Light scattering in Heisenberg paramagnets

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Two-spin light scattering in the disordered phase of Heisenberg antiferromagnets is investigated by means of a modified Markoffian approximation for the continued-fraction representation of the shape function. The necessary frequency moments are evaluated: they are found to be dominated by the contribution of zone-boundary wave vectors. The predicted spectral shapes are in good agreement with the experimental spectra in $RbMnF_3$ and $KNiF_3$ both at high temperatures and in the neighborhood of the Néel point.

I. INTRODUCTION

Raman scattering experiments in Heisenberg antiferromagnets show an intense band due to two-spin excitations[1,2]: the associated inelastic peak persists also above the Néel temperature T_N, up to $T \sim 1.4T_N$ and the spectrum becomes symmetrically centered about zero-frequency shift only in the limit of very high temperatures.[3] The shapes of the spectra and their relevant features like the frequency peak and the width have been satisfactorily accounted for through most part of the ordered region[4-6] where the scattering process turns out to be dominated by a couple of well-defined magnetic excitations with wave vector $\vec{k}$ in the antiferromagnetic zone-boundary region. In the paramagnetic phase the quantitative interpretation of the spectral shape is less clear: the magnon concept becomes less meaningful even at high $\vec{k}$ and this is reflected in the increasing overdamping of the inelastic peaks. Neutron inelastic scattering on single high-$\vec{k}$ excitations exhibits a quite similar behavior, as shown by the well-known three-peaked structure of the spectra.[7,8] Owing to this situation, for $T > T_N$ the usual many-body approach (e.g., Green's function formalism) appears much less powerful than other methods used in the statistical theories of the line shape. One of these approaches[9] is based on a continued-fraction expansion of the Kubo relaxation function for the scattering process: in the following we shall adopt this method.

The plan of the present work is the following. After an introduction (Sec. II) to the continued-fraction approach to two-spin Raman scattering, we discuss in Sec. III the limits of the previous approximations and present a modified Markoffian scheme which should work better for the involved frequency range. The necessary frequency moments for the light-scattering relaxation function are approximately evaluated in Sec. IV. Finally, in Sec. V the resulting theoretical cross section is compared with the experimental spectra of $RbMnF_3$ and $KNiF_3$ at various temperatures in the paramagnetic phase.

II. CONTINUED-FRACTION APPROACH FOR THE RAMAN CROSS SECTION

In the following we deal with Heisenberg antiferromagnets with Hamiltonian

$$\mathcal{H} = -\tfrac{1}{2}J \sum_{\vec{j},\,\vec{\delta}} \vec{S}_{\vec{j}} \cdot \vec{S}_{\vec{j}+\vec{\delta}} , \tag{1}$$

where the exchange integral J (<0) is limited to the r nearest-neighbor spins in the positions $\vec{\delta}$ around a given site $\vec{j}$. Simple cubic perovskites like $RbMnF_3$ ($S=\frac{5}{2}$) and $KNiF_3$ ($S=1$) are well described by this magnetic Hamiltonian.

Introducing space Fourier transforms of spin operators

$$\vec{S}_{\vec{k}} = \frac{1}{\sqrt{N}} \sum_{\vec{j}} \vec{S}_{\vec{j}} e^{-i\vec{k}\cdot\vec{j}}$$

the Hamiltonian (1) becomes

$$\mathcal{H} = -\tfrac{1}{2}Jr \sum_{\vec{k}} \gamma_{\vec{k}} (\vec{S}_{\vec{k}} \cdot \vec{S}_{-\vec{k}}) , \tag{2}$$

where

$$\gamma_{\vec{k}} = \frac{1}{r} \sum_{\vec{\delta}} \exp(i\vec{k}\cdot\vec{\delta})$$

for simple cubic lattices with spacing a takes the form

$$\gamma_{\vec{k}} = \tfrac{1}{3}(\cos k_x a + \cos k_y a + \cos k_z a) . \tag{3}$$

The two-spin light-scattering mechanism is ruled by a spin transition operator[10]

$$M = \sum_{\vec{k}} \Phi_{\vec{k}} (\vec{S}_{\vec{k}} \cdot \vec{S}_{-\vec{k}}) , \tag{4}$$

where for the sc case

$$\Phi_{\vec{k}} = \cos k_x a - \cos k_y a . \tag{5}$$

The quantity $\Phi_{\vec{k}}$ satisfies the relation

$$\sum_{\vec{k}} \Phi_{\vec{k}} \langle \vec{S}_{\vec{k}} \cdot \vec{S}_{-\vec{k}} \rangle = 0.$$

The Raman cross section is then proportional to the time Fourier transform of the correlation function $\langle MM(t) \rangle$, i.e., to

$$S(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_{\vec{k}\vec{k}'} \Phi_{\vec{k}} \Phi_{\vec{k}'} \times \langle (\vec{S}_{\vec{k}'} \cdot \vec{S}_{-\vec{k}'})(\vec{S}_{\vec{k}} \cdot \vec{S}_{-\vec{k}})(t) \rangle , \tag{6}$$

where $\omega > 0$ for Stokes scattering. Instead of $S(\omega)$ it is more convenient to deal with the normalized relaxation shape function $f_0(\omega)$:

$$f_0(\omega) = f_0(-\omega) = \frac{1}{2\pi} \frac{1}{R(t=0)} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} R(t) , \tag{7}$$

where

$$R(t) = \int_0^{\beta} d\lambda \langle e^{\lambda \mathcal{H}} M e^{-\lambda \mathcal{H}} M(t) \rangle \tag{8}$$

is the Kubo relaxation function for our problem, and $\beta = (k_B T)^{-1}$. The quantity $S(\omega)$ is related to $f_0(\omega)$ by

$$S(\omega) = R(t=0)[\omega/(1 - e^{-\beta\omega})]\, f_0(\omega) . \tag{9}$$

Here and in the following we use units $\hbar = 1$.

Mori[9] has derived a method for calculating the shape function $f_0(\omega)$. More precisely, his theory is in terms of $\hat{f}_0(z)$, the Laplace transform of $f_0(t) = R(t)/R(0)$: the shape function $f_0(\omega)$ is simply given by

$$f_0(\omega) = (1/\pi)\, \mathrm{Re}\, \hat{f}_0(z = i\omega).$$

Then Mori proves the following continued-fraction representation for $\hat{f}_0(z)$:

$$\hat{f}_0(z) = [\, z + \Delta_1 \hat{f}_1(z)]^{-1} , \tag{10}$$

where

$$\hat{f}_n(z) = [\, z + \Delta_{n+1} \hat{f}_{n+1}(z)] . \tag{11}$$

In Eqs. (10) and (11) the quantities Δ_n are connected with the even frequency moments $\langle \Omega^{2n} \rangle$ of the shape function $f_0(\omega)$. In particular, the first three Δ_n are given by

$$\Delta_1 = \langle \Omega^2 \rangle, \quad \Delta_2 = \langle \Omega^4 \rangle / \langle \Omega^2 \rangle - \langle \Omega^2 \rangle , \tag{12}$$

$$\Delta_3 = (1/\Delta_2)[\langle \Omega^6 \rangle / \langle \Omega^2 \rangle - (\langle \Omega^4 \rangle / \langle \Omega^2 \rangle)^2] .$$

The continued-fraction representation (10) and (11) is formally exact. In practice, however, only very few of the first Δ_n can be theoretically evaluated, and one must resort to definite approximation schemes for a termination of the continued fraction.

III. STATISTICAL TERMINATION OF THE CONTINUED FRACTION

Typical truncation schemes of the continued fraction depend both on the magnitude of the available Δ_n and on the frequency region of the spectra which is relevant to the particular physical problem.

In the paramagnetic phase the absence of any preferred direction simplifies the explicit calculation of the moments. Of course the continued-fraction approach has validity also in the antiferromagnetic phase where the longitudinal and transverse relaxation functions must be separately treated. However until $T \sim 0.8\, T_N$ the magnetic system can be described in terms of interacting bosons. For Stokes scattering the continued fraction can be stopped at the first stage by means of a Markoffian approximation recovering the results of the Green's-function formalism.[4]

In the time-domain Eq. (11) takes the form

$$\frac{df_n(t)}{dt} = -\Delta_{n+1} \int_0^t f_{n+1}(t-\tau) f_n(\tau)\, d\tau , \tag{13}$$

where $f_{n+1}(t)$ plays the role of a generalized memory function. In particular cases one can find from Eq. (13) the approximate behavior of $f_n(t)$ without a detailed knowledge of $f_{n+1}(t)$. Let us call τ_n and τ_{n+1} the typical decay times of $f_n(t)$ and $f_{n+1}(t)$ respectively. Then Eq. (13) can be approximately solved in the following limiting cases:

(i) $t \lesssim \tau_n \ll \tau_{n+1}$. In this small time approximation, one can safely put $f_{n+1}(t-\tau) \simeq f_{n+1}(t=0) = 1$ in Eq. (13). This yields

$$f_{n+1}(t) = \cos[(\Delta_{n+1})^{1/2} t] ,$$

i.e., an undamped oscillatory behavior. This solution corresponds to the so-called "wing approximation" for the frequency spectrum, which turns out to be composed of many δ-like spikes.

(ii) $\tau_n = \tau_{n+1}$ [actually, $f_n(t) \equiv f_{n+1}(t)$]. This yields

$$f_n(t) = J_1[2(\Delta_{n+1})^{1/2} t]/(\Delta_{n+1})^{1/2} t ,$$

i.e., a damped oscillatory behavior.

(iii) $\tau_{n+1} \ll \tau_n \lesssim t$. In this long-time limit Eq. (13) can be approximately written

$$\dot{f}_n(t) \simeq -\Delta_{n+1} \int_0^t f_{n+1}(\tau)\, d\tau\, f_n(t) , \tag{14}$$

where the upper integration limit can be taken as infinite since for $t \gg \tau_{n+1}$ $f_{n+1}(t)$ is negligibly small. Therefore one finds an exponential decay

$$f_n(t)=\exp\left[-\left(\Delta_{n+1}\int_0^\infty f_{n+1}(\tau)\,d\tau\right)t\right]\ . \quad (15)$$

In the frequency domain this means that $\hat{f}_{n+1}(z)\simeq\hat{f}_{n+1}(z=0)$ in the continued fraction (11). All the procedure yields the so-called $(n+1)$-pole approximation for the frequency spectrum.

However, in general, the time constants τ_n and τ_{n+1} are unknown. The quantities which may be known (for low n) are the coefficients of a small-time expansion of $f_n(t)$;

$$f_n(t)=1-(1/2!)\Delta_n t^2+(1/4!)\Delta_n(\Delta_n+\Delta_{n+1})t^4-\cdots\ , \quad (16)$$

so that a quantity of the order of $1/\sqrt{\Delta_n}$ can be a reasonable estimate for the *initial* time decay of $f_n(t)$. It is clear that this estimate may be very rough if one is interested in the whole detailed time behavior of $f_n(t)$.

A compromise between all these tendencies, which has the correct small-time behavior and satisfies the condition $\lim f_n(t)=0$ as $t\to\infty$ is given by

$$f_n(t)\simeq\exp(-\tfrac{1}{2}\Delta_{n+1}t^2)\ . \quad (17)$$

This Gaussian termination (essentially, the first term of a cumulant expansion[11]) can give good results for the high-frequency part of the spectral shape. It has been also used for $n=1$,[12] and $n=2$,[13] to explain the spectral shapes in inelastic neutron scattering spectra at various wave vectors in the paramagnetic region, but has met only a partial success, especially at low temperatures and high $\vec{k}$. In particular, both terminations are not able to account for the experimental peak frequencies.

The more interesting features of two-spin Raman spectra and of high-$\vec{k}$ neutron spectra for $T>T_N$ appear in a rather small frequency range around $\omega=0$. From this point of view, a long-time approximation for the behavior of a particular $f_n(t)$ should be a good termination for the continued fraction. Indeed, taking into account the three-peaked structure of high-$\vec{k}$ neutron spectra, a three-pole approximation [case (iii) for $n=2$] has been worked out.[14] However, there is no guarantee that really in the whole temperature range $T>T_N$ the memory function $f_3(t)$ decays much faster than $f_2(t)$, or in other words that $f_3(t)$ has a purely Markoffian behavior. As a matter of fact, this approximation does not give good results at very high temperatures, just where the theoretical starting point is better since the maximum number of frequency moments is exactly known.

We have recently worked out a modified long-time approximation[15] ("pseudo-three-pole approximation") which does not rely so heavily on an arbitrary Markoffian behavior of $f_3(t)$. For $n=2$, $z=i\omega$, Eq. (11) becomes

$$i\omega\hat{f}_2(z=i\omega)-1=-\Delta_3\hat{f}_3(z=i\omega)\hat{f}_2(z=i\omega)\ . \quad (18)$$

If $f_3(t)$ decays faster (but not necessarily *much* faster) than $f_2(t)$, a good approximate solution to Eq. (18) can be found expanding around $\omega=0$ the slowly varying function $\hat{f}_3(z=i\omega)$. Letting $\hat{f}_n(z=i\omega)=a_n(\omega)-ib_n(\omega)$, we obtain

$$a_3(\omega)\simeq a_3(0),\quad b_3(\omega)\simeq b_3'(0)\omega\ , \quad (19)$$

with

$$a_3(0)=\int_0^\infty f_3(t)\,dt,\quad b_3'(0)=\int_0^\infty t f_3(t)\,dt\ . \quad (20)$$

Higher-order terms like $\frac{1}{2}a_3''(0)\omega^2$ in the first of Eqs. (19) are neglected: for our problem, they yield a negligible contribution to the spectral shape (see Sec. V). The three-pole approximation is recovered in the limit $b_3'(0)\equiv 0$: the time constant $1/\tau$ of Ref. 14 is simply $\Delta_3 a_3(0)$.

Using the approximation (19) in the continued fraction (10) and (11), the spectral shape function is found to be

$$f_0(\omega)=\frac{1}{\pi}\frac{\Delta_1\Delta_2 a_2(\omega)}{\{\omega[\omega-\Delta_2 b_2(\omega)]-\Delta_1\}^2+[\omega\Delta_2 a_2(\omega)]^2} \quad (21)$$

with

$$a_2(\omega)=\frac{\Delta_3 a_3(0)[1-\Delta_3 b_3'(0)]^{-2}}{\omega^2+\{\Delta_3 a_3(0)/[1-\Delta_3 b_3'(0)]\}^2}\ , \quad (22)$$

$$b_2(\omega)=\frac{\omega[1-\Delta_3 b_3'(0)]^{-1}}{\omega^2+\{\Delta_3 a_3(0)/[1-\Delta_3 b_3'(0)]\}^2}\ . \quad (23)$$

Equations (21) and (23) are expected to give a reasonable approximation for the spectrum in a range of frequencies around $\omega=0$ smaller than the inverse of the time decay τ_3 of $f_3(t)$. They are not expected to hold in the less interesting high-frequency region where any long-time approximation breaks down. Equations (22) and (23) imply

$$f_2(t)=[1-\Delta_3 b_3'(0)]^{-1}\exp\left(-\frac{\Delta_3 a_3(0)}{1-\Delta_3 b_3'(0)}\,t\right)\ . \quad (24)$$

Therefore, not only the time-constant of the exponential decay is modified with respect to the three-pole-approximation result,[16] but there is also an amplitude factor different from unity. The presence of this factor is a direct consequence of the requirement of a better description of $f_2(t)$ at long times and therefore of the low-frequency part of the spectrum. Of course, for this purpose it is not relevant that the predicted short-time behavior of $f_2(t)$ is not correct: this is a general consequence of all long-time approximations.

IV. FREQUENCY MOMENTS

In order to evaluate the spectral shape as given by Eq. (21) it is necessary to know Δ_1 and Δ_2 and to have a reasonable estimate for the higher-order quantities $\Delta_3 a_3(0)$ and $\Delta_3 b_3'(0)$. In this section an approach to get Δ_1 and Δ_2 in the whole temperature region for the light-scattering case is discussed.

The frequency moments $\langle\Omega^{2n}\rangle$ can be in principle calculated by means of $2n-1$ commutators with the Hamiltonian

$$\langle\Omega^{2n}\rangle = \frac{1}{R(t=0)} \times \sum_{\vec{k}\vec{k}'} \Phi_{\vec{k}}\Phi_{\vec{k}'} \langle [[\cdots[\vec{S}_{\vec{k}}\cdot\vec{S}_{-\vec{k}},\mathcal{H}]\cdots,\mathcal{H}], \times \vec{S}_{\vec{k}'}\cdot\vec{S}_{-\vec{k}'}]\rangle . \tag{25}$$

Of course, at arbitrary temperatures this is a formidable expression even for $n=1, 2$. In order to bypass this difficulty in the simplest way, one can decouple the dynamic four-spin correlation function into all possible products of two-spin correlation functions, i.e.,

$$\langle(\vec{S}_{\vec{k}'}\cdot\vec{S}_{-\vec{k}'})(\vec{S}_{\vec{k}}\cdot\vec{S}_{-\vec{k}})(t)\rangle \simeq \tfrac{1}{3}\langle\vec{S}_{\vec{k}}\cdot\vec{S}_{-\vec{k}}(t)\rangle^2(\delta_{\vec{k}',\vec{k}}+\delta_{\vec{k}',-\vec{k}}) . \tag{26}$$

This decoupling approximation can be rough for the whole dynamics, but its use for the calculation of the first moments is reasonable. Static two-spin correlation can be calculated by means of the spherical model

$$\langle\vec{S}_{\vec{k}}\cdot\vec{S}_{-\vec{k}}\rangle = (\beta|J|\gamma)^{-1}(\mu^{-1}+\gamma_{\vec{k}})^{-1} , \tag{27}$$

where μ^{-1} is determined by the sum rule

$$\sum_{\vec{k}}\langle\vec{S}_{\vec{k}}\cdot\vec{S}_{-\vec{k}}\rangle = NS(S+1) .$$

By means of Eq. (26) the moments $\langle\Omega^2\rangle$ and $\langle\Omega^4\rangle$ can be expressed in terms of the moments $\langle\omega_{\vec{k}}^2\rangle$ and $\langle\omega_{\vec{k}}^4\rangle$ of the two-spin relaxation shape function corresponding to

$$R_{\vec{k}}(t) = \int_0^\beta d\lambda\,\langle e^{\lambda\mathcal{H}} S_{-\vec{k}}^z e^{-\lambda\mathcal{H}} S_{\vec{k}}^z(t)\rangle . \tag{28}$$

Therefore we straightforwardly obtain

$$\langle\Omega^2\rangle = 2\Big(\sum_{\vec{k}}\Phi_{\vec{k}}^2\langle\vec{S}_{\vec{k}}\cdot\vec{S}_{-\vec{k}}\rangle^2\langle\omega_{\vec{k}}^2\rangle\Big) \Big/ \sum_{\vec{k}}\Phi_{\vec{k}}^2\langle\vec{S}_{\vec{k}}\cdot\vec{S}_{-\vec{k}}\rangle^2 \tag{29}$$

and

$$\langle\Omega^4\rangle = 2\Big(\sum_{\vec{k}}\Phi_{\vec{k}}^2\langle\vec{S}_{\vec{k}}\cdot\vec{S}_{-\vec{k}}\rangle^2 \times(\langle\omega_{\vec{k}}^4\rangle + 3\langle\omega_{\vec{k}}^2\rangle^2)\Big) \Big/ \sum_{\vec{k}}\Phi_{\vec{k}}^2\langle\vec{S}_{\vec{k}}\cdot\vec{S}_{-\vec{k}}\rangle^2 . \tag{30}$$

Here, in order to connect the correlation and the relaxation functions, we have used a high-temperature approximation which is consistent with the spherical model. The moments $\langle\omega_{\vec{k}}^{2n}\rangle$ are exactly known at infinite temperature up to $n=3$,[17] at finite temperatures $\langle\omega_{\vec{k}}^2\rangle$ and $\langle\omega_{\vec{k}}^4\rangle$ are also approximately known.[12, 18]

At infinite temperature, taking into account the identities

$$\sum_{\vec{k}}\Phi_{\vec{k}}^2 = N, \quad \sum_{\vec{k}}\Phi_{\vec{k}}^2\gamma_{\vec{k}} = 0, \quad \sum_{\vec{k}}\Phi_{\vec{k}}^2\gamma_{\vec{k}}^2 = \frac{3N}{\gamma^2} , \tag{31}$$

and letting $\Omega_0^2 = \frac{2}{3}J^2\gamma S(S+1)$, the second moment $\langle\Omega^2\rangle = \Delta_1$ evaluated from Eq. (29) turns out to be $2\Omega_0^2$, i.e., the same value that comes from an exact calculation.[2] It must be noted that this value is exactly twice the antiferromagnetic zone-boundary value of $\langle\omega_{\vec{k}}^2\rangle$. Therefore at infinite temperature $\langle\Omega^2\rangle$ is wholly determined by zone-boundary wave vectors. It is interesting to examine whether this feature is verified also at finite temperatures, or in other words whether the ratio $G = \langle\Omega^2\rangle/2\langle\omega_{\vec{k}}^2\rangle^{ZB}$ is nearly 1 through all the paramagnetic region. Since a finite temperature calculation of $\langle\Omega^2\rangle$ is difficult even using Eq. (29), we have estimated the quantity G in an approximate way. An expansion of Eq. (27) in the quantity $\gamma_{\vec{k}}/\mu^{-1}$ for $r=6$ gives

$$G = [1+\tfrac{1}{12}\mu(1+\mu)]/(1+\tfrac{1}{4}\mu^2) . \tag{32}$$

Such a procedure yields exact results in the high-temperature limit. Typical values of the parameter G obtained in this way are 0.958 and 0.933 at $T=1.5\,T_N$ and $T=T_N$, respectively. Therefore one can conclude that within some percent $\langle\Omega^2\rangle$ can be satisfactorily replaced by its "zone boundarized" value $\Delta_1^{ZB} = 2\langle\omega_{\vec{k}}^2\rangle^{ZB}$ through all the paramagnetic region.

At infinite temperature the same statement can be approximately made also for the fourth moment $\langle\Omega^4\rangle$ and the related quantity Δ_2. As a matter of fact, using Eqs. (30) and (31) and the known value of $\langle\omega_{\vec{k}}^4\rangle$ at $T\to\infty$,[17] Δ_2 turns out to be $4.527\Omega_0^2$ to be compared with the value $\Delta_2^{ZB} = 4.152\Omega_0^2$ obtained using the zone-boundary expressions for $\langle\omega_{\vec{k}}^4\rangle$ and $\langle\omega_{\vec{k}}^2\rangle$. These figures actually refer to $S=\frac{5}{2}$ (the case of $RbMnF_3$), but the corrections for different S are very small; for $KNiF_3$ ($S=1$) one obtains $\Delta_2 = 4.479\Omega_0^2$ and $\Delta_2^{ZB} = 4.104\Omega_0^2$. At finite temperatures only approximate results for $\langle\omega_{\vec{k}}^4\rangle$ are available. Since the quantity

$$\delta_{2\vec{k}} = \langle\omega_{\vec{k}}^4\rangle/\langle\omega_{\vec{k}}^2\rangle - \langle\omega_{\vec{k}}^2\rangle \tag{33}$$

appears to be much less dependent on $\vec{k}$ than $\delta_{1\vec{k}} = \langle\omega_{\vec{k}}^2\rangle$ through all the paramagnetic region, even here it can be a good approximation to replace Δ_2

with Δ_2^{ZB}. Form Eqs. (29) and (30) with $\langle\omega_{\vec{k}}^2\rangle \simeq \langle\omega_{\vec{k}}^2\rangle^{ZB}$ and $\langle\omega_{\vec{k}}^4\rangle \simeq \langle\omega_{\vec{k}}^4\rangle^{ZB}$ one therefore obtains

$$\Delta_2 \simeq \Delta_2^{ZB} = \delta_{2\vec{k}}^{ZB} + 2\langle\omega_{\vec{k}}^2\rangle^{ZB} . \tag{34}$$

Using the recipe (26) it is also straightforward to derive an approximate expression for the sixth moment $\langle\Omega^6\rangle$ which turns out to be

$$\langle\Omega^6\rangle = 2\Big(\sum_{\vec{k}} \Phi_{\vec{k}}^2 \langle\vec{S}_{\vec{k}} \cdot \vec{S}_{-\vec{k}}\rangle^2 (\langle\omega_{\vec{k}}^6\rangle + 15\langle\omega_{\vec{k}}^2\rangle\langle\omega_{\vec{k}}^4\rangle)\Big) \Big/ \sum_{\vec{k}} \Phi_{\vec{k}}^2 \langle\vec{S}_{\vec{k}} \cdot \vec{S}_{-\vec{k}}\rangle^2 . \tag{35}$$

Unfortunately, the sixth moment $\langle\omega_{\vec{k}}^6\rangle$ is known[17] only in the $T \to \infty$ limit: at finite temperatures even an approximate expression for $\langle\omega_{\vec{k}}^6\rangle$ does not exist. Nonetheless, even here, at $T = \infty$ the related quantity Δ_3 does not differ substantially from its "zone boundarized" value Δ_3^{ZB} (for $S = \frac{5}{2}$ one finds $6.96\Omega_0^2$ and $6.725\Omega_0^2$, respectively).

V. MODIFIED MARKOFFIAN THEORY VERSUS EXPERIMENT

A. High temperatures (Ref. 19)

The first test to be made on the modified Markoffian theory discussed in Sec. III is based on the comparison with the Raman scattering data in $RbMnF_3$ at room temperature[3] ($T = 3.55T_N$). Here the experimental spectrum has a nearly Gaussian shape and is practically symmetrical around $\omega = 0$. Therefore these data are a convenient test for the theoretical $f_0(\omega)$ in the high-temperature limit: the small detailed-balance factor $\omega[1 - \exp(-\beta\omega)]^{-1}$ in Eq. (9) accounts for the slight asymmetry of the spectrum. Moreover, the test of the various theories is particularly significant in this $T \to \infty$ limit because of the better knowledge of the frequency moments and consequently of the quantities Δ_1, Δ_2, Δ_3.

According to their definition (20), the parameters $a_3(0)$ and $b_3'(0)$ are determined by the time behavior of $f_3(t)$. As the knowledge of this high-order memory function is very poor, it is more convenient to express $\Delta_3 a_3(0)$ and $\Delta_3 b_3'(0)$ by means of a small-frequency expansion of the lower-order memory functions, i.e., by a systematic stepping down of the continued fraction (10) and (11). In such a way one obtains

$$\begin{aligned} &\Delta_3 a_3(0) = 1/a_2(0), \\ &1 - \Delta_3 b_3'(0) = b_2'(0)/[a_2(0)]^2 , \end{aligned} \tag{36}$$

$$\begin{aligned} &\Delta_3 a_3(0) = \Delta_2 a_1(0), \\ &1 - \Delta_3 b_3'(0) = \Delta_2\{[a_1(0)]^2 - b_1'(0)\}, \end{aligned} \tag{37}$$

$$\begin{aligned} &\Delta_3 a_3(0) = (\Delta_2/\Delta_1)[a_0(0)]^{-1} , \\ &1 - \Delta_3 b_3'(0) = \{\Delta_2/\Delta_1[a_0(0)]^2\} \\ &\qquad \times\{1/\Delta_1 - [a_0(0)]^2 + b_0'(0)\}, \end{aligned} \tag{38}$$

where the stepping procedure has been pursued down to the second, first and zeroth stage, respectively. The quantities $a_j(0)$ and $b_j'(0)$ are given by

$$a_j(0) = \int_0^\infty f_j(t)\,dt, \quad b_j'(0) = \int_0^\infty t f_j(t)\,dt . \tag{39}$$

In the *high-temperature limit* the simplest approximation for $\Delta_3 a_3(0)$ and $\Delta_3 b_3'(0)$ can be based on the nearly Gaussian shape of the experimental spectrum. This implies a nearly Gaussian $f_0(t)$. Therefore, just for an estimate of $\Delta_3 a_3(0)$ and $\Delta_3 b_3'(0)$ one can assume

$$f_0(t) = \exp(-\tfrac{1}{2}\Delta_1 t^2) , \tag{40}$$

which also has the correct short-time behavior (16). Then Eq. (38) yields

$$\begin{aligned} &\Delta_3 a_3(0) = \Delta_2(2/\pi\Delta_1)^{1/2}, \\ &1 - \Delta_3 b_3'(0) = (4/\pi - 1)\Delta_2/\Delta_1 . \end{aligned} \tag{41}$$

Therefore all the parameters entering the modified-Markoffian result (21)–(23) can be evaluated in terms of Δ_1 and Δ_2. The result has been plotted in Fig. 1 (dotted curve) and is in good agreement with the experimental data. In order to probe the substantial validity of this estimate of $\Delta_3 a_3(0)$ and $\Delta_3 b_3'(0)$, one can take advantage of the mathematical fact[13] that the higher-order memory functions $f_n(t)$ of a purely Gaussian $f_0(t)$ show a more and more increasing oscillatory behavior as n is increased, eventually giving a limiting function of the Bessel type $J_1(x)/x$. Therefore an alternative estimate of the parameters can be done at the next stage [Eq. (37)] taking

$$f_1(t) = (1 - Ct^4)e^{-\Delta_2 t^2/2} , \tag{42}$$

which has a negative undershoot. The constant $C = \frac{1}{12}\Delta_2^2(1 - \Delta_3/2\Delta_2)$ has been evaluated requiring that $f_1(t)$ has the correct short-time behavior up to

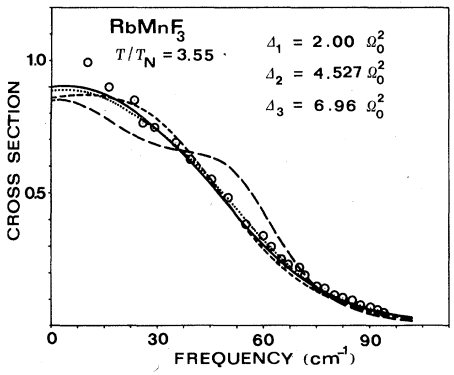

FIG. 1. Two-spin Stokes spectrum in $RbMnF_3$ at room temperature ($T = 3.55 T_N$). The long dashed line is the result of the purely Markoffian approximation which implies $\Delta_3 b_3'(0) = 0$. The other curves refer to the modified Markoffian theory with the parameters $\Delta_3 a_3(0)$ and $\Delta_3 b_3'(0)$ estimated stepping down the continued fraction at various stages (see text). Dotted, full, and short dashed lines refer to the stepping down at zeroth, first, and second stages, respectively. They yield $\Delta_3 a_3(0) = 2.55$, 2.51, 2.64 (in units of Ω_0), and $\Delta_3 b_3'(0) = 0.38$, 0.45, 0.50, respectively. The circles are the experimental data (Ref. 3).

t^4 terms. The parameters $\Delta_3 a_3(0)$ and $\Delta_3 b_3'(0)$ and the spectrum obtained in this way do not differ substantially from those given by the previous estimate (see full curve in Fig. 1). At the further stage, even the rather drastic assumption that $f_2(t)$ has already the limiting form, i.e.,

$$f_2(t) = J_1[2(\Delta_3)^{1/2} t\,]/(\Delta_3)^{1/2} t \tag{43}$$

is seen to give results in fair agreement with the experimental data (short dashed curve in Fig. 1). This is a clear indication of the convergence of the whole method.[20] Moreover, only very small changes in the spectrum are found if one conserves in the low-frequency expansion of $\hat{f}_3(z = i\omega)$ [Eq. (19)] also higher-order terms like $\frac{1}{2} a_3''(0)\omega^2$. Therefore, in this case the main non-Markoffian effects are already taken into account by a nonzero $b_3'(0)$.

For comparison, in Fig. 1 it is also plotted (long dashed curve) the purely Markoffian result[14] which implies $\Delta_3 b_3'(0) = 0$. Its disagreement with experimental data is a clear evidence of the breakdown of the main assumption of this approximation. In other words, the assumption of a very rapid decay of $f_3(t)$ is not valid in the high-temperature limit. All these features at $T \to \infty$ have already been noted in the neutron scattering case at large wave vectors.[15]

B. Finite temperatures

Experimental Stokes spectra[1,2,21,22] up to $T \sim 1.4\, T_N$ show a broad inelastic peak indicating the presence of overdamped collective excitations. In three-dimensional antiferromagnets there is also some evidence of a diffusive central peak although it is difficult to observe the precise shape of the spectrum near $\omega = 0$. The overall spectrum has probably a three-peaked structure, similar to that observed in neutron scattering at large wave vectors.

In the *neutron* case, attempts to explain this structure by means of Gaussian terminations (17) were unsuccessful.[12,13] A purely Markoffian, three-pole approximation[14] seems to give a fair agreement for the overall shape, even if the predicted inelastic peaks occur at frequencies somewhat larger than the experimental ones. This agreement is also borne out by a modified Markoffian theory[15] [Eq. (21)] in which the parameter $\Delta_3 b_3'(0)$ is determined in such a way to reproduce the experimental peak frequency: one finds that $\Delta_3 b_3'(0)$ fitted in this way has a very small value, thus empirically supporting the substantial validity of the Markoffian hypothesis $[\Delta_3 b_3'(0) = 0]$ in the neighborhood of T_N.

As already stated, very little can be told on the temperature dependence of the parameters $a_3(0)$ and $b_3'(0)$ according to their definitions (20), since even the initial time decay of $f_3(t)$—roughly of the order of $1/(\Delta_4)^{1/2}$—is completely unknown. Nonetheless, some qualitative remarks can be made even at this stage. The parameter $a_3(0)$ measures only the area under the $f_3(t)$ profile: therefore, for an evaluation of $a_3(0)$ a detailed knowledge of the temporal behavior of $f_3(t)$ is not necessary. On the other hand, according to its definition, $b_3'(0)$ weighs more strongly the intermediate time behavior of $f_3(t)$: therefore, here we require a much better knowledge of this memory function. In particular, let us assume a monotonous behavior for $f_3(t)$ with the correct initial time decay, e.g.,

$$f_3(t) = \exp(-\tfrac{1}{2}\Delta_4 t^2)\,. \tag{44}$$

This may still give a meaningful estimate for $a_3(0)$, whereas $b_3'(0)$ can be seriously overestimated if the actual $f_3(t)$ presents a negative undershoot at intermediate times. This feature limits the usefulness of any assumption based on the small-time behavior (16) even if the initial time decay of $f_3(t)$ were known.

In absence of any detailed knowledge of $f_3(t)$, any hope for a quantitative understanding of the behavior of $\Delta_3 a_3(0)$ and $\Delta_3 b_3'(0)$ at finite temperatures must rely on a stepping-down procedure of the continued fraction [Eqs. (36)–(38)]. In such a way, the problem is reduced to some guess for the lower-order functions $f_2(t)$, $f_1(t)$, or $f_0(t)$. Even here, it is apparent from Eqs. (32)–(38) that, whereas $\Delta_3 a_3(0)$ can be reasonably estimated by the know

ledge of the area of one of these $f_j(t)$ and of some low-order frequency moments, $\Delta_3 b_3'(0)$ requires a better description of these memory functions, since this parameter is determined by a delicate balance between $[a_j(0)]^2$ and $b_j'(0)$.

The quantity which has a more direct connection with the experimental spectra is $f_0(t)$. Since for $T < 1.4T_N$ the spectra show a broad inelastic peak, here the function $f_0(t)$ has a more or less defined oscillatory character: in particular, it must have a non-negligible negative undershoot. For neutron scattering in $RbMnF_3$ at high $\vec{k}$, such a behavior of $f_0(t)$ has been indeed found[13] at $T = 1.25T_N$ (analytical fit to the experimental data) and[8] at $T = 1.17T_N$ (a computer simulation). The simplest form for a $f_0(t)$ of this type is

$$f_0(t) = e^{-\Delta_1 t^2/2}(1 - Et^4) . \tag{45}$$

Then from Eqs. (45) and (39) one gets

$$\begin{aligned} a_0(0) &= (\pi/2\Delta_1)^{1/2}(1 - 3E/\Delta_1^2) , \\ b_0'(0) &= (1/\Delta_1)(1 - 8E/\Delta_1^2) . \end{aligned} \tag{46}$$

If the parameter E were determined requiring that $f_0(t)$ has the correct small-time expansion up to t^4 terms, one would obtain

$$E = \tfrac{1}{12}\Delta_1^2(1 - \Delta_2/2\Delta_1) . \tag{47}$$

However, this estimate of E is found to give a nearly Gaussian shape for $f_0(t)$ in Eq. (45): in particular, $f_0(t)$ vanishes at times $t = E^{-1/4}$ much higher than those obtained in the aforementioned neutron cases. As a consequence, the quantity $\Delta_3 b_3'(0)$ derived by means of Eqs. (46), (47), and (38) is found to slightly increase with respect to its high-temperature value, thus being unable to reproduce any inelastic peak. This circumstance is another evidence of the bad results of any procedure just based on the small-time quantities. As a matter of fact, the value of E obtained from the computer simulation[8] at $T = 1.17T_N$ turns out to be almost six times larger than that predicted by Eq. (47) and gives for $f_0(t)$ a much better description of the overall spin dynamics near T_N. If one phenomenologically accepts this large value of E in Eq. (46), one indeed finds for $\Delta_3 b_3'(0)$ a value substantially smaller than the high-temperature one, and about one half of that estimated by means of Eq. (47). On the other hand, the parameter $\Delta_3 a_3(0)$ turns out to be much less affected.

All these results support for the high-$\vec{k}$ neutron case the approximate validity of a Markoffian hypothesis in the neighborhood of T_N. Since two-spin Raman spectra are dominated by high wave vectors and show a shape very similar to that observed in neutron scattering, it appears reasonable to assume that $\Delta_3 b_3'(0) \simeq 0$ even in the Raman

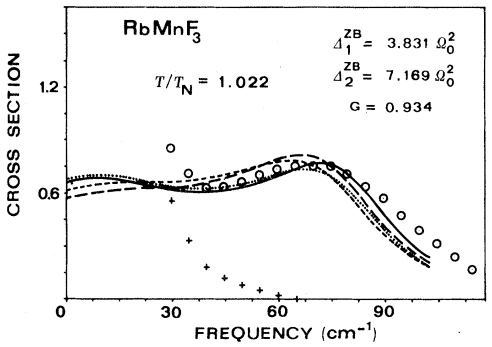

FIG. 2. Two-spin Stokes spectrum in $RbMnF_3$ at 84.5 °K ($T \sim 1.02T_N$). Long dashed and full curves refer to the purely Markoffian theoretical shapes in which the parameter $\Delta_3 a_3(0)$ has been evaluated according the first or the second way in Eq. (48), respectively. Short dashed and dotted curves refer to the same shapes in which band effects ($G \neq 1$) have been accounted for. The circles and the crosses are the experimental data for the spectrum and for the stray light respectively (Ref. 21). The exchange integral has been taken as $J = -4.73$ cm^{-1}.

case. Therefore it is very interesting to compare the theoretical shapes obtained using this Markoffian approximation and the evaluated frequency moments with the experimental spectra near T_N. For a meaningful comparison in this temperature range one must of course consider also the effect of the detailed balance factor in Eq. (9). Even here, we shall consider simple cubic antiferromagnets like $RbMnF_3$ and $KNiF_3$.

In Fig. 2 our theory is compared with the experimental Stokes spectrum[20] in $RbMnF_3$ at 84.5 °K ($T = 1.022\ T_N$). The experimental spectrum is unobservable at low-frequency shifts due to the strong stray light. The theoretical shapes refer to two simple Markoffian approximations [$\Delta_3 b_3'(0) = 0$] which differ only for the estimate of $\Delta_3 a_3(0)$. This parameter is evaluated by means of Eqs. (37) and (38) stepping the continued fraction down to the first and to the zeroth order. As $\Delta_3 a_3(0)$ is not much affected by the detailed behavior of $f_0(t)$ or $f_1(t)$, for the sake of simplicity we have chosen Gaussian behaviors. This yields

$$\Delta_3 a_3(0) = (\tfrac{1}{2}\pi\Delta_2)^{1/2}, \quad \Delta_3 a_3(0) = \Delta_2(2/\pi\Delta_1)^{1/2} \tag{48}$$

for the first and for the zeroth stage, respectively. Both approximations are in good agreement with the experimental spectrum. In particular, the experimental peak at 76 cm^{-1} is reproduced within few cm^{-1}. Figure 2 also shows the fair agreement of the same curves in which the deviation of the second moment Δ_1 from the zone-boundary value Δ_1^{ZB} has been taken into account through the factor G discussed in Sec. IV. If one considers that the

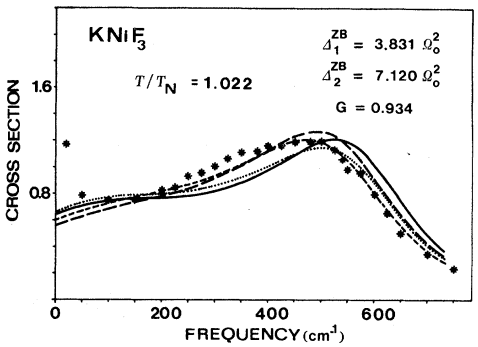

FIG. 3. Two-spin spectrum in $KNiF_3$ at 256 °K ($T \sim 1.02 T_N$). The theoretical shapes have the same meaning of Fig. 2. The stars are the experimental data (Ref. 22). The exchange integral has been taken as $J = -71$ cm^{-1}.

only fitting parameter which has been used is a common amplitude factor, the agreement confirms also in the Raman case the validity of the Markoffian theory in the neighborhood of T_N.

The same conclusion can be drawn looking at Fig. 3, which compares theory and the experimental spectrum in $KNiF_3$ at[21] $T = 256$ °K ($T \sim 1.02 T_N$). The parameter $\Delta_3 a_3(0)$ has been evaluated in the same way as before. The agreement is very good; moreover, in this case one can make a meaningful comparison also at frequency shifts comparatively lower than in $RbMnF_3$, since the experimental spectrum appears to be less affected by spurious quasielastic scattering.

At intermediate temperatures the experimental inelastic peak is hardly recognizable. In these conditions the quantity $\Delta_3 b_3'(0)$, which in a sense measures the deviation from the purely Markoffian behavior, begins to play a non-negligible role which increases more and more with temperature. Few experimental spectra have been published in this temperature region: in any case, just to give an idea of the effect of a finite $\Delta_3 b_3'(0)$ at intermediate temperatures, in Fig. 4 we have plotted the theoretical spectra for $KNiF_3$ at $T = 1.197 T_N$ obtained with a purely Markoffian hypothesis [$\Delta_3 b_3'(0) = 0$] and with $\Delta_3 b_3'(0) = 0.25$ [i.e., about one half of the $T \to \infty$ value $\Delta_3 b_3'(0) \sim 0.45$]. Comparing these shapes with the experimental Stokes spectrum at $T = 300$ °K, one indeed notes that the presence of a finite $\Delta_3 b_3'(0)$ leads to a better agreement.

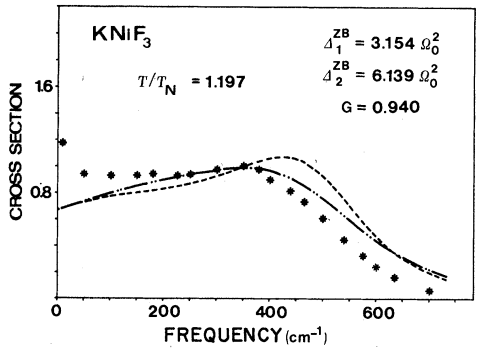

FIG. 4. Two-spin Stokes spectrum in $KNiF_3$ at 300 °K ($T \sim 1.20 T_N$). The theoretical shapes refer to the results of a purely Markoffian [$\Delta_3 b_3'(0) = 0$; dashed curve] and of a modified Markoffian approximation [$\Delta_3 b_3'(0) = 0.25$; dash double-dotted curve]. In both cases the parameter $\Delta_3 a_3(0)$ has been determined according the first of Eqs. (48). The stars are the experimental data (Ref. 22).

VI. CONCLUSIONS

In this paper we have worked out a modified long-time approximation for the spectral shape using its continued fraction representation established by Mori. The theory has been applied to the interpretation of two-spin Raman spectra in the paramagnetic region of simple cubic antiferromagnets like $RbMnF_3$ and $KNiF_3$. The relevant frequency moments have been evaluated by means of a simple decoupling procedure and turn out to be dominated by the contribution of zone-boundary wave vectors in the whole temperature range.

The temperature dependence and the main features of the experimental Raman spectra are quite analogous to those observed in inelastic neutron scattering at large wave vectors. This behavior can be understood within the framework of the modified long-time theory: in particular, its agreement with the experimental data at high temperatures is an evidence of the breakdown at $T \to \infty$ of any purely Markoffian hypothesis. The deviation from the Markoffian behavior [measured by the quantity $\Delta_3 b_3'(0)$] which is substantial at $T \to \infty$, decreases as the transition temperature T_N is approached. Even if a quantitative explanation of this temperature dependence is difficult, the main effect is due to the strong deviation of the main time correlation functions from a monotonous behavior as $T \to T_N$. The increasing validity of the Markoffian assumption is most clearly seen at $T \sim 1.02\ T_N$, where the theoretical spectra evaluated with $\Delta_3 b_3'(0) = 0$ are found to be in good agreement with the experimental ones in $RbMnF_3$ and $KNiF_3$: in particular, the inelastic peaks are well reproduced. As two-spin Raman spectra strongly weigh the wave vectors at the antiferromagnetic zone boundary, the whole method can give a basis for a consistent treatment of the spin dynamics at short distances through all the paramagnetic region.

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