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Magnetic properties of the spin trimer compound $Ca_3Cu_2Mg(PO_4)_4$ from susceptibility measurements

M. Ghosh, M. Majumder, K. Ghoshray,[*] and S. Banerjee
Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata 700064, India

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The effect of the substitution of one Cu^{2+} ion ($S=1/2$) by Mg^{2+} ion ($S=0$) on the magnetic property of the linear-chain spin trimer compound $Ca_3Cu_3(PO_4)_4$ was studied using dc magnetic susceptibility in $Ca_3Cu_2Mg(PO_4)_4$ together with those in $Ca_3Cu_3(PO_4)_4$ and $Ca_3Cu_2Ni(PO_4)_4$ for comparison. A remarkable difference is observed among the results obtained in the Mg and the Ni substituted compounds. A clear signature of the reduction in the net spin of the trimers in $Ca_3Cu_2Mg(PO_4)_4$ was found below 65 K, which is compatible with the presence of the Cu2-Cu1-Mg trimers in the singlet ground state, together with those of the type Cu2-Cu1-Cu2 and Mg-Cu1-Mg in the doublet state. However, no signature of the reduction in the net spin of the trimers was observed in $Ca_3Cu_2Ni(PO_4)_4$. This finding suggests that the type of trimers present in $Ca_3Cu_2Mg(PO_4)_4$ and $Ca_3Cu_2Ni(PO_4)_4$ are different. Furthermore, a singlet ground state is partially realized in a quantum spin trimer system $Ca_3Cu_2Mg(PO_4)_4$.

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I. INTRODUCTION

Study of the low-dimensional quantum magnets are still attracting attention not only for the unusual and interesting findings but also they are considered as model systems to study much complex phenomena such as high-temperature superconductivity in metal oxides and arsenides. One-dimensional (1D) antiferromagnets (AF) are expected not to have a long-range magnetic order in general. For integer spin S, there is an energy gap between the ground state and the first excited state and persists up to a critical field,[1] equal to the gap where Bose condensation of magnons occurs.[2] Such systems remain gapless from the critical field to the saturation field.[3] Whereas, $S=1/2$ Heisenberg AF (HAF) chain remains gapless from zero field up to the saturation field, where the ground state is fully polarized. In the $S=1/2$ 1D alternating exchange HAF the ground state is a singlet state, in which singlet dimers are coupled one dimensionally. The alternating interactions are sometimes caused by the spin-Peierls transition, in which the spin lattice coupling is important. On the other hand, examples of spin trimer systems are rare in nature. $La_4Cu_3Mo_3O_{12}$ is a model system in which the magnetic susceptibility and neutron-scattering studies showed that this compound is well described by the isolated Heisenberg triangle spin trimer model, where the trimers are weakly coupled quasi two dimensionally, with the AF intratrimer interactions are frustrated.[4] As a result the zero-temperature magnetic structure is very sensitive to intratrimer and intertrimer interaction. Whereas, $A_3Cu_3(PO_4)_4$ ($A=Ca,Sr,Pb$) can be represented as 1D array of trimers. There are two types of Cu sites. The Cu1 site has a square planer coordination and Cu2 site has a distorted square pyramidal coordination. It may be considered that the trimeric units made of a central Cu1 and two outer Cu2 are isolated on account of metal-metal distances. The superexchange paths between the Cu ions within a trimer and between the trimers, belonging to the neighboring chains are shown in Fig. 1, when trimers are projected in the ab plane. In this system the magnetic susceptibility and the specific-heat data showed that the net spin of a trimer reduces from $S=3/2$ to $S=1/2$ below 45 K,[5] due to the strong nearest-neighbor (NN) AF exchange. The intratrimer exchange J_1 was estimated to be of the order of 126 K, while intertrimer exchange J_2 about 3 K. Thus $A_3Cu_3(PO_4)_4$ is a model system of weakly coupled linear HAF trimer in which AF-coupled Cu^{2+} spins give rise to a doublet ground state.[6] By substituting a Cu^{2+} spin in the trimer by Ni^{2+} ($S=1$), Pomjakushin *et al.*[7] from powder inelastic neutron-scattering studies in $Ca_3Cu_{3-x}Ni_x(PO_4)_4$ ($x=1$), tried to see whether the doublet ground state could, in principle, be changed to a singlet ground state, offering the observation of Bose-Einstein condensation (BEC) in a quantum-spin trimer system similar to the field-induced BEC of the bosonic triplet state in spin dimer system $TlCuCl_3$ observed by the inelastic neutron scattering.[8] However, the spin singlet state was not realized in $Ca_3Cu_2Ni(PO_4)_4$. By analyzing the neutron-scattering results they have shown that

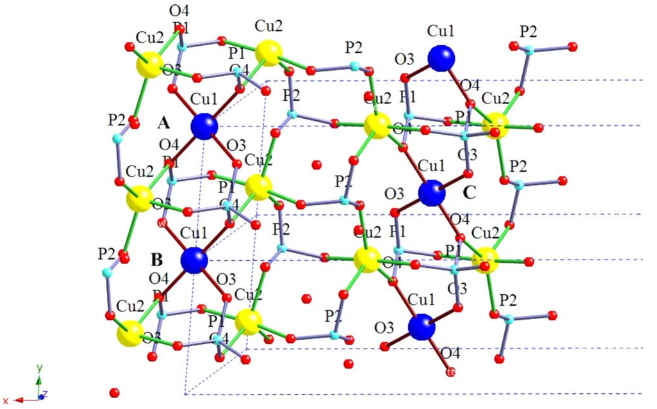

FIG. 1. (Color online) Three trimers (A, B, and C) in $Ca_3Cu_3(PO_4)_4$ viewed from z axis showing the possible superexchange paths between the trimers in the ab plane. The Cu1 and Cu2 atoms are shown by blue and yellow spheres, respectively. O and P atoms are shown by red and green spheres. Ca atoms have not been shown. The structure has been drawn using the coordinates given in Ref. 5.

in this compound there are three types of trimers viz. Cu2-Cu1-Cu2, Cu2-Cu1-Ni, and Ni-Cu1-Ni instead of only one type, with the Ni atom prefers to occupy the end position of a trimer. They suggested that this could be the reason for the failure of the observation of a singlet ground state. It is to be noted that in this compound, they have also measured the bulk susceptibility data which did not show a signature of the reduction in the net spin of the trimer units, which is expected to occur particularly, in case of Cu2-Cu1-Cu2 and Cu2-Cu1-Ni bonds, below a certain temperature, as seen in the pure compound ($x=0$) near 45 K, due to the presence of much stronger Cu-Cu nearest-neighbor AF exchange ($J1=-4.74$ meV) with a less probability of the reduction in net spin in Ni-Cu-Ni trimer with $J1_{\text{Ni-Cu}}=-0.85$ meV.[9] Thus it seems that the bulk susceptibility result in $Ca_3Cu_2Ni(PO_4)_4$ does not show the signature of the presence of three types of trimers as mentioned above.

This finding motivated us to study the effect on the magnetic property of $Ca_3Cu_3(PO_4)_4$, due to the substitution of one of the Cu ions by a nonmagnetic ion Mg^{2+} ($S=0$). If as in the Ni substituted compound, similar three types of bonds viz., Cu2-Cu1-Cu2, Cu2-Cu1-Mg, and Mg-Cu1-Mg, are formed, with the end positions being always occupied by Mg^{2+}, while the middle position by Cu1, then there is a possibility that those bonds of the type Cu2-Cu1-Mg will have singlet ground state with a spin gap, while those of the type Mg-Cu1-Mg and Cu2-Cu1-Cu2 will have the doublet ground state with $S=1/2$, if the NN AF exchange interaction remains same as in the parent compound. Then the measured susceptibility at low temperature should follow a combined behavior of spin singlet and doublet ground states. On the other hand if only one type of bond such as Cu2-Cu1-Mg is formed in that case the low-temperature susceptibility behavior should correspond to a singlet ground state separated from the excited triplet state by an energy gap. Furthermore, if instead of occupying the position of Cu2 atom (end position of a trimer), the Mg atom occupies the position of Cu1 atom (central position of a trimer), then the only possible type of trimer would be Cu2-Mg-Cu2. In this case there would be no possibility of the reduction in the net spin of the trimers below a certain temperature because of much weaker AF exchange between the two Cu atoms within a trimer. Therefore, it is expected that the magnetic-susceptibility measurement could provide some useful information about the effect of partial substitution of Cu^{2+} ion by Mg^{2+}/Ni^{2+} on the magnetic property of such trimer spin chain compound. Thus we have also measured the susceptibility in $Ca_3Cu_2Ni(PO_4)_4$ as well as in the parent system $Ca_3Cu_3(PO_4)_4$, in order to compare our results in the Mg-substituted compound.

II. EXPERIMENTAL

Polycrystalline samples of $Ca_3Cu_2Mg(PO_4)_4$, $Ca_3Cu_2Ni(PO_4)_4$, and $Ca_3Cu_3(PO_4)_4$ were synthesized by a solid-state reaction[6] of mixture of CuO, MgO/NiO, $CaCO_3$, and $NH_4H_2PO_4$ of purity 99.99% of Alfa Aesar. The mixture was heated slowly up to 600 °C and then annealed at 900 °C for 110 h with several intermediate grindings. The powder sample is then characterized by x-ray diffraction (XRD) study. Figure 2 shows the x-ray diffraction patterns of the pure, the Mg-substituted and the Ni-substituted systems. Using the least-square method all the lines could be indexed by considering the crystal symmetry to be monoclinic and belonging to the space group $P2_1/a$, as in the pure compound.[5] The lattice parameters for $Ca_3Cu_3(PO_4)_4$, $Ca_3Cu_2Ni(PO_4)_4$, and $Ca_3Cu_2Mg(PO_4)_4$ are shown in Table I. It is to be noted that the substitution of a Cu atom by Ni/Mg atom results in an expansion of the unit cell along the *a* direction and a compression along the *c* direction. Moreover, the lattice parameters for Ni- and Mg-substituted compounds are found to be very close to each other. The dc magnetic susceptibility was measured in $Ca_3Cu_3(PO_4)_4$,

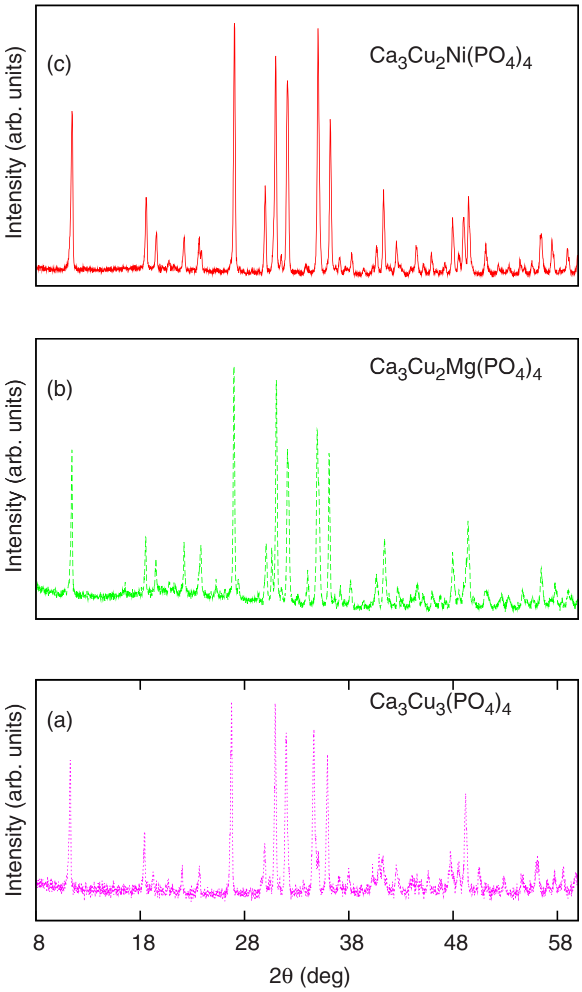

FIG. 2. (Color online) Typical XRD patterns for (a) $Ca_3Cu_3(PO_4)_4$, (b) $Ca_3Cu_2Mg(PO_4)_4$, and (c) $Ca_3Cu_2Ni(PO_4)_4$ samples.

TABLE I. Values of lattice parameters.

Compound	*a* (Å)	*b* (Å)	*c* (Å)	*β*
$Ca_3Cu_3(PO_4)_4$	17.615(3)	4.896(3)	8.912(4)	124.06(4)
$Ca_3Cu_2Ni(PO_4)_4$	17.714(4)	4.885(3)	8.845(4)	123.84(4)
$Ca_3Cu_2Mg(PO_4)_4$	17.719(3)	4.886(2)	8.830(2)	123.84(2)

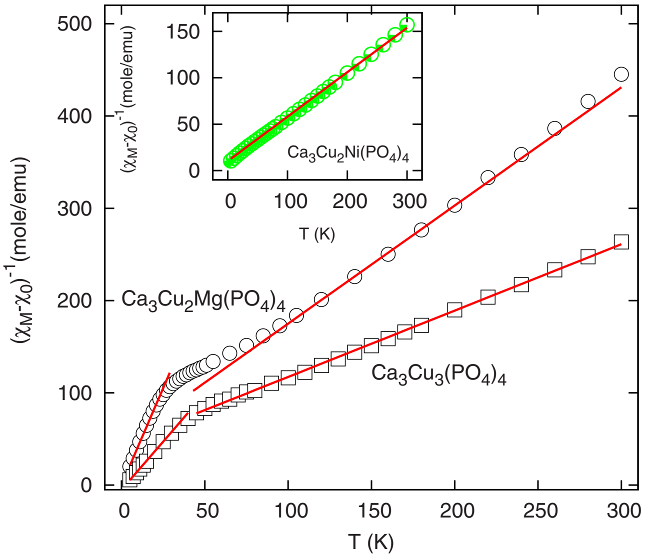

FIG. 3. (Color online) $(\chi_M-\chi_0)^{-1}$ vs temperature for $Ca_3Cu_2Mg(PO_4)_4$ and $Ca_3Cu_3(PO_4)_4$ with the straight lines corresponding to Curie-Weiss fit. Inset shows the same for $Ca_3Cu_2Ni(PO_4)_4$.

$Ca_3Cu_2Mg(PO_4)_4$, and $Ca_3Cu_2Ni(PO_4)_4$ in a superconducting quantum interference device magnetometer of Quantum Design [Magnetic Property Measurement System (MPMS)] in a magnetic field of 0.1 T, in the temperature range 5–300 K in the heating cycle.

III. RESULTS AND DISCUSSION

Figure 3 shows the inverse of molar susceptibility (χ_M^{-1}) versus temperature curves for pure compound $Ca_3Cu_3(PO_4)_4$, Mg-substituted compound $Ca_3Cu_2Mg(PO_4)_4$ and Ni-substituted compound $Ca_3Cu_2Ni(PO_4)_4$. For $Ca_3Cu_2Mg(PO_4)_4$, in the temperature range 100–300 K χ_M follows the equation

$$\chi(T) = \chi_0 + \chi_{cw}(T) = \chi_0 + C/(T - \theta) \qquad (1)$$

χ_0 is the temperature-independent contribution arising from core diamagnetic susceptibility of the individual ions[10] and the Van Vleck paramagnetic susceptibility of the compound. $\chi_{cw}(T)$ is the Curie-Weiss term. Below this range there is a clear signature of deviation from this law with a tendency of slow upturn in the range 30–100 K. Below 30 K, χ_M^{-1} again decreases linearly with T following Eq. (1). Whereas, in $Ca_3Cu_3(PO_4)_4$, as reported in the literature, the slope change occurs near 45 K, with no signature of upturn in the χ_M^{-1} vs T curve. While the same in $Ca_3Cu_2Ni(PO_4)_4$ varies linearly with a same slope in the range 5–300 K. Values of temperature-independent term, χ_0, Weiss constant, θ, and the Curie constant, C for the three compounds $Ca_3Cu_3(PO_4)_4$, $Ca_3Cu_2Ni(PO_4)_4$, and $Ca_3Cu_2Mg(PO_4)_4$ are given in Table II for comparison. In the table χ_0^{HT} indicates the values of χ_0 in the high-temperature range (45–300 K) for $Ca_3Cu_3(PO_4)_4$ and the same for $Ca_3Cu_2Mg(PO_4)_4$ in the range 100–300 K. While χ_0^{LT} represents the values of χ_0 in the low-temperature range, 5–45 K for $Ca_3Cu_3(PO_4)_4$ and 5–25 K for $Ca_3Cu_2Mg(PO_4)_4$. In a similar way, C^{HT}, C^{LT} and θ^{HT}, θ^{LT} denote the values of the Curie constant and Curie-Weiss temperature in the high- and low-temperature range as mentioned above.

In case of $Ca_3Cu_2Mg(PO_4)_4$ the paramagnetic spin value per magnetic site Cu^{2+}, calculated from this value of C is 0.52 which is in close agreement with the expected average spin value per magnetic site, 0.5. Negligible value of θ below 30 K, indicates that the Cu^{2+} spins are almost isolated within the chain. The ratio between the Curie constants at high- and low-temperature range, is 3.12. In this compound, the reduction in the magnitude of C below 30 K, would result not only from a reduction in the Cu^{2+} net spin within different trimers but also due to a reduction in the total number of Cu^{2+} ions with nonzero spins, (due to the strong NN AF exchange) if there are bonds of the type Cu-Cu-Mg, in addition to those of Cu-Cu-Cu and Mg-Cu-Mg types. As in case of $Ca_3Cu_3(PO_4)_4$, only one type of trimer viz., Cu-Cu-Cu is present, the one third reduction in the value of C below 45 K, corresponds to a change in the net spin value of each trimer, to one third of its value obtained in the range 45–300 K, due to the dominance of the NN AF exchange between the Cu atoms in each trimer. So in this case the total number of trimers with nonzero spin remains unchanged. However, in case of $Ca_3Cu_2Mg(PO_4)_4$, if more than one type of bonds are formed, as mentioned above, the reduced value of the spin in all types of bonds will not be the same. So in this case the obtained value of C in the range 5–30 K, will be an added effect of the different magnitude of the reduced spins in different types of bonds formed due to Mg substitution.

To understand the origin of the upward turn in the χ_M^{-1} versus T curve in $Ca_3Cu_2Mg(PO_4)_4$, in the range 30–100 K, we have subtracted the purely Curie-type contribution which appears below 30 K (as represented by the straight line in the range 5–30 K) from the measured susceptibility. Figure 4 shows that this contribution to the total susceptibility (represented by circle) increases continuously below 300 K and shows a broad peak around 75 K and then decreases continuously below 65 K. In order to see whether this decrease is a signature of the singlet ground state separated from the ex-

TABLE II. Values of different parameters of Curie-Weiss law.

Compound	χ_0^{HT} (emu/mole)	C^{HT}	θ^{HT} (K)	χ_0^{LT} (emu/mole)	C^{LT}	θ^{LT} (K)
$Ca_3Cu_3(PO_4)_4$	$1.4(4)\times10^{-4}$	1.38(1)	−62.9(1)	$1.04(4)\times10^{-4}$	0.48(2)	2.4(1)
$Ca_3Cu_2Ni(PO_4)_4$	$1.1(2)\times10^{-4}$	2.46(2)	−29.1(1)	$1.1(2)\times10^{-4}$	2.46(2)	−29.1(1)
$Ca_3Cu_2Mg(PO_4)_4$	$1.6(3)\times10^{-4}$	0.78(2)	−37(2)	$1.02(2)\times10^{-4}$	0.25(1)	0

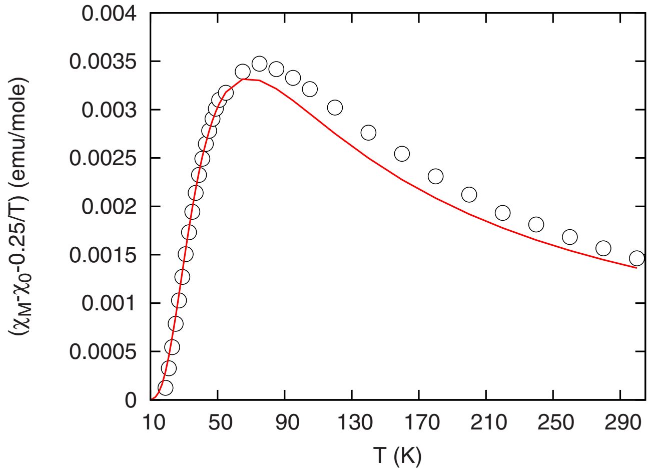

FIG. 4. (Color online) Variation in $\chi_M(T)-\chi_0-\chi_{low}(T)$ with T (represented by circles), where $\chi_{low}(T)=0.25/T$ is the Curie term below 25 K. The continuous line represents the theoretical curve corresponding to Eq. (2).

cited state by an energy gap Δ, in some trimers, we have theoretically fitted this susceptibility by using expression[11]

$$\chi_{spin}(T) = Ng^2\mu_B^2/k_BT[3+\exp(\Delta/k_BT)], \qquad (2)$$

where Δ is the energy gap between the singlet ground state and the triplet excited state. The theoretical curve with the value of $\Delta/k_B \sim 110$ K, is found to agree quite satisfactorily, with the experimental data below 65 K. The deviation of the theoretical curve from the experimental curve above 65 K, indicates that there are other bonds whose net spin values are not reduced to zero. Their contribution to the measured susceptibility would be responsible for the disagreement between the two curves above 65 K. Therefore, the present finding suggests that in $Ca_3Cu_2Mg(PO_4)_4$, there exists some bonds possibly of the type Cu2-Cu1-Mg, for which the net spin of the Cu ions reduces to zero, below 65 K. In addition to this, if there are bonds of the types Cu2-Cu1-Mg and Cu2-Cu1-Cu2 as suggested in case of $Ca_3Cu_2Ni(PO_4)_4$, these bonds would have the net spin $S=1/2$ in $Ca_3Cu_2Mg(PO_4)_4$ at low temperature, if the NN AF exchange interaction dominates. In that case the behavior of the overall susceptibility below a certain temperature is expected to be a superposition of both types of spins viz., $S=0$ and $S=1/2$.

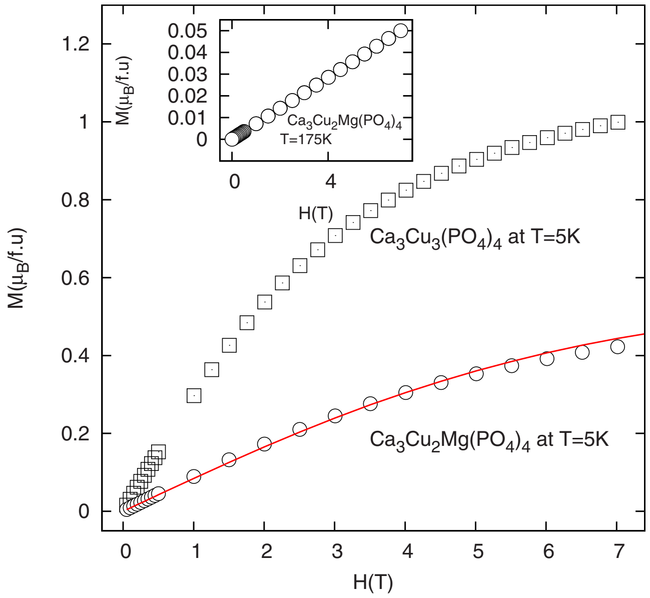

FIG. 5. (Color online) The M vs H curve at 5 K for $Ca_3Cu_2Mg(PO_4)_4$ and $Ca_3Cu_3(PO_4)_4$. Continuous line represents theoretical fitting of M-H curve with Brillouin function. Inset shows the M vs H curve at 175 K for $Ca_3Cu_2Mg(PO_4)_4$.

Figure 5 shows the M vs H curves in the magnetic field range of 0–7 T at $T=175$ K (inset) and at $T=5$ K in $Ca_3Cu_2Mg(PO_4)_4$. The same curve at $T=5$ K in $Ca_3Cu_3(PO_4)_4$ is also included for comparison. In $Ca_3Cu_2Mg(PO_4)_4$ the variation is perfectly linear at 175 K, however, there appears a nonlinearity above $H=3$ T for the curve at $T=5$ K. However, in case of $Ca_3Cu_3(PO_4)_4$, this curve at $T=5$ K starts to become nonlinear from a much lower field of $H=1$ T. In $Ca_3Cu_2Mg(PO_4)_4$ the curve at $T=5$ K, could be fitted satisfactorily by a Brillouin function of $S=1/2$, as shown by the continuous line. This further confirms that in this temperature region, all the bonds which possess a nonzero value of the net spin, is $S=1/2$. Moreover, the close agreement between the calculated and the experimental curve further confirms that these spins are uncorrelated and agrees with the observed nearly zero value for the Curie-Weiss temperature in the same temperature range. However, the M vs H curve in $Ca_3Cu_3(PO_4)_4$, cannot be fitted with a Brillouin function of $S=1/2$. A possible reason for this is the presence of short-range magnetic correlations among the $S=1/2$ spins in different trimers, as this system orders ferromagnetically at $T_C=0.9$ K. In this compound, the magnetization curve saturates at about $1.15-1.20$ μ_B/mol, which is one third of the expected saturation value, M_s, of 3.3 μ_B/mol for $S=3/2$ and $g=2.2$. This agrees with the results reported by Drillon *et al.*[5] The observed quantum state corresponds to $S=1/2$ per trimer, i.e., the spin per trimer unit becomes 1/2 due to the dominance of strong NN AF coupling below a certain temperature. Whereas, the magnetization curve for $Ca_3Cu_2Mg(PO_4)_4$ at 5 K saturate at about $0.5-0.52$ μ_B/mol. This value is one fourth of the expected saturation value, $M_s=2.2$ μ_B/mol for $S=1/2$ and $g=2.2$. This further reduction in M_s value compared to the amount of reduction in M_s, for pure compound, indicates that the spin of one type of bond [Cu(2)-Cu(1)-Mg] among the other types, becomes zero, below a certain temperature and thus corroborates with the findings from χ_M^{-1} versus T curve. It is to be noted that the value of the g factor indicates incomplete quenching of the orbital angular momentum of the Cu ions in this compound as was also reported for the pure compound.[5] One possible reason for this could be the different magnitude of quenching of the orbital angular momentum of the Cu1 and Cu2 sites, because of their different local crystalline environments, as mentioned in Sec. I and also shown in Fig. 1.

Thus the magnetic susceptibility data in $Ca_3Cu_2Mg(PO_4)_4$ indicates that the partial substitution of Cu by Mg in $Ca_3Cu_3(PO_4)_4$, creates more than one type of trimers, as was suggested in case of $Ca_3Cu_2Ni(PO_4)_4$. Surprisingly, the behavior of susceptibility in the latter do not corroborate with this prediction while the former supports this. One possible reason for such difference could be that the Ni ion does not occupy the position of Cu2 (the end position of a trimer) instead it occupies the position of Cu1 (the middle position of a trimer). In this case the only possible type of trimer would be Cu2-Ni-Cu2, where the exchange interaction between the two Cu2 ions would be much weaker and hence the possibility of reduction in the net spin of the trimer would be much less compared to the case when Ni occupies the Cu2 position. Such a difference in site occupancy may arise because the crystal chemistry may be different for Mg ion, a 2*p* element and the Ni ion having 3*d* orbitals. In this case the expected susceptibility behavior of $Ca_3Cu_2Ni(PO_4)_4$ could be similar to the experimental observation. Therefore, the present magnetization results in $Ca_3Cu_2Mg(PO_4)_4$, demands a detailed neutron-scattering study in this compound and a comparison of the same with those reported in $Ca_3Cu_2Ni(PO_4)_4$, which would be helpful to understand the reason behind the absence of the spin-singlet ground state in $Ca_3Cu_2Ni(PO_4)_4$.

IV. SUMMARY

We studied the effect of substitution of one Cu^{2+} ion ($S=1/2$) by a Mg^{2+} ion ($S=0$) on the magnetic properties of the linear-chain spin trimer compound $Ca_3Cu_3(PO_4)_4$. For this we measured the dc magnetic susceptibility in $Ca_3Cu_2Mg(PO_4)_4$, together with those in $Ca_3Cu_3(PO_4)_4$ and $Ca_3Cu_2Ni(PO_4)_4$ for comparison. In $Ca_3Cu_2Ni(PO_4)_4$, the nature of the χ_M^{-1} versus T curve in the range 5–300 K, did not give any signature of the reduction in the net spin value of the trimers below a certain temperature due to the dominance of NN AF exchange, as was reported for the pure compound $Ca_3Cu_3(PO_4)_4$, and also observed in the present study. Interestingly, the measurement in $Ca_3Cu_2Mg(PO_4)_4$, clearly shows the signature of the reduction in the net spin of each trimer below 65 K. These results further suggest, the existence of some bonds possibly of the type Cu2-Cu1-Mg, whose net spin gradually reduces to zero below 65 K, due to the dominance of NN Cu-Cu AF exchange interaction. The results further suggest that the rest of the bonds in this compound have the reduced value of the spin of $S=1/2$ below 65 K. Those bonds may be of the type Cu2-Cu1-Cu2 and Mg-Cu1-Mg. A comparison of the susceptibility data in the three compounds indicate that probably same types of bonds between Cu2, Cu1, and Ni/Mg are not formed due to Ni/Mg substitution in $Ca_3Cu_3(PO_4)_4$, or the strength of the NN exchange interaction between the Cu^{2+} ions are not same in these three compounds, probably smaller in case of $Ca_3Cu_2Ni(PO_4)_4$, which again does not corroborate with the prediction of higher value of $J_{\text{Cu-Cu}}$ in this compound from neutron scattering, compared to that in $Ca_3Cu_3(PO_4)_4$.

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*kajal.ghoshray@saha.ac.in

[1] F. D. M. Haldane, Phys. Rev. Lett. **50**, 1153 (1983).

[2] I. Affleck, Phys. Rev. B **43**, 3215 (1991).

[3] T. Sakai and M. Takahashi, Phys. Rev. B **43**, 13383 (1991).

[4] M. Azuma, T. Odaka, M. Takano, D. A. Vander Griend, K. R. Poeppelmeier, Y. Narumi, K. Kindo, Y. Mizuno, and S. Maekawa, Phys. Rev. B **62**, R3588 (2000).

[5] M. Drillon, M. Belaiche, P. Legoll, J. Aride, A. Boukhari, and A. Moqine, J. Magn. Magn. Mater. **128**, 83 (1993).

[6] A. A. Belik, A. Matsuo, M. Azuma, K. Kindo, and M. Takano, J. Solid State Chem. **178**, 709 (2005).

[7] V. Y. Pomjakushin, A. Furrer, D. V. Sheptyakov, E. V. Pomjakushina, and K. Conder, Phys. Rev. B **76**, 174433 (2007).

[8] C. Ruegg, N. Cavadini, A. Furrer, H. U. Gudel, K. Kramer, H. Mutka, A. K. Habicht, P. Vorderwisch, and A. Wildes, Nature (London) **423**, 62 (2003).

[9] A. Podlesnyak, V. Pomjakushin, E. Pomjakushina, K. Conder, and A. Furrer, Phys. Rev. B **76**, 064420 (2007).

[10] P. W. Selwood, *Magnetochemistry* (Interscience, New York, 1956).

[11] D. C. Johnston, R. K. Kremer, M. Troyer, X. Wang, A. Klumper, S. L. Bud'ko, A. F. Panchula, and P. C. Canfield, Phys. Rev. B **61**, 9558 (2000).