Neutron Scattering Investigation on Quantum Spin System $SrCu_2(BO_3)_2$

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In this paper we would like to review the zero field inelastic neutron scattering results obtained by using both the thermal and cold neutron triple axis instrument. The first single triplet state at around 3 meV is split due to the Dzyaloshinski-Moriya (DM) inter-dimer interaction with both the out-of-plane and in-plane components. The splitting between the $S_z = \pm 1$ states is of the order of 0.3 meV. The two triplets bound states also form a very flat bands at 4.9, 5.5 and 6.3 meV with finite line width of the order and/or twice of the DM splitting. Finally the higher energy range up to 13 meV can be also characterized by three rather broad, but flat bands at around 8, 10 and 12 meV with the line width roughly three times the DM splitting. These excitations can be probably assigned to three and more triplets bound state excitations.

§1. Introduction

After the discovery of $SrCu_2(BO_3)_2$ as being a potential realization of the 2-dimensional Shastry-Sutherland model by Kageyama et al.,[1)] and Miyahara and Ueda,[2)] many experimental and theoretical investigations have been undertaken to characterize and understand the spin liquid state of this compound. The magnetic properties of this compound are determined by Cu^{2+} ions carrying localized spins of $S = 1/2$. The network of the Cu^{2+} ions, as will be described below, has a structure for which strong frustration effects can be expected. This system shows indeed various unique magnetic behaviours. The magnetic susceptibility shows a maximum at around 20 K and rapidly drops toward zero with decreasing temperature and thus suggests the existence of a spin gap. But the Curie-Weiss constant estimated from the high temperature susceptibility is $\Theta = 102.5$ K and much larger than the spin

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gap $\Delta = 35$ K estimated from the low T behaviour.[3] High-field magnetization measurements have demonstrated the existence of the 1/3, 1/4 and 1/8 magnetization plateaux.[1),4] All these bulk measurements indicate that $SrCu_2(BO_3)_2$ is an excellent candidate of a frustrated antiferromagnetic quantum spin system. Furthermore the theoretical investigation following these experiments indicated the possible mapping of the system on to the Shastry-Sutherland model,[5] which then naturally leads to the question of the quantum phase transition from the non-magnetic singlet ground state for $J'/J < 1$ to magnetically ordered state for limiting $J = 0$ case, which is namely $S = 1/2$ AF square lattice with J', where J and J' are intra- and inter-dimer exchange, respectively[2] (For recent experimental and theoretical review, see Kageyama[6] and Miyahara and Ueda.[7]).

It is therefore interesting and important to obtain both the characteristics of the spin dynamics of $SrCu_2(BO_3)_2$ over the whole relevant energy scale and the details of the spin fluctuations to determine the essential exchange coupling determining the quantum critical behaviour. We therefore have been studying the spin excitations in this interesting 2-D system using both thermal and cold neutron inelastic scattering.

§2. Description of the system

The crystal structure is of tetragonal symmetry with a space group of I-42m (No. 121) and $a = 8.995$ Å, $c = 6.649$ Å at room temperature. Figure 1(a) shows the structure of $SrCu_2(BO_3)_2$ projected along the c-axis. Layers of $(BO_3)^{3-}$ groups and Cu^{2+} ions stack along the c-axis rotating by 90°, with nonmagnetic Sr^{2+} ions separating these layers. All copper ions with a localized spin $S = 1/2$ are crystallographycally equivalent, sitting on the 8i site. For a given $CuBO_3$ layer, the copper ions along with the oxygen ions of the BO_3 group form dimers of planer, edge-sharing CuO_4 groups. The spin dimers are connected orthogonally by triangular BO_3 groups. The antiferromagnetic intra-dimer (nearest neighbour, hereafter abbreviated as nn) and the inter-dimer (next nearest neighbour, hereafter abbreviated as nnn) exchange are designated as J and J', respectively (see Fig. 1(a)) and one immediately recognizes that the antiferromagnetic inter-dimer exchange J' is causing a strong frustration between the neighbouring dimers because of their orthogonal configuration.

A buckling of the $CuBO_3$ plane is observed below 395 K. The mutually orthogonal dimers form two different planes and these two planes are slightly shifted from each other, as indicated in Fig. 1(b). Because the super-exchange path between the plane goes via the closed shell of the Sr^{2+} ions the inter-planar exchange is expected to be much smaller than the above-mentioned intra-planar exchange. We therefore regard the $SrCu_2(BO_3)_2$ as a good realization of the two-dimensional orthogonal dimer model.

There are the following coupling constants proposed theoretically for the orthogonal dimer model describing $SrCu_2(BO_3)_2$ to explain macroscopic and microscopic experimental findings so far. Miyahara and Ueda proposed $J = 85$ K, $J' = 54$ K ($J'/J = 0.635$) and the averaged inter-planar exchange of ~ 8 K on the basis of the exact diagonalization results explaining the low-T magnetic susceptibility, specific

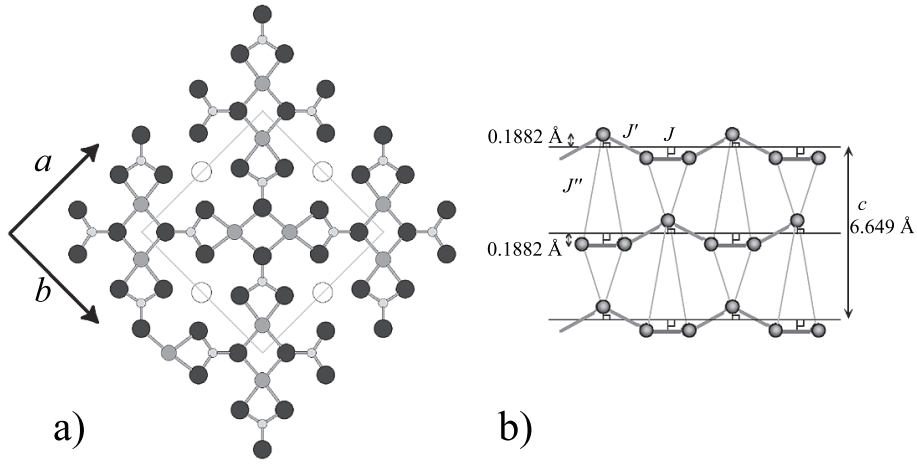

Fig. 1. (a) The structure of $SrCu_2(BO_3)_2$ projected on ab-plane. The open circles denote Sr^{2+}, black circles O^{2-}, large grey circles Cu^{2+} and small grey circles B^{3+} ions. (b) The buckling of the dimer plane.

heat results.[7] On the other hand $J = 71.5$ K, $J'/J = 0.603$, and inter-planar exchange of ~ 15 K are proposed by Knetter et al. from the triplet and bound state energies using the method of perturbative continuous unitary transformations.[8]

§3. Wide energy range investigation using thermal neutron triple axis instrument

We show first the results of the thermal neutron investigation covering the full range of the magnetic excitation with rather coarse resolution. The experimental results presented here are taken on IN22 spectrometer operated by CENG at ILL. The k_f was fixed at 2.663 $Å^{-1}$ and the horizontal collimations were 25'-40'-60'-60'. Higher order contaminations were suppressed using the PG filter after the sample. ^{11}B-enriched (99.6%) bulk single crystal of 3.6 g was used. The sample was oriented with its a- and b-axis in the scattering plane and cooled to $T = 1.5$ K using Orange-type pumped liquid Helium cryostat. We note that the inelastic neutron scattering results in the first report[9] were obtained under similar conditions using thermal neutron triple axis instrument PONTA at JRR-3M.

Figure 2 depicts typical spectra measured along [1,−1,0] direction starting at $Q = (0,-2,0)$. As has been already reported in Ref. 9), the prominent peak with a 3 meV energy gap can be clearly recognized in all spectra, corresponding to the lowest excitation from the singlet ground state to the triplet excited state (Excitation I). The increase in the counting rate below 2 meV energy transfer is caused by the incoherent scattering and is regarded as a temperature independent background. The horizontal bar in the figure indicates the instrumental resolution (~ 1.2 meV at 3 meV energy transfer) and it can be readily recognized that the lowest triplet excita-

tion is almost resolution limited at this moderate energy resolution. As discussed in Ref. 9) its almost dispersionless nature is the consequence of the localization of the triplet excitation due to the frustrated interdimer exchange between the orthogonal arrangement of the neighbouring dimers. We discuss the details of the lowest energy excitation below.

On the higher energy transfer side of this first gapped excited state a somewhat broader peak covering the energy regime of 4 to 7 meV can be clearly seen (We denote this group as excitation group II.). One also notices, that the position of the maximum intensity shifts roughly from 5 meV to 6 meV when Q is changed from $h = 0.1$ to 0.5. With insufficient counting statistics and limited number of Q points this can be interpreted as the evidence of the more dispersive excitation at around 5.5 meV, as in the previous thermal neutron experiment.[9] But looking more closely at the present data sequence with improved counting statistics (Fig. 2) reveals an asymmetry and line width change not compatible with a single dispersive peak, but rather a multi-peak structure covering this range of the energy transfer. As shown in Fig. 2 one could indeed fit the spectra in this energy range by two peaks, one with a energy width of ~ 0.4 meV at around 4.9 meV and the other with an energy width of ~ 0.8 meV at around 6.2 meV. While the intensity of the peak around 6.2 meV does not change by going from $Q = (0.1,-2.1,0)$ to $(0.5,-2.5,0)$, the intensity of the peak around 4.9 meV decreases and almost vanishes at $(0.5,-2.5,0)$, thus creating a clear separation of the lowest excited peak at 3 meV and the next higher excitation group at this Q. We address this point in the following section on high energy-resolution investigation of this energy range, where the excitations due to the bound state of two triplets are expected.

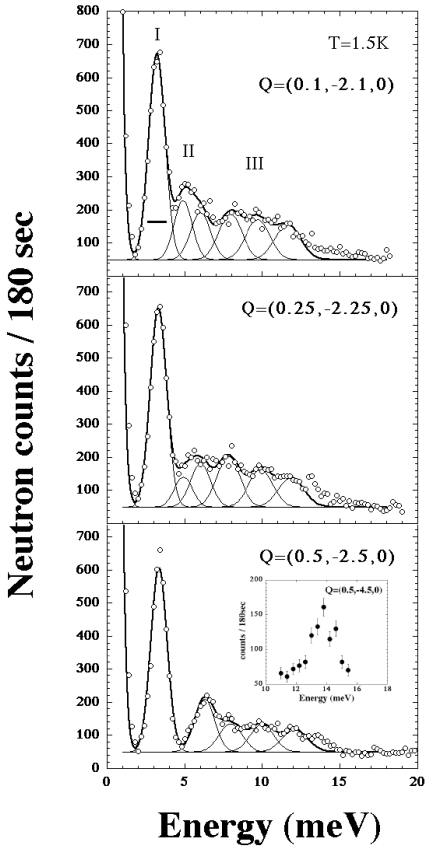

Fig. 2. Typical inelastic spectra as obtained using thermal neutron triple axis instrument. Inset shows the phonon peak around 14 meV at large Q.

The next excitation group, as designated group III, extend up to 13 meV and shows an even more broad feature. As indicated in Fig. 2, this group can be fitted with three broad gaussian peaks having an energy width of ~ 1 meV. The additional peak structure at around 14 meV is recognized as phonon contribution, as indicated

in the large Q experiment shown in the inset. The observed energy range for the magnetic excitations is also in accord with the calculation of the dynamical structure factor for the orthogonal dimer model by Miyahara et al.[10] using exact diagonalization for $Q = (2\pi, 2\pi)$, which shows an appreciable spectral weight extending up to about 150 K.

The observation that the magnetic excitations extend in the energy range up to 13 meV is further substantiated by looking at the difference of the low ($T = 2$ K) and high ($T = 24$ K) temperature spectra as shown in Fig. 3. A clear temperature dependent feature shows up in the energy range up to 13 meV and can be attributed to the magnetic contribution. But one should also note that there remains a broad scattering intensity up to 13 meV above background level even at $T = 24$ K, which is most probably of magnetic origin.

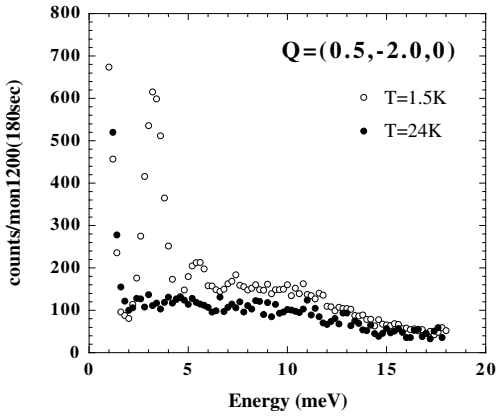

Fig. 3. The spectra for low ($T = 1.5$ K) and high ($T = 24$ K) temperature at $Q = (0.5,-2,0)$.

It is also surprising that the spectral feature is totally changing although the temperature 24 K corresponds to energy even less than the characteristic gap energy of 3 meV. If one would have an isolated dimer system with 3 meV gap, one would expect the intensity of the lowest excitation to drop only by roughly a factor 2 due to the thermally excited triplets states without changing the qualitative gap character of the dimer excitation, as has been observed e.g. in $BaCuSi_2O_6$[11] and $TlCuCl_3$.[12] In contrast to that the dynamics of the highly frustrated dimer system $SrCu_2(BO_3)_2$ changes qualitatively by going to temperatures above the susceptibility maximum and seems to develop the gap only below this temperature. Whether this feature is due to the implicit quantum character of the frustrated 2-D system or the 3-D effect caused by the weak inter-planar interaction is an object of further investigation.

§4. High energy-resolution results using cold neutron triple-axis instrument

4.1. *First excited triplet state*

We now turn to the high energy-resolution experiments on the 3 meV first excited triplet state and on the excitation group II. The high energy-resolution inelastic neutron scattering experiments were performed on the cold neutron triple axis instrument ISSP-HER at JRR-3M of Japan Atomic Energy Research Institute. The instrument is installed on a cold neutron guide and is equipped with vertically curved pyrolytic graphite PG(002) monochromator and horizontally curved

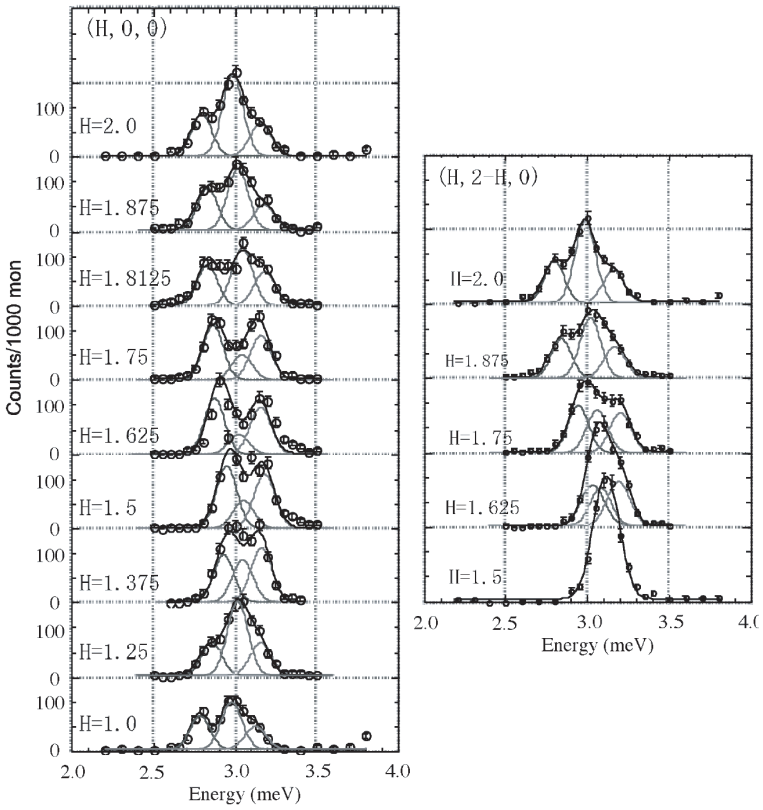

Fig. 4. Series of high-resolution energy scan at $T = 1.5$ K for different Q. Note, that the spectrum at $Q = (1,0,0)$ shows a three peak, at $Q = (1.5,0,0)$ a two peak and at $Q = (1.5,0.5,0)$ a single peak structure.

PG(002) analyser. A combination of PG Bragg reflection filter for $E_i > 5.1$ meV and cooled beryllium filter for $E_i < 5.1$ meV before the sample is used to suppress higher-order contamination. The experimental conditions were k_f being fixed at 1.22 Å^{-1} ($E_f = 3.10$ meV) and collimations after the monochromator being open-radial collimator-open. Figure 4 shows series of energy scans at different wave vectors in zero field. It can be recognized that the first excitation around 3 meV energy transfer indeed consists of at the maximum three excitation branches. Figure 5 summarizes the observed excitation energies of the branches in different directions. The energies were determined by fitting gaussian line shapes with resolution limited line widths as indicated by the thin solid lines in the spectra of Fig. 4. From the field dependent neutron scattering and ESR investigations it was demonstrated that the field dependent gap at $q = 0$ and the anisotropic behaviour can be well accounted for by introducing the Dzyaloshinski-Moriya (DM) inter-dimer interaction with the main component directed perpendicular to the *ab*-plane.[13] By combining the result of the perturbative calculation neglecting the frustrated nnn-coupling (J') valid in the weak coupling limit and the exact numerical diagonalization for limited q valid for the strong coupling limit, as is the case for the $SrCu_2(BO_3)_2$ ($J'/J \sim 0.62$), we

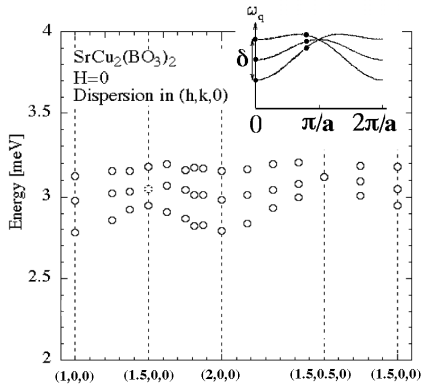

Fig. 5. Q dependence of the peak positions deduced from the spectra as shown in Fig. 4. Inset: Results of exact numerical diagonalization from Ref. 12).

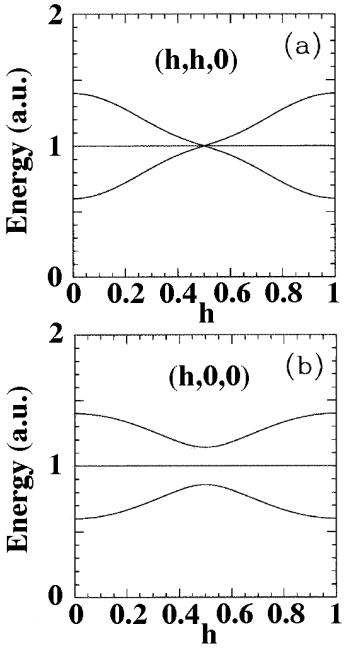

Fig. 6. Theoretical prediction of the splitting due to the DM exchange with both the out-of-plane and in-plane components in the $J' = 0$ limit in (a) [110] and (b) [100] direction.

obtained the dispersion relation for the first triplet excitation as indicated in the inset of Fig. 5. Notable features are the q-dependent splitting due to the anisotropic exchange and the finite bandwidth due to the nnn-coupling. The agreement of the dispersion as determined by the high energy-resolution investigation in [1,1,0] direction and the calculation is excellent and can be regarded as strong evidence for the importance of the anisotropic DM inter-dimer interaction in the spin dynamics of this quantum system. The splitting δ is renormalized by the finite J' and from the exact diagonalization for $J'/J = 0.62$, one obtains $\delta \sim 2.0D$. From the zero-filed splitting $\delta = 0.352 \pm 0.008$ meV at $q = 0$ (Q = (2,0,0)), the z-component of the DM interaction is estimated to be $D \sim 2.1$ K. This finding is in complete agreement with the recent chopper spectrometer investigation by Gaulin et al.[14] employing a slightly better energy resolution.

An anisotropic DM interaction with only z-component would predict a single peak behaviour both at $q_a = q_b = \pi/2$, e.g. (1.5,0.5,0) and $q_a = \pi/2$, $q_b = 0$, e.g. (1.5,0,0). The experiment however clearly shows at least a two peak structure at Q = (1.5,0,0). This suggests that the degeneracy at this point is lifted by another component of the DM interaction. Recalling that the 2-D dimer plane in $SrCu_2(BO_3)_2$ below room temperature is not totally flat, but shows some buckling (Fig. 1(b)), the

symmetry allows the introduction of the in-plane DM component, which may lift the degeneracy at (1.5,0,0), but leaves the result for [1,1,0] direction unchanged, as indicated by the weak coupling limit results depicted in Fig. 6. As shown in Ref. 15) the Zeeman splitting of the two peaks into the three peak structure observed at this Q can be also well accounted for by introducing the in-plane component of DM.

The high energy-resolution investigation of the lowest triplet excitation revealed that most of the observed band width is attributed to the anisotropic exchange inter-dimer DM interaction and the bandwidth due to the frustrated nnn-interaction J' is indeed very small and is of the order of 0.2 meV. Thus the strongly localized character of the triplet excitation in this orthogonal dimer system is again impressively demonstrated.

4.2. *Two triplets bound states*

We now turn to the high energy-resolution investigation of the excitation group II in the energy range of 4 to 7 meV. As already pointed out in the first section the first inelastic neutron scattering results on this energy range was interpreted as indicating a more dispersive nature of this higher energy mode and thus suggesting a correlated hopping of the two-triplets excited states. However the above-mentioned data with better statistic already indicated that the Q-dependence in (1,1,0) direction could be explained by number of flat modes displaying different structure factors. To substantiate this interpretation we performed high resolution experiment on the bound states in the energy range of 4 to 7 meV.[16] The experimental conditions were the same as for the previous high resolution experiment looking at the first triplet excitation.

Figure 7 depicts typical inelastic spectra in the energy range of 4 to 7 meV. With this high resolution it is obvious that the excitation group in this energy range consists at least of three peaks with finite widths. The solid lines in Fig. 7 show the results of fitting procedure assuming three gaussian peaks convoluted with the resolution function (in the fitting procedure another higher energy mode at around 8 meV is assumed, which we know from the coarse resolution experiment, see Fig. 2.). Figure 8 summarizes the fitting results. Figure 8(a) shows the Q-dependence of the energy positions and the bars represent the intrinsic line widths of the individual excitations. Figure 8(b) indicates the Q-dependent integrated intensity of the individual excitations. Following features clearly emerge from this analysis.

1) The excitations in the energy range of 4 to 7 meV should be described as collection of almost flat modes (bandwidth of at most 0.2 meV) at 4.8, 5.5 and 6.25 meV energy transfer with intrinsic line widths of 0.3, 0.5 and 0.5 meV, respectively.

2) The integrated intensities of the upper two modes show only small modulation with Q, but the intensity of the 4.8 meV mode shows a strong Q dependence, notably disappears at $Q = (2.5,0.5,0)$.

We remark that these findings are consistent with the coarse resolution measurement, where we approximated the observed spectra in this energy range by two flat modes at 4.9 and 6.2 meV energy transfer with line widths of 0.4 meV and 0.7 meV respectively (see Fig. 1).

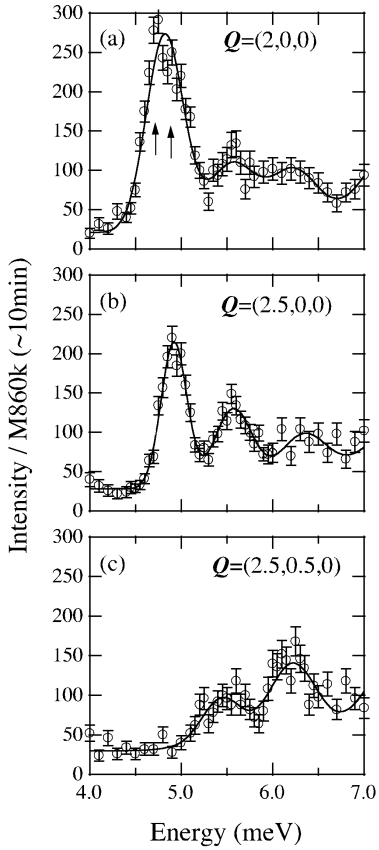

Fig. 7. Typical inelastic spectra at $T = 1.5$ K in the energy range of 4 to 7 meV. The solid lines are the results of fit procedure, as described in the text.

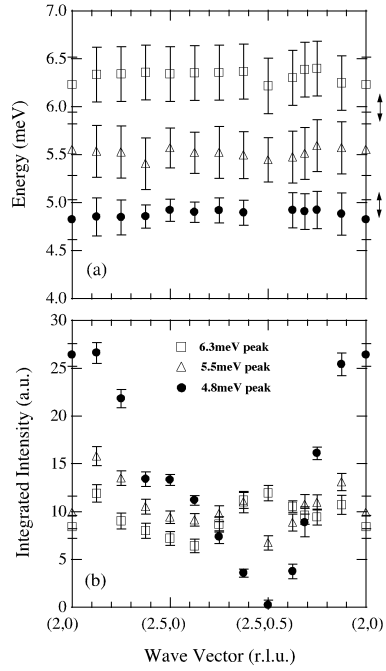

Fig. 8. (a) Q dependence of the peak positions. The vertical bars indicate the intrinsic line widths. (b) Integrated intensities of the individual peaks versus Q.

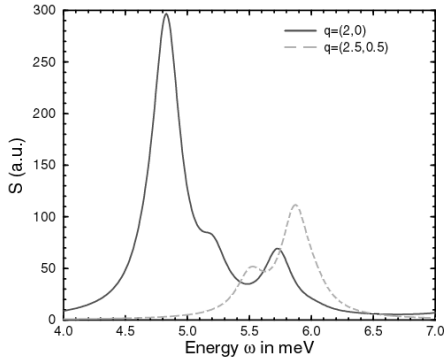

Fig. 9. Two-triplon contribution as calculated by Knetter and Uhrig using $J'/J = 0.603$ and $J = 71.5$ K. (by courtesy of Drs. Ch. Knetter and G. S. Uhrig)

Recently Knetter and Uhrig calculated the dynamic structure factor of the two-triplon sector of the two-dimensional spin 1/2 Shastry-Sutherland model using the method of perturbative continuous unitary transformations.[17] Their main conclusion is that the rather flat bands of the two-triplon state are distributed over the energy range of 4.5 to 7 meV. This energy range corresponds to the previously predicted range due to the correlated hopping. And since many bound states occur the strong level repulsion flattens

the bands so that no significant dispersion arises. Figure 9 reproduces their calculated spectra for Q = (2,0,0) and (2.5,0.5,0) with $J'/J = 0.603$ and $J = 71.5$ K. The qualitative agreement with the experimental spectra presented in Fig. 7 is striking. It can therefore be concluded that the rather flat bands of excitations in the energy transfer range of 4.9 to 6.3 meV should be associated with the number of flat two-triplon bound states distributed in this energy range showing very characteristic Q-dependent spectral weight.

§5. Conclusions

To summarize the inelastic neutron scattering investigations utilizing both thermal and cold neutron spectroscopy revealed the characteristic spin dynamics of the orthogonal dimer system $SrCu_2(BO_3)_2$. The negligible kinetic energy of the single triplet excitation due to the frustrated inter-dimer exchange renders each individual band a very small band width of at most 0.2 meV. The first single triplet state at around 3 meV is split due to the Dzyaloshinski-Moriya inter-dimer interaction with both the out-of-plane and in-plane components. The splitting between the $S_z = \pm 1$ states is of the order of 0.3 meV. The two triplets bound states also form a very flat bands at 4.9, 5.5 and 6.3 meV with finite line width of the order and/or twice of the Dzyaloshinski-Moriya splitting. Finally the higher energy range up to 13 meV can be also characterized by three rather broad, but flat bands at around 8, 10 and 12 meV with the line width three times the Dzyaloshinski-Moriya splitting. These excitations can be probably assigned to higher bound state excitations. The finite widths observed in the two triplets and higher bound states excitations may arise from the existence of numerous discrete excitations, as has been indicated by the ESR experiment by Nojiri et al.[18] Unfortunately the energy resolution of the present experiments does not allow to address this issue. We probably have to wait for the operation of a cold neutron chopper instrument at the MW-class spallation source to clarify this issue.

The series of the inelastic neutron investigations revealed the entire spin dynamics of $SrCu_2(BO_3)_2$ and should contribute to the deeper understanding of this 2-dimensional quantum system. Some of the prominent features of spin dynamics expected for the Shastry-Sutherland model are found in $SrCu_2(BO_3)_2$, but it is of great interest how the novel anisotropic Dzyaloshinski-Moriya exchange terms modify the quantum critical behaviour in this real system. And whether the origin of the unexpected temperature dependence of the spin dynamics is intrinsic to the 2-D system or a 3-D effect due to the finite inter-plane exchange awaits further experimental and theoretical investigations.

Acknowledgements

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