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High-field (40 T) magnetization studies of linear Heisenberg chains with alternating exchange

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We present susceptibility versus temperature, and high-field magnetization data on two Cu^{2+} chain compounds with alternating exchange constants.

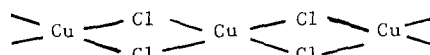
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In recent years a number of Cu^{2+} chain compounds have been discovered in which the exchange interactions between the copper spins $S = 1/2$ along the chain are alternating in strength, i.e. the chain is a 1-d assembly of weakly coupled dimers. Theoretical [1-3] and experimental [4] work on such magnetic systems is stimulated e.g. by the close relationship with the spin-Peierls dimerisation problem, where the uniform $S = 1/2$ antiferromagnetic chain becomes spontaneously dimerised below a certain transition temperature T_{sp} , due to the magneto-elastic coupling with the lattice [5]. For the alternating chains the exchange alternation is (in principle) independent of temperature and field, since it results from an inequivalency of super-exchange bonds along the chain. The interaction Hamiltonian may be written as :

$$H = -2J \sum_{i=1}^{1/2 N} (\vec{s}_{2i} \cdot \vec{s}_{2i+1} + \alpha \vec{s}_{2i} \cdot \vec{s}_{2i-1}) - g\mu_B \sum_{j=1}^N \vec{H} \cdot \vec{S}_j$$

The eigenvalues for finite chains and rings of spins 1/2 have been calculated [2,3] for this Hamiltonian, so that accurate predictions for the thermodynamic behavior exist. Note that $\alpha = 1$ and $\alpha = 0$ correspond to the uniform chain and the isolated dimer. Below, we compare these predictions with results on two Cu^{2+} chain compounds.

Our first example is $\text{CuCl}_2(\gamma\text{-picoline})_2$, where $\gamma\text{-picoline} \equiv \text{NC}_5\text{H}_4 - \text{CH}_3$. Its crystal structure [6] consists of chains of



These chains are well separated by the $\gamma\text{-picoline}$ groups similar as for $\text{CuCl}_2(\text{pyridine})_2$, which, however, is a uniform antiferromagnetic chain. Our magnetic susceptibility data vs temperature for $\text{CuCl}_2(\gamma\text{-picoline})_2$ are shown in fig. 1, together with predictions for $\alpha = 0$, $\alpha = 1$ and $\alpha = 0.6$, and using the parameters $J/k_B = -13.4$ K and $g = 2.14$. These values are close to those obtained by Hatfield and coworkers [7], likewise from χ data ($J/k_B = -13.8$ K ; $\alpha = 0.7$; $g = 2.17$). In addition, we have performed high-field magnetization experiments at 1.2 K - 4.2 K in the pulsed-field magnet of our laboratory, which is capable of reaching 40 - 50 T [8]. These data are shown in fig. 2, together with prediction for $T = 0$ and the same value of α , using $J/k_B = -13.8$ K and $g = 2.11$. In particular the experimental curve at $T = 1.2$ K ($k_B T / |J| \approx 0.087$) is in good agreement with the theory for $\alpha = 0.6$. We conclude that $J/k_B = -13.6 \pm 0.4$, $\alpha = 0.6 \pm 0.1$ for this material.

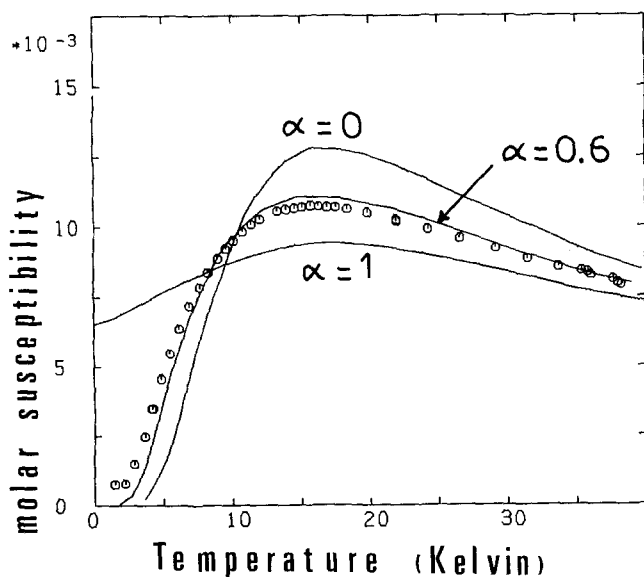


Fig. 1 : Powder-susceptibility of $\text{CuCl}_2(\gamma\text{-picoline})_2$.

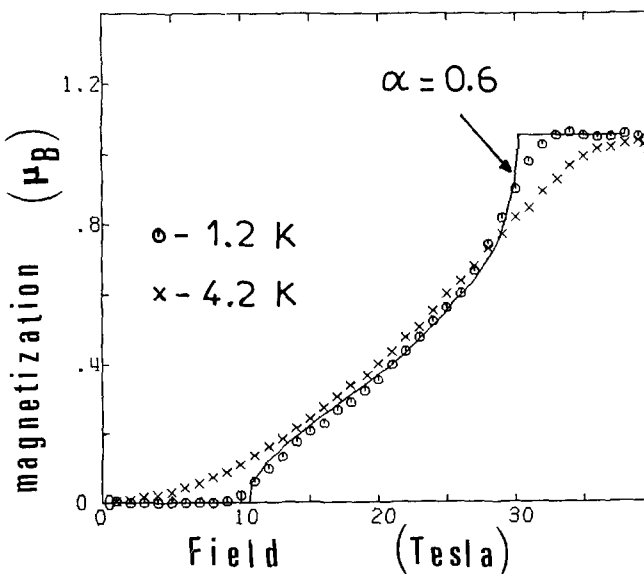


Fig. 2 : High-field magnetization of $\text{CuCl}_2(\gamma\text{-picoline})_2$ powder.

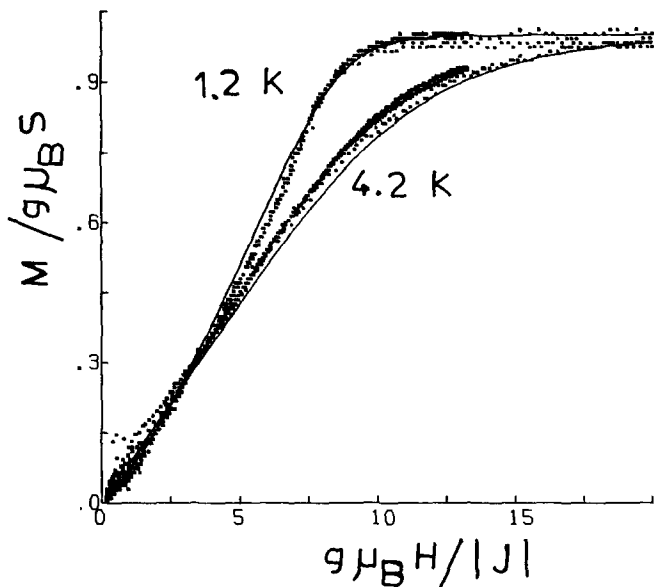


Fig. 3 : High-field magnetization of CuCl_3 (4-benzylpiperidinium) powder.

It is of interest that $\text{CuCl}_2(\gamma\text{-picoline})_2$ is an alternating chain, whereas $\text{CuCl}_2(\text{pyridine})_2$ is a uniform chain (note that $\gamma\text{-picoline} = 4\text{-methyl-pyridine}$, so that the compounds differ only by substitution of one of the H atoms attached to the pyridine ring by the CH_3 group). The room temperature crystal structures of both compounds are equivalent; in particular there is no evidence for an inequivalency of exchange paths along the chains in case of the substituted pyridine compound. The same problem was encountered in case of the isostructural compound $\text{CuCl}_2(\text{N-methyl-imidazole})_2$ for which the magnetic data evidenced an alternating exchange with $\alpha = 0.4$ [11], whereas such an alternation could not be traced to the room temperature crystal structure.

A possible explanation may be found in the fact that precisely for the two methyl substituted compounds anomalies in the dielectric constant have been found near about 50 K by Hatfield and coworkers [7]. Similar measurements taken at our laboratory [12] on $\text{CuCl}_2(4\text{-methyl-pyridine})_2$ confirm the conclusion of Hatfield, whereas data on $\text{CuCl}_2(\text{pyridine})_2$ show no

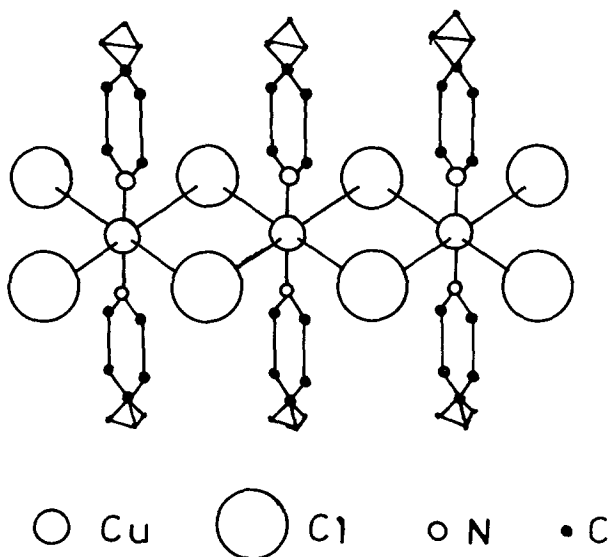


Fig. 4 : Sketch of the chain structure in $\text{CuCl}_2(4\text{-methyl-pyridine})_2$

anomaly in the same range of temperature. One is tempted to conclude that these anomalies arise from a freezing of the (hindered) methyl-group rotations. The accommodation of the static CH_3 tetrahedra in the chain structure, as sketched in fig.4, may quite well result in tilts and/or twists of the octahedra surrounding the Cu ions, leading to inequivalent superexchange bonds along the chains in an alternating fashion. Evidently, for $\text{CuCl}_2(\text{pyridine})_2$ with its fully flat pyridine molecules, such a problem does not arise. It is noteworthy in this respect that the lower symmetry of the N-methyl-imidazole molecule as compared to the methyl-pyridine molecule, leads to a stronger alternation ratio of $\alpha = 0.4$ for this compound.

Secondly, we have studied $\text{CuCl}_3(4\text{-benzylpiperidinium})$ which was shown recently by Willett and coworkers [9] to consist of ferromagnetic dimers, weakly coupled antiferromagnetically into chains. Their susceptibility data analyses led to $J/k_B = +30$ K for the intradimer exchange. Our high-field magnetization curves at $T = 1.2$ K - 4.2 K are shown in fig. 3. The theoretical curves have been calculated for a $S = 1$ antiferromagnetic Heisenberg chain, using the eigenvalues obtained by Blöte [10]. The application of this model is justified by the fact that at these low temperatures the excited singlet dimer state ($\Delta E/k_B \approx 60$ K) will be depopulated so that we may treat the dimers as effective spins $S' = 1$. The interdimer interaction following from the fit is $J'/k_B = -1.2$ K with $g = 2.24$, so that $\alpha = 0.04$. This value for J' agrees with $\Theta = -4$ K found from the Curie-Weiss plot at low temperatures in ref. 9.

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