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Nuclear-spin-lattice relaxation and magnetization of the ferromagnetic $S = \frac{1}{2}$ chain system $(\text{C}_6\text{H}_{11}\text{NH}_3)\text{CuBr}_3$: Contribution of magnons and solitons

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The spin-lattice relaxation rate (T_1^{-1}) of the hydrogen nuclei in $(\text{C}_6\text{H}_{11}\text{NH}_3)\text{CuBr}_3$ (CHAB) has been measured for $1.2 < T < 6.5$ K and applied fields $0 < B < 70$ kG along the crystallographic a , b , and c directions. For $\mathbf{B} \parallel \mathbf{c}$, in which case CHAB can be mapped to a sine-Gordon system, the contribution of linear and nonlinear excitations to T_1^{-1} has been investigated. The relaxation rate for $\sqrt{B}/T > 1$ is completely dominated by the two-magnon (Raman) process, whereas for $\sqrt{B}/T < 1$, a three-magnon term has to be included to obtain a fair description of the data. The quantitative effect of solitonlike excitations on T_1^{-1} is too small to be unambiguously identified. The magnetization was measured for $1.4 < T < 10$ K and fields $0 < B < 50$ kG along c . The data for $T/\sqrt{B} > 0.8$ exhibit systematic deviations from linear spin-wave theory, which can fully be explained by the effect of sine-Gordon solitons. The apparent discrepancies between the observed magnetization and various classical model predictions seem to originate primarily from the poor description of the linear excitations by these models.

I. INTRODUCTION

The static and dynamic properties of one-dimensional magnetic systems are strongly influenced by the presence of nonlinear excitations.¹ A physically appealing description of these excitations is possible for systems with easy-plane anisotropy in a transverse magnetic field, which can be mapped to the sine-Gordon (SG) equation, at least under certain approximations.² Apart from linear excitations (magnons), this equation has nonlinear solutions called kink solitons.³ A variety of experiments on quasi-one-dimensional compounds with easy-plane anisotropy have been interpreted in terms of the SG model. Among these we mention neutron-scattering studies on CsNiF_3 ($S=1$) (Ref. 4) and $(\text{CD}_3)_4\text{NMnCl}_3$ (TMMC, $S=\frac{5}{2}$),⁵ and nuclear-spin-lattice relaxation and heat-capacity measurements on CsNiF_3 ,^{6,7} TMMC,^{8,9} and $(\text{C}_6\text{H}_{11}\text{NH}_3)\text{CuBr}_3$ (CHAB, $S=\frac{1}{2}$).¹⁰ Although a satisfactory description of most of the data could be obtained, it has been questioned whether this fact should be regarded as a proof of the existence of solitons in these systems, since in some cases the observed effects can also be explained in terms of other elementary excitations. On the other hand, the effect of the various approximations involved with the mapping of the original magnetic system to the SG system is not clear. A recent analysis of the field-dependent part of the heat capacity of CHAB (Ref. 11) revealed that the nice description of the average data on this $S=\frac{1}{2}$ system by the classical SG model results from an accidental canceling of the quantum sine-Gordon corrections by the effect of spin components out of the easy plane.

In this paper we present a detailed analysis of the con-

tribution of linear and nonlinear excitations to the nuclear-spin-lattice relaxation time of the hydrogen nuclei in CHAB. For this purpose the data reported before¹⁰ were supplemented with measurements at higher temperatures and fields (up to 6.5 K and 70 kG, respectively) along each of the three crystallographic axes. This analysis will be given in Sec. IV, after a brief description of the crystallographic and magnetic properties of CHAB (Sec. II) and an outline of the theory (Sec. III).

Next, we will consider the magnetization of CHAB for fields applied along the crystallographic c direction. In contrast to the heat capacity of potentially soliton-bearing ferromagnetic chain systems, an analysis of the magnetization (M) in the paramagnetic region of such compounds in terms of the SG model has, to our knowledge, not been reported. In this respect we note that it has been stated¹² that the magnetization is a soliton-insensitive quantity. The majority of the data mentioned above, however, has been collected in a field and temperature region where the soliton density is rather large and hence—in our opinion—their effect on M may be significant. In Sec. V we compare our data on M with the predictions for various classical spin models and analyze the magnetization in terms of contributions of magnons and solitons. The paper will be concluded with a discussion in Sec. VI.

II. CRYSTALLOGRAPHIC AND MAGNETIC PROPERTIES

The crystallographic structure of $(\text{C}_6\text{H}_{11}\text{NH}_3)\text{CuBr}_3$ is orthorhombic, space group $P2_12_12_1$, with $a=19.84$ Å, $b=8.78$ Å, and $c=6.44$ Å, and four formula units in

the crystallographic unit cell.¹³ It consists of bibriged linear chains of CuBr_3^- ions running parallel to the c axis, which are effectively isolated in the a and b directions by the cyclohexylammonium complexes. From heat-capacity, magnetization,¹⁴ and ferromagnetic resonance¹⁵ experiments it was deduced that the individual chains in CHAB can be described by the Hamiltonian

$$\mathcal{H} = -2 \sum_i (J^{xx} S_i^x S_{i+1}^x + J^{yy} S_i^y S_{i+1}^y + J^{zz} S_i^z S_{i+1}^z), \quad (1)$$

with $J^{xx}/k_B = 55 \pm 5$ K, $J^{zz}/J^{xx} = 0.95$, and $1 - J^{yy}/J^{xx} \approx 5 \times 10^{-4}$. The y axis coincides with the crystallographic c axis, whereas the x axis is located within the ab plane at an angle ϕ from the b axis. Two symmetry-related types of chains are present, with $\phi = -25^\circ$ and $+25^\circ$, respectively. The interchain interactions are smaller than J^{xx}/k_B by 3 orders of magnitude, and give rise to a three-dimensional long-range-ordered state below $T_c = 1.50$ K. It is obvious from these results that CHAB is a very good realization of a one-dimensional (1D) $S = \frac{1}{2}$ ferromagnetic system. Mapping to the SG system is formally possible¹⁶ for external fields applied along the crystallographic c axis, which is located in the easy (XY) plane for both types of chains.

III. RELATION BETWEEN T_1^{-1} AND THE DYNAMIC STRUCTURE FACTORS

The dynamics of CHAB can be probed by nuclear-spin-lattice relaxation measurements on the ^1H ($I = \frac{1}{2}$) nuclei of the cyclohexylammonium complexes. The relaxation of these nuclei is mediated by the dipolar interaction between the nuclear moment and the electron-spin system. To enable a quantitative comparison of the contribution of the various elementary excitations to the nuclear-spin-lattice relaxation rate T_1^{-1} , we have chosen a unified description of both magnons and solitons. Their respective contributions are calculated by exploiting the relation between T_1^{-1} and the dynamic structure factors $S^{\alpha\beta}(q, \omega)$. This approach has the advantage that the contribution of the solitons can be evaluated without approximating their actual shape by, for instance, a rectangular profile.⁶ In this section we will give an outline of the derivation of the expression relating T_1^{-1} to the dynamic structure factors of the individual chains.

If the very small dipolar interactions between different hydrogen nuclei ($< 5 \times 10^{-6}$ K) are neglected, the Hamiltonian of the j th nucleus can be written as

$$\begin{aligned} \mathcal{H}_N(j) &= \mathcal{H}_s(j) + \mathcal{H}_f(j), \\ \mathcal{H}_s(j) &= -\hbar \gamma_N \mathbf{I}_j \cdot \mathbf{B}_{\text{eff}}(j) \\ &= -\hbar \gamma_N \mathbf{I}_j \cdot \left[\mathbf{B}_{\text{ex}} - (\hbar \gamma_N)^{-1} \sum_l \vec{\mathbf{A}}_{jl} \langle \langle \mathbf{S}_l \rangle \rangle \right], \end{aligned} \quad (2)$$

$$\mathcal{H}_f(j) = \sum_l \mathbf{I}_j \cdot \vec{\mathbf{A}}_{jl} \delta \mathbf{S}_l,$$

with

$$\delta \mathbf{S}_l = \mathbf{S}_l - \langle \langle \mathbf{S}_l \rangle \rangle, \quad (3)$$

$$\vec{\mathbf{A}}_{jl} = \frac{\mu_0}{4\pi} g \mu_B \gamma_N \hbar \frac{1}{|\mathbf{r}_{jl}|^3} \begin{bmatrix} 1 - 3x^2 & -3xy & -3xz \\ -3yx & 1 - 3y^2 & -3yz \\ -3zx & -3zy & 1 - 3z^2 \end{bmatrix}.$$

In these equations γ_N is the gyromagnetic ratio of the hydrogen nucleus ($\gamma_N/2\pi = 4.2576$ MHz/kG), $\mathbf{r}_{jl}$ is the position vector of the l th electron spin relative to the position of the j th nucleus, $\mathbf{x} = (x, y, z)$ is defined as $\mathbf{r}_{jl}/|\mathbf{r}_{jl}|$, and $\delta \mathbf{S}_l$ denotes the fluctuating part of the l th electron spin. The first term in the Hamiltonian, $\mathcal{H}_s(j)$, describes the interaction of the j th hydrogen nucleus with the static part of the local field $\mathbf{B}_{\text{eff}}(j)$ at the j th nuclear site. $\mathbf{B}_{\text{eff}}(j)$ is the sum of the applied field $\mathbf{B}_{\text{ex}}$ and a "static" internal field, induced by the surrounding electron spins, which depends both on the temperature and on the orientation and magnitude of $\mathbf{B}_{\text{ex}}$. The second term, $\mathcal{H}_f(j)$, describes the fluctuating part of the dipolar field at the j th nuclear site.

It is well known that the diagonalization of the static part of the Hamiltonian results in two eigenstates, with an energy splitting $\Delta E = \hbar \omega_N(j)$, where $\omega_N(j) = \gamma_N |\mathbf{B}_{\text{eff}}(j)|$ is the nuclear Larmor frequency. The Fourier component of the fluctuating part with frequency $\omega_N(j)$ causes transitions between the nuclear-spin levels and provides a relaxation mechanism for the hydrogen nuclear-spin system towards equilibrium with the electron-spin system. The transition probabilities and, consequently, $T_1^{-1}(j)$, can be expressed in terms of time-dependent two-spin correlation functions $\langle \langle \delta S_l^\alpha(t) \delta S_n^\beta(0) \rangle \rangle$ of the electron-spin system, using first-order time-dependent perturbation theory¹⁷ (see Appendix). The result reads

$$\begin{aligned} T_1^{-1}(j) &= \sum_{\alpha, \beta} \sum_{l, n} g^{\alpha\beta}(j, l, n) \\ &\quad \times \int_{-\infty}^{\infty} dt e^{i\omega_N(j)t} \langle \langle \delta S_l^\alpha(t) \delta S_n^\beta(0) \rangle \rangle + \text{c.c.}, \end{aligned} \quad (4)$$

where $\alpha, \beta = x, y, z$, and $g^{\alpha\beta}(j, l, n)$ are geometrical coefficients corresponding to the dipolar interaction. These coefficients, for which explicit expressions are given in the Appendix, depend on the position vectors of the l th and n th electron spins relative to the position of the j th nucleus, and also on the relative orientation of the quantization axes of the j th nuclear spin [$|\mathbf{B}_{\text{eff}}(j)|$] and the l th ($|\langle \langle \mathbf{S}_l \rangle \rangle|$) and n th ($|\langle \langle \mathbf{S}_n \rangle \rangle|$) electron spins.

From Eq. (4) it is obvious that $T_1^{-1}(j)$ probes the Fourier component with frequency $\omega_N(j)$ of all two-spin correlation functions. Since in CHAB, however, the interaction between two spins belonging to different chains is at least 3 orders of magnitude smaller than the nearest-neighbor intrachain interaction, we will follow the usual approach,^{6,8} and ignore the time-dependent correlations between spins on different chains, i.e., for those spins $\langle \langle \delta S_l^\alpha(t) \delta S_n^\beta(0) \rangle \rangle = 0$. Using this approximation it is straightforward to rewrite Eq. (4) in terms of dynamic structure factors. These are defined as

$$\mathcal{S}^{\alpha\beta}(\mathbf{q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} \times \frac{1}{N} \sum_j \sum_k e^{i(\mathbf{r}_k - \mathbf{r}_j) \cdot \mathbf{q}} \langle\langle S_j^\alpha(t) S_k^\beta \rangle\rangle, \quad (5)$$

where N is the number of spins, or, alternatively,

$$\mathcal{S}^{\alpha\beta}(\mathbf{q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle\langle S^\alpha(\mathbf{q}, t) S^\beta(-\mathbf{q}) \rangle\rangle, \quad (6)$$

where

$$S^\alpha(\mathbf{q}) = \frac{1}{\sqrt{N}} \sum_j e^{-i\mathbf{r}_j \cdot \mathbf{q}} S_j^\alpha. \quad (7)$$

For a one-dimensional magnetic lattice it can be easily deduced that

$$\begin{aligned} & \int_{-\infty}^{\infty} dt e^{i\omega t} \langle\langle \delta S_l^\alpha(t) \delta S_n^\beta(0) \rangle\rangle \\ &= \frac{2\pi}{N} \sum_q \mathcal{S}^{\alpha\beta}(\mathbf{q}, \omega) \cos(mqa) - 2\pi\delta(\omega) \langle\langle S_l^\alpha \rangle\rangle \langle\langle S_n^\beta \rangle\rangle, \end{aligned} \quad (8)$$

where N is the number of electron spins within a chain and $ma = |\mathbf{r}_l - \mathbf{r}_n|$, a being the distance between two adjacent spins. The second term in Eq. (8) yields no contribution to the relaxation rate since $\omega_N \neq 0$ and will therefore be omitted. In CHAB two symmetry-related sets of chains must be distinguished (cf. Sec. II). In general, the dynamic structure factors of these two sets are different for nonzero external fields. Our T_1^{-1} data, however, have been collected in fields directed along the crystallographic a , b , and c axes. In this case the dynamic structure factors of the two sets of chains are identical, because of the symmetry of the magnetic structure. For these particular directions of the field it is possible to obtain an expression for the relaxation rate by inserting Eq. (8) into Eq. (4):

$$\begin{aligned} T_1^{-1} &= \sum_\alpha \sum_\beta \sum_{m=-\infty}^{\infty} \left[\sum_{\text{chains}} \sum_l g^{\alpha\beta}(j, l, l+m) \right] \\ &\times \frac{2\pi}{N} \sum_q \mathcal{S}^{\alpha\beta}(\mathbf{q}, \omega_N(j)) \cos(mqa) \\ &+ \text{c.c.} \end{aligned} \quad (9)$$

Because of the translational invariance of the chains, the geometrical coefficients can be added according to the summations over the chains and over l in Eq. (9), where the sum over l runs over all electron spins belonging to a certain chain. The expression can be further simplified using the relation $\mathcal{S}^{\alpha\beta}(\mathbf{q}, \omega_N) = \mathcal{S}^{\alpha\beta}(-\mathbf{q}, \omega_N)$ and the “detailed-balance” condition

$$\mathcal{S}^{\alpha\beta}(\mathbf{q}, -\omega_N) = e^{-\hbar\omega_N/k_B T} \mathcal{S}^{\alpha\beta}(\mathbf{q}, \omega_N)$$

(Ref. 18). Since in the experimental field and temperature region $\hbar\omega_N/k_B T < 2 \times 10^{-3}$, we replace the exponential term by unity and finally obtain

$$\begin{aligned} T_1^{-1}(j) &= \sum_\alpha \sum_\beta \sum_{m=0}^{\infty} G^{\alpha\beta}(j, m) \\ &\times \frac{2\pi}{N} \sum_q \mathcal{S}^{\alpha\beta}(\mathbf{q}, \omega_N(j)) \cos(mqa), \end{aligned} \quad (10)$$

with

$$\begin{aligned} G^{\alpha\beta}(j, m) &= \sum_{\text{chains}} \sum_l [1 - \delta(m, 0)/2] \\ &\times [g^{\alpha\beta}(j, l, l+m) \\ &+ g^{\alpha\beta}(j, l, l-m) + \text{c.c.}], \end{aligned} \quad (10a)$$

where $\omega_N(j) > 0$ and $G^{\alpha\beta}(j, m)$ are the so-called geometrical factors. The term with $m=0$ in Eq. (10) corresponds to the contribution of the spin-autocorrelation functions ($l=n$), the term with $m=1$ to that of the nearest-neighbor spin pair-correlation functions ($l=n \pm 1$), etc. This equation will be used as the starting point of the interpretation of the T_1^{-1} measurements presented in Sec. IV.

IV. EXPERIMENTAL RESULTS

The nuclear-spin-lattice relaxation rate T_1^{-1} was determined from the recovery of the magnetization of the nuclear-spin system after demagnetization. This recovery is described by the relation

$$M_z(t) = M_z(t = \infty) (1 - e^{-t/T_1}), \quad (11)$$

where $M_z(t = \infty)$ corresponds to the equilibrium magnetization. The magnitude of $M_z(t)$ was measured by means of a spin-echo technique,¹⁹ using a sequence of incoherent rf pulses matching the Larmor frequency of the nuclear subsystem of interest. The time t was varied between $0.1T_1$ and $3T_1$. The spin-echo signals could be observed with a signal-to-noise ratio varying between 10 and 40, depending on frequency and temperature. From a fit of Eq. (11) to the data taken at different t , in principle, accurate estimates of T_1^{-1} can be obtained if the observed spin-echo signal originates from one well-defined subsystem of hydrogen nuclei. In CHAB, however, each crystallographic unit cell contains 56 hydrogen atoms. If the external field is directed along one of the crystallographic axes, 14 inequivalent sets of hydrogen nuclei remain. Because of the small dipolar interactions, these sets are subject to slightly different internal fields and hence possess different $\omega_N(j)$. Moreover, because the geometrical factors for these sets are not the same, each set may, in principle, have a different value of $T_1^{-1}(j)$. In some cases it was obvious that more than one set contributed to the spin-echo signal, since the variation of the echo intensity with time could not be described by a single exponent over more than one decade of t . Although these complications hamper a detailed quantitative comparison of the calculated relaxation rate with the data, they do not dramatically affect the characteristic field and temperature dependence of T_1^{-1} . We will return to this point in Sec. IV A.

FIG. 1. Field dependence of the ^1H nuclear spin-lattice relaxation rate in CHAB at several fixed temperatures. The solid curves represent the theoretical prediction for the Raman process, scaled by a factor 0.50, 0.83, and 0.73 for $\mathbf{B}||\mathbf{a}, \mathbf{b}, \mathbf{c}$, respectively. The dashed curves reflect the effect of inclusion of three-spin-wave processes.

A. The Raman relaxation process

The relaxation rate was measured as a function of the resonance frequency ($7.5 < \nu < 300$ MHz, corresponding to $1.75 < B < 70$ kG) at constant temperatures ($1.3 < T < 6$ K). The experimental results are presented in Fig. 1. The data exhibit a remarkably large field and temperature dependence: At a constant temperature the relaxation rate varies over almost five decades in the experimental field region, whereas at a constant field T_1^{-1} varies over two decades in the experimental temperature range. The scatter of the data shows that the errors in the determination of T_1 are substantially larger than the experimental inaccuracy (a few percent). As already indicated above, the data apparently represent an average relaxation rate of the inequivalent sets of hydrogen nuclei which are simultaneously excited. The errors arise from the fact that the hydrogen NMR spectra tend to broaden with increasing field and decreasing temperature and hence slight changes may occur in the relative contribution of the various sets of nuclei to the observed spin-echo intensity.

We will first calculate T_1 within the framework of linear spin-wave theory. Since the preferred directions

of the spins depend on the direction and magnitude of $\mathbf{B}$, the Hamiltonian of the individual chains [Eq. (1)] is transformed to a set of local axes, ξ, η, ζ , where the ζ axis coincides with the direction of the electron spins at $T=0$ K. If $\mathbf{B}$ is applied along a crystallographic axis the transformed Hamiltonian is identical for both sets of chains and can be written as

$$\begin{aligned} \mathcal{H} = & -2 \sum_i (J^{\xi\xi} S_i^\xi S_{i+1}^\xi + J^{\eta\eta} S_i^\eta S_{i+1}^\eta + J^{\zeta\zeta} S_i^\zeta S_{i+1}^\zeta) \\ & - \mu_B B^\zeta \sum_i S_i^\zeta \\ & - \sum_i (J^{\alpha\alpha} - J^{\text{zz}}) \sin(2\phi) (S_i^\alpha S_{i+1}^\zeta + S_i^\zeta S_{i+1}^\alpha) \\ & - \mu_B B^\alpha \sum_i S_i^\alpha, \end{aligned} \quad (12)$$

where $\alpha=x$ for $\mathbf{B}||\mathbf{a}, \mathbf{b}$ and $\alpha=y$ for $\mathbf{B}||\mathbf{c}$. ϕ denotes the angle of the direction of the spins ($||\zeta$) at $T=0$ K with the easy axis. Expressions for $J^{\xi\xi}$, $J^{\eta\eta}$, $J^{\zeta\zeta}$, B^ζ , and B^α are given in Table I.

Next, the spin operators in the Hamiltonian are replaced by boson operators using the Holstein-Primakoff transformation. The angle ϕ for which the terms that

TABLE I. Expressions for the parameters in the spin Hamiltonian (12). The meaning of the angles θ and ϕ is given in the text.

	$\mathbf{B} \mathbf{a}$	$\mathbf{B} \mathbf{b}$	$\mathbf{B} \mathbf{c}$
$J^{\xi\xi}$	$J^{xx} \cos^2 \phi + J^{zz} \sin^2 \phi$	$J^{xx} \cos^2 \phi + J^{zz} \sin^2 \phi$	J^{xx}
$J^{\eta\eta}$	J^{yy}	J^{yy}	$J^{yy} \cos^2 \phi + J^{zz} \sin^2 \phi$
$J^{\zeta\zeta}$	$J^{xx} \sin^2 \phi + J^{zz} \cos^2 \phi$	$J^{xx} \sin^2 \phi + J^{zz} \cos^2 \phi$	$J^{yy} \sin^2 \phi + J^{zz} \cos^2 \phi$
B^ζ	$g^{aa} B \cos(\theta - \phi)$	$g^{bb} B \cos(\theta - \phi)$	$g^{cc} B \cos(\theta - \phi)$
B^α	$g^{aa} B \sin(\theta - \phi)$	$g^{bb} B \sin(\theta - \phi)$	$g^{cc} B \sin(\theta - \phi)$

are linear in these operators vanish can be calculated from the relation

$$\begin{aligned} g^{aa,bb} \mu_B B \sin(\theta - \phi) &= 2S(J^{zz} - J^{xx}) \sin(2\phi) \quad (\mathbf{B} \parallel \mathbf{a}, \mathbf{b}), \\ g^{cc} \mu_B B &= 4S(J^{zz} - J^{yy}) \sin(\phi) \quad (\mathbf{B} \parallel \mathbf{c}), \end{aligned} \quad (13)$$

where θ denotes the angle of the applied field with the easy axis. Since no spin-wave (SW) renormalization is taken into account, Eq. (13) is identical to the classical torque-balance equation. After Fourier transformation of the boson operators the Hamiltonian is diagonalized by means of a Bogoliubov transformation, yielding

$$\mathcal{H}_{\text{SW}} = \sum_q \hbar \omega_q (\alpha_q^* \alpha_q + \frac{1}{2}) \quad \text{with } \hbar \omega_q = (A_q^2 - B_q^2)^{1/2}, \quad (14)$$

where

$$\begin{aligned} A_q &= 4J^{\xi\xi} S + \mu_B B^{\xi} - 2(J^{\xi\xi} + J^{\eta\eta}) S \cos(qa), \\ B_q &= 2(J^{\eta\eta} - J^{\xi\xi}) S \cos(qa). \end{aligned}$$

The dynamic structure factors were calculated in the usual way¹⁸ by expressing the spin-fluctuation operator $S^x(q)$ [cf. Eq. (7)] in a linear combination of the spin-wave creation and annihilation operators. If we insert the resulting expressions in Eq. (10), we obtain

$$T_1^{-1}(j) = [T_1^{-1}(j)]^D + [T_1^{-1}(j)]^S + [T_1^{-1}(j)]^R, \quad (15)$$

with

$$\begin{aligned} [T_1^{-1}(j)]^D &= \sum_{m=0}^{\infty} G^{\xi\xi}(j, m) \frac{\hbar}{k_B} \frac{2\pi}{N} \sum_q (v_q - u_q)^2 \langle\langle n_q + 1 \rangle\rangle \cos(mqa) \delta \left[\frac{\hbar \omega_N(j)}{k_B} - E_q \right] \\ &+ \sum_{m=0}^{\infty} G^{\eta\eta}(j, m) \frac{\hbar}{k_B} \frac{2\pi}{N} \sum_q (v_q + u_q)^2 \langle\langle n_q + 1 \rangle\rangle \cos(mqa) \delta \left[\frac{\hbar \omega_N(j)}{k_B} - E_q \right], \end{aligned} \quad (16)$$

$$\begin{aligned} [T_1^{-1}(j)]^S &= \sum_{m=0}^{\infty} G^{\xi\xi}(j, m) \frac{\hbar}{k_B} \frac{\pi}{N^2} \sum_{q_1} \sum_{q_2} (u_{q_1} v_{q_2} + u_{q_2} v_{q_1})^2 \\ &\times \langle\langle n_{q_1} + 1 \rangle\rangle \langle\langle n_{q_2} + 1 \rangle\rangle \cos[ma(q_1 + q_2)] \delta \left[\frac{\hbar \omega_N(j)}{k_B} - E_{q_1} - E_{q_2} \right], \end{aligned} \quad (17)$$

$$\begin{aligned} [T_1^{-1}(j)]^R &= \sum_{m=0}^{\infty} G^{\xi\xi}(j, m) \frac{\hbar}{k_B} \frac{2\pi}{N^2} \sum_{q_1} \sum_{q_2} (u_{q_1} u_{q_2} + v_{q_1} v_{q_2})^2 \\ &\times \langle\langle n_{q_1} + 1 \rangle\rangle \langle\langle n_{q_2} \rangle\rangle \cos[ma(q_1 + q_2)] \delta \left[\frac{\hbar \omega_N(j)}{k_B} + E_{q_2} - E_{q_1} \right]. \end{aligned} \quad (18)$$

In these equations E_q is the spin-wave energy at wave number q expressed in units of kelvins. u_q and v_q are the coefficients of the Bogoliubov transformation:

$$u_q = \left[\frac{A_q + \hbar \omega_q}{2\hbar \omega_q} \right]^{1/2}, \quad v_q = \left[\frac{A_q - \hbar \omega_q}{2\hbar \omega_q} \right]^{1/2}. \quad (19)$$

We note that a straightforward calculation shows that within the framework of (linear) spin-wave theory the terms in Eq. (10) involving the dynamic structure factors $\mathcal{S}^{\alpha\beta}(q, \omega)$ with $\alpha \neq \beta$ do not contribute to the relaxation rate. $[T_1^{-1}(j)]^D$ represents the contribution of the so-called one-spin-wave, or direct, relaxation process. $[T_1^{-1}(j)]^S$ is the contribution of the so-called two-spin-wave sum process, and $[T_1^{-1}(j)]^R$ is the contribution of the so-called two-spin-wave difference, or Raman, process. The δ functions in Eqs. (16)–(18) ensure the conservation of energy at the transition. Because of this energy-conservation requirement only the Raman relaxation process can occur in CHAB, at least within the present theoretical description, since the minimum spin-wave energy, i.e., the spin-wave gap, is much larger than $\hbar \omega_N / k_B$ (2×10^{-3} K for $B = 70$ kG).

The calculation of the contribution of the Raman process proceeds as follows. The δ function with respect to energy in Eq. (18) is replaced by a δ function with

respect to wave numbers using the relation²⁰

$$\delta(f(x)) = \sum_{x_0} \frac{1}{|f'(x_0)|} \delta(x - x_0), \quad (20)$$

where the summation runs over all nodes of $f(x)$, yielding

$$\begin{aligned} &\delta \left[\frac{\hbar \omega_N(j)}{k_B} + E_{q_2} - E_{q_1} \right] \\ &= |N(E_{q_0})| [\delta(q_0 - q_1) + \delta(q_0 + q_1)]. \end{aligned} \quad (21)$$

$q_0[q_2, \omega_N(j)]$ is the positive wave number for which $E_{q_0} = E_{q_2} + \hbar \omega_N(j) / k_B$ and $N(E_{q_0}) = [(\partial E_q / \partial qa)_{q_0}]^{-1}$ is the density of states of spin waves at wave number q_0 . With the use of Eq. (21) the summation over q_1 in Eq. (18) is trivial. Replacing the summation over q_2 by an integral and exploiting the inversion symmetry of the spin wave Hamiltonian [i.e., $N(E_q) = N(E_{-q})$, $E_q = E_{-q}$, $u_q = u_{-q}$, and $v_q = v_{-q}$], the following expression for $[T_1^{-1}(j)]^R$ can be deduced:

$$[T_1^{-1}(j)]^R = \sum_{m=0}^{\infty} G^{\xi\xi}(j, m) Z_{\text{SW}}(j, m), \quad (22)$$

with

$$Z_{\text{sw}}(j, m) = \frac{\hbar}{k_B \pi} \int_0^\pi d(q_2 a) N(E_{q_0}) (u_{q_0} u_{q_2} + v_{q_0} v_{q_2})^2 \\ \times \langle \langle n_{q_0} \rangle \rangle \langle \langle n_{q_2} + 1 \rangle \rangle \\ \times \cos(mq_0 a) \cos(mq_2 a) .$$

The integrals $Z_{\text{sw}}(j, m)$ were computed numerically. Although the state density $N(E_{q_0})$ exhibits a singularity at $q_0=0$, which is characteristic for a one-dimensional system, the integrals do not diverge, since q_0 will be always larger than zero because of the presence of the term $\hbar\omega_N(j)/k_B$ in Eqs. (18) and (21). We like to note that in the calculation of T_1 in CsNiF_3 by Goto⁶ this term is neglected. To avoid a divergence of the corresponding integrals, he introduced a cutoff by setting the lower limits of the integrals equal to $qa = \xi^{-1}$, where ξ is the correlation length of the planar classical spin model. Apart from the fact that in the presence of an external field such a cutoff is probably not justified, since in that case $q=0$ magnons are present,¹⁵ this procedure drastically affects the calculated field and temperature dependence of T_1 . We will return to this point in Sec. IV C.

The geometrical factors $G^{\xi\xi}(j, m)$ can be evaluated by a direct summation of the relevant geometrical coefficients $g^{\xi\xi}(j, l, n)$ [cf. Eq. (10)]. These coefficients depend both on the position vectors of the electron spins relative to the position of the j th hydrogen nucleus and on the orientation of the quantization axes of the electron spins and the nuclear spin. In our calculation the quantization axis of the electron spins was evaluated with the use of Eq. (13). The quantization axis of the nuclear spins is—in principle—different for each of the 14 inequivalent sets of nuclei, due to the different dipolar field at the corresponding hydrogen sites. However, since the dipolar field (< 500 G) is rather small compared to the applied external fields (> 2 kG), we simplified the problem by assuming that the quantization axis of the nuclei was parallel to the direction of the external field. The summation of the geometrical coefficients was performed over the lattice points within a volume of $3 \times 7 \times 11$ unit cells in the crystallographic a , b , and c directions, respectively, in which case the numerical values of $G^{\xi\xi}(j, m)$ are computed with an accuracy better than 1%. The magnitude of the geometrical factors decreases fairly rapidly for increasing m values. In the analysis of the data on CsNiF_3 (Ref. 6) only the terms with $m=0$ and 1 had to be taken into account. In CHAB, however, also terms with $m \geq 2$ appeared to contribute significantly to the relaxation rate. We truncated the summation in Eq. (18) at $m=10$, in which case the relaxation rates are computed with an accuracy better than 5%.

In order to compare the actually observed field and temperature dependence of T_1^{-1} with the theoretical prediction, we applied the following procedure. For each direction of $\mathbf{B}$ we selected first that set of nuclei that yielded the smallest difference between the calculated and observed magnitude of the relaxation rate. Since the

basic approximation of linear spin-wave theory, i.e., small numbers of excited spin waves, is expected to be most accurate at low temperatures and high fields, the theoretical curves were scaled to match the data collected in that region. The resulting scaling factors amount to 0.50, 0.83, and 0.73 for $\mathbf{B} \parallel \mathbf{a}, \mathbf{b}, \mathbf{c}$, respectively. The differences of these scaling factors from unity may be due to the fact that in the calculations of the geometrical factors the relative hydrogen positions reported for the chlorine isomorph²¹ were used. Apart from this, as already mentioned above, in some experiments more than one inequivalent set of hydrogen nuclei contributed to the spin-echo signal. Since the observed relaxation rate, however, varies over more than five decades in the experimental field and temperature region, we do not expect that these small uncertainties in the absolute value of the geometrical factors will seriously affect our interpretation.

The results of the procedure outlined above are represented by solid curves in Fig. 1. Inspection of this figure reveals that the overall field and temperature dependence of T_1^{-1} can be satisfactorily explained by the Raman relaxation process. Only for $\mathbf{B} \parallel \mathbf{c}$ do significant deviations occur at $T \geq 4.2$ K. These deviations suggest that, especially at low fields and high temperatures, other relaxation mechanisms contribute significantly. To elucidate this point we calculated the contribution of three-spin-wave relaxation processes and that of soliton-like excitations, which may be important for this particular field direction.

B. The three-spin-wave relaxation process

Within the framework of linear spin-wave theory the dynamic structure factors were evaluated by expressing the spin operators S_i^α in terms of boson creation and annihilation operators using the Holstein-Primakoff transformation, in which the operator quantity $(1 - a_i^* a_i / 2S)^{1/2}$ is replaced by the identity operator. In this case only one- and two-spin-wave processes, in principle, contribute to the relaxation rate [cf. Eqs. (15)–(18)]. To obtain three-spin-wave processes we expand this operator quantity up to second order in a_i^* and a_i in the calculation of the dynamic structure factors. Such an expansion only modifies the prediction for $\mathcal{S}^{\text{xx}}(q, \omega)$ and $\mathcal{S}^{\text{yy}}(q, \omega)$, but the calculation of the dynamic structure factors itself remains unaltered.

By inserting the modified predictions for $\mathcal{S}^{\text{xx}}(q, \omega)$ and $\mathcal{S}^{\text{yy}}(q, \omega)$ in Eq. (10), the following expression can be deduced:

$$T_1^{-1} = (1 - C) [T_1^{-1}(j)]^D + [T_1^{-1}(j)]^S \\ + [T_1^{-1}(j)]^R + [T_1^{-1}(j)]^T , \quad (23)$$

with

$$[T_1^{-1}(j)]^T = \sum_{m=0}^{\infty} [G^{\xi\xi}(j, m) X_{\text{sw}}(j, m) \\ + G^{\eta\eta}(j, m) Y_{\text{sw}}(j, m)] , \quad (24)$$

where

$$\begin{aligned}
X_{\text{sw}}(j, m) = & \frac{\hbar}{k_B} \frac{\pi}{16SN^3} \sum_{q_1} \sum_{q_2} \sum_{q_3} (\gamma_1 - \gamma_2)^2 \cos[m(q_2 + q_3 - q_1)a] \\
& \times \left[\langle\langle n_{q_1} + 1 \rangle\rangle \langle\langle n_{q_2} \rangle\rangle \langle\langle n_{q_3} \rangle\rangle \delta \left[\frac{\hbar\omega_N(j)}{k_B} + E_{q_1} - E_{q_2} - E_{q_3} \right] \right. \\
& \left. + \langle\langle n_{q_1} \rangle\rangle \langle\langle n_{q_2} + 1 \rangle\rangle \langle\langle n_{q_3} + 1 \rangle\rangle \delta \left[\frac{\hbar\omega_N(j)}{k_B} + E_{q_2} + E_{q_3} - E_{q_1} \right] \right], \quad (25)
\end{aligned}$$

$$\begin{aligned}
Y_{\text{sw}}(j, m) = & \frac{\hbar}{k_B} \frac{\pi}{16SN^3} \sum_{q_1} \sum_{q_2} \sum_{q_3} (\gamma_1 + \gamma_2)^2 \cos[m(q_2 + q_3 - q_1)a] \\
& \times \left[\langle\langle n_{q_1} + 1 \rangle\rangle \langle\langle n_{q_2} \rangle\rangle \langle\langle n_{q_3} \rangle\rangle \delta \left[\frac{\hbar\omega_N(j)}{k_B} + E_{q_1} - E_{q_2} - E_{q_3} \right] \right. \\
& \left. + \langle\langle n_{q_1} \rangle\rangle \langle\langle n_{q_2} + 1 \rangle\rangle \langle\langle n_{q_3} + 1 \rangle\rangle \delta \left[\frac{\hbar\omega_N(j)}{k_B} + E_{q_2} + E_{q_3} - E_{q_1} \right] \right]. \quad (26)
\end{aligned}$$

In these equations

$$C = \frac{1}{N} \sum_q [(2u_q^2 - u_q v_q) \langle\langle n_q \rangle\rangle + (2v_q^2 - v_q u_q) \langle\langle n_q + 1 \rangle\rangle],$$

$$\gamma_1 = -(u_{q_1} u_{q_2} u_{q_3} + v_{q_1} u_{q_2} v_{q_3} + v_{q_1} v_{q_2} u_{q_3}),$$

$$\gamma_2 = (u_{q_1} u_{q_2} v_{q_3} + u_{q_1} v_{q_2} u_{q_3} + v_{q_1} v_{q_2} v_{q_3}).$$

Calculations of the three-spin-wave process $[T_1^{-1}(j)]^T$ for the various field directions were performed in a similar way as those of the Raman relaxation rate. It appeared that for $\mathbf{B} \parallel \mathbf{a}, \mathbf{b}$ the contribution of the three-spin-wave process can be neglected with respect to that of the Raman process in the experimental field and temperature region. For $\mathbf{B} \parallel \mathbf{c}$ the calculated Raman relaxation rate is about a factor of 10 smaller, mainly because of the magnitude of the geometrical factors, and the three-spin-wave relaxation process yields a significant contribution at relatively high temperatures and low fields. In this respect, the experimental data corroborate our calculations, since the observed relaxation rate for $\mathbf{B} \parallel \mathbf{a}, \mathbf{b}$ is about a factor of 10 larger than that for $\mathbf{B} \parallel \mathbf{c}$. In Fig. 1 we plotted the calculated relaxation rate $T_1^{-1} = (T_1^{-1})^R + (T_1^{-1})^T$ (dashed curve) for the set of nuclei selected on basis of the Raman process. Inspection of this figure reveals that inclusion of the three-spin-wave processes leads to a substantial improvement of the theoretical description at higher temperatures.

C. Contribution of solitons to the relaxation rate

It is obvious from Fig. 1 that the data in the whole experimental field and temperature region can be satisfactorily explained by the combined action of the Raman and three-spin-wave relaxation processes. This result is, in a certain sense, surprising, since similar measurements on CsNiF_3 (Ref. 6) were reported to reveal a significant contribution of nonlinear excitations. However, as was already mentioned in Sec. IV A, in that analysis the term $\hbar\omega_N/k_B$ appearing in the expressions for the Raman and three-magnon processes was neglected, resulting in a divergence of the corresponding integrals. The cutoff that was introduced to avoid this divergence rather drastically affects the calculated field and temperature dependence of the spin-wave contribution to the relaxation rate, especially in the region where solitons were shown to be important. In view of this, we thought it worthwhile to consider the contribution of solitons to the relaxation rate in CHAB for $\mathbf{B} \parallel \mathbf{c}$ in more detail.

The starting point of our calculation is Eq. (1), in which we neglect the small easy-plane anisotropy. Assuming that the solitons behave as an ideal gas of thermally excited quasiparticles, it is possible to obtain expressions for the soliton contribution to the dynamic structure factors.^{22,23} By substitution of these expressions into Eq. (10) and taking the ζ axis as the easy axis, it can be deduced that the soliton contribution to T_1^{-1} is given by

$$[T_1^{-1}(j)]^{\text{sol}} = \frac{4\pi^2 aJS^2}{k_B cT} e^{-E_s^0/k_B T} \sum_{m=0}^{\infty} [G^{\xi\xi}(j, m) X_{\text{sol}}(j, m) + G^{\eta\eta}(j, m) Y_{\text{sol}}(j, m) + G^{\xi\xi}(j, m) Z_{\text{sol}}(j, m)], \quad (27)$$

with

$$\begin{aligned}
X_{\text{sol}}(j, m) &= \left[\frac{4E_0\omega_N(j)a}{\hbar c} \right]^2 \frac{1}{\pi} \int_0^\pi d(qa) \frac{1}{qa} e^{-\alpha/(qa)^2} \left[\frac{1}{Q \cosh(Q)} \right]^2 \cos(mqa), \\
Y_{\text{sol}}(j, m) &= \left[\frac{16S}{\pi} \right]^2 \frac{1}{\pi} \int_0^\pi d(qa) \frac{1}{qa} e^{-\alpha/(qa)^2} \left[\frac{Q}{\cosh(Q)} \right]^2 \cos(mqa), \\
Z_{\text{sol}}(j, m) &= \left[\frac{16S}{\pi} \right]^2 \frac{1}{\pi} \int_0^\pi d(qa) \frac{1}{qa} e^{-\alpha/(qa)^2} \left[\frac{Q}{\sinh(Q)} \right]^2 \cos(mqa),
\end{aligned} \tag{28}$$

where

$$Q = q/2m_s, \quad \alpha = E_s^0 \omega_N^2(j) a^2 / 2c^2 k_B T. \tag{29}$$

In these equations

$$\begin{aligned}
E_s^0 &= 8S(2Jg\mu_B BS)^{1/2}, \quad m_s = \frac{1}{a}(g\mu_B B/2JS)^{1/2}, \\
E_0 &= 2aJS^2, \quad c = 2aJS \left[\frac{2(J^{xx} - J^{zz})}{J^{xx}} \right]^{1/2}.
\end{aligned} \tag{30}$$

In the derivation of Eq. (27) we used the original expression for the soliton density given by Krumhansl and Schrieffer.²⁴ We have calculated the soliton contribution for the set of nuclei that was selected on basis of the Raman process. In the actual calculation we truncated the summation over m at $m = 10$ and evaluated the integrals in Eq. (28) numerically. It appeared that within the field and temperature region where these equations are formally valid, i.e., $k_B T/E_s^0 < 0.15$ [$\sqrt{B}/T > 0.6$ for CHAB (Ref. 11)], the numerical values of these integrals are almost independent of the applied field and temperature. This implies that if the relaxation rate would be solely due to the presence of solitons, it would be given by

$$T_1^{-1} \sim \frac{1}{T} e^{-E_s^0/k_B T}, \tag{31}$$

where $E_s^0/k_B = 10.95\sqrt{B}$. Equation (31) results in a linear relation between $\ln(TT_1^{-1})$ and $\sqrt{B}/T$ for all fields and temperatures. In Fig. 2 the experimental data collected for $\mathbf{B} \parallel c$ are represented in such a way. This figure reveals that the data almost perfectly collapse onto one universal curve. In a previous analysis of comparable data collected in a limited field range ($\sqrt{B}/T < 1.6$),¹⁰ it was noted that the data for $0.2 < \sqrt{B}/T < 1$ could be represented very well by a straight line. This behavior was attributed to the effect of solitons, since the value $E_s^0/k_B = 8.1\sqrt{B}$ inferred from the slope of the line agreed very well with the value $8.4\sqrt{B}$ deduced from measurements of the field-dependent part of the heat capacity. The present quantitative analysis of the various contributions to T_1^{-1} , however, demonstrates that this linear behavior of itself cannot be considered as a proof of the presence of solitons, since the spin-wave contribution to the relaxation rate, which can be represented by a single curve for low values of $\sqrt{B}/T$ [cf. the curves labeled $(T_1^{-1})^R + (T_1^{-1})^T$ is much larger than the soliton contribution [dashed line labeled $(T_1^{-1})_{\text{KS}}^{\text{sol}}$], at least in the re-

gion $\sqrt{B}/T > 0.6$ where Eq. (27) is valid. This is more clearly illustrated in the inset of the figure, where we plotted the various contributions to the relaxation rate separately for low values of $\sqrt{B}/T$. We like to emphasize that in order to obtain a meaningful comparison of the theoretical results with the data, we scaled all con-

FIG. 2. ^1H nuclear spin-lattice relaxation rate T_1^{-1} in CHAB for $\mathbf{B} \parallel c$ plotted as $\log_{10}(TT_1^{-1})$ against $\sqrt{B}/T$. The contributions from the Raman and three-spin-wave relaxation processes are denoted by $(T_1^{-1})^R$ and $(T_1^{-1})^T$, respectively. The contribution from solitons is represented by lines labeled $(T_1^{-1})^{\text{sol}}$. The dashed line labeled $(T_1^{-1})_{\text{KS}}^{\text{sol}}$ represents the contribution calculated using the original soliton density given by Krumhansl and Schrieffer (Ref. 24). The dashed-dotted line in the inset labeled $(T_1^{-1})_{\text{ST}}^{\text{sol}}$ is obtained using the soliton density reported by Sasaki and Tsuzuki (Ref. 25). The curve in the inset labeled $(T_1^{-1})_{\text{tot}}$ represents the sum of both magnon and soliton contributions.

tributions with the same scaling factor of 0.73 (cf. Fig. 1). The formal validity range of Eq. (27) may be extended to $\sqrt{B}/T > 0.5$ by replacing the expression for the soliton density²⁴ used in the derivation of this equation by the finite-temperature expansion reported by Sasaki and Tsusuki.²⁵ The resulting soliton contribution to the relaxation rate is depicted by the dashed-dotted line labeled $(T_1^{-1})_{\text{ST}}^{\text{sol}}$, which appears to differ only slightly from the original prediction. The figure reveals that the inclusion of a soliton contribution yields a slightly better description of the behavior of T_1^{-1} in the appropriate $\sqrt{B}/T$ region [solid curve labeled $(T_1^{-1})_{\text{tot}}$], but the resulting improvement is not very significant and does therefore not yield solid evidence for the presence of solitonlike excitations in this compound.

V. MAGNETIZATION

As already mentioned in the Introduction, the magnetization of soliton-bearing systems has not been studied very extensively. For this reason we have supplemented our previously reported¹⁴ experiments on CHAB with magnetization measurements in applied fields up to 50 kG along the crystallographic c direction, which is located within the easy plane for both sets of chains (cf. Sec. II). The magnetization (M) was measured with a commercial (Princeton Applied Research) vibrating-sample magnetometer. Sample temperatures between 1.4 and 10 K could be achieved with a typical stability of 50 mK. The accuracy of the measured value of M did amount to 2%. A sample with a mass of 52.3 mg was used in most of the experiments. The data collected at various fixed temperatures are plotted in Fig. 3 as a function of B . No demagnetization corrections were applied, since they amount to at most 100 G. Inspection of the figure shows that in the experimental field range saturation of M is reached at temperatures below 3 K. From the saturation value M_s , which was checked with measurements on five different samples, a value $g^{cc} = 2.01 \pm 0.02$ can be deduced. Within experimental uncertainty this is equal to the value $g^{cc} = 2$, which is used in the interpretation of the experimental data on CHAB up until now. Similar measurements for $B \parallel b$ yielded $g^{bb} = 2.06 \pm 0.04$. For

FIG. 3. Field dependence of the magnetization of CHAB for $B \parallel c$ at several fixed temperatures.

$B \parallel a$ no saturation was reached in fields up to 50 kG, which is consistent with the XY character of this compound.

Since for several magnetic model systems, including the SG model, M/M_s has been reported to be an universal function of $T/\sqrt{B}$,^{12,26,27} at least within a certain range of fields and temperatures, we have plotted our experimental results accordingly in Fig. 4. From this figure it appears that the data collected above 3 K almost perfectly collapse onto a single curve. At lower temperatures systematic deviations occur, the origin of which will be discussed later on. In the figure we have included several theoretical predictions, based on transfer-matrix calculations on a discrete chain of classical spins,²⁸ which will now successively be considered.

First, the magnetization was calculated using the spin Hamiltonian given in Eq. (1), with parameters appropriate to CHAB, and a spin length $\tilde{S}$ equal to S . In this calculation the number of nonzero spin components, denoted by n , is equal to 3. The results are represented by the two curves in Fig. 4 labeled $n=3$, $\tilde{S}=0.5$. The solid and dashed curves correspond to $T=10$ and 4.2 K, respectively. It is obvious that the predicted magnetization is about a factor of 2 smaller than the experimental data at the highest values of $T/\sqrt{B}$. Apart from this, the calculated results do not show universal behavior, a tendency also observed in similar calculations on CsNiF_3 .¹² If a semiclassical spin length $\tilde{S} = \sqrt{S(S+1)}$ is used instead of the classical value $\tilde{S}=S$, the transfer-matrix calculations yield results that are reflected by the

FIG. 4. Reduced magnetization of CHAB for $B \parallel c$ plotted against $T/\sqrt{B}$. The various sets of curves represent the results of transfer-matrix calculations on a chain of classical spins with length S having two ($n=2$) or three ($n=3$) nonzero components. Solid and dashed curves correspond to $T=10$ and 4.2 K.

two curves in the figure labeled $n=3$, $\tilde{S}=0.87$. The solid and dashed curves again correspond to $T=10$ and 4.2 K, respectively. Inspection of the figure shows that this choice of $\tilde{S}$ shifts the predicted magnetization to values which are substantially larger than the experimental data. For comparison, we also included the results of similar transfer-matrix calculations on a planar ($n=2$) system, i.e., a chain of classical spins having only two nonzero (XY) spin components, and $\tilde{S}=S$. These results are represented by the two curves in Fig. 4 labeled $n=2$. Although this prediction agrees much better with the data than the $n=3$ transfer-matrix calculations, significant deviations occur at low values of $T/\sqrt{B}$.

Before continuing with the interpretation of the observed magnetization, we would like to discuss the nonuniversal behavior of the data collected at low temperatures. This behavior cannot be caused by the small in-plane anisotropy $1-J^{yy}/J^{xx} \simeq 5 \times 10^{-4}$ in this compound, because similar deviations were found in CsNiF_3 ,²⁷ which has perfect axial symmetry. On the other hand, the transfer-matrix calculations show an *increase* of M/M_s at lower T , in contrast to the data. This suggests that the systematic deviations of the data from universal behavior at these temperatures originate from the small interactions between the chains, which become important close to T_c .

Now we turn to the interpretation of the magnetization in terms of the SG model. First, we compare our data with numerical results on the magnetization of this model reported by Schneider and Stoll,²⁶ since similar

calculations on the excess heat capacity $\Delta C = C(B) - C(B=0)$ of CHAB yielded a fair description of the corresponding data.¹¹ In the mapping of the spin Hamiltonian of this compound to the SG model we used the classical values for the mass parameter and the soliton rest energy [cf. Eq. (30)]. The resulting prediction for M/M_s , which is a universal function of $T/\sqrt{B}$, is plotted in Fig. 5, together with the experimental results. Inspection of the figure shows that the overall agreement between this prediction (dotted curve) and the data is fairly good, but the qualitative behavior at low $T/\sqrt{B}$ is remarkably different from the experimental results. Possibly, this is caused by the presence of spin components out of the easy (XY) plane, which are not taken into account in this model. However, the prediction lies outside the region covered by the results of the $n=2$ transfer-matrix calculations (cf. Fig. 4). In this respect, the magnetization seems to differ fundamentally from the excess heat capacity.¹¹ To obtain more information about the possible origin of these differences we have described the magnetization with the same model that we used in the interpretation of our T_1 measurements, i.e., a model in which the basic elementary excitations are magnons and solitons.

Both magnons and solitons cause the magnetization at finite temperatures to decrease with respect to its saturation value M_s . The decrease ΔM_{SW} caused by magnons was calculated using the same spin-wave Hamiltonian as that given in Sec. IV [cf. Eqs. (12)–(14)], and can be expressed as

$$\Delta M_{\text{SW}} = g\mu_B \sum_q (u_q^2 \langle\langle n_q \rangle\rangle + v_q^2 \langle\langle n_q + 1 \rangle\rangle), \quad (32)$$

where the coefficients u_q and v_q have already been defined in Eq. (19). The corresponding prediction for $\Delta M_{\text{SW}}/M_s$, based on the exchange parameters appropriate to CHAB, is represented by the dashed curve in Fig. 5. Inspection of the figure shows that this prediction agrees very well with the experimental data up to $T/\sqrt{B} \simeq 1.2$. At higher values of $T/\sqrt{B}$ the predicted decrease of M is too small, the difference increasing to about 10% of M_s (30% of M) at $T/\sqrt{B} \simeq 3$. This suggests that other elementary excitations may contribute significantly in this region.

The decrease of the magnetization ΔM_{sol} caused by solitonlike excitations was calculated from the expansion of the soliton free energy F_{sol} given by Sasaki and Tsuzuki,²⁵

$$F_{\text{sol}} = -k_B T n_s, \quad (33)$$

$$n_s = \left[\frac{8}{\pi} \right]^{1/2} m a t^{-1/2} e^{-1/t} \left(1 - \frac{7}{8} t - \frac{59}{128} t^2 \right).$$

In this expression n_s is the number of solitons per unit length and $t = k_B T / E_s^0$. The other parameters have already been defined in Eq. (30). This expansion of F_{sol} is believed to be fairly accurate up to $t = 0.3$ ($T/\sqrt{B} = 3.3$ for CHAB). By straightforward differentiation of Eq. (33) with respect to B we obtain

FIG. 5. Reduced magnetization of CHAB for $\mathbf{B} \parallel \mathbf{c}$ plotted against $T/\sqrt{B}$. The dotted curve reflects numerical results for a classical SG system. The dashed curve represents the reduction of M according to linear spin-wave theory, whereas the dashed-dotted curve denotes the additional reduction resulting from kink solitons. The solid curve reflects the combined effect of the latter two types of elementary excitations.

$$\Delta M_{\text{sol}} = -4Ng\mu_B S \left[\frac{8}{\pi} \right]^{1/2} t^{-1/2} e^{-1/t} \times (1 - \frac{19}{8}t - \frac{3}{128}t^2 - \frac{59}{256}t^3). \quad (34)$$

The resulting prediction is represented by the dashed-dotted curve in Fig. 5. From this figure it appears that the decrease of M caused by solitons is negligible for $T/\sqrt{B} < 1$, whereas it has a maximum at $T/\sqrt{B} \simeq 3.2$.

Within the framework of the classical SG model, the total free energy F_{tot} of a system can be written²⁵ as $F_{\text{tot}} = F_m + F_{\text{sol}}$, where F_{sol} is given by Eq. (33) and F_m reflects the contribution of linear excitations (magnons). Following a similar approach as that underlying the interpretation of our T_1^{-1} data given above, we replace, in first order, the classical contribution F_m by its quantum-mechanical counterpart, based on linear spin-wave theory, and add ΔM_{SW} [cf. Eq. (32)] to ΔM_{sol} . The corresponding result is represented by the solid curve in Fig. 5. It is obvious that this approach yields a very good description of the data, especially since one has to recall that no adjustable parameters were used in the corresponding calculations. A possible physical explanation of the good agreement between this model and the experimental results will be presented in Sec. VI.

VI. DISCUSSION

From the evidence presented in Sec. IV it is obvious that the variation of the nuclear spin-lattice relaxation rate in CHAB with field and temperature can be described satisfactorily by linear spin-wave theory, using the set of parameters appropriate to this compound. From a quantitative comparison of the contribution of magnons and solitons to the relaxation rate for $\mathbf{B} \parallel \mathbf{c}$ it was found that the effect of solitons on T_1^{-1} is too small to be identified unambiguously. This is in marked contrast to CsNiF_3 , where solitons have been reported⁶ to contribute significantly to the relaxation rate. As demonstrated in Sec. IV, however, the quantitative details of that interpretation are subject to some reservations. It may therefore be worthwhile to reanalyze the T_1^{-1} data on CsNiF_3 according to the procedure outlined in this paper, in order to investigate the effect of nonlinear processes in that compound more precisely.

Attempts to describe the observed behavior of the reduced magnetization for $\mathbf{B} \parallel \mathbf{c}$ by a classical model, i.e., numerical results for the SG model or transfer-matrix calculations on discrete classical spin systems, did not yield a satisfactory agreement with the data. Deviations between these calculations and the data appear to persist for $T/\sqrt{B} < 1$, in which region nonlinear excitations have a negligible statistical weight [cf. Eqs. (33) and (34)]. This indicates that at least the linear excitations cannot properly be described by a classical model. Such a conclusion is supported by the behavior of the heat capacity. In that case the classical model predictions for $n=2$ or 3 are dominated by a magnon contribution, having a nonphysical zero-temperature limiting value of $Nk_B/2$ or Nk_B , respectively. In this respect, it may

seem surprising that the excess heat capacity of CHAB could be described fairly well by the classical SG model.¹¹ However, in contrast to the heat capacity itself, the excess heat capacity in CHAB is dominated by nonlinear excitations, as can be inferred from a comparison of the predicted soliton contribution to ΔC (Ref. 25) with the numerical results for the SG model or, alternatively, by a direct calculation of the magnon contribution to ΔC using linear spin-wave theory.¹⁴ Apart from this, it has been shown that in the compound the quantum SG corrections to the heat capacity are compensated for by the effect of spin fluctuations out of the easy plane.

Inspection of Fig. 5 reveals that the behavior of the magnetization is largely dominated by the linear excitations. This may explain the fact that for a proper description of M/M_s we had to use an approach in which the linear excitations were calculated from linear spin-wave theory and the nonlinear excitations from the classical SG model. With respect to this approach two remarks seem appropriate. First, the contribution of the spin waves to M/M_s is calculated without any renormalization of the magnon dispersion relation. Such a procedure is correct for low values of $T/\sqrt{B}$, and yielded a satisfactory description of the T_1^{-1} data, but formally it is not quite clear whether it is justified in the whole experimental field and temperature region. Secondly, all nonlinear effects are attributed to solitonlike excitations and are calculated within the framework of the classical SG model. Although this approach obviously results in a very good description of the reduced magnetization of CHAB, this nice agreement may partly be the result of a cancellation of quantum effects and out-of-plane components, similar to that observed for the excess heat capacity.

Concluding, we would like to note that the contribution of nonlinear excitations to the decrease of M with respect to its saturation value amounts to about 10% of M_s (cf. Fig. 5). This indicates that the statement of Pini *et al.*¹² that the magnetization is a soliton-insensitive quantity is, in general, not valid. Apart from this, they argued that a classical model is not applicable to the soliton-bearing system CsNiF_3 . In view of the present results it may be worthwhile to investigate whether also in that compound the observed discrepancies can be explained by the poor description of, in particular, the linear excitations by such a model.

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APPENDIX: GENERAL EXPRESSION FOR THE NUCLEAR SPIN-LATTICE RELAXATION RATE

By treating the fluctuating part of the dipolar interaction between the j th nuclear spin and the electron spins $\mathcal{H}_f(j)$ [Eq. (2)] as a perturbation, an expression for the

transition probability $w_j(m_I, \nu \rightarrow m_I', \nu')$, where m_I is the nuclear-spin quantum number and ν denotes the quantum numbers specifying the eigenstates of the electron-spin system, can be readily obtained by first-order time-dependent perturbation theory,¹⁷ yielding

$$w_j(m_I, \nu \rightarrow m_I', \nu') = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt \langle m_I, \nu | \mathcal{H}_f(j, t) | m_I', \nu' \rangle \times \langle m_I', \nu' | \mathcal{H}_f(j, 0) | m_I, \nu \rangle. \quad (\text{A1})$$

The time dependence of $\mathcal{H}_f(j, t)$ is determined by $\mathcal{H}_s(j)$ [cf. Eq. (2)] and the Hamiltonian of the electron-spin system. The thermal transition probabilities $w_j(\pm \frac{1}{2} \rightarrow \mp \frac{1}{2})$ follow from Eq. (A1) by multiplying the expression by the statistical weight $\exp(-E_\nu/k_B T)/Z$ of the initial state ν and taking the sum over all possible initial and final states ν and ν' . The result reads

$$w_j(\pm \frac{1}{2} \rightarrow \mp \frac{1}{2}) = \sum_{\nu} \sum_{\nu'} w_j(\pm \frac{1}{2}, \nu \rightarrow \mp \frac{1}{2}, \nu') e^{-E_\nu/k_B T} / Z. \quad (\text{A2})$$

In order to evaluate these thermal transition probabilities it is convenient to transform $\mathbf{I}_j$ and $\delta \mathbf{S}_j$ occurring in the expression for $\mathcal{H}_f(j, t)$ to the reference frames ξ, η, ζ and x', y', z' defined in Fig. 6. The z' and ζ axes of these reference frames are chosen such that they coincide with the quantization axes of the j th nuclear spin ($\|\mathbf{B}_{\text{eff}}\rangle$) and the electron spins ($\|\langle \mathbf{S}_j \rangle\rangle$), respectively. If Θ_l, Φ_l and Θ_j, Φ_j are the spherical coordinates of $\langle \mathbf{S}_l \rangle$ and $\mathbf{B}_{\text{eff}}$ with respect to the crystallographic abc coordinate system, this transformation can be expressed as follows:

$$\begin{aligned} (I_j^a, I_j^b, I_j^c) &= (I_j^{x'}, I_j^{y'}, I_j^{z'}) \tilde{\mathbf{R}}(\Theta_j, \Phi_j), \\ (\delta S_l^a, \delta S_l^b, \delta S_l^c) &= (\delta S_l^{\xi}, \delta S_l^{\eta}, \delta S_l^{\zeta}) \tilde{\mathbf{R}}(\Theta_l, \Phi_l), \end{aligned} \quad (\text{A3})$$

$$\mathcal{H}_f(j, t) = \hbar \sum_l (I_j^+ e^{-i\omega_N(j)t}, I_j^- e^{i\omega_N(j)t}, I_j^z) \tilde{\mathbf{Z}}(j, l) \begin{pmatrix} \delta S_l^{\xi}(t) \\ \delta S_l^{\eta}(t) \\ \delta S_l^{\zeta}(t) \end{pmatrix}, \quad (\text{A6})$$

with

$$\tilde{\mathbf{Z}}(j, l) = \frac{\mu_0}{8\pi} g \mu_B \gamma_N \frac{1}{|\mathbf{r}_{jl}|^3} \begin{pmatrix} 1 & -i & 0 \\ 1 & i & 0 \\ 0 & 0 & 2 \end{pmatrix} \tilde{\mathbf{R}}(\Theta_j, \Phi_j) \tilde{\mathbf{A}} \tilde{\mathbf{R}}^T(\Theta_l, \Phi_l), \quad (\text{A7})$$

where

$$\tilde{\mathbf{A}} = \begin{pmatrix} 1-3x^2 & -3xy & -3xz \\ -3yx & 1-3y^2 & -3yz \\ -3zx & -3zy & 1-3z^2 \end{pmatrix}. \quad (\text{A8})$$

In Eq. (A7) $\mathbf{r}_{jl}$ is the position vector of the l th electron spin relative to the position of the j th hydrogen nucleus within the crystallographic abc coordinate frame and $\mathbf{x}=(x, y, z)$ is defined as $\mathbf{r}_{jl}/|\mathbf{r}_{jl}|$. Insertion of Eq. (A6) into (A2) yields—after some algebraic manipulations—the following expressions for the thermal transition probabilities:

FIG. 6. Definition of the reference frames x', y', z' (nuclear spin j) and ξ, η, ζ (electron spins).

where $\delta S_l^a = S_l^a - \langle S_l^a \rangle$ and $\tilde{\mathbf{R}}$ is defined as

$$\tilde{\mathbf{R}}(\Theta, \Phi) = \begin{pmatrix} \sin\Theta & -\cos\Theta & 0 \\ \cos\Theta \cos\Phi & \cos\Theta \sin\Phi & -\sin\Theta \\ \sin\Theta \cos\Phi & \sin\Theta \sin\Phi & \cos\Theta \end{pmatrix}. \quad (\text{A4})$$

Using Eq. (A3) and the well-known relations

$$\begin{aligned} I_j^+(t) &= I_j^{x'}(t) + i I_j^{y'}(t) = I_j^+ e^{-i\omega_N(j)t}, \\ I_j^-(t) &= I_j^{x'}(t) - i I_j^{y'}(t) = I_j^- e^{i\omega_N(j)t}, \\ I_j^z(t) &= I_j^z, \end{aligned} \quad (\text{A5})$$

with $\omega_N(j) = \gamma_N |\mathbf{B}_{\text{eff}}(j)|$, it readily follows that $\mathcal{H}_f(j, t)$ [Eq. (2)] can be rewritten as

$$w_j(-\frac{1}{2} \rightarrow +\frac{1}{2}) = \sum_{\alpha} \sum_{\beta} \sum_n \sum_l g^{\alpha\beta}(j, l, n) \int_{-\infty}^{\infty} dt e^{i\omega_N(j)t} \left[\sum_{\nu} \sum_{\nu'} \frac{1}{Z} e^{-E_{\nu}/k_B T} \langle \nu | \delta S_l^{\alpha}(t) | \nu' \rangle \langle \nu' | \delta S_n^{\beta}(0) | \nu \rangle \right]. \quad (\text{A9})$$

$$w_j(+\frac{1}{2} \rightarrow -\frac{1}{2}) = \sum_{\alpha} \sum_{\beta} \sum_n \sum_l g^{\alpha\beta}(j, l, n)^* \int_{-\infty}^{\infty} dt e^{-i\omega_N(j)t} \left[\sum_{\nu} \sum_{\nu'} \frac{1}{Z} e^{-E_{\nu}/k_B T} \langle \nu | \delta S_l^{\alpha}(t) | \nu' \rangle \langle \nu' | \delta S_n^{\beta}(0) | \nu \rangle \right]. \quad (\text{A10})$$

where $\alpha, \beta = \xi, \eta, \zeta$ and $g^{\alpha\beta}(j, l, n)$ are the so-called geometrical coefficients, which are given by

$$\vec{g}(j, l, n) = \begin{pmatrix} Z_{11}(j, l)Z_{21}(j, n) & Z_{11}(j, l)Z_{22}(j, n) & Z_{11}(j, l)Z_{23}(j, n) \\ Z_{12}(j, l)Z_{21}(j, n) & Z_{12}(j, l)Z_{22}(j, n) & Z_{12}(j, l)Z_{23}(j, n) \\ Z_{13}(j, l)Z_{21}(j, n) & Z_{13}(j, l)Z_{22}(j, n) & Z_{13}(j, l)Z_{23}(j, n) \end{pmatrix}. \quad (\text{A11})$$

In this equation $Z_{\alpha\beta}(j, l)$ are the elements of Eq. (A7). Since the term in large parentheses in Eqs. (A9) and (A10) is just the thermal expectation value of $\delta S_l^{\alpha}(t)\delta S_n^{\beta}(0)$, this completes the derivation of the expression for the relaxation rate of the j th hydrogen nucleus given in Sec. III [Eq. (4)].

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