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Haldane-gap modes in the $S=1$ antiferromagnetic chain compound $CsNiCl_3$

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For the antiferromagnetically coupled integer-spin Ni^{2+} chains of $CsNiCl_3$ the Haldane gap is found by neutron scattering to be a singlet-to-triplet spin excitation. It has a 2π periodicity in momentum space with a dispersion relation that falls to a value of order twice the gap energy as $Q\rightarrow 2\pi$. When the coupled Ni^{2+} chains undergo the transition to three-dimensional order, a set of longitudinal modes is found to occur that are not present in conventional theory where the excitations are transverse spin waves. Our calculations of the intensities show that near the ordering wave vector $(\frac{1}{3},\frac{1}{3},1)$ the new modes agree with the field theory of Affleck but not with spin-wave theory. At larger interchain wave vectors both field theory and spin-wave theory break down.

The mass gap predicted by Haldane[1] for integer-spin Heisenberg antiferromagnetic (HAFM) chains was first observed[2] in $CsNiCl_3$, a quasi-one-dimensional (quasi-1D) material with chains of Ni^{2+} ($S=1$) ions. Due to weak interchain interactions, a 3D long-range order develops at $T_N=4.4$ K in which the Ni^{2+} magnetic moments are canted within a plane containing the hexagonal c axis. Since the orbital angular momentum of Ni^{2+} is quenched, the superexchange interaction between Ni^{2+} ions is predominantly isotropic and can be represented by the following Hamiltonian:

$$H=2J\sum_i \mathbf{S}_i\cdot\mathbf{S}_{i+1}+J'\sum_{i\neq j}\mathbf{S}_i\cdot\mathbf{S}_j+D\sum_i (S_i^z)^2 , \qquad (1)$$

where D is negative and small. The strengths J and J' of the nearest-neighbor intrachain and interchain interactions deduced from the spin-wave frequencies of the 3D phase are antiferromagnetic with the values 0.345 and 0.006 THz, respectively.[3] The last term arises from anisotropy in the local crystal fields: it is weak because it influences the orbitally nondegenerate ground state only via the spin-orbit coupling to excited states. Direct determination of D from the spin-flop magnetic field[4] gives a small easy-axis anisotropy where $|D|<0.0026$ THz. Inelastic neutron-scattering measurements by Morra *et al.*[3] in the 3D phase ($T<4.4$ K) showed a Goldstone mode and a gap mode near the ordering wave vector $(\frac{1}{3},\frac{1}{3},1)$ where the interion phase factor between nearest Ni^{2+} ions is π (AFM zone center). They showed that the gap mode could be reproduced by linear spin-wave theory only if a very large anisotropy $D=-0.013$ THz (finite-D model) was phenomenologically introduced in (1). It was suggested that this unusual size of $|D|$ was a reflection of Haldane gap effects in the 3D phase rather than the true anisotropy. For the spin spectrum in the 1D phase ($T\gg 5$ K) a simple model of weakly coupled chains, each with an intrinsic 1D gap of 0.32 THz, was found to account well for the residual 3D dispersion present above the Néel point. It was then argued that the energy gap of 0.32 THz for isolated chains must be the Haldane gap because it was much too large to be explained by even the large phenomenological $|D|$.

The *ad hoc* approach of Morra *et al.*[3] of course does not describe how the Haldane-gap mode of the 1D phase is connected with the modes of the 3D phase. Since the gap in the 1D phase arises from a many-body quantum effect that embodies quite different physics and energy scale than the weak interchain interaction, we generally expect the gap to persist in the 3D phase. The need for such a theory became very clear when it was subsequently shown[5,6] that describing all the modes in the 3D phase by the finite-D model[3] gave a wrong polarization for the gap at $(\frac{1}{3},\frac{1}{3},1)$.

Until recently, theory[1] was only available for isolated chains for which a triplet mass gap of magnitude $\Delta=0.41(2J)$ was predicted by numerical simulations.[7] The first prediction related to spin-wave dispersion was the first- and second-moment calculation of Arovas, Auerbach, and Haldane[8] for an extended Heisenberg Hamiltonian that Affleck *et al.*[9(a)] had shown gave rise to the valence-bond solid state. Although this exactly solvable model predicts similar properties to those of the actual Heisenberg model, namely, a triplet mass gap with 2π periodicity, its first moment, which rises monotonically as $Q \to 0$ (or 2π), has been shown to be in disagreement with neutron-scattering data,[6] which show a spin-wave peak that falls as $Q \to 2\pi$. More recently the spin-wave dispersion of a $N=32$, $S=1$ chain was calculated by Takahashi[10] by the projector Monte Carlo method. It gave the magnitude of the gap $\Delta = 0.415(2J)$ at $Q=\pi$, in agreement with previous numerical simulations,[7] and a gap of 2Δ at $Q=0$ (or 2π). (The 2Δ gap is seen also in numerical calculations by Haldane[9(b)] for the model of Affleck *et al.*[9(a)]) However, the zone boundary ($Q=\pi/2$ or $3\pi/2$) frequency calculated was $5.31J$ instead of $4J$ as expected for a spin-1 AFM chain.

The only theory for the excitations in the 3D phase of the Heisenberg model is the recent work of Affleck[11] based on a long-wavelength limit field-theory approach. To calculate the effect of the 3D ordering on the spectrum, Affleck simplified the problem by mapping the long-wavelength behavior given by the $(1+1)$-dimensional quantum field theory of the isotropic (i.e., $D=0$) Heisenberg chain onto a classical Lagrangian containing an explicit mass term. Even for an isolated 1D chain this model predicts a gap of 2Δ as $Q \to 0$ corresponding to two-magnon excitations. In the 1D phase the model gives rise, near $Q=\pi$, to a triplet gap mode above the singlet ground state. One of the triplet members corresponds to fluctuations in the length of the field variable $|\boldsymbol{\phi}|$, i.e., to longitudinal fluctuations. In the 3D phase, near $(\frac{1}{3},\frac{1}{3},1)$, the longitudinal mode persists as a gap mode, while the two transverse modes become Goldstone modes identical to the modes of linear theory. Note that Affleck's longitudinal mode cannot be obtained from any site-based model, since magnetic sites are assumed to be occupied by fixed-$|\mathbf{S}|$ particles.

In this paper we report inelastic neutron-scattering results that demonstrate the predicted properties of the Haldane gap in the 1D phase, i.e., its energy, triplet character, and 2π periodicity. In the *3D* phase we have calculated the intensities from spin-wave theory and from the recent field theory of Affleck.[11] Near the ordering wave vector $(\frac{1}{3},\frac{1}{3},1)$ only the intensity ratios given by the field theory are shown to be in agreement with experiment. Another new result is that the field-theory approach[11] does not provide a satisfactory explanation of the 3D phase magnons at wave vectors away from $(\frac{1}{3},\frac{1}{3},1)$. Constant-**Q** scans were performed on single crystals of $CsNiCl_3$ with a triple-axis spectrometer at the National Research Universal (NRU) reactor, Chalk River. All measurements were carried out in the (hhl) zone and, for polarized neutron scans, the sample was subjected to a $[1\bar{1}0]$ vertical magnetic field (taken to be the $\hat{\mathbf{y}}$ direction) strong enough to produce a single-domain sample with spins canted only in the xz plane. (Note that $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$ form a Cartesian coordinate system, which, of course, is different from the hexagonal unit cell.) In this geometry Affleck's longitudinal mode is always of $\langle xz \rangle$ symmetry, while the transverse modes can be of $\langle xz \rangle$ (fluctuation within the canting plane) or $\langle y \rangle$ (fluctuations out of the canting plane) symmetry.

The highest-frequency mode near $(\frac{1}{3},\frac{1}{3},1)$, i.e., the gap mode, is shown in Fig. 1 to occur in the spin-flip (SF) channel indicating that it is of $\langle xz \rangle$ symmetry. This disagreement with the predicted $\langle y \rangle$ symmetry of finite-D theory[3] was first observed by Steiner *et al.*[5] in a polarized neutron scan at (0.2767,0.2767,1). The field theory[10] predicts the gap mode to be a longitudinal fluctuation of the correct $\langle xz \rangle$ symmetry. The intensity ratio between the two low-frequency Goldstone modes, $I\langle y \rangle : I\langle xz \rangle$, is predicted to be 1:0.45 in the finite-D theory, whereas the observed ratio is about 1:0.29, in agreement with the field theory. Thus the highest-frequency mode is indeed a member of the predicted new class of longitudinal spin excitations.

The finite-D theory predicts three magnon branches of significant spectral weight at frequencies 0.3298, 0.4493, and 0.5181 THz for the wave vector of Fig. 2. The lowest-frequency mode is a $\langle z \rangle$ mode and, hence, cannot be seen at (001) but ought to be seen near (111). Yet no strong scattering is observed near (111) at the expected frequency in Fig. 2(a). Subsequent polarization analysis of the peak, carried out with relaxed resolution in order to maximize neutron intensity [Fig. 2(b)], showed it consisted of non-spin-flip (NSF) scattering and SF scattering both centered at 0.44 THz and with intensity ratio of $I\langle y \rangle : I\langle xz \rangle = 2:1$. This observation is in clear disagreement with the field theory, which predicts two transverse

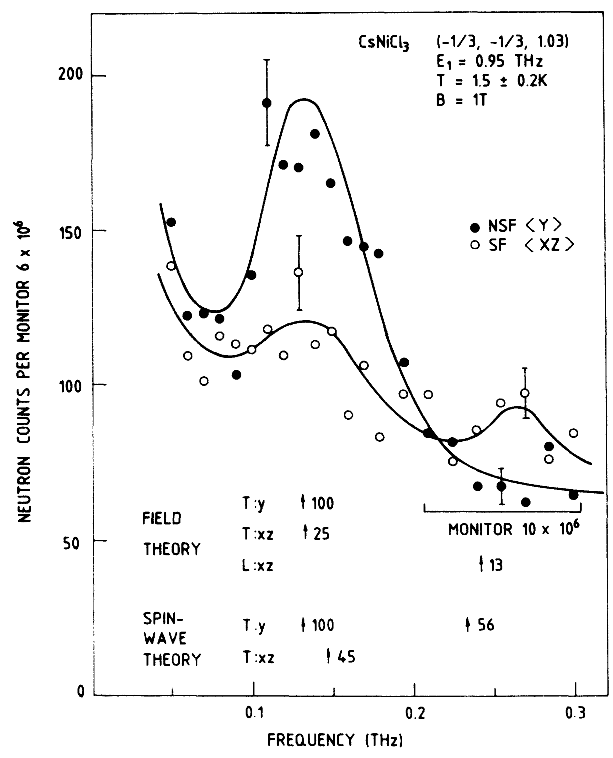

FIG. 1. Constant-**Q** scan performed with polarized neutrons near the 3D ordering wave vector $(\frac{1}{3},\frac{1}{3},1)$. The predicted magnon frequencies (arrows) and relative intensities normalized to the strongest mode (numbers) are from the spin-wave theory of Morra *et al.* (Ref. 3) with a large anisotropy D (finite-D theory) and the quantum field theory of Affleck (Ref. 11). Note that the highest-frequency mode at 0.26 THz appears in the spin-flip (SF) channel consistent with the longitudinal mode (L:xz) prediction of the field theory.

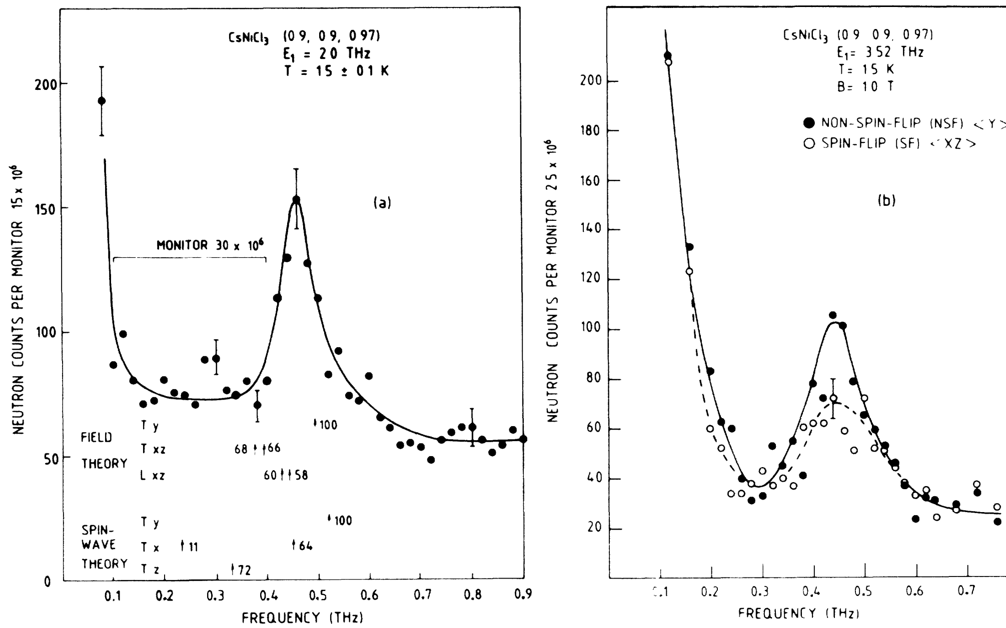

FIG. 2. Constant-**Q** scan in the 3D phase at (0.9,0.9,0.97); (a) high-resolution unpolarized scan and (b) low-resolution scan with polarized neutrons. The arrows are the magnon frequencies predicted by spin-wave theory with large anisotropy (Ref. 3) (finite-D theory) and by quantum field theory (Ref. 11).

modes and one longitudinal mode near (111). The predicted ratio of the two transverse frequencies, $\sqrt{2}$, is a general result for a triangular lattice in the limit of an isotropic HAFM Hamiltonian. It is therefore hard to explain the observations in Fig. 2 without invoking interaction between spin waves or some overdamping near (111), but current theory does not predict such behavior.

The polarized neutron scans shown in Fig. 3 were carried out in the 3D phase (1.4 K) and in the 1D phase (7.6 K) but at the same position in **Q** space. Since **Q** is almost along $\hat{\mathbf{z}}$ at (0.2,0.2,1) the in-plane transverse fluctuations observed are mostly of $\langle x \rangle$ symmetry. The equal intensities in the SF and NSF channels at 7.6 K [Fig. 3(b)] then suggest that $\langle S^yS^y\rangle = \langle S^xS^x\rangle$. Similar polarized neutron scans made by Steiner *et al.*[5] in higher zones further suggest $\langle S^zS^z\rangle = \langle S^yS^y\rangle = \langle S^xS^x\rangle$, i.e., the excitation is unpolarized. From this observation we can conclude that the Haldane gap is a triplet above a singlet ground state. The singlet follows because it has been shown earlier[2,3] that there is no quasielastic scattering. The triplet excited state is then deduced from the fact that the excitation is unpolarized. The triplet symmetry is a further sign that we are dealing with a system with a Haldane gap. It cannot occur within spin-wave theory for a $S=1$ system. In the 3D phase [Fig. 3(a)] the agreement for the $\langle y \rangle$ mode frequency (NSF channel) predicted by field theory[10] is very good, while the broad peak seen in the SF channel is consistent with the superposition of the four $\langle xz \rangle$ modes. We therefore find that the quantum field theory is in agreement with the observed spectra if the comparison is made near the ordering wave vector but not all (001).

In the 1D phase of an integer-spin HAFM chain the periodicity of the gap mode in **Q** space (i.e., along Q_c in $CsNiCl_3$) is expected to be 2π, since the translational symmetry of the chain remains unbroken. The 2π periodicity is seen in numerical calculations by Takahashi,[10] which give the energy gap at the nuclear zone center ($Q_c=2\pi$) 2Δ, where Δ, the energy gap at the magnetic zone center ($Q_c=\pi$), is $0.415(2J)$. The field theory,[11] valid for small q_c vectors near $Q_c=\pi$ and 2π, also predicts that the excitations at 2π are two-magnon processes with a frequency 2Δ.

Figure 4 shows the 1D phase gap mode frequency and full width at half maximum (FWHM) measured at $(0.19,0.19,\eta)$ points. The basal plane components of 0.19 were particularly chosen because the Fourier transform

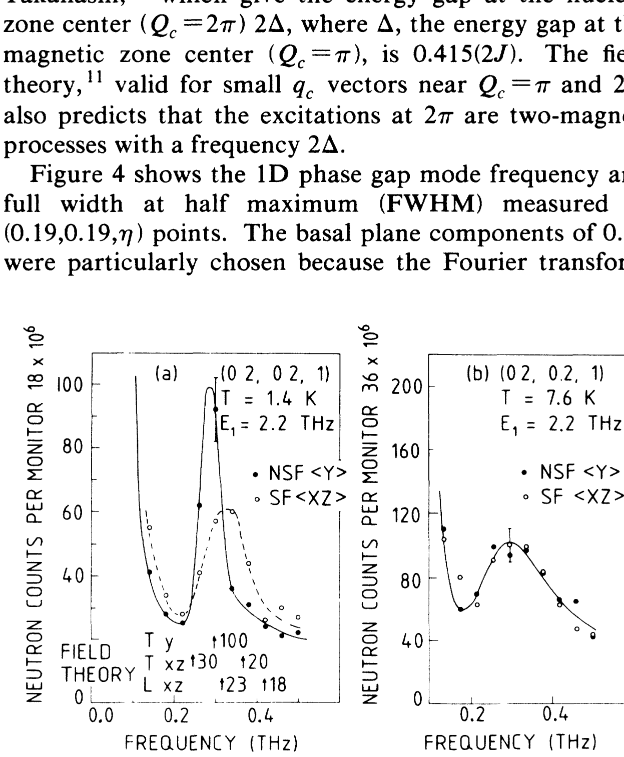

FIG. 3. Polarized neutron constant-**Q** scans in 3D phase (a) and 1D phase (b) at (0.2,0.2,1). In the 1D phase, scattering intensities in non-spin-flip (NSF) and spin-flip (SF) channels are identical indicating that the gap mode is unpolarized.

of interchain coupling vanishes identically at such wave vectors [i.e., $J'(Q_a,Q_b)\equiv 0$] giving a neutron response similar to that of an isolated chain. Measurements in the nuclear zone ($Q_c > 1.5\pi$) were actually carried out at $(0.5,0.5,\eta)$ positions in order to avoid low-frequency phonons but have been renormalized[12] to $Q_a = Q_b = 0.19(2\pi)$. The observed frequencies in the nuclear zone are consistently higher than the corresponding frequencies in the magnetic zone even though they are the same within errors. Although no data are shown beyond $Q_c = 1.8\pi$ because of the decreasing intensity, our results can be interpreted as tending to a gap of 0.6 ± 0.3 THz, i.e., centered on 2Δ. The width of the gap mode is much wider in the nuclear zone than in the magnetic zone (shaded area) even if the change in the spectrometer resolution is taken into account. This may indicate that the triplet degeneracy is partially lifted in the nuclear zone. Both the frequency and the width show that the true periodicity of the excitation is indeed 2π and not π as in a system with broken Néel symmetry.

The crosses in Fig. 4 are the result of projector Monte Carlo calculation[10] with the predicted magnitude of the gap $\Delta = 0.415(2J)$, which we associate with the measured gap of 0.32 THz. This normalization of Takahashi's energy scale gives the predicted zone-boundary frequency much higher than experiment (2.05 THz instead of 1.45 THz). The disagreement is probably caused by the fact that the calculated dispersion in the ground state ($T=0$) has been scaled to the $Q_c = \pi$ frequency measured at 10 K. Since this frequency is expected to have renormalized upward with temperature,[11] Takahashi's zone-boundary frequency appears to be too high. In fact it lies at $5.31J$, 33% above the $4J$ of linear theory, comparable to the $(\pi - 2)/4$ or 28% enhancement for an $S=1$ chain when the interactions between spin waves are taken into account.[13] Alternatively, if $5.31J$ is identified as the measured zone-boundary frequency we would predict an energy gap of only 0.23 THz. This may be considered as an estimate of Δ at $T=0$, since the measured zone-boundary frequency is independent of temperature to a very good approximation (compare Fig. 4 with Ref. 3). We then have the following estimates of the upward renormalization of Δ with temperature: $\Delta = 0.23$, 0.28 (Ref. 11), and 0.32 THz at $T=0$, ~ 2, and ~ 10 K, respectively. We stress, however, that further neutron-scattering experiments, perhaps a series of constant-Q scans at (0.19,0.19,1) at various temperatures in the 1D phase, are required to confirm this behavior of Δ.

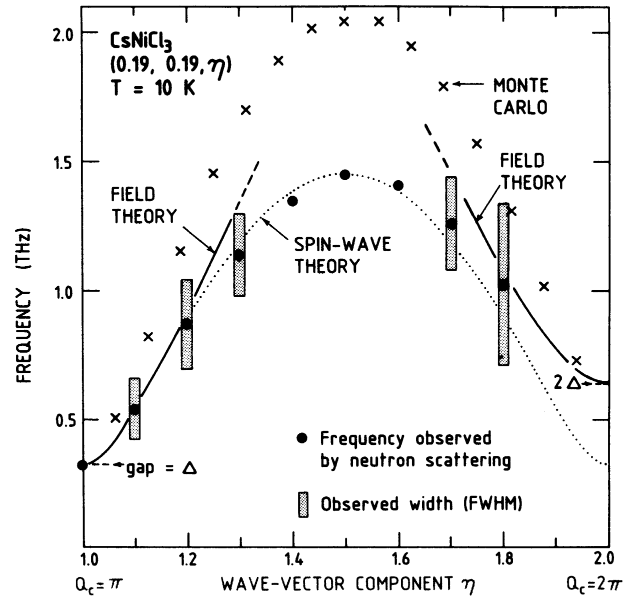

FIG. 4. Measured frequencies (circles) and FWHM (shaded regions) of the mass gap in the 1D phase between the AFM zone center ($Q_c = \pi$) and the nuclear zone center ($Q_c = 2\pi$). The bold solid lines are the field theory of Ref. 11 with energy gap Δ at $Q_c = \pi$ and 2Δ at $Q_c = 2\pi$. The crosses are from Monte Carlo calculation (Ref. 10) normalized to the observed Haldane-gap frequency at $Q_c = \pi$.

We conclude from the neutron-scattering experiment taken with available theories that (1) a Haldane gap is confirmed in $CsNiCl_3$ and by implication in other $S=1$ antiferromagnetic chains, (2) the spin excitations in the 1D phase are of triplet symmetry and their periodicity is 2π, since no symmetry of the chain has been broken, (3) the spin excitations of a set of coupled $S=1$ chains below their transition to 3D long-range order are composed not only of the usual transverse spin waves, but also of a new excitation in which the spin fluctuates in length, and (4) current field theory[11] gives a good account of the excitations near the ordering wave vector but fails for large out-of-phase interchain excitations.

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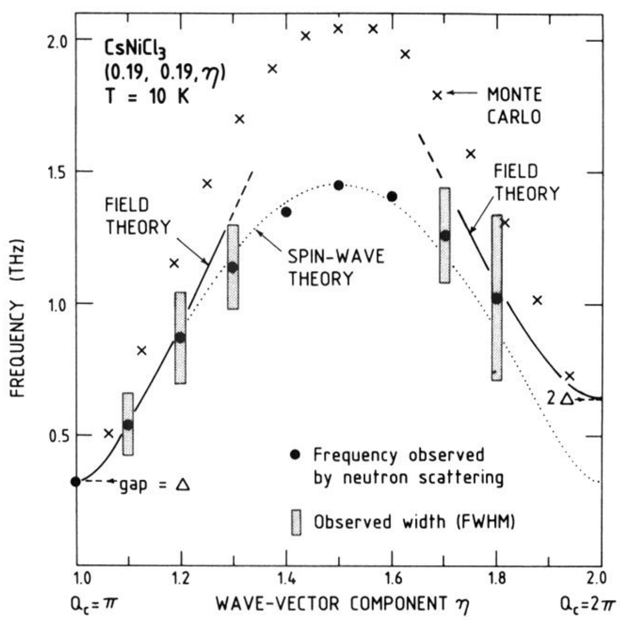
[12]The normalization, done by the formula

$$\omega^2(Q_a,Q_b,Q_c)=\omega(Q_c)[\omega(Q_c)+2J'(Q_a,Q_b)S(Q_a,Q_b,Q_c)] ,$$

is small in the nuclear zone, since $S(\mathbf{Q})$ becomes very small as $Q_c \to 0$. Absolute renormalization is obtained by scaling $S(\mathbf{Q})$ to the observed intensities so that the above equation is exact at $Q_c=\pi$. In the magnetic zone the single-chain frequency, $\omega(Q_c)$, is measured directly at $(0.19,0.19,Q_c)$, where $J'(Q_a,Q_b)=0$.

[13]We have calculated the enhancement from the equation given by T. Oguchi, Phys. Rev. **117**, 117 (1960) for the case of $S=1$ in one dimension.



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