Magnetic Excitations in Strongly Correlated Electrons
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Neutron Scattering Studies on Quantum Spin Systems - Spin Excitations in $KCuCl_3$ and NaV_2O_5 -

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We present the results of inelastic neutron scattering experiments on quantum spin systems $KCuCl_3$ and NaV_2O_5. Both compounds show non-magnetic singlet ground state behaviour at low temperature. An important insight into the origin of the spin excitation gap can be obtained by looking at the wave vector dependence of the magnetic excitations in these systems without a Néel order. $KCuCl_3$ turns out to be a weakly coupled dimer system, in contrast to the initially assumed zig-zag chain or ladder system. NaV_2O_5 on the other hand was first thought to be a linear chain system undergoing a spin-Peierls transition, but it turns out to be most likely a zig-zag charge ordered ladder system at low temperature.

KEYWORDS: $KCuCl_3$, NaV_2O_5, quantum spin system, spin excitations, neutron scattering

§1. Introduction

The quantum fluctuations leading to a ground state, which cannot be expected in a classical spin system, continue to attract interests of both theoretical and experimental physicists. Isolated antiferromagnetic spin dimer systems[1)] have been known for quite a while to posses a non-magnetic singlet ground state. The alternating exchange chain system can be regarded as a one-dimensional arrangement of dimers, hence the existence of the spin excitation gap was obvious. It was the Haldane conjecture[2)] which ignited a controversy on the spin excitation gap in an antiferromagnetic(AF) Heisenberg linear chain with integer spin value S. Many experimental and theoretical efforts have been invested to understand the Haldane state.[3,4)]

Meanwhile many other low-dimensional spin systems displaying singlet ground state behaviour have been discovered and intensively studied. Besides the above mentioned systems, there are e.g. spin Peierls,[5)] spin ladder[6)] and spin plaquette[7)] systems. In some cases the origin of the spin singlet ground state is obvious by looking at the structure of the compound. But in many cases it is a priori not clear by what kind of exchange paths the magnetic ions are predominantly connected. Since these systems do not order even at zero temperature, the study of the excited state only gives the information on the microscopic magnetic exchange path scheme leading to the observed singlet ground state. Neutron inelastic scattering experiments in zero and applied field thus greatly contribute to the physical understanding of the ground state by revealing the wave vector dependence and degeneracy of the excited states. In this paper we would like to demonstrate this aspect by presenting inelastic neutron scattering results on $KCuCl_3$ and NaV_2O_5 in zero and applied field.

§2. $KCuCl_3$

$KCuCl_3$ crystallizes in a monoclinic structure belonging to the space group $P2_1/c$. The lattice parameters are a=4.029Å, b=13.785Å, c=8.736Å and β=97°20'. The main feature of the crystal structure is the double chain of edge-sharing octahedra of $CuCl_6$ along the a-axis as shown in Fig.1a). 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. Figure 1b) schematically shows the possible exchange interactions between the neighbouring Cu^{2+} ions in the double chains. Depending on the ratios of J_i values, one could regard the double chain system e.g. as a ladder system (J_1(AF)~J_3(AF) >>J_2), a zig-zag (alternating) chain with next-nearest neighbour exchange (J_2(AF)~J_3(AF)> J_1(AF)), or as two independent linear chains (J_1(AF) >>J_2,J_3). The susceptibility measurement by Tanaka et al. [8] showed no anomaly pointing to a magnetic phase transition, but rather a broad maximum around 30K. The susceptibility then vanishes exponentially towards zero temperature. They therefore suggested that the ground state of $KCuCl_3$ is essentially the same as those of a

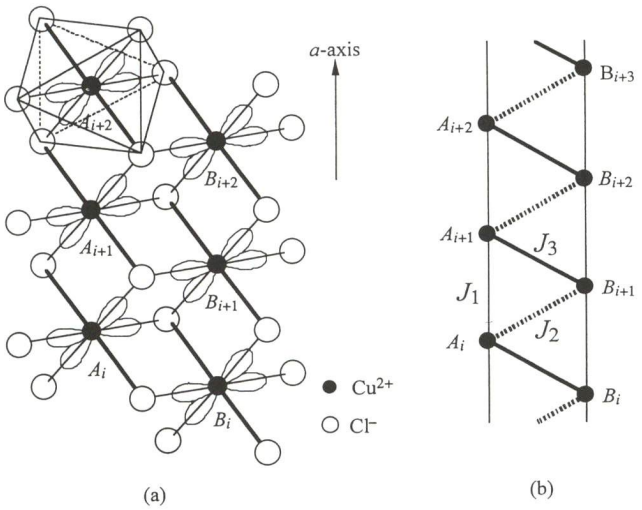

Fig.1. a) Double chain structure in $KCuCl_3$ and the configuration of the hole orbital $d(x^2-y^2)$ of the Cu^{2+} ion.
b) Possible exchange interactions in the double chain.

S=1/2 spin ladder or alternating chain, because both systems are known to exhibit a singlet ground state with excitation gap. To verify this picture we performed inelastic neutron scattering experiment on a large single crystal of $KCuCl_3$, grown from a melt by the Bridgeman technique. The experiment in zero applied field was performed using the ISSP-PONTA spectrometer installed at the research reactor JRR-3M, JAERI, Tokai. The scattering plane was selected to be the a^*-c^* plane of the crystal. Figure 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 origin of this excitation is verified by looking at the temperature dependence. As can be seen from Fig.2 at T=57K 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. Figure 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 2.7meV by averaging the values for Q=(0,0,-1) and the equivalent points at Q=(1,0,±1). This value is very closeto the gap energy of 2.74 meV deduced from the previous magnetization measurements.[9] 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 coupled antiferromagnetic dimer system rather than a quasi one-dimensional double spin chain, as initially proposed based on the chemical intuition.[8]

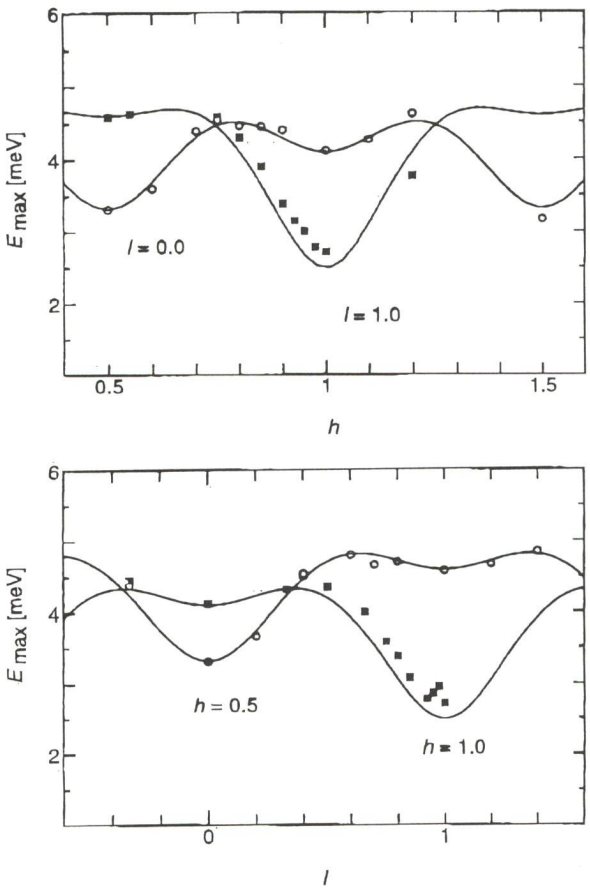

Fig.3. Summary of the observed excitation peak positions for different Q=(h,0,l). The solid lines indicate calculated dispersion relations, as explained in the text.

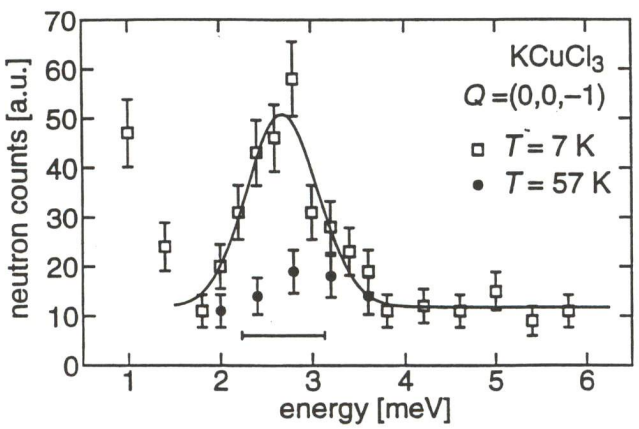

Fig.2. Typical constant-Q inelastic spectra from $KCuCl_3$ at T=7 and 57K.

To clarify the nature of the excited state we performed inelastic neutron scattering under applied field. The experiment was performed on the thermal neutron triple axis instrument E1 installed at the research reactor BER-II of Hahn-Meitner Institut, Berlin. Magnetic fields up to 14 Tesla were applied vertically to the scattering plane, which included a^*- and c^*-axes of the sample. Figure 4 shows the inelastic spectra at Q=(0.05,0,-0.9) in zero and 10.5 Tesla applied field. In zero field a single excitation peak at 3.4 meV can be observed consistent with the above neutron scattering results. Under the applied field of 10.5 Tesla the excitation splits into three modes. The field dependence of the splitting is depicted in Fig. 5. These results clearly show that the excited state is a triplet state and support the strong antiferromagnetic dimer character causing the singlet-triplet excitations.

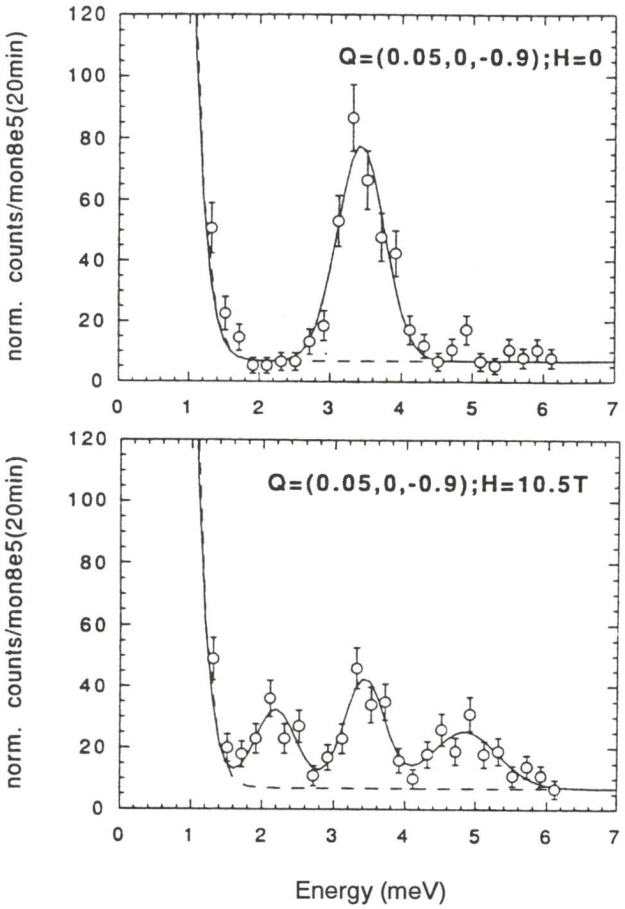

Fig.4. Inelastic spectra at Q=(0.05,0,-0.9) in zero and 10.5 Tesla applied field.

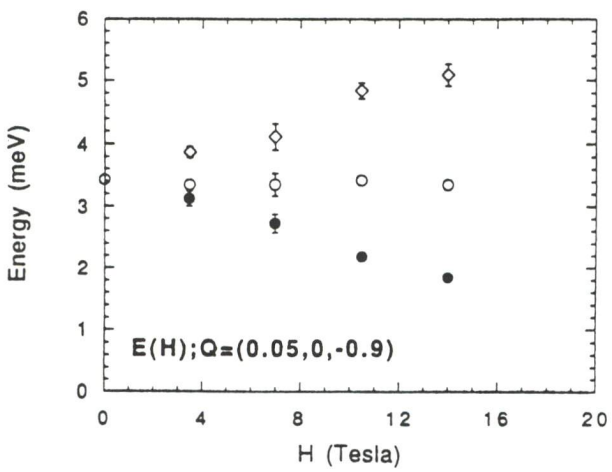

Fig.5. Field dependence of the excitations energies at Q=(0.05,0, -0.9).

The dispersion relation of such a weakly coupled dimer system can be modeled within the random phase approximation.[8] Assuming the exchange constant J_2 as the dominant dimer forming antiferromagnetic interaction J_d, the exchange constants as shown in Table I can be introduced to describe the experimentally observed excitation energies[10]. The solid lines in Fig. 3 indicate the calculated dispersion relations with these parameters in good agreement with the experimental findings.

Table I. 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

These results clearly show that $KCuCl_3$ is a weakly coupled dimer system with the dominant antiferromagnetic intradimer exchange of J_d= -4.11meV and weak interdimer exchanges, which, 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.[11] and their results are consistent with those presented here.

§2. NaV_2O_5

The vanadium oxide NaV_2O_5 is a mixed valence compound. According to the earlier structural study by Carpy and Galy,[12] it has an orthorhombic structure of the space group $P2_1mn$ and lattice parameters a=11.30Å, b=3.61Å and c=4.80Å at room temperature. The layers

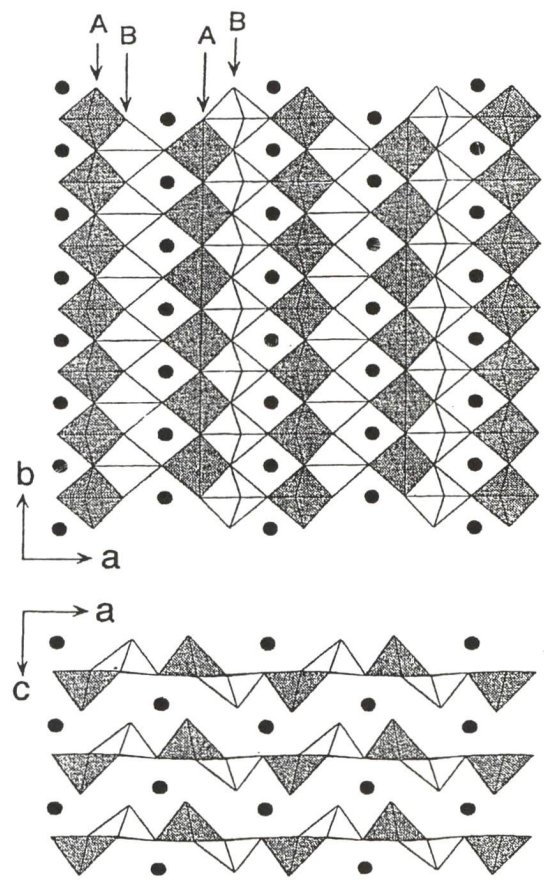

Fig.6. Schematic crystal structure of NaV_2O_5 projected onto the a-b plane and a-c plane. The white and shaded square pyramids show two kinds of VO_5 pyramids. A and B indicate the $V^{4+}O_5$ and $V^{5+}O_5$ chains, respectively.

of the VO_5 pyramids connected in the *a-b* plane are stacked along the c direction and the sodium atoms are located between these layers as intercalants. There are two crystallographically inequivalent vanadium sites belonging to two kinds of VO_5 pyramid chains along b-axis. The chains formed by magnetic V^{4+}(S=1/2) ions are separated by chains containing non magnetic V^{5+} (S=0) ions. (Fig. 6)

The magnetic susceptibility shows a broad maximum at around 350K and decreases abruptly to zero below 35K, indicating a transition to a non-magnetic singlet ground state. It was the above linear chain structure of magnetic V^{4+} ions and the almost perfect agreement of the high-temperature susceptibility with the Bonner-Fisher prediction using the intrachain exchange value of J=-560K, which led to the suggestion that this transition may be a spin-Peierls(SP) transition per excellence.[13] The observation of the structural superlattice reflections with the modulation vector q=(1/2,1/2,1/4) by means of X-ray diffraction and the magnetic excitation gap of ~10meV by means of powder inelastic neutron scattering below 35K further supported the one-dimensional (1-D) SP scenario.[14] However the serious deviation from the BCS-scaling of $2\Delta/(k_B T_{sp})$~3.5, Δ being the gap energy and T_{sp} being the SP transition temperature, obeyed in almost all the SP systems so far discovered, even in the first inorganic SP system $CuGeO_3$, and the Q-dependent intensity at the gap energy of 10meV in the powder averaging, pointing to a not purely 1-D character of spin excitations, are inconsistent with this scenario.

Again to obtain more detailed information on the microscopic magnetic exchange path scheme leading to the observed non-magnetic ground state, we performed inelastic neutron scattering experiments at low temperature (low-T) using single crystal sample. The experiments were carried out on the ISSP-PONTA spectrometer at the research reactor JRR-3M of JAERI. Eight single crystals of the total volume of ~0.5cc were aligned with their a^* and b^* axes in the scattering plane.

Figure 7 shows constant-energy scans around Q=(3,0.5,0) in the b^* chain direction. Consistent with the previous powder measurement, there is only a flat background observed at 7meV energy transfer, while at 10meV a strong intensity centered around the 1-D antiferromagnetic zone centre at k=0.5 is observed. As the energy transfer is increased, the peak broadens first and at 15meV energy transfer a two peak structure reflecting the strong AF dispersion along b^*-axis can be seen. The solid lines in Fig. 7 are the resolution convoluted spectra of a 1-D AF dispersion along b^* axis with the gap energy of 9.8meV and the zone boundary energy of 59.5meV, corresponding to the exchange constant of $|J|$=37.9meV.[15] These results clearly demonstrate that the magnetic excitation shows a strong dispersion along b^*-direction.

Figure 8 shows series of energy scans at Q=(h,0.5,0) for $1<h<4$. If the interchain interaction would be negligible and the system one-dimensional, one would expect almost h-independent spectra. But in contrast we recognize two remarkable features in Fig. 8:

1) A single peak structure around 10meV is observed when h is an integer, while two peaks are clearly observed in between these h-values.

2) There is a strong intensity modulation along h, which explains the peculiar Q-dependent gap energy intensity in the previous powder experiment.[14]

Figure 9 shows the energy positions of the two peaks between $2<h<3$. It shows the lowest and highest energy position of about 8.5meV and 11.5meV, respectively. This energy difference of 3meV gives the energy scale of the interaction perpendicular to the chain direction and is indeed much smaller than that of the exchange constant along b^*-direction. This finding clearly underlines the strong anisotropic character of the magnetic excitations in

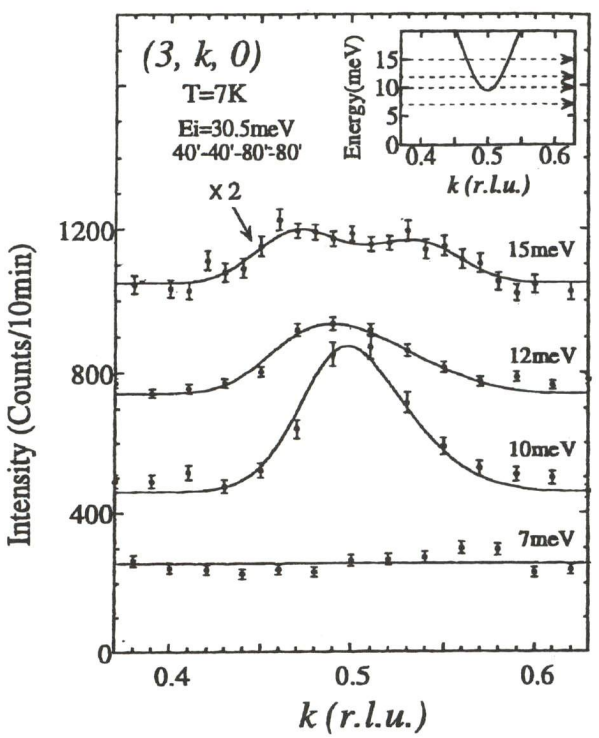

Fig.7. Constant-energy scans around Q=(3,0.5,0) in the b^* chain direction at different energy transfers. The zero levels of the intensity axes for different energy transfers are shifted by arbitrary amounts. Inset: The solid line shows 1-D AF dispersion along b^* axis with the gap energy of 9.8meV and the zone boundary energy of 59.5meV. The broken arrows indicate the constant-energy scans performed.

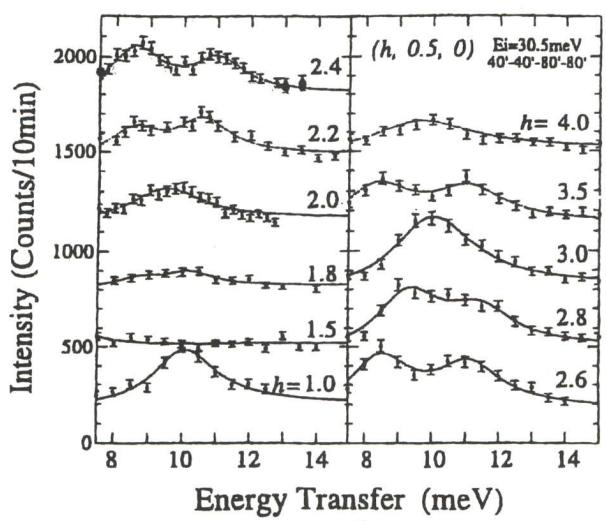

Fig.8. Energy spectra at Q=(h,0.5,0) for different h -values.

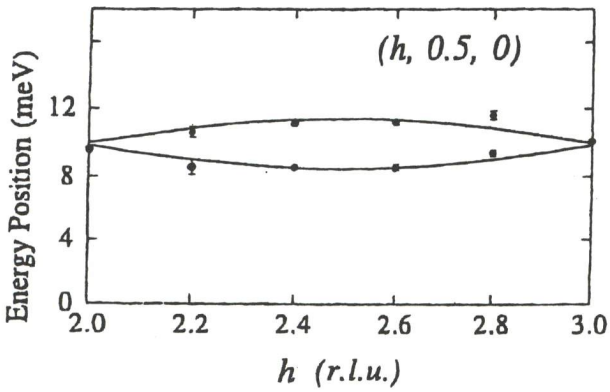

Fig.9. Energy peak positions of the excitations at Q=(h,0.5,0) for 2<h<3. The solid line indicates dispersion relation calculated by Gros and Valenti [18] for a zig-zag charge order.

low-T phase of NaV_2O_5, in contrast to the above $KCuCl_3$ case, but it also rules out a simple independent SP chain model.

To clarify the nature of these two excitation branches we performed inelastic neutron scattering experiment under applied field. Figure 10 shows the spectra at Q=(2.4,0.5,0) in zero and applied field of 5.5Tesla. A clear broadening of both peaks in accord with the expected 0.7meV Zeeman splitting of two triplet peaks can be observed.

More recently it is proposed that NaV_2O_5 in high-T phase should be regarded as a quarter filled ladder compound.[16] In this interpretation the electron spins are not localized at V-ions, but distributed over V-O(1)-V molecules in high-T phase. It was Seo and Fukuyama[17] who proposed a zig-zag type charge disproportionation along the ladders of V-ions at low-T, which is stabilized as a ground state due to the interatomic Coulomb interaction.

According to Gros and Valenti[18] the splitting of the spin excitation branches along a direction as observed by inelastic neutron scattering is induced by a specific zig-zag charge ordering in the quarter filled ladder system. They calculated threefold degenerate magnon-dispersion relations for acoustic and optic mode in accord with the above neutron scattering results (see Fig. 9). Thus the zig-zag charge ordered state in the quarter filled ladder is a promising candidate for explaining the non-magnetic ground state in NaV_2O_5. Unfortunately the dynamical structure factor cannot be yet calculated in the same theoretical frame and hence the intensity modulation along a-direction is yet to be explained consistently. But it is clear that a full understanding of the novel ground state in NaV_2O_5 can only be achieved by taking into account the microscopic magnetic exchange scheme consistent with the neutron scattering results.

§3. Summary

These two inelastic neutron scattering investigations on $KCuCl_3$ and NaV_2O_5 impressively demonstrate the importance of the method to determine the microscopic origin of the non-magnetic singlet ground state realized in these systems. In both cases the direct observation of the wave vector dependent magnetic excitations by means of inelastic neutron scattering added important insights into the microscopic magnetic exchange path schemes leading to the observed singlet ground states, which in both cases turned out to be counter-intuitive to the initial geometrical considerations.

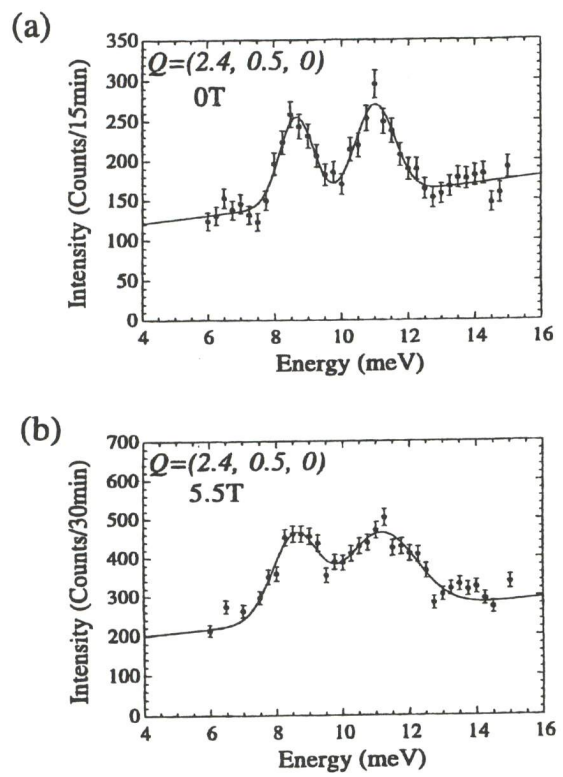

Fig.10. Spectra at Q=(2.4,0.5,0) in zero (a) and applied field of 5.5 Tesla (b).

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