The nature of spin trimer in $Ca_3Cu_2Ni(PO_4)_4$

M. Ghosh and K. Ghoshray

ECMP Division, Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata 700064, India
E-mail: kajal.ghoshray@saha.ac.in

The nature of spin trimer and $3d$ spin dynamics in $Ca_3Cu_2Ni(PO_4)_4$ was studied using ^{31}P NMR measurements. This material is obtained replacing one of the Cu ions by a Ni ion in one dimensional spin trimer compound $Ca_3Cu_3(PO_4)_4$. NMR spectrum suggests the presence of two types of magnetically inequivalent phosphorous atoms as in the parent compound. This finding reveals the presence of only one type of trimer viz. Cu2–Ni–Cu2 rather than three types viz., Cu2–Cu1–Cu2, Cu2–Cu1–Ni and Ni–Cu1–Ni as suggested from neutron scattering. Hence the ground state of $Ca_3Cu_2Ni(PO_4)_4$ appears to be a quintet. The present finding also explains the magnetic susceptibility behavior showing no indication of the reduction of net spin of a trimer in $Ca_3Cu_2Ni(PO_4)_4$, as expected for $J_{Ni–Cu} = -0.85$ meV compared to $J_{Cu–Cu} = -4.74$ meV, reported from neutron scattering. The spin lattice relaxation rate suggests that the three magnon mediated scattering process, dominant in $Ca_3Cu_3(PO_4)_4$, is reduced in $Ca_3Cu_2Ni(PO_4)_4$.

1. Introduction

Low-dimensional quantum spin systems have attracted considerable attention due to the possible emergence of novel magnetism such as quantum critical phenomena [1], formation of Haldane gap [2], field induced Bose–Einstein condensation [3]. Enhancement of quantum fluctuations due to low dimensionality could suppress the magnetic ordering and give rise to several such unusual phenomena. Recently it has been suggested that in $S = 1/2$ antiferromagnetic (AF) chain with period 3, exchange coupling shows a plateau in the magnetization curve where the magnetization stays constant at a fractional value of the saturation over a finite range of magnetic field [4–6]. This phenomenon in quantum spin chains is analogous to the quantum Hall effect-topological quantization of a physical quantity under a changing magnetic field. A trimer chain is the first spin system that has been predicted to show a magnetization plateau. However, the spin trimer systems are rare in nature. Among the few such systems, $La_4Cu_3MoO_{12}$ is a 2D AF system in which the three Cu^{2+} spins form a triangle, so that the AF intra trimer interactions are frustrated [7], nevertheless the system undergoes an AF ordering near 2.6 K. Due to strong nearest neighbor (NN) AF exchange, the net spin of the trimer reduces from 3/2 to 1/2 below 250 K, as revealed from the inverse susceptibility χ^{-1} curve.

$A_3Cu_3(PO_4)_4$ (A ≡ Ca, Sr, Pb) is another spin trimer system, in which Cu2–Cu1–Cu2 trimers are arranged in linear chain, with the intertrimer AF exchange interaction J_2 is 3 K while the intra trimer NN AF exchange interaction, J_1 is about 126 K [8,9]. As a result, below 45 K, the χ^{-1} vs T curve shows a clear signature of a reduction of the net spin of a trimer from 3/2 to 1/2 [10]. So the ground state is a doublet, and is a model system of linear HAF trimer. In principle, such a doublet ground state can be changed into a singlet ground state by substituting a Cu^{2+} ($S = 1/2$) spin in the trimer by Ni^{2+} ($S = 1$) provided only one type of trimer viz., Ni–Cu1–Cu2/Cu–Cu1–Ni is formed. This would offer for the first time an opportunity of realizing a gapped quantum spin trimer system, with the possibility of observing Bose–Einstein condensation (BEC) above a certain critical value of an external magnetic field. BEC was observed in the spin dimer system $TlCuCl_3$ from inelastic neutron scattering [10,11]. To investigate this in $Ca_3Cu_3(PO_4)_4$ Podlesnyak *et al.* [12] studied inelastic neutron scattering in $Ca_3Cu_3(PO_4)_4$. Unfortunately the singlet state was not realized. From these studies it was also suggested that the middle position is exclusively occupied by Cu^{2+}, whereas, the end positions are statistically populated by Cu^{2+} and Ni^{2+}; thus three types of trimer: Cu2–Cu1–Cu2, Cu2–Cu1–Ni and Ni–Cu1–Ni are created with the ground states of doub-

let, triplet, and quintet respectively, instead of only one type Cu2–Cu1–Ni with the ground state being a triplet. The same was also pointed out from elastic neutron scattering study [13]. From these findings it was concluded that the possible reason for the failure of the observation of a singlet ground state in $Ca_3Cu_2Ni(PO_4)_4$, is the formation of three types of trimers. Moreover, it was also shown that, $J_{Cu–Cu}$ in $Ca_3Cu_2Ni(PO_4)_4$ is enhanced to –4.92 meV from –4.74 meV observed in $A_3Cu_3(PO_4)_4$ and $J_{Ni–Cu} = -0.85$ meV. Surprisingly, the magnetic susceptibility data in $Ca_3Cu_2Ni(PO_4)_4$ [13,14] in the range 2–300 K, did not show the expected signature of the reduction of the net spins of the trimers Cu2–Cu1–Cu2 and Cu2–Cu1–Ni, due to the presence of strong NN AF exchange between the Cu^{2+} spins, as was seen in $Ca_3Cu_2(PO_4)_4$, where only one type of trimer Cu2–Cu1–Cu2 is present, with less stronger NN AF exchange as mentioned above. Whereas, the same in $Ca_3Cu_2Mg(PO_4)_4$ indicated the presence of more than one type of trimer with a clear signature of reduction of the net spins of certain type of trimers [14]. A comparison of the susceptibility data in $Ca_3Cu_2(PO_4)_4$, $Ca_3Cu_2Ni(PO_4)_4$ and $Ca_3Cu_2Mg(PO_4)_4$, indicated that Ni atom in $Ca_3Cu_2Ni(PO_4)_4$ probably occupies the middle position instead of end positions, of a trimer. Whereas, the Mg atom in $Ca_3Cu_2Mg(PO_4)_4$ occupies the end position. In this connection it may be mentioned that Pomjakushin *et al.* [13] also suggested from neutron scattering in $Ca_3Cu_2Ni(PO_4)_4$ that the valance of Ni has reasonable value if it occupies the middle position of the Cu2–Cu1–Cu2 trimer, according to the bond valence sum (BVS) calculation, and therefore, in this respect Ni could occupy the middle position. Thus the possibility of the formation of only one type of trimer Cu2–Ni–Cu2 with a quintet ground state can not be neglected in case of $Ca_3Cu_2Ni(PO_4)_4$.

To understand this further, presently we have performed the ^{31}P NMR study in polycrystalline sample of $Ca_3Cu_2Ni(PO_4)_4$. Fig. 1 shows the only one type of trimer, Cu2–Cu1–Cu2, present in the unit cell of $Ca_3Cu_2(PO_4)_4$, when projected in the *ab* plane, along with the bonding of the two types of phosphorous (P) atoms, via the oxygen atom. P1 is bonded with two nearest neighbor magnetic ions within a trimer and P2 is bonded with the magnetic ions between the two trimers. Now if in $Ca_3Cu_2Ni(PO_4)_4$, the Ni ion occupies the Cu2 site, resulting in three types of trimers as mentioned above, from Fig. 1 it follows that the local magnetic environments of all the P1 atoms in the unit cell will not be identical and same would be true for P2. As a result, the resonance line positions of all the P1 atoms would not superimpose at a particular frequency, and same would be true for P2. This would produce a complicated ^{31}P NMR spectrum compared to that observed in $Ca_3Cu_3(PO_4)_4$ [15] where it is a superposition of two resonance lines corresponding to P1 and P2 indicating that all the P1 nuclei experience the same local magnetic field, and same is true for P2. On the other hand if Ni atom oc-
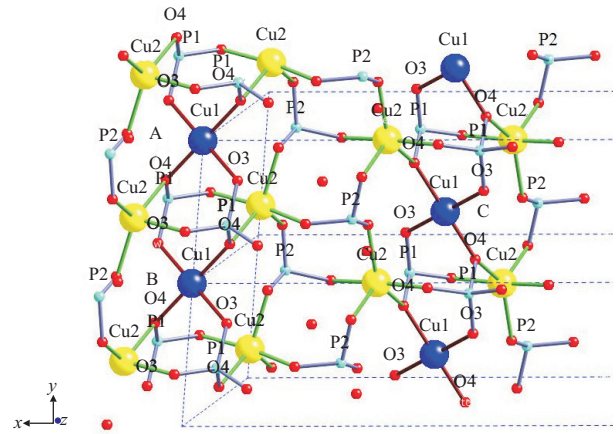

Fig. 1. (Color online) Three trimers (A, B, and C) in $Ca_3Cu_2(PO_4)_4$, viewed from *z* axis showing the possible superexchange paths between the trimers in the *ab* plane. Cu1 and Cu2 atoms are shown by the blue and yellow spheres, respectively. O and P atoms are shown by red and green spheres. Ca atoms are not shown. The structure has been drawn using the coordinates given in Ref. 13.

cupies the Cu1 position, then there will be only one type of trimer viz., Cu2–Ni–Cu2. In such case from Fig. 1 it follows that all the P1 atoms will be linked with Cu2 on one side and with Ni on other side within a trimer, and therefore, have identical magnetic environment. While all the P2 atoms will be bonded on both sides with Cu2 atoms of the trimers of the two consecutive chains. In this case ^{31}P resonance line in $Ca_3Cu_2Ni(PO_4)_4$ would be a superposition of two lines similar to that in the pure compound. Therefore, it is expected that NMR study could provide some valuable information about the possible type of trimer formed in $Ca_3Cu_2Ni(PO_4)_4$, and hence the magnetic ground state of this system. Apart from this, ^{31}P nuclear spin lattice relaxation rate could provide additional information about the effect of Ni substitution on one dimensional spin dynamics, which is a current topic of great interest.

2. Experiment

Polycrystalline sample of $Ca_3Cu_2Ni(PO_4)_4$ was synthesized using solid state reaction method, by heating a stoichiometric mixture of CuO (99.99%), NiO (99.99V), CaCO$_3$ (99.99%) and $NH_4H_2PO_4$ (99.99%) very slowly up to 600 °C and then annealed at 900 °C during 120 h, with several intermediate grindings. The sample is characterized at room temperature using x-ray diffraction (XRD) with CuK$_\alpha$ radiation (λ = 1.5406 Å). All the peaks can be indexed on the basis of monoclinic structure with space group $P2_1/a$ and cell parameters: a = 17.718(1) Å, b = 4.888(2) Å, c = 8.84(1) Å and β = 123.8(1)° which agree satisfactorily with the reported values [13]. The NMR measurements were carried out in the fields of H =1.39 T (ν_R = 24.005 MHz) and at H = 7.04 T (ν_R = 121.423 MHz)

using a conventional phase-coherent Thamway PROT4103 pulse spectrometer. The spectrum was recorded by changing the frequency step by step and recording the spin-echo intensity by applying a $\pi/2 - \tau - \pi/2$ solid echo sequence. The temperature variation studies in the range 4–300 K were performed in an Oxford continuous flow dynamic cryostat with a ITC503 controller. Shift is measured with respect to the position of the ^{31}P NMR line (ν_R) in H_3PO_4 solution.

3. Results and discussion

3.1. NMR spectra and shift parameters

Figure 2 shows the ^{31}P NMR spectrum in $Ca_3Cu_2Ni(PO_4)_4$ at 300 K in a field of 7 T along with the same in $Ca_3Cu_3(PO)_4$ [14] and $Ca_3CuNi_2(PO_4)_4$ [14] for comparison. The spectrum in $Ca_3Cu_2Ni(PO_4)_4$ shows a typical overlap of two powder patterns for nuclear spin $I = 1/2$ having different component of shift parameters, similar to that observed in the other two compounds. It is to be noted that the position of the resonance line for P2 in $Ca_3Cu_3(PO)_4$ and in $Ca_3Cu_2Ni(PO_4)_4$ are close to each other, whereas, in $Ca_3CuNi_2(PO_4)_4$ the shift of the line for P2 is higher. In case of $Ca_3CuNi_2(PO_4)_4$, a higher value of the shift is expected, as the P2 atom is bonded on both sides with Ni^{2+} ions with $S = 1$. On the other hand in $Ca_3Cu_3(PO_4)_4$, P2 is bonded on both sides with Cu^{2+} ions of $S = 1/2$. In $Ca_3Cu_2Ni(PO_4)_4$ if the Ni atom occupies the Cu1 position, with the end positions of the trimer being occupied by Cu2 atoms, then P2 in this compound will also be bonded with Cu2 atoms on both sides, as a result the local

magnetic field experienced by P2 in this compound would also be similar to that of the pure compound. Moreover, if only Cu2–Ni–Cu2 trimer is present in $Ca_3Cu_2Ni(PO_4)_4$, then P1 atom would be bonded with Cu2 on one side and Ni on the other side, similar to that in $Ca_3CuNi_2(PO_4)_4$, where the only type of trimer viz., Ni–Cu2–Ni is present. In such case, the local magnetic field at the P1 site in $Ca_3CuNi_2(PO_4)_4$ and $Ca_3Cu_2Ni(PO_4)_4$ would be almost same. Interestingly, it is seen from Fig. 2 that the position of the resonance line of P1 in $Ca_3Cu_2Ni(PO_4)_4$ and $Ca_3CuNi_2(PO_4)_4$ are very close to each other. These observations indicate that the Ni atom in $Ca_3Cu_2Ni(PO_4)_4$ most probably occupies the Cu1 position of the trimer in $Ca_3Cu_2Ni(PO_4)_4$, resulting in only one type of trimer Cu2–Ni–Cu2 to be present in this compound. In order to determine the shift parameters, the experimental spectra in $Ca_3Cu_2Ni(PO_4)_4$ in the whole temperature range were fitted to the equation

$$\nu = \nu_R[1 + K_{iso} + K_{ax}(\cos^2\theta - 1) + K_{an}\sin^2\theta\cos 2\phi] \quad (1)$$

where K_{iso}, K_{ax} and K_{an} are the isotropic, axial and the anisotropic parts of the shift respectively, arising from H_{local} produced at the ^{31}P nucleus site, due to the electron nuclear hyperfine and the dipolar interaction. ν_R is the reference frequency as mentioned earlier. θ and ϕ are the Euler angles between the principal axes of the hyperfine coupling tensor and the direction of the external magnetic field (Zeeman field).

Figure 3 shows the ^{31}P NMR spectra at different temperatures in the range 4–300 K in $Ca_3Cu_2Ni(PO_4)_4$ along with the theoretical spectra. The experimental lines below 300 K are also well fitted with two constituent lines. This further suggests that the internal magnetic fields at each type of P sites, change identically throughout the range
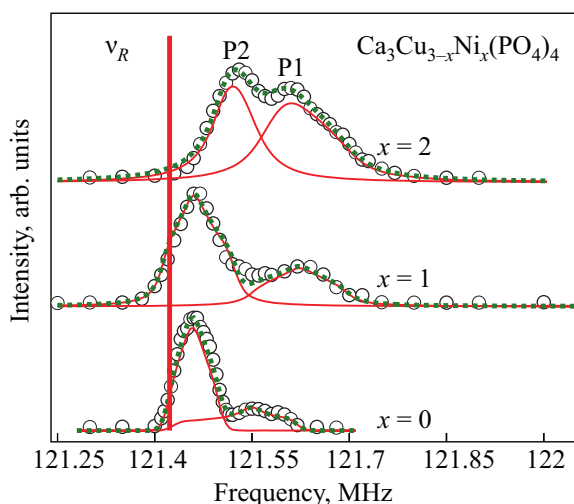

Fig. 2. (Color online) ^{31}P NMR spectra of polycrystalline $Ca_3CuNi_2(PO_4)_4$ [14], $Ca_3Cu_2Ni(PO_4)_4$ and $Ca_3Cu_3(PO_4)_4$ [14] at 300 K recorded at $H = 7$ T (represented by open-circles). Theoretical line (dashed) calculated using Eq. (1), along with two constituent lines (continuous) corresponding to resonance lines of two inequivalent phosphorous atoms are also shown. Vertical line represents reference position at frequency 121.42 MHz.
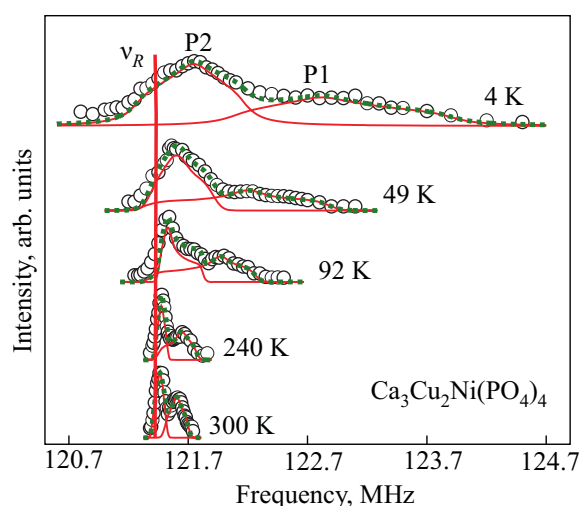

Fig. 3. (Color online) ^{31}P NMR spectra of polycrystalline $Ca_3Cu_2Ni(PO_4)_4$ at different temperatures recorded at $H = 7$ T. Legends are same as in Fig. 2.

4–300 K. Therefore from the spectral features, in the whole temperature range, it is also emerged that the Ni atom occupies the Cu1 position in Cu2–Cu1–Cu2 trimer, as discussed above. Figure 4 shows the variation of K_{iso}, K_{ax} and K_{an} with T with the insets showing the variation of these parameters with respect to the bulk susceptibility.

We have also performed the NMR experiment at a much lower resonance frequency of 24 MHz with $H = 1.39$ T. The shift parameters obtained by fitting the spectra recorded at $H = 1.39$ T in the range 160–300 K, are also included in Fig. 4. The close agreement between the values obtained by analyzing the spectra at two widely different resonance frequencies justifies the accuracy of the obtained parameters.
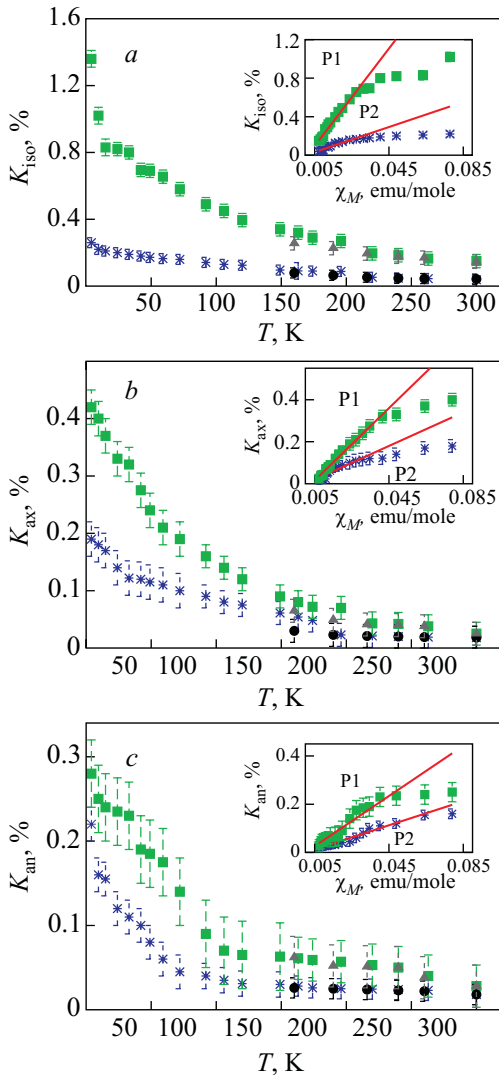

Fig. 4. (Color online) Temperature variation in: K_{iso} (*a*), K_{ax} (*b*), and K_{an} (*c*), measured in a field of $H = 7$ T: filled squares are for P1 site and stars are for P2 site. For $H = 1.39$ T: triangles are for P1 site and filled circles are for P2 site. Inset shows the variation in K_{iso} (*a*), K_{ax} (*b*), and K_{an} (*c*) for both P1 and P2 sites against χ_M with temperature as an implicit parameter.

The shift is related to χ_{spin} by the relation

$$K = K_0 + \frac{H_{hf}}{N\mu_B}\chi_{spin}(T) \qquad (2)$$

where H_{hf} is the hyperfine field, K_0 is the chemical shift, N is the Avogadro number and $\chi_{spin}(T)$ is the contribution of electronic spin to the magnetic susceptibility. As long as hyperfine field remains constant, K should follow $\chi(T)$. Contribution to H_{hf} arises from the transferred hyperfine interaction, which is a property of the electronic structure, and the dipolar interaction, neither of which is temperature dependent. Although $K(T)$ need not have the same symmetry as $\chi(T)$, the temperature dependence of $K(T)$ should reflect that of $\chi(T)$. The inset of Fig. 4,*a–c* shows that K_{iso}, K_{ax} and K_{an} vary linearly with $\chi(T)$ in the range 15–300 K. The linearity suggests unique hyperfine coupling constant over this temperature range. Below 15 K, there is a deviation from linearity. By using Eq. (1), we determine the values of isotropic, axial and the anisotropic parts of the hyperfine field for these two sites. Table 1 shows the values of H_{hf}^{iso}, H_{hf}^{ax} and H_{hf}^{an} for the P1 and P2 sites for the compound $Ca_3Cu_2Ni(PO_4)_4$ together with those obtained in $Ca_3Cu_3(PO_4)_4$ (from our measurement) [14], for comparison.

Table 1. Values of ^{31}P hyperfine-fields

Parameters, kOe/μ_B	$Ca_3Cu_3(PO_4)_4$	$Ca_3Cu_2Ni(PO_4)_4$
H_{hf}^{iso} for P1	1.28 ± 0.03	1.32 ± 0.02
H_{hf}^{iso} for P2	0.43 ± 0.03	0.35 ± 0.03
H_{hf}^{ax} for P1	0.44 ± 0.01	0.41 ± 0.01
H_{hf}^{ax} for P2	0.16 ± 0.01	0.20 ± 0.02
H_{hf}^{an} for P1	0.50 ± 0.02	0.32 ± 0.02
H_{hf}^{an} for P2	0.15 ± 0.01	0.13 ± 0.01

3.2. Nuclear spin-lattice relaxation rates

In order to investigate the effect on the electron spin dynamics due to the replacement of one of the Cu^{2+} ions by a Ni^{2+} ion, in a trimer of $Ca_3Cu_3(PO_4)_4$, we measured the ^{31}P nuclear spin-lattice relaxation rate $1/T_1$, which is a very sensitive probe of the low energy electron spin fluctuations. $1/T_1$ is measured by the saturation recovery method using a single $\pi/2$ pulse. Measurements were performed in presence of the external magnetic fields of 7 T in the temperature range 4–300 K and at 1.39 T in the range 160–300 K, in order to see whether the strong field dependence of $1/T_1$ observed in case of $Ca_3Cu_3(PO_4)_4$ [16], as well as in isostructural $Sr_3Cu_3(PO_4)_4$ [16] in the high temperature range, is also present in $Ca_3Cu_2Ni(PO_4)_4$. Figure 5 shows the $1/T_1$ vs T curves for one type of phosphorous site (P2), measured in magnetic fields of 7 T and 1.39 T for
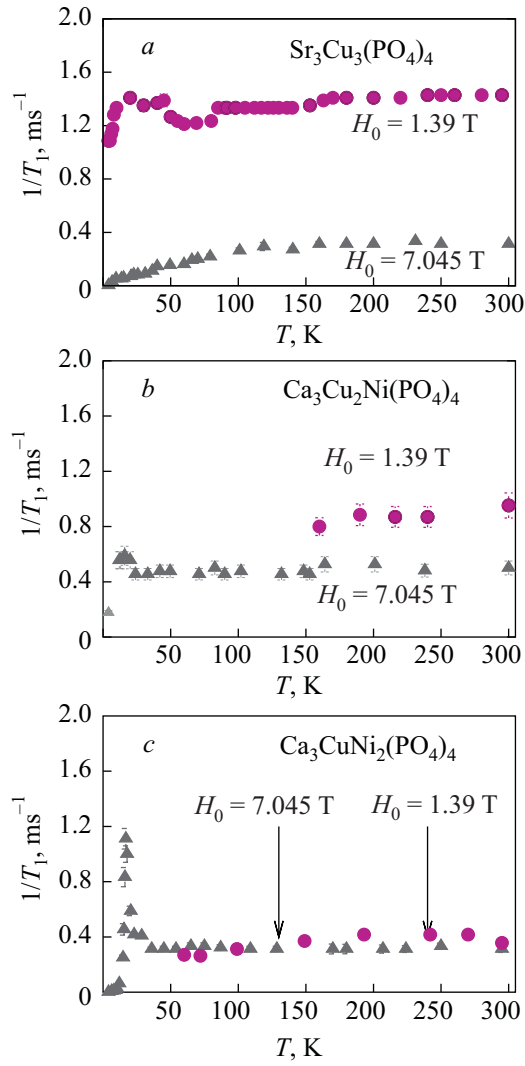
Fig. 5. (Color online) Variation in $1/T_1$ with T in $Sr_3Cu_3(PO_4)_4$ [16] (*a*), $Ca_3Cu_2Ni(PO_4)_4$ (*b*) and $Ca_3CuNi_2(PO_4)_4$ [17] (*c*) for two fields: solid triangle is for $H = 7.045$ T, solid circle is for $H = 1.39$ T. The error bar in each data corresponds to the size of the symbol.

$Ca_3Cu_2Ni(PO_4)_4$ together with those in $Sr_3Cu_3(PO_4)_4$ [16] and $Ca_3CuNi_2(PO_4)_4$ [17] for comparison. It is seen that $1/T_1$ in $Sr_3Cu_3(PO_4)_4$ is strongly field dependent as reported in case of isostructural $Ca_3Cu_3(PO_4)_4$, whereas, the same in $Ca_3CuNi_2(PO_4)_4$ shows negligible field dependence. On the other hand $1/T_1$ in $Ca_3Cu_2Ni(PO_4)_4$, still remains field dependent with the influence of H being reduced compared to that in the pure compound. This shows that the substitution of Ni^{2+} ($S = 1$) in place of Cu^{2+} ($S = 1/2$) strongly affects the ^{31}P nuclear relaxation mechanism. $1/T_1$ in such compounds is governed by the thermal excitations of the $3d$ spins, and can be written as

$$\frac{1}{T_1} = 2\gamma_n^2 k_B T \Sigma \mid A(\mathbf{q}) \mid^2 \chi''(\mathbf{q}, \omega_n) / \omega_n, \quad (3)$$

where γ_n is the nuclear gyromagnetic ratio, $A(\mathbf{q})$ is the wave vector dependent hyperfine coupling, and $\chi''(\mathbf{q}, \omega_n)$, is the dissipative component of the chain dynamic susceptibility evaluated at the nuclear Larmor frequency ω_n [18].

The values of $1/T_1$ in $Ca_3Cu_2Ni(PO_4)_4$ remain almost constant in the temperature range 6.5–300 K for $H = 7$ T. Below 6.5 K it showed a decreasing trend which is also confirmed from the change in the nature of the ^{31}P nuclear magnetization recovery curves from 6.5 to 4 K (Fig. 5). Whereas, in the pure compound $1/T_1$ remained constant in the range 50–300 K and decreased continuously below this range. In $Ca_3CuNi_2(PO_4)_4$ $1/T_1$, remained constant in the range 26–300 K and showed a peak at 16 K due to antiferromagnetic transition. The T independent behavior of $1/T_1$ is typical feature of fast spin fluctuation ($\omega_e \gg \omega_n$) of the paramagnetic moments. A comparison of such behavior in the three compounds suggests that substitution of one copper ion in a trimer by a Ni ion reduces the extent of field dependence and also increases the T independent range of $1/T_1$. This indicates a reduction of the magnetic field dependent three magnon mediated relaxation process, with an enhancement of two magnon contribution, in $Ca_3Cu_2Ni(PO_4)_4$, with the former contribution being still present. However, replacement of two Cu ions by Ni ions reduces the T independent range of $1/T_1$, due to the appearance of magnetic ordering at 16 K, with the H dependence being completely suppressed, indicating that $1/T_1$ is governed only by the two magnon mediated Raman process. Within the localized spin model in a high temperature limit [18], the value of $1/T_1$ at a non magnetic nucleus can be written as

$$\frac{1}{T_1} = \sqrt{2\pi}(2\gamma_n H_{hf})^2 z' S(S+1)/(3\omega_{ex}) \quad (4)$$

with the exchange frequency of local spins $\omega_{ex} = (2/3) \times \times (J^2/\hbar^2) \times [zS(S+1)]$. The constants $z = 2$ and $z' = 2$ correspond to the numbers of exchange-coupled local spins
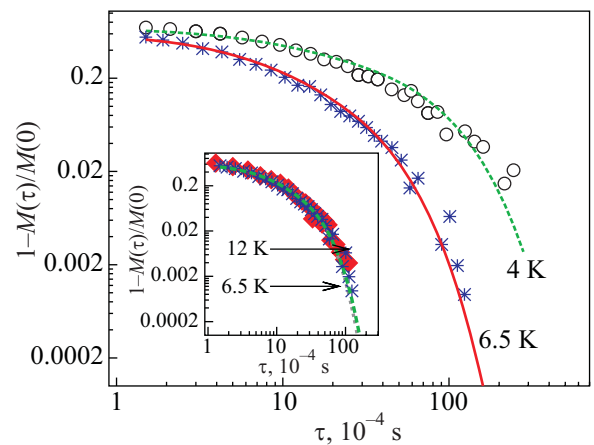

Fig. 6. (Color online) The nuclear magnetization recovery curves at 4 and 6.5 K. The inset shows the same at 12 and 6.5 K.

and those of the local spins interacting with the probing nucleus, and J is the exchange constant respectively [18].

Taking $\gamma_n = 1.083 \cdot 10^8$ s$^{-1} \cdot$T^{-1} for the phosphorous nucleus, and the values of H_{hf}^{iso} from Table I, we have calculated the value of $1/T_1$ in Ca$_3$Cu$_2$Ni(PO$_4$)$_4$ and Ca$_3$CuNi$_2$(PO$_4$)$_4$. In case of Ca$_3$Cu$_2$Ni(PO$_4$)$_4$, if we consider Ni atom occupies the middle position of the trimer, then P1 will experience the effect of intra trimer exchange interaction between Cu2 and Ni. The strength of this exchange interaction J_{Ni-Cu} was reported from neutron scattering [12]. We have used this value for calculating $T1$ of P1 in Ca$_3$Cu$_2$Ni(PO$_4$)$_4$. In this compound, then P2 will be bonded with Cu2 ions of adjacent trimers. Since the inter trimer Cu2–Cu2 exchange constant was not reported by Podlesnyak *et al.* [12] we have used this J_{Cu-Cu} (–0.258 meV) reported from magnetic susceptibility data [9] in Ca$_3$Cu$_3$(PO$_4$)$_4$ to calculate T_1 of P2 in Ca$_3$Cu$_2$Ni(PO$_4$)$_4$. The obtained value (Table 2) is in close agreement with the experimental one. However, in Ca$_3$CuNi$_2$(PO$_4$)$_4$, since P2 is bonded on both sides with Ni ions and inter trimer J_{Ni-Ni} is not reported from neutron scattering as well as from magnetic susceptibility, therefore, we could calculate T_1 only for P1 (Table 2). In this case also the agreement of experimental and the theoretical values are quite satisfactory. So our findings from spin-lattice relaxation data further supports our suggestion from ^{31}P line shape analysis in Ca$_3$Cu$_2$Ni(PO$_4$)$_4$, that Ni atom most probably occupies the middle position of a trimer so that there is only one type of trimer Cu2–Ni–Cu2 is present instead of three types Cu2–Cu1–Cu2, Cu2–Cu1–Ni and Ni–Cu2–Ni as suggested from neutron scattering. So the ground state of this compound would be a quintet.

Table 2. Values of T_1 at room temperature for two compounds

Parameters, ms	Ca$_3$Cu$_2$Ni(PO$_4$)$_4$	Ca$_3$CuNi$_2$(PO$_4$)$_4$
$T_{1\infty}^{theo}$ for P1	0.69	1.61
$T_{1\infty}^{exp}$ for P1	0.85	1.82
$T_{1\infty}^{theo}$ for P2	5.94	
$T_{1\infty}^{exp}$ for P2	2.0	3.2

4. Conclusion

We have studied the static and the dynamic magnetic properties of the trimer spin chain compound Ca$_3$Cu$_2$Ni(PO$_4$)$_4$ which remains in the paramagnetic phase in the temperature range 4–300 K, using ^{31}P NMR studies in the temperature range 4–300 K in presence of the external magnetic field of 7 T and in the temperature range of 160–300 K for $H = 1.39$ T. At any temperature the spectrum corresponds to a typical overlap of two powder patterns, indicating the presence of two types of P atoms present in the unit cell similar to that in Ca$_3$Cu$_3$(PO$_4$)$_4$ and Ca$_3$CuNi$_2$(PO$_4$)$_4$. This finding together with the spin lattice relaxation data indicate that most probably only one type of trimer viz., Cu1–Ni–Cu2 is present in Ca$_3$Cu$_2$Ni(PO$_4$)$_4$, which could also explain satisfactorily the magnetic susceptibility behavior, which did not give any signature of the reduction of net spin of any trimer, as the NN J_{Ni-Cu} is an order of magnitude smaller than that of NN J_{Cu-Cu} [12]. Therefore, the present NMR results indicate that the ground state of Ca$_3$Cu$_2$Ni(PO$_4$)$_4$ is a quintet. The behavior of spin lattice relaxation rate suggests that the replacement of one of the Cu ion by a Ni ion in a trimer, partially reduces the three magnon scattering process mediated relaxation mechanism which is the dominant contribution in case of Ca$_3$Cu$_3$(PO$_4$)$_4$.

1. S. Sachdev, *Quantum Phase Transition*, Cambridge University Press, New York (1999).
2. F.D.M. Haldane, *Phys. Rev. Lett.* **50**, 1153 (1983).
3. T. Giamarchi, C. Ruegg, and O. Tchenyshyov, *Nature Phys.* **B4**, 198 (2008).
4. K. Hida, *J. Phys. Soc. Jpn.* **63**, 2359 (1994).
5. H. Kageyama, K. Yoshimura, R. Stern, N.V. Mushnikov, K. Onizuka, M. Kato, K. Kosuge, C.P. Slichter, T. Goto, Y. Ueda, *Phys. Rev. Lett.* **82**, 3168 (1999).
6. T. Ono, H. Tanaka, H.A. Katori, F. Ishikawa, H. Mitamura, and T. Goto, *Phys. Rev.* **67**, 104431 (2003).
7. M. Azuma, T. Odaka, M. Takano, D.A. Vander Griend, K.R. Poeppelmeier, Y. Narumi, K. Kindo, Y. Mizuno, and S. Maekawa, *Phys. Rev.* **B62**, R3588 (2000).
8. M. Drillon, M. Belaiche, P. Legoll, J. Aride, A. Boukhari, A. Moqine, *J. Magn. Magn. Mater.* **128**, 83 (1993).
9. A.A. Belik, A. Matsuo, M. Azuma, K. Kindo, and M. Takano, *J. Solid State Chem.* **178**, 709 (2005).
10. M. Azuma, Z. Hori, M. Takano, K. Ishida, and Y. Kitaoka, *Phys. Rev. Lett.* **73**, 3463 (1994).
11. H. Kageyama, M. Nishi, N. Aso, K. Onizuka, T. Yosihama, K. Nukui, K. Kodama, K. Kakurai, and Y. Ueda, *Phys. Rev. Lett.* **84**, 5876 (2000).
12. A. Podlesnyak, V. Pomjakushin, E. Pomjakushina, K. Conder, and A. Furrer, *Phys. Rev.* **B76**, 064420 (2007).
13. V.Yu. Pomjakushin, A. Furrer, D.V. Sheptyakov, E.V. Pomjakushina, and K. Conder, *Phys. Rev.* **B76**, 174433 (2007).
14. M. Ghosh, M. Majumder, K. Ghoshray, and S. Banerjee, *Phys. Rev.* **B81**, 094401 (2010).
15. S. Yamamoto, H. Hori, Y. Furukawa, Y. Nishisaka, Y. Sumida, K. Yamada, K. Kumagai, T. Asano, and Y. Inagaki, *J. Phys. Soc. Jpn.* **75**, 074703 (2006).
16. M. Ghosh, K. Ghoshray, B. Pahari, R. Sarkar, and A. Ghoshray, *J. Phys. Chem. Solids* **68**, 2183 (2007).
17. M. Ghosh, K. Ghoshray. M. Majumder, B. Bandyopadhyay, and A. Ghoshray, *Phys. Rev.* **B81**, 064409 (2010).
18. T. Moriya, *Prog. Theor. Phys.* **16**, 23 (1956).