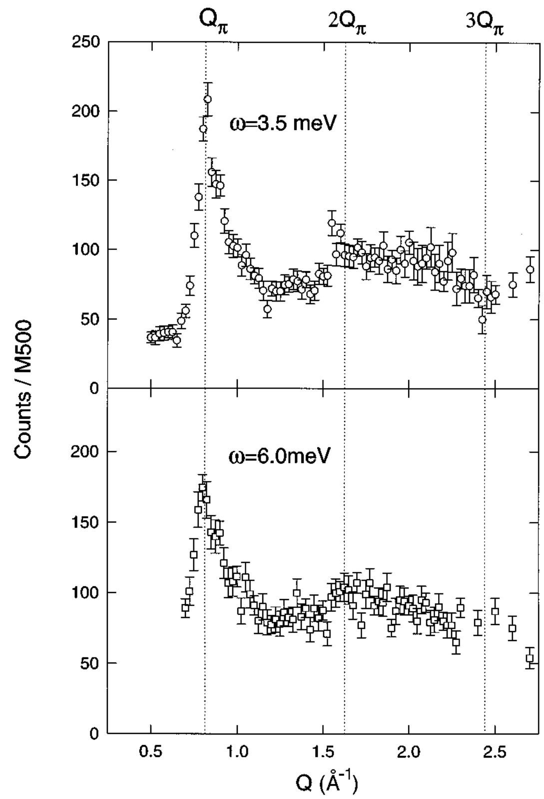

FIG. 3. Constant energy scans of scattering intensity versus momentum transfer Q at $\omega=3.5$ meV (upper panel) and $\omega=6.0$ meV (lower panel), normalized to 500 monitor units. The dashed vertical lines show the values of $Q=nQ_\pi$ corresponding to one-dimensional nuclear (n even) and magnetic (n odd) zone centers. Note the strong peaking at $Q=Q_\pi$ in both cases. Measurements were done at HB1A with fixed incident energy $E_i=14.728$ meV and collimation 40′-40′-40′-70′.

expected because of the reduction of the magnetic form factor at large Q. For the V^{4+} ion in VOPO, $|f^{\mathrm{mag}}(3Q_\pi)|^2\approx 0.5|f^{\mathrm{mag}}(Q_\pi)|^2$.

Constant Q scans at $Q=3Q_\pi$ and $Q=5Q_\pi$ at a temperature of 1.6 K are presented in the lower panel of Fig. 4. The scans were carried out at HB3 with fixed scattered neutron energy, which allowed measurements over a wide range of energy transfers. The scattering at both wave vectors exhibits a broad maximum near 13 meV. The origin of this broad scattering is unknown, but since magnetic scattering at $Q=5Q_\pi$ is expected to be weak, it is probably not magnetic in origin. Unfortunately, kinematic restrictions did not allow the same energy scan at lower Q, particularly at $Q=Q_\pi$ where the magnetic features should be most prominent. Inspection of the lower panel of Fig. 4 shows that the $3Q_\pi$ scan has features which were not observed in the $5Q_\pi$ scan. In repetitions (not shown) of the $3Q_\pi$ scan at $T=45$ K and $T=100$ K the extra features are not clearly visible, and only the broad maximum remains. The Q and T dependence of the scattering strongly suggests that the additional features seen at $3Q_\pi$ arise from magnetic excitations. To investigate this possibility further the $Q=5Q_\pi$ intensity was subtracted from the $Q=3Q_\pi$ intensity on a point-by-point basis; the result is shown in the upper panel of Fig. 4. The solid line is a fit of this difference spectrum to a sum of three Gaussians

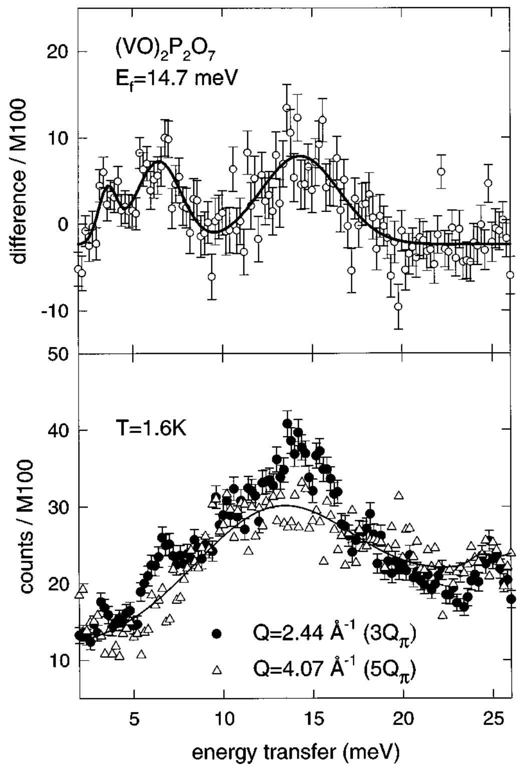

FIG. 4. Constant Q scans at $Q=3Q_\pi$ and $Q=5Q_\pi$ at $T=1.6$ K (lower panel) and the subtracted difference scattering (upper panel). The scattering intensity is normalized to 100 monitor units. The line in the lower panel is a guide to the eye through the $5Q_\pi$ data. The solid line in the upper panel is a least-squares fit of the difference to a sum of three Gaussians and a constant background, with fitted centers equal to 3.62(13) meV, 6.46(16) meV, and 14.32(22) meV. The measurements were carried out at HB3 using a fixed scattered neutron energy $E_f=14.7$ meV and collimation 40′-40′-40′-120′.

and a constant background, revealing features near 3.6 meV and 6.5 meV, approximately consistent with the magnetic excitations observed at Q_π. The fit also shows a higher-energy peak at 14.3 meV. An earlier neutron scattering experiment[9] also saw indications of enhanced scattering near 15 meV and $Q=0.8$ Å^{-1}, although the details were unclear.

Since 14 meV is close to the predicted onset of the $k=\pi$ two-magnon continuum as well as the maximum energy of the one-magnon band (shown in Fig. 1) in the SHAL model, it is tempting to associate the magnetic scattering with either or both of these features. However, a detailed comparison of experiment with the excitation spectrum predicted by the SHAL model is problematical, since it did not anticipate the 6 meV mode.

IV. DISCUSSION

In this experiment we have found clear evidence for two low-lying magnetic excitations in VOPO, at energies of approximately 3.5 meV and 6.0 meV, and some additional magnetic scattering near 14 meV. The low-lying excitations peak strongly at $Q=0.8$ Å^{-1}, near the $Q_\pi=2\pi/a$ point in VOPO, which suggests that these are $k=\pi$ modes of the VOPO spin ladder. Although the 3.5 meV mode and the 14 meV scattering are similar to expectations in the spin-ladder model, the presence of two low-lying modes at $k=\pi$ is unexpected, and argues against the validity of the SHAL model (1) for VOPO.

In view of this disagreement we should recall the assumptions which led to (1) and determine whether they are justified. The Heisenberg model assumes that each magnetic ion can be treated as a localized spin with $S=1/2$, interacting with neighboring ions through an isotropic interaction. Whether or not this is true in practice depends on the ground state and low-lying excited states of the magnetic ion.

An isolated V^{4+} ion in an octahedral field, as is approximately realized by the O octahedra in VOPO, has a t_{2g} triplet ground state;[15] this triplet is split by the spin-orbit interaction and by departures from octahedral symmetry, including the formation of (VO) units along the chains.[12] For isolated V^{4+} ions in ruby the single-ion excited t_{2g} levels are known to lie just 3.5 meV and 6.6 meV above the ground state,[16] comparable to the energy scales of the magnetic modes observed in VOPO. This raises the possibility that one or more of the magnetic modes observed in VOPO could be crystal field levels, which might explain the peak at 6 meV. There is however experimental evidence against this possibility, based on the Q dependence of the scattering and the bulk magnetic susceptibility.

Single-ion excitations do not normally display a strong dependence of either frequency or scattering intensity on Q (other than the magnetic form factor). Since we observed a rather sharp peak at $Q=0.8$ Å^{-1} in the constant-E scan (Fig. 3), it appears likely that the 6 meV feature arises from a collective mode. If it is a band of crystal field excitations, they exhibit an unusually strong exchange coupling.

Magnetic susceptibility measurements also argue strongly against the presence of t_{2g} V^{4+} excited orbitals at these low energy scales. The observed high temperature limit of the susceptibility [known to about 350 K (Ref. 1)] is consistent with that expected for paramagnetic spins with $S=1/2$ and $g=2$. The presence of additional t_{2g} degrees of freedom would modify the temperature dependence of the susceptibility. Thus there is no indication of excited t_{2g} levels in VOPO to 350 K, corresponding to ≈ 30 meV. Further experimentation, including infrared spectroscopy and EPR measurements, is desirable to locate these t_{2g} levels.

Another possibility is that VOPO actually can be modelled as an $S=1/2$ spin ladder at low energy scales, but there are important additional spin interactions not present in (1) which produce the two separate bands we observe at 3.5 meV and 6.0 meV. There are various possibilities for such terms, including ladder-ladder interactions, chain dimerization, departures from isotropy, next-nearest-neighbor interactions and so forth. Elucidation of the form of these interactions is impractical using a powder specimen.

In conclusion, our observation of two low-lying modes, at 3.5 and 6.0 meV, indicates that a different Hamiltonian than the SHAL model is required to describe magnetic excitations in VOPO. The determination of the appropriate spin Hamiltonian would be facilitated by more detailed experimental studies of the low-lying bands, in particular by inelastic neutron scattering studies of VOPO single crystals. The technical difficulty of growing adequate crystals has precluded such studies previously. Some progress has recently been made in this area, and we hope to report results from neutron scattering experiments on VOPO single crystals in the near future.

ACKNOWLEDGMENTS

We would like to acknowledge useful communications with E. Dagotto, R.S. Eccleston, D.C. Johnston, A. Moreo, J. Riera, and C. Torardi. We thank J. Zarestky and J. Fernandez-Baca for valuable assistance with HB1 and HB3. Expert technical assistance was provided by S. Moore and G.B. Taylor. This work was supported in part by the United States Department of Energy under Contract No. DE-FG05-96ER45280 at the University of Florida, and by Oak Ridge National Laboratory, managed for the U.S. D.O.E. by Lockheed Martin Energy Research Corporation under Contract No. DE-AC05-96OR22464.

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