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A quantitative determination of magnetic fluctuations in $CuGeO_3$

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Abstract. A polarised neutron scattering investigation has been carried out on a powder sample of $CuGeO_3$ within the temperature range of 1.5 K to 600 K. The magnetic scattering has been separated from all other contributions by using polarised neutrons and polarisation analysis and placed onto an absolute scale. At low temperatures the long wavelength components of the paramagnetic response are suppressed consistent with the formation of Cu dimers in which the magnetic moments are correlated antiferromagnetically. This form of the scattering persists to temperatures well above the dimerisation temperature $T_{sp} \sim 14$ K. However as the temperature is raised the intensity of the long wavelength spin fluctuations increases and above ∼150 K they are the dominant feature in the wave vector dependence of the response. At all temperatures the observed scattering extrapolates smoothly to the $Q = 0$ value given by the uniform susceptibility. Consequently the thermal variation of the uniform susceptibility arises from the evolution of the long wavelength magnetic fluctuations. At large wave vectors the energy dependence of the scattering revealed that the response occurs below 16 meV in agreement with the reported maximum magnetic excitation energy at the zone boundary in the ground state. However the total magnetic scattering is significantly less than that expected for a local moment system suggesting that the spectrum of thermal and quantum fluctuations overlap.

PACS. 75.20.Ck Nonmetals – 75.40.Gb Dynamic properties (dynamic susceptibility, spin waves, spin diffusion, dynamic scaling, etc.) – 78.70.Nx Neutron inelastic scattering

Introduction

Low dimensional systems exhibit many unusual physical properties due to the increased importance of fluctuation phenomena of both quantum as well as thermal origin. These fluctuations are strongest in 'one' dimension but still have important consequences in 'quasi one' dimensional systems in which the coupling to the other spatial dimensions is weak. Interest in these quasi one-dimensional systems has increased, the inorganic compound $CuGeO_3$ having gained most attention. This compound is typically labelled as a 'spin-Peierls' system. The effect occurs in crystals containing antiferromagnetically coupled one-dimensional chains of spin 1/2 ions for which Peierls predicted the occurrence of an instability towards a modulated phase, the simplest case being a dimerisation. If the modulation is driven by the dependence of the exchange interaction on atomic distance, as a result of magneto-elastic coupling, the transition is known as spin-Peierls. Initially this interest focussed on organic compounds such as TTF-CuBDT [1], TTF-AuBDT [2] or MEM(TCNQ) [3] where unpaired electrons on TTF^+ or TCNQ-ions with localised spin 1/2 are responsible for the dimerisation. More recently inorganic insulating compounds $CuGeO_3$ [4] and NaV_2O_5 [5] have also been reported to exhibit a transition to a dimerised phase below T_{sp}. The dimerisation process is primarily observed in the lattice properties leading to a lowering of the crystal symmetry without the occurrence of long-range magnetic order. However the microscopic origin for the phase transition remains unresolved. An open question still remains as to whether the magnetic moments are the dominant variables causing the lattice to dimerise through the dependence of the exchange interactions on atomic distance. A precondition for this scenario to hold is that the integrated magnetic response must remain close to the sum rule $\gamma NS(S+1)$ where S is the value of the spin, N the number of spins present and the factor γ is of order 4/3 1.7 barn. This last value corresponds to the total cross section expected for $S = 1/2$ without correction for the Cu^{2+} magnetic form factor. An alternative scenario is that the Cu atoms become non magnetic in the dimerised phase, with the lattice itself providing the dominant variables for the change in crystal symmetry. This would be revealed by a marked decrease of the integrated magnetic response when lowering the temperature with the magnetic fluctuations being transferred to higher energies than that

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expected for a Heisenberg model. These two possibilities can be investigated using polarised neutron scattering with polarisation analysis to determine the temporal and spatial dependence of the magnetic response as a function of temperature. By placing the magnetic scattering onto an absolute scale, and integrating over all wave vectors in the Brillouin zone and up to the characteristic energy scale set by the magnetic coupling, the magnitude of the response can be determined and the influence of quantum fluctuations established. The results of such an investigation on $CuGeO_3$ at temperatures between 1.5 and 600 K are reported here.

Physical properties

Boucher and Regnault (1996) [6] have published a comprehensive review of the properties of $CuGeO_3$. Above the transition $CuGeO_3$ crystallises in an orthorhombic structure with space group (Pbmm) and lattice parameters at room temperature of $a = 4.81$ Å, $b = 8.47$ Å and $c = 2.941$ Å [7]. With two formula units in the primitive cell, the structure comprises of CuO_2 and GeO_4 chains along the c axis. "$Cu^{2+}(S = 1/2)$" ions are located at the centre of edge sharing oxygen atoms forming a square. The nearest neighbour intra chain coupling occurs by weak covalent Cu-O-Cu exchange paths. The magnetic chains are separated by distorted GeO_4 octahedra along the b axis producing an exchange path of Cu-O-Ge-O-Cu and along the a-axis Cu-O-O-Cu. This would lead to antiferromagnetic coupling along the b and c-axes being stronger than that along a. On cooling to 20 K the $Cu(O(2))_2$ ribbons are reported to rotate around the c-axis thus modifying the exchange paths [8]. X-ray [9] and neutron diffraction measurements [10] have revealed superlattice reflections resulting from the dimerisation of the lattice. Under the influence of a magnetic field three structurally distinct phases are found to occur in the low temperature dimerised phase [11]. Below the transition $T_{sp} \sim 14$ K the exchange interaction alternates along the chain and a finite energy gap is reported to open. The uniform magnetic susceptibility in the principal crystallographic directions drops rapidly to zero [4] as the temperature is reduced below 60 K. In the ground state no static long-range magnetic order occurs. The thermal variation of the magnetic susceptibility $\chi(T)$ is similar to that expected for a low dimensional Heisenberg system. However there is poor agreement with the observed $\chi(T)$ and the predictions of the Bonner-Fisher model [12] nor is the thermal variation consistent with Curie-Weiss behaviour [13]. The discrepancy is thought to arise from a coupling of the magnetic and lattice degrees of freedom or frustration arising from antiferromagnetic nearest neighbour interactions [14]. Significant magnetostriction is observed at the transition [15,16] and specific heat measurements reveal that the transition is depressed to lower temperatures under the influence of an external magnetic field [17]. Magnetic excitations take place by population of states with an energy gap of 2.1 meV at 0 K. The magnetic response has been investigated using a number of techniques including neutron scattering [18,19] and ESR [20,21]. The dispersion along the principal crystallographic axis has been determined yielding an antiferromagnetic intra chain exchange constant J_c of ∼121 K and inter chain interactions of $J_b/J_c \sim 0.1$, which is close to T_{sp}, and $J_a/J_c \sim -0.01$. A continuum of excitations was found to lie above the dispersive modes [22] and more recently a new magnetic mode (optic mode) has been reported [23].

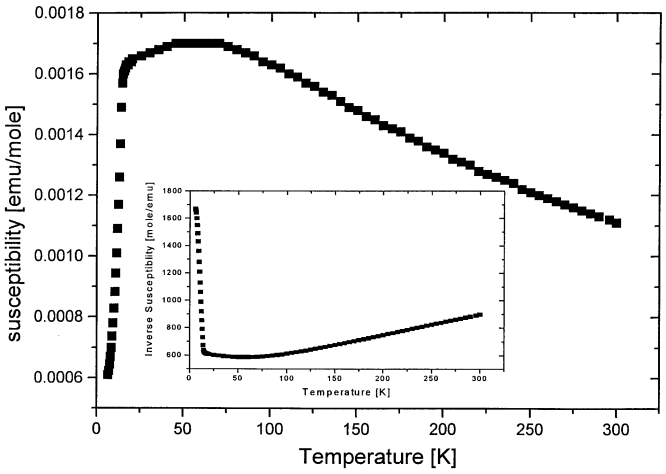

Fig. 1. The magnetic susceptibility and inverse susceptibility (inset) of $CuGeO_3$ as a function of temperature. If a Curie-Weiss variation is assumed above ∼100 K this leads to a spin $S \sim 0.8$.

Experimental

A polycrystalline powder sample of $CuGeO_3$ was prepared by reacting in air CuO and GeO_2 powder at 1000 °C in a platinum crucible. The starting powders were both of $5N$ purity and purchased from Johnson Matthey. X-ray and neutron diffraction measurements confirmed that the resultant sample of $CuGeO_3$ was single phase with the reported orthorhombic crystallographic structure. The bulk susceptibility was measured in a field of 0.1 T over the temperature range 4 to 300 K using a SQUID magnetometer manufactured by Quantum Design. The results, which are presented in Figure 1, are in excellent agreement with those reported by other groups [4,13].

20g of the powder were used for the polarised neutron measurements on D7 at the ILL in Grenoble. The availability of polarised neutrons and polarisation analysis combined with a multidetector facility makes D7 a powerful instrument for the study of magnetic fluctuations, particularly if the cross section is small. Using a wavelength of 4.84 Å (3.5 meV) the 32 detectors enabled a simultaneous measurement of the response over the wave vector range $0.1 < Q < 2.5$ Å^{-1}. Polarisation of the incident beam and analysis of the scattered beam, by each of the 32 detectors, was made using polarising supermirrors. A coil placed in the incident beam before the sample allowed the neutron spin to be reversed. Three mutually

perpendicular Helmholtz coils around the specimen position enabled the incident neutron spin to be rotated along the axis of the three coils. The efficiency of the 32 detectors was determined using the scattering from a standard vanadium specimen. A quartz glass sample was used to determine the polarisation efficiency of each detector/mirror arrangement. The average flipping ratio of the 32 detector systems was found to be 30 ± 1.5. For measurements below 300 K the powder sample was contained in a thin walled aluminium tube located in a helium flow cryostat. A non-inductively wound furnace was used for the high temperature measurements at 600 K. The scattering from the sample was placed on an absolute scale using the vanadium normalisation. This procedure was verified using the nuclear spin incoherent scattering from the sample. Despite the uncertainty in the reported values of the nuclear spin incoherent cross section of germanium the observed nuclear incoherent scattering falls within the range of values quoted in the literature [24,25].

An unambiguous separation of the paramagnetic scattering from all other contributions was made using the XYZ method [26] and the vector nature of the magnetisation-neutron interaction. Only the magnetic component is dependent on the relative orientation of the scattering vector, so by measuring the spin flip (SF) and non spin flip (NSF) scattering associated with the X, Y and Z directions the magnetic contribution can be extracted by subtracting the following partial cross sections

$$\langle \mathrm{d}\sigma_{\mathrm{para}} \rangle = \left\langle \mathrm{d}\sigma_x^{\mathrm{NSF}} \right\rangle + \left\langle \mathrm{d}\sigma_y^{\mathrm{NSF}} \right\rangle - 2 \left\langle \mathrm{d}\sigma_z^{\mathrm{NSF}} \right\rangle \quad (1)$$

and

$$\langle \mathrm{d}\sigma_{\mathrm{para}} \rangle = - \left\langle \mathrm{d}\sigma_x^{\mathrm{SF}} \right\rangle - \left\langle \mathrm{d}\sigma_y^{\mathrm{SF}} \right\rangle + 2 \left\langle \mathrm{d}\sigma_z^{\mathrm{SF}} \right\rangle, \quad (2)$$

where the z-axis is taken to be vertical.

The paramagnetic component can be obtained from either the spin flip or the non-spin flip scattering. Usually the spin flip channel is used to extract the magnetic scattering since it contains fewer contributions, essentially only the magnetic and nuclear spin incoherent components.

The polarised neutron technique not only enables the isothermal determination of the magnetic cross section but also its spatial and temporal dependence. If the scattering is placed on an absolute scale then the measurements provide a powerful test of theory. The experiment on $CuGeO_3$ was concerned with both the wave vector and energy dependence of the magnetic response.

If relativistic effects are unimportant and spin is conserved the observed scattering will extrapolate to the cross section at $Q = 0$ given by the uniform susceptibility χ *i.e.* the $\omega = 0$ susceptibility. Thus as $Q \to 0$ the spectrometer D7 is able to integrate over all scattering for all temperatures used in the study. The spin-spin correlation function $\langle \mathbf{S_q} \cdot \mathbf{S_{-q}} \rangle$ at $Q = 0$ is given by $\sum_j \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle = 3 k_{\mathrm{B}} \chi T$ which is related to the partial differential cross section by $\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \sum_j \frac{2}{3} \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle (r_0 \gamma)^2 f^2$ where $(r_0 \gamma) = 0.54 \times 10^{-13}$ cm and f is the form factor which is unity at $Q = 0$.

The magnetic correlation function

$$S(\mathbf{q}, \omega) = \int_{-\infty}^{\infty} \mathrm{d}t \mathrm{e}^{-\mathrm{i}\omega t} \sum_{i,j} \mathrm{e}^{\mathrm{i}\mathbf{q}(\mathbf{R}_i - \mathbf{R}_j)} \langle \mathbf{S}_i(t) \cdot \mathbf{S}_j(0) \rangle \quad (3)$$

is related to the imaginary part of the dynamic susceptibility *via*

$$S(\mathbf{q}, \omega) = \frac{1}{1 - \mathrm{e}^{-\frac{\hbar\omega}{kt}}} \chi''(\mathbf{q}, \omega). \quad (4)$$

For a system of local magnetic moments a sum rule for the scattering can then be defined

$$\sum_{\mathbf{q}} \int_{-\infty}^{\infty} \mathrm{d}\omega S(\mathbf{q}, \omega) = \int_{-\infty}^{\infty} \mathrm{d}\omega \sum_{\mathbf{q}} \int_{-\infty}^{\infty} \mathrm{d}t \mathrm{e}^{-\mathrm{i}\omega t} \times \sum_{i,j} \mathrm{e}^{\mathrm{i}\mathbf{q}(\mathbf{R}_i - \mathbf{R}_j)} \langle \mathbf{S}_i(t) \cdot \mathbf{S}_j(0) \rangle \quad (5)$$

which yields

$$N \langle S^2 \rangle = NS(S+1). \quad (6)$$

Typically the sum rule is obtained by integrating the scattering up to some finite energy, which for a system with an ordered ground state is usually the maximum spin wave energy $\sim k_{\mathrm{B}} T_{\mathrm{N}}$. At finite temperatures the moments become directionally disordered but their magnitudes remain fixed. Thus the paramagnetic phase is characterised by disordered local moments and if the same range in q and ω integration is carried out the sum rule is conserved. In the paramagnetic phase the response is diffusive centred on $\omega = 0$ with a width $\Delta\omega$ that increases from zero at $q = 0$ to its maximum value at the zone boundary. However local moments are meaningful variables only if the magnetic excitation spectrum ω_{mag} and charge excitation spectrum ω_{ch} are separated, namely $\omega_{\mathrm{mag}} \ll \omega_{\mathrm{ch}}$. This situation is usually satisfied for ionic magnets such as MnF_2 in which the Coulomb forces giving rise to Hund's rule moments are much stronger than the thermal energies $k_{\mathrm{B}} T_{\mathrm{N}}$ characterising magnetic fluctuations [27]. For some systems, such as itinerant electron magnets or spin 1/2 antiferromagnets fluctuations of either charge or spin become important arising from the quantum nature of the electrons. These are driven not by temperature but arise due to the fact that the relevant expectation value is not a sharp quantum number. For metallic systems the spectra of charge and spin fluctuations overlap and the concept of a local moment is not well defined. Although $CuGeO_3$ is a wide gap insulator, $\rho(300\ \mathrm{k}) \sim 10^{13}\ \Omega$ cm, the effects of pure quantum fluctuations are particularly important owing to the small value of the spin. The spectral distribution of quantum fluctuations, especially those of a longitudinal nature, is largely unknown. The dynamics of the ground state investigated by inelastic neutron scattering are characterised by dispersive modes with a maximum energy of $\sim$16 meV $\sim$180 K at the zone boundary. Thus since the incident neutron energy on D7 is 3.5 meV the inelasticity of the response was investigated in the up scattering regime

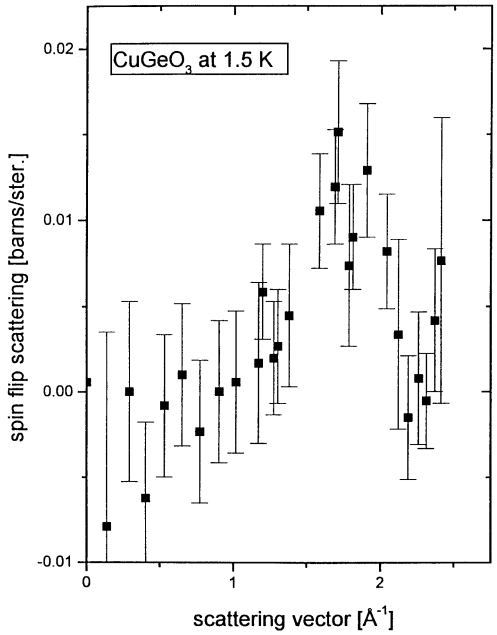

Fig. 2. The magnetic scattering from $CuGeO_3$ at 1.5 K. The $Q = 0$ value is obtained from the uniform susceptibility.

for temperatures greater than 200 K. These measurements were able to cover the extended range in energy at large wave vectors thus enabling an estimate of the amplitude associated with the Cu atoms to be made. Since the level of scattering for a spin 1/2 system is expected to be small ($\sim$1.7 barns per Cu-atom) and since $CuGeO_3$ undergoes a structural phase transition at 14 K, the polarised neutron technique which enables an isothermal determination of the magnetic response is essential.

Results

The wave vector dependence of the scattering measured at low temperatures is shown in Figures 2 and 3, for $T = 1.5$ and 15 K respectively. From these figures it may be seen that the scattering is wave vector dependent and at 1.5 K there is negligible scattering as Q tends to zero. Consequently there is a maximum in the scattering at a finite wave vector corresponding to the nearest neighbour separation of copper atoms. As the temperature is increased the paramagnetic scattering at small wave vectors gains in intensity with the response becoming essentially independent of the scattering vector at 60 K as shown in Figure 4. For the experimental energy integration the limits are set on the energy loss side by the kinetic energy of the neutron (*i.e.* 3.5 meV) and on the neutron energy gain side by the thermal energy, k_BT, of the sample. Although this limits the range of integration it may be seen from Figures 2 to 8 that the data extrapolates to the uniform susceptibility as $Q \to 0$ at all temperatures. The inelasticity of the paramagnetic response and the value of the total integrated scattering will be discussed later.

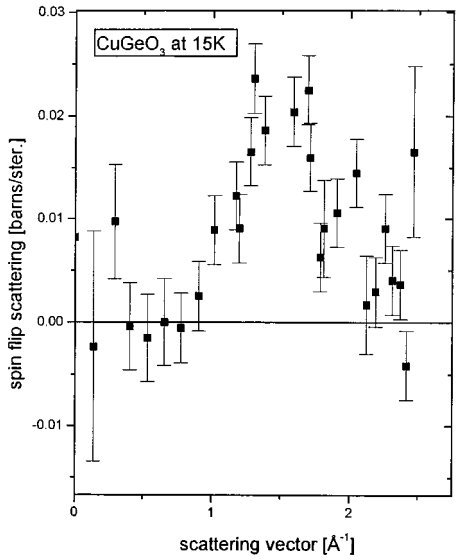

Fig. 3. The paramagnetic scattering from $CuGeO_3$ at 15 K slightly above the dimerisation temperature. The $Q = 0$ value is obtained from the uniform magnetic susceptibility.

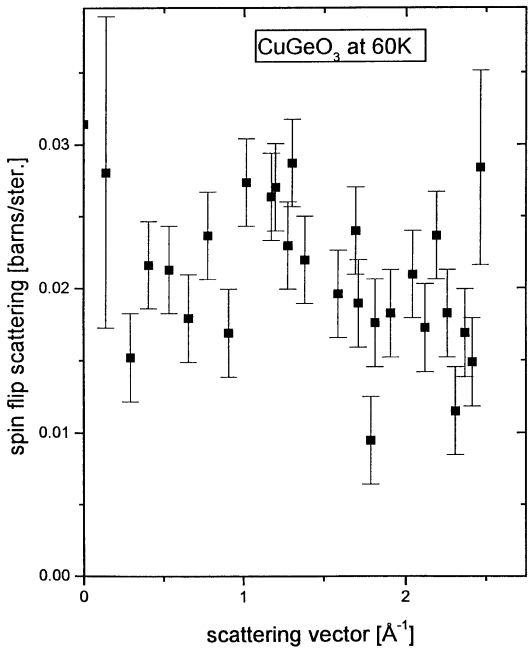

Fig. 4. The paramagnetic scattering from $CuGeO_3$ at 60 K. The $Q = 0$ value is obtained from the uniform susceptibility.

On increasing the temperature further, the magnetic scattering is found to be enhanced in the forward direction. The magnetic scattering observed at 60, 100, 200, 300 and 600 K is shown in Figures 4 to 8. From these figures it is evident that the scattering at large wave vectors does not appear to change with temperature, being essentially the same as that observed at low temperatures. The enhancement at small Q is indicative of the presence of ferromagnetic correlations with the increase being consistent with the variation of the uniform magnetic susceptibility. Owing to the phase space factor the

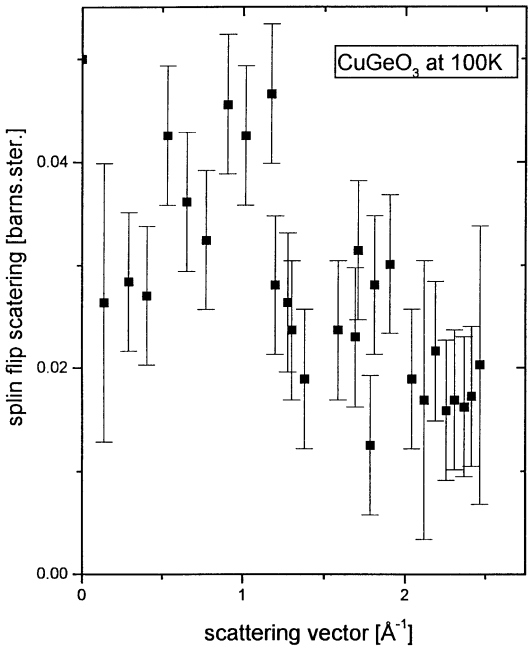

Fig. 5. The paramagnetic scattering from $CuGeO_3$ at 100 K. The $Q = 0$ value is obtained from the uniform susceptibility.

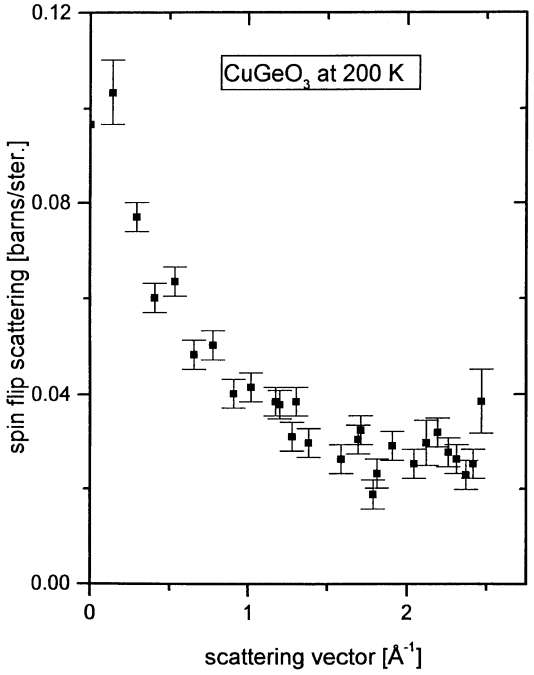

Fig. 6. The paramagnetic scattering from $CuGeO_3$ at 200 K. The $Q = 0$ value is obtained from the uniform susceptibility.

enhanced forward scattering does not contribute significantly to the amplitude and the level of scattering remains essentially unchanged.

As emphasised earlier it is essential to establish over which energy range the paramagnetic response extends. A time of flight experiment was therefore carried out at 600 K using full polarisation analysis. As expected the response was found to be centred on $\omega = 0$. Although the thermal energy of 600 K corresponds ∼50 meV the paramagnetic scattering occurs below 16 meV. This observation is consistent with the maximum magnetic excitation energy [19,22] determined at the zone boundary in the ground state. The total scattering corresponds to 20% of the scattering expected for a moment of 1 μ_B per Cu atom, a value normally associated with a Cu^{2+} atom.

Discussion

The occurrence of antiferromagnetic correlations at low temperatures is not unexpected. The system is reported to dimerise below T_{sp} and although no long- range magnetic order occurs inelastic neutron measurements have established the dispersion of magnetic excitations which are of an antiferromagnetic nature. The measurements reported here indicate that the magnetic correlations extend up to temperatures well into the non-dimerised phase. Antiferromagnetically correlated magnetic moments associated with the Cu atoms are clearly visible at twice the dimerisation temperature. This observation is consistent with inelastic neutron measurements which report an excitation at the Brillouin zone boundary, which develops above T_{sp} but becomes sharp below this temperature [22]. At high

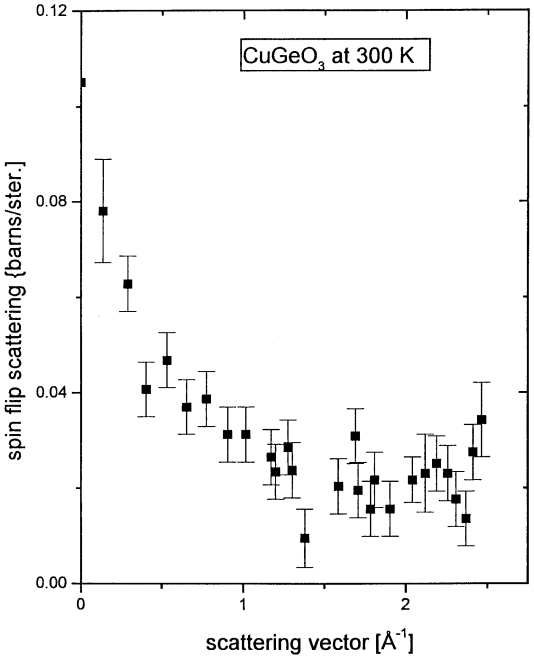

Fig. 7. The paramagnetic scattering from $CuGeO_3$ at 300 K. The $Q = 0$ value is obtained from the uniform susceptibility.

temperature the scattering peaks in the forward direction and in the temperature range between 300 and 600 K the forward peak is found not to change. As the temperature is lowered and the enhanced forward scattering weakens and the antiferromagnetic correlations set in, it is difficult to estimate the correlation length. As may be seen from Figures (2 to 7) the observed scattering can be extrapolated

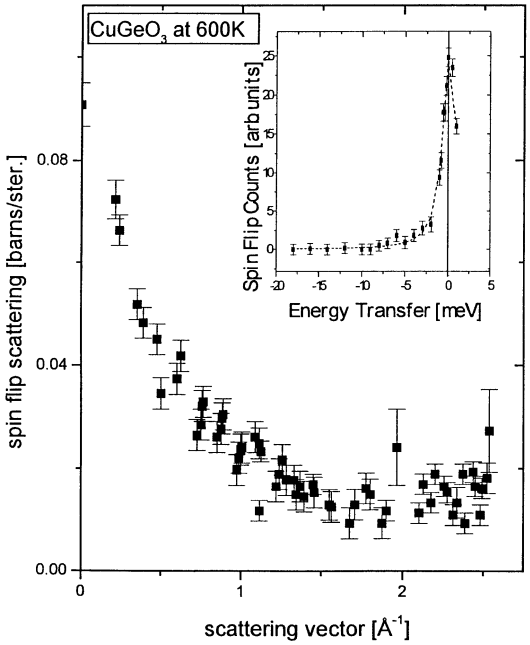

Fig. 8. The paramagnetic scattering from $CuGeO_3$ at 600 K. The inset shows the inelasticity of the paramagnetic scattering at large wave vectors.

smoothly to the $Q = 0$ value given by the uniform susceptibility. This value is indicated in Figures 2 to 8 by the experimental value at $Q = 0$. From this observation it is apparent that the thermal variation of the uniform susceptibility is determined by the evolution of the long wavelength spin fluctuations. These fluctuations are not contained in the Bonner-Fisher model and therefore discrepancies are to be expected if it is used to interpret the thermal variation of the observed susceptibility. As the temperature is raised from the ground state the ferromagnetic correlations grow in importance. However, only for temperatures greater than 100 K do the ferromagnetic correlations begin to dominate the wavevector dependence of the response. The dynamics of the ground state are reported to be those of a "singlet- triplet" nature. However the modes have strong dispersion indicating that a model of isolated dimers is inappropriate for $CuGeO_3$. To make this point clearer it is necessary to consider the scattering which can be expected from isolated dimers coupled by exchange interaction J and separated by distance R. The two spins couple to a ground state and an excited triplet with the only possible excitation energy being the energy difference $J = \Delta$. From equation (3) the cross section for an isolated dimer is

$$S(\mathbf{Q},\omega) = \frac{3}{2Z}\left(\delta(\hbar\omega - \Delta)(1 - \cos(\mathbf{Q}\cdot\mathbf{R})) + \mathrm{e}^{-\beta\Delta}\begin{bmatrix}\delta(\hbar\omega)2(1-\cos(\mathbf{Q}\cdot\mathbf{R}))\\ +\delta(\hbar\omega+\Delta)(1-\cos(\mathbf{Q}\cdot\mathbf{R}))\end{bmatrix}\right) \quad (7)$$

where

$$Z = 1 + 3\mathrm{e}^{-\beta\Delta} \qquad \text{and} \qquad \beta = 1/k_{\mathrm{B}}T. \quad (8)$$

Inelastic transitions can occur at all temperatures for energy transfers $\hbar\omega = \pm\Delta$ and at high temperatures elastic scattering ($\hbar\omega = 0$) can also occur. For $T = 0$ $S(\mathbf{Q},\omega)$ vanishes at $\mathbf{Q} = 0$ and is a maximum for $\mathbf{Q}\cdot\mathbf{R} = \pi$. At high temperatures ($\beta\Delta \to 0$) the energy integrated scattering becomes independent of $\mathbf{Q}$. Although such a model gives qualitative agreement with the wavevector dependence of the response in the ground state it is unable to account for the enhancement of the long-wavelength components as a function of increasing temperature.

The size of the moment as determined in the experiment appeared to not change with temperature with the observed scattering being approximately a factor 5 smaller than that expected for disordered local moments of spin 1/2. The inelastic measurement carried out at 600 K clearly indicates that the magnetic response is contained within an energy range of 16 meV. Although the thermal energy scale of 600 K corresponds to 50 meV the dynamics of the paramagnetic response are characterised by the magnetic coupling constants which at low temperature give rise to a maximum zone boundary excitation energy of ∼16 meV. The inelastic experiment was carried out in the up scattering regime *i.e.* neutron energy gain in which only the thermal fluctuations are measured. These measurements revealed that the response was centred around $\omega = 0$ and that the majority of the weight occurred well below 16 meV *i.e.* within 3.5 meV. This is consistent with the observation that the level of scattering in the energy-integrated mode at high Q did not increase significantly with increasing temperature. From this result it may be concluded that the local moment picture is inappropriate and that the spectrum of thermal and quantum fluctuations overlap. A similar observation has been reported in other oxides, namely the high temperature superconductor $YBa_2Cu_3O_{7-\delta}$ [29] and the metal-insulator compound V_2O_3 [30]. In the latter compound magnetic correlations were found to change abruptly from antiferromagnetic to ferromagnetic at the Mott transition. Once the ferromagnetic correlations become established in the metallic phase at ∼170 K they persist beyond 600 K with very little change in form. In $CuGeO_3$ the change from an antiferromagnetically to a ferromagnetically correlated system takes place more gradually but once established *i.e.* above ∼100 K the ferromagnetic correlations do not appear to vary.

An indication for the stability of a local moment can be inferred from thermal expansion measurements and the variation of the atomic volume. A loss of moment is signalled by a large change in volume, more than a 3% change in YMn_2 [31] and V_2O_3 [30]. Thermal expansion measurements on $CuGeO_3$ reveal anomalies in the thermal expansion coefficients at T_{sp} with the greatest change occurring along the b axis. Although there is a volume anomaly at T_{sp} above and below the transition the volume increases smoothly with temperature. On this evidence it would appear that the dimerisation transition is not accompanied

by a significant change in the local moment. However the polarised neutron measurements clearly indicate that the local moment is significantly smaller than the anticipated 1 μ_B as a result of quantum fluctuations.

Conclusions

The ground state in the dimerised phase is reported to be of a "singlet" nature with magnetic excitations occurring through transitions to the "triplet states". However the dispersion of these modes clearly indicate that the "singlet states" are not isolated. A similar conclusion may be drawn from the paramagnetic response and its thermal evolution. At low temperatures $T < T_{sp}$ the response is antiferromagnetically correlated but with increasing temperature ferromagnetic correlations develop and characterise the variation of the uniform susceptibility. For temperatures greater than 150 K the ferromagnetic correlations dominate the response persisting beyond 600 K. An estimate of the correlation length from the width of the forward scattering suggests that it does not vary substantially. It is the thermal evolution of the long wavelength fluctuations which gives rise to the temperature variation of the uniform susceptibility. Whether this observation is specific to $CuGeO_3$ or a more general property of low dimensional spin 1/2 systems merits further investigation. Since the measurements were carried out on a powder sample it is not possible to identify the precise atomic nature and direction of the correlations. However the correlations are not simply of a thermodynamic nature involving spins of fixed amplitude. Inelastic measurements show that the paramagnetic response is contained within an energy range given by the magnetic coupling determined in the ground state. Integrating this scattering leads to a moment per Cu atom significantly less than the expected 1 μ_B for localised Cu^{2+} spins indicating the importance of quantum fluctuations. On the basis of these results, any model put forward to describe the properties of $CuGeO_3$ can not be based on the Heisenberg Hamiltonian alone but must take into consideration the dynamics of the Cu moments, the change in coupling between them and the coupling to the lattice.

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References

1. J.W. Bray, H.R. Hart, L.V. Interrante, I.S. Jacobs, J.S. Kasper, G.D. Watkins, S.H. Wee, J.C. Bonner, Phys. Rev. Lett. **35**, 744 (1975).
2. J.A. Northby, H.A. Groenendijk, L.V. de Jongh, J.C. Bonner, I.S. Jacobs, L.V. Interrante, Phys. Rev. B **25**, 3215 (1982).
3. S. Huizinga, J. Kommandeur, G.A. Savatzky, B.T. Thole, W.J.M. de Jongh, J. Roos, Phys. Rev. B **19**, 4723 (1979).
4. M. Hase, I. Terasaki, K. Uchinokura, Phys. Rev. Lett. **70**, 3651 (1993).
5. M. Isobe, Y. Ueda, J. Phys. Soc. Jpn **65**, 1178 (1996).
6. J.P. Boucher, L.P. Regnault, J. Phys. I France **6**, 1939 (1996).
7. H. Völlenkle, A. Wittmann, H. Nowotny, Monatsh. Chem. **98**, 1352 (1967).
8. M. Braden, G. Wilkendorf, J. Lorenzana, M. Ain, G.J. McIntyre, M. Behruzi, G. Heger, G. Dhalaenne, A. Revcolevischi, Phys. Rev B **54**, 1105 (1996).
9. Q.J. Harris, Q. Feng, R.J. Birgeneau, K. Hirota, K. Kakurai, J.E. Lorenzo, G. Shirane, M. Hase, K. Uchinokura, Phys. Rev. B **50**, 1266 (1994).
10. L.P. Regnault, M. Aïn, B. Hennion, G. Dhalenne, A. Revcolevschi, Phys. Rev. B **53**, 5579 (1996).
11. V. Kiryukhin, B. Keimer, Phys. Rev. B **52**, R-704 (1995).
12. J. Bonner, M.E. Fisher, Phys. Rev. A **135**, 640 (1964.)
13. J. Riera, A. Dobry, Phys. Rev. B **51**, 16098 (1995).
14. G. Castilla, S. Chakravarty, V.J. Emergy, Phys. Rev. Lett. **75**, 1823 (1995).
15. L. Gladczuk, R. Szymczak, A. Nablialek, I. Krynetskii, G. Petrakovskii, K. Sablina, A. Vorotunov, H. Szymczak, Czech. J. Phys. **46**, 1969 (1996).
16. M. Saint-Paul, G. Reményi, N. Hegman, P. Monceau, G. Dhalenne, A. Revcolevschi, Phys. Rev. B **52**, 15298 (1995).
17. G. Reményi, S. Sahling, J.C. Lasjaunias, N. Hegman, J.P. Brison, A.I. Busdin, G. Dhalenne, A. Revcolevschi, J. Low Temp. Phys. **107**, 243 (1997).
18. M. Nishi, O. Fujita, J. Akimitsu, Phys. Rev. B **50**, 6508 (1994).
19. L.P. Regnault, M. Aïn, B. Hennion, G. Dhalenne, A. Revcolevschi, Phys. Rev. B **53**, 5579 (1996).
20. T.M. Brill, J.P. Boucher, J. Voiron, G. Dhalenne, A. Revcolevschi, J.P. Renard, Phys Rev. Lett. **73**, 1545 (1994).
21. I. Yamada, M. Nishi, J. Akimitsu, J. Phys. Cond. Matt. **8**, 2625 (1996).
22. M. Fujita, M. Arai, M. Motokawa, O. Fujita, J. Akimitsu, S.M. Bennington, Czech. J. Phys. **46**, 1967 (1996).
23. J.E. Lorenzo, L.P. Regnault, J.P. Boucher, B. Hennion, G. Dhalenne, A. Revcolevschi, Europhys. Lett. **45**, 619 (1999).
24. V.F. Sears *Thermal Neutron Scattering Lengths and Cross Sections for Condensed Matter Research* (Chalk River, 1984).
25. V.F. Sears, Neutron News **3**, 29 (1992).
26. O. Schärpf, H. Capellmann, Phys. Stat. Sol. A **135**, 359 (1993).
27. K.R.A. Ziebeck, P.J. Brown, J. Deportes, D. Givord, P.J. Webster, J.G. Booth, Helvetica Physica Acta **56**, 117 (1983).
28. H. Capellmann, J. Lötfering, O. Schärpf, Z. Phys. B **88**, 181 (1992).
29. T.J. Smith, K.H. Andersen, U. Beck, H. Capellmann, R.K. Kremer, K.-U. Neumann, O. Schärpf, A. Simon, K.R.A. Ziebeck, J. Superconductivity **12**, 95 (1999).
30. J.W. Taylor, T.J. Smith, K.H. Andersen, H. Capellmann, R.K. Kremer, K.-U. Neumann, O. Schärpf, A. Simon, K.R.A. Ziebeck, Eur. Phys. J. B **12**, 312 (1999).
31. Y. Nakamura, M. Shiga, S. Kawano, Physica B **120**, 212 (1983).