Static properties of a ferromagnetic S=1/2 chain system with orthorhombic exchange anisotropy

Static properties of a ferromagnetic $S=1/2$ chain system with orthorhombic exchange anisotropy: Comparison of numerical results and experimental data on $[C_6H_{11}NH_3]CuCl_3$

K. Kopinga
Department of Physics, Eindhoven University of Technology, NL-5600 MB Eindhoven, The Netherlands

T. Delica, H. Leschke, and I. Riedel
Institut für Theoretische Physik, Universität Erlangen-Nürnberg, D-8520 Erlangen, Germany
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Results of the numerical quantum-transfer-matrix method (QTM) are compared with experimental data on $[C_6H_{11}NH_3]CuCl_3$, a quasi-one-dimensional ferromagnetic $S=\frac{1}{2}$ system with orthorhombic exchange anisotropy. The experimentally observed static properties of this system, such as magnetization, susceptibility, and heat capacity, generally can be described with an accuracy comparable to the experimental error. At temperatures extending up to a few kelvin above the three-dimensional-ordering temperature systematic deviations between theory and the data are found; they are attributed to the (very small) coupling between the chains in this compound.

The static and dynamic properties of one-dimensional (1D) $S=\frac{1}{2}$ systems with a dominant nearest-neighbor interaction have been the subject of a large number of investigations. These systems display a large variety of quite interesting features, which are not present in systems with a higher dimensionality.[1] These features strongly depend on the type of anisotropy in the magnetic intrachain interaction and the magnitude and direction of the external field.[2,3] In particular, not only do the linear excitations contribute significantly to the thermodynamic properties of these systems, but in a certain range of fields and temperatures nonlinear excitations may have a large statistical weight.

In the past few years, the compound $[C_6H_{11}NH_3]CuBr_3$(CHAB) has been studied very extensively. The ferromagnetic intrachain interaction in this substance contains about 5% easy-plane anisotropy.[4] For this type of anisotropy, the excitation spectrum may contain local, nonlinear excitations called kink solitons.[5]

Since CHAB is an almost ideal one-dimensional magnetic system, it has been used as a test case for numerical computations of the thermodynamic properties, which are based on the actual quantum-mechanical spin Hamiltonian. Since exact solutions of this Hamiltonian for the infinite system are not available, either approximations involving the numerical diagonalization of the Hamilton matrix for finite chains[6,7] or procedures based on the mapping of the one-dimensional quantum system to a two-dimensional array of classical (Ising) spins[8] have been used. The properties of the resulting classical system were evaluated by Monte Carlo simulations[9] or by a numerically exact transfer-matrix method (QTM).[10] A very detailed analysis of the thermodynamic properties of CHAB has recently been performed by a comparison of the experimental data with results obtained using the latter approach.[11] For one consistent set of exchange and anisotropy parameters an almost perfect agreement was found, which indicates that this numerical approach yields accurate results, at least in the case of easy-plane anisotropy.

A second almost ideal realization of a ferromagnetic $S=\frac{1}{2}$ chain system is the chlorine isomorph of CHAB, $[C_6H_{11}NH_3]CuCl_3$(CHAC). The intrachain interaction in this compound is of the same order of magnitude as that in CHAB, but, instead of an easy-plane character, the anisotropy in CHAC has an orthorhombic or XYZ symmetry.[12] Such a change of anisotropy is known to have a dramatic effect on the static and dynamic properties at low temperatures.[1,2] In particular, the excitation spectrum in an XYZ system is predicted to consist mainly of (linear) magnons and bound complexes of two or more magnons, so-called magnon bound states.[2] Some experimental evidence for the presence of these magnon bound states in CHAC has been obtained from ferromagnetic resonance (FMR) measurements.[13] A recent analysis of the differential magnetic susceptibility of this compound indicates that also the thermodynamic properties are dominated by these excitations in a certain range of fields and temperatures.[14] A quantitative agreement between theory and experiment is, however, still lacking. It is not clear whether this is due to inadequacies in the theory or to uncertainties in the values of the exchange and anisotropy parameters. Therefore we thought it worthwhile to compare experimental data on the static properties of CHAC with numerical QTM results for the corresponding model system. An analysis of these data will provide rather accurate estimates of the intrachain interaction parameters in CHAC, allowing reliable checks of the validity of various theoretical predictions for the excitation spectrum in XYZ systems. Apart from this, such an analysis may serve to test the accuracy of the (extrapolated) QTM results for systems with this type of symmetry.

The Hamiltonian describing the individual chains in CHAC is given by

$$\mathcal{H}=-2\sum_i (J^{xx}S_i^xS_{i+1}^x+J^{yy}S_i^yS_{i+1}^y+J^{zz}S_i^zS_{i+1}^z) -\mu_B\sum_i \mathbf{S}_i g\mathbf{B}\ , \quad (1)$$

where $J^{\alpha\alpha}(\alpha=x,y,z)$ denote the components of the intrachain interaction tensor and **B** is the applied magnetic field. From FMR experiments the anisotropy of the interaction tensor has been deduced[12] as $(J^{xx}-J^{zz})/k_B=1.03$ K, $(J^{xx}-J^{yy})/k_B=0.53$ K, whereas the principal components of the g tensor have been determined from electron-spin-resonance (ESR) experiments.[15] The magnitude of J^{xx}/k_B is estimated from zero-field heat-capacity[4] and susceptibility[15] measurements to range between 45 and 70 K. The crystal structure of CHAC is orthorhombic. The y axis in Eq. (1) corresponds to the crystallographic c axis, whereas the x axis lies in the ab plane at an angle φ from the b axis. Two symmetry-related types of chains are present, with $\varphi=+17°$ and $-17°$, respectively. Three-dimensional antiferromagnetic ordering in CHAC occurs at $T_N=2.214$ K.

The present version of the QTM[16] has been described in detail in Ref. 17. All calculations have been performed on open chains of $N=150$ spins and Trotter numbers up to $M=10$. A further increase of N had no significant effect on the calculated results. The results presented here were obtained by extrapolating data for $M=7,8,9$ or $M=8,9,10$ to $M=\infty$ using the $1/M^2$ rule.[8] Typically, the various extrapolations agreed within a few percent for temperatures down to $T=3$ K. At higher temperatures, the uncertainty in the extrapolations becomes negligibly small.

To obtain a reliable set of exchange and anisotropy parameters we have concentrated on the reduced magnetization M/M_S. This property was chosen because experimentally full saturation was observed at $T=1.2$ K for all directions of B, and hence systematic errors in the absolute magnitude of M cancel out. Apart from this, the numerical results for M are very accurate and the g values can be treated as fixed parameters, since they have been deduced directly from ESR experiments.[15] Moreover, small deviations of CHAC from ideal model behavior are expected to be of minor importance at higher fields and temperatures.

In Fig. 1 we have plotted the experimentally observed magnetization of CHAC for all three crystallographic directions as M/M_S. The full curves represent the results of QTM calculations, using the set of parameters given above, except for the anisotropy $(J^{xx}-J^{yy})/k_B$, which was modified to 0.8 K to obtain an acceptable description of the data at higher temperatures. This suggests a somewhat more pronounced Ising-like anisotropy than that deduced from FMR measurements in the ordered state.[12] The value of the intrachain coupling was optimized to $J^{xx}/k_B=56.5$ K, which falls within the range quoted above. The overall agreement between the QTM results and the experimental data is very good; the deviations occurring at low temperatures are attributed to deviations of CHAC from ideal 1D model behavior due to the small interchain interactions. The description of the data at $T=4.2$ K can be improved by using the value $(J^{xx}-J^{yy})/k_B=0.53$ K, determined from FMR at $T=1.2$ K, which suggests that these (largely dipolar) interchain interactions induce a change of the effective anisotropy at lower temperatures.

Next, we will consider the excess heat capacity $\Delta C=C(\mathbf{B})-C(\mathbf{0})$. The experimental data for **B** along the b and c axes are plotted in Fig. 2, together with the QTM results calculated for the same set of parameters as the magnetization. The figure reveals very good agree-

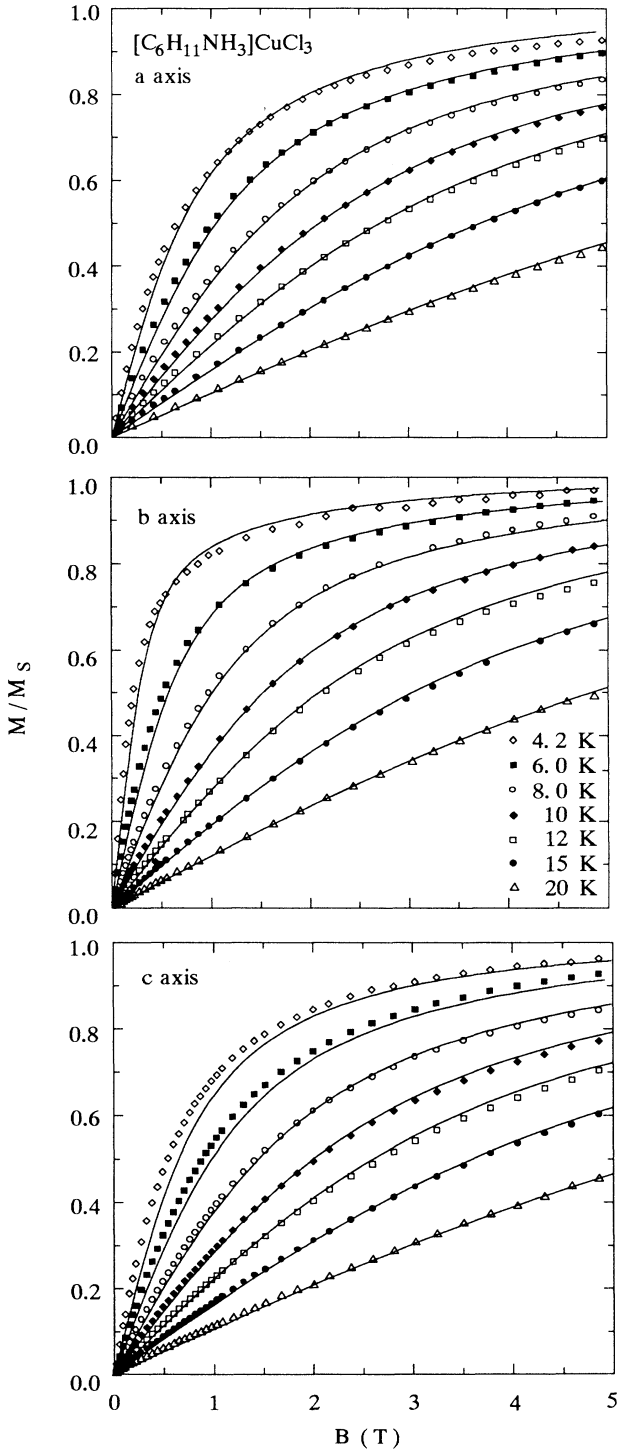

FIG. 1. Reduced magnetization of CHAC for **B** along the a, b, and c axes at various temperatures. Full curves denote the corresponding QTM results.

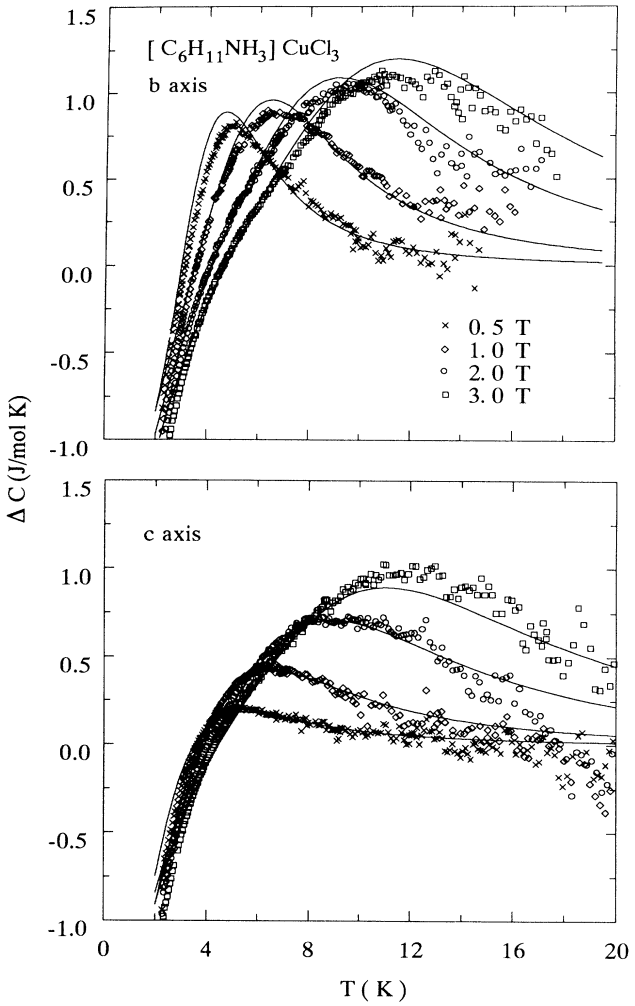

FIG. 2. Excess heat capacity of CHAC for fields $B = 0.5$, 1, 2, and 3 T along the b and c axes. Full curves denote the corresponding QTM results.

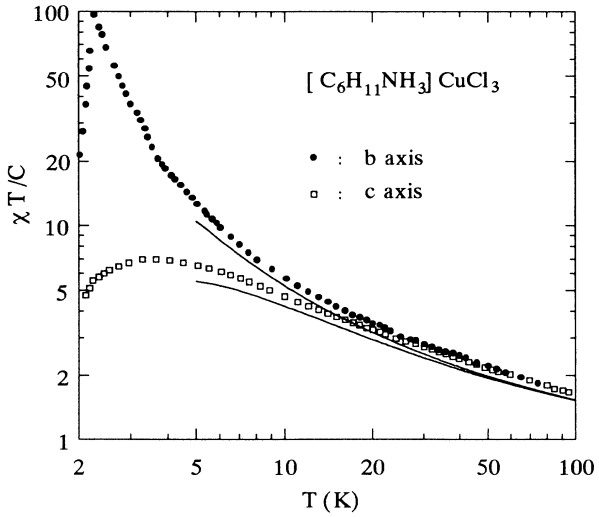

FIG. 3. Zero-field susceptibility of CHAC along the b and c axes. Data are taken from Ref. 15, whereas the drawn curves denote the corresponding QTM results.

ment between theory and experiment, supporting the applicability of the QTM for canted fields as well as the very good one-dimensional characteristics of the model system CHAC.

We have also calculated the zero-field susceptibility of CHAC along all three crystallographic axes, again using the same set of parameters. The QTM results are plotted in Fig. 3, together with the reported experimental data.[15] Inspection of this figure shows a very nice qualitative agreement, but the experimental data for both the b and c axes are about 8% higher than the numerical results. This systematic deviation also persists in the temperature region above 10 K, where the QTM method is very accurate. The agreement can be improved by increasing J^{xx}/k_B to 70 K, but this would deteriorate the description of M/M_S in an unacceptable way. Probably, the deviations result from uncertainties in the calibration of the

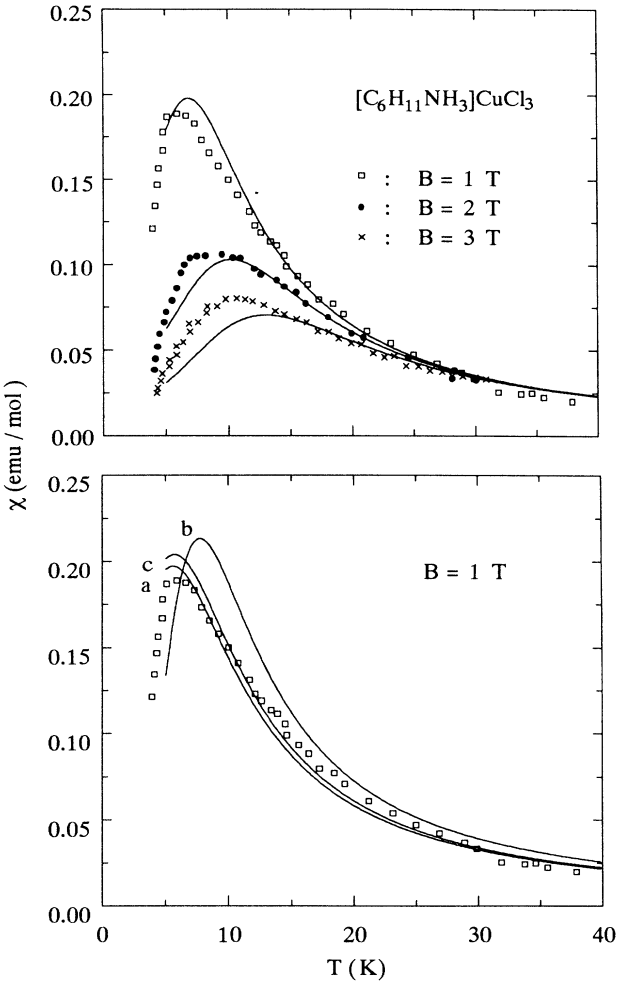

FIG. 4. Differential susceptibility of a powdered sample of CHAC for $B = 1$, 2, and 3 T. Data are taken from Ref. 14, whereas the drawn curves denote the corresponding QTM results. In the lower part of the figure the data for $B = 1$ T are plotted, together with the QTM results for the crystallographic a, b, and c axes.

experimental equipment, since a comparable systematic difference between theory and experiment has also been observed for CHAB.[11]

In Fig. 4 we have plotted the experimentally observed differential susceptibility ($\partial M/\partial B$) of CHAC (Ref. 14) at various fields and temperatures. The reported data have been collected on powdered samples. The curves in the upper half of the figure denote the corresponding QTM results calculated for the same set of parameters as deduced above and assuming a uniform distribution of the orientation of the individual crystallites in the sample. Although the overall agreement between theory and experiment is very satisfactory, some systematic deviations occur, which probably arise from texture in the sample. To illustrate the possible effect of such a texture, we have plotted the QTM results for the individual crystallographic axes and $B = 1$ T in the lower half of Fig. 4.

In conclusion, we state that a comparison of the QTM results with the relevant experimental data on CHAC yields a very good agreement. The deviations that are observed are comparable with the experimental uncertainties. This suggests that the present QTM results, based upon extrapolation of the numerical data for Trotter numbers up to $M = 10$, are very reliable and may therefore be used to check the applicability of various analytical approximations for the behavior of systems with an orthorhombic or Ising-like anisotropy. Among these we mention in particular predictions for those thermodynamic properties that are dominated by nonlinear excitations, e.g., magnon bound states.

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