**LETTER TO THE EDITOR**

# Models of excitations in CuGeO₃

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**Abstract.** The excitations of CuGeO₃ are discussed using a model in which pairs of Cu spins are in a spin-singlet state and excitations are made to the excited triplet states. Unless the exchange constants are known independently, the dispersion curves cannot be distinguished experimentally from those of conventional spin waves. The models and conventional spin-wave theory give very different values for the exchange constants which are calculated. Extensions of the calculations to include multi-excitation processes and other systems are suggested.

Ever since Hase *et al* (1993) reported that CuGeO₃ undergoes a spin–Peierls transition, there has been renewed interest in the properties of materials undergoing this type of transition and whether spin–Peierls states might occur in other materials. In this letter we discuss the nature of the excitations from a spin–Peierls state and the extent to which they can be distinguished from the excitations of a conventional antiferromagnet. The excitations of CuGeO₃ were measured by Nishi *et al* (1994) and by Regnault *et al* (1995) using neutron scattering techniques and were interpreted in terms of the linear spin-wave theory for antiferromagnets. We show that the measurements can also be interpreted in terms of a linearized theory of the triplet excitations from a dimerized spin–Peierls state, and deduce the values for the exchange constants of this model.
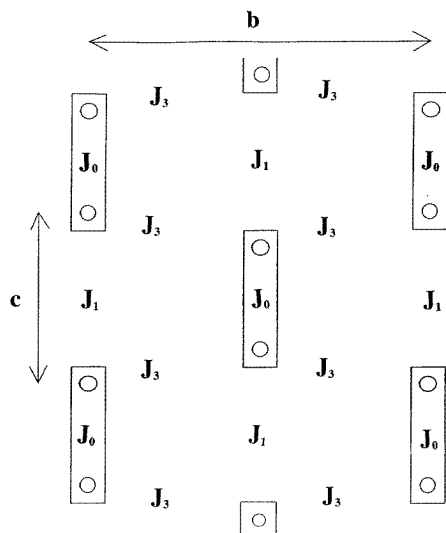


**Figure 1.** The *bc* plane of CuGeO₃ showing only the Cu atoms. The rectangular boxes show the dimerized pairs, and the exchange constants are listed between the appropriate Cu atoms.

Above 14 K, CuGeO$_3$ has an orthorhombic crystal structure. There are strong antiferromagnetic exchange interactions between the Cu atoms in the $c$-direction due to the O ligands between them, leading to a nearly one-dimensional magnetic system. Below 14 K, new Bragg reflections with indices $(h/2, k, \ell/2)$ were observed by Kamimura *et al* (1994) and by Pouget *et al* (1994) and the low-temperature structure was solved by Hirota *et al* (1994) and is shown in figure 1. The Cu atoms along the $c$-axis chains are dimerized leading to two different intra-chain exchange constants. Hase *et al* (1993) showed that this dimerization results in a spin–Peierls structure below 14 K. which has no average magnetic moment but pairs of Cu $(S = \frac{1}{2})$ spins forming a spin-singlet state.

The magnetic model that we have used for CuGeO$_3$ is illustrated in figure 1 with exchange interactions between the $S = \frac{1}{2}$ spins having Heisenberg character. The intra-chain interactions are described by the Hamiltonian

$$\mathcal{H} = \sum_\ell J_0 \boldsymbol{S}(2\ell) \cdot \boldsymbol{S}(2\ell + 1) + \sum_\ell J_1 \boldsymbol{S}(2\ell + 1) \cdot \boldsymbol{S}(2\ell + 2) \tag{1}$$

where we shall assume $J_0 > J_1$ and $\ell$ is the index of the dimerized unit cell along the chain. The model also includes Heisenberg exchange interactions between nearest neighbours in the $a$-direction, $J_2$, and $b$-direction, $J_3$, as shown in figure 1.

In the spin–Peierls state the two Cu spins at $2\ell$ and $2\ell + 1$ form a spin singlet, $\phi_g(\ell)$, with $T(\ell) = |\boldsymbol{S}(2\ell) + \boldsymbol{S}(2\ell + 1)| = 0$, and an energy of $-\frac{3}{4}J_0$. The excited states of the pair are a spin triplet of states with an energy above the ground state of $J_0$, $T(\ell) = 1$, and wavefunctions $\phi_{-1}(\ell)$, $\phi_0(\ell)$ and $\phi_1(\ell)$ where the indices give the eigenvalues of $T_z(\ell)$ in the arbitrary $z$-direction. The excitations of the linear chain—equation (1)—have been discussed by several authors using Hartree–Fock techniques and computer simulations as reviewed by Bonner and Blotze (1982). We shall use the pseudo-boson techniques developed by Grover (1964) and others but extended to apply to the spin–Peierls state. The method proceeds by introducing operators $a_{-1}^+(\ell)$, $a_0^+(\ell)$ and $a_1^+(\ell)$ which excite the spins in the $\ell$th unit cell to one of the excited triplet states of pair $\ell$ while analogous annihilation operators destroy these excitations. When the Hamiltonian is rewritten in terms of these operators the terms involving $J_0$ become

$$\mathcal{H}_1 = -\frac{3}{4}J_0 + J_0 \sum_\ell \left( a_{-1}^+(\ell)a_{-1}(\ell) + a_0^+(\ell)a_0(\ell) + a_1^+(\ell)a_1(\ell) \right). \tag{2}$$

The second term in equation (1) can also be rewritten in terms of these operators but the results are both more complex and more approximate. The operator $S_z(2\ell)$ has a matrix element of $\frac{1}{2}$ connecting the states $\phi_g(\ell)$ and $\phi_0(\ell)$ while that of $S_z(2\ell + 1)$ has a matrix element of $-\frac{1}{2}$, so within this manifold

$$S_z(2\ell) = \frac{1}{2} \left( a_0^+(\ell) + a_0(\ell) \right) + \cdots \mathrm{O}(a^3) \tag{3}$$

$$S_z(2\ell + 1) = -\frac{1}{2} \left( a_0^+(\ell) + a_0(\ell) \right) + \cdots \mathrm{O}(a^3).$$

Using these results the $S_z$-part of the second term in equation (1) becomes

$$\mathcal{H}_2 = -\frac{1}{4}J_1 \sum_\ell \left( a_0^+(\ell) + a_0(\ell) \right) \left( a_0^+(\ell + 1) + a_0(\ell + 1) \right). \tag{4}$$

Similar expressions can be obtained for the $S_x$- and $S_y$-terms and these involve $a_1(\ell)$ and $a_{-1}(\ell)$.

The energy of the excitations can now be found from equations (2) and (4) for the $T_z = 0$ part of the triplet states by diagonalizing the pseudo-boson Hamiltonian to give

$$(\hbar\omega(\boldsymbol{q}))^2 = J_0 \left( J_0 - 2J(\boldsymbol{q}) \right) \tag{5}$$
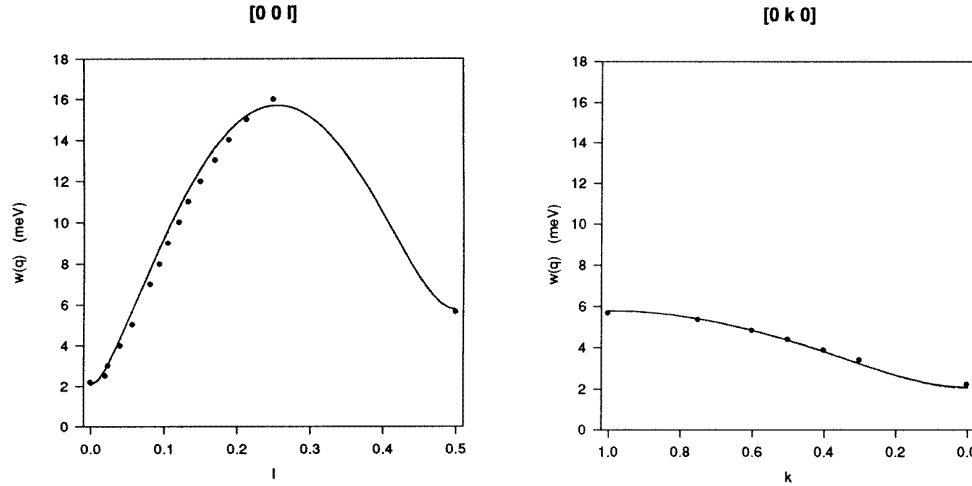
**[0 0 l]**            **[0 k 0]**



**Figure 2.** The dispersion relations for the excitations in $CuGeO_3$ calculated for the model illustrated in figure 1. The solid points show the energies measured by Nishi *et al* (1994).

where, if we extend the analysis to include the inter-chain terms in the model,

$$J(\boldsymbol{q}) = \tfrac{1}{2} J_1 \cos(2\boldsymbol{q} \cdot \boldsymbol{c}) + J_2 \cos(\boldsymbol{q} \cdot \boldsymbol{a}) \cos(\boldsymbol{q} \cdot \boldsymbol{c}) + J_3 \cos(\boldsymbol{q} \cdot \boldsymbol{b}/2) \cos(\boldsymbol{q} \cdot \boldsymbol{c}). \tag{6}$$

This result can only be valid if the structure is stable against these excitations, which implies that

$$J_0 > J_1 + 2|J_2| + 2|J_3|.$$

Equations (5) and (6) were deduced for the excitations to the $T_z = 0$ part of the triplet. Since the magnetic system is isotropic in spin space, the other two branches must have identical excitation energies, so the predicted excitation spectrum is a triplet branch, as was shown experimentally by Fujita *et al* (1995) by observing the splitting of the excitations on application of a magnetic field. In figure 2 we show the dispersion relation calculated with the exchange constant chosen to have the values

$$J_0 = 11.5 \pm 0.2 \text{ meV}$$
$$J_1 = 9.9 \pm 0.2 \text{ meV}$$
$$J_2 = 0 \pm 0.03 \text{ meV}$$
$$J_3 = 0.63 \pm 0.05 \text{ meV}$$

which were chosen to give a good description of the experimental measurements by Nishi *et al* (1994) and Regnault *et al* (1995).

The exchange constants satisfy the stability criterion. The difference in the exchange constant along the chain direction due to the dimerization is 14% even though the difference in the atomic distances is only 0.85% (Hirota *et al* 1994), showing that the exchange constants are very much dependent upon small changes in the local environment. The constant $J_2$ is small but possibly ferromagnetic showing that the magnetic system would favour a ferromagnetic arrangement of the dimers in the chains separated by the lattice constant $a$ as found for the magnetic structures of doped $CuGeO_3$ by Lussier *et al* (1995). The antiferrodistortive coupling between the chains separated in the $a$-direction of pure $CuGeO_3$ presumably arises because the coupling to the lattice gives the minimum

of the total—lattice and magnetic—energy for the wavevector in reciprocal-lattice units $q = (\frac{1}{2}, 1, \frac{1}{2})$ rather than for the wavevector favoured by the purely magnetic system, $q = (0, 1, \frac{1}{2})$.
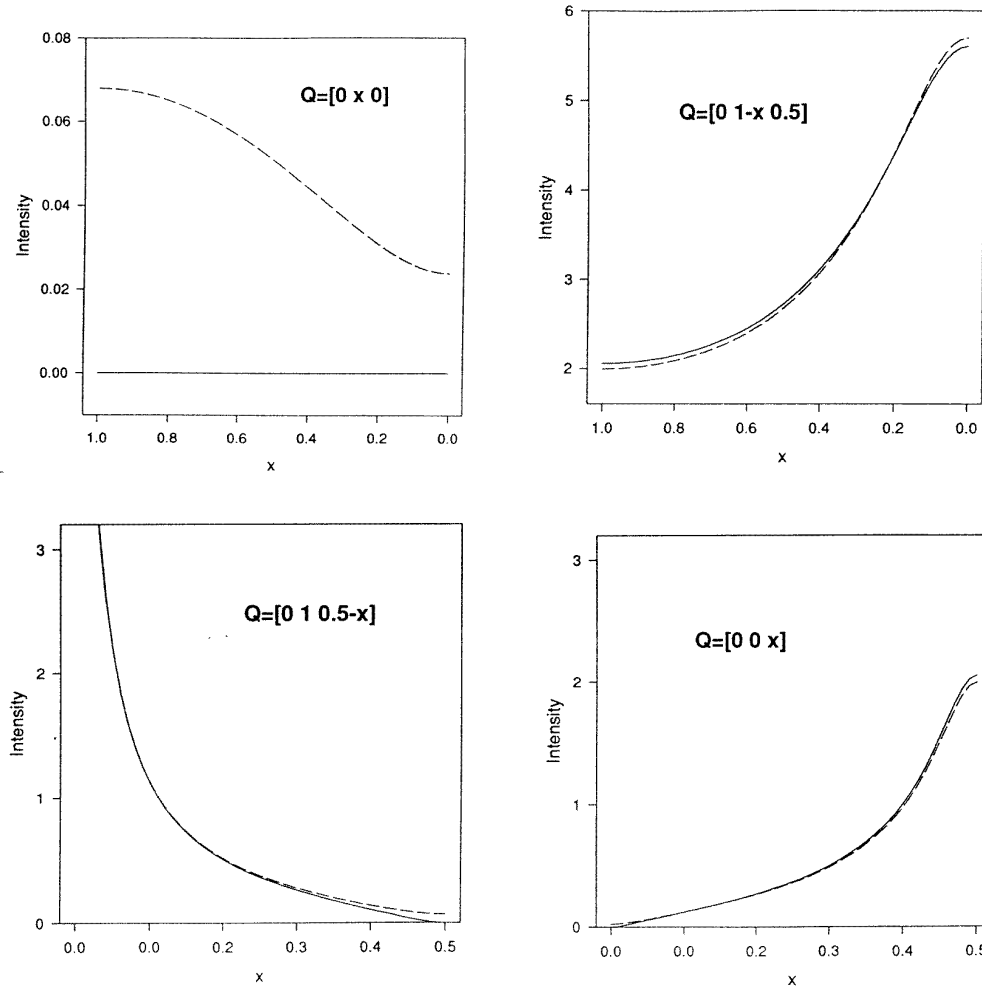


**Figure 3.** The magnitude of the $\langle S_z S_z \rangle$ correlation functions for various directions in reciprocal space (solid line). The dashed line shows $\frac{2}{3} \langle S_x S_x \rangle$ calculated using the linearized spin-wave model described in the text.

The model can also be used to calculate the intensity of the neutron scattering as a function of the wavevector transfer, $Q$. The amplitude of the scattering depends for the $T_z = 0$ excitations on the amplitude

$$\sum_\ell S_z(\ell) \exp \mathrm{i} Q \cdot R(\ell).$$

This expression is transformed to creation and annihilation operators by using equation (3) and summing over the dimerized pairs of spins. The creation operators are evaluated to

give the $\langle S_z S_z \rangle$ part of the scattering cross-section as

$$\tfrac{1}{2} \sin^2 \left( \frac{\boldsymbol{Q} \cdot \boldsymbol{c}}{2} \right) (J_0 - \hbar\omega(\boldsymbol{q}))^2 \big/ \big( \hbar\omega(\boldsymbol{q}) \, (J_0 - J(\boldsymbol{q}) - \hbar\omega(\boldsymbol{q})) \big) \tag{7}$$

where we have assumed that the change in the atomic positions is negligible on dimerization. These intensities are illustrated in figure 3 as functions of the wavevector, and the intensity is zero whenever the $Q_c = 2n\pi/c$, due to the form factor of the dimers.

It is interesting to compare these results with those for a simple antiferromagnetic ordering. The molecular-field energy in the fully antiferromagnetically ordered state is $-\tfrac{1}{4}(J_0 + J_1 + 2J_2 + 2J_3)$ for each pair of spins, which for the parameters of CuGeO$_3$ gives a state that is less stable than the spin–Peierls state $(-\tfrac{3}{4}J_0)$ discussed above. Following Nishi *et al* (1994), the excitations can be modelled if $J_0$ and $J_1$ are taken to be equal at $j_0$ and a single-site anisotropy, $E_A$, is introduced. Linearized spin-wave theory then gives the spin-wave energies as

$$(\hbar\omega_{sw}(\boldsymbol{q}))^2 = (E_A + j_0 + j_2 + j_3)^2 - \left( j_0 \cos(\boldsymbol{q} \cdot \boldsymbol{c}) + j_2 \cos(\boldsymbol{q} \cdot \boldsymbol{a}) + j_3 \cos\left( \boldsymbol{q} \cdot \frac{\boldsymbol{b}}{2} \right) \right) \tag{8}$$

where we have denoted the exchange constants by $j_0$, $j_2$ and $j_3$. At first sight this expression is very different from that given by equations (4) and (5) and so a measurement of the excitation frequencies might provide a way of distinguishing between the different ground states and models. There is, however, no independent way of determining the exchange constants, and equation (8) can be rewritten as

$$\begin{aligned}
(\hbar\omega_{sw}(\boldsymbol{q}))^2 = {} & \left( (E_A + j_0 + j_2 + j_3)^2 - \frac{j_0^2}{2} \right) - \frac{j_0^2}{2} \cos(2\boldsymbol{q} \cdot \boldsymbol{c}) \\
& - 2j_0 \cos(\boldsymbol{q} \cdot \boldsymbol{c}) \left( j_2 \cos(\boldsymbol{q} \cdot \boldsymbol{a}) + j_3 \cos\left( \boldsymbol{q} \cdot \frac{\boldsymbol{b}}{2} \right) \right) \\
& - \left( j_2 \cos(\boldsymbol{q} \cdot \boldsymbol{a}) + j_3 \cos\left( \boldsymbol{q} \cdot \frac{\boldsymbol{b}}{2} \right) \right)^2
\end{aligned} \tag{9}$$

where it is apparent that the first three terms have exactly the same structure as equations (5) and (6) and with appropriate choice of the exchange constants become identical. Indeed we have calculated the energies given by equation (8) with $j_0 = 15.08$ meV, $j_2 = 0$, $j_3 = 0.48$ meV and $E_A = 0.136$ meV, which parameters give energies for the excitations with $\boldsymbol{q} = (0, 0, 0)$, $(0, 0, 0.25)$ and $(0, 1, 0)$ identical to those shown in figure 2. The results for the energies of the excitations for the two models then differ by no more than 0.03 meV for any wavevector examined. Clearly it is not possible to distinguish between these two models in figure 2 or by measuring the excitation energies, unless there is an independent way of determining the exchange constants. Despite this similarity, the values of the intra-chain exchange constants obtained from the spin-wave model are approximately $\sqrt{2}$ larger than those of the spin-triplet model. This difference is apparent if the expressions for the maximum energies of the excitations are compared. For the singlet–triplet model, this energy is approximately $\sqrt{2}J_0$ and for the spin-wave model it is $j$. This can also be compared with the result $\pi J/2$ for the maximum energy of the $S = \tfrac{1}{2}$ antiferromagnetic chain obtained by des Cloizeaux and Pearson (1962). Since $\sqrt{2}$ and $\pi/2$ are fairly similar it suggests that the ground state of the antiferromagnetic chain is composed largely of spin singlets and is closer to a spin–Peierls state than to the fully aligned antiferromagnetic state.

The intensity of the scattering from the excitations has been calculated using the spin-wave model, and in figure 3 the results for $\frac{2}{3}\langle S_x S_x \rangle$ are compared with those for the singlet–triplet model. The results are strikingly similar except for when $Q_c = 0$, figure 3, or $nc^*$ in an extended-zone scheme when, in the singlet–triplet model, the form factor of the dimer, $\sin^2(Q \cdot c/2)$ of equation (7) is zero, while the corresponding intensity of the spin-wave model is small but non-zero. In a more refined calculation the zero of the intensity would enable the separation of the dimers to be determined and would not occur precisely at $nc^*$ but would be displaced due to the dimerization. It would therefore be of interest to measure the intensities of the excitations close to the 'nuclear' lattice points as these differ for the two models, but the intensities are very weak and difficult to measure.

Apart from these differences in the intensities, the clearest difference between the excitations from a spin-singlet state and those from an antiferromagnetic state is that the former are a triplet of states and the latter a doublet and that they can be split by a magnetic field as shown by Fujita *et al* (1995) for CuGeO$_3$. Another difference is in the angular dependence of the intensities, because the spin-triplet intensities are the same for the $\langle S_x S_x \rangle$, $\langle S_y S_y \rangle$ and $\langle S_z S_z \rangle$ correlation functions, whereas if the spin direction for the antiferromagnetic state is the $z$-direction, the spin-wave excitations occur only in the $\langle S_x S_x \rangle$ and $\langle S_y S_y \rangle$ correlation functions. In order to normalize for this difference in figure 3 we plotted two thirds of the intensity calculated for the $\langle S_x S_x \rangle$ correlation function. In practice the scattering is composed of only the spin components perpendicular to the wavevector transfer, $Q$, and so for the spin-wave intensities the appropriate factor is $\frac{1}{2}(1 + Q_z^2/Q^2)$ instead of $\frac{2}{3}\langle S_x S_x \rangle$. This angular dependence of the intensities arises directly from the broken symmetry of the antiferromagnetic phase.

The spin–Peierls singlet–triplet model can be extended in several different ways. One is to include the effects of many excitation processes on the scattering. The expansion of the $S_z$-operators in equation (3) has only included the leading linear terms but the next terms are of third order in the boson operators. It therefore follows that there are no direct two-excitation processes and that the leading many-excitation process extends in energy up to three times the maximum energy of equations (5) and (6). Also the dimer form factor $\sin(Q \cdot c/2)$ applies to the multi-excitation processes and so these are predicted to have negligible intensity when $Q_c = 2\pi n/c$. We plan to perform detailed calculations, but both predictions are consistent with recent measurements made by Arai *et al* (1995).

Secondly, the theory can be extended to the region where neither the spin–Peierls nor the fully aligned antiferromagnetic state is the ground state.

$$J_0 < J_1 + 2J_2 + 2J_3 < 2J_0.$$

The ground state is then an admixture of the dimer ground state $\phi_g$ and of one of the triplet states and has a net ordered antiferromagnetic moment, but that moment is considerably less than the total spin (Bleaney 1963). The ordered moment splits the degeneracy of the triplet of excited states leading to a pair of transverse spin waves and a singlet longitudinal mode. Such a model might be applicable to systems where there is a reduced moment and in which there is one particular strong exchange interaction.

In conclusion we have calculated the excitation spectrum of CuGeO$_3$ using a singlet spin ground state and a triplet of excited states. The results are very difficult to distinguish experimentally from those of linearized spin-wave theory. They do nevertheless give a good description of the excitations in CuGeO$_3$ and allow us to make a number of predictions about the intensities and the properties of the excitations. The theory can be extended and is applicable to other systems in which there is a large difference in the exchange interactions.

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