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Magnetic specific heat of the nearly-one-dimensional system tetramethyl ammonium nickel trichloride (TMNC)

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The specific heat of tetramethyl ammonium nickel trichloride (TMNC) for $3.5 < T < 20$ K has been analyzed using the scaled lattice contribution of the isomorphous cadmium and manganese compounds and a magnetic contribution represented by the Hamiltonian $\mathcal{H} = -2J \sum_i \vec{S}_i \cdot \vec{S}_{i+1} - D \sum_i [S_{iz}^2 - S(S+1)/3]$. The resulting parameter values $J/k = +1.7 \pm 0.3$ K, and $D/k = -3.3 \pm 0.5$ K are qualitatively in agreement with the results from susceptibility measurements.

INTRODUCTION

Tetramethyl ammonium nickel trichloride (TMNC) can be considered as isomorphous with tetramethyl ammonium manganese trichloride (TMMC) and tetramethyl ammonium cadmium trichloride (TMCC).^{1,2} TMMC, especially, has been the subject of a considerable number of experimental investigations because the magnetic properties of this compound were found to display almost pure one-dimensional characteristics.³⁻⁸ The magnetic intrachain interaction was found to be antiferromagnetic with a magnitude of about -6.7 K, while the ratio of the interchain and intrachain interactions (J'/J) was estimated to range between 10^{-3} and 10^{-5} .

The magnetic interactions in TMNC do not seem to be very well established. The powder susceptibility has been measured for 1.6 – 79 K by Gerstein *et al.*,⁹ who reported deviations from a Curie-Weiss behavior $\chi = C/(T - \Theta)$ with $\Theta = +4.80 \pm 5.25$ K below 30 K. Their data strongly suggest that the dominant interaction is *ferromagnetic*. Specific-heat measurements for $0.64 < T < 27.4$ K performed by Hurley and Gerstein¹⁰ reveal a three-dimensional ordering peak at $T_c \approx 1.21$ K superimposed on a broad bump with a maximum of 4.5 J/mole K at $T_m \approx 1.5$ K. The critical entropy amounts to $0.21R$ (19%), which is low compared to the values predicted for various three-dimensional $S=1$ models.¹¹ This suggests a rather low-dimensional character of the magnetic properties, which was already conjectured from the isomorphy with TMMC. In order to account for the magnitude of the heat-capacity maximum, Hurley and Gerstein interpreted the data with the spin-1 linear Heisenberg model proposed by Weng and Griffiths,¹² but this yielded an *antiferromagnetic* intrachain interaction, which clearly is in disagreement with powder suscepti-

bility measurements.

Single-crystal susceptibility measurements in the liquid-hydrogen and helium region were performed by Dupas *et al.*¹³ They analyzed their data within the framework of a Hamiltonian describing a Heisenberg linear-chain system with uniaxial single-ion anisotropy

$$\mathcal{H} = -2J \sum_i \vec{S}_i \cdot \vec{S}_{i+1} - D \sum_i [S_{iz}^2 - \frac{1}{3}S(S+1)] \quad (1)$$

This resulted in $J/k = +1.1$ K and $D/k = -2.1$ K. The interchain interactions were estimated from χ_1 in the ordered state and from a Green's-function method,¹⁴ which yielded a J'/J value of 3×10^{-2} and 7×10^{-2} , respectively, confirming the conjectured one-dimensional magnetic behavior at high temperatures.

SPECIFIC HEAT

Recently^{15,16} the magnetic heat capacity of linear $S=1$ systems described by Eq. (1) has been calculated numerically, which—in principle—enables us to analyze the specific-heat data in more detail. Moreover, a reliable separation of the magnetic and lattice contribution to the heat capacity in TMNC seems possible, since the lattice heat capacity of the isomorphous TMCC and TMMC has been determined fairly accurately.⁸ The magnetic contribution C_M was obtained by subtracting the scaled heat capacity of TMCC. The scaling factor, which was assumed to be temperature independent in the region under consideration, was determined by the conditions $C_M > 0$ and $\partial C_M / \partial T < 0$ for $T > 20$ K. This resulted in a scaling factor 1.230 ± 0.005 . The total evaluated magnetic entropy increase, including the extrapolated contribution $0.02R$ below $T = 0.64$ K, did amount to $1.09R$, which corresponds

FIG. 1. Experimental magnetic heat capacity of TMNC. The circles are the data obtained by subtracting the scaled heat capacity of TMCC. The crosses represent the data obtained by subtracting the scaled lattice heat capacity of TMMC. The drawn curve denotes the best fit with $J/k = +1.7$ K, $D/k = -3.3$ K. The dashed part of the curve indicates the estimated low-temperature behavior of the magnetic specific heat (Refs. 15 and 16).

within 1% to the theoretical value $R \ln 3$.

Since the mass difference between the Ni^{2+} and the Cd^{2+} ion is rather large, use of a temperature-independent scaling factor may produce some systematic deviations. In order to check the accuracy of the procedure outlined above we determined C_M in a similar way using the inferred lattice contribution of TMMC,⁸ which resulted in a scaling factor 1.125 ± 0.005 . The results of both scaling procedures are plotted in Fig. 1. Both sets of data are quite consistent; significant differences are found for $T > 12$ K only. The data for $3.5 < T < 20$ K could be described within the experimental uncertainty with the Hamiltonian (1) with $J/k = +1.7 \pm 0.3$ K, and $D/k = -3.3 \pm 0.5$ K. The parameters were obtained by a least-squares fit to the experimental C_M data. The best fit is shown as a drawn curve in Fig. 1. Below $T \approx 3$ K the observed magnetic specific heat rises systematically above the theoretical prediction, indicating that interchain

interactions in this compound are presumably no longer negligible. This is supported by the fact that the three-dimensional ordering temperature is comparable to the temperature corresponding to the maximum of C_M predicted for a linear chain model.

DISCUSSION

The values for J and D obtained from different experimental techniques are listed in Table I. It appears that the present values are somewhat higher than those reported by Dupas *et al.*,¹³ which is most likely explained by the fact that their interpretation is based upon a Curie-Weiss behavior of the susceptibility at liquid-hydrogen temperatures. This is inconsistent with earlier measurements of Gerstein *et al.*,⁹ which reveal a Curie-Weiss behavior at temperatures above $T = 30$ K only. In general, a $1/\chi$ vs T plot at temperatures low compared to the region in which the Curie-Weiss law $\chi = C/(T - \Theta)$ strictly holds will yield an extrapolated intersection Θ^* on the temperature axis with $\Theta^* < \Theta$. This indicates that the parameter values obtained from the single crystal susceptibility measurements are too low indeed.

The intrachain interaction in TMNC is found to be ferromagnetic, whereas this interaction in the isomorphous TMMC is strongly antiferromagnetic. As each magnetic ion is linked with its nearest neighbors within the chain by three chlorine bridges with a bond angle of about 80° , this behavior is not inconsistent with the model of Anderson,¹⁷ which predicts, for a 90° bridge, a decreasing importance of the antiferromagnetic contributions to the superexchange going from $3d^5$ to $3d^8$.

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TABLE I. Magnitude of the intrachain exchange interaction and the single-ion anisotropy in TMNC obtained from different experimental techniques.

Technique	J/k (K)	D/k (K)	Comment	
Powder susceptibility	$+1.8 \pm 2.0$	...	Ref. 9: Θ value	30–80 K
	+1.9	...	Ref. 9: Ising $S=1$	3–80 K
	+1.0	...	Ref. 9: Fisher $S=1$	2–80 K
Specific heat	-2.73	...	Ref. 10	6–20 K
Single-crystal susceptibility	$+1.1 \pm 0.1$	-2.1 ± 0.5	Ref. 13	13–20 K
Specific heat	$+1.7 \pm 0.3$	-3.3 ± 0.5	Present work	3.5–20 K

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