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Zero-point fluctuation in quasi one-dimensional antiferromagnets: theory and experiment

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Abstract. A systematic comparison is given of the quantum reduction in the ordered spin of quasi one-dimensional Heisenberg antiferromagnets as predicted by spin-wave theory and as measured in ionic systems with known spin-wave parameters. Simple linear theory yields a leading term $[1/(2\pi)]\ln(C|J/J'|) - \frac{1}{2}$ where further terms can be neglected for practical purposes if $|J'/J| < 10^{-2}$; such expressions are listed for ferromagnetic and antiferromagnetic square and triangular lattices of antiferromagnetic chains with zero anisotropy. For half-integer-spin systems with $\frac{1}{2} \leqslant S \leqslant \frac{5}{2}$, excellent agreement with experiment is found over the range $10^{-2} > |J'/J| > 10^{-4}$ when a known correction for 'kinematical interactions' is applied. It should thus be possible to identify covalency reductions in excess of 10%. For the $S = 1$ system $CsNiCl_3$, however, the measured spin reduction may indicate extra quantum fluctuations related to the Haldane effect. From the susceptibility behaviour, the quantum ground state for progressively smaller $|J'/J|$ is argued to increasingly resemble a singlet separated from other states by an energy gap.

1. Introduction

The experimenter who wants to interpret a magnetic moment value measured on an antiferromagnetic compound is faced with the task of separating covalency reduction from zero-point quantum fluctuation effects. According to antiferromagnetic spin-wave theory [1, 2], the quantum reduction can be formulated as a reciprocal-space integral involving the spin-wave dispersion, and in quasi-one-dimensional (1D) systems it may become arbitrarily large. A numerical evaluation for such systems, however, is rendered difficult by the singular nature of the integrand, and ready-to-use analytical results for quantitative experiment analysis are not available in the literature. Moreover, a systematic test of the theoretical prediction for quasi-1D systems that takes into account the body of experimental data collected since 1975 seems to be missing. Early reviews [3] cited experimental evidence for reduced moments in quasi-1D antiferromagnets, but questioned the prediction from spin-wave theory, or paid no attention to quantitative aspects.

The present article aims to make more easily accessible, and to establish some trust in, the spin-wave theoretical prediction of the zero-point spin reduction in quasi-1D Heisenberg antiferromagnets. Thus, in the context of a brief review of the theoretical background (section 2), an analytical treatment of the reduction is given and explicit formulae are listed for simple lattices. The prediction is then checked (section 3) against a compilation

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of available measurements on ionic chain systems with known spin-wave dispersion parameters, which calls for some discussion of contradictory data and data at variance with spin-wave theory. Finally, in an attempt to shed light on the fluctuating quantum magnetic ground-state (section 4), implications of spin-wave theory for the magnetic susceptibility close to the limit of vanishing inter-chain coupling are considered.

2. Theory

For the Heisenberg spin Hamiltonian we use

$$\mathcal{H} = -2\sum_{\langle ij\rangle} J_{ij} S_i S_j - D\sum_i (S_i^{\parallel})^2 \tag{1}$$

where the exchange sum runs over interacting spin pairs and $\parallel$ denotes an arbitrary anisotropy direction. The spin positions are assumed to be on a Bravais lattice, and the ordered-state configuration is assumed to be an antiferromagnetic spiral†, so that the spin angle at site $\boldsymbol{r}_i$ may be expressed as $\boldsymbol{k}_0 \cdot \boldsymbol{r}_i$ in terms of a pitch vector $\boldsymbol{k}_0$. In an extended zone scheme, the Holstein–Primakoff formalism then takes the Hamiltonian into [1]

$$\mathcal{H}_{\mathrm{lin}} = \sum_k A_k a_k^+ a_k^- + \sum_k \tfrac{1}{2}(B_k a_k^+ a_{-k}^+ + B_k^* a_k^- a_{-k}^-) \tag{2}$$

where a_k^+ and a_k^- are Bose operators that create and annihilate spin waves of wavevector $\boldsymbol{k}$, A_k and B_k may be readily written down in terms of J_{ij} and $\boldsymbol{r}_j - \boldsymbol{r}_i$ (see table 1), and terms higher than bilinear in $a_k^{\pm}$ are neglected. This Hamiltonian yields the spin-wave energies $E_k = (A_k^2 - |B_k|^2)^{1/2}$, with all distinct modes following from folding the non-magnetic Brillouin zone into the antiferromagnetic one. The resulting zero-point spin reduction is [1]

$$\Delta S_{\mathrm{lin}} = \frac{1}{2}\int_0^1\int_0^1\int_0^1 \left(\frac{A_k}{E_k} - 1\right) \mathrm{d}h\,\mathrm{d}k\,\mathrm{d}l \tag{3}$$

where (h, k, l) are the components of $\boldsymbol{k}$ in reciprocal-lattice coordinates (with respect to the original Bravais lattice).

In table 1, A_k and B_k are listed for the four cases (referred to as SLF, SLAF, TLF, and TLAF) of linear spin chains with antiferromagnetic exchange $J < 0$ being arranged on square or triangular lattices (SL, TL) with ferromagnetic or antiferromagnetic inter-chain coupling, $J' > 0$ or $J' < 0$ (F, AF). The case of free chains ($J' = 0$) with a non-zero easy-axis anisotropy $D > 0$ [4,5] is included for comparison. In the quasi-1D limit $|J'| \ll |J|$, the numerator A_k in the integrand determining the spin reduction (3) may be approximated by $-2J \times 2S$, and A_k/E_k can then be written as (chains assumed along z)

$$\frac{-2J \times 2S}{\sqrt{(A_k + |B_k|)(A_k - |B_k|)}} = \frac{1}{\sqrt{[1 + \cos(2\pi l) + p(h,k)][1 - \cos(2\pi l) + q(h,k)]}} \tag{4}$$

with $0 < p, q \ll 1$. In this limit, the intra-chain (i.e. l) integration yields‡

$$\Delta S_{\mathrm{lin}} \approx \int_0^1\int_0^1 \left(\frac{1}{2\pi}\ln\frac{8}{\sqrt{p(h,k)\,q(h,k)}} - \frac{1}{2}\right) \mathrm{d}h\,\mathrm{d}k. \tag{5}$$

† Note that this includes simple two-sublattice order.

‡ The integration leads to a complete elliptic integral of the first kind [6], which for $p, q \ll 1$ can be replaced by a logarithm and whose prefactor and argument can be simplified correspondingly.

Table 1. The energies A_k and B_k of the linearized spin-wave Hamiltonian (2) and the resulting zero-point spin reduction ΔS_{lin} for simple quasi-1D antiferromagnets with zero anisotropy and for free chains with finite easy-axis anisotropy. SL and TL denote square and triangular lattices of chains; (h, k, l) and the ordering vectors k_0 refer to primitive tetragonal and primitive hexagonal lattices. $u = \cos(2\pi l)$, $v = \cos(2\pi h) + \cos(2\pi k)$ and $w = \cos(2\pi h) + \cos(2\pi k) + \cos(2\pi h + 2\pi k)$.

Case	k_0	$A_k/2S$	$B_k/2S$	ΔS_{lin}
SL, $J' > 0$	$(0, 0, \frac{1}{2})$	$-2J + 4J' - 2J'v$	$-2Ju$	$\frac{1}{2\pi}\ln\left\lvert 4\frac{J}{J'}\right\rvert - \frac{1}{2} + 0.035^{a}$ $(J' \ll \lvert J\rvert)$
SL, $J' < 0$	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$-2J - 4J'$	$-2Ju - 2J'v$	$\frac{1}{2\pi}\ln\left\lvert 4\frac{J}{J'}\right\rvert - \frac{1}{2} + 0.035^{a}$ $(\lvert J'\rvert \ll \lvert J\rvert)$
TL, $J' > 0$	$(0, 0, \frac{1}{2})$	$-2J + 6J' - 2J'w$	$-2Ju$	$\frac{1}{2\pi}\ln\left\lvert \frac{8J}{3J'}\right\rvert - \frac{1}{2} + 0.028$ $(J' \ll \lvert J\rvert)$
TL, $J' < 0$	$(\frac{1}{3}, \frac{1}{3}, \frac{1}{2})$	$-2J - 3J' - \frac{1}{2}J'w$	$-2Ju - \frac{3}{2}J'w$	$\frac{1}{2\pi}\ln\left\lvert \frac{16J}{3J'}\right\rvert - \frac{1}{2} + 0.050$ $(\lvert J'\rvert \ll \lvert J\rvert)$
$J' = 0$, $D > 0$		$-2J + D$	$-2Ju$	$\frac{1}{2\pi}\ln\left\lvert 16\frac{J}{D}\right\rvert - \frac{1}{2}^{b}$ $(D \ll \lvert J\rvert)$

[a] The additive numerical constants for the two SL cases are identical and may be expressed analytically as $(1/2\pi)\sum_{n>0}[2^{-2n}\binom{2n}{n}]^2/2n$.

[b] The result for free chains with easy-axis anisotropy differs from that given by Kubo [4] (and cited in [1]), but agrees with that by Montano *et al* [5] when their elliptic integral is replaced by a limiting logarithm.

For the simple cases mentioned, this leads to expressions of the type $\Delta S_{\text{lin}} \approx [1/(2\pi)]\ln(C|J/J'|) - \frac{1}{2}$ which are also given in table 1. With the particular choice of logarithmic terms taken there, equivalent to substituting mean values of $p(h, k)$ and $q(h, k)$ in (5), small additive corrections from the inter-chain modulation remain that are all but negligible for practical purposes.

An analytical treatment thus furnishes simple general expressions for the zero-point spin reduction ΔS in Heisenberg antiferromagnets near the 1D limit. Being based on linear spin-wave theory, (3), these are independent of the spin quantum number S (still, the quantum effect $\Delta S/S$ properly vanishes on S approaching infinity). From (5), the leading logarithmic behaviour is obviously universal, while our approximations ignore linear and higher order terms in J'/J. Yet, for $|J'/J| < 10^{-2}$ the analytical results virtually coincide with the exact spin reduction (3), as may be seen for the SLAF case from figure 1 where the limiting formula is depicted along with a numerical evaluation of the integral for $|J'/J| \geqslant 10^{-2}$. Also shown is the corresponding behaviour for the $D > 0$ case [5]. For most real chain systems, the analytical expressions can therefore replace the cumbersome 3D numerical integration which is complicated by the singular nature of the integrand. This difficulty should explain why the SLAF numerical data of Ishikawa and Oguchi [2] for $|J'/J| < 0.01$ fall systematically short of the SLAF analytical result from table 1.

Coupled spin chains with additional anisotropy or with second-neighbour interactions between them can be dealt with in the same manner, unless a new ordered spin configuration prevents the analytical diagonalization of the spin-wave Hamiltonian (this happens e.g. for the TLAF case with easy-axis anisotropy [7]). For example, the decisive logarithm for SLF or SLAF coupling combined with easy-axis ($D > 0$) anisotropy becomes $\ln[16|J|/(4|J'|+D)]$, and for TLAF coupling with easy-plane ($D < 0$) anisotropy $\ln[16|J|/(3|J'|(3|J'|+|D|))^{1/2}]$. It is seen that the effect of additional anisotropy is not dramatic if $|D| < |J'|$, and that an

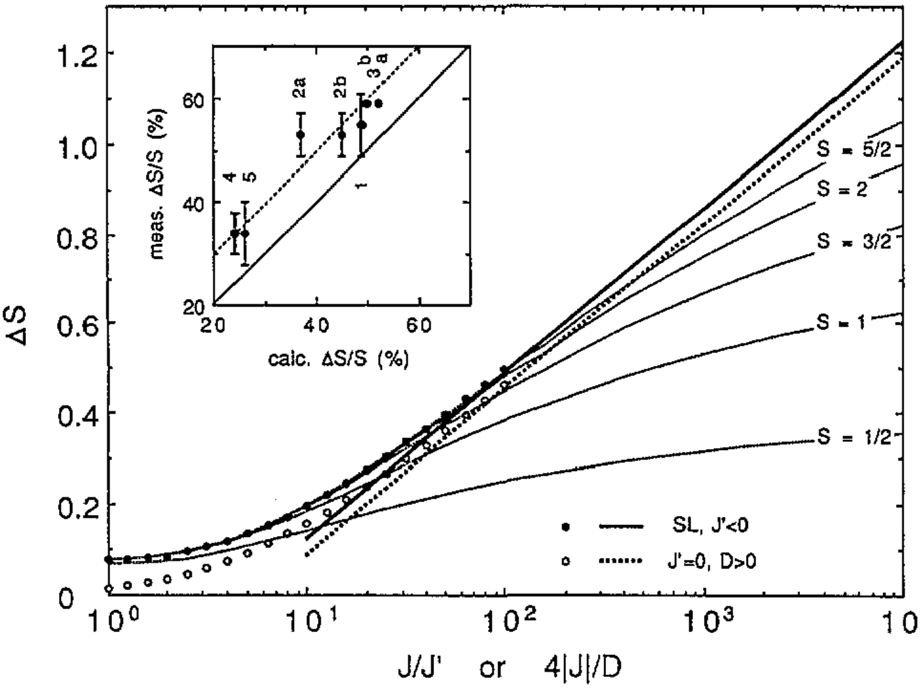

Figure 1. Zero-point spin reduction from linear spin-wave theory for quasi-1D tetragonal antiferromagnets with $J' < 0$ (full circles) and for free chains with easy-axis anisotropy $D > 0$ (empty circles); the straight slopes represent limiting analytical results from table 1. A spin-dependent correction [2] for 'kinematical interactions' is illustrated for the $J' < 0$ case (dotted curves); it leads to good agreement with measurements on ionic compounds (table 2) if covalency reductions up to 10% are allowed for (inset). The one outside point (2a) is from $S = 1$ $CsNiCl_3$.

easy-plane anisotropy together with $J' = 0$ yields an infinite spin reduction, reflecting its inability to stabilize an ordering direction in free chains at $T = 0$. The remaining additive correction here interpolates between the respective J'-only and D-only values given in table 1; for the easy-plane TLAF case it approaches +0.014 for $|D| \gg |J'|$.

The divergent logarithmic behaviour as J' and D tend to zero looks grossly unphysical, yet it correctly indicates the failure of linear spin-wave theory for large spin deviations from the assumed ordered state, and must be regarded as a useful rather than as a bad sign. By incorporating in an approximate way the effect of 'kinematical interaction' terms from the original Heisenberg Hamiltonian (1), which are neglected in the Holstein–Primakoff treatment, Ishikawa and Oguchi [2], expanding on work by Herbert [2], for the SLAF case obtained the improved spin reduction

$$\Delta S_{\text{ren}} = \Delta S_{\text{lin}} - (2S+1)(\Delta S_{\text{lin}})^{2S+1}/[(1+\Delta S_{\text{lin}})^{2S+1} - (\Delta S_{\text{lin}})^{2S+1}] \qquad (6)$$

where ΔS_{lin} is the estimate (3) from linear spin-wave theory. This prescription renormalizes any ΔS_{lin} (which can easily exceed S for small spins) to below S, as it must be, and leads to a vanishing ordered spin $S - \Delta S$ as J' and D go to zero. The same result can be derived [8] for an arbitrary two-sublattice antiferromagnet† by the Green-function technique with

† In the following, we will ignore that an extension to non-collinear antiferromagnets is without verification, and simply use (6) for TLAF systems as well.

random-phase decoupling. The subtractive correction in (6) depends on the spin S; its effect is illustrated for the SLAF case in figure 1 by dotted curves for $S = \frac{1}{2}$ up to $S = \frac{5}{2}$.

3. Experiment

For ionic chain antiferromagnets for which the required data are available [9–28], the calculated spin reductions ΔS_{lin} from (5)† and ΔS_{ren} from (6) are compared in table 2 with experimental reductions ΔS_{exp} from magnetic moment values $\mu = g\mu_B(S - \Delta S)$ measured by neutron diffraction (and extrapolated to $T = 0$ where necessary). Appropriate Landé g-factors were used as listed. The exchange ratios $|J'/J|$ involve parameters extracted via linear spin-wave models, $E_k = (A_k^2 - |B_k|^2)^{1/2}$, from excitation energies directly observed in inelastic neutron scattering, and thus incorporate quantum renormalization effects from higher order terms omitted in the Hamiltonian (2). An exception is the compound K_2FeF_5 [24–26], which shows undulating chains in an orthorhombic structure: here $|J'/J|$ has been deduced from the measured intra-chain exchange J and Néel temperature T_N via the Oguchi relation [29] for a SLF case. In spite of this shortcoming, K_2FeF_5 is included in table 2 because of its unique position as a highly ionic chain compound with a large spin and collinear magnetic order.

Table 2. Available experimental data on the zero-point spin reduction in ionic quasi-1D antiferromagnets, ΔS_{exp}, compared with the linear spin-wave prediction, ΔS_{lin}, and an improved prediction [2] incorporating 'kinematical interactions', ΔS_{ren}. See the inset of figure 1 for a plot of $\Delta S_{\text{exp}}/S$ versus $\Delta S_{\text{ren}}/S$ where the systems are identified by the line numbers from this table.

	System	(Type)	S	g	μ/μ_B	ΔS_{exp}	$\lvert J'/J\rvert$	ΔS_{lin}	ΔS_{ren}	Ref.
1	$KCuF_3$	(SLF)	$\frac{1}{2}$	2.17	0.49(7)	0.27	1.0×10^{-2}	0.50	0.25	[9–11]
2a	$CsNiCl_3$	(TLAF)	1	2.25	1.05(10)	0.53	1.7×10^{-2}	0.48[a]	0.37[a]	[12–15]
2b							6.0×10^{-3}	0.63	0.45	[16]
3a	$CsVCl_3$	(TLAF)	$\frac{3}{2}$	1.97	≈ 1.2	≈ 0.9	2.7×10^{-4}	1.12	0.78	[17, 18]
3b							2.9×10^{-4}[b]	1.05[c]	0.75[c]	[19]
4	K_2FeF_5	(SLF)[d]	$\frac{5}{2}$	≈ 2.0	3.3(2)[e]	0.85	3.3×10^{-3}[f]	0.62[g]	0.60[g]	[24–26]
5	$CsMnBr_3$	(TLAF)	$\frac{5}{2}$	≈ 2.0	3.3(3)[h]	0.85	2.2×10^{-3}	0.66[i]	0.64[i]	[27, 28]

[a] Ignores an easy-axis anisotropy $D/|J| = 3.8 \times 10^{-2}$ in compliance [15] with a small spin-flop field of ≈ 20 kG.
[b] From the model of [19] with $J/k = -169$ K taken from [18].
[c] Includes the effect of easy-plane anisotropy, $D/|J| = -5.7 \times 10^{-4}$.
[d] The SLF model approximates an actual orthorhombic structure.
[e] Mössbauer hyperfine field variation [25] used in extrapolating 4.2 K magnetic moment [24] to $T = 0$.
[f] Obtained from $T_N \approx 10$ K and $J/k = -9.45$ K via the Oguchi relation $kT_N \approx 2.1S(S+1)(|J||J'|)^{1/2}$.
[g] Includes the effect of easy-axis anisotropy, $D/|J| = 2.8 \times 10^{-3}$, derived [26] from a spin-flop field of 37 kG.
[h] Error as given for the 4.5 K data used [27] in extrapolating to $T = 0$.
[i] Includes the effect of easy-plane anisotropy, $D/|J| = -1.6 \times 10^{-2}$.

The spin-wave energies for the SLF system $KCuF_3$ reveal [11] an anisotropy that is negligible compared to J', whereas for TLAF $CsMnBr_3$ [28] an appreciable easy-plane term is found, which has been included in computing ΔS. For K_2FeF_5, an easy-axis anisotropy $D \approx J'$ derived from the measured spin-flop field [26] has been incorporated in the computation.

† The full integral (3) has been used where $|J'/J| \geqslant 10^{-2}$. For $|J'/J| = 1.7 \times 10^{-2}$ in TLAF $CsNiCl_3$ (table 2), for instance, the approximation (5) underestimates ΔS_{lin} by about 0.013, and ΔS_{ren} (6) by about 0.007.

Discrepant anisotropy parameters have been reported [18–20] for TLAF $CsVCl_3$, springing from somewhat different interpretations of basically compatible spin-wave dispersion data (noted [18, 20] deviations from the neutron scattering cross section predicted by linear theory should not affect the parameters derived). Two models, one [18] with negligible anisotropy and one [19] with a noticeable easy-plane term $D \approx 2J'$, are represented in table 2; as the intra-chain exchange could not be determined by the latter authors, the value $J/k = -169$ K of the former, well confirmed recently [21], has been taken for both. In spite of the anisotropy being taken into account, the calculated ΔS_{lin}, and particularly ΔS_{ren}, are closely similar. Another model with a much larger $D \approx 12J'$ has been discussed [20] without direct evidence for the flat upper magnon branch implied†, and is ignored here. Also, the moment value $\mu = 1.9\ \mu_B$ of [23], corresponding to $\Delta S_{exp} = 0.55$, from the context of the present compilation (table 2) turns out to be implausible.

Of special interest is the integer-spin TLAF system $CsNiCl_3$ for which standard spin-wave theory apparently fails to describe the measured inter-chain excitations [14, 16], and whence the derived ratio $|J'/J|$ depends on the (inter-chain) wavevector used for fitting‡. Two models, relying on the magnetic zone boundary $(0, 0, \frac{1}{2})$ [14] and zone centre $k_0 = (\frac{1}{3}, \frac{1}{3}, \frac{1}{2})$ [16], are represented in table 2. In the first model, an appreciable easy-axis anisotropy $D/|J| \approx 3.8 \times 10^{-2}$ was originally introduced to achieve agreement at the zone centre, but the measured spin-flop field value [15] as well as neutron polarization analysis [16] require that this be replaced by a much smaller $D/|J| < 2 \times 10^{-3}$, which can be neglected here. The failure of spin-wave theory for $CsNiCl_3$ has been attributed [31] to the Haldane excitation gap [32, 33] of free $S = 1$ antiferromagnetic chains also affecting the ordered state of weakly coupled chains. Interestingly, even though the observed energies are much better reproduced by the first spin-wave model, the agreement with experiment of the reduction ΔS_{ren} calculated from the second model fits in better with the other systems of table 2.

Setting aside the problematic case of $S = 1$ $CsNiCl_3$, an inspection of table 2 nevertheless shows that the linear prediction ΔS_{lin} does not correlate well with ΔS_{exp}, the experimental reduction being significantly exceeded for $KCuF_3$ and $CsVCl_3$ (as well as for the second model of $CsNiCl_3$). In contrast, the improved estimates ΔS_{ren} fall consistently short of ΔS_{exp} by small amounts of up to $\approx 10\%$ in S (inset of figure 1), which correspond to the effect of covalency expected in transition-metal halides [34]. As the uncertainties from the error bounds quoted for the magnetic moments μ are of the same order, and as the moment values may be affected further by assumptions about the magnetic form factors, more detailed conclusions about covalency cannot be drawn from the data. It is clear, however, that the improved spin-wave estimate gives a satisfactory description of the experimental zero-point spin reduction over a wide range of exchange ratio $10^{-2} > |J'/J| > 10^{-4}$ and spin $\frac{1}{2} \leqslant S \leqslant \frac{5}{2}$. A calculation of ΔS_{ren} may thus be applied to identify cases of substantial covalency among quasi-1D Heisenberg antiferromagnets, as was recently reported [35] for the chalcogenide $TlFeS_2$ ($\approx 40\%$ covalency reduction).

4. Susceptibility

In view of the measured spin reductions ΔS_{exp} in table 2, there can be no doubt about

† The large anisotropy [20] would imply that spin 'condensation' into the anisotropy plane [30] ($kT_c \approx 2S(S+1)(|J||D|)^{1/2}$) appears around $T_c \approx 66$ K, in contradiction to the measured [17, 22] susceptibility ($T_c \lesssim 18$ K); compare TMMC [30] and $CsMnBr_3$ [27].

‡ The parameters employed in an early explanation of ΔS_{exp} by Montano *et al* [5], a negligible J' and a large easy-axis D, are unacceptable today.

the importance of zero-point quantum fluctuation in quasi-1D antiferromagnets. Since the fluctuations must be interpreted [1] as corrections to the ordered ground state used as the starting point of spin-wave theory, large deviations are implied from the very foundation on which the calculated spin reductions rest. In this light, the predictive power of spin-wave theory for progressively smaller inter-chain coupling, as demonstrated by the improved estimates ΔS_{ren} for reductions up to $\approx$ 50%, seems remarkable. In order to further characterize the quantum ground state for small $|J'/J|$, let us therefore turn to other consequences of spin-wave theory for Heisenberg antiferromagnets.

According to standard antiferromagnetic spin-wave theory [1, 36], zero-point fluctuations cause a reduction in the perpendicular static susceptibility, $\chi_\perp = M_s/H_E$, at $T = 0$ in proportion with the reduction in the ordered spin; the effect occuring relative to the molecular-field result $\chi_\perp^\infty = N(g\mu_B)^2/8|J|$ where J incorporates quantum renormalization (J' neglected). Thus, for increasing fluctuation in quasi-1D systems, the ordered-state $\chi_\perp(T = 0)$ can be expected to approach a value well below $\chi_\perp^\infty$ (if not zero), while the disordered state of free 'gapless' half-integer-spin chains† shows [37] a finite $\chi(0)$ close to $\frac{2}{3}\chi_\perp^\infty$. Figure 2 qualitatively reconciles such a shrinking $\chi_\perp \propto S - \Delta S$ with the requirement that at any $T > 0$ the susceptibility for decreasing $|J'/J|$ must ultimately approach the free-chain result. Here, the peaked susceptibility curve estimated for free $S = \frac{3}{2}$ chains [3, 37], the Oguchi relation for SL systems, $kT_N/[S(S+1)|J|] \approx 2.1|J'/J|^{1/2}$ (with $S = \frac{3}{2}$) [29], and a monotonic T-square like behaviour of $\chi_\parallel$ and $\chi_\perp$ below T_N as given by two-sublattice spin-wave theory [1, 36] have been used as quantitative ingredients. It is seen that the decreasing $\chi_\perp(T = 0)$ together with the monotonic variation of $\chi_\perp(T)$ eventually necessitates a matching depression in the paramagnetic susceptibility immediately above T_N.

For many quasi-1D antiferromagnets, the observed behaviour above T_N confirms this non-rigorous reasoning from spin-wave theory. A susceptibility depression below the free-chain curve is hinted at for K_2FeF_5 [24] and $CsMnBr_3$ [27] with spin reductions around $\approx$ 25%, and becomes unmistakable for $CsVCl_3$ [17, 22] (as well as integer-spin $CsNiCl_3$ [12]) where the reduction reaches $\approx$ 50% (table 2)‡. The effect may be easily recognized from an incompatibility of the $\chi_{max}/\chi(0)$ ratios with those of 'gapless' free chains, which range [3, 37] between 1.45 for $S = \frac{1}{2}$ and 1.20 for classical spins. As an example, the $CsVCl_3$ susceptibility from [22], as measured perpendicular to the chain axis, is reproduced in figure 2, where the data have been corrected for a core contribution of $\approx -1 \times 10^{-4}$ cm^3 mol^{-1} and an estimated Van-Vleck term of $\approx +2.5 \times 10^{-4}$ cm^3 mol^{-1}, and where a 'bare' exchange, $J/k = -130$ K, and $g = 1.97$, has been used for the ordinate and abscissa scales. Obviously, the depression must be related to the presence of inter-chain magnetic correlations above T_N, and in the case of a strongly fluctuating ordered state, as for $CsVCl_3$, it appears from the susceptibility that the incipient order in quasi-1D antiferromagnets is heralded by precursors of zero-point fluctuation.

When $|J'/J|$ decreases to zero, the growing depression below the free-chain curve in figure 2 implies a final discontinuity in the low-temperature susceptibility immediately above T_N indicating that the strongly fluctuating ordered state fundamentally differs from the free-chain disordered ground state, in spite of the decay of the ordered magnetic

† Though $\chi(0)$ is exactly known [37] for $S = \frac{1}{2}$ and classical spin chains only, similar non-zero values are expected for any half-integer S, whereas for $S = 1$ a singlet ground state with a Haldane excitation gap [33] of $\approx 0.41|2J|$ implies $\chi(0) = 0$.

‡ For the compound $KCuF_3$ from table 2, the entire low-temperature susceptibility [9] is masked by paramagnetic contributions.

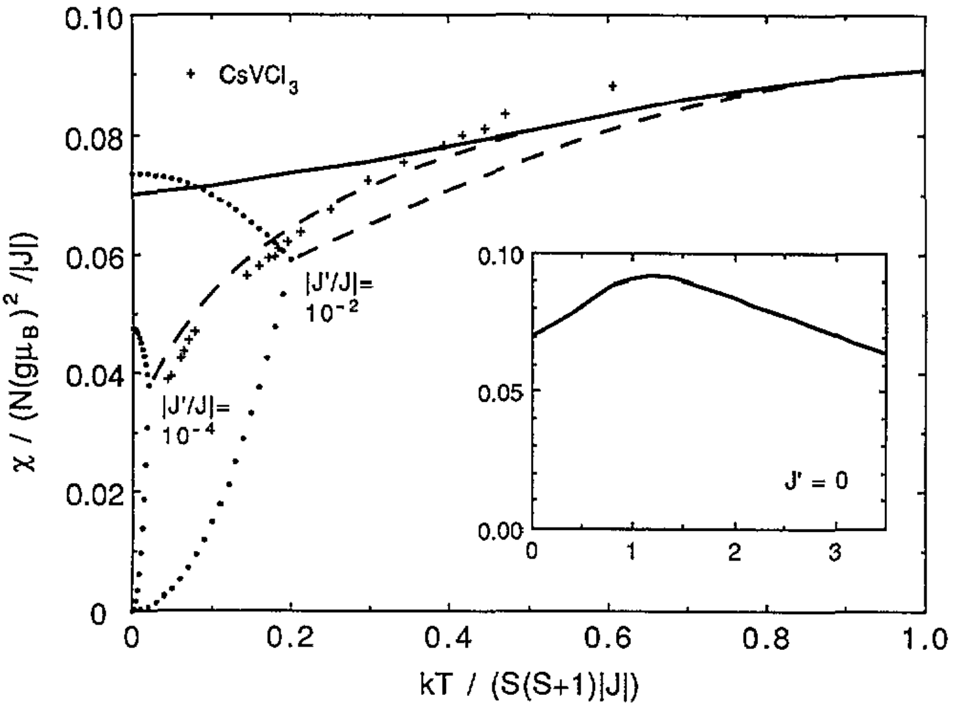

Figure 2. Expected behaviour of the perpendicular and parallel static susceptibilities below T_N (dotted) and their continuation above T_N (broken) as $|J'/J|$ in quasi-1D antiferromagnets approaches zero, quantitatively based on relations for tetragonal $S = \frac{3}{2}$ systems. The crosses represent data [22] from hexagonal $CsVCl_3$ above T_N; they are corrected for core and Van-Vleck contributions and plotted for $J/k = -130$ K and $g = 1.97$. An overview of the $S = \frac{3}{2}$ free-chain curve ($J' = 0$) appears in the inset.

moment. This can be understood from the fact that long-range magnetic order in free chains is destroyed [32] by 'topological soliton' excitations (i.e. domain walls) rather than by collective magnons. Close to the $|J'/J| = 0$ limit, the expected susceptibility curve bears a marked resemblance to that shown by singlet ground-state systems, such as quantum antiferromagnetic dimers or free $S = 1$ (Haldane) chains, the final discontinuity being reminiscent of the closing of the singlet–triplet gap in dimerized quantum spin chains becoming uniform [38]. By analogy, one might conclude that, as $J' \to 0$, the magnetic ground state increasingly behaves like a singlet with a decreasing finite excitation gap.

As the ground state of quasi-1D antiferromagnets deviates more and more from the ordered state underlying the linearized spin-wave Hamiltonian (2), the emergence of new excitations, lost in the Holstein–Primakoff treatment, is a possibility to be considered. The resemblance to a singlet state with a finite excitation energy in particular suggests that, as for the case of weakly coupled $S = 1$ chains [31], longitudinal gap modes might appear in addition to the conventional transverse spin waves.

5. Conclusions

In conclusion, spin-wave theory is seen to provide an adequate quantitative description of the zero-point spin reduction in quasi-1D half-integer-spin antiferromagnets when 'kinematical interactions' are taken into account in the manner of Ishikawa and Oguchi [2]. The present analytical treatment should facilitate the application for the experimentalist, and has already proved useful in confirming a substantial covalency reduction in the chain chalcogenide $TlFeS_2$. However, further data on ionic systems (such as an error bound on the $CsVCl_3$ magnetic moment or a spin-wave determination of J'/J and D/J for K_2FeF_5) would be worth collecting to strengthen the case.

A marginal but possibly significant deviation is found for the integer-spin system $CsNiCl_3$. While the exchange ratio $|J'/J| = 1.7\times10^{-2}$ reasonably accounts for the observed spread of inter-chain magnon energies, it leaves 16(4)% of the measured spin reduction to be explained by covalency, rather than the 6–10% typical of the other halides. Corroborating the known failure of standard spin-wave theory for the inter-chain excitations, this may point to additional quantum fluctuations related to the occurrence of a singlet ground state in free $S = 1$ chains. A theoretical estimate of this effect would be useful.

Finally, the qualitative behaviour of the magnetic susceptibility expected from spin-wave theory for quasi-1D antiferromagnets is noted to conform with experiment. For decreasing inter-chain coupling, a growing depression below the susceptibility of free half-integer-spin chains at low temperatures implies that the fluctuating magnetic ground state increasingly resembles a singlet separated from other states by an energy gap.

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