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# SUSCEPTIBILITY BEHAVIOUR OF $CuGeO_3$: COMPARISON BETWEEN EXPERIMENT AND THE QUANTUM TRANSFER MATRIX APPROACH

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Thermodynamical properties of one-dimensional $S = 1/2$ Heisenberg model with dimerized nearest- and uniform next-nearest-neighbour interactions are studied by the numerically exact quantum transfer matrix method and the results are applied to $CuGeO_3$. Suzuki–Trotter formula is used to obtain a classical system with spin $\sigma = 3/2$ and effective interactions between nearest-neigbours only. Magnetic susceptibility curve is calculated and compared with new experimental results performed in a wide temperature range, revealing the presence of frustration in the model proposed for $CuGeO_3$.

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## 1. Introduction

Both experimental and theoretical interest in quasi one-dimensional frustrated quantum spin systems has been strongly enhanced since 1993, when it was shown [1] that the magnetic susceptibility of $CuGeO_3$ measured in all crystal directions drastically drops below $T_{SP} = 14.3$ K. It was attributed to the spin-Peierls (SP) phase transition, which manifests itself when a system of quasi one-dimensional quantum spin chains undergoes dimerization due to a lattice distortion. Below the SP transition point $T_{SP}$, a finite energy gap $\Delta$ opens between the non-magnetic singlet ground state and the first excited triplet state and reaches the maximum value $\Delta \simeq 2.1$ meV at $T = 0$ K.

To describe the properties of $CuGeO_3$, a $S = 1/2$ one-dimensional antiferromagnetic Heisenberg model with nearest-neigbour (nn) and next-nearest-neigbour (nnn) interactions was proposed [2, 3] with the Hamiltonian in the form

$$H = -J \sum_{i=1}^{N} (S_i S_{i+1} + \alpha S_i S_{i+2}) + \sum_{i=1}^{N} (-1)^i \delta S_i S_{i+1}, \tag{1}$$

where $N$ denotes the size of the chain, $J(< 0)$ and $\alpha(> 0)$ are the nn exchange integral and the ratio of the nnn exchange integral to the nn one, respectively. The parameter $\delta$ describes the dimerization. Below $T_{SP}$, the value of $\delta$ is non-zero and the alternation of $J$ has to be taken into account.

In this paper we report new experimental susceptibility measurements and the application of the quantum transfer matrix (QTM) technique to calculate the thermodynamical properties of $CuGeO_3$ and to evaluate the best-fit values of $J$ and $\alpha$.

## 2. Experiment

The single crystalline $CuGeO_3$ samples (section $4 \times 8$ mm$^2$, thickness 1 mm) used in this study were cleaved along the (100) plane from large crystals several cm long, grown from the melt using a floating zone method associated with an image furnace. Magnetic susceptibility was measured using a home-made superconducting quantum interference device (SQUID) magnetometer operating in the temperature range 1.8–350 K and in the magnetic field range 0–8 T. The experiments were performed in a field parallel to the $c$ crystal axis, i.e. the Cu chain direction. The sample was mounted in a capsule placed in a straw and the applied magnetic field was equal to 1 kOe. The correction for a negligibly small diamagnetic contribution due to the capsule was not taken into account. For a more detailed description of our experimental work refer to Ref. [4].

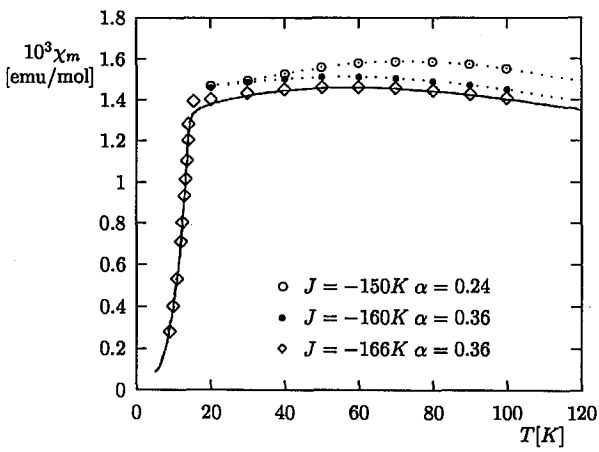


Fig. 1. Temperature behaviour of magnetic susceptibility for $CuGeO_3$. Solid line corresponds to the experimental measurements along the $c$ direction. Our best numerical fit is plotted with diamonds. Solid and open circles mark the QTM estimates obtained for alternative sets of parameters [2, 3].

The temperature behaviour of the molar susceptibility in the range 5–120 K is shown in Fig. 1 (solid line). Below $T_{SP}$, the susceptibility data $\chi(T)$ have been fitted to the following relation:

$$\chi(T) = \chi_0 + \chi_{PARA}(T) + \chi_{SP}(T), \tag{2}$$

where $\chi_0$ is a constant including the diamagnetic contribution of the sample holder and the sample itself, $\chi_{\mathrm{PARA}}$ is the paramagnetic contribution of a small amount of free spins (coming from impurities and chain breaks), and $\chi_{\mathrm{SP}}$ represents the spin-Peierls contribution of the Cu spins.

## 3. QTM technique

The QTM technique has been applied successfully to a number of the linear spin systems [5–7]. In order to perform numerical calculations for a macroscopic chain, we have first divided the Hamiltonian (1) into two parts $H = H_A + H_B$

$$H_A = H_{1,4} + H_{5,8} + H_{9,12} + \dots$$

$$H_B = H_{3,6} + H_{7,10} + H_{11,14} + \dots \tag{3}$$

Then we used the Trotter expansion to obtain the $m$-th classical approximant $Z_m$ of the partition function $Z$ of the classical system of $2m \times N$ spins with the effective interactions grouped into eight-spin blocks

$$Z_m = \sum_{\{S_{r,i}\}} \prod_{r=1}^{m} \prod_{i=1}^{N/4} \langle S_{r,i} \dots {}_{r,i+3} \,|\, \exp(-\beta/m H_{i,i+3}) | S_{r+1,i} \dots S_{r+1,i+3} \rangle. \tag{4}$$

Secondly, we introduced an effective classical spin $\sigma = 3/2$ to replace pairs of $S = 1/2$ spins distributed along each row $r$

$$(S_{r,i}, S_{r,i+1}) \longrightarrow \sigma_{r,j}, \quad \text{where} \quad j = 1 \dots N/2. \tag{5}$$

At the same step, we rewrote the local transfer matrix in the basis of $\sigma$. This allowed us to reverse the transfer direction by defining a new local transfer matrix

$$\langle \sigma_{r,j} \sigma_{r+1,j} | V_{r,r+1} | \sigma_{r,j+1} \sigma_{r+1,j+1} \rangle =$$

$$\langle \sigma_{r,j} \sigma_{r,j+1} | \exp(-\beta/m H_{j,j+1}) | \sigma_{r+1,j} \sigma_{r+1,j+1} \rangle. \tag{6}$$

Since then, the global transfer matrices $W_1$ and $W_2$ (defined for odd and even columns of spins, respectively) have been expressed by the corresponding products of $V_{r,r+1}$. And finally, the $m$-th classical approximation to the partition function of (1) was written in the form

$$Z_m = \mathrm{Trace}\, [W_1 W_2]^{N/4}. \tag{7}$$

## 4. Results

In order to estimate the $J$ and $\alpha$ values we calculated the magnetic susceptibility along the $c$ crystal direction and compared it to the experimental results described above. In the calculations, we choose the $g_c$ factor equal to 2.07.

Above $T_{\mathrm{SP}}$, the best fit was obtained for the following set of parameters:

$$J = -166 \text{ K} \pm 2 \text{ K} \quad \text{and} \quad \alpha = 0.36 \pm 0.01. \tag{8}$$

As shown in Fig. 1, our results very well fit the experimental data, drawn by the full line, down to the low-temperature region.

Our estimate to $\alpha$ proposed for $CuGeO_3$ is significantly greater than the critical value $\alpha_c = 0.2411$ [3] and confirms the existence of frustration in the spin

model proposed for $CuGeO_3$. This conclusion is fully consistent with those following from the exact diagonalization technique. Especially, we would like to refer to the susceptibility calculations performed above 20 K by Fabricius et al. [8], which were compared to the experimental data similar to those we used.

Subsequently, using the parameters (8), we have fitted the experimental susceptibility curve below $T_{SP}$ imposing the temperature dependence of the dimerization parameter $\delta$. The estimates of $\sigma$ show a sharp increase in the region close to $T_{SP}$ and the saturation as $T$ tends to zero. This behaviour is in good agreement with the power law for the gap $\Delta \sim \delta^{2/3}$.

## 5. Conclusions

We have performed the single-crystal susceptibility measurements for pure $CuGeO_3$ and have shown that the modified QTM technique can be successfully used for characterization of frustrated $S = 1/2$ antiferromagnetic quantum chains. The application to the SP compound $CuGeO_3$ gives numerical results fully consistent with the experimental susceptibility data and the best-fit values of the exchange integrals in $CuGeO_3$ spin model within 2%.

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