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NMR study of low dimensional spin system $Cu_2(PO_3)_2CH_2$

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Abstract

The low dimensional spin system $Cu_2(PO_3)_2CH_2$ has been investigated by means of NMR spectroscopy. ^{31}P NMR measurements were performed in the temperature range 2–200 K. Above $T_c \sim 10$ K the ^{31}P NMR spectra consist of two distinct peaks which coincides with two non equivalent crystallographic P sites. Below 10 K a convergence of both peaks is observed. The chemical shift tends to approach the constant value at $T \to 0$ evidencing for the gap formation in the magnetic excitation spectrum. These results are analyzed in frames of both alternating spin chain and dimer models.
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Keywords: NMR; Low dimensional magnetism; Spin gap

1. Introduction

Quasi one-dimensional spin 1/2 systems with different mechanisms of ground state formation provide the opportunity to understand the interplay between the lattice features and spin, orbital and charge degrees of freedom [1–3]. The crystal structure of the recently discovered spin 1/2 compound $Cu_2(PO_3)_2CH_2$ [4] contains pairs of isolated edge-shared CuO_4 plaquettes connected with each other by PO_4 pyramids (Fig. 1). From the crystallographic point of view, this compound could be considered either as an alternating spin chain or as a dimer system. To provide a more detailed analysis of its ground state properties, we performed the NMR investigations.

2. Experimental

The single phase powder sample $Cu_2(PO_3)_2CH_2$ was prepared from the aqueous solution of $Cu(CH_3COO)_2$-H_2O, H_3BO_3 and methylenediphonic acid with molar ratio of 2:1:2 via hydrothermal process. The crystal structure was determined by X-ray diffraction as the orthorhombic Pnma group with the lattice constants $a = 13.696(2)$ Å, $b = 8.0103(13)$ Å and $c = 4.9034(7)$ Å.

The NMR measurements were performed with the conventional pulsed NMR spectrometer (Tecmag Apollo) in the temperature range 1.8–200 K. ^{31}P NMR spectra were obtained by the Fourier transformation of a half of the spin-echo in an external magnetic field of 4.093 T.

3. Results and discussion

Above $T_c \sim 10$ K the ^{31}P NMR spectra consist of two distinct peaks and were approximated by Gaussian lines with almost equal integral intensity. This coincides with two crystallographic P sites with the same occupation factor. Below 10 K both peaks become undistinguishable (Fig. 2). The two peaks of the ^{31}P NMR spectrum have the same temperature dependence of the line shift. The frequency line shift K as a function of temperature for the right line is shown in Fig. 3. Since the temperature dependent component of the line shift is proportional to the spin

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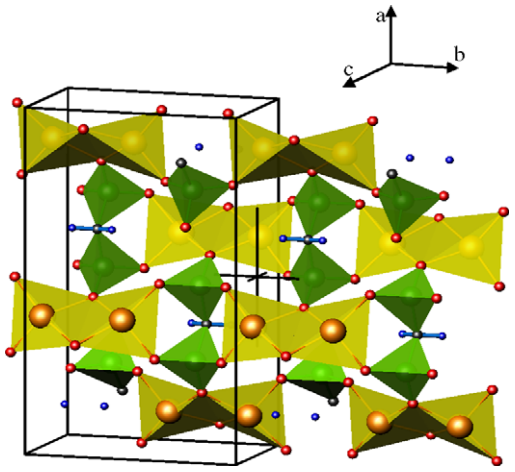

Fig. 1. Crystal structure of $Cu_2(PO_3)_2CH_2$.

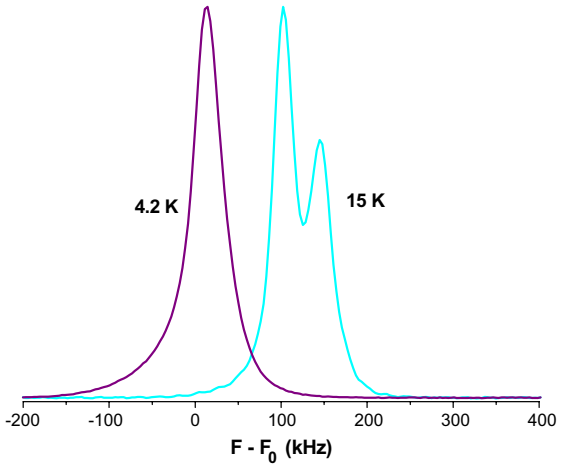

Fig. 2. ^{31}P NMR spectra at 4.2 and 15 K in $Cu_2(PO_3)_2CH_2$. The reference frequency $F_0 = 70.0$ MHz.

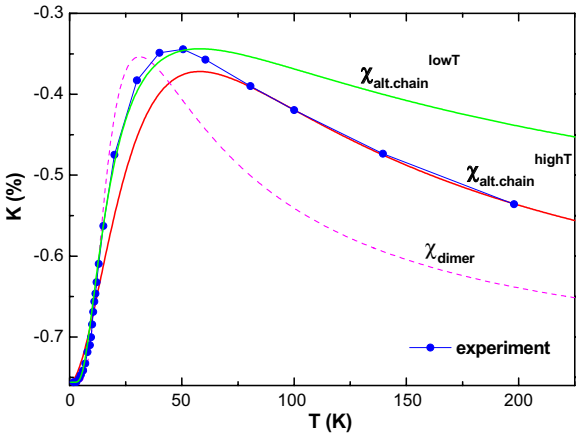

Fig. 3. Temperature dependence of the line shift K of the right ^{31}P NMR line. The best fits for the dimer model (dot line) and alternating spin chain model (solid lines) are shown.

part of the susceptibility, it enables us to avoid the impurity upturn observed at low temperatures in magnetic susceptibility measurements. The $K(T)$ dependence is typical for low dimensional systems, exhibiting broad maxima at 40–50 K and rapid decrease at low temperatures. Such behaviour is a clear evidence for a singlet ground state with a gap in the magnetic excitation spectrum. The formation of a singlet ground state depends on the hierarchy of exchange interactions and chain topology. The spin gap in the magnetic excitation spectrum could be the consequence of next-nearest-neighbour (NNN) exchange interaction in the uniform spin chain as well as the alternation of the exchange interaction. From crystallographic point of view, the alternation of the exchange interaction scenario is more preferable.

The fitting procedure of the $K(T)$ dependence was performed by the following models: dimer spin system and alternating spin chain interaction [5]. The fitting according to dimer model showed systematic deviation from the experimental data (Fig. 3). Since for alternated spin chain model there is no uniform equation for the magnetic susceptibility in entire temperature range, the low and high temperature limits were used. The values of exchange interaction $J_1 = 85$ K and alternating parameter $\alpha = J_2/J_1 = 0.95$ were obtained from the high temperature approximation. From low temperature fitting the gap value of $\Delta = 28$ K was extracted. It is worth to note, that α is close to 1 (uniform spin 1/2 Heisenberg chain) that means the interaction between nearest Cu atoms and interaction between Cu via P are very similar. Moreover, relatively low gap value provides evidence that the gap is reduced due to frustration effects caused by competing exchange interactions.

In conclusion, singlet ground state was observed in $Cu_2(PO_3)_2CH_2$. Based on crystallographic data and experimental results, the spin gap formation is caused by alternated spin chain interaction and frustration effects.

Acknowledgements

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