\textbf{$^{31}$P NMR study of Na$_2$CuP$_2$O$_7$: a $S = 1/2$ two-dimensional Heisenberg antiferromagnetic system}

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Abstract

The magnetic properties of Na$_2$CuP$_2$O$_7$ were investigated by means of $^{31}$P nuclear magnetic resonance (NMR), magnetic susceptibility, and heat capacity measurements. We report the $^{31}$P NMR shift, the spin-lattice ($1/T_1$), and spin-spin ($1/T_2$) relaxation-rate data as a function of temperature $T$. The temperature dependence of the NMR shift $K(T)$ is well described by the $S = 1/2$ square lattice Heisenberg antiferromagnetic (HAF) model with an intraplanar exchange of $J/k_B \simeq (18 \pm 2)$ K and a hyperfine coupling $A = (3533 \pm 185)$ Oe/$\mu_B$. The $^{31}$P NMR spectrum was found to broaden abruptly below $T \sim 10$ K signifying some kind of transition. However, no anomaly was noticed in the bulk susceptibility data down to 1.8 K. The heat capacity appears to have a weak maximum around 10 K. With decrease in temperatures, the spin-lattice relaxation rate $1/T_1$ decreases monotonically and appears to agree well with the high temperature series expansion expression for a $S = 1/2$ 2D square lattice.

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I. INTRODUCTION

Low-dimensional spin systems with antiferromagnetic interactions have received considerable attention because of pronounced quantum mechanical effects which result in magnetic properties which are quite different from those of the three-dimensional (3D) antiferromagnetic substances. According to the Hohenberg-Mermin-Wagner theorem, one-dimensional (1D) and two-dimensional (2D) spin systems with Heisenberg interaction and finite-range coupling between spins cannot have long-range order (LRO) at any temperature different from zero. In 1D systems it does not occur even at zero temperature. However for 2D systems at zero temperature, LRO is not forbidden by this theorem. In fact, LRO has been rigorously established for spin $S > 1/2$, on a square lattice with nearest-neighbor coupling. For the case of $S = 1/2$, there is no solid proof but there are strong theoretical arguments that LRO exists.

The case of a $S = 1/2$ system on a square lattice, with nearest-neighbor antiferromagnetic coupling, has been of special interest because of its proximity to the high-$T_c$ cuprates. The interest in quasi-1D spin systems has been stimulated by the hope that better understanding of 1D systems might lead to insights into the 2D systems and high-temperature superconductivity.

So far, a large number of $S = 1/2$ compounds have been experimentally investigated, which could effectively be described by 2D HAF models. Among the important ones are cuprate compounds such as La$_2$CuO$_4$ and YBa$_2$Cu$_3$O$_6$ which have CuO planes. In La$_2$CuO$_4$, the intraplanar exchange coupling $J/k_B$ was reported to be 1800 K. In spite of a small interplanar coupling $J' \approx 10^{-5}J$, the large correlations in CuO planes lead to 3D magnetic order at the Néel temperature $T_N \sim 300$ K. In the above cases $T_N$ is strongly dependent on $J'/J$ ratio.

Most recently, KCuF$_3$ has been experimentally investigated as one of the quasi-1D HAF compounds. Unfortunately, this material has a relatively large coupling ratio $J'/J \sim 1.0 \times 10^{-2}$, due to which, the $T_N/J$ ratio ($\sim 39$ K/203 K) was found to be large. Later Sr$_2$CuO$_3$ was reported to be another 1D HAF system with a significantly reduced $T_N/J$ ratio of $\sim 5$ K/2200 K $\sim 2 \times 10^{-3}$. Due to the relatively small $T_N$ value compared to the exchange coupling $J/k_B$, 1D behavior is observed over a wide range of temperature. Recently, Nath et al. have reported that Sr$_2$Cu(PO$_4$)$_2$ and Ba$_2$Cu(PO$_4$)$_2$ are two 1D HAF
systems, which do not appear to undergo Néel ordering even at a very low temperature ($T \sim 0.02$ K). Their exchange coupling constants have been reported to be 165 K, and 151 K respectively. It is thus of interest to synthesize and characterize additional $S = 1/2$ 1D or 2D HAF compounds to improve our understanding of such systems. In this paper, we present a detailed study of the magnetic properties of Na$_2$CuP$_2$O$_7$ via susceptibility and $^{31}$P nuclear magnetic resonance (NMR) experiments. Our objective is to report detailed magnetic measurements on a new potentially low-dimensional system and to analyse the data based on available models. An additional objective is then to motivate the theorists to model real (and more complex) systems as the ones we report and compare the result of their simulations with our data. Our results indicate that the magnetic properties of Na$_2$CuP$_2$O$_7$ are consistent with the 2D square-lattice $S = 1/2$ HAF model somewhat better than the 1D model. In the next section, an overview of the schematic structure is presented which motivated us to work on this system. This is followed by details of our experiments. The "experimental details" section is followed by results of our magnetic and heat capacity measurements accompanied by an analysis and a conclusion.

II. STRUCTURE

The structural properties of Na$_2$CuP$_2$O$_7$ have been reported by Etheredge et al. and Erragh et al. It (the high-temperature phase) crystallizes in a monoclinic unit cell with space group C$_2$/c. The reported lattice constants are 14.715 Å, 5.704 Å, and 8.066 Å respectively along $a$-, $b$- and $c$- directions. From the schematic diagram of the structure shown in Fig. 1 (a) and (b), it is seen that the exchange interaction between Cu$^{2+}$ ions could arise due to two interaction paths: (i) each CuO$_6$ octahedron shares its corners with two similar kinds of PO$_4$ groups. The corner sharing takes place in one direction forming [Cu(PO$_4$)$_2$]$_\infty$ chains along the $c$-direction and in this case the magnetic properties would be those of a 1D HAF chain. (ii) alternatively, there exist (nearly) 180° Cu-O-Cu linkages in the $bc$ plane. Depending on the orientation of the $d_{x^2-y^2}$ orbitals (i.e. whether perpendicular to the $bc$ plane or in the $bc$ plane), the system will behave either as a chain-like or a planar magnetic system. In the latter case however, one should note that the Cu$^{2+}$ ions are arranged in a face centered manner (see Fig. 1(b)). One can, therefore, think of the $bc$ plane as comprising of two sub-planes (shown in Fig. 1(b) by thick and thin lines). While the Cu$_1$–O–Cu$_1$
(or Cu$_2$–O–Cu$_2$) bond angle is almost 180°, the Cu$_1$–O–Cu$_2$ bond angle is somewhat less than 90°. The deviation of the magnetic properties of Na$_2$CuP$_2$O$_7$ from the square planar case would depend on the relative strength of the Cu$_1$–O–Cu$_2$ interaction with respect to that of the Cu$_1$–O–Cu$_1$ (or Cu$_2$–O–Cu$_2$) interaction. Further, the interaction between the $bc$ planes is expected to be weak since the distance between them is about 8 Å which is nearly twice the Cu$^{2+}$–Cu$^{2+}$ intraplanar distance of 4 Å. Also, unlike the 180° Cu$_1$–O–Cu$_1$ intraplanar bonds, there appear to be no similar interaction paths perpendicular to the $bc$ plane.

III. EXPERIMENTAL DETAILS

Polycrystalline sample of Na$_2$CuP$_2$O$_7$ was prepared by solid state reaction technique using NaH$_2$PO$_4$.H$_2$O (98% pure) and CuO (99.99% pure) as starting materials. The stoichiometric mixtures were fired at 800 °C for 120 hours, in air, with several intermediate grindings and pelletization. Formation of nearly single phase sample was confirmed from x-ray diffraction, which was performed with a Philips Xpert-Pro powder diffractometer. A Cu target was used in the diffractometer with $\lambda_{av} = 1.54182$ Å. An impurity phase was identified to be Na$_3$P$_3$O$_9$ and the intensity ratio ($I_{imp}/I_{max}$) was found to be 0.05, where $I_{imp}$ is the intensity of the most intense diffraction peak for Na$_3$P$_3$O$_9$ and $I_{max}$ is that of Na$_2$CuP$_2$O$_7$. Lattice parameters were calculated using a least-square fit procedure. The obtained lattice constants are 14.703 (4) Å, 5.699 (2) Å, and 8.061 (3) Å, respectively along $a$-, $b$- and $c$-directions. These are in agreement with previously reported values. Magnetization ($M$) data were measured as a function of temperature $T$ (1.8 K $\leq T \leq$ 400 K) and applied field $H$ (0 $\leq H \leq$ 50 kG) using a SQUID magnetometer (Quantum Design). The heat capacity was measured with a PPMS set-up (Quantum Design). The NMR measurements were carried out using pulsed NMR techniques on $^{31}$P nuclei (nuclear spin $I = 1/2$ and gyromagnetic ratio $\gamma/2\pi = 17.237$ MHz/Tesla) in a temperature range 2 K $\leq T \leq$ 300 K using a $^4$He cryostat (Oxford Instruments). We have done the measurements in an applied field of about 55 kG, which corresponds to a radio frequency (rf) of about 95 MHz. Spectra were obtained by plotting the echo integral (following a $\pi/2 - \pi$ pulse sequence with a $\pi/2$ pulse of width 4 μs) as a function of the field at a constant frequency of 95 MHz. The NMR shift $K(T) = [H_{ref} - H(T)]/H(T)$ was determined by measuring the resonance field.
of the sample \((H(T))\) with respect to a reference \(H_3\text{PO}_4\) solution (resonance field \(H_{\text{ref}}\)). The \(^{31}\text{P}\) nuclear spin-lattice relaxation rate \((1/T_1)\) was determined by the inversion-recovery method. Nuclear spin-spin relaxation rate \((1/T_2)\) was obtained by measuring the decay of the transverse nuclear magnetization with a variable spacing between the \(\pi/2\) and the \(\pi\) pulse.

VI. RESULTS AND DISCUSSION

We first present the results of our \(^{31}\text{P}\) NMR measurements in \(\text{Na}_2\text{CuP}_2\text{O}_7\). Since there is a unique \(^{31}\text{P}\) site, the \(^{31}\text{P}\) NMR spectra consist of a single spectral line at high temperatures \((T \geq 5 \text{ K})\) as is expected for \(I = 1/2\) nuclei. The observed peak position shifts with respect to \(H_{\text{ref}}\) in the field-sweep spectra. The temperature dependence of the \(^{31}\text{P}\) NMR shift apparently arises due to the temperature dependence of the spin susceptibility \(\chi_{\text{spin}}(T)\) via a hyperfine coupling to the \(\text{Cu}^{2+}\) ions. The NMR shift is not affected by small amounts of extrinsic paramagnetic impurities whereas in the bulk susceptibility they give rise to Curie terms. NMR shift data as a function of temperature are shown in Fig. 2, for \(5 \text{ K} \leq T \leq 300 \text{ K}\). They exhibit a broad maximum at 20 K, indicative of short-range ordering. As explained earlier, the dominant magnetic behavior of \(\text{Na}_2\text{CuP}_2\text{O}_7\) could be that of a HAF chain or a plane. Consequently, we tested both the 2D (planar) and 1D (chain) models to fit the NMR shift data. A high temperature \((\frac{k_B T}{J} \gtrsim 0.7)\) series expansion for the inverse susceptibility \(1/\chi_{\text{spin}}(T)\) for 2D \(S = 1/2\) HAF square lattice was given by Rushbrooke and Wood\(^{15}\), which has the form,

\[
\frac{1}{\chi_{\text{spin}}(T)} = \frac{J}{N_A \mu_B^2 g^2} \left[ 4x + \sum_{n=1}^{6} \frac{C_n}{(\frac{4}{3}x)^{n-1}} \right]
\]

(1)

where \(x = \frac{k_B T}{J}\), \(g\) is the Landé \(g\)-factor, \(\mu_B\) is the Bohr magneton, \(N_A\) is the Avogadro number, and \(C_n\) are the coefficients listed in Table 1 of Ref. 13. Similarly Johnston\(^{16}\) parametrized the low-temperature \((\frac{k_B T}{J} \leq 1)\) simulations of Takahashi\(^{17}\) and Makivic and Ding\(^{18}\) to obtain

\[
\chi_{\text{spin}}(T) = \frac{N_A \mu_B^2 g^2}{J} \left[ 0.043669 + 0.039566x - 0.5341x^3 + 4.684x^4 - 11.13x^5 + 10.55x^6 - 3.56x^7 \right]
\]

(2)

For 1D HAF chains, the temperature dependence of the susceptibility \(\chi_{\text{spin}}(T)\) was numerically calculated by Bonner and Fisher\(^{19}\) which accurately predicts the susceptibility for high
temperatures \( (\frac{J}{k_B}T \geq 0.5) \). Below, we use the form as given by Estes et al.\textsuperscript{20}.

\[
\chi_{\text{spin}}(T) = \frac{Ng^2\mu_B^2}{k_Bx} \times \frac{(0.25 + 0.074975x^{-1} + 0.075235x^{-2})}{(1 + 0.9931x^{-1} + 0.172135x^{-2} + 0.757825x^{-3})} \tag{3}
\]

Since the temperature dependence of the \( \chi_{\text{spin}}(T) \) is reflected in the NMR shift \( K(T) \), one can determine the exchange coupling \( J/k_B \) and the hyperfine interaction \( A \) simultaneously by fitting the temperature dependence of \( K \) to the following equation,

\[
K(T) = K_0 + \left( \frac{A}{N_A\mu_B} \right) \chi_{\text{spin}}(T) \tag{4}
\]

where \( K_0 \) is the chemical shift. Figs. 2 and 3 show fitting of the \(^{31}\)P NMR shift data to Eq. 4 taking \( \chi_{\text{spin}} \) for HAF square lattice (Eq. 1) and linear chain (Eq. 3) respectively. In Fig. 2, the fitting to the 2D high-temperature series expansion was done for \( 15 \text{K} \leq T \leq 300 \text{K} \) whereas in Fig. 3, the experimental data were fitted to the linear chain model in the temperature range \( 5 \text{K} \leq T \leq 300 \text{K} \). The parameters extracted from the fit are listed in Table I. The Landé \( g \)-value was found to be \( g = 2.1 \), which is a typical value for cuprates.

**TABLE I:** Values of the parameters obtained from the fitting of NMR shift to Eq. 4 considering 2D square planar HAF (Eq. 1) and 1D HAF (Eq. 3) models.

<table>
<thead>
<tr>
<th></th>
<th>( K_0 ) (ppm)</th>
<th>( A ) (Oe/( \mu_B ))</th>
<th>( \frac{J}{k_B} ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. 2</td>
<td>100 ± 50</td>
<td>3533 ± 185</td>
<td>18 ± 2</td>
</tr>
<tr>
<td>Fig. 3</td>
<td>143 ± 60</td>
<td>3479 ± 200</td>
<td>28 ± 5</td>
</tr>
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</table>

From Figs. 2 and 3 it is seen that our \( K(T) \) data fit somewhat better to the 2D HAF model. At low temperature \( (T \leq 25 \text{K}) \), the 1D fit deviates from the experimental data. In Fig. 2, we have also plotted the simulated low temperature curve using Eqs. 2 and 4 with the parameters \( K_0, A, \) and \( J/k_B \) obtained from the high temperature fit along with our experimental data. It is clearly seen that our experimental data do not deviate significantly from the simulated curve down to \( T \sim 10 \text{K} \) while a large deviation is seen below 10 K. This suggests some transition or crossover below 10 K.

An observation of the \(^{31}\)P NMR lineshapes below 10 K (shown in Fig. 4) reveals a huge broadening at lower temperatures. Further, the lineshape develops shoulder-like features and finally at 2 K the overall extent of the spectrum is about five times that at 10 K, with
at least three distinct peaks. Either a structural or a magnetic transition might be the cause for this. No anomaly is seen in the bulk susceptibility (see below) which seems to suggest against the occurrence of 3D LRO.

Magnetic susceptibility $\chi(T) = M/H$ of Na$_2$CuP$_2$O$_7$ was measured as a function of temperature in an applied field of 5 kG (Fig. 5). The amount of ferromagnetic impurity present in our sample was estimated from the intercept of $M$ vs. $H$ isotherms at various temperatures and was found to be 19 ppm of ferromagnetic Fe$^{3+}$ ions. The data in Fig. 5 have been corrected for these ferromagnetic impurities. As shown in the figure, $\chi(T)$ exhibit a broad maximum at 20 K, indicative of low-dimensional magnetic interactions. With a further decrease in temperature, susceptibility increases in a Curie-Weiss manner. This possibly comes from defects and extrinsic paramagnetic impurities present in the samples. No obvious features associated with LRO are seen for 1.8 K $\leq T \leq$ 400 K.

The broad maximum in $\chi(T)$ at 20 K could be reproduced by assuming that

$$\chi = \chi_0 + \frac{C}{T + \theta} + \chi_{\text{spin}}(T)$$  \hspace{1cm} (5)

where $\chi_{\text{spin}}(T)$ is the uniform spin susceptibility for a $S = 1/2$ 2D HAF system obtained from Eq. 4 $\chi_0$ is temperature independent and consists of diamagnetism of the core electron shells ($\chi_{\text{core}}$) and Van-Vleck paramagnetism($\chi_{\text{vv}}$) of the open shells of the Cu$^{2+}$ ions present in the sample. The Curie-Weiss contribution is $\frac{C}{T + \theta}$ (where $C = \frac{Ng^2\mu_B^2S(S+1)}{3k_B}$) due to paramagnetic species in the sample. The parameters were determined by fitting our experimental $\chi(T)$ data to Eq. 4 in the high temperature regime 15 K $\leq T \leq$ 400 K. The extracted parameters are $\chi_0 = (-7 \pm 2) \times 10^{-5}$ cm$^3$/mole, $C = (13 \pm 3) \times 10^{-3}$ cm$^3$/mole, $\theta = 1.7$ K, $\frac{C}{k_B} = (18 \pm 2)$ K, and $g = 2.07$. Adding the core diamagnetic susceptibility for the individual ions$^{21}$ (Na$^{1+}$ = $-5 \times 10^{-6}$ cm$^3$/mole, Cu$^{2+}$ = $-11 \times 10^{-6}$ cm$^3$/mole, P$^{5+}$ = $-1 \times 10^{-6}$ cm$^3$/mole, O$^{2-}$ = $-12 \times 10^{-6}$ cm$^3$/mole), the total $\chi_{\text{core}}$ was calculated to be $-1.07 \times 10^{-4}$ cm$^3$/mole. The Van-Vleck paramagnetic susceptibility estimated by subtracting $\chi_{\text{core}}$ from $\chi_0$ is about $3.7 \times 10^{-5}$ cm$^3$/mole, which is comparable to that found in Sr$_2$CuO$_3$ ($\sim 3.4 \times 10^{-5}$ cm$^3$/mole)$^{14}$. The Curie contributions present in the sample corresponds to a defect spin concentration of 3.5 % assuming defect spin $S = 1/2$.

Further, we did heat capacity measurements on Na$_2$CuP$_2$O$_7$ to look for signs of any anomalies at low temperature, signaling a magnetic transition. As seen in the data (Fig. 6), no sharp peaks are visible which seems to rule out LRO. However, a look at the
derivative of the specific heat as a function of temperature (see inset of Fig. 6) clearly shows a local maximum at about 7 K and a local minimum around 10 K. This suggests that the specific heat has an anomaly/peak between 7 K and 10 K. In the 2D HAF model, a broad maximum in the heat capacity is expected at about $T = 0.58J/k_B^{18}$ (i.e. at about 10 K in the present case) whereas in the 1D HAF model, a broad maximum is expected at about $T = 0.48J/k_B^{23}$ (i.e. at about 16 K in the present case). This further suggests the applicability of the 2D HAF model in the present case.

The time dependence of the longitudinal nuclear magnetization $M(t)$ for $^{31}$P at three different temperatures is shown in the inset of Fig. 7. For a spin-1/2 nucleus this recovery is expected to follow a single exponential behavior,

$$\frac{M(\infty) - M(t)}{M(\infty)} = A \exp \left( -\frac{t}{T_1} \right) + C$$

Our experimental data show good single exponential behaviour over two decades. The spin-lattice relaxation rate $1/T_1$ was extracted from the fitting of the experimental data at various temperatures (down to 5 K) to Eq. 6. Due to the large line broadening we could not saturate the nuclear magnetization below 5 K and hence could not extract reliable $1/T_1$ below this temperature. The temperature dependence of $^{31}$P nuclear spin-lattice relaxation rate thus obtained is presented in Fig. 7. With decrease in temperature, it decreases monotonically.

For $S = 1/2$ 2D square lattice, a high temperature series expansion for $1/T_1$ was given by Moriya$^{24}$ which has the form,

$$1/T_1 = \frac{1}{T_{1\infty}} \frac{1}{(1 + J/(4k_B T))^{1/2} \exp [(J/(2k_B T))^2(1 + J/(4k_B T))]}$$

where, $T_{1\infty} = (A_{th}^2/\gamma^2)(\sqrt{\pi k_B})$ taken from Ref. 20. Here, $A_{th} = 2\hbar\gamma$ where $A$ is the total hyperfine coupling obtained from the experiment. In Moriya’s expression a term of the order of $(J/k_B T)^2$ occurs in the prefactor and has a negligible effect and hence is not included in Eq. 7. Using Eq. 7 and the relevant $A$ and $J/k_B$ values obtained from the fit of NMR shift to 2D model, we simulated the theoretical curve for Na$_2$CuP$_2$O$_7$ and it is plotted with our experimental data in Fig. 7. Clearly, at high temperatures ($T \geq 25$ K), the experimental data agree reasonably well with the simulated curve. In the case of a $S = 1/2$ 1D HAF chain model, $1/T_1$ is expected to be temperature independent at low temperatures ($T \ll J/k_B$) due to a dominant contribution from the fluctuations of the staggered susceptibility of the 1D chain. We are unable to probe this region of temperature due to the large broadening
of our NMR spectra seen there. At higher temperatures, from fluctuations of the uniform susceptibility of the 1D chain, one expects a linear variation of $1/T_1$ with temperature. This should eventually saturate at even higher temperatures when the spin-susceptibility becomes Curie-like. Qualitatively speaking, the observed $1/T_1$ data could be explained based on the above. However, an analytical expression for the temperature dependence of $1/T_1$ is not available in the temperature regime of our experiment and hence no curve-fit is shown in the figure.

The spin-spin relaxation was measured as a function of separation time $t$ between $\pi/2$ and $\pi$ pulses by monitoring the decay of the transverse magnetization. $1/T_2$ at different temperatures was obtained by fitting of the spin-echo decay to the following equation,

$$M(2t) = M_0 \exp\left[-2\left(\frac{t}{T_2}\right)^2\right] + C$$

Inset of Fig. 8 shows the spin-echo decays for different temperatures. The extracted spin-spin relaxation rates $1/T_2$ are plotted as a function of temperature in Fig. 7. It is to be seen that below about 55 K, the spin-spin relaxation rate $1/T_2$ falls sharply towards low temperatures. No indication of 3D LRO was found down to 6 K. The origin of this temperature dependence $1/T_2$ is not clear yet.

V. CONCLUSION

Our $^{31}$P NMR shift and susceptibility data fitted reasonably well to the high temperature series expansion for 2D HAF model whereas the fitting to the 1D model was not as good, especially in the $T \leq 25$ K regime. From the $^{31}$P NMR shift analysis, the $J/k_B$ value was estimated to be about $(18 \pm 2)$ K. The large broadening of the $^{31}$P NMR spectra at $T \leq 5$ K points towards a transition. However, no evidence of magnetic LRO was found in susceptibility and heat capacity measurements down to 2 K. Further experiments are required to really understand the detailed nature of this transition. $^{31}$P NMR $1/T_1$ shows a good agreement with the theory of 2D HAF square lattice. The results reported in this paper thus suggest a variety of experiments and a need for a better theoretical understanding of quasi-low dimensional Heisenberg antiferromagnets.
Acknowledgments

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This temperature range is not low enough for the "$T^3$" approximation of the lattice heat capacity to be valid. We tried to determine the lattice contribution to the specific heat by fitting the high-temperature data (say, between 40 K and 70 K, where the magnetic contribution may be expected to be negligible) to the exact expression of the Debye model. However, this fit (not shown) deviated significantly from the data when extrapolated to higher and lower temperatures. Considering larger ranges of temperature for the fit, required us to use a temperature dependent (we tried a second order polynomial form with coefficients as fitting parameters) Debye temperature. This too did not appear to be helpful in reliably extracting the magnetic contribution at low temperatures (below 15 K).

FIG. 1 (a) A schematic figure of the $bc$ plane in Na$_2$CuP$_2$O$_7$ with [Cu(PO$_4$)$_2$]$_\infty$ linear chains propagating along $c$-direction indicated. A possible coupling path Cu-O-P-O-Cu is also indicated. (b) The arrangement of Cu and O in the $bc$-plane is shown. Two planes formed by Cu$^{2+}_1$ and Cu$^{2+}_2$ ions are represented by thick and thin bonds respectively.

FIG. 2 $^{31}$P NMR shift $K$ vs temperature $T$ for Na$_2$CuP$_2$O$_7$. The solid line is fit to Eq. 4 in the temperature range, $15 \leq T \leq 300$ K, where $\chi_{spin}$ is the high temperature series expansion for susceptibility of HAF square plane (Eq. 1). The dashed line is the simulated curve from Eq. 2 using the parameters obtained from the high-$T$ fit. In the inset we have displayed the data at low temperatures on a logarithmic scale in order to show the deviation of experimental data from low-$T$ series expansion.

FIG. 3 $^{31}$P NMR shift $K$ vs temperature $T$ for Na$_2$CuP$_2$O$_7$. The solid line is fit to Eq. 4 in the temperature range, $5 \leq T \leq 300$ K taking $\chi_{spin}$ for HAF chain (Eq. 3). In the inset we have displayed the data on a logarithmic scale in order to show the deviation of experimental data from the theory around the broad maximum region.
FIG. 4 Low-$T$ field sweep $^{31}$P NMR spectra for Na$_2$CuP$_2$O$_7$ are shown at different temperatures $T$ around 5 K. It also shows the sudden change in line width and appearance of several distinct peaks.

FIG. 5 Magnetic susceptibility ($M/H$) vs temperature $T$ measured at $H = 5$ kG for Na$_2$CuP$_2$O$_7$. The solid line is best fit of the data to Eq. 5 in the $15 \text{ K} \leq T \leq 400 \text{ K}$ range taking $\chi_{\text{spin}}$ for HAF square plane (Eq. 1).

FIG. 6 Normalised specific heat $C_p/(N_Ak_B)$ of Na$_2$CuP$_2$O$_7$ is displayed as a function of temperature $T$. The inset has $d[C_p/(N_Ak_B)]/dT$ as a function of $T$ showing an anomaly around 10 K.

FIG. 7 The $^{31}$P nuclear spin-lattice relaxation rate $1/T_1$ vs temperature $T$ for Na$_2$CuP$_2$O$_7$. The open circles are our experimental results and the solid line represents the simulated curve of Eq. 7. In the inset, the magnetization recoveries are plotted as a function of pulse separation $t$ and the solid line is an exponential fit to Eq. 6.

FIG. 8 The $^{31}$P spin-spin relaxation rate $1/T_2$ is plotted as a function of temperature $T$. In the inset, spin-echo decays are plotted as a function of $t$ at three different temperatures for Na$_2$CuP$_2$O$_7$. The solid lines show the fitting to a exponential function (Eq. 8).
Fig. 1 (a), R. Nath et al.
Fig. 1 (b), R. Nath et al.
Na$_2$CuP$_2$O$_7$, $^{31}$P NMR

Fig. 3, R. Nath et al.
Fig. 4, R. Nath et al.
Na$_2$CuP$_2$O$_7$

H = 5 kG

- exp
- 2D HTSE

Fig. 5, R. Nath et al.
Fig. 6, R. Nath et al.