Magnetic Properties of the Novel Low-Dimensional Cuprate Na₅RbCu₄(AsO₄)₄Cl₂

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The magnetic properties of a new compound, Na₅RbCu₄(AsO₄)₄Cl₂, are reported. The material has a layered structure comprised of square Cu₄O₄ tetramers. The Cu ions are divalent and the system behaves as a low-dimensional S=1/2 antiferromagnet. Spin exchange in Na₅RbCu₄(AsO₄)₄Cl₂ appears to be quasi-two-dimensional and non-frustrated. Measurements of the bulk magnetic susceptibility and heat capacity are consistent with low-dimensional magnetism. The compound has an interesting, low-entropy, magnetic transition at T = 17 K.

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Introduction

The occurrence of high-temperature superconductivity in doped spin-1/2 square planar antiferromagnets has stimulated the quest for new families of low-dimensional magnetic materials. We have studied and report here the first results from a new compound, Na₅RbCu₄(AsO₄)₄Cl₂, whose spin exchange interactions are confined to two-dimensional layers. Na₅RbCu₄(AsO₄)₄Cl₂ is a nearly-tetragonal insulating magnetic material with a remarkable crystal structure. It is a two-dimensional, layered compound with a square-planar arrangement of copper and oxygen ions. The copper valence state is 2+, so the Cu ions are magnetic with spin 1/2. The copper and oxygen ions form square tetramer units, Cu₄O₄, which are connected by the AsO₄ bridging units to form nearly-tetragonal two-dimensional layers, as illustrated in Fig. 1. Thus the spin exchange of Na₅RbCu₄(AsO₄)₄Cl₂ is expected to be essentially two-dimensional in nature (see below for details).

Experiment

Single-crystals of Na₅RbCu₄(AsO₄)₄Cl₂ were synthesized by conventional solid state reaction using molten-salt methods. Details of the synthesis are reported elsewhere. The crystals are transparent, blue and plate-like. Typical crystal dimensions are 1 mm × 1 mm × 200 µm. The crystal structure was determined by employing single-crystal X-ray diffraction techniques.

The materials were characterized by specific heat and magnetization measurements. Special care was required for these measurements because of the small size of the sample materials. We used a Quantum Design SQUID magnetometer for the magnetization studies and were careful to first measure an empty sample holder—with mounting grease—each time before affixing the sample. Even with the largest sample (2 mm × 2.3 mm × 500 µm) of Na₅RbCu₄(AsO₄)₄Cl₂, the diamagnetic background signal from the tiny amount of silicone vacuum grease was nearly 20% of the measured signal, necessitating
the careful subtraction. Nevertheless, it was possible to determine the anisotropy of the magnetization with good precision.

The specific heat measurements presented an even greater challenge. The largest crystals weigh only 3 milligrams and have a total heat capacity of only 25 \( \mu \text{J/K} \) at \( T = 15 \text{ K} \). Nevertheless, we have constructed a calorimeter capable of resolving bulk heat capacities to a resolution of nearly 100 nanoJoules-per-Kelvin. With this apparatus, it was possible to measure single-crystal samples.

Susceptibility data for \( \text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2 \) are shown in Fig. 2. The measurements were carried out with the magnetic field applied along different symmetry axes of the crystal. The magnetic susceptibility is slightly higher when the magnetic field is applied along the a- or c-directions than along the b-direction. No hysteresis was detected at any temperature. Above \( T = 100 \text{ K} \), it follows a Curie-Weiss law with an antiferromagnetic Curie-Weiss temperature of -86 K with \( g = 1.97 \), consistent with crystal-field quenching of the orbital angular momentum. At \( T = 50 \text{ K} \), the susceptibility reaches a broad maximum before decreasing at lower temperatures. The solid curve shows a qualitative fit to a high-temperature series expansion[2, 3] for the magnetic susceptibility of the uniform two-dimensional nearest-neighbor Heisenberg model, yielding an effective single value for the magnetic coupling, \( J = 4.77 \text{ meV} \).

The susceptibility data shows a phase transition at \( T = 17 \text{ K} \). As shown in the inset to Fig. 2, the susceptibility drops by approximately 30 to 40 \% at the transition temperature and becomes much more anisotropic. Below the transition, the susceptibility is smallest when measured with the magnetic field aligned perpendicular to the layers of the crystal. It seems likely that the magnetic transition upon cooling through 17 K involves the onset of antiferromagnetic order.

Specific heat measurements taken on single crystals of \( \text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2 \) are shown in Fig. 3. From these data, we find a Debye temperature of 320 K. We also observed a second-order phase transition at \( T = 17 \text{ K} \) as seen clearly in the inset to Fig. 3. The transition temperature seen in the specific heat corresponds to the temperature at which we observe the phase transition in the magnetic susceptibility. We also find that the entropy loss per spin upon cooling through the transition amounts to only a small fraction, less than 10 \%, of the total free spin entropy, \( R \ln 2 \), per \( \text{Cu}^{2+} \).

We performed a careful search for a phase transition, magnetic or otherwise, between 20 K and room temperature using ac calorimetry. No transition was found. Additionally, the susceptibility was measured at \( T = 4.2 \text{ K} \) in magnetic fields up to 33 T using a cantilever susceptometer to detect metamagnetic or spin-flop transitions at the National High Magnetic Field Laboratory. No field-induced transitions were found.

**Discussion**

Because of its layered structure, the magnetic properties of \( \text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2 \) should be governed primarily by the spin exchange interactions between neighboring \( \text{Cu}^{2+} \) ions within the same \( \text{Cu}_4(\text{AsO}_4)_4 \) layer. Spin exchange between the layers of the compound should be very small because the interlayer O–O distances are long.
tetramers are connected by AsO$_4$ bonds, causing the intratetramer superexchange couplings to be much smaller than in cuprates having straight, 180° Cu–O–Cu bonds.

There are two intra-tetramer coupling constants, $J_a$ and $J_c$, to consider because the a- and c-directions are not equivalent (see Fig. 4). As shown in Fig. 4, the Cu$_4$O$_4$ tetramer units are buckled. The Cu–O–Cu bonds are far from straight, the bond angle being 110.9° along the a-axis and 108.7° along the c-axis instead of 180°. This significantly reduces the strength of the superexchange coupling between adjacent copper ions, which can exceed 120 meV in compounds having colinear Cu–O–Cu bonds.

Significant inter-tetramer interactions are possible through the Cu–O–Cu super-exchange paths if the Cu–O–Cu bond distances are short. Analysis of the layer structure suggests that such super-exchange interactions should occur between adjacent tetramers along the in-plane diagonals. There are two inter-tetramer coupling constants, $J'_a$ and $J'_c$, to consider (see Fig. 4).

Values for the four different Heisenberg couplings can be estimated on the basis of spin dimer analysis of the bond angle being 110.9° along the a-axis and 108.7° along the c-axis instead of 180°. This significantly reduces the strength of the superexchange coupling between adjacent copper ions, which can exceed 120 meV in compounds having colinear Cu–O–Cu bonds.

Our calculations indicate that inter-tetramer interactions are as important as the intra-tetramer interactions. We found that the spin exchange interactions through other spin exchange paths are negligible. Thus the spin exchange interactions in Na$_5$RbCu$_4$(AsO$_4$)$_4$Cl$_2$ cannot be approximated by a model of weakly interacting tetramers. The calculations indicate that spin-exchange in Na$_5$RbCu$_4$(AsO$_4$)$_4$Cl$_2$ is quasi-two-dimensional and non-frustrated.

As described above, ac calorimetry confirmed the absence of any cooperative phase transition above 20 K. Only when the material was cooled below 17 K were the spins observed to order magnetically. This phase transition at 17 K has some peculiar features which appear to distinguish it from conventional antiferromagnetic transitions. The first is that the observed ordering temperature is much smaller, by a factor of five, than the measured Curie-Weiss temperature, $|\theta| = 86$ K. This is probably understandable because of the anisotropy of the spin-exchange in Na$_5$RbCu$_4$(AsO$_4$)$_4$Cl$_2$: the magnetic ordering necessarily involves the much weaker magnetic coupling along the b-direction.

We note that the total entropy involved in the second-order transition is smaller—by an order of magnitude—than is common for three-dimensional antiferromagnetic-ordering transitions. It is obvious that the transition does involve some sort of spin ordering because of its effects on the magnetic susceptibility (Fig. 3 inset), which means that the low entropy must be accounted for. The most likely explanation would be that much of the spin degeneracy had already been lifted at higher temperatures.

FIG. 4: Close-up view of a single Cu$_4$O$_4$ tetramer showing the bent Cu–O–Cu bonds. The bond angle is close to 110°, causing the intratetramer superexchange couplings to be much smaller than in cuprates having straight, 180° Cu–O–Cu bonds.

FIG. 5: Non-frustrated Heisenberg antiferromagnetic spin exchange interactions between neighboring Cu$^{2+}$ ions in the Cu$_4$(AsO$_4$)$_4$ layers of Na$_5$RbCu$_4$(AsO$_4$)$_4$Cl$_2$. The calculations indicate that spin-exchange couplings between adjacent tetramers.

orbitals by comparing a set of experimental $J$ values with the corresponding calculated $t^2$ values for Nd$_2$CuO$_4$ and La$_2$CuO$_4$. Thus from the hopping integrals calculated for the four exchange paths shown in Fig. 4, their spin-exchange coupling constants are estimated as follows: $J_a \approx 6$ meV, $J_c \approx 3$ meV, $J'_a \approx 6$ meV, and $J'_c \approx 5$ meV.
as the spin degrees of freedom develop low-dimensional correlations upon cooling below $T \approx J/k_B$.

In summary, $\text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2$ is a new layered cuprate antiferromagnet, in which spin exchange interactions are largely confined to well-separated layers. The bilinear, Heisenberg spin exchange interactions appear to be non-frustrated.

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