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A dimer theory of the magnetic excitations in the ordered phase of the alternating-chain compound CuWO_4

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Abstract. A theory is developed to model the excitations in a dimerized, spin-1/2 system with a magnetically ordered ground state and where the dimer exchange constant is antiferromagnetic. This method starts by considering the energy levels of a single dimer in the effective, staggered magnetic field due to the mean-field ordering of the surrounding dimers. Pseudo-boson operators are introduced which create and annihilate these excitations, and the Hamiltonian of the magnetic system can be rewritten in terms of these operators and then diagonalized to yield one doubly degenerate transverse mode and a longitudinal singlet mode for each non-equivalent dimer in the magnetic unit cell. The dimer theory has been used to model the measured dispersion relations in the antiferromagnetically ordered phase of the alternating-chain compound CuWO_4 . It provides a good fit to the data and is as successful as spin-wave theory in accounting for the transverse excitations although with different values of the exchange constants. In addition the transition temperature and the size of the reduced moment at $T = 0$ K calculated in the dimer theory are closer to the experimental values of CuWO_4 than those calculated by spin-wave theory. An important difference between these two models lies in their predictions of the longitudinal excitations: whereas in spin-wave theory these are regarded as two-magnon events resulting in a continuum of scattering, in the dimer theory one well defined mode is expected. An experimental measurement of the longitudinal excitations should distinguish between these models.

1. Introduction

There has been recently much interest in low-dimensional, spin-1/2 antiferromagnets. One reason for this is that conventional theories of magnetism, for example spin-wave theory and mean-field theory, are often inadequate in describing the excitations and magnetic features of these compounds. The susceptibility of these systems displays a broad maximum well above the transition temperature indicating the existence of short-range order far above the long-range ordering temperature. The transition temperature itself is often low compared to the value calculated from mean-field theory and sometimes there is no ordering at all pointing to the importance of quantum fluctuations. In the antiferromagnetic phase, the experimentally measured ordered moment in these compounds is usually substantially less than that expected in the Néel state, suggesting that the true ground state differs significantly from the Néel state. Finally the excitations above and sometimes even below the transition temperature have frequently been found to form continua spread out in energy. This feature suggests the existence of strong quantum fluctuations and is in marked contrast to the predictions of linear spin-wave theory where only well defined excitations are expected.

A typical low-dimensional, spin-1/2 antiferromagnet is the uniform quasi-one-dimensional Heisenberg system, KCuF_3 . This compound has a reduced moment in its

ordered phase that is 54% of the value expected in a fully aligned Néel state [1] and its magnetic excitations form a two-spinon continuum rather than well defined spin-waves [2]. Field theory techniques have been used [3], and these account well for the excitation continuum. Another type of low-dimensional antiferromagnet is a dimerized, spin-1/2 system, such as CuGeO_3 in its spin–Peierls phase. In this phase CuGeO_3 consists of weakly coupled, alternating chains. At low temperature it does not order magnetically [4], but rather has a spin-singlet ground state.

The low-lying magnetic excitations in CuGeO_3 form a well defined, triply degenerate mode which is characterized by an energy gap at the zone-centre [5]. This energy gap exists only in the spin–Peierls phase and rapidly tends to zero above the transition temperature [6] implying that it arises as a direct consequence of the dimerization. Recent measurements on CuGeO_3 also show evidence of a continuum [7], which lies above the mode and is separated from it by another energy gap. This feature has been predicted to exist in the uncoupled, alternating-chain system [8]. Spin-wave theory can reproduce the well defined excitations in CuGeO_3 but cannot account for the energy gap (without artificially introducing anisotropy), triplet degeneracy of the mode or the continuum. The inadequacy of spin-wave theory is exposed by its inability to explain the excitations of an isolated dimer. An isolated dimer has a spin-singlet ground state and a triplet of excited states separated by an energy gap from the ground state (table 1). When spin-wave theory is applied to this system it incorrectly predicts that there are four energy levels all lying at the same energy and that there is no energy gap.

Table 1. The eigenfunctions and corresponding eigenvalues of an isolated dimer where $-J_0$ is the dimer exchange constant which is defined as antiferromagnetic. The ground state $|G\rangle$ has energy $-3J_0/4$ and the excited states $|0\rangle$, $|-1\rangle$ and $|+1\rangle$ form a triplet at energy $J_0/4$. In the notation $|\uparrow\downarrow\rangle$ is the state where the first spin in the dimer points up and the second spin points down with respect to an arbitrary z axis.

Eigenfunction	Eigenvalue	Spin	State
$ G\rangle = \frac{1}{\sqrt{2}}\{ \uparrow\downarrow\rangle - \downarrow\uparrow\rangle\}$	$-\frac{3}{4}J_0$	$S^T = 0, S^z = 0$	ground state
$ -1\rangle = \downarrow\downarrow\rangle$	$\frac{1}{4}J_0$	$S^T = 1, S^z = -1$	excited state
$ +1\rangle = \uparrow\uparrow\rangle$	$\frac{1}{4}J_0$	$S^T = 1, S^z = +1$	excited state
$ 0\rangle = \frac{1}{\sqrt{2}}\{ \uparrow\downarrow\rangle + \downarrow\uparrow\rangle\}$	$\frac{1}{4}J_0$	$S^T = 0, S^z = 0$	excited state

To overcome some of the deficiencies of spin-wave theory an alternative formulation for CuGeO_3 was introduced in [9]. Using pseudo-boson operators acting on dimer rather than spin operators, a Hamiltonian was constructed. Ignoring higher-order terms and diagonalizing the bilinear terms gave well defined excitations. Although this bilinear theory could not account for the continuum observed in CuGeO_3 , it was successful in explaining the well defined excitations as well as providing a physically appealing picture that captured some of the essential characteristics of CuGeO_3 .

Within a bilinear approximation, the pseudo-boson operator (dimer) formulation has distinct advantages over the spin-wave formulation. Firstly the dimer model is based on a spin-singlet ground state whereas spin-wave theory is based on the fully aligned Néel state: as CuGeO_3 does not magnetically order [4], dimer theory is based on a more realistic ground state. Secondly, dimer model excitations form a triply degenerate mode due to rotational invariance. In spin-wave theory rotational symmetry is artificially broken by specifying an ordering direction and the excitations are doublets. Measurements of CuGeO_3 in a magnetic field show triply rather than doubly degenerate modes [10]. Thirdly, the dimer model has

a zone-centre energy gap which is a function of exchange constants alone. However the excitations in spin-wave theory are gapless in the absence of an artificially introduced anisotropy. As the energy gap displayed by CuGeO_3 in the spin-Peierls phase, where the chains are alternating, goes to zero above the transition temperature [6] where the chains are uniform, it is clear that the gap arises from dimerization rather than anisotropy. Fourthly in the dimer model the fitted intrachain exchange constants for CuGeO_3 are approximately $\sqrt{2}$ smaller than those in spin-wave theory. It is interesting to compare this factor of $\sqrt{2}$ to the factor of $\pi/2$ between spin-wave theory and the exact theory of des Cloizeaux and Pearson for the low-lying excitations of a uniform, spin-1/2, antiferromagnetic chain [11].

In this paper we shall apply the dimer model to CuWO_4 ; this is an antiferromagnetic, spin-1/2, dimerized compound which, unlike CuGe_3 , develops long-range antiferromagnetic order at low temperatures. CuWO_4 consists of weakly coupled, alternating, antiferromagnetic chains running in the $[2, -1, 0]$ direction [12], as illustrated in figure 1. Unlike CuGeO_3 , dimerization in CuWO_4 is a direct consequence of the low crystal symmetry and of having four magnetic ions in the magnetic unit cell. These features mean that most exchange interactions when taken on their own couple the Cu ions into dimers rather than chains or planes and several different interactions are required for one-, two- or three-dimensional coupling. CuWO_4 has a number of features in common with low-dimensional, spin-1/2 antiferromagnets. Firstly the ordered moment on the Cu ion was found by neutron diffraction [13] to be 67% of the value expected in the Néel state, indicating that the true ground state differs significantly from the Néel state. Secondly the susceptibility of CuWO_4 displays a broad maximum at 85.5 K far above the transition temperature of 24.0 K [14], suggesting the existence of short-range order at temperatures well above the onset of long-range order.

There is no exact theory of the magnetic excitations in a dimerized, antiferromagnetically ordered, spin-1/2 compound like CuWO_4 , although spin-wave theory can adequately model the excitations below the transition temperature [12]. In this paper the dimer theory used in [9] is extended for the ordered case and applied to CuWO_4 . A comparison with spin-wave theory is also made. The dimer theory will be discussed at some length because this is the first time it has been presented for the case of a compound with an antiferromagnetically ordered ground state.

This paper is organized as follows: in the next section the dimer theory is outlined and the features of CuWO_4 are described; the dimer theory is then applied to CuWO_4 and the details of the calculation are given with the help of two appendices. In the final section spin-wave theory and the dimer theory are compared as models for CuWO_4 and the reduced moment, value of the transition temperature and longitudinal scattering predicted by the two models are discussed.

2. Theory

In this section the dimer theory is developed for a dimerized, spin-1/2 compound with an antiferromagnetically ordered ground state and is used as a model of the excitations in CuWO_4 . In part 2.1 the theory is outlined and in part 2.2 the magnetic features of CuWO_4 are discussed, and then part 2.3 describes the dimer theory as applied to CuWO_4 in detail.

2.1. Dimer theory for an antiferromagnetically ordered compound

We start by considering an isolated dimer in which two spin-1/2 Cu ions are coupled by an antiferromagnetic exchange $-J_0$. This system has a spin-singlet ground state $|g\rangle$ with

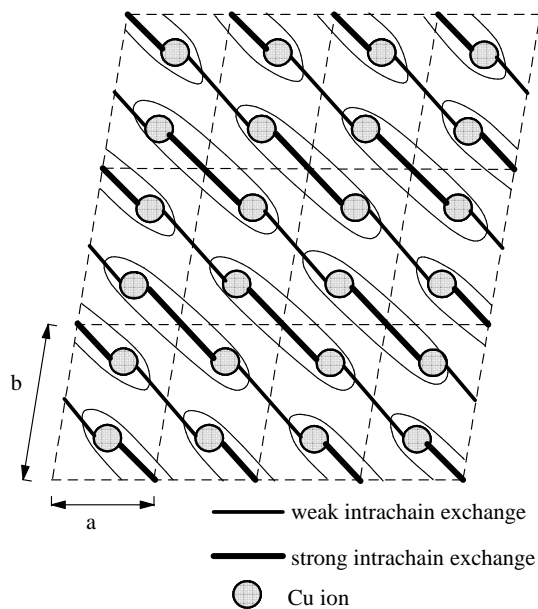


Figure 1. The alternating chains in CuWO_4 are illustrated in the a - b plane where the strong intrachain exchange is represented by the thick black line and the weaker intrachain exchange is represented by the thin black line. The dimer pairs are circled and the dashed lines indicate the structural unit-cell boundaries.

an energy $-3J_0/4$ and a triplet of excited states at an energy J_0 above the ground state. The excited states have total spin $S = 1$ and wavefunctions $|-1\rangle$, $|0\rangle$ and $|+1\rangle$ where the notation indicates the eigenvalues of S^z in an arbitrary z direction. The eigenstates and eigenvalues are listed in table 1, and were used as the basis in which to model the excitations in [9].

In a dimerized, spin-1/2 crystal where the ground state is weakly antiferromagnetically ordered, each dimer is in the effective magnetic field due to the antiferromagnetic ordering of the neighbouring dimers. Using mean-field theory, the interaction energy of each dimer with the surrounding dimers is given by

$$E_I = F(S_1^z - S_2^z) \quad (1)$$

where the ordering parameter F is given by

$$F = -J_t |\langle S_1^z \rangle|. \quad (2)$$

In these expressions J_t is the sum of the modulus of all the exchange interactions that couple each Cu ion to the other Cu ions in the crystal excluding the dimer exchange constant and this quantity is the same for both Cu ions in the dimer. S_1^z and S_2^z are the components of the spin operators of the first and second Cu ions in the dimer in the ordering direction (assumed to be the z direction). Lastly the quantity $|\langle S_1^z \rangle|$ is the modulus of the expectation value of the ordered spin of the first Cu ion where it has been assumed that this quantity is the same for the second Cu ion, $|\langle S_2^z \rangle| = |\langle S_1^z \rangle|$. From equations (1) and (2), the effective magnetic field is a staggered field with strength

$$B_I = B_I^z = F/g_s \mu_B. \quad (3)$$

The effect of introducing this staggered field is to mix the isolated dimer eigenstates $|G\rangle$ and $|0\rangle$ resulting in a new ground state $|G'\rangle$ and longitudinal excitation $|0'\rangle$. The transverse excitations $| - 1\rangle$ and $| + 1\rangle$ are the same as in the isolated dimer case. The eigenfunctions and corresponding eigenvalues are given in table 2. The expectation value of the spin of the first Cu ion in the dimer is also listed in table 2 for each eigenstate, and this quantity can be used to calculate the ordering parameter $F(T)$ (where T is temperature). In this paper we shall concentrate on the low-temperature magnetic behaviour where most of the dimers in the magnetic system are in their spin-singlet ground states and so $F(T)$ can be approximated by

$$F(T = 0) = -J_t |\langle S_1^z(T = 0) \rangle| = -J_t |\langle G' | S_1^z | G' \rangle| \quad (4)$$

from table 2

$$\langle G' | S_1^z | G' \rangle = \frac{1}{2} \sin(2\theta) = \frac{1}{2} \frac{\sqrt{J_t^2 - J_0^2}}{J_t}. \quad (5)$$

An important deduction from equation (5) is that antiferromagnetic ordering can only occur in the dimer model if $J_t > J_0$, this is the condition for the square root in the expression to be positive. A uniform antiferromagnetic chain where $J_t = J_0$ is therefore on the point of developing long-range order at $T = 0$ K, a feature suggested by other theories which predict quasi-long-range order at $T = 0$ K [15]. In contrast an alternating chain with $J_t < J_0$ is not expected to show antiferromagnetic ordering at any temperature. Another significant conclusion is that for all dimerized systems where antiferromagnetic ordering does occur the ordered spin moment is reduced from the value expected in the fully aligned Néel state, since the quantity $\sqrt{J_t^2 - J_0^2}/J_t$ in equation (5) is always less than one.

Table 2. The eigenfunctions and corresponding eigenvalues for a dimer in a staggered magnetic field of strength $F/g_s\mu_B$ where F is the ordering parameter. The expectation value of the spin on the first Cu ion in the dimer has also been given for each eigenstate.

Eigenstate	Eigenvalue	$\langle n S_1^z n \rangle$	State
$ G'\rangle = \cos(\theta) G\rangle + \sin(\theta) 0\rangle$	$-\frac{1}{4}J_0 - \frac{1}{2}\sqrt{J_0^2 + 4F^2}$	$\frac{1}{2}\sin(2\theta)$	ground state
$ - 1\rangle$	$\frac{1}{4}J_0$	$-\frac{1}{2}$	transverse excitation
$ + 1\rangle$	$\frac{1}{4}J_0$	$\frac{1}{2}$	transverse excitation
$ 0'\rangle = -\sin(\theta) G\rangle + \cos(\theta) 0\rangle$	$-\frac{1}{4}J_0 + \frac{1}{2}\sqrt{J_0^2 + 4F^2}$	$-\frac{1}{2}\sin(2\theta)$	longitudinal excitation
	where $\tan \theta = \frac{1}{2F}(J_0 - \sqrt{J_0^2 + 4F^2})$		

The dimer eigenfunctions and eigenvalues have been calculated at $T = 0$ K in terms of the quantities J_t and J_0 using equations (4) and (5), and are listed in table 3. Note that the longitudinal excitation has a higher energy than the transverse excitations. These states form a useful basis in which to model the low-temperature magnetic behaviour of a dimerized compound with an antiferromagnetically ordered ground state, and pseudo-boson operators are introduced which act on the $T = 0$ dimer eigenfunctions.

The dimer theory developed here is analogous to spin-wave theory. When spin-wave theory is applied to an antiferromagnetic spin-1/2 system, the basis states consist of the ground state which is the Néel state and the excitations which correspond to individual spins being reversed. Pseudo-boson operators are introduced to create and annihilate these excitations giving one doubly degenerate transverse mode for each pair of sublattices in the

Table 3. The eigenfunctions and corresponding eigenvalues for a dimer in a weakly antiferromagnetically ordered environment at $T = 0$ K where the effective magnetic field is $-\sqrt{J_t^2 - J_0^2}/2g_s\mu_B$. The quantity J_t is the sum of the modulus of all the exchange interactions that couple each Cu ion in the dimer to other Cu ions in the magnetic system excluding the dimer exchange constant.

Eigenstate	Eigenvalue	State
$ G\rangle = \cos(\theta) G\rangle + \sin(\theta) 0\rangle$	$-\frac{1}{4}(J_0 + 2J_t)$	ground state
$ -1\rangle$	$\frac{1}{4}J_0$	transverse excitation
$ +1\rangle$	$\frac{1}{4}J_0$	transverse excitation
$ 0'\rangle = -\sin(\theta) G\rangle + \cos(\theta) 0\rangle$	$-\frac{1}{4}(J_0 - 2J_t)$	longitudinal excitation

where $\cos(2\theta) = \frac{J_0}{J_t}$ and $\sin(2\theta) = \frac{\sqrt{J_t^2 - J_0^2}}{J_t}$

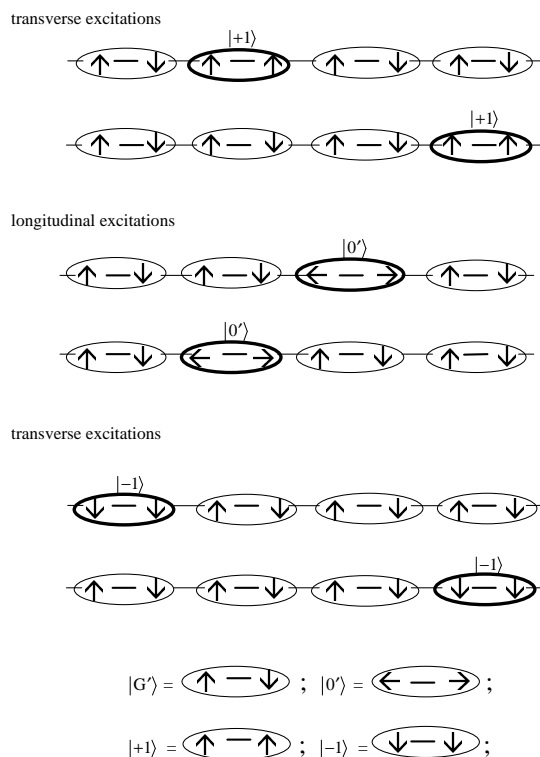


Figure 2. A number of different dimer excitations are illustrated on a one-dimensional, alternating chain. Each dimer is circled and the excitations are labelled as $|0'\rangle$, $|+1\rangle$, and $|-1\rangle$. The collective excitations of dimers coupled together in an antiferromagnetically ordered system can be regarded as the superposition of single dimer excitations like those illustrated here.

compound. In the same way that a spin-wave excitation is a linear superposition of states in which a single spin in the crystal is reversed from its ground state position, the dimer excitations presented here are superpositions of single dimer excitations. Figure 2 shows a series of single dimer excitations on a one-dimensional alternating chain. The excitations

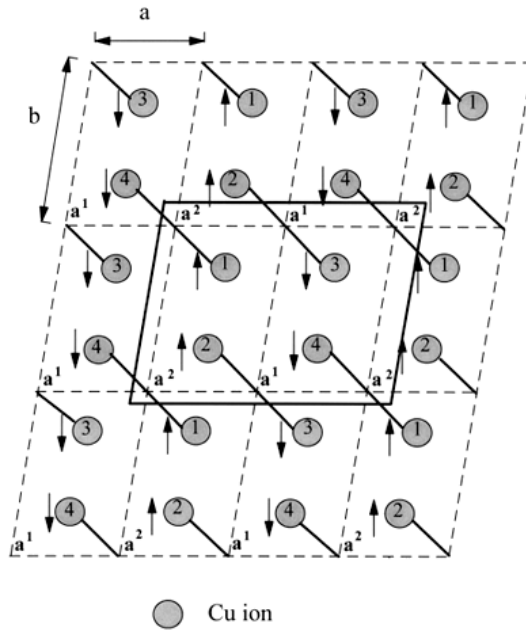
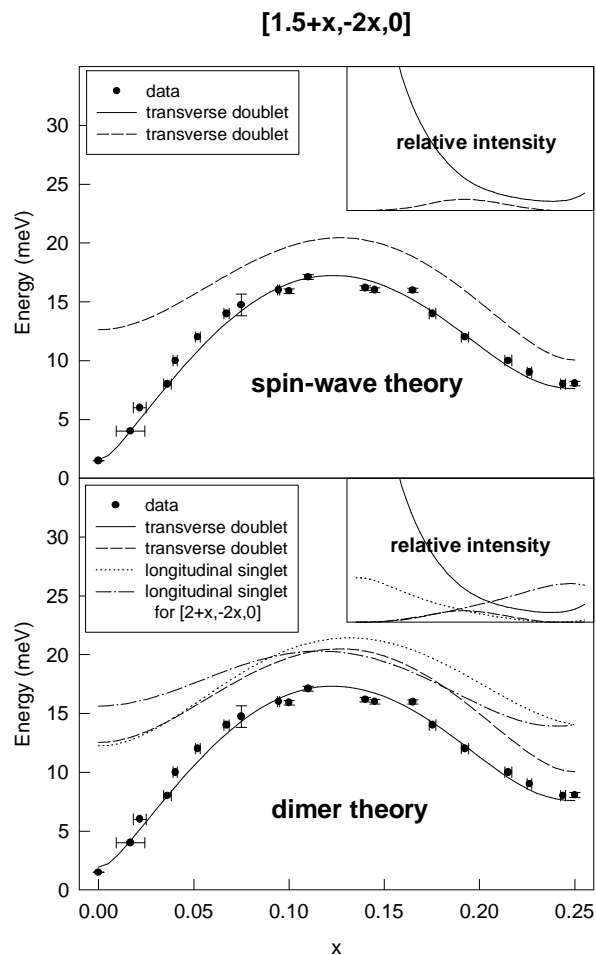


Figure 3. The a - b plane of CuWO_4 is illustrated: the dashed line shows the structural unit cell boundaries and the solid box surrounds one magnetic unit cell. The four Cu ions within the magnetic cell are labelled 1, 2, 3 and 4, and their relative spin ordering directions are indicated by the arrows. The two Cu ions forming each dimer pair are connected by a solid line and the dimers are labelled a^1 or a^2 .

Table 4. The possible exchange interactions in CuWO_4 are listed in the first column of this table and the corresponding exchange paths for which they are responsible are given in the second column. In the third column the interaction is described as ferromagnetic or antiferromagnetic.

Exchange	Ions linked	Type
$J_{a[ijk]}$	$\text{Cu } 1, \mathbf{r} \rightarrow \text{Cu } 1, \mathbf{r} + [i, j, k]$ $\text{Cu } 2, \mathbf{r} \rightarrow \text{Cu } 2, \mathbf{r} + [i, j, k]$ $\text{Cu } 3, \mathbf{r} \rightarrow \text{Cu } 3, \mathbf{r} + [i, j, k]$ $\text{Cu } 4, \mathbf{r} \rightarrow \text{Cu } 4, \mathbf{r} + [i, j, k]$	ferromagnetic
$J_{b[ijk]}$	$\text{Cu } 1, \mathbf{r} \rightarrow \text{Cu } 2, \mathbf{r} + [i, j, k]$ $\text{Cu } 3, \mathbf{r} \rightarrow \text{Cu } 4, \mathbf{r} + [i, j, k]$	ferromagnetic
$J_{c[ijk]}$	$\text{Cu } 1, \mathbf{r} \rightarrow \text{Cu } 3, \mathbf{r} + [i, j, k]$ $\text{Cu } 2, \mathbf{r} \rightarrow \text{Cu } 4, \mathbf{r} + [i, j, k]$ $\text{Cu } 3, \mathbf{r} \rightarrow \text{Cu } 1, \mathbf{r} + [2 + i, j, k]$ $\text{Cu } 4, \mathbf{r} \rightarrow \text{Cu } 2, \mathbf{r} + [2 + i, j, k]$	antiferromagnetic
$J_{d[ijk]}$	$\text{Cu } 1, \mathbf{r} \rightarrow \text{Cu } 4, \mathbf{r} + [i, j, k]$ $\text{Cu } 3, \mathbf{r} \rightarrow \text{Cu } 2, \mathbf{r} + [2 + i, j, k]$	antiferromagnetic

resulting from the dimer theory are collective excitations of the magnetic system as a whole and can be regarded as a linear superposition of states like those illustrated.

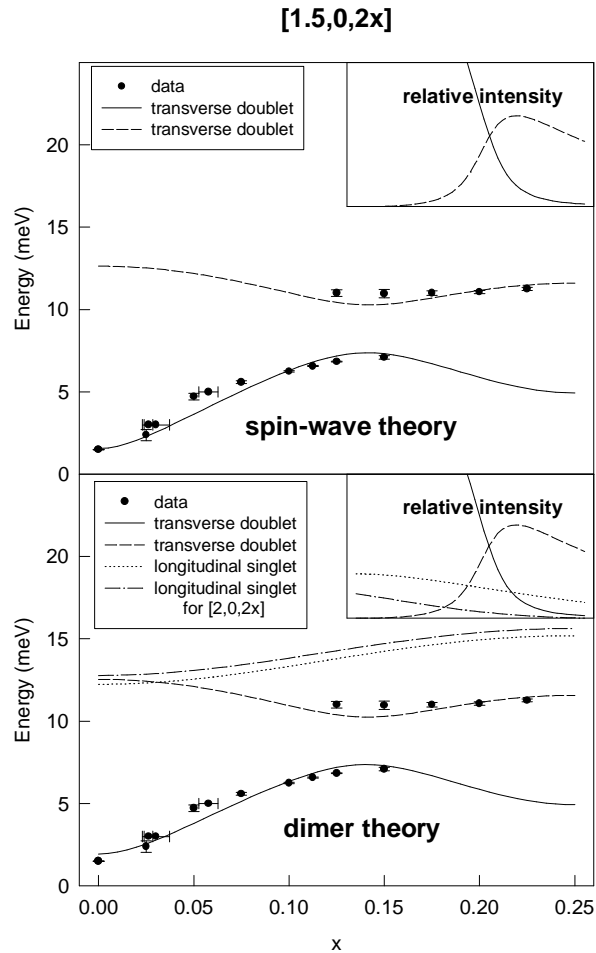


(a)

Figure 4. The upper graph shows the spin-wave theory fit to the CuWO_4 data for the direction indicated in the title and the inset plot is a simulation of the intensities of the modes in this model using the fitted exchange constants. The lower graph shows the dimer theory fit to the data and the inset plot is a simulation of the dimer model intensities. The longitudinal mode has been given for an additional reciprocal space direction indicated by the dot-dashed line: this direction is stated in the legend.

2.2. The magnetic features of CuWO_4

CuWO_4 has triclinic symmetry with space group $P\bar{1}$ [16] and there are two Cu ions per structural unit cell which are related to each other by inversion symmetry. Below its transition temperature of 24.0 K [14] CuWO_4 exhibits long-range antiferromagnetic order with a magnetic propagation vector $(0.5, 0, 0)$ [17, 18]. The two Cu ions within the structural unit cell align ferromagnetically, and the Cu ions in successive unit cells along the a direction align antiferromagnetically leading to a magnetic unit cell that is double the size of the structural unit cell in the a direction. Figure 3 shows the a - b plane of CuWO_4 and the solid box surrounds one magnetic unit cell. The four magnetic ions are labelled 1, 2, 3 and 4 and their relative spin directions in the ordered phase are indicated by the arrows.

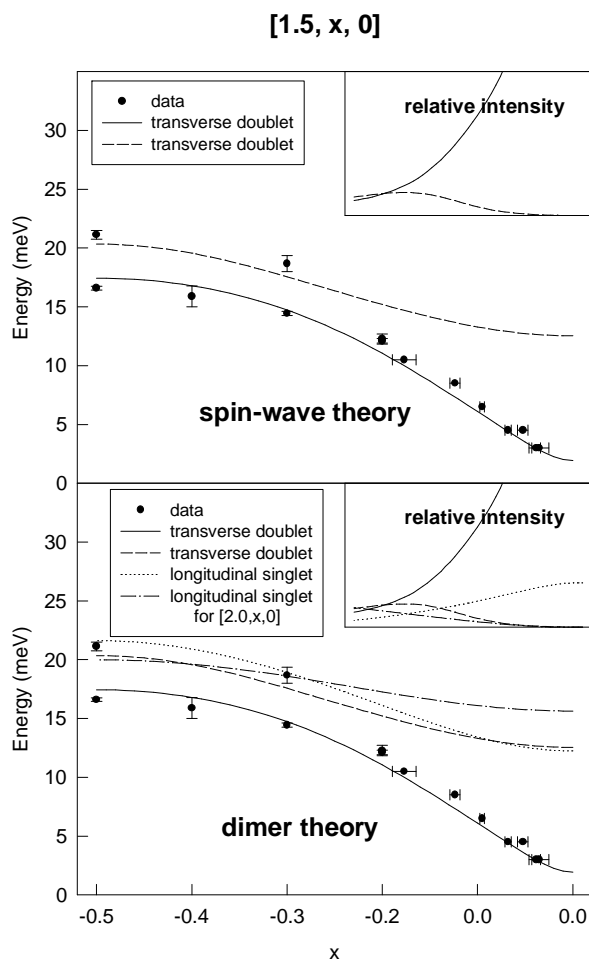


(b)

Figure 4. (Continued)

There are many possible exchange interactions in CuWO_4 , and the possible interactions can be divided into four categories according to which sublattices they couple. These interactions are quoted in the first column of table 4 and the corresponding exchange paths associated with each interaction are listed in the second column of table 4; the notation used here is the same as that used in a previous paper [12]. For example the exchange interaction $J_{d[i,j,k]}$ links the Cu ions on sublattice 1 in each magnetic unit cell (the Cu 1 type ions) to the Cu 4 type ions in the magnetic cell at displacement vector $[i, j, k]$, and is also responsible for coupling each Cu 3 type ion to the Cu 2 type ion in the magnetic cell displaced by a vector $[2+i, j, k]$. In the third column of table 4 the exchange interaction is described as ferromagnetic or antiferromagnetic where it has been assumed that interactions linking Cu ions whose spins are aligned parallel to each other are ferromagnetic, while those linking Cu ions whose spins are antiparallel are antiferromagnetic.

The magnetic excitations of CuWO_4 were measured using neutron scattering [12]. Two well defined modes were observed in the antiferromagnetic phase as a direct consequence



(c)

Figure 4. (Continued)

of having four magnetic ions in the magnetic unit cell in the same way that the number of phonon branches is related to the number of atoms in the structural unit cell. By analogy with the phonon case the lower mode is called the acoustic mode and the upper mode the optic mode. The measured dispersion relations were fitted to spin-wave theory to extract the exchange interactions responsible for these excitations, and two possible models arose from the fitting both providing an equally good account of the data. In both models there are weakly coupled alternating chains running in the $[2, -1, 0]$ direction. Some of the dispersion curves are shown in the upper graphs of figure 4 along with the spin-wave theory fit; figure 4(a) shows the dispersion along the chain direction where the energies are large, while perpendicular to this direction the excitations are lower in energy, figure 4(b). The spin-wave intensities calculated using the fitted exchange constants are plotted on the inset graphs and explain why the modes were observed at some points in reciprocal space and not others.

In this paper we shall concentrate on one of the two spin-wave models that explain the excitations in CuWO_4 : this corresponds to model 1 in a previous publication [12] and the

Table 5. The fitted exchange constants from both spin-wave theory and the dimer theory are listed; the same set of exchange interactions are required by both models to fit the data although the values of the exchange constants are different in the two models. The calculated ordered moment and transition temperature obtained from the models have also been tabulated.

	Spin-wave theory	Dimer theory
Intrachain exchanges (meV) $J_{d[-2,1,0]}$	33.6	12.96
$J_{d[0,0,0]}$	8.34	12.49
Intrachain exchanges (meV) $J_{b[0,1,0]}$	-0.52	-0.72
$J_{b[0,0,-1]}$	-2.96	-4.28
Ordered moment (μ_B)	0.550	0.671
Transition temperature (K)	130.7	62.37

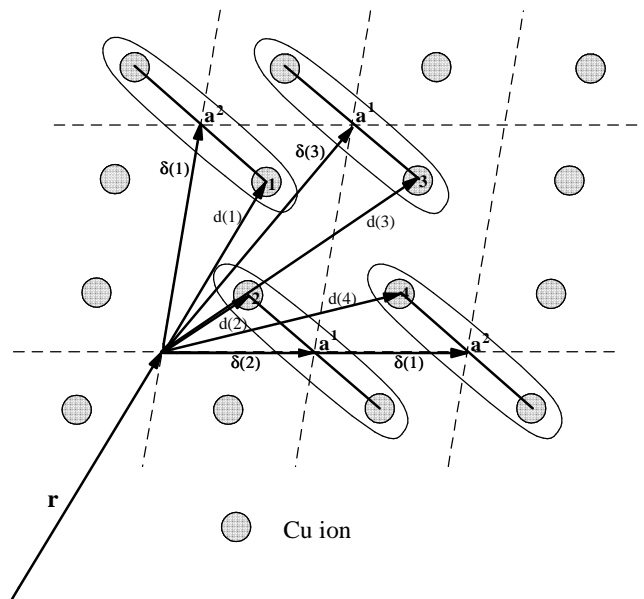


Figure 5. The four Cu ions in the r th magnetic cell are shown; each ion forms part of a dimer and these dimers are also illustrated. The position vectors of the Cu ions of type 1, 2, 3 and 4 are $d(1)$, $d(2)$, $d(3)$ and $d(4)$ respectively and these are marked on the diagram as are the position vectors of the dimers with which they are associated, $\delta(1)$, $\delta(2)$, $\delta(3)$ and $\delta(4)$.

exchange constants for this model are listed in table 5. This model suggests that CuWO_4 can be considered as a dimerized crystal with one large exchange interaction $J_{d[-2,1,0]}$ which couples the Cu ions into antiferromagnetic pairs. This interaction creates two inequivalent dimers per magnetic unit cell which are labelled a^1 and a^2 in figure 3. The a^1 dimers couple Cu 3 type ions to Cu 2 type ions and the a^2 dimers couple Cu 1 type ions to Cu 4 type ions; throughout this paper care has been taken to keep the labelling of the ions within the magnetic unit cell and the notation of the exchange interactions the same as in the previous publication [12].

2.3. The dimer theory applied to CuWO₄

The dimer theory assumes that CuWO₄ is a dimerized compound with a dimer exchange interaction $J_{d[-2,1,0]}$ while its ground state has long-range, antiferromagnetic order. The general Hamiltonian with all possible exchange interactions included, and where the dimer exchange constant is fixed as $J_{d[-2,1,0]}$, is given by

$$H = H_0 + H_1 \quad (6)$$

$$H_0 = \sum_{\mathbf{r}} J_0 [\mathbf{S}_{1,\mathbf{r}+d(1)} \cdot \mathbf{S}_{4,\mathbf{r}+[-2,1,0]+d(4)} + \mathbf{S}_{3,\mathbf{r}+d(3)} \cdot \mathbf{S}_{2,\mathbf{r}+[0,1,0]+d(2)}] \\ - \frac{1}{2} \sum_{\mathbf{r}} \sqrt{J_t^2 - J_0^2} [\mathbf{S}_{1,\mathbf{r}+d(1)}^z + \mathbf{S}_{2,\mathbf{r}+d(2)}^z - \mathbf{S}_{3,\mathbf{r}+d(3)}^z - \mathbf{S}_{4,\mathbf{r}+d(4)}^z] \quad (7)$$

$$H_1 = \sum_{\mathbf{r}} \sum_{i,j,k} [H_{a,\mathbf{r}[i,j,k]} + H_{b,\mathbf{r}[i,j,k]} + H_{c,\mathbf{r}[i,j,k]} + H_{d,\mathbf{r}[i,j,k]}] \\ + \frac{1}{2} \sum_{\mathbf{r}} \sqrt{J_t^2 - J_0^2} [\mathbf{S}_{1,\mathbf{r}+d(1)}^z + \mathbf{S}_{2,\mathbf{r}+d(2)}^z - \mathbf{S}_{3,\mathbf{r}+d(3)}^z - \mathbf{S}_{4,\mathbf{r}+d(4)}^z] \quad (8)$$

where the quantities J_0 and J_t are

$$-J_0 = J_{d[-2,1,0]} \quad (9)$$

$$J_t = \sum_{i,j,k} (2|J_{a[i,j,k]}| + |J_{b[i,j,k]}| + 2|J_{c[i,j,k]}| + |J_{d[i,j,k]}|) - |J_0|. \quad (10)$$

The terms $H_{a,\mathbf{r}[i,j,k]}$, $H_{b,\mathbf{r}[i,j,k]}$, $H_{c,\mathbf{r}[i,j,k]}$ and $H_{d,\mathbf{r}[i,j,k]}$ involve the exchanges categories $J_{a[i,j,k]}$, $J_{b[i,j,k]}$, $J_{c[i,j,k]}$ and $J_{d[i,j,k]}$ respectively and are given by

$$H_{a,\mathbf{r}[i,j,k]} = -J_{a[i,j,k]} [\mathbf{S}_{1,\mathbf{r}+d(1)} \cdot \mathbf{S}_{1,\mathbf{r}+[i,j,k]+d(1)} + \mathbf{S}_{2,\mathbf{r}+d(2)} \cdot \mathbf{S}_{2,\mathbf{r}+[i,j,k]+d(2)}] \\ + \mathbf{S}_{3,\mathbf{r}+d(3)} \cdot \mathbf{S}_{3,\mathbf{r}+[i,j,k]+d(3)} + \mathbf{S}_{4,\mathbf{r}+d(4)} \cdot \mathbf{S}_{4,\mathbf{r}+[i,j,k]+d(4)}] \quad (11)$$

$$H_{b,\mathbf{r}[i,j,k]} = -J_{b[i,j,k]} [\mathbf{S}_{1,\mathbf{r}+d(1)} \cdot \mathbf{S}_{2,\mathbf{r}+[i,j,k]+d(2)} + \mathbf{S}_{3,\mathbf{r}+d(3)} \cdot \mathbf{S}_{4,\mathbf{r}+[i,j,k]+d(4)}] \quad (12)$$

$$H_{c,\mathbf{r}[i,j,k]} = -J_{c[i,j,k]} [\mathbf{S}_{1,\mathbf{r}+d(1)} \cdot \mathbf{S}_{3,\mathbf{r}+[i,j,k]+d(3)} + \mathbf{S}_{3,\mathbf{r}+d(3)} \cdot \mathbf{S}_{1,\mathbf{r}+[2+i,j,k]+d(1)}] \\ + \mathbf{S}_{2,\mathbf{r}+d(2)} \cdot \mathbf{S}_{4,\mathbf{r}+[i,j,k]+d(4)} + \mathbf{S}_{4,\mathbf{r}+d(4)} \cdot \mathbf{S}_{2,\mathbf{r}+[2+i,j,k]+d(2)}] \quad (13)$$

$$H_{d,\mathbf{r}[i,j,k]} = -J_{d[i,j,k]} [\mathbf{S}_{1,\mathbf{r}+d(1)} \cdot \mathbf{S}_{4,\mathbf{r}+[i,j,k]+d(4)} + \mathbf{S}_{3,\mathbf{r}+d(3)} \cdot \mathbf{S}_{2,\mathbf{r}+[2+i,j,k]+d(4)}]. \quad (14)$$

In this Hamiltonian ferromagnetic exchange interactions are defined as positive and antiferromagnetic exchange interactions as negative. The sum over \mathbf{r} is over all the magnetic unit cells in the crystal and $\mathbf{S}_{p,\mathbf{r}+d(p)}$ is the spin operator of the Cu p type ion in the \mathbf{r} th magnetic unit cell at position vector $\mathbf{r} + d(p)$ (figure 5 and table 6). The Hamiltonian has been written as the sum of two terms, H_0 which involves the dimer exchange interaction, and H_1 which involves all the other interactions in the crystal. For the purposes of this dimer theory calculation a term giving the interaction energy of each dimer with the effective, staggered, magnetic field due to the mean-field ordering of the surrounding dimers at $T = 0$ K has been added to H_0 and then subtracted from H_1 . This effective field was discussed in section 2.1 and equations (3), (4) and (5) show that it is of strength $-\sqrt{J_t^2 - J_0^2}/2g_s\mu_B$.

One set of pseudo-boson operators is introduced for each dimer in the crystal. Each set consists of a creation operator and corresponding annihilation operator for the longitudinal excitation and two creation operators and their corresponding annihilation operators for the transverse excitations. There are two different categories of operators in CuWO₄ because of the two inequivalent dimers in each magnetic unit cell: the a^1 operators create and annihilate excitations in the dimers consisting of Cu 3 and Cu 2 ions, while the a^2 operators create and annihilate excitations in the dimers consisting of Cu 1 and Cu 4 ions. The corresponding creation operators are defined by

$$a_{0',\rho}^{n+} |G'_{n,\rho}\rangle = |0'_{n,\rho}\rangle \quad a_{+1',\rho}^{n+} |G'_{n,\rho}\rangle = | + 1_{n,\rho}\rangle \quad a_{-1',\rho}^{n+} |G'_{n,\rho}\rangle = | - 1_{n,\rho}\rangle. \quad (15)$$

Table 6. The position vectors of the four Cu ions within the r th magnetic unit cell $\mathbf{d}(1)$, $\mathbf{d}(2)$, $\mathbf{d}(3)$ and $\mathbf{d}(4)$ are listed along with the types of dimer with which they are associated and the positions of these dimers $\delta(1)$, $\delta(2)$, $\delta(3)$ and $\delta(4)$. The dimer vector δ is the vector connecting the two ions that form each dimer.

Spin	Position of spin	Type of dimer	Position of dimer
$S_{1,r}$	$\mathbf{r} + \mathbf{d}(1)$	a^2	$\mathbf{r} + \delta(1) = \mathbf{r} + \mathbf{d}(1) - \delta/2$
$S_{2,r}$	$\mathbf{r} + \mathbf{d}(2)$	a^1	$\mathbf{r} + \delta(2) = \mathbf{r} + \mathbf{d}(2) - \delta/2$
$S_{3,r}$	$\mathbf{r} + \mathbf{d}(3) = \mathbf{r} + \mathbf{d}(1) + [1, 0, 0]$	a^1	$\mathbf{r} + \delta(3) = \mathbf{r} + \mathbf{d}(1) - \delta/2 + [1, 0, 0]$
$S_{4,r}$	$\mathbf{r} + \mathbf{d}(4) = \mathbf{r} + \mathbf{d}(2) + [1, 0, 0]$	a^2	$\mathbf{r} + \delta(4) = \mathbf{r} + \mathbf{d}(2) + \delta/2 + [1, 0, 0]$
			the dimer vector is $\delta = \mathbf{d}(1) - \mathbf{d}(2) + [1, -1, 0]$

The index n indicates the type of dimer being operated on (1 or 2) and the vector ρ gives the position of this dimer; for example $a_{0',\rho}^{1+}$ excites the a^1 type dimer which is at position vector ρ from the ground state $|G'_{1,\rho}\rangle$ to the longitudinal excited state $|0'_{1,\rho}\rangle$. The destruction operators are similarly defined

$$a_{0',\rho}^{n-} |0'_{n,\rho}\rangle = |G'_{n,\rho}\rangle \quad a_{+1',\rho}^{n-} |1_{n,\rho}\rangle = |G'_{n,\rho}\rangle \quad a_{-1',\rho}^{n-} |1_{n,\rho}\rangle = |G'_{n,\rho}\rangle. \quad (16)$$

For the purposes of calculation these operators adopt Bose statistics and obey the commutation relations

$$[a_{k,\rho}^{n-}, a_{k',\rho'}^{n'+}] = \delta_{\rho,\rho'} \delta_{k,k'} \delta_{n,n'} \quad [a_{k,\rho}^{n-}, a_{k',\rho'}^{n'-}] = 0 \quad [a_{k,\rho}^{n+}, a_{k',\rho'}^{n'+}] = 0 \quad (17)$$

where n and k can take the values $n = 1, 2$; $k = 0, +1, -1$.

Each spin in CuWO₄ forms part of a dimer. Figure 5 shows the r th magnetic cell where the position vectors within the cell of the Cu ions of type 1, 2, 3 and 4 are labelled $\mathbf{d}(1)$, $\mathbf{d}(2)$, $\mathbf{d}(3)$ and $\mathbf{d}(4)$ and the corresponding positions of the dimers they are associated with are labelled $\delta(1)$, $\delta(2)$, $\delta(3)$ and $\delta(4)$. The spin positions are listed in table 6 along with the positions of their corresponding dimers and each dimer is described as type a^1 or a^2 .

The Hamiltonian of CuWO₄ can be transformed from spin operators to dimer operators. The part H_0 which is the sum of the energies of the individual dimers throughout the system becomes

$$H_0 = \sum_r \left(J_t [a_{0',r+\delta(2)}^{1+} a_{0',r+\delta(2)}^{1-} + a_{0',r+\delta(1)}^{2+} a_{0',r+\delta(1)}^{2-}] + \left(\frac{J_t + J_0}{2} \right) [a_{+1,r+\delta(2)}^{1+} a_{+1,r+\delta(2)}^{1-} + a_{-1,r+\delta(2)}^{1+} a_{-1,r+\delta(2)}^{1-} + a_{+1,r+\delta(1)}^{2+} a_{+1,r+\delta(1)}^{2-} + a_{-1,r+\delta(1)}^{2+} a_{-1,r+\delta(1)}^{2-}] \right). \quad (18)$$

H_1 can also be written in terms of dimer operators by rewriting each spin operator in terms of the operators of the dimer with which it is associated. For Cu ions on sublattices $p = 1$ and 2 $S_{p,r+d(p)}^+$ is given by

$$S_{p,r+d(p)}^+ = \frac{1}{\sqrt{2}} (\cos \theta + \sin \theta) (a_{-1,r+\delta(p)}^{n-} + a_{+1,r+\delta(p)}^{n+}) a_{0',r+\delta(p)}^{n-} + \frac{1}{\sqrt{2}} (\cos \theta - \sin \theta) (a_{0',r+\delta(p)}^{n+} a_{-1,r+\delta(p)}^{n-} - a_{+1,r+\delta(p)}^{n+}) \quad (19)$$

where the quantity θ is

$$\cos 2\theta = \frac{J_0}{J_t}. \quad (20)$$

In this equation Cu 1 type ions have $p = 1$ and $n = 2$, while Cu 2 type ions have $p = 2$ and $n = 1$. For Cu ions on sublattices 3 and 4 the transformation is

$$S_{p,r+d(p)}^+ = \frac{1}{\sqrt{2}} (\cos \theta + \sin \theta) (a_{+1,r+\delta(p)}^{n+} + a_{0',r+\delta(p)}^{n+} a_{-1,r+\delta(p)}^{n-}) + \frac{1}{\sqrt{2}} (\cos \theta - \sin \theta) (a_{+1,r+\delta(p)}^{n+} a_{0',r+\delta(p)}^{n-} - a_{-1,r+\delta(p)}^{n-}) \quad (21)$$

where Cu 3 type ions have $p = 3$ and $n = 1$, while Cu 4 type ions have $p = 4$ and $n = 2$. Expressions for $S_{p,r+d(p)}^-$ are found by taking the adjoint of $S_{p,r+d(p)}^+$. The transformation for the $S_{p,r+d(p)}^z$ spin operators on all sublattices is

$$S_{p,r+d(p)}^z = \pm \frac{1}{2} \cos 2\theta (a_{0',r+\delta(p)}^{n-} + a_{0',r+\delta(p)}^{n+}) + \frac{1}{2} a_{+1,r+\delta(p)}^{n+} a_{+1,r+\delta(p)}^{n-} - \frac{1}{2} a_{-1,r+\delta(p)}^{n+} a_{-1,r+\delta(p)}^{n-} \pm \frac{1}{2} \sin 2\theta (1 - 2a_{0',r+\delta(p)}^{n+} a_{0',r+\delta(p)}^{n-} - a_{+1,r+\delta(p)}^{n+} a_{+1,r+\delta(p)}^{n-} + a_{-1,r+\delta(p)}^{n+} a_{-1,r+\delta(p)}^{n-}). \quad (22)$$

The upper sign is taken for Cu 1 and 2 type ions and the lower sign for Cu 3 and 4 type ions. Again Cu 1 type ions have $p = 1, n = 2$; Cu 2 type ions have $p = 2, n = 2$; Cu 3 type ions have $p = 3, n = 1$ and Cu 4 type ions have $p = 4, n = 2$.

Once the Hamiltonian has been expressed in terms of dimer operators (keeping terms of up to order two) it is found to be the sum of two separate Hamiltonians, one depending on the longitudinal operators $a_{0',r+\delta(p)}^{n\pm}$ and the other depending on the transverse operators $a_{+1,r+\delta(p)}^{n\pm}$ and $a_{-1,r+\delta(p)}^{n\pm}$.

$$H = H^L(a_{0',r+\delta(p)}^{n\pm} (n = 1, p = 2, 3; n = 2, p = 1, 4)) + H^T(a_{+1,r+\delta(p)}^{n\pm}, a_{-1,r+\delta(p)}^{n\pm} (n = 1, p = 2, 3; n = 2, p = 1, 4)). \quad (23)$$

H^L arises from the terms S^z and $S^z S^z$ in the Hamiltonian where all the transverse operators cancel leaving just longitudinal operators, while H^T arises from the terms $S^x S^x$ and $S^y S^y$. H^L is the longitudinal part of the Hamiltonian and gives the energy of the longitudinal modes, whereas H^T is the transverse Hamiltonian which governs the behaviour of the transverse modes.

2.3.1. The transverse Hamiltonian. In order to solve the transverse Hamiltonian and obtain the energies of the transverse excitations, the Hamiltonian must undergo two further transformations. First of all, the dimer operators are converted to their Fourier transforms which are given by

$$a_{+1,r+\delta(p)}^{n\pm} = \frac{1}{\sqrt{N}} \sum_Q e^{\pm iQ \cdot (r+\delta(p))} a_{+1,Q}^{n\pm}, \quad a_{-1,r+\delta(p)}^{n\pm} = \frac{1}{\sqrt{N}} \sum_Q e^{\mp iQ \cdot (r+\delta(p))} a_{-1,Q}^{n\pm}. \quad (24)$$

The operator $a_{k,Q}^{n\pm}$ is the Fourier transform, at wavevector Q , of the dimer operator $a_{k,r+\delta(p)}^{n\pm}$ for dimer type n and excitation k ; the upper sign is for creation operators and the lower sign for annihilation operators. When $n = 1, p$ can take the values 2 and 3, while for $n = 2, p$ can take the values 1 and 4. The transverse Hamiltonian is given in terms of $a_{k,Q}^{n\pm}$ in appendix A. The Hamiltonian can be diagonalized to yield the excitations by introducing another transformation which is also described in the appendix. The transverse excitations are found to consist of two doubly degenerate modes with energies $E_{Q,1}^T$ and $E_{Q,2}^T$, given by equations (A13) and (A14). The existence of two excitation branches is a direct consequence of having two dimers per magnetic unit cell.

The excitation energies resulting from the dimer theory have been fitted to the experimentally measured dispersion relations of CuWO_4 by varying the values of the

exchange constants, and are successful in modelling the excitations. The data along with the best fit are shown for some reciprocal space directions in the lower graphs of figure 4 and the fitted exchange constants are listed in table 5. It is interesting to observe that, while an energy gap is predicted by the dimer theory to exist in a dimerized compound with a spin-singlet ground state as a direct consequence of the exchange interactions alone, no gap is predicted by this theory when the ground state is antiferromagnetically ordered. CuWO₄ does in fact have a small energy gap of 1.4 meV (at $T = 13$ K) which probably has its origin in residual unquenched orbital angular momentum. To describe this an extra anisotropy term has been included in the Hamiltonian.

The intensities of the transverse modes have also been calculated in the dimer theory: they are given by the neutron scattering cross-section

$$\frac{d^2\sigma}{d\Omega d\omega} \propto (1 - \hat{Q}_x \hat{Q}_x) S^{xx}(\mathbf{Q}, \omega) + (1 - \hat{Q}_y \hat{Q}_y) S^{yy}(\mathbf{Q}, \omega) \quad (25)$$

where \hat{Q}_x (\hat{Q}_y) is the x (y) component of a unit vector in the direction of \mathbf{Q} . The spin correlation functions $S^{xx}(\mathbf{Q}, \omega)$ and $S^{yy}(\mathbf{Q}, \omega)$ are obtained in appendix A and are given by equation (A15), (A16) and (A17). The intensities of the excitations, computed using the fitted exchange constants for CuWO₄, are shown on the inset graphs in figure 4.

2.3.2. The longitudinal Hamiltonian. The longitudinal Hamiltonian is solved for the longitudinal excitations in a similar way to the transverse Hamiltonian. First of all the dimer operators are converted to their Fourier transforms.

$$a_{0,r+\delta(p)}^{n\pm} = \frac{1}{\sqrt{N}} \sum_{\mathbf{Q}} e^{\pm i\mathbf{Q}\cdot(r+\delta(p))} a_{0,\mathbf{Q}}^{n\pm} \quad (26)$$

and then the Hamiltonian is diagonalized as described in appendix B. The excitations are found to consist of two modes with energies $E_{\mathbf{Q},1}^L$ and $E_{\mathbf{Q},2}^L$ given by equations (B12) and (B13).

The intensities of these modes are given by the neutron scattering cross-section

$$\frac{d^2\sigma}{d\Omega d\omega} \propto (1 - \hat{Q}_z \hat{Q}_z) S^{zz}(\mathbf{Q}, \omega) \quad (27)$$

where \hat{Q}_z is the z component of a unit vector in the direction of \mathbf{Q} and the spin correlation function $S^{zz}(\mathbf{Q}, \omega)$ is given by (B15) and (B16). Only one of the two modes has non-zero intensity at any one point in reciprocal space as discussed in appendix B. One mode is non-zero in the vicinity of the magnetic peaks with reciprocal lattice vectors $\boldsymbol{\tau} = [h_\tau, k_\tau, l_\tau]$ where h_τ is integral, and the other mode is observed around the magnetic peaks where h_τ is half-integral. The resulting single longitudinal mode has a periodicity in reciprocal space that corresponds to the structural unit cell rather than the magnetic unit cell. The longitudinal energies have been calculated using the exchange constants obtained by fitting the transverse modes and are shown in the bottom graphs of figure 4 while the intensity is displayed on the inset plot. The dotted line shows the mode position for a scan in the vicinity of $h_\tau = 1.5$ while the dot-dashed line shows the corresponding scan around $h_\tau = 2.0$. For most wavevectors the longitudinal mode lies above both transverse modes and is generally of lower intensity.

3. Discussion

The dimer theory is successful in accounting for the transverse excitations of CuWO₄. This can be seen from the lower graphs in figure 4 where the energies are correctly reproduced.

The intensities also agree with experimental measurements, for example, in figure 4(b) the lower, transverse acoustic mode was observed from $x = 0$ to $x = 0.15$ where the dimer theory predicts it is strong, but it was not seen at larger x where it is predicted to be weaker; similarly the upper, transverse optic mode was only observed in the region $x = 0.12$ to $x = 0.25$ again in accordance with the intensity simulation. The dimer theory fits can be compared to the spin-wave theory fits which are shown in the upper graphs of figure 4: as can be seen there is negligible difference between the two and it is clearly not possible to distinguish between them from a measurement of the transverse excitations.

The same exchange interactions are required to describe the dispersions of CuWO_4 in the two theories but the values of the constants are different with the intrachain interactions in the dimer theory being both less dimerized and on average of lower strength than those of spin-wave theory, table 5. This is similar to the case of the dimerized spin-singlet system CuGeO_3 where the average of the intrachain exchange constants is approximately a factor of $\sqrt{2}$ smaller in dimer theory than in spin-wave theory, a result that is close to the renormalization factor of $\pi/2$, calculated exactly by des Cloiseaux and Pearson, for the low-lying excitations of a uniform, spin-1/2 chain [11]. The difference in the degree of dimerization between the two models can in part be explained by the fact that in the dimer theory the requirement for antiferromagnetic ordering is $J_t > J_0$, a condition that automatically limits the amount of dimerization that can occur in a weakly coupled, alternating-chain system. In spin-wave theory there is no such constraint and the exchange constants can take any value.

The dimer theory exchange constants are much closer to the values necessary to fit the susceptibility data of CuWO_4 than those of spin-wave theory. The susceptibility of a powdered sample was measured by Doumerc *et al* [14] between 4.2 K and 650 K and the data showed a broad maximum at 85.5 K well above the transition temperature of 24.0 K. These data were compared to the numerical calculations of Duffy and Barr [19] where the susceptibility of an infinite, alternating, spin-1/2 chain was obtained by extrapolation from simulations of finite chains with length of up to ten spins. The fitted exchange constants, $J_0 = -11.56$ meV and $J_1 = -9.246$ meV, are similar to those of the dimer model but do not agree with either the strength or amount of dimerization required by spin-wave theory.

Both the dimer theory and spin-wave theory can be used to determine the transition temperature of CuWO_4 using mean-field theory. The expression for T_N given by spin-wave theory is

$$T_{N,SW} = \frac{1}{4k}(J_t + J_0) \quad (28)$$

where k is the Boltzmann constant. Using the fitted exchange constants (28) gives $T_{N,SW} = 130.67$ K.

The transition temperature of CuWO_4 has also been calculated from the dimer theory. Each dimer in the system is considered as being in the effective, staggered, magnetic field due to the ordering of the surrounding dimers where this ordering is a function of temperature. This effective field was discussed in section 2.1 for the case of $T = 0$ K where it was given by equations (3), (4) and (5). At a finite temperature the field becomes

$$B_I(T) = B_I^z(T) = F(T)/g_s\mu_B \quad (29)$$

$$F(T) = -J_t|\langle S_1^z(T) \rangle| \quad (30)$$

where the ordering parameter $F(T)$ is now calculated from the modulus of the temperature dependent expectation value of the ordered spin of the first Cu ion in the dimer given by the Boltzmann weighting of the expectation value of S_1^z in each of the dimer eigenstates.

These expectation values are listed in the third column of table 2 and the resulting value of $F(T)$ is

$$F(T) = \frac{-J_t \sin(2\theta)}{2} \frac{[e^{\alpha/2kT} - e^{-\alpha/2kT}]}{[e^{\alpha/2kT} + e^{-\alpha/2kT} + 2e^{-J_0/2kT}]} \quad (31)$$

where

$$\tan \theta = \frac{1}{2F} (J_0 - \alpha) \text{ and } \alpha = \sqrt{J_0^2 + 4F^2}. \quad (32)$$

Close to the transition temperature F is small and $\tan \theta \approx -F(T)/J_0$, $\sin \theta \approx -F(T)/J_0$ and $\cos \theta \approx 1$; using these approximations equation (31) becomes

$$1 = \frac{J_t [1 - e^{-J_0/kT}]}{J_0 [1 + 3e^{-J_0/kT}]} \quad T \rightarrow T_{N,D}. \quad (33)$$

The transition temperature calculated from equation (33), using J_t and J_0 obtained from the dimer theory fitting (table 5), is $T_{N,D} = 62.37$ K.

Both the values of the transition temperature calculated in the dimer theory and spin-wave theory are substantially higher than the experimental transition temperature of 24.0 K [14] as is always the case when mean-field theory is applied to a quasi one-dimensional system because mean-field theory cannot account for the quantum fluctuations that disrupt the ordering and lower T_N . Nevertheless it is interesting to note that the transition temperature obtained from the dimer model is significantly closer to the true value than that calculated by spin-wave theory.

Another way in which these two theories can be compared is in terms of the ground state they predict for CuWO₄. The ground state of spin-wave theory is initially assumed to be the Néel state and the excitations are seen as spin-deviations from full spin alignment. When the Hamiltonian is diagonalized the normal modes or magnons are linear combinations of these spin-deviations. The expectation value of the ordered moment at $T = 0$ K can be calculated in the basis of the magnon states [20] and is reduced from the Néel state value due to zero-point fluctuations. For CuWO₄ $\mu_{SW} = 0.19 \mu_B$ (i.e. 19% of the Néel state value) which is much lower than the experimental value of $0.67 \mu_B$ [13]. Linear spin-wave theory overestimates the spin reduction because higher-order terms in the Holstein–Primakoff transformation which would restrict the spin-deviations to lie between the physical limits of S and $-S$ have been neglected. When these terms are incorporated within a mean-field approximation [21] the ordered moment becomes $0.55 \mu_B$ which is much closer to the experimental value.

Unlike spin-wave theory, a reduction in the spin moment is built into the dimer theory right from the start and the staggered magnetic field, equation (3), acting on each dimer to account for the ordering of the surrounding dimers, is proportional to this moment. The spin moment can be calculated from the dimer eigenstates, table 5, and is given by equation (5). Since the condition for antiferromagnetic ordering is $J_t > J_0$, equation (5) is always less than $1/2$ implying that the spin moment is always reduced from its Néel state value of $1/2$. Using the fitted exchange constants for CuWO₄, the ordered moment is found to be $\mu_D = 0.671 \mu_B$, a value that is remarkably close to the experimental value and which is significantly better than the spin-wave result.

The most significant difference between the dimer theory and spin-wave theory is their prediction of longitudinal excitations. The dimer theory predicts one well defined longitudinal mode in CuWO₄ which lies above the transverse modes and has lower intensity than them figure 4. In contrast no longitudinal excitations are expected in linear spin-wave theory although longitudinal scattering can occur if higher-order terms are considered. The

spin correlation function $S^{zz}(\mathbf{Q}, \omega)$ then allows two-magnon processes to occur [22] and this scattering appears as a broad continuum extending above the transverse excitations [23]. The existence of longitudinal modes in dimerized compounds which develop long-range antiferromagnetic order is interesting because such modes are usually only observed close to a magnetic phase transition. A longitudinal mode has however recently been predicted by Schulz in the antiferromagnetic phase of the weakly coupled, spin-1/2, uniform chain compound KCuF_3 [24]. In this calculation the coupling between chains has been treated in mean-field theory. This mode lies above the transverse mode and has an energy of 10.6 meV at the zone-centre and 54 meV at the zone boundary. The dimer theory can also be applied to KCuF_3 , even though this is not a dimerized compound, and it accurately models the transverse modes and predicts an ordered moment of size $0.43 \mu_B$ which is reasonably close to the experimental value of $0.54 \mu_B$. It also predicts a longitudinal mode similar to that of Schulz with an energy of 16.9 meV at the zone-centre and 55.5 meV at the zone boundary. The presence of a longitudinal mode in KCuF_3 is yet to be confirmed experimentally. Inelastic neutron scattering measurements show increased intensity at the zone-centre around 13 meV which could be attributed to this mode although the existing data has been explained adequately by higher-order spin-wave theory [23].

The longitudinal excitations could also be investigated in CuWO_4 in order to find out whether spin-wave theory or the dimer theory provides the best model of this compound. Figure 4 shows that the longitudinal mode predicted by the dimer theory is strongest at the antiferromagnetic zone-centre $[1.5, 0, 0]$ and other regions where it may be observable are around $[2.25, -0.5, 0]$ and $[1.5, 0, 0.5]$. Measurements at equivalent wavevectors in different Brillouin zones could be used to establish whether any observed scattering was longitudinal in nature. It would also be appropriate to search for the longitudinal mode in a dimerized compound where there is a large reduction in the ordered spin moment. This is because the intensity of the scattering increases as the spin reduction increases making the mode easier to find. A suitable compound would be Zn-doped CuGeO_3 , small amounts of Zn reduce the spin-Peierls transition temperature and cause an additional phase transition to long-range antiferromagnetic order at low temperatures. For example 2.4% Zn-doped CuGeO_3 has $T_{s-p} = 11.6$ K and $T_N = 4.4$ K and the ordered moment at $T = 0.5$ K is $0.24 \mu_B$ [25] a value that is considerably lower than that of either CuWO_4 or KCuF_3 .

Finally the dimer theory can be compared to theories of uncoupled, spin-1/2 antiferromagnetic chains. A characteristic feature of these theories is deconfinement where a spin-1 magnon type excitation is unstable and disintegrates into two spin-1/2 solitons which can move apart. Experimentally this is observed as a continuum of scattering. The top diagrams in figure 6 show a spin-1/2, Ising chain: this has two alternative Néel states that are degenerate and are labelled $|N1\rangle$ and $|N2\rangle$ on chains A and B. Excitations are formed by reversing spins from their Néel state positions. On chain C a single spin has been flipped over from its position in the $|N1\rangle$ Néel state and the resulting excitation has spin = 1 and energy = J , where J is the intrachain exchange constant. A state where several consecutive spins are reversed can have exactly the same values of spin and energy as the single-spin-flip state. For example the excitation illustrated on chain D where five spins (marked in bold) have been flipped over also has an energy of J . An alternative way of describing these excitations is as two spin-1/2 domain walls enclosing a region with an alternative Néel states. For an Ising chain where there is also a small transverse exchange the eigenstates are formed from combinations of states like those illustrated and can be regarded as moving domain walls or solitons [26]. In the spin-1/2 Heisenberg chain there is a similar deconfinement of spin waves into spin-1/2 solitons called spinons [27]. These spinons which are analogous to the domain walls in the Ising system are only allowed to

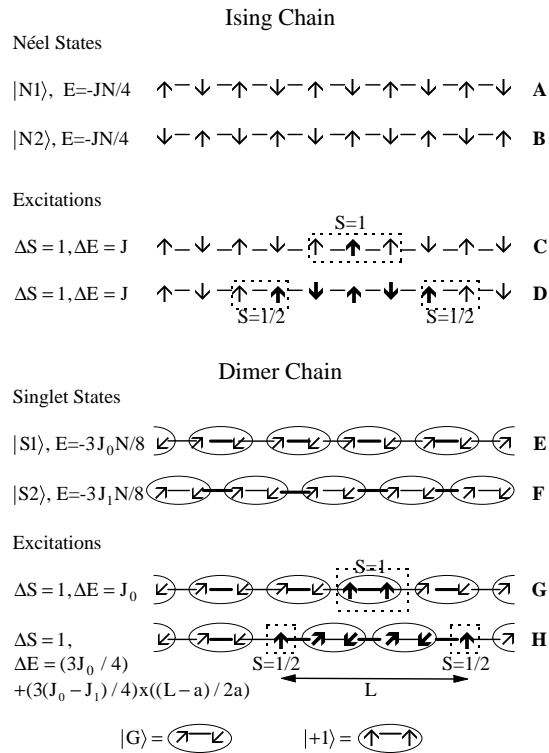


Figure 6. The two degenerate Néel states and possible excited states of an Ising chain are illustrated and the values of spin and energy of the excitations are also given. Similarly the two alternative singlet states and possible excitations of a dimer chain are shown. The singlet states have different energies as indicated and the excitation pictured on chain H has an energy proportional to L , the separation of the free spins.

exist over half the Brillouin zone and are created and destroyed as pairs. Experimentally they are observed as a continuum of scattering spread out in energy.

In any real, one-dimensional compound there is always interchain coupling which often results in long-range, three-dimensional, antiferromagnetic order at low temperatures. Ordering reduces deconfinement because the interaction energy of the reversed spins with their neighbours on nearby chains must now be considered, and this energy is proportional to the number of these spins. For example, with interchain coupling, the excitation on chain D, figure 6, would have a higher energy than that on chain C, because more spins are reversed against the mean field of the neighbouring chains. The lowest-lying eigenstates now correspond to superpositions of single-spin-flip states like C, with only a limited mixing of the higher-order states which lead to deconfinement, like D. The excitations are therefore often adequately approximated as well defined, spin-1, magnons.

The dimer theory presented in this paper has similarities with the resonating valence bond concept first developed for insulating antiferromagnets by Anderson [28], which has been successful in accounting for the ground state energies in a number of magnetic systems. The idea is that the ground state is a superposition of states where all the spins are paired up into singlets, different states being characterized by different pairing combinations. In the dimer theory only one of these states is chosen as the ground state: this is the lowest-lying

state where the singlets are between spins connected by the dimer exchange interaction as shown on the alternating chain, diagram E, figure 6; here the energy per spin is $-3J_0/8$. In the next-lowest-lying state the singlets are between spins coupled by the weaker intrachain exchange interaction, chain F, figure 6, which has an energy of $-3J_1/8$ per spin. An excitation can be created by exciting a dimer into one of its excited triplet levels chain G, and the analogy, for a singlet ground state, of the excitations shown on chain D of the Ising system is illustrated on chain H where two free spins surround a region of the alternative singlet ground state (marked in bold). Unlike in the Ising chain, the energy of chain H increases as the separation L of the two free spins increases because the two ground states have different energies: this energy is given in figure 6. Large separations are not favoured energetically and the lowest-lying eigenstates of the dimer chain are dominated by single dimer excitations like G, with contributions from states like H limited by the degree of alternation in the exchange interactions along the chain. As a result the deconfinement is reduced from that of a uniform, spin-1/2 antiferromagnet and the excitations should be less spread out in energy. For a compound like CuWO_4 , where there is both alternation along the chains and long-range antiferromagnetic order, the excitations are well defined as is indeed observed experimentally [12]. As a consequence, our approximation of working with only the linear terms in the Hamiltonian which are responsible for these magnon type excitations is justified and the higher-order terms which would produce a continuum of excitations are much less important.

Both spin-wave and the dimer theory presented here are mean-field theories which are best suited to higher-dimensional systems. It would therefore be interesting to consider the action of the higher-order terms in the spin-Hamiltonian [30] in order to quantify the validity of the bilinear approximation and further theoretical work on this issue would be most welcome. The structure of these terms are dependent on the geometry of the spin system and cancellations of terms may occur as happens for the trilinear terms in a spin-ladder geometry [31].

4. Summary

A theory has been presented for a dimerized, spin-1/2 magnetic system which has an antiferromagnetically ordered ground state. The excitations calculated by this method consist of one doubly degenerate transverse mode and one longitudinal singlet for each non-equivalent dimer in the magnetic unit cell. This dimer theory has been used to model the measured dispersion relations in the antiferromagnetic phase of the alternating-chain compound CuWO_4 and provides a good fit to the data. Detailed comparison has been made between this theory and spin-wave theory and, whereas both are successful in describing the excitations, the values of the transition temperature and the reduced moment at $T = 0$ K calculated in the dimer theory are closer to the experimental values than those calculated in spin-wave theory. An important difference between the two models lies in their prediction of longitudinal excitations; in spin-wave theory these are seen as two-magnon events resulting in a continuum of scattering, while in the dimer theory one well defined mode is predicted. A measurement of the longitudinal excitations should distinguish between these models.

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Appendix A

In this appendix the transverse Hamiltonian of CuWO₄ is diagonalized and the transverse excitations are derived; the spin correlation functions are also calculated in terms of the normal mode co-ordinates. The transverse Hamiltonian written in terms of the Fourier transforms of the dimer operators has the form

$$H^T = \sum_Q H_Q^T. \quad (A1)$$

If we consider those terms that are quadratic in the operators and ignore higher-order terms the H_Q^T are

$$H_Q^T = \sum_{t,t'} \frac{1}{2} \alpha_{Q,t,t'} c_{t,Q}^+ c_{t',Q}^+ + \frac{1}{2} \alpha_{Q,t,t'}^* c_{t,Q}^- c_{t',Q}^- + \beta_{Q,t,t'} c_{t,Q}^+ c_{t',Q}^- \quad (A2)$$

where in this notation $c_{1,Q}^\pm = a_{+1,Q}^{1\pm}$, $c_{2,Q}^\pm = a_{-1,Q}^{1\pm}$, $c_{3,Q}^\pm = a_{+1,Q}^{2\pm}$, and $c_{4,Q}^\pm = a_{-1,Q}^{2\pm}$. For CuWO₄ the $\alpha_{Q,t,t'}$ and $\beta_{Q,t,t'}$ are given by

$$\beta_{Q,1,1} = \beta_{Q,2,2} = \beta_{Q,3,3} = \beta_{Q,4,4} = \left(\frac{J_0 + J_t}{2} \right) + \sum_{i,j,k} (-J_{a[i,j,k]} \cos(\mathbf{Q} \cdot \mathbf{d}_{a[i,j,k]}) + \frac{1}{2} J_{d[i,j,k]} \cos(2\theta) \cos(\mathbf{Q} \cdot \mathbf{d}_{d[i,j,k]})) \quad (A3)$$

$$\alpha_{Q,1,4} = \alpha_{Q,4,1} = \alpha_{Q,2,3} = \alpha_{Q,3,2} = \sum_{i,j,k} (-J_{c[i,j,k]} \cos(\mathbf{Q} \cdot \mathbf{d}_{c[i,j,k]}) + \frac{1}{2} J_{b[i,j,k]} \cos(2\theta) \cos(\mathbf{Q} \cdot \mathbf{d}_{b[i,j,k]})) \quad (A4)$$

$$\beta_{Q,1,3} = \beta_{Q,3,1} = \beta_{Q,2,4} = \beta_{Q,4,2} = + \sum_{i,j,k} \left(-\frac{1}{2} J_{b[i,j,k]} [\cos(\mathbf{Q} \cdot \mathbf{d}_{b[i,j,k]}) + i \sin(2\theta) \sin(\mathbf{Q} \cdot \mathbf{d}_{b[i,j,k]})] + J_{c[i,j,k]} \cos(2\theta) \cos(\mathbf{Q} \cdot \mathbf{d}_{c[i,j,k]}) \right) \quad (A5)$$

$$\alpha_{Q,1,2} = \alpha_{Q,2,1} = \alpha_{Q,3,4}^* = \alpha_{Q,4,3}^* = \sum_{i,j,k} \left(-\frac{1}{2} J_{d[i,j,k]} [\cos(\mathbf{Q} \cdot \mathbf{d}_{d[i,j,k]}) - i \sin(2\theta) \sin(\mathbf{Q} \cdot \mathbf{d}_{d[i,j,k]})] + J_{a[i,j,k]} \cos(2\theta) \cos(\mathbf{Q} \cdot \mathbf{d}_{a[i,j,k]}) \right) \quad (A6)$$

where

$$\mathbf{d}_{a[i,j,k]} = -[i, j, k]; \mathbf{d}_{b[i,j,k]} = -[1+i, j-1, k]; \mathbf{d}_{c[i,j,k]} = -[i+i, j, k]; \mathbf{d}_{d[i,j,k]} = [2+i, j-1, k]. \quad (A7)$$

This Hamiltonian is solved by introducing a third transformation to diagonalize it [26]

$$c_{t,Q}^- = \sum_s (\zeta_{s,Q}^- u_{t,s,Q} + \zeta_{s,Q}^+ v_{t,s,Q}^*) \quad c_{t,Q}^+ = \sum_s (\zeta_{s,Q}^+ u_{t,s,Q}^* + \zeta_{s,Q}^- v_{t,s,Q}) \quad (A8)$$

where $\zeta_{s,Q}^+$ ($\zeta_{s,Q}^-$) is the creation (annihilation) operator of the s th mode. The $u_{t,s,Q}$ and $v_{t,s,Q}$ in equation (A8) are related to each other and the energies by the following set of homogeneous equations:

$$\begin{aligned} \sum_{t'} ((\beta_{Q,t,t'} - E_{Q,s}^T \delta_{t,t'}) u_{t',s,Q} + \alpha_{Q,t,t'} v_{t',s,Q}) &= 0 \\ \sum_{t'} ((\alpha_{Q,t,t'}^* u_{t',s,Q} + (\beta_{Q,t,t'}^* + E_{Q,s}^T \delta_{t,t'})) v_{t',s,Q}) &= 0 \end{aligned} \quad (A9)$$

where $E_{Q,s}^T$ is the energy of the s th transverse mode and $u_{t',s,Q}$ and $v_{t',s,Q}$ are subject to the following conditions:

$$\sum_t (u_{t,s,Q} u_{t,s',Q}^* - v_{t,s,Q} v_{t,s',Q}^*) = \delta_{s,s'} \quad \sum_t (u_{t,s,Q} v_{t,s',Q} - u_{t,s',Q} v_{t,s,Q}) = 0 \quad (\text{A10})$$

The equations (A9) form a matrix equation which can be split into two identical matrix equations of the form

$$\begin{pmatrix} \beta_{Q,1,1} & \beta_{Q,1,3} & \alpha_{Q,1,2} & \alpha_{Q,1,4} \\ \beta_{Q,1,3}^* & \beta_{Q,1,1} & \alpha_{Q,1,4} & \alpha_{Q,1,2}^* \\ -\alpha_{Q,1,2}^* & -\alpha_{Q,1,4} & -\beta_{Q,1,1} & -\beta_{Q,1,3}^* \\ -\alpha_{Q,1,4} & -\alpha_{Q,1,2} & -\beta_{Q,1,3} & -\beta_{Q,1,1} \end{pmatrix} \begin{pmatrix} u_{s,Q}^1 \\ u_{s,Q}^2 \\ v_{s,Q}^1 \\ v_{s,Q}^2 \end{pmatrix} = E_{Q,s}^T \begin{pmatrix} u_{s,Q}^1 \\ u_{s,Q}^2 \\ v_{s,Q}^1 \\ v_{s,Q}^2 \end{pmatrix}. \quad (\text{A11})$$

The eigenvectors in these two equations are

$$\begin{pmatrix} u_{s,Q}^1 \\ u_{s,Q}^2 \\ v_{s,Q}^1 \\ v_{s,Q}^2 \end{pmatrix} = \begin{pmatrix} u_{1,s,Q} \\ u_{3,s,Q} \\ v_{2,s,Q} \\ v_{4,s,Q} \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} u_{s,Q}^1 \\ u_{s,Q}^2 \\ v_{s,Q}^1 \\ v_{s,Q}^2 \end{pmatrix} = \begin{pmatrix} u_{2,s,Q} \\ u_{4,s,Q} \\ v_{1,s,Q} \\ v_{3,s,Q} \end{pmatrix}. \quad (\text{A12})$$

Equation (A10) can be solved to obtain the eigenvalues $E_{Q,s}^T$ and the eigenvectors $\{u_{s,Q}^n, v_{s,Q}^n\}$. For CuWO_4 the transverse Hamiltonian yields two doubly degenerate modes with energies given by

$$E_{Q,1}^T = \sqrt{C_{1,Q}^T - C_{2,Q}^T} \quad E_{Q,2}^T = \sqrt{C_{1,Q}^T + C_{2,Q}^T} \quad (\text{A13})$$

where the quantities $C_{1,Q}^T$ and $C_{2,Q}^T$ are

$$\begin{aligned} C_{1,Q}^T &= \beta_{Q,1,1}^2 - \alpha_{Q,1,4}^2 + \beta_{Q,1,3} \beta_{Q,1,3}^* - \alpha_{Q,1,2} \alpha_{Q,1,2}^* \\ C_{2,Q}^T &= (4\beta_{Q,1,1}^2 \beta_{Q,1,3} \beta_{Q,1,3}^* - 2\beta_{Q,1,3} \beta_{Q,1,3}^* \alpha_{Q,1,2} \alpha_{Q,1,2}^* + 4\alpha_{Q,1,4}^2 \alpha_{Q,1,2} \alpha_{Q,1,2}^* \\ &\quad + (\alpha_{Q,1,2}^* \beta_{Q,1,3})^2 + (\alpha_{Q,1,2} \beta_{Q,1,3}^*)^2 - 4\beta_{Q,1,1} \alpha_{Q,1,2} \alpha_{Q,1,4} \beta_{Q,1,3} \\ &\quad - 4\beta_{Q,1,1} \alpha_{Q,1,2} \alpha_{Q,1,4} \beta_{Q,1,3}^*)^{1/2}. \end{aligned} \quad (\text{A14})$$

The spin correlation functions can be calculated for these modes: they are given by

$$\begin{aligned} S^{xx}(\mathbf{Q}, \omega) &= \sum_s |\langle E_{Q,s}^T | S_Q^x | \Gamma \rangle|^2 \delta(\hbar\omega - E_{Q,s}^T) \\ \text{and} \quad S^{yy}(\mathbf{Q}, \omega) &= \sum_s |\langle E_{Q,s}^T | S_Q^y | \Gamma \rangle|^2 \delta(\hbar\omega - E_{Q,s}^T) \end{aligned} \quad (\text{A15})$$

where $|E_{Q,s}^T\rangle$ is the wavefunction of the state with eigenvalue $E_{Q,s}^T$ and $|\Gamma\rangle$ is the ground state. $S_{Q,s}^x$ and $S_{Q,s}^y$ are the Fourier transforms of the x and y components of the spin and are calculated by passing the spin operators through the same transformations that were used in the energy calculation given by equations (19), (21), (24) and (A8). The quantities $|\langle E_{Q,s}^T | S_Q^x | \Gamma \rangle|$ and $|\langle E_{Q,s}^T | S_Q^y | \Gamma \rangle|$ expressed in terms of the eigenvectors $\{u_{s,Q}^n, v_{s,Q}^n\}$ are

$$|\langle E_{Q,s}^T | S_Q^x | \Gamma \rangle|^2 = |\langle E_{Q,s}^T | S_Q^y | \Gamma \rangle|^2 = \Lambda \Lambda^* \quad (\text{A16})$$

where

$$\begin{aligned} \Lambda &= \frac{1}{2\sqrt{2}} e^{-i\tau \cdot d(1)} e^{-iQ' \cdot \delta/2} [(\cos\theta + \sin\theta)[u_{s,Q'}^2 + (-1)^{2h_\tau} v_{s,Q'}^1] \\ &\quad - (\cos\theta + \sin\theta)[v_{s,Q'}^2 + (-1)^{2h_\tau} u_{s,Q'}^1] - \frac{1}{2\sqrt{2}} e^{-i\tau \cdot d(2)} \\ &\quad \times e^{+iQ' \cdot \delta/2} [(\cos\theta + \sin\theta)[u_{s,Q'}^1 + (-1)^{2h_\tau} v_{s,Q'}^2] \\ &\quad - (\cos\theta + \sin\theta)[v_{s,Q'}^1 + (-1)^{2h_\tau} u_{s,Q'}^2]]. \end{aligned} \quad (\text{A17})$$

Q' and τ are defined by $Q = Q' + \tau$, where τ is a reciprocal lattice vector of the magnetic unit cell such that Q' is a vector lying within the first Brillouin zone; τ is given by $\tau = [h_\tau, k_\tau, l_\tau]$. δ is the vector connecting the two Cu ions in the dimer and is equal to $\delta = d(1) - d(2) + [1, -1, 0]$. The intensities of the transverse modes can be computed from the neutron scattering cross-section, equation (25), using these spin correlation functions.

Appendix B

In this appendix the longitudinal Hamiltonian of CuWO₄ is diagonalized and the longitudinal excitations are derived; the spin correlation function is also calculated in terms of the normal mode co-ordinates. The longitudinal Hamiltonian written in terms of the Fourier transforms of the dimer operators has the form

$$H^L = \sum_Q H_Q^L. \quad (B1)$$

If we consider only terms that are quadratic in the operators and ignore higher-order terms the H_Q^L are

$$H_Q^L = \sum_{t,t'} \frac{1}{4} \alpha_{Q,t,t'} [c_{t,Q}^- c_{t',-Q}^- + c_{t,-Q}^- c_{t',Q}^- + c_{t,Q}^+ c_{t',-Q}^+ + c_{t,-Q}^+ c_{t',Q}^+] \\ + \frac{1}{2} \beta_{Q,t,t'} [c_{t,Q}^+ c_{t',Q}^- + c_{t,-Q}^+ c_{t',-Q}^-] \quad (B2)$$

where in this notation $c_{1,Q}^\pm = a_{0,Q}^{1\pm}$, $c_{2,Q}^\pm = a_{0,Q}^{2\pm}$. For CuWO₄ the $\alpha_{Q,t,t'}$ and $\beta_{Q,t,t'}$ are given by

$$\beta_{Q,1,1} = \beta_{Q,2,2} = J_t + \sum_{i,j,k} \frac{1}{2} \cos^2(2\theta) [2J_{a[i,j,k]} \cos(Q \cdot d_{a[i,j,k]}) - J_{d[i,j,k]} \cos(Q \cdot d_{d[i,j,k]})] \quad (B3)$$

$$\beta_{Q,1,2} = \beta_{Q,2,1} = \sum_{i,j,k} \frac{1}{2} \cos^2(2\theta) [J_{b[i,j,k]} \cos(Q \cdot d_{b[i,j,k]}) - 2J_{c[i,j,k]} \cos(Q \cdot d_{c[i,j,k]})] \quad (B4)$$

$$\alpha_{Q,1,1} = \alpha_{Q,2,2} = \sum_{i,j,k} \frac{1}{2} \cos^2(2\theta) [2J_{a[i,j,k]} \cos(Q \cdot d_{a[i,j,k]}) - J_{d[i,j,k]} \cos(Q \cdot d_{d[i,j,k]})] \quad (B5)$$

$$\alpha_{Q,1,2} = \alpha_{Q,2,1} = \sum_{i,j,k} \frac{1}{2} \cos^2(2\theta) [J_{b[i,j,k]} \cos(Q \cdot d_{b[i,j,k]}) - 2J_{c[i,j,k]} \cos(Q \cdot d_{c[i,j,k]})] \quad (B6)$$

where

$$d_{a[i,j,k]} = -[i, j, k]; d_{b[i,j,k]} = -[1+i, j-1, k]; d_{c[i,j,k]} = -[i+i, j, k]; \\ d_{d[i,j,k]} = [2+i, j-1, k]. \quad (B7)$$

This Hamiltonian can be solved by introducing another transformation to diagonalize it which is

$$c_{t,Q}^- = \sum_s (\zeta_{s,Q}^- u_{t,s,Q} + \zeta_{s,-Q}^+ v_{t,s,Q}^*) \quad c_{t,-Q}^+ = \sum_s (\zeta_{s,-Q}^+ u_{t,s,Q}^* + \zeta_{s,Q}^- v_{t,s,Q}) \quad (B8)$$

where $\zeta_{s,Q}^+$ ($\zeta_{s,Q}^-$) is the creation (annihilation) operator of the s th mode. The $u_{t,s,Q}$ and $v_{t,s,Q}$ in equation (B8) are related to each other and the energies by the following set of homogeneous equations:

$$\sum_{t'} ((\beta_{Q,t,t'} - E_{Q,s}^L \delta_{t,t'}) u_{t',s,Q} + \alpha_{Q,t,t'} v_{t',s,Q}) = 0 \\ \sum_{t'} ((\alpha_{Q,t,t'} u_{t',s,Q} + (\beta_{Q,t,t'} + E_{Q,s}^L \delta_{t,t'}) v_{t',s,Q}) = 0. \quad (B9)$$

The reality of the matrix elements $\alpha_{Q,t,t'}$ and $\beta_{Q,t,t'}$, and their invariance to the transformation $Q \rightarrow -Q$ has been used in simplifying the expressions $E_{Q,s}^L$ is the energy of the s th longitudinal mode and the $u_{t',s,Q}$ and $v_{t',s,Q}$ are subject to the conditions

$$\sum_t (u_{t,s,Q} u_{t,s',Q}^* - v_{t,s,Q} v_{t,s',Q}^*) = \delta_{s,s'} \quad \sum_t (u_{t,s,Q} v_{t,s',Q} - u_{t,s',Q} v_{t,s,Q}) = 0. \quad (\text{B10})$$

The equations (B9) form the matrix equation

$$\begin{pmatrix} \beta_{1,1} & \beta_{1,2} & \alpha_{1,1} & \alpha_{1,2} \\ \beta_{1,2} & \beta_{1,1} & \alpha_{1,2} & \alpha_{1,1} \\ -\alpha_{1,1} & -\alpha_{1,2} & -\beta_{1,1} & -\beta_{1,2} \\ -\alpha_{1,2} & -\alpha_{1,1} & -\beta_{1,2} & -\beta_{1,1} \end{pmatrix} \begin{pmatrix} u_{1,s,Q} \\ u_{2,s,Q} \\ v_{1,s,Q} \\ v_{2,s,Q} \end{pmatrix} = E_{Q,s}^L \begin{pmatrix} u_{1,s,Q} \\ u_{2,s,Q} \\ v_{1,s,Q} \\ v_{2,s,Q} \end{pmatrix}. \quad (\text{B11})$$

This can be solved to obtain the eigenvalues $E_{Q,s}^L$ and the eigenvectors $\{u_{t,s,Q}, v_{t,s,Q}\}$. For CuWO_4 the longitudinal Hamiltonian yields two modes with energies given by

$$E_{Q,1}^L = \sqrt{C_{1,Q}^L - C_{2,Q}^L} \quad E_{Q,2}^L = \sqrt{C_{1,Q}^L + C_{2,Q}^L} \quad (\text{B12})$$

where the quantities $C_{1,Q}^L$ and $C_{2,Q}^L$ are

$$\begin{aligned} C_{1,Q}^L &= (\beta_{Q,1,1})^2 + (\beta_{Q,1,2})^2 - (\alpha_{Q,1,1})^2 - (\alpha_{Q,1,2})^2 \\ C_{2,Q}^L &= \beta_{Q,1,1}\beta_{Q,1,2} - \alpha_{Q,1,1}\alpha_{Q,1,2} \end{aligned} \quad (\text{B13})$$

and the eigenvectors take the form

$$\begin{pmatrix} u_{1,1,Q} \\ u_{2,1,Q} \\ v_{1,1,Q} \\ v_{2,1,Q} \end{pmatrix} = \begin{pmatrix} u_{1,Q} \\ u_{1,Q} \\ v_{1,Q} \\ v_{1,Q} \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} u_{1,2,Q} \\ u_{2,2,Q} \\ v_{1,2,Q} \\ v_{2,2,Q} \end{pmatrix} = \begin{pmatrix} u_{2,Q} \\ -u_{2,Q} \\ v_{2,Q} \\ -v_{2,Q} \end{pmatrix}. \quad (\text{B14})$$

The spin correlation function can be calculated for these modes: it is given by

$$S^{zz}(Q, \omega) = \sum_s |\langle E_{Q,s}^L | S_Q^z | \Gamma \rangle|^2 \delta(\hbar\omega - E_{Q,s}^L) \quad (\text{B15})$$

where $|E_{Q,s}^L\rangle$ is the wavefunction of the state with eigenvalue $E_{Q,s}^L$, and $|\Gamma\rangle$ is the ground state. S_Q^z is the Fourier transform of the z component of the spin and is calculated by passing the spin operators through the same transformations that were used in the energy calculation, equations (22), (26) and (B8). The quantity $\langle E_{Q,s}^L | S_Q^z | \Gamma \rangle$, expressed in terms of the eigenvectors $\{u_{s,Q}, v_{s,Q}\}$ is

$$\begin{aligned} \langle E_{Q,s}^L | S_Q^z | \Gamma \rangle &= \frac{1}{2} \cos(2\theta) e^{-i\tau \cdot d(1)} e^{-iQ' \cdot \delta/2} [u_{s,Q} + v_{s,Q}] [1 \pm (-1)^{2h_\tau}] \\ &\quad + \frac{1}{2} \cos(2\theta) e^{-i\tau \cdot d(2)} e^{-iQ' \cdot \delta/2} [u_{s,Q'} + v_{s,Q'}] [1 \pm (-1)^{2h_\tau}]. \end{aligned} \quad (\text{B16})$$

Q' and τ are defined by $Q = Q' + \tau$ where τ is a reciprocal lattice vector of the magnetic unit cell such that Q' is a vector lying within the first Brillouin zone; τ is given by $\tau = [h_\tau, k_\tau, l_\tau]$. δ is the vector connecting the two Cu ions in the dimer and is equal to $\delta = d(1) - d(2) + [1, -1, 0]$. The upper sign in this expression is for the mode $s = 1$ and the lower sign is for $s = 2$. The intensities of the longitudinal excitations can be computed from the neutron scattering cross-section, equation (25), using this spin correlation function. Because of the term $[1 \pm (-1)^{2h_\tau}]$ only one of the longitudinal modes has non-zero intensity at any one point in reciprocal space: the $s = 1$ mode is non-zero when h_τ is integral and the $s = 2$ mode is non-zero when H_τ is half-integral.

References

- [1] Hutchings M T, Samuelson E J, Shirane G and Hirakawa K 1969 *Phys. Rev.* **188** 919
- [2] Tennant D A, Cowley R A, Nagler S E and Tsvetik A M 1995 *Phys. Rev. B* **52** 13 368
- [3] Schultz H J 1986 *Phys. Rev. B* **34** 6372
- [4] Hase M, Terauchi I and Uchinokura K 1993 *Phys. Rev. Lett.* **70** 3651
- [5] Nishi M, Fujita O and Akimitsu J 1994 *Phys. Rev. B* **50** 6508
- [6] Regnault L P, Aïn M, Hennion B, Dhahenne G and Revcolevschi A 1996 *Phys. Rev. B* **53** 5579
- [7] Regnault L P, Lorenzo J E, Grenier B, Aïn M, Hennion B, Renard J P, Dhahenne G and Revcolevschi A at press
- [8] Uhrig G S and Schultz H J 1996 *Phys. Rev. B* **53** R9624
- [9] Cowley R A, Lake B and Tennant D A 1996 *J. Phys.: Condens. Matter* **8** L179
- [10] Fujita O, Akimitsu J, Nishi M and Kakurai K 1995 *Phys. Rev. Lett.* **74** 1677
- [11] des Cloizeaux J and Pearson J J 1962 *Phys. Rev. B* **128** 2131
- [12] Lake B, Tennant D A, Cowley R A, Axe J D and Chen C K 1996 *J. Phys.: Condens. Matter* **8** 8613
- [13] Forsyth J B, Wilkinson C and Zvyagin A I 1991 *J. Phys.: Condens. Matter* **3** 8433
- [14] Doumerc J P, Dance J M, Chaminade J P, Pouchard M, Hagemuller P and Krussanova M 1981 *Res. Bull.* **16** 985
- [15] Affleck I 1989 *J. Phys.: Condens. Matter* **1** 3047
- [16] Kilhborg L and Gebert E 1970 *Acta Crystallogr. B* **2** 1020
- [17] Weitzel H 1970 *Solid State Commun.* **8** 2071
- [18] Wilkinson C and Sprague M J 1977 *Z. Kristallogr.* **145** 96
- [19] Duffy W and Barr K P 1967 *Phys. Rev. B* **165** 647
- [20] Anderson P W 1952 *Phys. Rev. B* **86** 694
- [21] Ishikawa T and Ogouchi T 1975 *Prog. Theor. Phys.* **54** 1281
- [22] Heilmann I U, Kjems J K, Endoh Y, Reiter G F, Shirane G and Birgeneau R J 1981 *Phys. Rev. B* **24** 3939
- [23] Tennant D A, Nagler S E, Welz D, Shirane G and Yamada K 1995 *Phys. Rev. B* **52** 13 381
- [24] Schulz H J 1996 *Phys. Rev. Lett.* **77** 2790
- [25] Coad S, Lussier J-G, McMorro D F and Paul D McK 1996 *J. Phys.: Condens. Matter* **8** 6251
- [26] Ishimura N and Shiba H 1980 *Prog. Theor. Phys.* **63** 743
- [27] Faddeev L D and Takhtajan 1981 **85A** 375
- [28] Anderson P W 1973 *Mater. Res. Bull.* **8** 153
- [29] Vonsovskii S V *Magnetism* vol 2 (New York: Halsted-Wiley) ch 22
- [30] Chubnikov A V 1991 *Phys. Rev. B* **43** 3337
- [31] Tennant D A 1997 private communication