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Neutron scattering experiments on low-dimensional quantum spin systems—Spin excitations in $KCuCl_3$ and $SrCu_2(BO_3)_2$

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Abstract

We present the results of inelastic neutron scattering experiments on quantum spin systems $KCuCl_3$ and $SrCu_2(BO_3)_2$. Both compounds show non-magnetic singlet ground state behaviour at low temperature. $KCuCl_3$ turns out to be a weakly coupled dimer system without any strong frustrating interdimer interactions. $SrCu_2(BO_3)_2$, on the other hand, should be regarded as a strongly coupled dimer system with a strong frustration originating from the orthogonal arrangement of the neighbouring dimers. The characteristics of the spin excitations in these two dimer systems are compared and discussed.

Keywords: A. Inorganic compounds; C. Neutron scattering; D. Magnetic properties

1. Introduction

The quantum fluctuations leading to a ground state, which cannot be expected in a classical spin system, continues to attract the interest of both theoretical and experimental physicists. The interest has been revived by the discovery of 2D $S = 1/2$ spin correlation in high T_c superconducting cuprates. In the course of these studies, many new low-dimensional magnetic systems with singlet ground state have been discovered, e.g. Haldane, spin Peierls, ladder, plaquette systems [1–4]. The spin dynamics of these systems show a spin excitation gap from the non-magnetic singlet ground state to the first excited triplet state, which may be regarded as a direct consequence of the quantum spin fluctuations. However, little is known about the frustration effect in these extreme quantum spin systems. For example, the magnitude of the role played by the finite next-nearest neighbour interaction in the spin Peierls compound $CuGeO_3$ in establishing the observed singlet ground state, remains controversial [5,6]. It is therefore, interesting to study the frustration effect on spin dynamics in similar quantum systems with and without strong frustrations.

Inelastic neutron scattering experiment on $KCuCl_3$ revealed that this compound can be regarded as a weakly coupled dimer system [7]. $SrCu_2(BO_3)_2$, on the other hand, should be regarded as a strongly coupled dimer system with a strong frustration originating from the orthogonal arrangement of the neighbouring dimers [8,9]. A comparative inelastic neutron scattering investigation of these two dimer systems may give some insight into the frustration effect on spin dynamics, of quantum magnets.

In this paper, we thus compare the characteristics of spin excitations in two dimer systems, namely $KCuCl_3$ as a prototype of a weakly coupled system and $SrCu_2(BO_3)_2$ as a prototype of a strongly coupled, frustrated system.

2. $KCuCl_3$

$KCuCl_3$ crystallises in a monoclinic structure belonging to the space group $P2_1/c$. The lattice parameters are $a = 4.029$, $b = 13.785$, $c = 8.736$ Å and $\beta = 97°20'$. The main feature of the crystal structure is the double chain of

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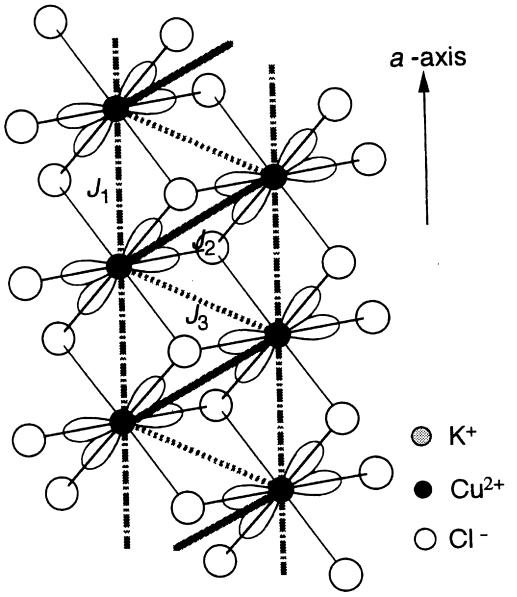

Fig. 1. Double chain structure in $KCuCl_3$ and the configuration of the hole orbital $d_{x^2}-y^2$) of the Cu^{2+} ion.

edge-sharing octahedra of $CuCl_6$ along the *a*-axis as shown in Fig. 1. All the octahedra are distorted due to the Jahn–Teller effect, and their elongated axes are aligned in the same direction. Hence, all the Cu^{2+} ions in a double chain are magnetically equivalent. The susceptibility result by Tanaka et al.[10] shows no anomaly pointing to a magnetic phase transition, rather a broad maximum around 30 K. The susceptibility then vanishes exponentially towards zero temperature.

To clarify the nature of this singlet ground state behaviour we performed the inelastic neutron scattering experiment on a large single crystal of $KCuCl_3$, grown from a melt by the Bridgeman technique. The experiment was performed using the thermal neutron triple axis spectrometer ISSP-PONTA installed at the research reactor JRR-3M, JAERI, Tokai. The scattering plane was selected to be the a^*–c^* plane of the crystal. Fig. 2 shows a typical energy spectrum taken at $Q = (0, 0, -1)$ reciprocal point. A resolution limited single excitation peak is observed at around 3 meV. The magnetic

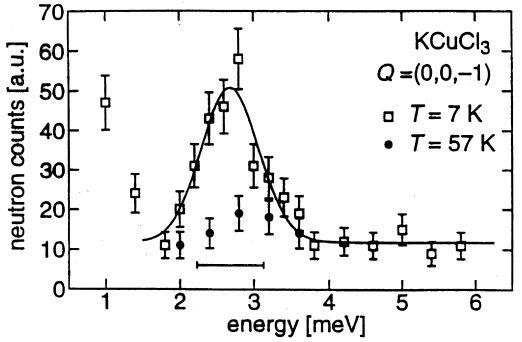

Fig. 2. Typical constant-Q inelastic spectra from $KCuCl_3$ at $T = 7$ and 57 K. (From Ref. [7].)

origin of this excitation is verified by looking at the temperature dependence. As can be seen from Fig. 2, at $T = 57$ K there is no appreciable peak above the background level. The energies of the magnetic excitations at different Q are deduced by fitting a Gaussian peak, as indicated by the solid line in Fig. 2. Fig. 3 shows the summary of the excitation energies at different wave vectors. The lowest excitation energy for the reciprocal points in the a^*–c^* plane is evaluated to be 2.7 meV by averaging the values for $Q = (0, 0, -1)$ and the equivalent points at $Q = (1, 0, \pm 1)$. This value is very close to the gap energy of 2.74 meV deduced from the previous magnetisation measurements [11]. Furthermore, we see that the dispersion, parallel and perpendicular to the chemical double chains, i.e. in a^*- and c^*-direction, show band widths of the same order of magnitude, and that the excitation gap is almost as large as the dispersion band width. Thus, $KCuCl_3$ should be described as a weakly coupled antiferromagnetic dimer system rather than a quasi one-dimensional double spin chain, as initially proposed based on chemical intuition [10].

The dispersion relation of such a weakly coupled dimer system can be modelled within the random phase approximation [12].

Assuming the exchange constant J_2 as the dominant dimer forming antiferromagnetic interaction J_d, the exchange constants as shown in Table 1 can be introduced to describe the observed excitation energies [13]. The solid lines in Fig.

Table 1
Values of the intradimer exchange constant J_d and the effective interdimer exchange constants J_i with the path direction vector r_i

Exchange constants	Path direction vector r_i (lattice unit vector)	Absolute values of exchange constants (meV)
J_d	(0 0 0)	4.11 ± 0.02
J_{a2c}	± (2 0 1)	0.37 ± 0.02
J_{abc}	± (1 1/2 1/2), ±(1 −1/2 1/2)	0.32 ± 0.02
J_a	± (1 0 0)	0.26 ± 0.01
J_{bc}	± (0 1/2 1/2), ±(0 −1/2 1/2)	0.02 ± 0.01

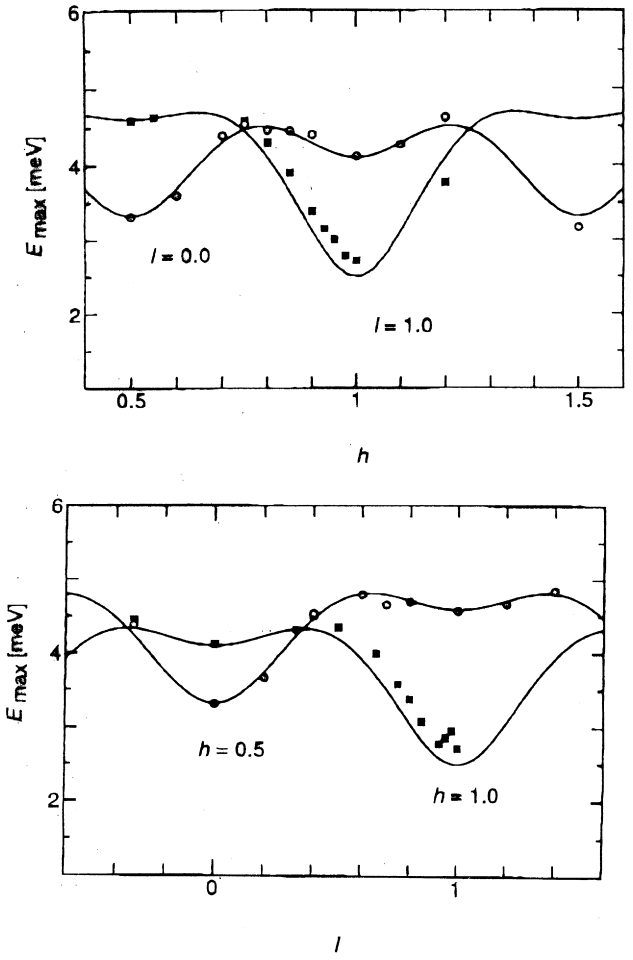

Fig. 3. Summary of the observed excitation peak positions for different $Q = (h,0,l)$. The solid lines indicate calculated dispersion relations, as explained in the text.

3 indicate the calculated dispersion relations with these parameters, in good agreement with the experimental findings.

One should note that the measured susceptibility of $KCuCl_3$ is well reproduced by the isolated dimer susceptibility with the above mentioned intradimer exchange energy, consistent with the conclusions derived from the inelastic neutron scattering results.

These results clearly show that $KCuCl_3$ is a weakly coupled dimer system with the dominant antiferromagnetic intradimer exchange of $J_d = -4.11$ meV and weak interdimer exchanges, which when compared to the intradimer exchange are smaller roughly by an order of magnitude. We note that, an independent inelastic neutron scattering investigation on the same compound has been performed by Cavadini et al. [14] and their results are consistent with those presented here. Fig. 4 shows the temperature dependence of the excitation peak intensity at $Q = (0, 0, -1)$. It can be seen that the peak structure disappears at around $T =$ 30 K, corresponding roughly to the observed energy gap of 2.7 meV.

3. $SrCu_2(BO_3)_2$

$SrCu_2(BO_3)_2$ has a tetragonal unit cell (D_{2d}) with lattice parameters $a = b = 8.995$ and $c = 6.649$ Å at room temperature. It consists of alternately stacked Sr- and $CuBO_3$-planes. A neighbouring pair of planar rectangular CuO_4 forms a spin dimer and the dimers are connected orthogonally by a triangular BO_3 (Fig. 5). The solid and broken lines connecting the Cu-ions in Fig. 5 denote the intradimer J_d and interdimer J' interactions, respectively. Miyahara and Ueda [9] showed that this 2D lattice in the a–b plane of the compound is topologically equivalent to the Shastry–Sutherland lattice studied earlier [15], and pointed out that this system has an exact dimer ground state even when $J' \neq 0$.

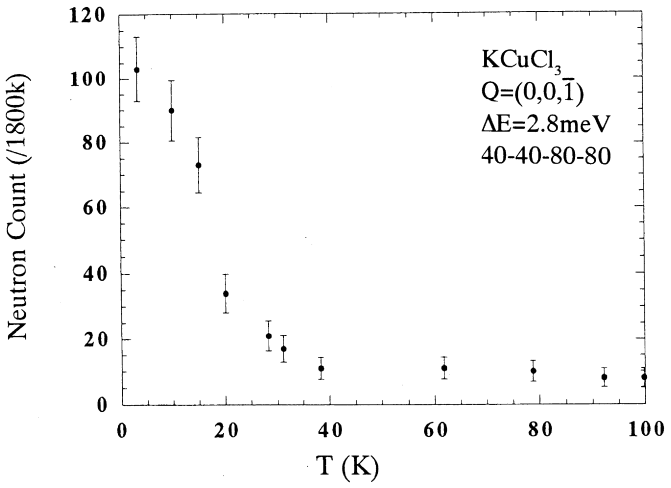

Fig. 4. Temperature dependence of the peak intensity of the excitation at $Q = (0, 0, -1)$.

As can be seen from Fig. 5, the orthogonal arrangement of the dimers with J'-exchanges introduce spin frustration. It turned out that, the experimental data of the magnetic susceptibility [8] cannot be reproduced by an isolated dimer model in which J' is neglected. Fig. 6 shows the temperature dependence of the magnetic susceptibility in $SrCu_2(BO_3)_2$. The solid line indicates the isolated dimer susceptibility, in which the intradimer exchange is chosen such that the maximum is located at the same temperature as the experimental result. The failure of the model is evident. Miyahara and Ueda showed, by the numerical diagonalization of a finite size Shastry–Sutherland model, that the observed susceptibility can be quite well reproduced by choosing $J_d = 100$ and $J' = 68$ K [9]. The ratio of the exchange constants, $J'/J_d = 0.68$, is just below the critical boundary of $(J'/J_d)c = 0.70$ [9] (or 0.69 [16]), beyond which the system is expected to exhibit a Néel ordered state.

The first inelastic neutron scattering experiments were performed using the thermal neutron triple-axis spectrometer ISSP-PONTA [17]. Vertically curved pyrolytic graphite (PG) monochromator and analyser were used and the final neutron energy was fixed at $E_f = 14.7$ meV($k_f = 2.67$ Å^{-1}). A PG filter was placed after the sample to

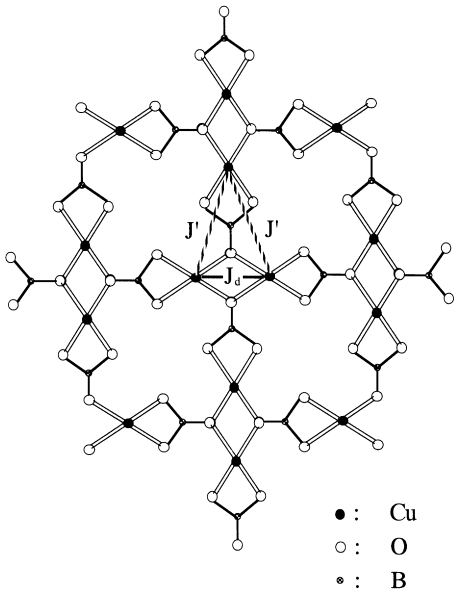

Fig. 5. Schematic drawing of the $CuBO_3$ plane in $SrCu_2(BO_3)_2$.

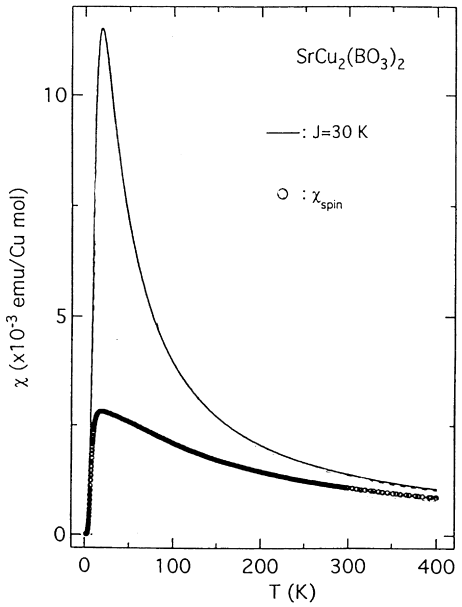

Fig. 6. Magnetic susceptibility of $SrCu_2(BO_3)_2$ depicted by open points. The solid line indicates the calculated susceptibility for an isolated dimer model displaying the maximum at the same temperature as the experimental result.

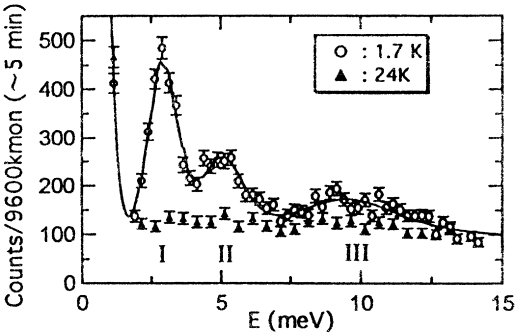

Fig. 7. Typical energy scans at $Q = (2,0,0)$ for $T = 1.7$ (open points) and $T = 24$ K (triangles). (From Ref. [13]).

suppress the higher-order contamination. The horizontal collimations were chosen as open-40′-sample-80′-80′. In order to minimise the neutron absorption by ^{10}B, we prepared a ^{11}B-enriched sample $SrCu_2(^{11}BO_3)_2$. Bulk single crystals were prepared from the travelling solvent floating zone method using the flux $Li^{11}BO_2$ [18]. Two pieces of the single crystals with a total volume of ~1.5 cm^3 were aligned

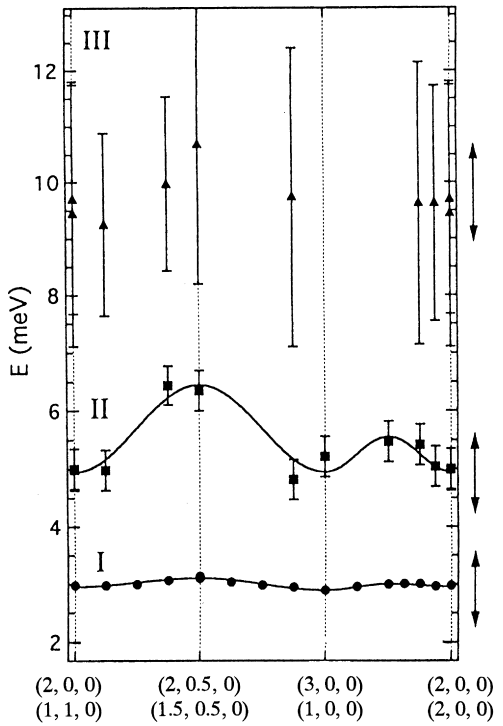

Fig. 8. Q-dependence of the excitation energies of mode I, II and III obtained at $T = 1.7$ K. The upper and lower Q-values indicate the scattering vectors, at which the lowest mode I and the other modes II and III are observed. The arrows represent the energy resolutions of the instrument (FWHM), at these energy transfers. The solid lines are only guides to the eyes. The vertical bars represent the intrinsic line widths (FWHM) of mode II and III.

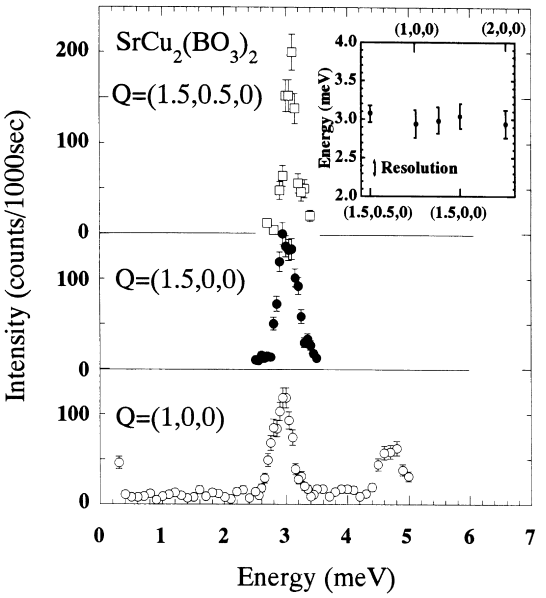

Fig. 9. High resolution spectra at $Q = (1,0,0)$, (1.5,0,0) and (1.5,0.5,0). Inset: the peak positions of excitation mode I as determined by Gaussian fits. The vertical bars represent the line widths (FWHM) as obtained by Gaussian fits.

within 20 min. The sample was mounted with its a- and b-axis in the scattering plane.

Fig. 7 shows a typical profile of the energy scan for the scattering vector of $Q = (2,0,0)$ measured at 1.7 K (open points). The 1.7 K spectrum is characterised by three modes of excitations; namely a sharp peak at 3 meV, a somewhat broader peak at around 5.0 meV and a very broad signal in the energy range of 6–12 meV, which we shall designate as excitations I, II and III, respectively. The spectrum at 24 K, in contrast, has no appreciable peak structures, indicating that excitations I, II and III are of magnetic origin.

As already confirmed, for example, by ESR [19], the excitation mode I is the lowest triplet excitation from the singlet ground state, and the gap energy $\Delta = 3.0$ meV is consistent with the values estimated from different measurements [19–22].

Fig. 8 depicts the Q-dependence of the energy centers of these excitation modes. The vertical bars do not represent error bars, but indicate the observed intrinsic line widths of the excitations. Besides the small gap energy compared with the estimated intradimer exchange energy of 100 K, it is remarkable that the first excited states show an almost flat dispersion despite the large interdimer exchange energy value.

To measure the band width of the lowest excitation mode more reliably, we performed a cold neutron triple axis experiment on IN12 at Institut Laue Langevin. The chosen spectrometer condition was E_f fixed at 5 meV with horizontal collimations after the vertically focused PG

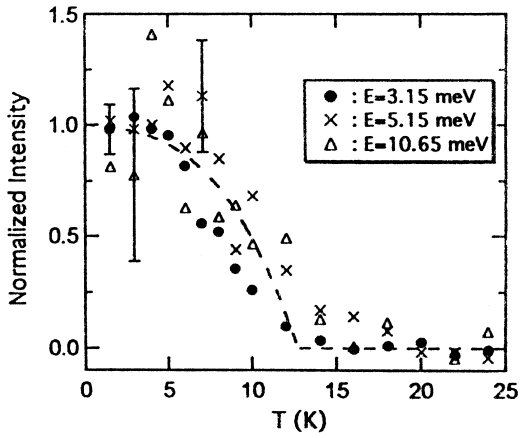

Fig. 10. Temperature dependence of the peak intensities at $\Delta E = 3.15$, 5.15 and 10.65 meV, at $Q = (1.5,0.5,0)$ for the first and (2,0,0)for the next two. The intensities are normalised at low temperature. The broken line is a guide to the eyes only. (From Ref. [13]).

monochromator 40-sample-open-open, to allow the use of the horizontally curved PG analyser. A cooled Be-filter was inserted in the scattered beam, to eliminate higher order contamination. Fig. 9 shows three typical spectra at different Q vectors, which include the extrema suggested by the thermal neutron experiment. The inset of Fig. 9 shows the peak positions at these wave vectors, and it can be clearly seen from this high resolution measurement that the 3 meV mode has indeed a very small band width of 0.2 meV. It should be noted that the 3 meV excitation peak at $Q = (1, 0, 0)$ has a small intrinsic line width of the order of 0.2 meV, while the peak at $Q = (1.5, 0.5, 0)$ is resolution limited even with this high energy resolution. (Note, that the vertical bars in the inset represent the line widths (FWHM) of Gaussian fits.) Furthermore, it is clear from the spectrum at $Q = (1, 0, 0)$, that there is a clear energy gap between the 3 and 5 meV excitations.

Fig. 10 shows the temperature dependence of the peak intensities at 3.15, 5.15 and 10.65 meV energy transfer, as obtained by the thermal neutron experiment. All peak structures disappear at about 13 K, corresponding to an energy much smaller than even the lowest gap energy of 34 K.

4. Discussion

The experimental findings presented above indicate that the spin dynamics in both systems can be interpreted as that of exchange connected dimers. In the case of $KCuCl_3$, the dimers are weakly coupled and the interdimer exchanges are not strongly frustrating. Hence, the excited triplet state on a dimer can propagate due to the interdimer exchange and exhibits a dispersive behaviour with a band width of the order of $2\sqrt{J_d \cdot J'}$, where J_d and J' are characteristic intra and interdimer exchange energies, respectively. The size of J_d is reflected in the averaged gap energy of the first triplet excitation.

In the case of $SrCu_2(BO_3)_2$, however, the dimers are strongly coupled but the two interdimer exchange paths form a triangular lattice together with the intradimer exchange due to the orthogonal arrangement of the dimers, thus causing a strong frustration. This frustration then gives the first triplet excitation a very strong localised nature, which is reflected in the dispersion with a narrow band width of 0.2 meV at most. This fact is consistent with the recent theoretical consideration by Miyahara and Ueda, where they prove that a hopping of the single-triplet excitation from one site to the neighbouring site within the plane, is possible only from the sixth order in the perturbation calculation. The gap energy is much smaller than the intradimer exchange energy, because the system is located close to the critical ratio of interdimer and intradimer exchange of $J'/J_d = 0.7$, where, according to Miyahara and Ueda [9], a phase transition from the singlet ground state to a Néel state is expected. One should mention here that Weihong et al. [17] calculated the single-triplet excitation using the series expansion method and they predicted a prominent J'/J_d-dependence of the bandwidth near the critical ratio, which is not in accord with our experimentally observed small band width.

The next striking difference between the spectrum of $KCuCl_3$ and $SrCu_2(BO_3)_2$ is the visibility of many higher energy excitation branches or continuum in the latter, while in the former the spectrum is dominated by the single excitation branch associated with the first excited triplet state. The excitation mode II in $SrCu_2(BO_3)_2$ at around 5 meV can be interpreted as the second triplet state associated with the coupled two-triplets excitation. The continuum like excitations at even higher energies up to 12 meV then can be understood as multi-triplets excitations. One may therefore conclude, that the spectral weight of these multi-triplets excitations is considerably enhanced in a frustrated system, rather than in a weakly coupled, hence unfrustrated, system. In the light of this interpretation, the 'second triplet state' at 5 meV in $SrCu_2(BO_3)_2$ may be related to the observation of the 'second gap' in $CuGeO_3$, where the frustration due to the next-nearest neighbour exchange coupling is thought to play an important role to form the singlet ground state.

The temperature dependence of the excitation spectrum in $SrCu_2(BO_3)_2$ is also different from that of $KCuCl_3$. In $KCuCl_3$, the excitation peak structure disappears roughly at a temperature corresponding to the smallest gap energy, as one would commonly expect; while in $SrCu_2(BO_3)_2$, the excitation peak structure including the multi-triplet excitations disappears at a much lower temperature than the smallest gap energy given by the single-triplet excitation.

A quantitative calculation of the dynamical structure factor and its temperature dependence for $SrCu_2(BO_3)_2$ is

highly desirable, to verify whether the large spectral weight of the multi-triplets excitations and the peculiar temperature dependence are indeed consequences of the strong frustration.

5. Summary

To summarise, we reported inelastic neutron scattering investigations on $KCuCl_3$ and $SrCu_2(BO_3)_2$. The two systems can be regarded as examples of quantum systems with singlet ground state. Both systems can be described as coming from interconnected dimers, but while in $KCuCl_3$ the dimers are only very weakly coupled and unfrustrated, in $SrCu_2(BO_3)_2$ they are strongly coupled and frustrated. The characteristics in the excitation spectrum and its temperature dependence of the latter may be attributed to the frustration effect and the near criticality, which are absent in the former system.

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