Spin-wave analysis of pseudo-one-dimensional antiferromagnet CsMnCl₃·2H₂O

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The low-temperature specific heat, sublattice magnetization, zero-point spin reduction, and ground-state energy of CsMnCl₃·2H₂O have been confronted with a spin-wave calculation, which was based upon the particular magnetic structure of this compound. In this numerical calculation the effect of small interchain interactions and a temperature-dependent anisotropy gap have been included. A good agreement with the experimental heat capacity was obtained for an intrachain interaction $J/k = -3.0$ K and a ratio of the inter- to intrachain interaction $|J'/J| = 8 \times 10^{-3}$. These values compare favorably with the results from other studies. The predicted sublattice magnetization, including the zero-point spin reduction of 19%, is in good agreement with the experimental evidence. The calculated ground-state energy corresponds with the value obtained by direct integration of the experimental magnetic heat capacity. It was concluded that unrenormalized spin-wave theory offers a fair description of the magnetic behavior of CsMnCl₃·2H₂O up to $\sim 0.6\,T_N$.

I. INTRODUCTION

Cesium manganese trichloride dihydrate (CsMnCl₃·2H₂O) can be considered as a fair representation of a linear-chain Heisenberg antiferromagnet. The one-dimensional behavior, especially at higher temperatures, has been reported in a large number of publications. They include susceptibility and magnetization,[1,2] magnetic specific heat,[3] and electron-spin-resonance[4] results. The reported values for the intra- and interchain interactions indicate that the system can be characterized by $J_1/k = -3.3 \pm 0.3$ K and $(J_2+J_3)/J_1 \simeq 10^{-2}$– 10^{-4}. The small interchain interactions J_2 and J_3 give rise to a three-dimensional ordered antiferromagnetic state below $T_N = 4.89$ K with a magnetic space group $P_{2b}c'ca'$.[5] Inelastic-neutron-scattering experiments[6] by Skalyo *et al.* showed that also in this ordered state the spin-wave dispersion relation strongly reflected the pseudo-one-dimensionality of the system. Recently Nishihara *et al.*[7] reported that the proton spin-lattice relaxation time in CsMnCl₃·2H₂O could be satisfactorily explained on the basis of a detailed calculation of the spin-wave dispersion relation taking into account the influence of the interchain interactions. The influence of these (small) interchain interactions may be anticipated to be important in the *ordered* state because in the (nonphysical) limit of the (ordered) purely one-dimensional chain the density of states diverges in the origin of $\vec{k}$ space. In view of this it seemed worthwhile to analyze the other thermodynamic quantities as well. In this article we will focus our attention on the specific heat, sublattice magnetization, spin-reduction and ground-state energy. In a recent article Iwashita and Uryû[8] performed a similar analysis of the sus- ceptibilities and the temperature dependence of the sublattice magnetization.

II. THEORY

Since the magnetic structure of CsMnCl₃·2H₂O is well established[5,6] the calculation of the spin-wave spectrum is rather simple if only nearest-neighbor interactions are taken into account. The magnetic structure is shown in Fig. 1. The intrachain interaction along the a axis is denoted by J_1; J_2 and J_3 represent the interchain interactions. It is evident that all interactions are antiferromagnetic and all neighboring spins belong to different sublattices. The system is therefore described by the Hamiltonian

$$\mathcal{H} = -2\sum_{lm} J_{lm}\vec{S}_l \cdot \vec{S}_m - g\mu_B H_A\left(\sum_l S_l^z - \sum_m S_m^z\right). \quad (1)$$
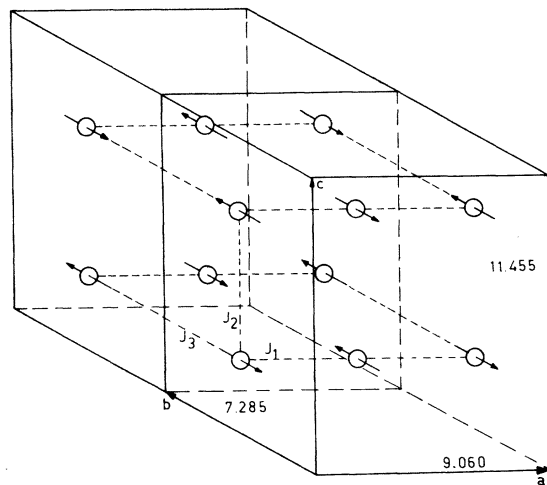

FIG. 1. Spin array of CsMnCl₃·2H₂O in the ordered state.

The anisotropy field H_A arises from — relatively small — dipolar and crystal-field effects and the indices l, m run over the "+" and "–" sublattice, respectively. Within the Holstein-Primakoff[9] formalism the Hamiltonian can be written in terms of creation and annihilation operators. If all terms which are of higher order than quadratic in these operators are omitted, the conventional diagonalization procedure yields[10, 11]

$$E_{n,p} = NS(S+1)\sum_h J(\vec{r}_h) - g\mu_B H_A N(S + \tfrac{1}{2})$$

$$+ \sum_k (n + \tfrac{1}{2})\epsilon(\vec{k}) + \sum_k (p + \tfrac{1}{2})\epsilon(\vec{k}),$$

$$n, p = 0, 1, 2, \ldots \quad (2)$$

In this expression $\vec{r}_h = \vec{r}_l - \vec{r}_m$,

$$\epsilon(\vec{k}) = \{\epsilon_m^2 - [b(\vec{k})]^2\}^{1/2},$$

$$\epsilon_m = -2S\sum_h J(\vec{r}_h) + g\mu_B H_A, \quad (3)$$

$$b(\vec{k}) = -2S\sum_h J(\vec{r}_h)e^{i\vec{k}\cdot\vec{r}_h}.$$

ϵ_m corresponds to the maximum energy of the spin-wave spectrum, which is twofold degenerate in zero applied field. If the slight zig-zag of the chains along the a direction is ignored, we obtain

$$\sum_h J(\vec{r}_h) = 2(J_1 + J_2 + J_3),$$
$$\quad (4)$$
$$\sum_h J(\vec{r}_h)e^{i\vec{k}\cdot\vec{r}_h} = 2(J_1\cos\tfrac{1}{2}k_a a + J_2\cos\tfrac{1}{2}k_c c + J_3\cos k_b b).$$

The density function $N(\epsilon)$ may now be calculated for a given set of exchange constants according to the procedure described by Nishihara et al.[7] In Fig. 2 some representative results are plotted. ϵ_0 denotes the minimum energy of the magnon spectrum, corresponding to $\vec{k} = 0$. As anticipated before, the low-energy part of the spectrum appears to be very sensitive to the ratio $|J_2/J_1|$. It seems likely that these low-dimensional characteristics will also be reflected by the thermodynamic properties at low temperatures.

The magnetic specific heat is related to the normalized spin-wave spectrum by

$$C_M(T) = R\int_{\epsilon_0}^{\epsilon_m}\left(\frac{\epsilon}{kT}\right)^2 e^{\epsilon/kT}(e^{\epsilon/kT} - 1)^{-2}N(\epsilon)\,d\epsilon. \quad (5)$$

The integral may be evaluated numerically. In the actual calculation, one should note that from neutron-diffraction experiments[6] the energy gap ϵ_0 has been found to be temperature dependent. The observed temperature dependence could be described by assuming a renormalization of ϵ_0 proportional to the sublattice magnetization. In the calculations in this paper, the observed variation
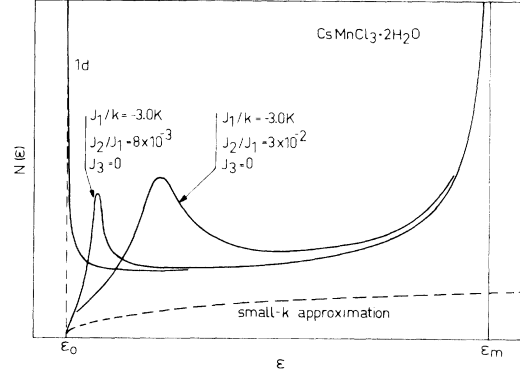

FIG. 2. Magnon density of states $N(\epsilon)$ vs ϵ calculated for CsMnCl$_3\cdot$2H$_2$O for different sets of exchange constants. The curve marked $1d$ denotes the purely one-dimensional limit $(J_2 = J_3 = 0)$. The dashed curve indicates the small-k approximation for a representative set of exchange constants.

of the energy gap has been taken into account explicitly by adapting the value of H_A.

The magnetic ground-state energy E_g may be obtained by considering Eq. (2) for $T = 0$, which yields

$$E_g = 2NS(S+1)(J_1 + J_2 + J_3) - g\mu_B H_A N(S + \tfrac{1}{2})$$

$$+ \frac{N}{2}\int_{\epsilon_0}^{\epsilon_m}\epsilon N(\epsilon)\,d\epsilon, \quad (6)$$

if the density function is normalized to 1. Since it has been shown[10] that the inclusion of fourth-order terms in the spin-wave Hamiltonian produces an increase of only 0.5% in E_g for a $S = \tfrac{5}{2}$ antiferromagnetic linear-chain model, Eq. (6) will very likely offer a good estimate of the actual ground-state energy of CsMnCl$_3\cdot$2H$_2$O.

The sublattice magnetization M_s may be found rather directly by differentiating the energy (2) with respect to its conjugate thermodynamic variable. This variable is the "staggered" field H_{st}, which points along the preferred direction of spin alignment, being positive at the "+" lattice sites and negative at the "–" lattice sites. As can easily be seen, H_{st} enters in the Hamiltonian (1) in the same way as H_A, and hence it may be added to H_A in the final solution (2) and (3). In zero applied field the result is

$$M_s = \tfrac{1}{2}Ng\mu_B\left(S + \tfrac{1}{2} - \int_{\epsilon_0}^{\epsilon_m}\frac{\epsilon_m N(\epsilon)}{2\epsilon}d\epsilon\right.$$

$$\left. - \int_{\epsilon_0}^{\epsilon_m}\frac{\epsilon_m N(\epsilon)}{\epsilon(e^{\epsilon/kT} - 1)}d\epsilon\right), \quad (7)$$

which is, in fact, equivalent to the expression given by Kubo.[10]

III. RESULTS AND DISCUSSION

The magnetic heat capacity has already been reported in a previous publication.[3] The data at low

temperatures are presented in detail in Fig. 3 by
open circles. They are obtained by subtracting the
inferred lattice contribution from the experimen-
tal data. Because in this temperature region the
lattice heat capacity amounts to less than 6% of the
total specific heat, the result will reflect the mag-
netic contribution rather accurately. The drawn
curve corresponds to the best fit of the spin-wave
prediction (5) to the data. Since the theoretical be-
havior at these temperatures was found to depend
on $|J_2 + J_3|$ rather than on J_2 and J_3 separately, and
several experimental studies indicate that $|J_3|$
$\ll |J_2|$, the problem has been simplified by putting
J_3 equal to zero. The result obtained from the set
of exchange constants reported by Iwashita and
Uryû[8] from their fit of the spin-wave prediction to
the low-temperature susceptibility is represented
by a dashed curve. For comparison the predic-
tions from some purely one-dimensional models
are also given. The curve marked "1d_{sw}" repre-
sents the estimate from linear spin-wave theory
given by Kubo[10] for $J/k = -3.0$ K, the curve marked
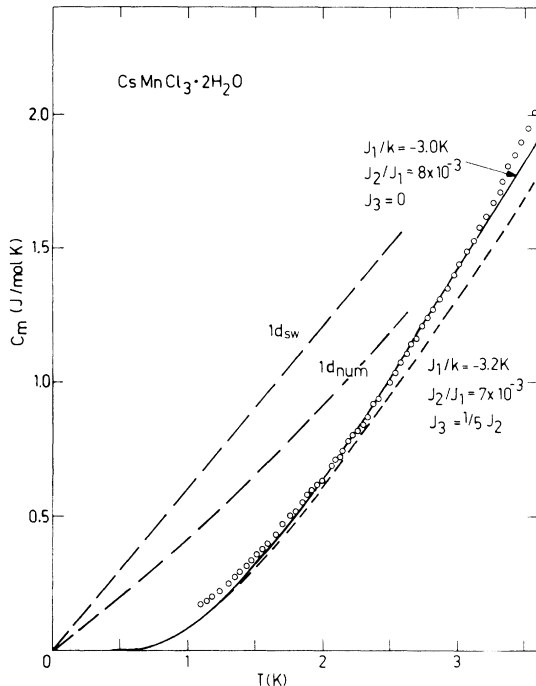"1d_{num}" corresponds to the low-temperature be-

havior of a $S = \frac{5}{2}$ Heisenberg antiferromagnetic lin-
ear-chain system, inferred from recent numerical
calculations.[12] As might have been expected, these
curves are systematically too high. Three-dimen-
sional spin-wave theory, however, is found to give
a fair description of the data up till $\sim 0.6 T_N$. The
intra- and interchain interactions, which gave the
best over-all fit with the experimental results are

$$J_1/k = -3.0 \text{ K}, \quad |J_2/J_1| = 8 \times 10^{-3}, \quad J_3 \simeq 0,$$

and they compare favorably with the values cited
in literature.

Inspection of Fig. 3 shows that the agreement be-
tween theory and experiment gets worse at the low-
est temperatures, although one would expect a spin-
wave analysis to be most accurate in this region.
This systematic deviation partially arises from the
high-temperature tail of the nuclear Schottky
anomaly of the Mn^{++} ions caused by the hyperfine
coupling $\vec{S} \cdot \overleftrightarrow{A} \cdot \vec{I}$ in the magnetically ordered state.
Assuming $|A|/k = 0.012$ K, a value which can be
considered as representative for Mn^{++} ions in an
octahedral environment,[13] we arrive at a nuclear
contribution to the specific heat of about 0.02
J/mol K at 1 K, which accounts for $\sim 30\%$ of the ob-
served deviation. The remaining discrepancy may
presumably be removed by the introduction of
small nonuniaxial terms in the anisotropy. Suscep-
tibility experiments[2] have indicated the existence
of such terms.

Substitution of H_A and the set of exchange con-
stants given above in the expression for the
ground-state energy E_g (8) yields $E_g = -357$ J/mol.
If we assert that the dominant contribution to E_g
will arise from the large intrachain interaction,
this value may be confronted with the rigorous
bounds given by Anderson[14] for $z = 2$ and J/k
$= -3.0$ K. The result is $-312 > E_g > -374$ J/mol,
which is consistent with the value calculated above.
Of course, the ground-state energy may be calcu-
lated directly from the experimental data by inte-
grating the C_M-vs-T curve. If such an integration
is performed for the magnetic heat capacity given
in Ref. 3 for $J/k = -3.0$ K, we obtain $E_g = -361$ J/
mol, which is in excellent agreement with the pre-
diction from linear spin-wave theory.

The behavior of the sublattice magnetization
M_{subl} has been determined from NMR measure-
ments on the hydrogen nuclei. From the variation
of the proton absorption frequency as a function of
temperature the *relative* behavior of M_{subl} may be
found. In order to obtain an estimate of the *abso-
lute* value of M_{subl}, the observed local fields at the
proton sites can be compared with the calculated
internal fields originating from the magnetic di-
pole moments on the Mn^{++} ions. Whether such a
dipole sum really reflects the actual local magnet-

FIG. 3. Magnetic heat capacity of CsMnCl$_3 \cdot$2H$_2$O at low
temperatures. The open circles correspond to the ex-
perimental data corrected for the lattice contribution.
The drawn curve denotes the best fit of the spin-wave
prediction to the experimental results. The result ob-
tained from the set of interactions reported in Ref. 8 is
represented by a dashed curve. The curve marked 1d_{sw}
reflects the prediction from purely one-dimensional spin-
wave theory. The result of a numerical calculation of the
heat capacity of an infinite linear chain (Ref. 12) is rep-
resented by 1d_{num}.

ic fields at the proton sites depends on a number of conditions, which have already been pointed out[15] and will therefore be summarized only briefly. First, the direction of the magnetic dipole moments (or M_{subl}) has to be known exactly. In $CsMnCl_3 \cdot 2H_2O$ this is given by symmetry as the b axis. Second, the hydrogen positions should be known with a sufficient degree of accuracy. Furthermore, the hyperfine interaction of the hydrogen nuclei with the Mn^{++} spins should be small compared to the dipolar interaction, a condition which is reasonably met in this kind of Mn^{++} compound.[15] If we compare the calculated dipole sums at the proton sites, corresponding to the magnetic space group $P_{2b}c'ca'$, with the experimentally determined internal fields, a magnetic moment of 4.0 μ_B on the Mn^{++} ions is required to fit the experimental fields extrapolated to $T = 0$. Given the small uncertainty of both the hydrogen positions and the hyperfine contribution, we conclude that a zero-point spin reduction of $(20 \pm 4)\%$ is present. The corresponding temperature dependence of the sublattice magnetization is given by open circles in Fig. 4. The dashed curve in this figure is obtained from Eq. (7) by substitution of the values for the exchange interactions $J_1/k = -3.0$ K, $|J_2/J_1| = 8 \times 10^{-3}$, $J_3 = 0$ found from the analysis of the heat capacity. The prediction resulting from the exchange constants reported by Iwashita and Uryû[8] almost coincides with this curve, and has not been shown separately. The drawn curve corresponds to the best fit of (7) to the experimental data, given
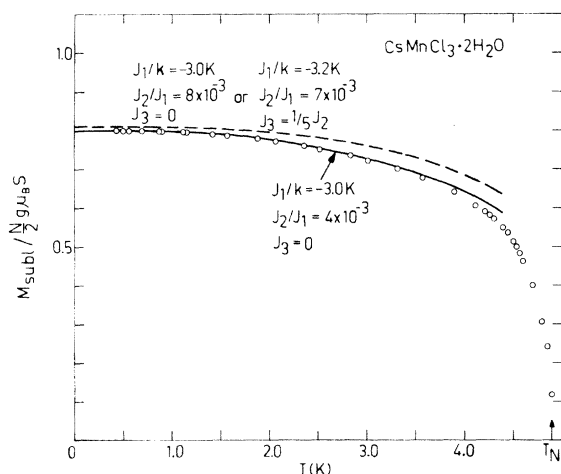

FIG. 4. Sublattice magnetization of $CsMnCl_3 \cdot 2H_2O$. The open circles denote the experimental behavior deduced from proton-NMR measurements. The dashed curve represents the spin-wave prediction for the set of exchange constants inferred from the heat-capacity measurements as well as the prediction resulting from the set of exchange constants reported in Ref. 8. The drawn curve is obtained by a small readjustment of the interchain interaction.

a fixed value of J_1 and the observed temperature dependence of ϵ_0. The value of $|J_2/J_1|$ resulting from this fit is somewhat smaller than the value obtained from the low-temperature specific heat. The calculated spin reduction, however, is in excellent agreement with the experimental evidence.

In view of the results of the present analysis of both heat capacity and sublattice magnetization as well as the interpretation of the susceptibility in the ordered state,[8] we would like to conclude that linear spin-wave theory offers a fair description of the magnetic behavior of $CsMnCl_3 \cdot 2H_2O$ in the ordered state. Unlike the purely three-dimensional case, where considerable renormalization effects occur as T_N is approached, the validity range of the linear spin-wave approximation in this pseudo one-dimensional case extends up to 0.6 T_N. The only renormalization effect that has been considered in the present treatment is the observed temperature dependence of the energy gap ϵ_0. The fact that no other renormalization effects have been taken into account does not seriously impair the description of the thermodynamic properties, as can be seen as follows. First, for spin waves propagating in the direction of the chains, Skalyo et al.[6] have shown that energy renormalization at the zone boundary is only detectable far above T_N, and hence ϵ_m may safely be considered as being constant in the temperature region below T_N. Moreover, the calculation of the magnetic properties at these temperatures involves mainly the density of states for low values of ϵ. For spin waves propagating perpendicular to the chain direction, an energy renormalization of 10% was observed at the zone boundary. This would give rise to a small shift of the bump in the low-energy part of the spin-wave spectrum. As can be seen from Fig. 2, however, such a shift may — to a certain extent — be compensated by a readjustment of the value of $(J_2 + J_3)/J_1$. This probably explains the slightly different sets of exchange constants used to describe the behavior of the various magnetic properties. Since these differences are not very significant, we are tempted to conclude that linear spin-wave theory may provide very realistic estimates for both the intra- and interchain interaction in pseudo-one-dimensional magnetic systems.

Note added in proof. When this article was in preparation it came to our attention that Iwashita and Uryû also performed a spin-wave analysis of the specific heat of CsMnCl₃·2H₂O. Their treatment is based on a Hamiltonian including single-ion anisotropy terms. The results of this analysis are in agreement with the present one.

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