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Elastic and inelastic neutron study of $CuGeO_3$

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Abstract. Elastic and inelastic neutron scattering was used to probe the structural and magnetic properties of polycrystalline $CuGeO_3$. The diffraction data show that the chemical lattice remains stable in the measured temperature range $1.5\ K \leqslant T \leqslant 296\ K$. At low temperature the inelastic experiments revealed a well defined magnetic excitation at 15 meV, which persists up to $T = 50$ K. The analysis of the spin-wave spectrum is based on a one-dimensional Heisenberg model within the spin-wave theory. On the other hand, no evidence of energy-gap opening, which would result from a dimerization of the Cu chains, could be found at low temperature.

1. Introduction

The magnetic properties of one-dimensional antiferromagnets have attracted a lot of interest, both from the experimental and from the theoretical point of view [1]. In particular, it has been shown that the magnetic excitations of a uniform antiferromagnetic chain described by the isotropic Heisenberg Hamiltonian are characterized by an energy gap when the spin quantum number is an integer [2]. On the other hand, this gap disappears for $S = \frac{1}{2}$ and the spin-wave dispersion is given by the des Cloiseaux–Pearson [3] expression. Moreover, as displayed in figure 1, an $S = \frac{1}{2}$ uniform antiferromagnetic chain can undergo a second-order phase transition at low temperatures accompanied by a displacement of the paramagnetic ions. Accordingly, the magnetic exchange-coupling parameters between first and second neighbours alternate. This phase transition is called a spin–Peierls transition. The ground state is a singlet (hence non-magnetic) separated from the excited states by an energy gap [4]. The size of the gap depends on the degree of dimerization and on the temperature [5].

So far, the spin–Peierls transition could only be observed in some organic compounds [6]. Recently, Hase *et al* [7] proposed that the inorganic compound $CuGeO_3$ displays the characteristics of such a transition at temperatures lower than $T_{SP} = 14$ K. Their conclusions are based on the behaviour of the susceptibility curve, which disappears exponentially as the temperature is lowered towards $T = 0$ K. Independent susceptibility and electron-paramagnetic-resonance measurements confirmed these results [8]. On the other hand, Petrakovskii *et al* [9] reported that $CuGeO_3$ exhibits three-dimensional antiferromagnetic ordering below $T_N = 7$ K. Moreover, recent muon spin-rotation studies of $CuGeO_3$ could not confirm the spin–Peierls transitions at low temperatures [10].

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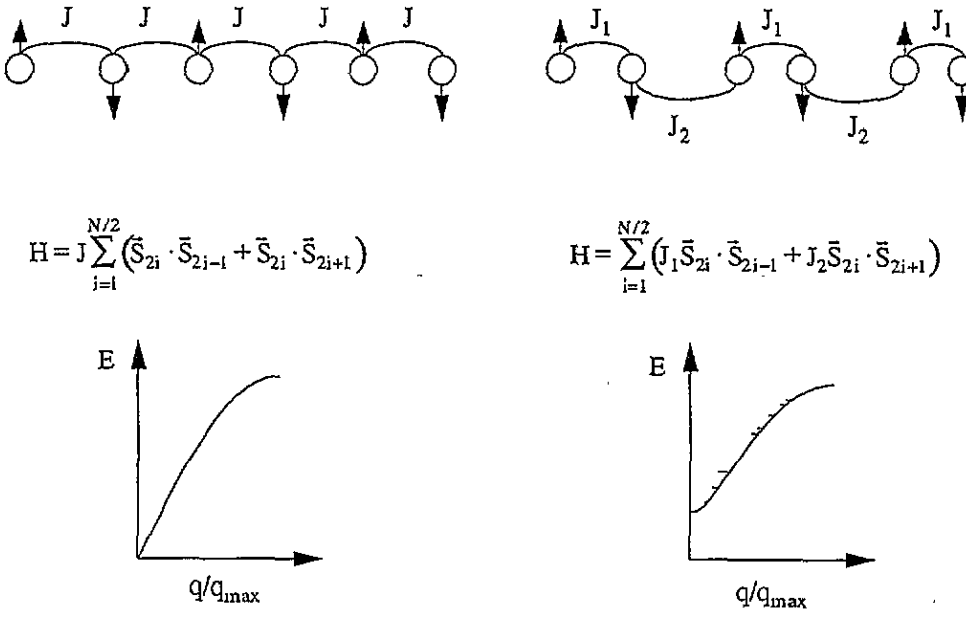

Figure 1. A schematic representation of a spin–Peierls transition. For temperatures lower than the transition temperature, the chain dimerizes and the magnetic excitations are characterized by an energy gap.

In order to obtain information on an atomic scale on crystal structure and on magnetic properties, a polycrystalline sample of $CuGeO_3$ was investigated by both elastic and inelastic neutron scattering in the temperature range 1.5 K $\leqslant T \leqslant$ 296 K. In this report we summarize the results.

2. Experimental details

The sample consisted of small single crystals of blue colour which were crushed to a powder. For the neutron-diffraction experiments we used both the multi-counter diffractometer DMC [11] (vertically curved monochromator Ge 311, $\lambda = 1.7037$ Å) of the Saphir reactor in Switzerland, and the high-resolution powder diffractometer HRPD ($\lambda = 1.8857$ Å) of the Brookhaven National Laboratory, USA. Considerable preferred orientation along the a axis was taken into account for the refinement of the diffraction data with the program of Wiles and Young [12]. The inelastic experiments were performed on the triple-axis spectrometer IN5 [13] at the Saphir reactor operated in the constant-final-energy mode ($E_f = 14.95$ meV). For the inelastic measurements, a graphite filter was placed between the sample and the analyser in order to reduce higher-order contamination. Scans were performed with a maximum energy transfer of 30 meV. These measurements revealed a single excitation at $E \simeq 15$ meV. The temperature dependence of this excitation was investigated between 1.2 K and 70 K.

3. Neutron diffraction

Figure 2 shows the neutron-diffraction pattern of $CuGeO_3$ obtained at room temperature.

$CuGeO_3$ has orthorhombic symmetry described by the space group *Pbmm*. At $T = 296$ K the lattice parameters are $a = 4.801\,40(19)$ Å, $b = 8.472\,81(15)$ Å and $c = 2.942\,15(5)$ Å. Position parameters of the atoms in the chemical cell are summarized in table 1. The chemical structure of $CuGeO_3$ is visualized in figure 3. It consists of GeO_3 chains parallel to the c axis. The Cu ions are located in the centres of squares formed by O atoms. The O form octahedra connected along the b and c axes. Comparison of the diffraction patterns obtained at $T = 1.5$ K and $T = 20$ K with use of the DMC diffractometer operated in the high-intensity mode did not reveal any superstructure reflections at low temperatures. We therefore observed neither a modification of the chemical structure nor antiferromagnetic ordering associated with the Cu sublattice. Yet, experimental limitations impose an upper limit on the Cu magnetic moment of $\mu \lesssim 0.2\mu_B$ and any attempt to measure superstructure reflections due to antiferromagnetic ordering is intensity limited in a powder-diffraction experiment. The same restrictions hold in the case of a lattice distortion and may explain why our results do not confirm recently published diffraction data for a single crystal of $CuGeO_3$ where superstructure reflections (presumably of nuclear origin) with indices $[0, \frac{1}{2}, 1]$ and $[0, \frac{1}{2}, 3]$ were observed at $T \leqslant 3.8$ K [14].

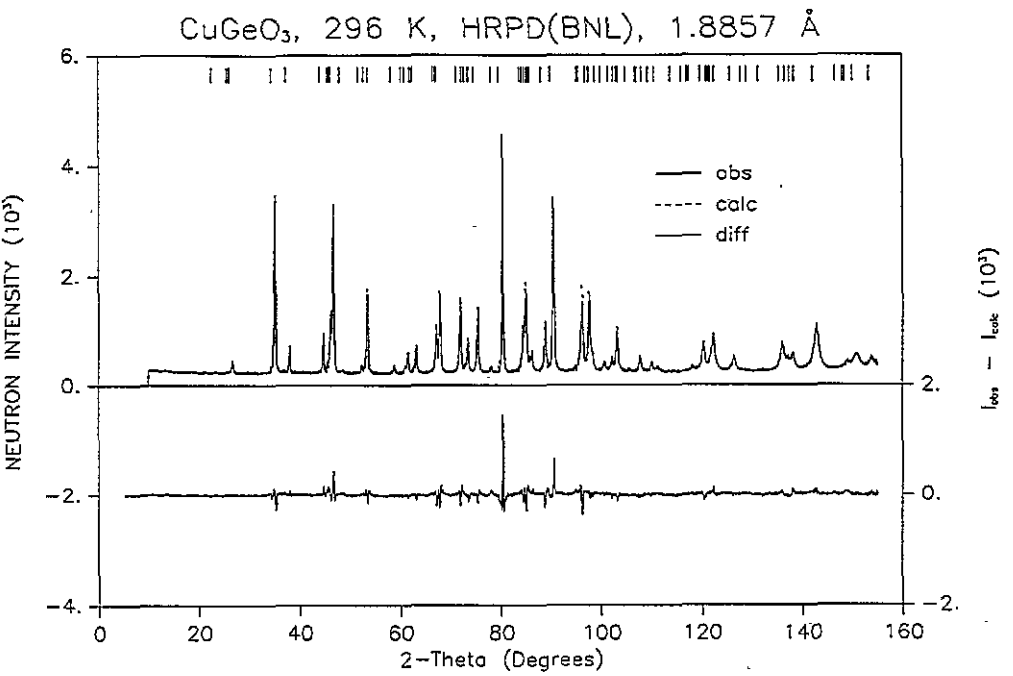

Figure 2. The observed, calculated and difference neutron-diffraction patterns of $CuGeO_3$.

4. Inelastic neutron scattering

The inelastic-neutron-scattering experiments performed for $CuGeO_3$ revealed a magnetic excitation at $E \simeq 15$ meV as shown in figure 4. The asymmetric lineshape indicates the

Table 1. Structural parameters of $CuGeO_3$ at 296 K.

	x	y	z
Cu	0.5	0.0	0.0
Ge	0.073 65(74)	0.25	0.5
O(1)	0.868 90(64)	0.25	0
O(2)	0.281 61(48)	0.082 26(15)	0.5

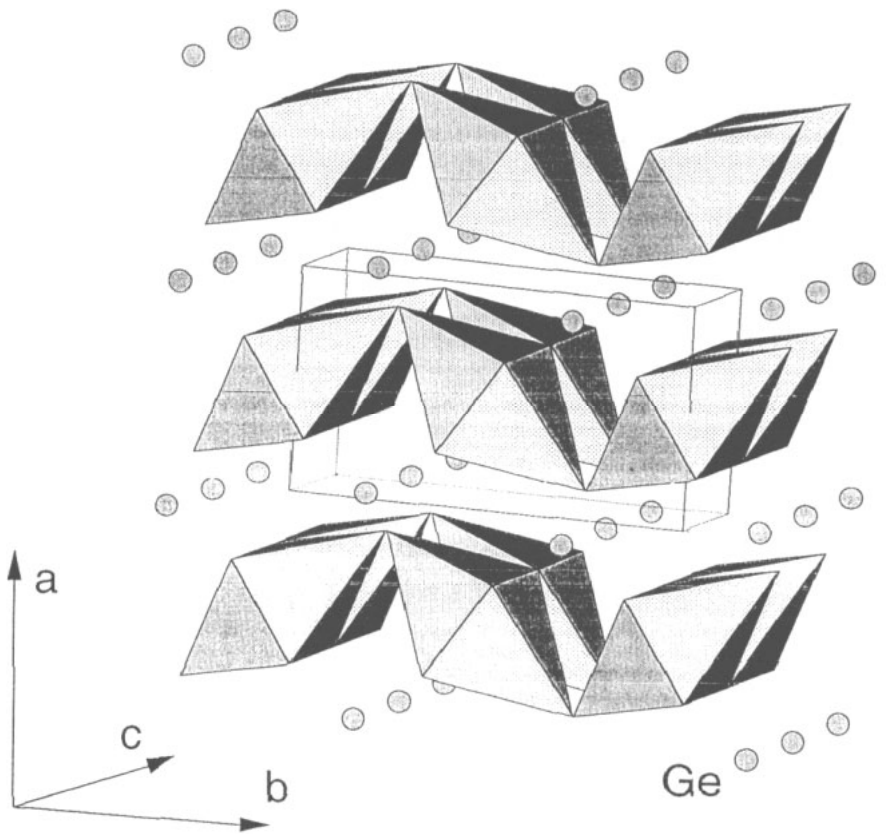

Figure 3. The chemical structure of $CuGeO_3$.

dispersive character of the excitation. For a polycrystalline sample, the response function corresponds to the total scattering averaged in Q space:

$$S(Q,\omega) = \frac{1}{4\pi Q^2} n(\omega) f^2(Q) \int_{|Q|} S(\boldsymbol{Q},\omega)\,\mathrm{d}\boldsymbol{Q} \tag{1}$$

where $n(\omega)$ is the Bose population factor and $f(Q)$ the magnetic form factor. $S(\boldsymbol{Q},\omega)$ is the Fourier transform in space and time of the spin–spin correlation function. The interpretation of the observed energy spectra was based on the isotropic Heisenberg spin Hamiltonian with nearest-neighbour exchange $H = J\sum_{i,j} \boldsymbol{S}_i \cdot \boldsymbol{S}_j$ and the magnetic excitations were calculated in the linear spin-wave approximation. We obtain the dispersion relation

$$\omega(q) = 2JS\sin(qc) \tag{2}$$

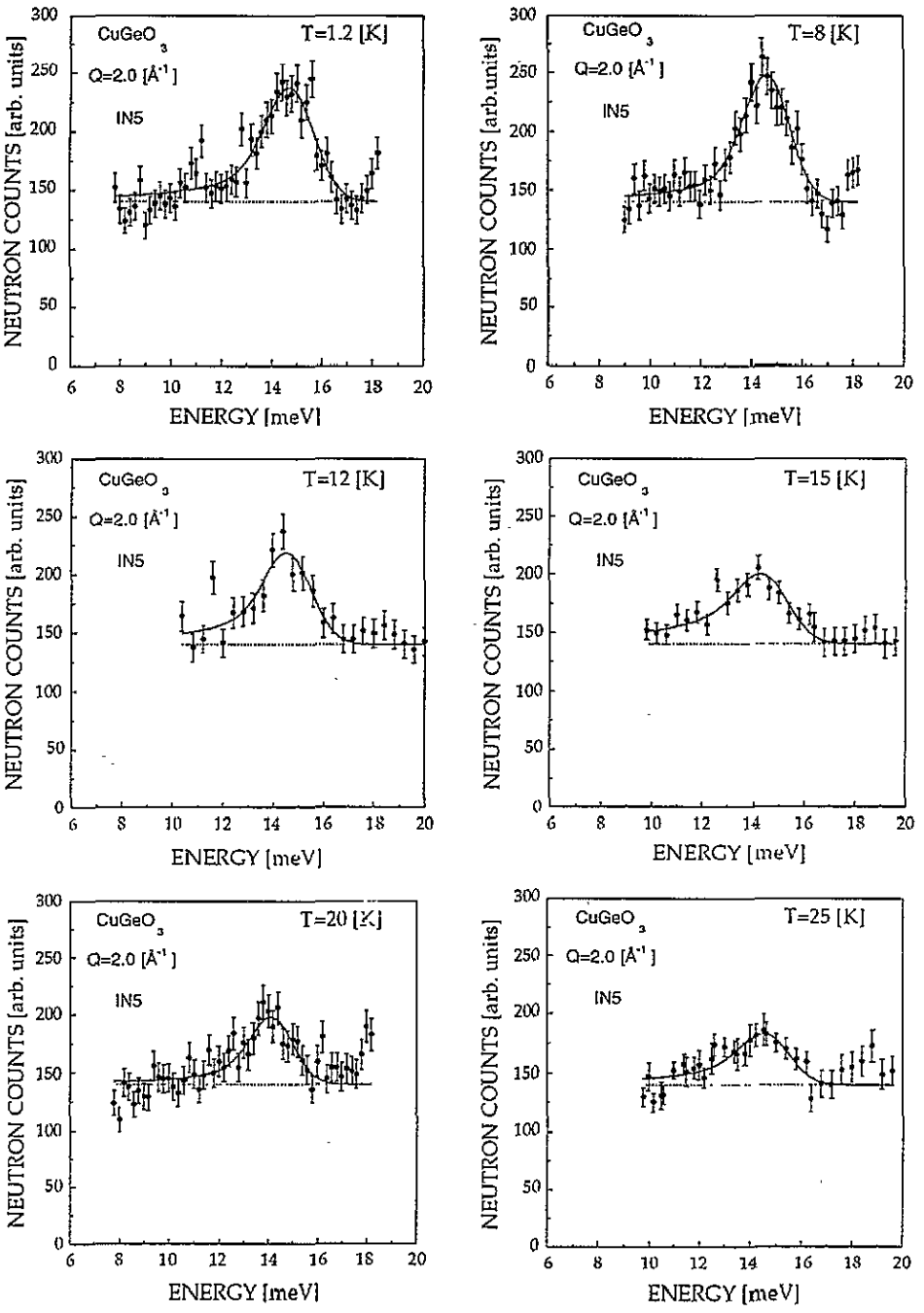

Figure 4. The magnetic excitation measured in polycrystalline $CuGeO_3$ at different temperatures. The line corresponds to the calculations explained in the text.

and the corresponding correlation function

$$S(q,\omega) = \{\sin(qc)/[1+\cos(qc)]\}\delta(\omega-\omega(q)) \tag{3}$$

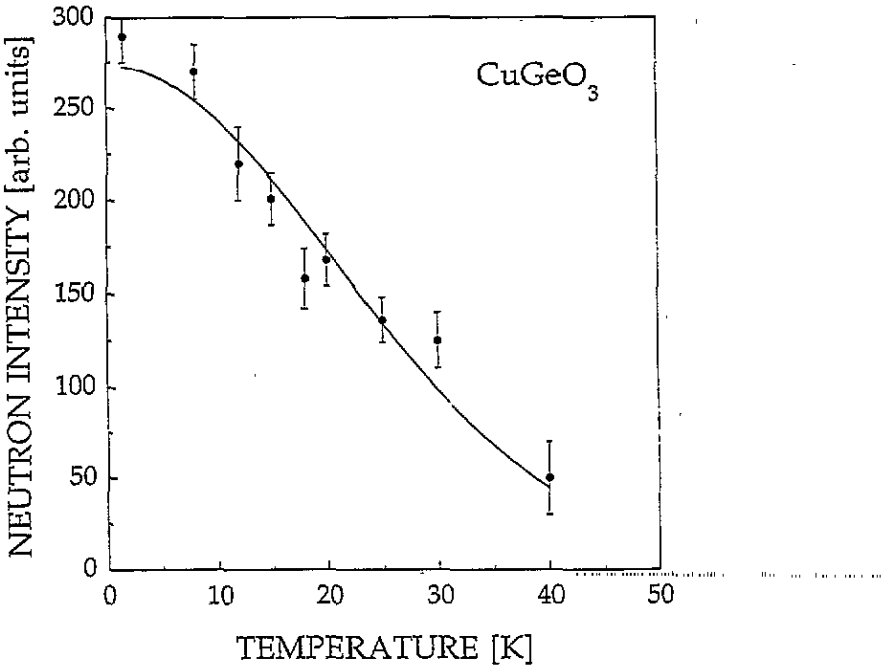

Figure 5. The temperature dependence of the magnetic excitations measured in $CuGeO_3$. The line is a guide to the eye.

for $q = Q - \tau$, where τ is a reciprocal lattice vector and c is the nearest-neighbour distance between Cu ions. The energy dependence of the intensity is obtained by evaluating the integral of (1), which is equivalent to the determination of the density of states $g(\omega)$. The variation of the neutron intensity is then given by

$$S(Q,\omega) = \frac{1}{4\pi Q^2} n(\omega) f^2(Q) \frac{1}{2JSc} \frac{\omega/2JS}{1 \pm \sqrt{1-(\omega/2JS)^2}} \frac{1}{\sqrt{1-(\omega/2JS)^2}}. \tag{4}$$

(4) shows that the main contribution to the inelastic spectrum originates from the singularity of the density of states where the dispersion has a maximum. Consequently, the principal features of the magnetic excitations in a one-dimensional antiferromagnet can be obtained even from a polycrystalline sample. We calculated the convolution of (4) with the known resolution function of the spectrometer and applied a least-squares procedure to the data measured from $CuGeO_3$. The results are shown in figure 4. We obtain the value of the magnetic exchange parameter $J = 15.0 \pm 0.2$ meV at $T = 1.2$ K. Within experimental precision, no relevant energy shift or broadening of the inelastic spectrum was observed in the temperature range 1.2 K $< T <$ 30 K. Figure 5 shows that the temperature dependence of the experimental intensity does not follow the usual Bose occupation factor $n(\omega)$ of (1): the intensity is a maximum at $T = 1.2$ K, decreases as the temperature is increased and eventually disappears at $T \simeq 50$ K. This reveals a strong temperature dependence of the correlation function and an onset of magnetic correlations between the Cu ions at $T \simeq 50$ K in $CuGeO_3$. The detailed theory of the temperature dependence of the spin-correlation function for the one-dimensional antiferromagnetic chain can be found e.g. in [15]. The main difference with spin-wave theory consists in replacing the delta function in (3) by a

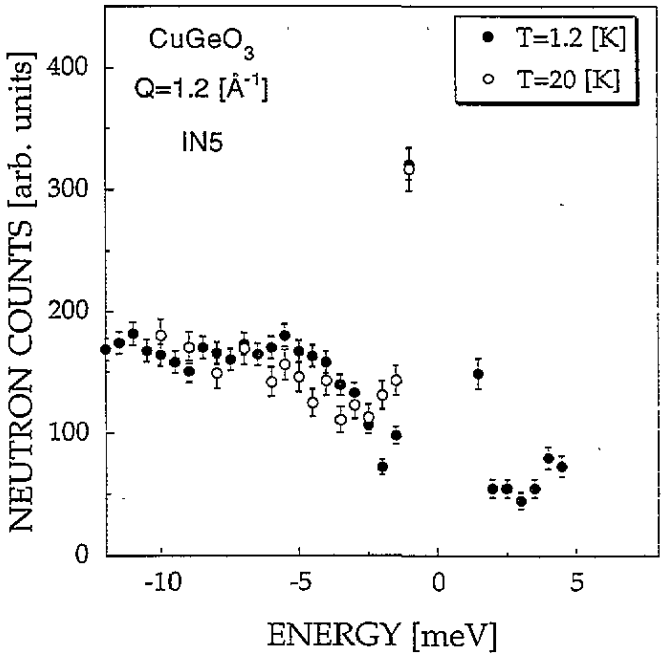

Figure 6. The low-energy part of the inelastic spectrum measured in $CuGeO_3$ at $Q = 1.2$ Å^{-1} for $T = 1.2$ K and $T = 20$ K.

Lorentzian line-shape with a temperature-dependent width. This results in the decrease of the neutron intensity observed in figure 5 as function of temperature.

We present in figures 6 and 7 the low-energy part of the inelastic neutron spectrum measured from $CuGeO_3$ at different values of momentum transfer and temperature. If a spin–Peierls phase transition occurred in $CuGeO_3$ as the temperature was lowered to $T = 1.2\ \mathrm{K} < T_{SP}$, the progressive dimerization of the uniform antiferromagnetic chain would cause an energy gap in the spin-wave spectrum. With the solution of [4] for the alternating one-dimensional antiferromagnetic chain (i.e. with dispersion of the magnetic excitations along one crystallographic direction only!), a singularity is expected in the inelastic neutron pattern as the density of states diverges at the energy transfer corresponding to the gap value. Such an effect has been observed in $AgVP_2S_6$ [16]. On the other hand, figures 6 and 7 do not reveal any strong inelastic response close to the elastic line. However, the temperature and Q dependences of neutron intensities presented in figures 6 and 7 show evidence of magnetic scattering around $E = 4 \pm 1$ meV and an absence of magnetic intensity close to the elastic line at $T = 1.2$ K. The intensity cut-off observed at low temperature at this particular energy transfer can be interpreted as an energy gap if the magnetic correlations are not exactly one dimensional in $CuGeO_3$: in a polycrystalline sample the sampling points at $q = 0$ are small in that case. Yet, at the present stage we have no quantitative interpretation for this effect, and inelastic neutron investigations in single-crystal $CuGeO_3$ are needed to obtain detailed information about the low-energy part of the inelastic spectrum.

5. Conclusion

The diffraction and inelastic neutron measurements performed in polycrystalline $CuGeO_3$

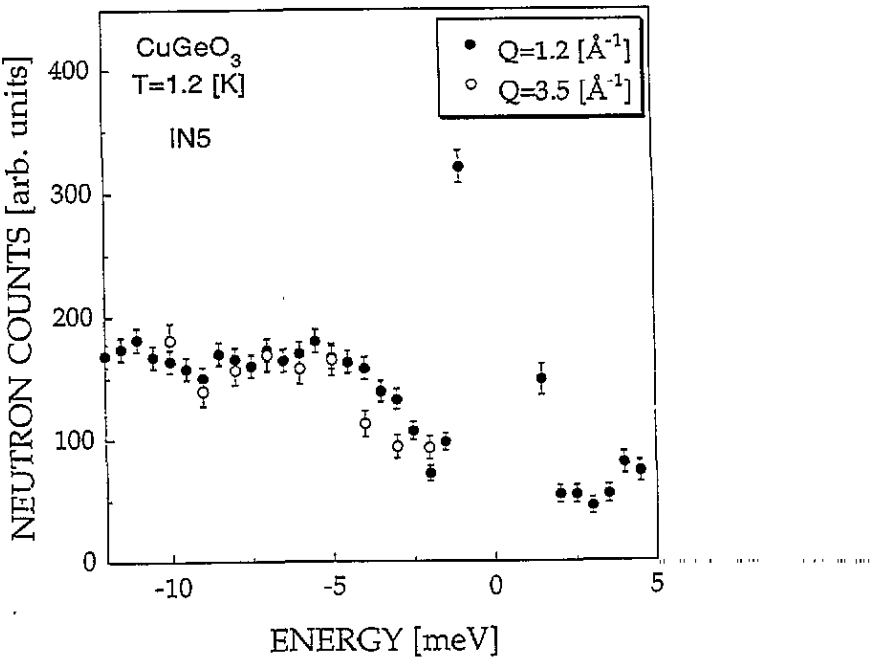

Figure 7. The low-energy part of the inelastic spectrum measured in $CuGeO_3$ at $Q = 1.2$ Å^{-1} and $Q = 3.5$ Å^{-1}.

could not confirm the spin–Peierls phase transition observed by Hase *et al* [7]. No modification of the chemical structure or evidence of an antiferromagnetic phase transition could be observed in the temperature range $1.5\ \text{K} \leqslant T \leqslant 296\ \text{K}$. The calculation of the spin-wave spectrum is based on a Heisenberg operator taking into account the resolution of the spectrometer. The asymmetric profile of the inelastic neutron intensity is due to powder averaging necessary for scattering in polycrystalline samples. We find the antiferromagnetic exchange constant $J = 15.0 \pm 0.2$ meV. On the other hand, the opening of an energy gap at the zone centre could not be unambiguously observed, even at the lowest achievable temperature.

Acknowledgments

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