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Failure of the classical approximation for $CsNiF_3$

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An exact numerical-transfer-matrix method is used to calculate the thermodynamic properties of an easy-plane Heisenberg ferromagnet with in-plane magnetic field. The results clearly show that the often-adopted classical approximation is totally inadequate for $CsNiF_3$ in typical experimental circumstances. In particular, it is shown that a quantum treatment of the out-of-plane fluctuations is crucial.

The properties of a ferromagnetic chain with easy-plane anisotropy in a symmetry-breaking external field

$$\mathscr{H}=-2J\sum_{i=1}^{N}\vec{S}_i\cdot\vec{S}_{i+1}+D\sum_{i=1}^{N}(S_i^z)^2-g\mu_BH\sum_{i=1}^{N}S_i^y \qquad (1)$$

have attracted much interest in recent years. On one hand, there is a material, $CiNiF_3$, which is described by (1); on the other hand, in the classical limit the Hamiltonian (1) may be approximated (in the continuum limit and for $D\rightarrow\infty$) by the sine-Gordon (SG) one.[1] The classical SG is a prototype system for studying linear excitations as well as nonlinear excitations, breathers, and topologically stable solitons and how they affect the thermodynamic and scattering properties.[1,2]

However, much experimental work[3,4] on $CsNiF_3$ addressed to provide a direct evidence of the role of nonlinear modes has not been interpreted in a univocal way.[5,6] Also, more recent theories that start with the full Hamiltonian (1) have not yet clarified the problem. In particular, various authors have estimated in the continuum limit the effect due to out-of-plane fluctuations on the thermodynamic properties.[7–9] These theories, which lead to a reduction of about 20–30% of the SG soliton energy, assume the classical approximation to be valid for $CsNiF_3$ in typical experimental circumstances.[10]

In this paper we show that the universal behavior of the experimental data for the magnetization[11] (a soliton-insensitive quantity) on the parameter $k_BT/(\tilde{H}J)^{1/2}$, with $\tilde{H}=g\mu_BH$, unexplicable by classical models, is reproduced at low temperatures by a simple *quantum* spin-wave theory. In particular, we find that even at $T=0$, owing to zero-point motion, the out-of-plane fluctuations are very strong. Consequently, the applicability of the classical model to describe $CsNiF_3$ is suspect. In order to analyze the validity of this approximation, we calculate the thermodynamic properties for the classical system with Hamiltonian (1) using a numerical-transfer-matrix (TM) method. Since this method is exact, from the comparison with the experimental data, we conclude that the classical approximation is absolutely inadequate for $CsNiF_3$ in the range of parameters (field and temperature) of interest. Finally, the validity of some theoretical predictions[9] is examined by a comparison with our exact TM results.

Before discussing the various thermodynamic properties, we briefly describe the TM method. Let us take a magnetic chain described by a symmetric Hamiltonian with nearest-neighbor (NN) interaction

$$H=\sum_i H(\vec{S}_i,\vec{S}_{i+1};H(\vec{S}_i,\vec{S}_{i+1})=H(\vec{S}_{i+1},\vec{S}_i) \ ,$$

with periodic condition for the classical spin vectors. By means of the transfer-integral formalism[12] any thermodynamic property can be expressed in terms of eigenvalues and eigenfunctions of the integral equation

$$\int d\vec{S}_{i+1}\exp[-\beta H(\vec{S}_i,\vec{S}_{i+1})]\psi_n(\vec{S}_{i+1})=\lambda_n\psi_n(\vec{S}_i) \ . \qquad (2)$$

The explicit expressions of the thermodynamic quantities in terms of λ_n and $\psi_n(\vec{S}_i)$ have been quoted elsewhere.[12] For an axially symmetric system an angular integration can be done analytically and the remaining integration can be simply performed by a Gaussian method.[12] However, for the model (1) the lack of axial isotropy makes the solution more complicated owing to the double integration that requires much computer time. To overcome this difficulty we have performed the integral (2) using McLaren's 72-point, 14th degree formula for integrals over the surface of a sphere, a method already used by Pandit and Tannous[13] for the classical canted antiferromagnetic chain. The accuracy of this method can be checked by comparing the results obtained for $H=0$ or $D=0$ with those obtained by using the standard technique: consistent results have indeed been found in all ranges of interest of the parameters. In addition, our results exactly reproduce the magnetization data obtained by Loveluck, Schneider, Stoll, and Jauslin,[6] for $H=5$ kG, carrying the double integration.

In all our calculations we have assumed values of parameters appropriate for $CsNiF_3$: $J=11.8$ K, $S=1$, $g=2.4$. For the easy-plane anisotropy, consistently with the classical approximation, we have taken $D=4.5$ K.

(i) Magnetization. Cibert[12] has analyzed the experimental data by Rosinski and Elschner[14] of the magnetization $\langle S^y\rangle$ finding that it is a universal function of $k_BT/(\tilde{H}J)^{1/2}$. It is known that classical planar[15] and classical Heisenberg models[16] show universality for low H/J, while the classical easy-plane model is close to the planar one at low temperatures and exhibits a crossover towards the Heisenberg limit for high temperatures. In order to understand this behavior we have calculated $\langle S^y\rangle$ by TM as well as by a quantum

linear-spin-wave (LSW) theory. Following Reiter,[5] at the lowest order we obtain the diagonalized Bose Hamiltonian

$$H_B=\sum_k \omega_k b_k^\dagger b_k \ , \tag{3}$$

with $b_k^\dagger$ and b_k Bose operators and

$$\omega_k=S[(J_0-J_k)^2+2(\tilde{D}+\tilde{H})(J_0-J_k)+2\tilde{D}\tilde{H}+\tilde{H}^2]^{1/2} \ ,$$

where $J_k=4J\cos k$, $\tilde{D}=D(S-\frac{1}{2})/S=4.5$ K. The magnetization is given by

$$\langle S^y\rangle=S-N^{-1}\sum_k[(\alpha_k^2+\beta_k^2)n_k+\beta_k^2] \ , \tag{4}$$

where $\alpha_k=\cosh\theta_k$, $\beta_k=\sinh\theta_k$, and $\tanh(2\theta_k)=\tilde{D}(J_0-J_k+\tilde{D}+\tilde{H})^{-1}$; n_k is the Bose factor. In Fig. 1 we report the predictions of quantum LSW and the TM results for $\langle S^y\rangle$ vs $k_BT/(\tilde{H}J)^{1/2}$. It is evident that, whereas the classical results in no case are universal function, the existence of a scaling law for the quantum results is clearly demonstrated. The agreement with the experimental data is very good as far as $k_BT(\tilde{H}J)^{1/2}\sim 2$. These results clearly show that a correct quantum treatment of the out-of-plane fluctuations is required. In order to elucidate the different behavior of these fluctuations in the classical and quantum case, we have calculated the quantity $\langle(S_i^z)^2\rangle$ which in the quantum LSW theory is given by

$$\langle(S_i^z)^2\rangle^q=(S/2)N^{-1}\sum_k(\alpha_k-\beta_k)^2(2n_k+1) \ . \tag{5}$$

This quantity is shown in Fig. 2 together with its classical counterpart

$$\langle(S_i^z)^2\rangle^{cl}=Sk_BT[(J_0S+2DS+\tilde{H})^2-(J_0S)^2]^{-1}$$

and with TM results versus T for $H=15$ kG. In the classical case $\langle(S_i^z)^2\rangle$ vanishes for $T\rightarrow 0$ and increases almost linearly with T. This strong variation explains the crossover found by TM methods[6] between the planar model at low T and the Heisenberg one at high T for the magnetization. In the quantum case at $T=0$ the out-of-plane fluctuations for the easy-plane model (1) are very large: $\langle(S_i^z)^2\rangle\sim 0.424$ for $H=15$ kG, to be compared with the value 0.5 (independent of H) for the isotropic Heisenberg model. The thermal increment is extremely slow in the range of temperatures examined, thus explaining the universal behavior experimentally found for the magnetization of $CsNiF_3$. Our quantum results for $\langle(S_i^z)^2\rangle$ are found to be in agreement with the exact finite chain calculation by Tammetta and Oitmaa[17] at low temperatures.

These results for the quantum easy-plane system (1) strongly suggest the inadequacy of the classical model to describe $CsNiF_3$.

(ii) Specific heat. Ramirez and Wolf in their measures of specific heat[4] notice the presence of an extra contribution to the specific-heat difference $\Delta C=C_H-C_{H=0}$, where C_H is the specific heat measured in a symmetry-breaking external field. This anomaly is not reproducible by a quantum LSW theory, that would give a negative ΔC_{SW}^q and is attributed to thermal soliton excitations.[4,8,9] By means of the TM method we have calculated the classical specific heat for the model (1) both for $H=0$ and $H\neq 0$. It should be noted

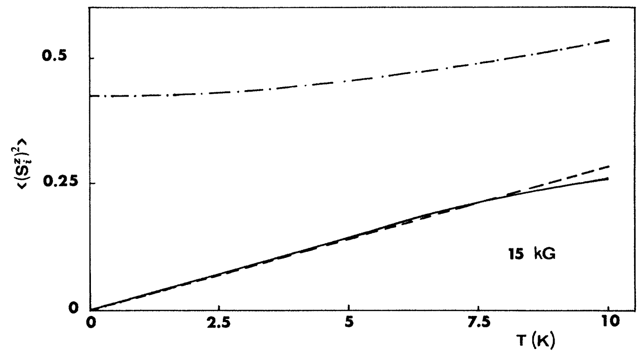

FIG. 2. Temperature dependence of the out-of-plane fluctuations $\langle(S_i^z)^2\rangle$ for $H=15$ kG. Full line: TM data. Dashed line: classical LSW results. Dashed-dotted line: quantum LSW results.

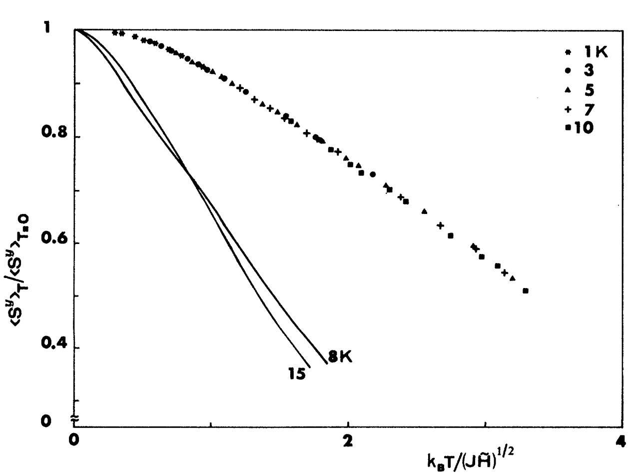

FIG. 1. Universal plot for reduced magnetization $\langle S^y\rangle_T/\langle S^y\rangle_{T=0}$ vs $k_BT/(\tilde{H}J)^{1/2}$. Curves: TM data. Symbols: quantum LSW theory results.

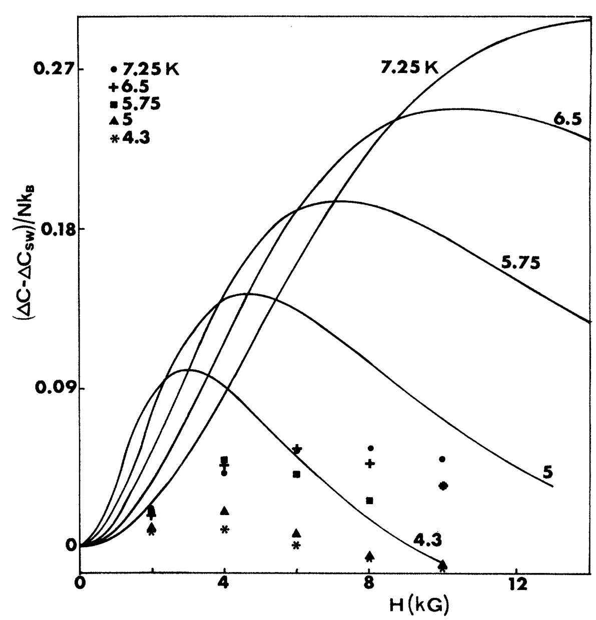

FIG. 3. Field dependence of $(\Delta C-\Delta C_{SW})/Nk_B$ at different values of T. Full line: TM data. Symbols: experimental data (Ref. 4) for $CsNiF_3$.

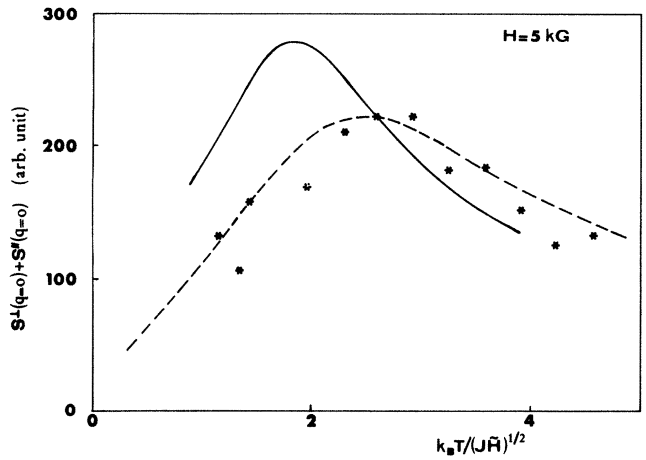

FIG. 4. Universal plot for

$$S^{\perp}(q=0)+S^{\parallel}(q=0)=\langle S^x_{q=0}S^x_{q=0}\rangle+\langle S^y_{q=0}S^y_{q=0}\rangle$$

vs $k_B T/(\tilde{H}J)^{1/2}$ at $H=5$ kG. Full line: TM data for model (1). Dashed line: TM data for the planar model. Symbols: experimental data (Ref. 19) for $CsNiF_3$.

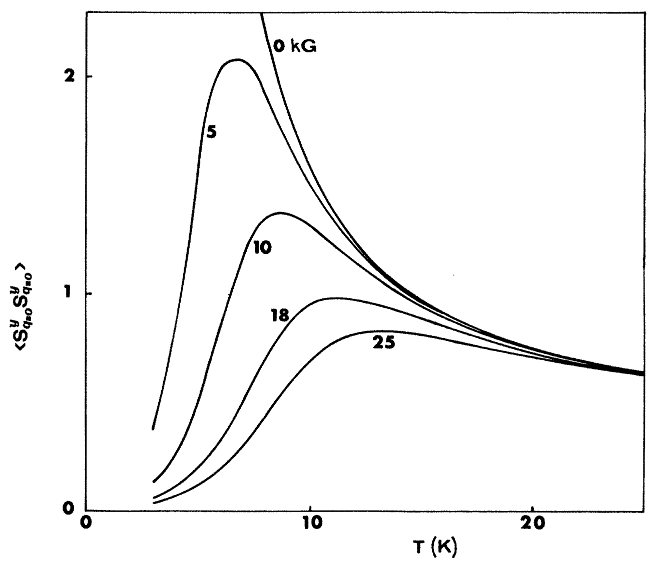

FIG. 5. TM data for the temperature dependence of $S^{\parallel}(q=0)$ at different fields.

that in both cases classical LSW theory gives an erroneous constant value NK_B for the specific heat. Therefore, for a meaningful comparison between TM results and experimental data (which obviously give $C\rightarrow 0$ for $T\rightarrow 0$), it is necessary to subtract the classical LSW contribution from the former and its quantum counterpart from the latter. In Fig. 3 we report the TM and experimental results for $\Delta C-\Delta C_{\rm SW}$ versus magnetic field for different temperatures. In spite of the addition of the positive quantity $-\Delta C^q_{\rm SW}$ to the Ramirez and Wolf's experimental data, these remain much smaller than the numerical results. Also, the peak positions are quite different. The specific heat of $CsNiF_3$ is therefore impossible to understand within a classical model, at variance with the results obtained for tetramethyl manganese chloride (TMMC).[18]

(iii) Susceptibility. This property has been measured by Kakurai and Steiner[19] using the quasielastic neutron scattering technique. The susceptibility at $q=0$ shows a broad maximum in its temperature dependence. In Fig. 4 we report the TM data obtained for the model (1). As it can be easily seen these data do not reproduce the experimental results, thus confirming that the classical model is inadequate for describing $CsNiF_3$. The good agreement that we find using the classical planar model (spin dimensionality $=2$), as shown in Fig. 4, as well as that found by Kakurai and Steiner[19] for the SG one, seems then to be fortuitous.

Besides the experimental data, it is interesting to compare the TM results with the predictions of the theories of Fogedby, Hedegård, and Svane[8] and Leung and Bishop,[9] who find divergence in the soliton contribution to thermodynamic quantities for a critial value $b_c=\frac{1}{3}$ of the ratio $b=\tilde{H}/2DS$. Although these divergences are attributed to the inadequacy of the approximations close to the critical field, Leung and Bishop[9] suggest that an "incipient divergence" should be experimentally observable in $CsNiF_3$, where $H_c=18$ kG. As we have just observed that the classical model (1) is unreliable in explaining the experimental data for $CsNiF_3$, we believe that only TM results should be used to verify the presence of anomalous contributions. The property where the most striking effect was expected by Leung and Bishop[9] was the component along the magnetic field direction of the susceptibility. In Fig. 5 the TM results for the correlation function $\langle S^y_{q=0}S^y_{q=0}\rangle$ are reported versus T at different fields. For $H=0$ we find a divergence for $T\rightarrow 0$ which, as it is well known, indicates the establishment of long-range order. Since the application of a magnetic field suppresses spin fluctuations, we observe a gradual decrease of the correlation functions at fixed T when the field is increased and no anomalous behavior is observed in the range 5–25 kG. Consequently, the validity of the theory[9] appears to be restricted to ranges of the parameters much more limited.

In conclusion, in this Rapid Communication we have demonstrated the inadequacy of the classical approximation for $CsNiF_3$, since the exact numerical TM data strongly disagree with the experimental results for magnetization, specific heat, and susceptibility, and consequently the necessity of a quantum treatment. In particular, we have shown that the quantum out-of-plane fluctuations are very strong demonstrating the inadequacy of a mapping of Hamiltonian (1) to the quantum SG model.[20] Also, approaches which include only the leading-order deviations from planar behavior[21] are to be regarded only as starting points for the treatment of the real system $CsNiF_3$.

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