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# Magnetic properties of a molecular-based spin-ladder system: $(5IAP)_2CuBr_4 \cdot 2H_2O$

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We have synthesized and characterized a spin-1/2 Heisenberg antiferromagnetic ladder: bis 5-iodo-2-aminopyridinium tetrabromocuprate (II) dihydrate. X-ray diffraction studies show the structure of the compound to consist of well isolated stacked ladders and the interaction between the $Cu^{2+}$ atoms to be due to direct Br···Br contacts. Magnetic susceptibility and magnetization studies show the compound to be in the strong-coupling limit, with the interaction along the rungs ($J' \approx 13$ K) much greater than the interaction along the rails ($J \approx 1$ K). Magnetic critical fields are observed near 8.3 and 10.4 T, respectively, establishing the existence of the energy gap.

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Quantum spins interacting antiferromagnetically on a lattice form one of the simplest systems with which to explore cooperative effects in many body systems. The behavior can be particularly rich when the parameters in the Hamiltonian can be tuned to a zero-temperature quantum critical point.[1] It is thought that high-temperature superconductivity exists due to its Hamiltonian's proximity to such a point.[2,3] It has recently become clear[4–6] that a spin ladder forms a remarkable system with which to explore quantum effects in antiferromagnets. An even leg ladder has a cooperative singlet ground state, with a finite-energy gap $\Delta$ in the spin excitation spectrum. By application of a magnetic field, the size of the gap can be reduced until it disappears at $H_{c1}$, at which point the system is at a quantum critical point. In addition, holes injected into an even-leg ladder are predicted to pair and possibly lead to superconductivity.[4–6]

Few physical realizations of two-leg ladders are known, and only one has been explored at the critical point. Among the most extensively studied two-leg ladders are $SrCu_2O_3$ (Refs. 7–9) and $[(DT\text{-}TTF)_2][Au(mnt)_2]$,[10,11] but the strong exchange constants of these compounds produce gaps too large to be overcome with available magnetic fields. Only $Cu_2(C_5H_{12}N_2)_2Cl_4$ has exchange strengths small enough to produce an experimentally accessible critical point, $\mu_o H_{c1} = 7.5$ T.[12–17]

We report here on the second two-leg spin ladder with an accessible critical point at $\mu_o H_{c1} = 8.3$ T. This material, bis 5-iodo-2-aminopyridinium tetrabromocuprate (II) dihydrate $[(5IAP)_2CuBr_4 \cdot 2H_2O]$, is the one of four spin ladders we have developed through the use of molecular-based magnetism[18] and fully characterized by high-field measurements. The structure of the compound will readily permit dilution of the magnetic lattice, by which the stability of the critical point can be explored further.

The structure of $(5IAP)_2CuBr_4 \cdot 2H_2O$ consists of twin molecular chains cross linked to form a ladder. The spin ladders are well isolated from one another by the bulk of the organic molecule. As determined by x-ray diffraction, the crystallographic structure of $(5IAP)_2CuBr_4 \cdot 2H_2O$ is triclinic, space group P1, $a = 6.7505$ Å, $b = 9.8433$ Å, $c = 16.7581$ Å, $\alpha = 78.512°$, $\beta = 84.962°$, and $\gamma = 88.512°$.

The exchange interaction between the $Cu^{2+}$ ions takes place through Br···Br direct contacts,[19–21] as shown by dashed and dotted lines in Fig. 1. The interaction strength drops rapidly with the Br···Br distance $r$, typically as $r^{-10}$, and depends also on the geometry of the superexchange pathway through such parameters as the mean trans angle $\theta$ of the distorted $CuBr_4$ tetrahedra, and the dihedral angle $\tau$ between the two Cu-Br···Br planes.[22,23] The mean *trans* angle of the $CuBr_4$ tetrahedra in our system is $\theta = 132.7°$. The exchange pathway along the rungs of the ladder is characterized by a distance between the Br atoms $r = 3.58$ Å, and by a dihedral angle $\tau = 180°$. Along the rails the distance between the Br atoms is $r = 4.23$ Å, and the dihedral angle is $\tau = 98.0°$. The next shortest distance in the system between Br atoms is 5.74 Å, along the diagonal of the ladder, too large to allow for an interaction.

The model Hamiltonian for a spin ladder consisting of two coupled spin-1/2 Heisenberg chains is

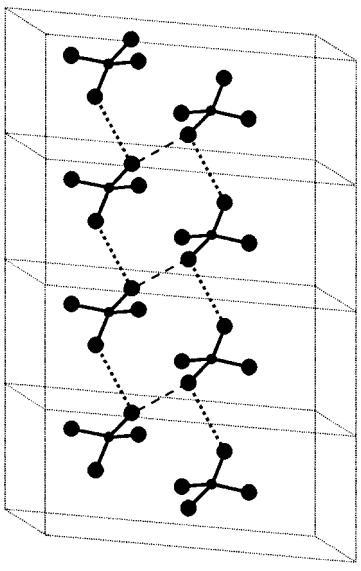

FIG. 1. Crystal packing of the $Cu^{2+}$ metal ions, along with the path of exchange interaction. The $Cu^{2+}$ ions are the small circles, the $Br^-$ ions are the larger circles. The Br-Br contacts are 3.58 Å (rung) and 4.23 Å (rail) with the rails aligned vertically along the page. The organic molecules are not shown.

 

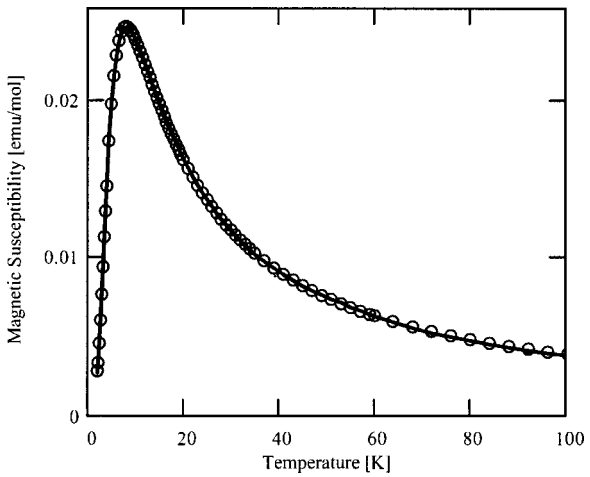


FIG. 2. Temperature dependence of the powder dc magnetic susceptibility for $(5IAP)_2CuBr_4 \cdot 2H_2O$. The solid line is a fit (5) to the susceptibility of a spin-ladder plus a paramagnetic contribution.

$$\mathcal{H} = J \sum_a \sum_i \boldsymbol{S}_{i,a} \cdot \boldsymbol{S}_{i+1,a} + J' \sum_i \boldsymbol{S}_{i,1} \cdot \boldsymbol{S}_{i,2} - g\mu_B H \sum_a \sum_i S^z_{i,a}, \tag{1}$$

where $\boldsymbol{S}_{i,a}$ is the spin operator at site $i$ (the index $i$ runs along the chains) on the rail $a$ ($a=1,2$). $H$ is an external magnetic field in the $z$ direction. The exchange constants $J$ (along the rails) and $J'$ (along the rungs) are positive, corresponding to antiferromagnetic coupling.

The powder dc magnetic susceptibility of $(5IAP)_2CuBr_4 \cdot 2H_2O$ has been measured on a Quantum Design MPMS superconducting quantum interference device magnetometer, in a magnetic field of 1 T, from 2 K up to 300 K. The data have been corrected for the core diamagnetic ($-379*10^{-6}$ emu/mol) and temperature-independent paramagnetic ($60*10^{-6}$ emu/mol) contributions. The magnetic susceptibility, plotted in Fig. 2, shows a rounded peak around 8 K, characteristic of low-dimensional antiferromagnetic compounds, and a sharp drop at very low temperatures, characteristic to gapped systems. There is no sign of a structural phase transition at low temperatures. Fitting a Curie-Weiss law $[\chi = C/(T-\Theta)]$ to high-temperature data ($T \geqslant 20$ K) gives $\Theta = -5.3$ K and $C = 0.416$ emu K/mol. The sign of $\Theta$ confirms antiferromagnetic coupling between the spins. The Curie constant predicted from powder electron paramagnetic resonance measurements ($g = 2.10$) is 0.412 emu K/mol, in good agreement.

Susceptibility data have been initially fitted using a high-temperature expansion series for a spin ladder system.[14] Because it was determined in this way that the exchange interaction $J'$ along the rungs is much greater than the exchange interaction $J$ along the rails, we have been able to fit the data over the full temperature range by using an analytical formula resulted from third-order perturbation theory.[9] Gu, Yu, and Shen[17] considered a dimer chain, in which the spin dimers are only weakly coupled, and calculated the perturbative corrections to the free energy due to the interactions of the dimers along the chain. From this expression for the free energy one can directly obtain the molar magnetic susceptibility in zero field (2). This expression reproduces with very high accuracy the quantum Monte Carlo simulations of Johnston *et al.*,[9] as long as the ratio $J/J'$ does not exceed 0.1.

$$\chi(T) = \frac{4C}{T}\left\{ \frac{1}{3+e^{2\beta}} - \frac{J}{J'}\left[\frac{2\beta}{(3+e^{\beta})^2}\right] - \left(\frac{J}{J'}\right)^2\left[\frac{3\beta(e^{2\beta}-1) - \beta^2(5+e^{2\beta})}{4(3+e^{\beta})^3}\right] - \left(\frac{J}{J'}\right)^3\left[\frac{3\beta(e^{2\beta}-1)}{8(3+e^{\beta})^3} - \frac{9\beta^2 e^{\beta}(1+3e^{\beta}) - \beta^3(7e^{2\beta}-9e^{\beta}-12)}{12(3+e^{\beta})^4}\right]\right\}, \tag{2}$$

where $C$ is the Curie constant for $Cu^{2+}$ ions

$$C = \frac{Ng^2\mu_B^2}{4k_B}, \tag{3}$$

and $\beta$ is the reduced temperature

$$\beta = \frac{k_B T}{J'}. \tag{4}$$

In addition to the expression (1) we have also allowed for a small paramagnetic impurity, to be determined from the fit:

$$\chi_{total}(T) = (1-x)\chi(T) + x\chi_{imp}, \tag{5}$$

where $x$ is the concentration of the paramagnetic $Cu^{2+}$ ions. The exchange constants resulted from fitting our experimental data in this way are $J' = 12.95$ K and $J = 0.75$ K. The small paramagnetic component can be attributed to a contribution from 0.62% of $Cu^{2+}$ ions due to lattice imperfections or impurity phases. The accuracy of the estimate of $J'$ and $J$ is affected by the strong correlation of the exchange parameters to the Curie constant.[9]

The intrinsic part of the susceptibility $\chi$ of our dimerlike ladder system is estimated by subtracting the paramagnetic component, and is plotted in Fig. 3 with open circles. The abrupt decrease of $\chi$ toward zero clearly suggests the presence of an energy gap in the spin excitation spectrum. This gap, for $J \ll J'$, can be directly evaluated from a strong-coupling series expansion[24]

$$\Delta = J' - J + \frac{J^2}{2J'} + \frac{J^3}{4J'^2} - \frac{J^4}{8J'^3} + \mathcal{O}(J^5); \tag{6}$$

for our system $\Delta = 12.23$ K.

According to a theoretical study of the two-leg Heisenberg ladder system,[25] if the continuum of the first excited states has a parabolic dispersion, and if magnon interactions

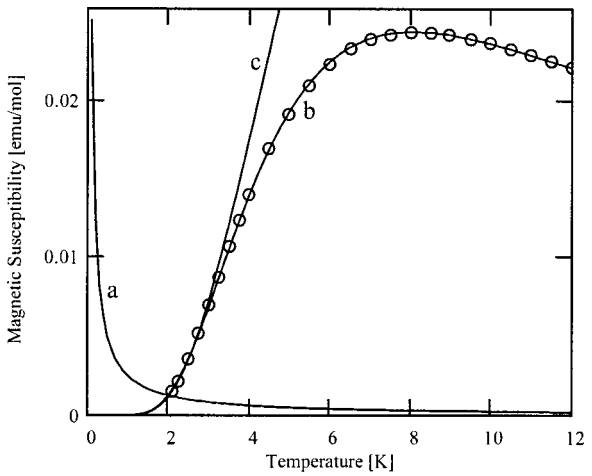


FIG. 3. Low-temperature behavior of the powder dc magnetic susceptibility for $(5IAP)_2CuBr_4 \cdot 2H_2O$. The circles are the experimental data from which we have subtracted the paramagnetic impurity contribution. This paramagnetic contribution is plotted as line (a). Line (b) is the perturbative expression (2), and line (c) is the low-temperature expression (7).

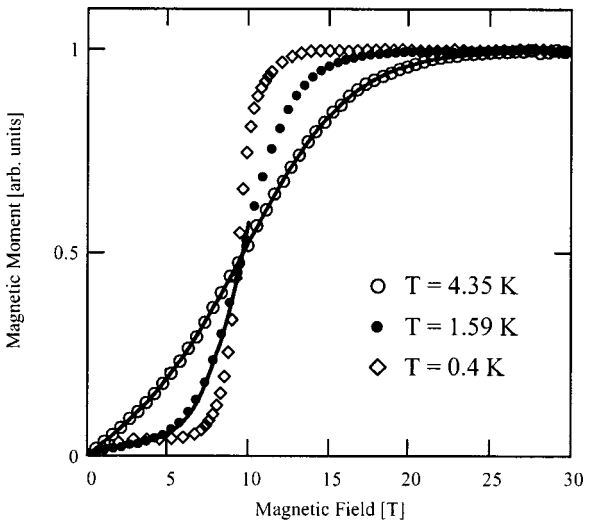


FIG. 4. High-field magnetization curve for different temperatures for $(5IAP)_2CuBr_4 \cdot 2H_2O$. $T=0.4$ K for the diamonds, $T=1.59$ K for the filled circles, and $T=4.35$ K for the open circles. Only representative points of the full data sets have been plotted. The black lines are theoretical predictions for $J'=12.99$ K, $J=1.15$ K, and $x=3.2\%$.

are ignored, at low enough temperatures $T \ll \Delta$ the magnetic susceptibility as a function of temperature should be

$$\chi(T) = \frac{\alpha}{\sqrt{T}} \exp\left(-\frac{\Delta}{T}\right), \tag{7}$$

where $\alpha$ is a constant corresponding to the dispersion of the excitation energy. As seen in Fig. 3 the solid line (c) calculated using $\Delta=12.23$ K and $\alpha=0.746$ $K^{1/2}$ emu/mol reproduces the experimental data rather well, and is indistinguishable from the curve given by Eq. (2) for temperatures up to 3.75 K, corresponding to $T/\Delta \leqslant 0.3$. Equation (7) can fit the susceptibility data for even higher temperatures, but the energy gap is not accurately obtained in this way.[7]

Due to the weak exchange constants involved, we have been able to fully saturate the magnetization of our sample in high magnetic fields. These measurements have been performed at the two facilities of the National High Magnetic Fields Laboratory. A sample of $(5IAP)_2CuBr_4 \cdot 2H_2O$ was studied in Tallahassee in dc fields up to 30 T, at temperatures of 4.35 and 1.59 K, and in Los Alamos in pulsed fields up to 50 T, cooled down to 0.4 K. The data are shown in Fig. 4. At low fields and at the lowest temperatures, the spin-ladder system is in the nonmagnetic singlet ground state, and the small moment observed is due only to the paramagnetic impurity phase. At the lower critical field $H_{c1}$ the gap is closed, and the magnetization increases almost linearly with field up to the second critical field $H_{c2}$, where the system is saturated. At the higher temperature $T=4.35$ K the critical fields are less evident, due to thermal population of the excited states.

An expression for the magnetization of a ladder as a function of temperature and magnetic field has been obtained from the free energy[17] previously mentioned. The perturbation series for the magnetization involves powers of $J/J'$ and $J/k_BT$. For good convergence of the series, we should have $J \ll k_BT$. The magnetic field enters the magnetization expression as the exponent $ng\mu_BB/k_BT$, where $n$ is an integer, increasing with the order of perturbation. Consequently, the calculated expression of the magnetization departs from the experimental data for low temperatures ($T=1.59$ K) and high magnetic fields ($B>10$ T), due to poor convergence of the series. For the data set at the higher temperature $T=4.35$ K, the calculated and the experimental magnetization agree well for the full magnetic field range.

We need only three parameters to reproduce the reduced magnetization $M/M_{sat}$. These parameters are $J$, $J'$, and the percentage of paramagnetic spins. Because a 1/2 spin ladder has a gap in the energy spectrum, at very low temperatures and magnetic fields the system will be in the singlet ground state with no magnetic moment. The only contribution to the magnetization will come from the paramagnetic impurities. This contribution is clearly identified for the $T=0.4$ K and $T=1.59$ K data at low fields. The two exchange constants and the impurity percentage have been extracted from a fit of the $T=4.35$ K data to the calculated magnetization, and the values obtained are $J'=12.99$ K and $J=1.15$ K, corresponding to a gap of $\Delta=11.90$ K. The concentration of the paramagnetic spins extracted from the magnetization fit is 3.2% of the $Cu^{2+}$ ions. The higher value is justified by the fact that we have used a different sample than in the susceptibility measurements. The purer batch has been obtained by a slower growth, minimizing the concentration of impurities.

The magnetization fit, unlike the susceptibility fit, is not affected by uncertainties in the nature of the impurities. This is most clearly seen from the analysis of the two critical fields $H_{c1}$ and $H_{c2}$.[13,26] At the lowest temperature (0.4 K) the magnetization of the spin ladder is close to zero up to the lower critical field $H_{c1}$ where the energy gap is closed by the magnetic field. If one assumes that the first excited states are triplets, then $\mu_oH_{c1}=\Delta/(g\mu_B) \approx (J'-J)/(g\mu_B)=8.39$ T.

The ground state is fully aligned above the higher critical field $\mu_o H_{c2} = (J' + 2J)/(g\mu_B) = 10.83$ T, where the magnetization reaches its saturation value. The critical fields determined from the $T = 0.4$ K data are $\mu_o H_{c1} \approx 8.3$ T and $\mu_o H_{c2} \approx 10.4$ T. The magnetization increases almost linearly between $H_{c1}$ and $H_{c2}$. The exchange constants are unambiguously linked to the position and slope of this domain in which the magnetization increases almost linearly.

In summary, $(5\mathrm{IAP})_2\mathrm{CuBr}_4 \cdot 2\mathrm{H}_2\mathrm{O}$ has been shown to behave as a $S = 1/2$ antiferromagnetic ladder with a dominant rung interaction $J' = 13.0(1)$ K and a rail interaction $J = 1.0(2)$ K. The ratio $J/J' = (7.7 \pm 1.5)\%$ is about 40% of the value found for $\mathrm{Cu}_2(\mathrm{C}_5\mathrm{H}_{12}\mathrm{N}_2)_2\mathrm{Cl}_4$.[13] The two critical fields near 8.3 and 10.4 T are within the range of common superconducting magnets, and hence it will be possible to examine the behavior of this quantum system when the gap has been closed ($H > H_{c1}$), as has been recently done for $\mathrm{Cu}_2(\mathrm{C}_5\mathrm{H}_{12}\mathrm{N}_2)_2\mathrm{Cl}_4$.[26–28]

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