Two-dimensional tetramer-cuprate Na₅RbCu₄(AsO₄)₄Cl₂: phase transitions and AFM order as seen by $^{87}$Rb NMR

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Abstract

We report the $^{87}$Rb nuclear magnetic resonance (NMR) results in a recently synthesized Na₅RbCu₄(AsO₄)Cl₂ complex novel two-dimensional (2D) cuprate is a unique magnetic material, which contains layers of coupled Cu₄O₄ tetramers. In zero applied magnetic field, it orders antiferromagnetically via a second-order low-entropy phase transition at $T_N = 15(1)$ K. We characterise the ordered state by $^{87}$Rb NMR, and suggest for it a non-collinear rather than collinear arrangement of spins. We discuss the properties of Rb nuclear site and point out the new structural phase transition(s) around 74 K and 110 K.

Key words: tetramer, cuprate, NMR, antiferromagnetic order
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The occurrence of high-temperature superconductivity in doped spin-1/2 square planar antiferromagnets has stimulated the search for new families of low-dimensional magnetic materials. We have studied the compound Na₅RbCu₄(AsO₄)Cl₂, whose spin exchange interactions are confined to 2D layers. The compound has a layered structure comprised of square Cu₄O₄ tetramers [1]. The Cu ions are divalent and the system behaves as a low-dimensional $S = 1/2$ antiferromagnet. Spin exchange in Na₅RbCu₄(AsO₄)Cl₂ appears to be quasi-2D and nonfrustrated [2].

In this report we present $^{87}$Rb NMR results of the compound. The experiments are performed in $B_0 = 8.45$ T and 14.1T magnetic field in a temperature ($T$) range 4 K $< T < 300$ K. A single crystal of Na₅RbCu₄(AsO₄)Cl₂ (1 × 1 × 0.2 mm) was used.

The NMR spectra of $^{87}$Rb ($I = \frac{3}{2}$) central transition ($\pm \frac{1}{2} \leftrightarrow \mp \frac{1}{2}$) in Fig. 1(left) for the orientation of a crystal $B_0 \parallel b$ show a direct observation of the tran-

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The complicated double-horn line shape that the real magnetic structure of the compound is not simple at all. The transitions at 74 K and 110 K. The splitting of the line in $B_0 \perp b$ direction reflects a small anisotropy of $K$ in ac-plane. Below $T = 74$ K the resonance lines in both directions show remarkable distortions which we attribute to the change of a local symmetry at Rb site. A clear indication of a symmetry change is the discontinuity of the $T$-dependence of the quadrupolar coupling constant around that $T$ (Panel (b)). Since $\nu_Q$ describes local electric field gradient, it is highly sensitive to structural changes. The $T$-dependence of spin-lattice relaxation rate $T^{-1}_{1}$ of $^{87}$Rb central transition shows also a Néel temperature at $T_N=14.8$ K and a broad peak around $T^*=110$K for $B_0 \perp b$ (Panel (c)). Similar $T$-dependence of $T^{-1}_{1}$ was measured in 14.1 T field. The relaxation is caused by local fluctuating magnetic fields that have to be aligned perpendicular to the applied field to see the transitions. The same location of the maximum at 110 K in both fields suggests strongly that not the fluctuation spectrum but the crystal structure is changing at this $T$. We do not know the resulting low-$T$ crystal structure in details yet, but the new structure may have crucial implications for the distinct magnetic order below $T_N$.

In conclusion, using $^{87}$Rb NMR we have shown the antiferromagnetic ordering and two high-$T$ phase transitions in Na$_3$RbCu$_4$(AsO$_4$)Cl$_2$. The studies to clarify the nature of those phase transitions using NMR of $^{23}$Na, $^{35}$Cl, and $^{63,65}$Cu are currently in progress.

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References
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