Inelastic Neutron Scattering from the Spin Ladder Compound $(VO)_2P_2O_7$

R. S. Eccleston,[1] T. Barnes,[2] J. Brody,[3] and J. W. Johnson[3]

[1]*The ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, OXON OX11 0QX, United Kingdom*

[2]*Physics Division and Center for Computationally Intensive Physics, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831 and Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996*

[3]*Corporate Research Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801*

(Received 23 May 1994)

We present results from an inelastic neutron scattering experiment on the candidate Heisenberg spin ladder vanadyl pyrophosphate, $(VO)_2P_2O_7$. We find evidence for a spin-wave excitation gap of $E_{gap} = 3.7 \pm 0.2$ meV at a band minimum near $Q = 0.8$ Å^{-1}. This is consistent with expectations for triplet spin waves in $(VO)_2P_2O_7$ in the spin-ladder model and represents the first confirmation in nature of a Heisenberg antiferromagnetic spin ladder.

PACS numbers: 75.10.Jm, 75.25.+z, 75.30.Ds, 75.50.Ee

The recent interest in the excitation spectrum of Heisenberg antiferromagnetic spin chains dates from Haldane's suggestion that integer- and half-integer spins might lead to qualitatively different physics [1,2]. This conjecture, that only half-integer-spin chains are gapless, is now generally regarded as confirmed by inelastic neutron scattering experiments [3]. The subsequent discovery of two-dimensional Heisenberg spin systems in the copper-oxygen planes of the high temperature superconductors, and the possibility that the superconductivity is a result of the behavior of dynamical holes in these systems [4], has further increased the interest in lower-dimensional Heisenberg antiferromagnets.

To gain further insight into the physics of one-dimensional spin chains and the two-dimensional high-T_c spin systems, one may study systems which are intermediate between these two cases. The simplest of these is the "Heisenberg spin ladder," which consists of two chains of magnetic ions coupled by an interaction of strength $J_\parallel$ along the chains and $J_\perp$ between them, described by the Hamiltonian

$$H = J_\parallel \sum_{\text{chains}} \mathbf{S}_i \cdot \mathbf{S}_j + J_\perp \sum_{\text{rungs}} \mathbf{S}_i \cdot \mathbf{S}_j \,. \qquad (1)$$

Recent theoretical work has addressed the properties of spin excitations of this system and its behavior under hole doping. Dagotto and co-workers [5] first found evidence for superconductivity in the hole-doped spin ladder, analogous to results for the 2D t-J model of the high-T_c materials. Barnes *et al.* [6] noted the presence of a gap for all $J_\perp/J_\parallel > 0$ and discussed other properties of the excitation spectrum of the undoped spin system. In these references it was noted that the orthorhombic antiferromagnet vanadyl pyrophosphate [7–12], $(VO)_2P_2O_7$, might be an accurate realization of this spin system and hence was interesting as a possible analogue of the 2D copper-oxygen high-T_c spin systems.

Many other theoretical studies of antiferromagnetic Heisenberg spin ladders have subsequently appeared in the literature [13–21], and two additional candidate ladder systems have been discussed, a $Sr_{n-1}Cu_{n+1}O_{2n}$ series [22,23] (expected to consist of coupled ladders with a frustrated "trellis" coupling [17]) and a $La_{4+4n}Cu_{8+2n}O_{14+8n}$ series [24] (another coupled-ladder system). In a parallel series of investigations [25–29] the properties of spin ladders with ferromagnetic rung couplings (which are more closely related to spin-1 chains) have also been discussed. Despite the interest in this subject and the existence of many candidate materials, to our knowledge no example of a spin ladder has previously been confirmed [30–33]. Ideally this would involve an experimental study of magnetic excitations, for example using inelastic neutron scattering.

The candidate spin ladder $(VO)_2P_2O_7$ clearly shows a ladder configuration of $S = \frac{1}{2}$ V^{+4} ions in its crystal lattice [8,10,12] (Fig. 1, adapted from Ref. [12], shows the ladder of vanadium ions and associated oxygens), with spacings of $a_\parallel = 3.864(2)$ Å between chain V ions and $a_\perp = 3.19(1)$ Å between rung V ions. The susceptibility of this material is fitted surprisingly well by an alternating chain model [12] with $J_1 = 11.3$ meV and $J_2 = 7.9$ meV, although this need not eliminate the ladder model if the thermodynamic similarities previously noted for ladder and alternating chain models of copper nitrate [31] apply in the $(VO)_2P_2O_7$ parameter regime as well. A recent theoretical study [14] confirmed this similarity and found that the $(VO)_2P_2O_7$ susceptibility was also accurately described by a ladder model, with nearly equal interactions, $J_\parallel = 7.76$ meV and $J_\perp = 7.82$ meV. The singlet-triplet gap at $J_\perp/J_\parallel = 1.0077$ is given by [34] $E_{gap}/J_\parallel = 0.50759(1)$, corresponding to $E_{gap} = 3.94$ meV with these parameters.

One may test the ladder model of $(VO)_2P_2O_7$ directly in a neutron scattering experiment, through a determination of characteristic properties of the spin-wave excitation spectrum. In the ladder model with the parameters quoted above, the singlet-triplet gap was predicted [14] to be $\approx$3.9 meV at a momentum transfer of $Q = \pi/a_\parallel$ [equivalent to $Q = 0.813$ Å^{-1} in $(VO)_2P_2O_7$]. This one-magnon band reaches a maximum energy of 16 meV near 0.3 and 1.3 Å^{-1}, and a crossing spin-triplet two-magnon band gives

 0031-9007/94/73(19)/2626(4)$06.00 © 1994 The American Physical Society

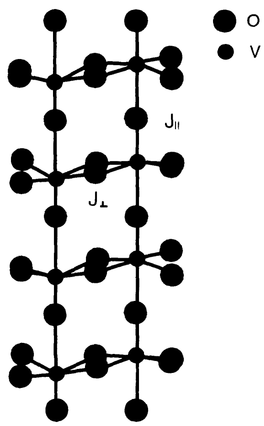

FIG. 1. The ladder of magnetic $S = \frac{1}{2}$ V^{+4} ions in $(VO)_2P_2O_7$ and associated oxygen ions.

a secondary gap of 7.9 meV at $Q = 0$ and 1.63 Å^{-1} and a broad plateau at 17–18 meV centered on $Q = 0.81$ Å^{-1}. (See Fig. 2.) Structure factor calculations on finite clusters [35] indicate that the strongest neutron scattering should occur near $Q = \pi/a_{\parallel}$, and higher levels above these two triplet bands should not be strongly excited. In contrast, a fit of the alternating chain model to the susceptibility predicts a somewhat higher gap of 4.9 meV, and the associated momentum transfer is problematical (it depends on an unspecified alternating-chain pathway) and need not have any simple relation to the $Q = 0.813$ Å^{-1} expected in the ladder model.

At present, single crystals of vanadyl pyrophosphate of a sufficient volume for inelastic neutron scattering experiments are not available; however, several experiments have demonstrated that neutron scattering experiments on polycrystalline samples of one-dimensional magnetic systems can yield considerable information [36]. This is particularly true when using time-of-flight spectrometers, which can access a wide range of $(\mathbf{q}, \omega)$ simultaneously. The powder average of the structure factor observed experimentally is given by [36]

$$S(Q,\omega) = T(\omega)\,|F(Q^2)| \times \frac{1}{4\pi Q^2}\int_{\mathbf{q}=\mathbf{q}_{\parallel}+\mathbf{q}_{\perp},|\mathbf{q}|=Q} S(\mathbf{q}_{\parallel},\mathbf{q}_{\perp},\omega)\,d\mathbf{q}\,, \quad (2)$$

where $T(\omega)$ is the temperature factor

$$T(\omega) = [1 - \exp(-\hbar\omega/k_BT)]^{-1}\,, \quad (3)$$

$F(Q)$ is the ionic form factor, and $\mathbf{q}_{\parallel}$ and $\mathbf{q}_{\perp}$ are the parallel and perpendicular projections of the total momentum transfer $\mathbf{q}$ relative to the chain axis. Clearly for any given Q all values of $|\mathbf{q}_{\parallel}| \leq Q$ will contribute to the scattered spectrum. Thus a mode which requires $|\mathbf{q}_{\parallel}| = q_1$ along the chain axis to be excited will first appear experimentally at $Q = q_1$, but will persist at values $Q > q_1$, because these can excite systems with oblique orientations such that $|\mathbf{q}_{\parallel}| = q_1$.

Measurements of the excitation spectrum of a polycrystalline sample of $(VO)_2P_2O_7$ were performed on HET, a direct geometry chopper spectrometer on the ISIS pulsed neutron source at the Rutherford Appleton Laboratory. A rotating Fermi chopper phased to the neutron pulse monochromates the incoming neutron beam. Banks of detectors at 4 and 2.5 m cover the angular ranges of $\phi = 3°$ to 7° and $\phi = 9°$ to 29°, respectively. A further two banks at these lengths are situated at average angles of 118° and 130° and are used for estimating nonmagnetic background scattering.

The sample was prepared by Brody, in a manner similar to that described by Johnston *et al.* [12]. The final annealing was performed under flowing He at 973 K for 7 d. For this experiment it was mounted on the cold finger of a closed cycle refrigerator in a sachet of aluminum foil. All data described hereafter were collected while the sample was at a temperature of 13 K, using incident energies of 15, 25, 35, and 100 meV.

Data collected simultaneously across the full angular range of the forward scattering banks using an incident energy of 25 meV were combined to produce the contour plot of scattering intensity shown in Fig. 2. The dispersion relation predicted by Barnes and Riera [14] has been superimposed on the plot to compare the ladder model to the experimental data and to demonstrate the effect of powder averaging, which spreads the scattering over larger Q values than the minimum required for excitation. The predicted cutoff of the scattering at approximately 18 meV energy transfer is clearly seen, and at lower energies there is evidence of scattering consistent with the theoretical dispersion relation, particularly in the region $Q \gtrsim 0.8$ Å^{-1}; the one-magnon band can be seen as it passes through a minimum energy near $Q = 0.8$ Å^{-1}, where there is an increase in intensity as expected from a peak in the density of states and in $S(\mathbf{q}, \omega)$.

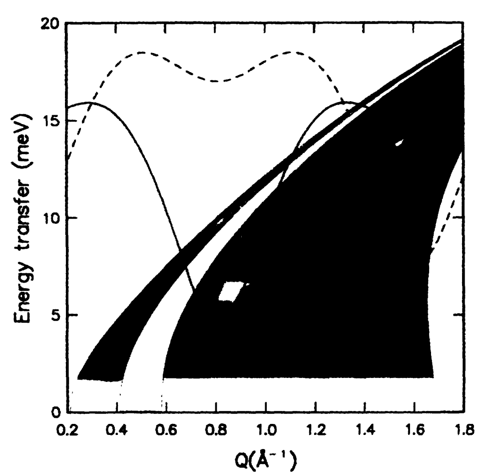

FIG. 2. Contour plot of the scattering intensity from $(VO)_2P_2O_7$ at 13 K using an incident energy of 25 meV. Contours of intensity run from 0.5 to 1.3 in steps of 0.1 (arbitrary units). The one-magnon (solid curve) and two-magnon (dashed curve) bands predicted by Barnes and Riera [14] are superimposed on the data.

Using a lower incident energy of 15 meV, the resolution is sufficient to resolve a gap between the elastic peak and the inelastic magnetic scattering. Figure 3 shows data summed over an angular range of $\phi = 14.3°$ to $18.7°$, which at an energy transfer of 3.7 meV represents a Q range of 0.72 Å^{-1} to 0.88 Å^{-1} (see Fig. 3 inset). The data have been corrected for k_f/k_i and detector efficiency. The figure clearly shows the onset of inelastic magnetic scattering above an energy transfer of approximately 3 meV. The low-energy onset of the inelastic magnetic scattering has been fitted with a Lorentzian convoluted with the resolution function, which yields a value of

$$E_{\text{gap}} = 3.7 \pm 0.2 \text{ meV} \tag{4}$$

for the gap. This is illustrated in Fig. 3 by a dashed curve in the upper graph and by a solid curve in the lower graph, which shows the data after subtraction of the elastic and quasielastic components. The smaller dashed curve on the lower graph represents the resolution function and suggests that the spectrum has an intrinsic width, as expected if we are exciting a band rather than a discrete level.

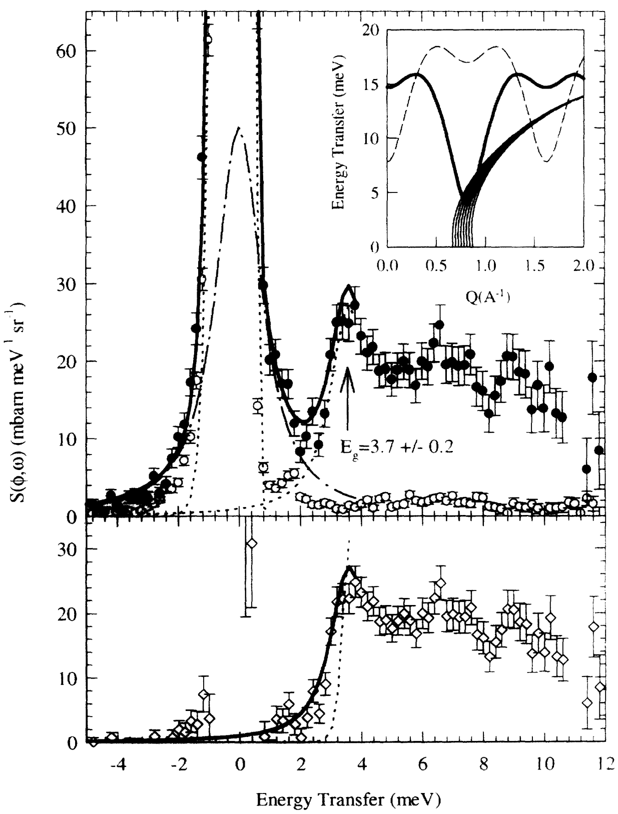

FIG. 3. A constant ϕ scan across the predicted band minimum. Data from eight detectors which trace out the trajectories shown in the inset have been summed. The upper graph shows the data (filled circles) and the fit as described in the text, together with data from the high angle bank of detectors (open circles), which have been multiplied by an empirical scale factor of 0.2 to provide an estimate of the nonmagnetic background scattering. The lower graph represents the magnetic scattering after subtraction of the elastic and quasielastic components.

The open symbols on the upper graph represent the data which were collected in the 2.5 m detectors at $\phi = 130°$. At these high angles and thus high Q values the magnetic scattering is negligible, due to the falloff of the ionic form factor, and the observed inelastic scattering arises from single and multiple phonon scattering processes. This data has been multiplied by an empirical scale factor of 0.2 (determined in previous experiments) to provide an indication of the amount of nonmagnetic background scattering underlying the magnetic scattering data collected at low Q values. The nonmagnetic inelastic scattering contribution estimated in this way is clearly very small, and there are no features coincident with the observed magnetic scattering. The nonmagnetic background scattering has not been subtracted from the data presented in the lower plot.

The resolution function of the spectrometer is made up of a contribution from the moderator and a contribution from the transmission of the chopper. The former is described by a Gaussian convoluted with an exponential, the later simply by a Gaussian. The data below an energy transfer of 4 meV has been fitted using the FRILLS least squares fitting routine [37]. The elastic scattering is well described by the resolution function (dotted), but there appears to be a second broad component under the elastic contribution, which we have fitted to a Lorentzian convoluted with the resolution function (dash-dotted). The origin of this scattering is not yet understood and may involve scattering from magnetic defects in the sample.

The overlap of the one- and two-magnon bands in the ladder model should give rise to considerable structure in the scattering above the gap energy, notably contributions from two-magnon production at $\omega \approx 8$ and 17 meV. We do see some evidence for these higher excitations, including significant scattering above 10 meV near $Q = 0.8$ Å^{-1} in our 35 meV and 100 meV data. The 100 meV data indicate that this higher energy $Q \approx 0.8$ Å^{-1} scattering is strongest around 15 meV and may therefore be due to the two-magnon band expected at 17 meV. Because of the gaps in experimental coverage we cannot be certain about the interpretation of these higher-energy excitations.

Ideally one should analyze the data using a powder average of the structure factor (2), as was done by Mutka *et al.* [36] for $AgVP_2S_6$. In the present experiment we did not carry out this analysis, in part because the ladder dispersion relation $\omega(\mathbf{q})$ is not yet well established and also because we found an obvious discrepancy: The observed scattering above $Q = \pi/a_{\parallel}$ was considerably stronger than expected from numerical studies of $S(\mathbf{q}, \omega)$ on small lattices [35]. This is the single feature of our data which does not appear to be in accord with current expectations for the ladder model. If data were available across a broader Q range and without the null region evident in Fig. 2 (which is a consequence of the space between the 2.5 m and 4 m banks of detectors), it should be possible to observe the dispersion relations of the two branches and to investigate the indications of anomalous behavior in $S(\mathbf{q}, \omega)$. Such an experiment is planned for the near future. Ideally these experiments should be carried out using a single crystal.

In summary, we have presented results from an inelastic neutron scattering experiment on the antiferromagnet vanadyl pyrophosphate. We found evidence for a band of triplet spin waves, with a minimum excitation energy of $E_{gap} = 3.7 \pm 0.2$ meV at a momentum transfer near $Q = 0.8$ Å^{-1}. These values are consistent with the expectations of the spin ladder model of $(VO)_2P_2O_7$, which predicted $E_{gap} = 3.9$ meV at $Q = 0.813$ Å^{-1}. There is some evidence for the dispersion relation $\omega(\mathbf{q})$ of spin excitations from approximately 0.6 to 1.5 Å^{-1} in our data, which is also consistent with expectations for the lowest one-magnon band in the ladder model. These results confirm that $(VO)_2P_2O_7$ to a good approximation is a realization of the antiferromagnetic Heisenberg spin ladder.

We are grateful to M. E. Hagen for assistance with the data visualization, J. Berlinsky, E. Dagotto, J. Greedan, W. E. Hatfield, H. A. Mook, H. Mutka, J. Riera, and S. R. White for related discussions, and M. A. Sokolov for a translation of Ref. [10]. We acknowledge the provision of neutron beam time by the EPSRC (formerly SERC). This study was supported in part by the Quantum Structure of Matter Project at Oak Ridge National Laboratory, funded by the U.S.D.O.E. Office of Scientific Computation under Contract No. DE-AC05-840R21400, managed by Martin Marietta Energy Systems Inc.

[1] F. D. M. Haldane, Phys. Lett. **93A**, 464 (1983).
[2] I. Affleck, J. Phys. **1**, 3047 (1989).
[3] See, for example, R. M. Morra, W. J. L. Buyers, R. L. Armstrong, and K. Hirakawa, Phys. Rev. B **38**, 543 (1988).
[4] For a recent review, see E. Dagotto, Rev. Mod. Phys. **66**, 763 (1994).
[5] E. Dagotto, J. Riera, and D. Scalapino, Phys. Rev. B **45**, 5744 (1992); see also E. Dagotto and A. Moreo, Phys. Rev. B **38**, 5087 (1988); **44**, 5396(E) (1991).
[6] T. Barnes, E. Dagotto, J. Riera, and E. S. Swanson, Phys. Rev. B **47**, 3196 (1993).
[7] H. Seeboth, G. Ladwig, B. Kubias, G. Wolf, and B. Luecke, Ukr. Chem. J. **43**, 842 (1977), and references cited therein.
[8] N. Middlemiss, Ph.D. thesis, McMaster University 1978.
[9] E. Bordes and P. Courtine, J. Catal. **57**, 236 (1979), and references cited therein.
[10] Y. Gorbunova and S. A. Linde, Dokl. Akad. Nauk SSSR **245**, 584 (1979).
[11] D. C. Johnston and J. W. Johnson, J. Chem. Soc. Chem. Commun. **1985**, 1720.
[12] D. C. Johnston, J. W. Johnson, D. P. Goshorn, and A. J. Jacobson, Phys. Rev. B **35**, 219 (1987).
[13] J. Riera, Phys. Rev. B **49**, 3629 (1994).
[14] T. Barnes and J. Riera, Phys. Rev. B **50**, 6817 (1994).
[15] R. M. Noack, S. R. White, and D. J. Scalapino, Phys. Rev. Lett. **73**, 882 (1994).
[16] S. R. White, R. M. Noack, and D. J. Scalapino, Phys. Rev. Lett. **73**, 886 (1994).
[17] S. Gopalan, T. M. Rice, and M. Sigrist, Phys. Rev. B **49**, 8901 (1994).
[18] M. Sigrist, T. M. Rice, and F. C. Zhang, Phys. Rev. B **49**, 12 058 (1994).
[19] H. Tsunetsugu, M. Troyer, and T. M. Rice, Phys. Rev. B **49**, 16 078 (1994).
[20] D. Poilblanc, H. Tsunetsugu, and T. M. Rice, Phys. Rev. B **50**, 6511 (1994).
[21] M. Azzouz, L. Chen, and S. Moukouri, Phys. Rev. B **50**, 6233 (1994).
[22] Z. Hiroi, M. Azuma, M. Takano, and Y. Bando, J. Solid State Chem. **95**, 230 (1991).
[23] M. Takano, Z. Hiroi, M. Azuma, and Y. Takeda, Jpn. J. Appl. Phys. **7**, 3 (1992).
[24] R. J. Cava *et al.,* J. Solid State Chem. **94**, 170 (1991).
[25] K. Hida, J. Phys. Soc. Jpn. **60**, 1347 (1991).
[26] S. Takada and H. Watanabe, J. Phys. Soc. Jpn. **61**, 39 (1992).
[27] H. Watanabe, K. Nomura, and S. Takada, J. Phys. Soc. Jpn. **62**, 2845 (1993).
[28] H. Watanabe, "Numerical Diagonalization Study of an $S = 1/2$ Ladder Model with Open Boundary Conditions," University of Tsukuba (unpublished).
[29] H. Watanabe, Ph.D. thesis, University of Tsukuba, 1994.
[30] Although copper hydrazinium chloride [32,33] is not a complete spin ladder, it apparently does form a closely related antiferromagnetic "sawtooth," in which Cu^{+2} and Cl^{-1} ions occupy alternate ladder sites.
[31] J. C. Bonner, S. A. Friedberg, H. Kobayashi, D. L. Meier, and H. W. J. Blöte, Phys. Rev. B **27**, 248 (1983), and references therein.
[32] D. B. Brown, J. A. Donner, J. W. Hall, S. R. Wilson, D. J. Hodgson, and W. E. Hatfield, Inorg. Chem. **18**, 2635 (1979).
[33] W. E. Hatfield, J. Appl. Phys. **52**, 1985 (1981).
[34] S. R. White (private communication).
[35] J. Riera (private communication).
[36] See, for example, H. Mutka, C. Payen, P. Molinie, J. L. Soubeyeroux, P. Colombet, and A. D. Taylor, Phys. Rev. Lett. **67**, 497 (1991), and references cited therein.
[37] R. Osborn, Rutherford Appleton Laboratory Report No. RAL-91-011.

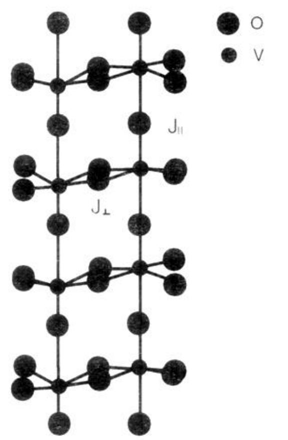

FIG. 1. The ladder of magnetic $S = \frac{1}{2}$ V^{+4} ions in $(VO)_2P_2O_7$ and associated oxygen ions.

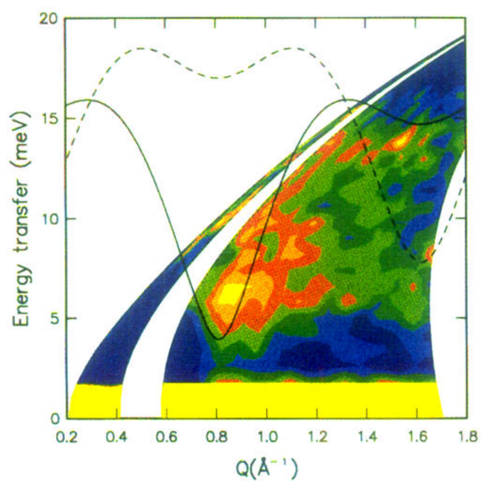

FIG. 2. Contour plot of the scattering intensity from $(VO)_2P_2O_7$ at 13 K using an incident energy of 25 meV. Contours of intensity run from 0.5 to 1.3 in steps of 0.1 (arbitrary units). The one-magnon (solid curve) and two-magnon (dashed curve) bands predicted by Barnes and Riera [14] are superimposed on the data.