

DMRG Approach to a Molecular-Based Bimetallic Chain Containing Re(IV) and Cu(II) Ions

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The bimetallic chain complex [Cu(tren)]ReCl₆ is numerically analysed on the basis of the anisotropic quantum Heisenberg model without the mean-field corrections by the density-matrix renormalization group approach. The high accuracy results of our simulations have been fitted to the corresponding experimental susceptibility data above the crossover regime. The set of model parameters comprising the strength of antiferromagnetic couplings, the single-ion anisotropy term and the corresponding g factors have been found: $J/k_B = 3.5 \pm 0.5$ K, $D/k_B = 35 \pm 5$ K, $g_{Cu} = 2.07 \pm 0.05$ and $g_{Re} = 1.73 \pm 0.01$.

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1. Introduction

With respect to magnetic properties, the complexes with the second and the third series of transition elements are less examined than complexes with the lighter element of the group. Polymetallic complexes synthesised by using the rhenium ions (building anionic blocks) and copper(II) ions (building cationic blocks) belong to the first group. We have studied theoretically the bimetallic chain complex [Cu(tren)]ReCl₆, where the used tren [tris(2-aminoethyl)amine] is a tetradentate ligand [1]. The rhenium(IV) complex forms octahedral compounds, whereas the above ligands are able to block four coordination sites around the potentially octahedral Cu^{II} ion, leaving two coordination sites for other ligands.

The magnetization vs. temperature curve measured at 50 Oe, has revealed the presence of spontaneous magnetization below the transition temperature $T \approx 3.15$ K. Spontaneous magnetization appears as the result of switching on the interchain exchange interactions at low temperatures that leads to $3d$ magnetic ordering of ferrimagnetic chains. Since we limit our study to temperatures above the crossover from the $3d$ to the $1d$ behaviour, the interchain interactions can be neglected. Therefore we can analyse the experimental results on the basis of the one-dimensional quantum Heisenberg model. It is worth stressing that the molecular field corrections are absent in the $1d$ phase because of the vanishing magnetization. So far [1], the compound has been studied qualitatively on the basis of the Ising model and simplified expressions for the longitudinal and perpendicular magnetic susceptibilities.

2. Model

For our analysis of the magnetic properties of the rhenium(IV) complex the following Hamiltonian is used:

$$\begin{aligned} \mathcal{H} = & \sum_{i=1}^{L/2} [J(s_{2i-1}^x S_{2i}^x + s_{2i-1}^y S_{2i}^y + s_{2i-1}^z S_{2i}^z \\ & + S_{2i}^x s_{2i+1}^x + S_{2i}^y s_{2i+1}^y + S_{2i}^z s_{2i+1}^z) + D(S_{2i}^z)^2 \\ & + \mu_B H^x (g_{Cu} s_{2i-1}^x + g_{Re} S_{2i}^x) \\ & + \mu_B H^z (g_{Cu} s_{2i-1}^z + g_{Re} S_{2i}^z)], \end{aligned} \quad (1)$$

where spins $s = 1/2$ and $S = 3/2$ are located on the odd and even sites and refer to Cu^{II} and Re^{IV} ions, respectively, and L stands for the length of the chain. In our model the magnetic interactions are isotropic and the rhenium(IV) ions are subject to the single-ion anisotropy. We assume that $g_x = g_y$ for both ions and the thermodynamic properties are isotropic in the xy plane. The Zeeman terms depend on the field directions but it is enough to consider the x and z orientations.

The thermodynamic quantities, as the free energy or magnetization, can be calculated by means of the partition function $Z = \text{Tr} \exp(-\mathcal{H}/k_B T)$, where k_B is the Boltzmann constant. To consider the macroscopic limit $L \rightarrow \infty$, the quantum transfer matrix approach (QTM) is referred here [2–4]. Under the Suzuki–Trotter formula the partition function of the quantum chain can be converted into a series of approximants Z_M of the equivalent two-dimensional classical system, where M is called the Trotter number. In practice, computations of Z_M are possible for relatively small M which can spoil the

reliable estimations of the thermodynamic functions in a low-temperature region. In order to overcome this restriction and cover the entire experimental 10–300 K temperature range, the density-matrix renormalization group approach (DMRG) is applied [5–7]. It is worth noting that only the presence of $3d$ magnetic order prevents us from studies at lower temperatures, because there, our $1d$ model is no valid anymore. In general, the method can be successfully applied in much lower temperatures [8].

The DMRG method is a type of variational method, where the main idea is to find a representation of the Hilbert space of states in a restricted space which is much smaller than the original one. Both the QTM and DMRG methods are free from statistical errors and the negative sign problem which hampers convergence of physical quantities at low temperatures. For one-dimensional quantum systems DMRG approach offers a very efficient iterative truncation algorithm for constructing the effective transfer matrices with large Trotter numbers M [8, 9]. Naturally, the lower temperature, the stronger quantum character of phenomena and higher M has to be taken into account. Although the majority of our results are provided with $M = 5$, we have checked that higher $M = 7$ does not improve the results (the corrections do not exceed 0.001%) so that the DMRG technique leads to the accurate reliable numerical results.

3. Results and discussions

In our analysis the magnetic susceptibility data measured at the field $H = 0.5$ T [1] are reanalysed. We have scanned the positive and negative values of J confirming the antiferromagnetic interactions between nonequivalent magnetic centers, although our estimate $J/k_B = -3.5$ (± 0.5) K is somewhat lower than that found before [1]. In parentheses the uncertainty of a given value is defined. In Fig. 1 we present a comparison between experiment and our results, where the continuous lines refer to $D > 0$ and the dashed line to $D < 0$. The dashed line occurs if it can be distinguished from the continuous line. In the main part, the χT product is plotted in the experimental temperature region, whereas in the inset, in the susceptibility versus temperature is shown. Fitting the experimental susceptibility data available, only the absolute value $|D/k_B| = 35$ K (± 5 K) can be determined. This means that for the powder susceptibility data, where only the average $\chi_{av} = 2/3\chi_x + 1/3\chi_z$ can be measured [8], it is not possible to distinguish between the results following from the ground state Kramers doublet $m = \pm 1/2$ or $m = \pm 3/2$. For the positive D , the ground state of the Re(IV) ion corresponds to $m = \pm 1/2$, whereas for the negative D , it corresponds to $m = \pm 3/2$. As expected [1, 10] for the Re(IV) ion, the anisotropy is strong with respect to the exchange coupling. As to the g factors, we have estimated $g_{Cu} = 2.07 \pm 0.05$ and $g_{Re} = 1.73 \pm 0.01$.

It is worth mentioning that the sign of the rhenium(IV) single-ion anisotropy could be determined from

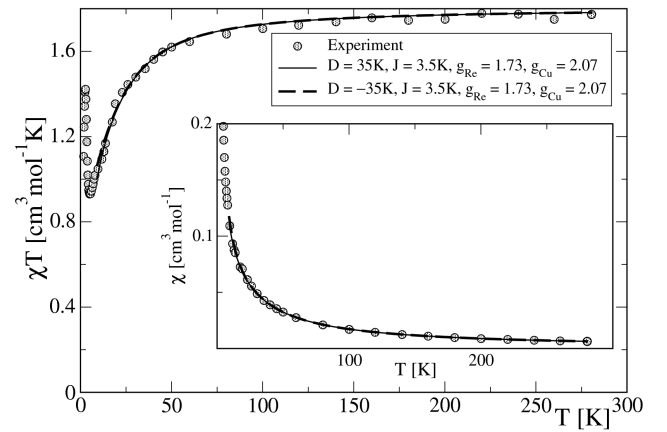


Fig. 1. Temperature dependence of the magnetic susceptibility for the CuRe sample. The inset presents the average magnetic susceptibility vs. temperature.

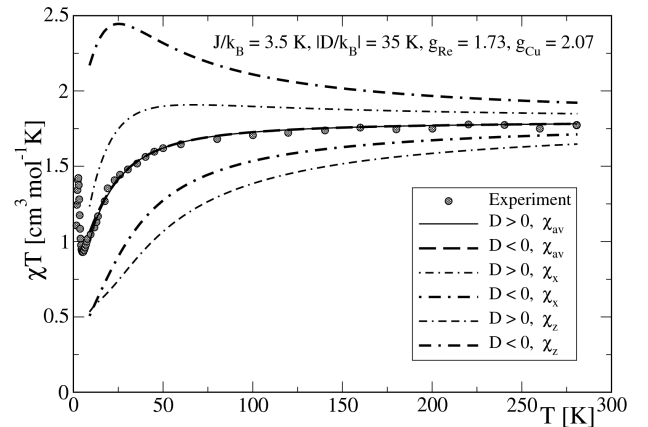


Fig. 2. Temperature dependence of the average, longitudinal and perpendicular magnetic susceptibilities for the CuRe model sample.

the single-crystal magnetometry. This possibility is demonstrated by the results of our calculations of the longitudinal and perpendicular susceptibility (see Fig. 2). As one can see, the components have substantially different temperature behaviour. So, if we had measurements for the crystal, we could distinguish the two cases.

4. Conclusions

The experimental evidence of the absence of spontaneous magnetization above $T = 3.15$ K enables us to apply a one-dimensional model and neglect the interchain interactions. To take into account the quantum nature of spin, we use intrinsically quantum Heisenberg model and simulations which preserve the quantum properties of the model.

Our analysis confirms the weak antiferromagnetic coupling between the Cu^{II} and Re^{IV} ions and reveals the importance of the anisotropy term for the rhenium(IV) ions. Our estimates of the parameters are consistent with

the previous findings but are based on the Heisenberg coupling between the Cu^{II} and Re^{IV} ions and reliable DMRG-based simulations.

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