Excitations and Possible Bound States in the $S = 1/2$ Alternating Chain Compound $(VO)_2P_2O_7$

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Abstract

Magnetic excitations in an array of $(VO)_2P_2O_7$ single crystals have been measured using inelastic neutron scattering. Until now, $(VO)_2P_2O_7$ has been thought of as a two-leg antiferromagnetic Heisenberg spin ladder with chains running in the a-direction. The present results show unequivocally that $(VO)_2P_2O_7$ is best described as an alternating spin-chain directed along the crystallographic b-direction. In addition to the expected magnon with magnetic zone-center energy gap $\Delta = 3.1$ meV, a second excitation is observed at an energy just below 2Δ. The higher mode may be a triplet two-magnon bound state. Numerical results in support of bound modes are presented.

Keywords: Bound Magnons, Alternating Heisenberg Chain.

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The S=1/2 alternating Heisenberg chain (AHC) is a fascinating quantum system that is currently the subject of much interest. We have established [1] that the material $(VO)_2P_2O_7$, previously considered to be a spin ladder, is in fact an excellent realization of the AHC. The physics of the AHC is also very relevant to spin-Peierls materials such as CuGeO3 [2]. Recent theoretical work [3] on the AHC underscored the potential importance of two-magnon bound modes. In this paper, we review our neutron scattering experiments on the alternating chain material $(VO)_2P_2O_7$. In addition to the expected one-magnon excitations, we observe an extra mode, which may be a two-magnon bound state. We follow with a discussion of some related theoretical issues.

The crystal structure of $(VO)_2P_2O_7$ is nearly orthorhombic, with a slight monoclinic distortion so that the space group is $P2_1$ [4]. The room temperature lattice parameters are a=7.73Å, b=16.59Å, c=9.58Åand β=89.98°. The magnetic properties of $(VO)_2P_2O_7$ arise from $S = 1/2$ V^{4+} ions situated within distorted VO_6 octahedra. Face-sharing pairs of VO_6 octahedra are stacked in two-leg ladder structures oriented along the a-axis. The ladders are separated by large, covalently bonded PO_4 complexes. The structure is illustrated schematically in figure 1.

The susceptibility of $(VO)_2P_2O_7$ powder [5] can be accurately reproduced by either a spin ladder (with $J_{\|} \approx J_{\perp}$) or by an alternating chain [5,6], but the expectation that the PO_4 group would provide a weak superexchange path led to a general acceptance of the spin ladder interpretation of $(VO)_2P_2O_7$. Pulsed inelastic neutron scattering measurements on $(VO)_2P_2O_7$ powders [7] showed a spin gap of 3.7 meV, which was interpreted as further support for the ladder model.

Beltrán-Porter *et al.* [8] examined the superexchange pathways in several vanadyl phosphate compounds, and were led to question the spin-ladder interpretation of $(VO)_2P_2O_7$. Instead they proposed that an alternating V-O-V-PO_4-V chain in the b-direction was a more likely magnetic system. The observation of a second spin excitation near 6 meV (not predicted by the ladder model) in a recent triple-axis neutron scattering experiment [9] on

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$(VO)_2P_2O_7$ powder, and the discovery of strong superexchange through PO_4 groups in the precursor compound $VODPO_4 \cdot 1/2D_2O$ [10], also cast doubt on the spin ladder interpretation. For these reasons we undertook studies of the spin dynamics in $(VO)_2P_2O_7$ single crystals.

Measurements of the excitations were made using a single crystal array of approx. 200 oriented $(VO)_2P_2O_7$ crystals of typical size 1x1x0.25 mm^3. The resulting sample had an effective mosaic spread of $8 - 10°$ FWHM. Inelastic neutron scattering measurements were carried out using triple-axis spectrometers at the HFIR reactor, Oak Ridge National Laboratory; full experimental details can be found in [1].

Scans [1] at $T = 10$K showed two modes of roughly equal strength at the antiferromagnetic zone-centre $(0, \pi, 0)$ at energies of $\Delta_l = 3.12(3)$ meV and $\Delta_u = 5.75(2)$ meV. Full resolution convolutions with the fitted dispersion showed these modes to be resolution limited. The disappearance of both modes at higher temperatures confirmed their magnetic origin. The modes were found to track approximately in Q close to $(0, \pi, 0)$ (see Figure (2)). At the zone-boundary $(0, \pi/2, 0)$ only a single mode was observed at an energy of ≈ 15meV. Because of poor instrumental resolution it was not possible to tell whether the modes had coalesced or were simply not resolved.

Fig. 2 shows the measured dispersion for both modes along a^*, b^* and c^*. The excitation energy is almost independent of Q_c (middle panel), implying a very weak coupling along c. The dependence of energy on Q_a is much weaker than on Q_b and is ferromagnetic. The strong Q_b dependence implies that the exchange coupling is dominantly one-dimensional along the b-direction, confirming the V-O-V-PO_4-V alternating chain proposed in [8] and [10].

For any exchange alternation – as occurs with the two inequivalent exchanges along b – a gap should appear in the dispersion (as observed) and the absence of magnetic ordering in $(VO)_2P_2O_7$ is consistent with a singlet ground state. However the observation of an extra mode requires a more thorough theoretical investigation. Since the high temperature limit

of the magnetic susceptibility [5] is consistent with expectations for simple $S = 1/2$, $g = 2$ spins, the possibility that the upper mode is an additional low lying single ion excitation can be ruled out. Two other plausible explanations of the second peak are (a) splitting due to an exchange anisotropy, and (b) a physical two-magnon bound state.

Although a pseudo-Boson calculation including exchange anisotropy gave an excellent fit to the dispersion [1] – the solid line in Figure (2) is a fit to this model [1] – considerable exchange anisotropy ($\approx$ 15%) was necessary to account for the mode splitting. Recent single crystal magnetic susceptibility measurements [11] were quantitatively consistent with the previous powder results [5] and found little if any evidence for anisotropy. Also the coupling in the precursor compound $VODPO_4 \cdot 1/2D_2O$ was found to be consistent with isotropic exchange [10] suggesting that one should seek another explanation for the second mode, and because the energy of the upper mode at $(0, \pi, 0)$, Δ_u, is just below $2\Delta_l$, a bound two-magnon mode may provide a good explanation. In support of this explanation, preliminary high-field measurements show splitting of both modes which is consistent with both modes being triplets [12].

To gain some insight into the formation of two-magnon modes in $(VO)_2P_2O_7$ we have studied the $S = 1/2$ AHC using numerical techniques. The isotropic AHC Hamiltonian is

$$H = \sum_{i=1}^{L/2} J\, \vec{S}_{2i-1} \cdot \vec{S}_{2i} + \alpha J\, \vec{S}_{2i} \cdot \vec{S}_{2i+1}\ , \tag{1}$$

where $J > 0$ and $1 \geq \alpha \geq 0$. Equation (1) has been studied analytically and numerically over many years, but it had not been appreciated until recently that $S = 0$ and $S = 1$ bound magnon states may form. Uhrig and Schulz [3] have used field theory and RPA methods to study these modes at $k = \pi/2$ and $k = 0, \pi$. The existence of these bound states depends subtly on the kinetic and potential energies of pair formation, and occur for only certain values of k.

Perturbation theory in α about the dimer limit ($\alpha = 0$) provides a quantitative basis for understanding the excitations for small α, and also provides insight into the competition between potential and kinetic energy effects in bound states [13]. Figure (3) shows the one-

and two-magnon excitation spectra calculated within a simplified approximate first order (one- and two-magnon manifold) treatment of the AHC. At $k = \pi/2$ there is a node in the two-magnon continuum which corresponds to a degeneracy in the total kinetic energy $\omega(k_1) + \omega(\pi/2 - k_1)$ of two magnons. The $S = 0$ and $S = 1$ bound states lie well below the continuum lower boundary. However at $k = 0$ and π only the $S = 0$ bound state is seen. The continuum is much broader at $k = 0, \pi$ indicating larger mixing effects which disrupt the $S = 1$ bound state. Although no $S = 1$ bound state forms, the attractive potential still leads to a strongly enhanced scattering cross-section $S(Q, \omega)$ at the continuum lower boundary [13], see dashed line in Figure (4). The $S = 1$ bound state appears clearly at the $k = \pi/2$ point (solid line in Figure (4)). It should be noted that the neutron scattering cross-section for the $S = 0$ mode is zero, however this mode may be visible by light scattering [13].

Harris [14] used a reciprocal space perturbation theory to calculate the ground state and excited state energy up to $O(\alpha^3)$. This gives a $k = 0, \pi$ energy gap of $E_{gap} = J(1 - \alpha/2 - 3\alpha^2/8 + \alpha^3/32)$. However these results can be derived more easily in real space [13], and in the case of the ground state energy, we have extended the calculation to $O(\alpha^5)$,

$$e_0(\alpha)/J = -3/2^3 - (3/2^6) \cdot \alpha^2 - (3/2^8) \cdot \alpha^3$$
$$-(13/2^{12}) \cdot \alpha^4 - (95/3) \cdot (1/2^{14}) \cdot \alpha^5 - O(\alpha^6). \quad (2)$$

The perturbation series appears to be rapidly converging for $\alpha \leq 0.5$, and may have a radius of convergence of unity.

Because $(VO)_2P_2O_7$ has $\alpha \approx 0.8$ [1], we have used a numerical Lanczos algorithm on finite $L = 4n$ lattices of up to $L = 28$ and with approximately 14 place accuracy to study the ground states and binding energies up to similar values of α. Full details will be given elsewhere [13]. Figure (4) shows the calculated binding energies of the $S = 0$ bound mode at $k = \pi/2$, and $k = 0$, as well as those for the $S = 1$ bound mode at $k = \pi/2$. The results show strong binding at $\alpha = 0.8$ of the $S = 0$ mode at $k = \pi/2$ but the situation is not clear for $k = 0$. They also suggest weak binding for the S=1 mode at $\pi/2$ at the alternation for $(VO)_2P_2O_7$. Unfortunately finite size effects precluded an accurate determination of this

binding energy.

In order to make a quantitative comparison with $(VO)_2P_2O_7$ $S(Q,\omega)$ is required for the bound modes and continuum. We are currently undertaking calculations to quantify this. The effects of interchain coupling have been neglected and these may enhance the binding. Next-nearest neighour exchange within the chains may have a similar effect. The α perturbation theory provides a useful quantitative guide to such effects, and further theoretical studies are in progress. We also note that similar dynamics are also important in many other low-dimensional Hamiltonians such as spin ladders and we shall present some work on those in the future.

In conclusion, we have measured an extra mode in the alternating chain system $(VO)_2P_2O_7$. The evidence suggests that this is a two-magnon bound state. Perturbation theory and Lanczos calculations give an insight into the formation of bound modes.

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Figure Captions

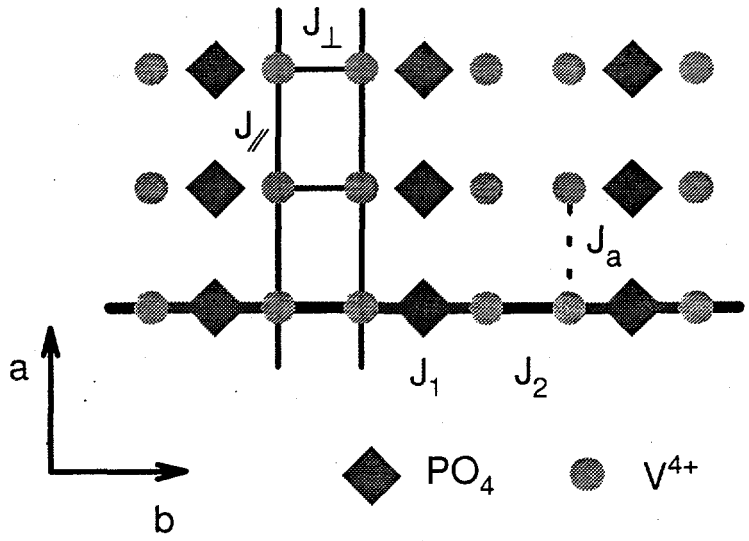
Figure 1. Schematic depiction of the structure and magnetic interactions in VOPO. The spin ladder model previously thought to describe VOPO has nearest neighbor exchange constants $J_{\|}$ along the a ("ladder") direction and $J_{\perp}$ along the b ("rung") direction. In the alternating chain model, nearest neighbor V^{4+} ions are alternately coupled by constants J_1 and J_2 along the b (chain) direction. Neighboring spins in adjacent chains are coupled by J_a. Magnetic coupling in the c direction is negligible.

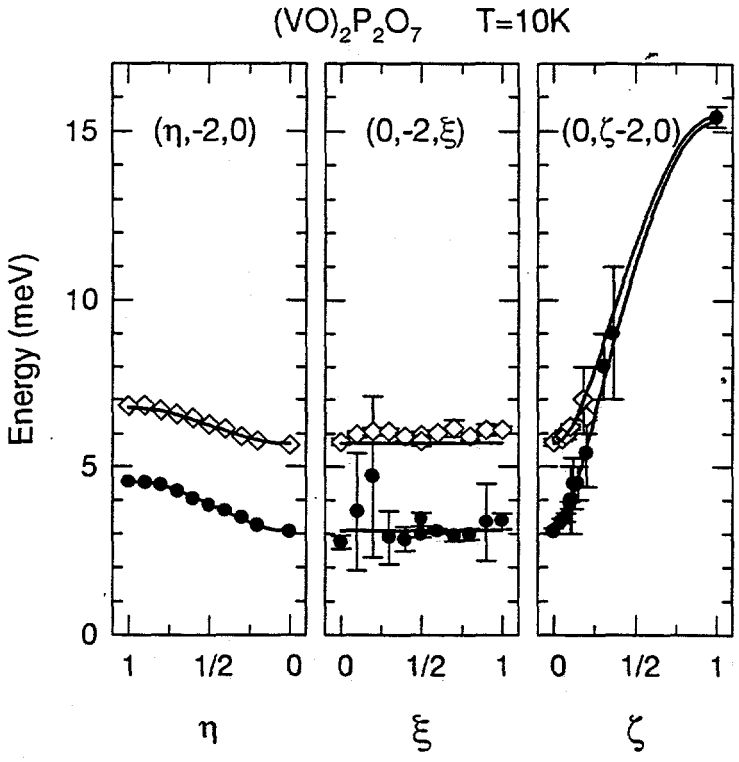
Figure 2. Measured dispersion of magnetic excitations in VOPO at T = 10K. When not visible error bars are smaller than the size of the plotted symbols. Filled circles (open diamonds) are points from the lower (upper) energy mode. The solid lines are dispersion curves calculated using parameters obtained by fitting to a pseudo-Boson model [1]. Wavevectors are plotted in units corresponding to the VOPO reciprocal lattice.

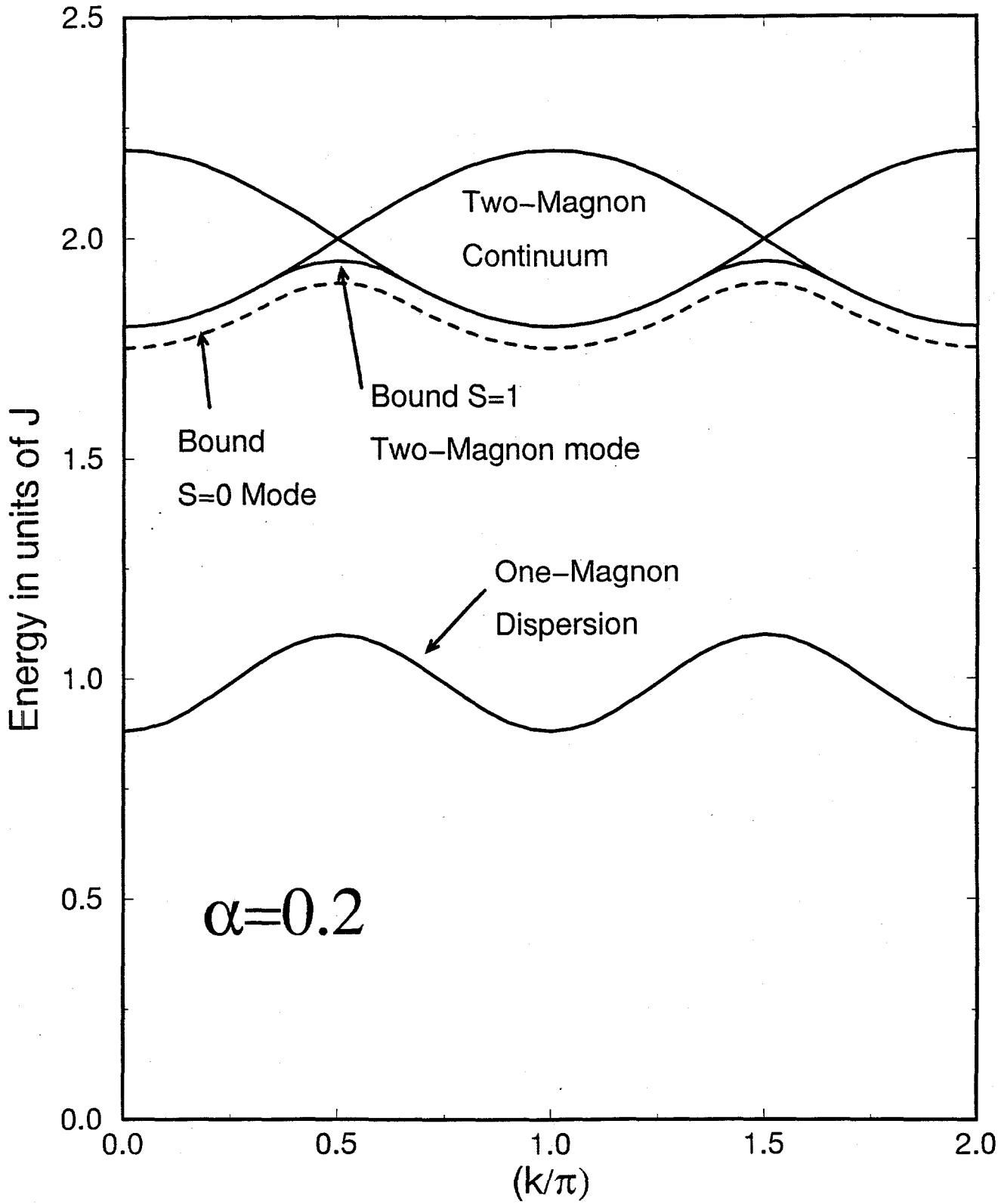
Figure 3. Schematic depiction of the one- and two-magnon excitation spectra of the $S = 1/2$ AHC with an alternation of $\alpha = 0.2$. An $S = 1$ bound mode appears below the continuum at $k \approx \pi/2$. The more deeply bound $S = 0$ mode (dashed line) is not visible to neutrons scattering.

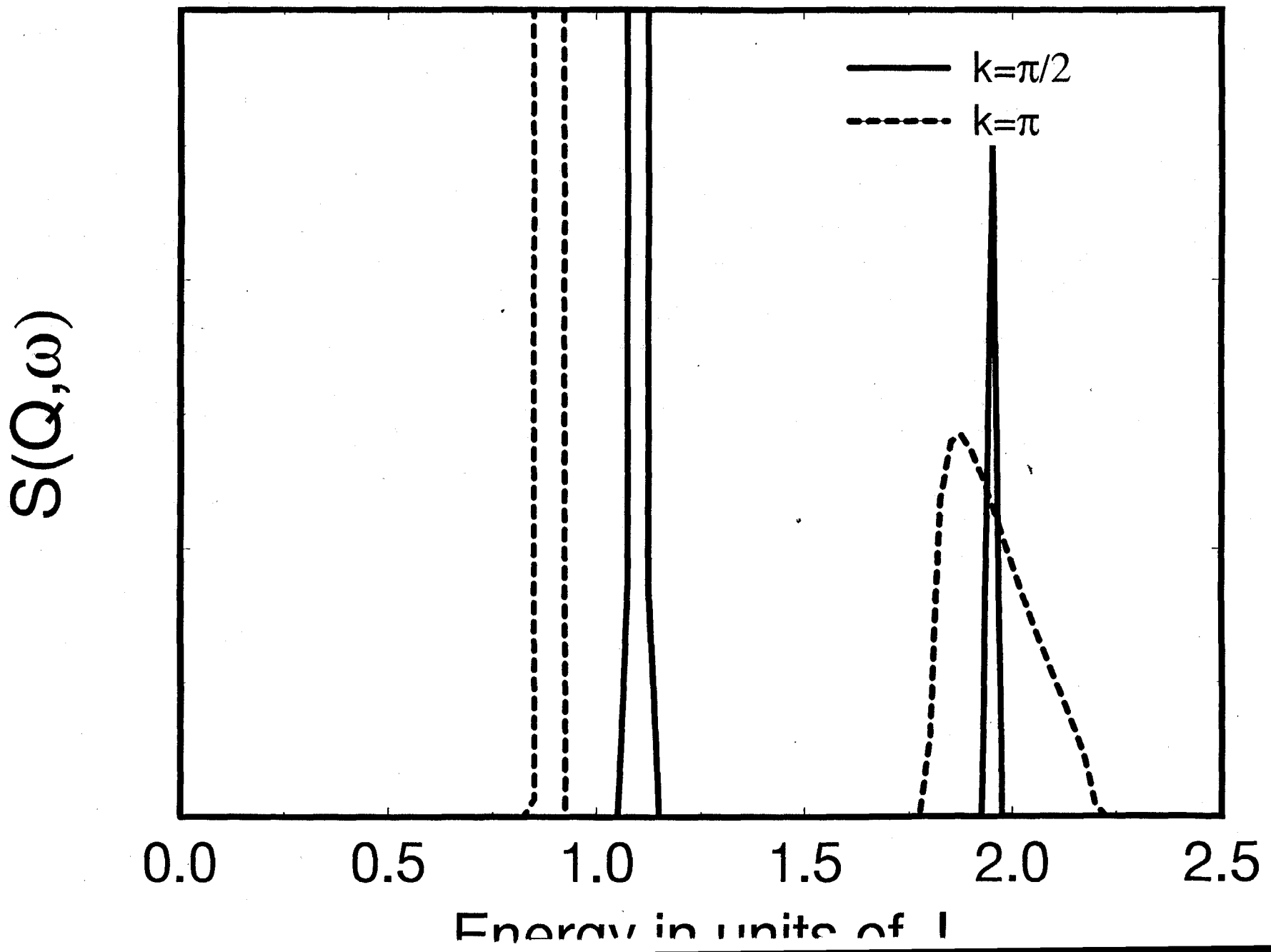
Figure 4. Calculated $S(Q, \omega)$ for constant-Q scans at $k = \pi/2$ (solid line) and $k = \pi$ (dashed line) using the first order perturbation approach with $\alpha = 0.2$.

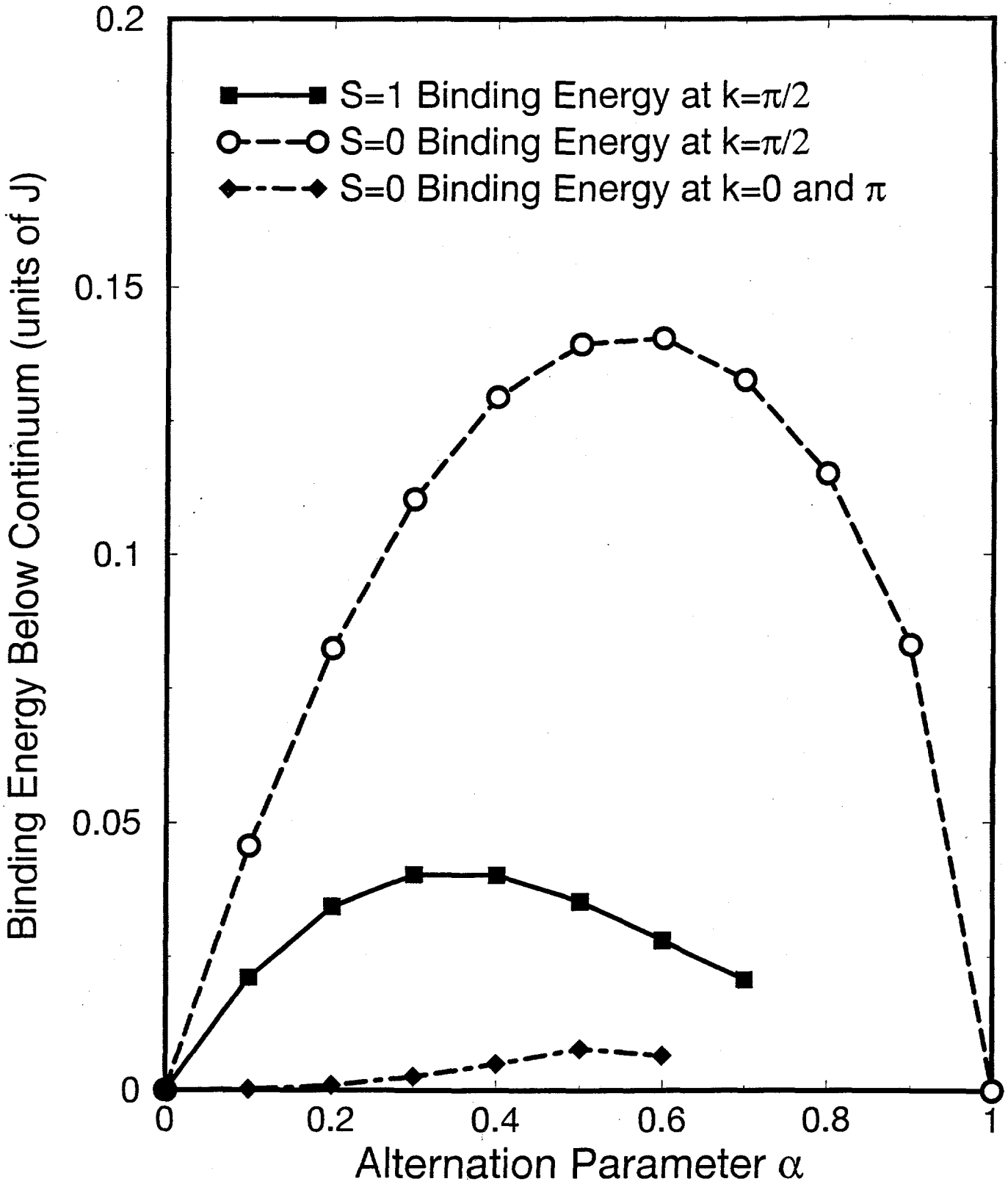
Figure 5. Calculated binding energies of the $S = 0$ and $S = 1$ bound states using a Lanczos method [13] at $k = 0$ and $\pi/2$. The binding energies are given in units of J.


$J_\perp$
$J_{/\!/}$
J_a
J_1
J_2
a
b
PO_4
V^{4+}


(VO)2P2O7 T=10K
(η,-2,0)
(0,-2,ξ)
(0,ζ-2,0)
Energy (meV)
15
10
5
0
1
1/2
0
0
1/2
1
0
1/2
1
η
ξ
ζ


2.5
2.0
1.5
1.0
0.5
0.0
0.0
0.5
1.0
1.5
2.0
(k/π)
Energy in units of J
Two−Magnon
Continuum
Bound S=1
Two−Magnon mode
Bound
S=0 Mode
One−Magnon
Dispersion
α=0.2


k=π/2
k=π
S(Q,ω)
0.0
0.5
1.0
1.5
2.0
2.5
Energy in units of J


S=1 Binding Energy at k=π/2
S=0 Binding Energy at k=π/2
S=0 Binding Energy at k=0 and π
Binding Energy Below Continuum (units of J)
0.2
0.15
0.1
0.05
0
0
0.2
0.4
0.6
0.8
1
Alternation Parameter α