Synthesis and magnetic properties of spin-$\frac{3}{2}$

$\gamma$-phase of SrCo$_2$(PO$_4$)$_2$ antiferromagnet

Arvind Yogi,*† T. Chakrabarty,† P. L. Paulose,† Ruta Kulkarni,†

Mayanak Kumar Gupta,‡ and Arumugam Thamizhavel†

†Department of Condensed Matter Physics and Materials Science, Tata Institute of
Fundamental Research, Homi Bhabha Road, Colaba, Mumbai 400005, India
‡Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India

E-mail: yogi.arvind2003@gmail.com

Abstract

We report on the synthesis of a new $\gamma$-phase of the spin $S = \frac{3}{2}$ compound SrCo$_2$(PO$_4$)$_2$
together with a detailed structural, magnetic and thermodynamic properties. The $\gamma$-
phase of SrCo$_2$(PO$_4$)$_2$ crystallizes in a triclinic crystal structure with the space group $P\bar{1}$. Susceptibility and specific heat measurements reveal that SrCo$_2$(PO$_4$)$_2$ orders
antiferromagnetically below $T_N \simeq 8.5$ K and the nature of ordering is three dimension-
(3D). The magnetic isotherm at temperatures below $T_N$ shows a field-induced
spin-flop transition, related to the magnetocrystalline anisotropy, at an applied field
of $\sim 4.5$ Tesla. Remarkably, heat capacity shows magnetic-field-induced transitions at
$T_{N1} = 3.6$ K and $T_{N2} = 7.4$ K. The magnetic long range ordering (LRO) is also con-
firmed in both the Knight shift and spin-lattice relaxation rate ($1/T_1$) of the $^{31}$P-NMR
measurements. However, below the LRO we have not detected any NMR signal due
to faster relaxation. We have detected two structurally different phosphorous sites in
$\gamma$-phase of SrCo$_2$(PO$_4$)$_2$ and they shift differently with temperature.
Introduction

Magnetic properties of the transition metal ion (M)-based oxide materials are strongly depended on the coordination polyhedra of the magnetic ion such as octahedron (MO$_6$), pentahedron (MO$_5$), and tetrahedron (MO$_4$). Such magnetic materials have attracted considerable attention because of their anomalous field-induced critical behaviors.$^{1-5}$ The ground state of such spin systems with antiferromagnetic (AFM) ordering gets modified by quantum fluctuations, which can be driven by small value of spin, geometric frustration, low-dimensionality or application of magnetic field as well. Anomalous field-induced behaviour observed in the magnetic properties of these materials also depends on the nature of exchange interaction and magneto-crystalline anisotropy.$^6$ One such fascinating family of compounds, which has general formula AM$_2$(XO$_4$)$_2$ [A = Ba, Sr, Pb; M = Cu, Ni, Co, Mn; and X = P, V, As], has been studied extensively. These studies unveiled a plethora of interesting magnetic properties.$^7$-$^{11}$

Several antiferromagnets, including isotropic spin gap systems PbNi$_2$V$_2$O$_8$$^{12}$ and TlCuCl$_3$$^{13}$ manifest field-induced disorder-to-order transition. Where as strong anisotropic field-induced behaviour observed for BaCo$_2$V$_2$O$_8$ in longitudinal and transverse field directions.$^{14}$ In other vanadium based compounds BaMn$_2$V$_2$O$_8$, PbCo$_2$V$_2$O$_8$, and SrCo$_2$V$_2$O$_8$ show field-induced quantum phase transition.$^{15}$-$^{20}$ Resembling with the aforementioned families of antiferromagnetic compounds, the phosphorous based systems with the nominal composition of AB$_2^+$(PO$_4$)$_2$ (A = Ca, Sr, Ba, and Pb; B = divalent transition metals) show large variations in crystal structures and their magnetic properties.$^{21}$-$^{34}$

To our knowledge, there are no reports on the synthesis and magnetic behavior of high temperature (HT) γ- phase (named) for SrCo$_2$(PO$_4$)$_2$ till date. Here, we report the structural, magnetic and spin dynamic properties of the newly discovered γ-phase for spin-$\frac{3}{2}$ compound SrCo$_2$(PO$_4$)$_2$ with non-negligible 3D interactions. The phases of SrCo$_2$(PO$_4$)$_2$ compound are highly sensitive and its synthesis strongly depends on the heat treatment conditions. α-phase of SrCo$_2$(PO$_4$)$_2$ was first prepared by Elbali et al.$^{23}$ and the magnetic
properties have been reported by He et al. The β-phase of SrCo2(PO4)2 was recently synthesized and magnetic properties have been reported by Yang et al. The magnetic properties are distinctly different for both α- and β-phases. The existence of γ-phase of the compound has been confirmed by differential thermal analysis (DTA) and x-ray diffraction studies, while the magnetic property of this phase was studied by measuring the magnetization, heat capacity, and 31P-NMR. This HT phase shows a clear magnetic ordering at \( T_N \approx 8.5 \) K; significantly lower than that of the previously reported α- and β-phases. γ-SrCo2(PO4)2 also exhibits sequence of field-induced magnetic transitions in an applied external magnetic field.

**Experimental Section**

The title compound γ-SrCo2(PO4)2 was synthesized by high temperature solid-state reaction route by using Sr2CO3 (99.99%, Alfa Aesar), CoO (99.99%, Alfa Aesar) and NH4H2PO4 (99.99%, Alfa Aesar) as starting materials. The starting materials were mixed in acetone medium and ground in an agate mortar and loaded into a high quality recrystallized alumina (99.9%) crucible. The contents in the crucible was then heat treated at 450 °C for 6 h and at 650 °C for 24 h in air in order to release H2O, NH3, and CO2. The resulting powder was then ground and heat treated at several different temperatures such as 800 °C, 850 °C, 900 °C, 950 °C, 1000 °C and 1050 °C for 24 h with several intermediate grindings to obtain the HT γ-phase. After each heating, the sample was cooled down (120 °C/h) to room temperature to ensure more complete absorption of oxygen by the lattice and reground to improve homogeneity. The synthesized compound was found to melt above 1050 °C, which was clearly observed in differential thermal analysis (DTA) measurement. The synthesized HT-phase γ-SrCo2(PO4)2 was dark blue in color. The progress of the reactions was followed by powder x-ray diffraction (P-XRD) and final reaction just below the melting of the material renders the pure powder sample.
Differential thermal analysis (DTA) was measured on a NETZSCH 449C thermal analyzer instrument with the temperature ranging from 30 to 1400 °C under N₂ atmosphere using a heating rate of 10 °C/min. To ensure the phase purity of the sample, powder x-ray diffraction was performed at room temperature in a PANalytical x-ray diffractometer with CuKα radiation of λave = 1.5441 Å. The x-ray diffraction pattern was refined by the Rietveld method. Magnetic susceptibility χ(T) measurements were performed using SQUID (Quantum Design) and heat capacity Cₚ(T) measurements were performed using a commercial Physical Property Measurement System (PPMS, Quantum Design). The NMR measurements of γ-SrCo₂(PO₄)₂ [³¹P-gyromagnetic ratio 2\textit{γ}/\textit{\pi} = 17.234 MHz Tesla⁻¹ and nuclear spin \textit{I} = \frac{1}{2}] were carried out using a fixed frequency of 27 MHz and with a varying field. As the spectra is broad, we have measured the spectra in field-sweep mode and each point is measured by integrating the area under the spin-echo magnitude and averaging it over multiple scans. We used a \( \frac{\pi}{2} - \tau - \frac{\pi}{2} \) (solid echo) sequence for measuring spectra where \( \tau \) is the gap between the pulses. We adjusted the pulse-width at different temperatures depending on the width of the spectra. From room temperature (300 K) to 10 K it was varied from 7 µs to 5 µs respectively. The ³¹P nuclear spin-lattice relaxation rate (1/T₁) was measured by the saturation recovery method using a \( \frac{\pi}{2} - t - \frac{\pi}{2} - \tau - \pi \) pulse sequence with \( \tau = 60 \mu s \) and a variable delay (t). Similar to spectra measurements, we varied the pulse-width here as well according to the change of the spectral width of the NMR signal with temperature.

Results and discussion

X-ray diffraction and thermal analyses

The structure of γ-SrCo₂(PO₄)₂ phase was solved using Rietveld method of the room temperature x-ray diffraction pattern as shown in the Fig. 1(a) by Fullprof software. In order to identify the single phase nature of γ-SrCo₂(PO₄)₂, initial parameters were taken from the previously reported structure. Rietveld analysis confirms that the γ-phase of the title
Figure 1: (a) Rietveld refined x-ray powder diffraction pattern for $\gamma$-SrCo$_2$(PO$_4$)$_2$ at room temperature. The observed and calculated patterns are shown by filled red circles and solid black line, respectively. The difference between observed and calculated patterns is shown by the thin blue line at the bottom. The vertical bars are the allowed Bragg peak positions. (b) Projection of the crystal structure of $\gamma$-SrCo$_2$(PO$_4$)$_2$ in the $bc$ plane is shown. The structure is composed of two inequivalent distorted trigonal bipyramids of Co$_2$O$_5$ and Co$_2$O$_5$ with two inequivalent P(1)O$_4$ and P(2)O$_4$ tetrahedra, which are separated by Sr atoms.

The compound also crystallizes in the triclinic structure with space group $P\overline{1}$ (space group No. 2) akin to both $\alpha$- and $\beta$-phases. The obtained values of cell-parameters are different from both phases but closer to $\alpha$-phase. The refined values of various structural parameters such as lattice constants, fractional atomic coordinates, and isotropic thermal parameters of
all crystallographic sites are given in Table 1. All the crystallographic sites were considered to be fully occupied during the refinement. The Co-O and P-O bond lengths, and bond angles are given in Table 2.

The crystal structure of $\gamma$-SrCo$_2$(PO$_4$)$_2$ consists of layers of five-coordinated cobalt (CoO$_5$) and (PO$_4$)$_{−3}$ groups within the $ab$ and $bc$ planes, which are isolated by strontium (Sr$^{2+}$) ions [Fig. 1(b)]. Co(1) and Co(2) are surrounded by five oxygen ions which construct Co(1)O$_5$ and Co(2)O$_5$ trigonal bipyramids having irregular 5-fold polyhedron, different from $\alpha$- and $\beta$-phases. Within a given layer, CoO$_5$ polyhedron are connected by corner sharing of two different types of PO$_4$ tetrahedra thus resulting in a 3D magnetic lattice. Additionally, Co(1)O$_5$ units form dimers among themselves via edge-sharing and results Co$_2$O$_{10}$ units. The detailed view of the crystal structure of $\gamma$-SrCo$_2$(PO$_4$)$_2$ in $bc$-plane is shown in Fig. 1(b).

The phase purity of SrCo$_2$(PO$_4$)$_2$ has been investigated by DTA and P-XRD measurements. DTA is a very sensitive and useful technique to know about the various physical transformations occurring in the solids such as melting, sublimation etc. Figure 2(a) reveals the phase changes in SrCo$_2$(PO$_4$)$_2$ occurring in four stages which involves different possible phases at different temperatures. There are four endothermic peaks at 805°C, 860°C, 955°C, and 1050°C. To know about the respective phases, we have performed P-XRD of the compounds synthesized at 800°C, 850°C, 875°C, 900°C, 950°C and 1050°C and are shown in Fig. 2(b). The subtle analysis of the powder x-ray diffraction data renders that out of the four endothermoc peaks, the 805°C and 955°C peaks in DTA curve are the $\beta$- and $\alpha$-phases, respectively. The HT-phase exists at 1050°C, named as $\gamma$-phase. The P-XRD pattern of $\gamma$-phase is very much similar to the $\alpha$-phase, we have compared it with the $\alpha$-phase in Fig. 2(b) where few additional peaks are marked by stars and a single missing peak is marked by an arrow. The HT $\gamma$-phase can be explained by the triclinic structure with space group $P\bar{1}$. A reasonably good fit of the P-XRD data has been obtained for $\gamma$-phase from the Rietveld analysis as shown in Fig. 1(a). The endothermic peak marked by star at 860°C in the DTA curve [Fig. 2(a)] also represents some intermediate unknown phase ($x$) of
SrCo$_2$(PO$_4$)$_2$, and is an open issue of future research. A schematic sketch of the synthesis method and the phase formation as a function of time and temperature are shown in Fig. 3. Heating mixtures of Sr$_2$CO$_3$, CoO and NH$_4$H$_2$PO$_4$ to sufficiently high temperatures leads to the formation of $\gamma$-SrCo$_2$(PO$_4$)$_2$ under release of H$_2$O, NH$_3$, and CO$_2$, which often referred to as calcination process. The $\alpha$ and $\beta$-phases are the relatively low temperature phases of SrCo$_2$(PO$_4$)$_2$ which are separated by another unknown ($\gamma$) phase (stripe pattern in the Fig. 3) with small temperature window between 805 °C to 860 °C [Fig. 2 (a)].

Figure 2: (Color online) Evaluation of different phases of SrCo$_2$(PO$_4$)$_2$ from DTA curve (a) P-XRD pattern of SrCo$_2$(PO$_4$)$_2$ at different temperatures are shown.

Magnetization and Magnetic Susceptibility

The magnetic susceptibility $\chi(T)$ data for $\gamma$-SrCo$_2$(PO$_4$)$_2$ measured at $H = 1$ T is presented in Fig. 4(a). At high temperatures $T > 30$ K, $\chi(T)$ follows a Curie-Weiss law. The susceptibility increases with decreasing temperature, while a sharp peak is observed at 8.5 K, indicating the onset of AFM ordering as shown in the inset of Fig. 4(a) by the derivative of susceptibility which is characteristic of LRO. The magnetic properties and the transition observed for $\gamma$-SrCo$_2$(PO$_4$)$_2$ are different from those of $\alpha$- and $\beta$-phases. In $\gamma$-SrCo$_2$(PO$_4$)$_2$, LRO is observed at much lower temperature compared to that of the $\alpha$- and $\beta$-phases [35,36]. A typical Curie-Weiss behaviour observed above 55 K for $\gamma$-SrCo$_2$(PO$_4$)$_2$, is shown in
Figure 3: (Color online) Schematic description of the synthesis method and temperature profile of SrCo$_2$(PO$_4$)$_2$ for different phases ($\alpha$, $\beta$, and $\gamma$). The formation of $\gamma$-phase takes place at $T= 955^\circ$C–1050$^\circ$C. The unknown phase ($x$) of SrCo$_2$(PO$_4$)$_2$ is shown by stripe pattern.
Table 1: Crystallographic parameters for $\gamma$-SrCo$_2$(PO$_4$)$_2$ at room temperature are obtained from Rietveld refinement. $\gamma$-SrCo$_2$(PO$_4$)$_2$ has triclinic structure, with space group $P-1$ and obtained lattice parameters are $a = 5.02080(6)$ Å, $b = 8.65940(10)$ Å, and $c = 9.72680(10)$ Å; $\alpha = 118.188^\circ(4)$, $\beta = 75.066^\circ(5)$, and $\gamma = 87.078^\circ(5)$ compared to the reported values $a = 5.014(2)$ Å, $b = 8.639(4)$ Å, and $c = 9.691(1)$ Å; $\alpha = 118.04^\circ(3)$, $\beta = 75.09^\circ(4)$, and $\gamma = 86.90^\circ(4)$. Wyckoff symbol and relative atomic coordinate of each atom is listed in the table. All atoms occupy at the $2i$ crystallographic site and all the atomic sites are found to be fully occupied. The goodness of fit: $\chi^2 = 2.51$. The numbers in the parentheses are the respective error bars.

| Atom | Wyckoff | $x/a$   | $y/b$   | $z/c$   |
|------|---------|---------|---------|---------|
| Sr   | 2i      | 0.161(20)| 0.324(12)| 0.054(12)|
| Co1  | 2i      | 0.024(3) | 0.193(2) | 0.590(17)|
| Co2  | 2i      | 0.533(3) | 0.209(19)| 0.290(17)|
| P1   | 2i      | 0.879(6) | 0.027(4) | 0.807(3) |
| P2   | 2i      | 0.593(6) | 0.599(4) | 0.306(3) |
| O11  | 2i      | 1.119(13)| 0.028(7) | 0.835(6) |
| O12  | 2i      | 0.750(11)| −0.138(7)| 0.797(6)|
| O13  | 2i      | 0.668(11)| 0.198(8) | 0.951(6) |
| O14  | 2i      | 0.984(11)| 0.002(7) | 0.634(7) |
| O21  | 2i      | 0.573(9) | 0.752(7) | 0.478(7) |
| O22  | 2i      | 0.282(12)| 0.614(6) | 0.326(6) |
| O23  | 2i      | 0.710(11)| 0.636(6) | 0.179(6) |
| O24  | 2i      | 0.742(10)| 0.412(6) | 0.299(6) |
Table 2: The Co–O and P–O bond lengths and bond-angles for the $\gamma$-SrCo$_2$(PO$_4$)$_2$ at 300 K. The bond lengths and bond angles indicate that neither the CoO$_5$ trigonal bipyramids nor the PO$_4$ tetrahedra are regular.

|                  | Bond lengths (Å) | Bond angles (°) |
|------------------|------------------|-----------------|
| Co1–Co1          | 3.01(2)          |                 |
| Co2–Co2          | 4.68(18)         |                 |
| Co1–Co2          | 3.41(2)          |                 |
| Co1–O14          | 1.89(8)          | O22–Co1–O23     | 132(15) |
| Co1–O14          | 2.05(6)          | O22–Co1–O14     | 122(5)  |
| Co1–O21          | 2.12(5)          | O14–Co1–O23     | 94(4)   |
| Co1–O22          | 1.91(5)          |                 |
| Co1–O23          | 2.78(6)          |                 |
| Co2–O11          | 2.23(6)          | O21–Co2–O13     | 173(5)  |
| Co2–O12          | 1.39(4)          | O21–Co2–O11     | 139(4)  |
| Co2–O13          | 3.14(7)          | O12–Co2–O13     | 110(3)  |
| Co2–O21          | 2.03(7)          |                 |
| Co2–O24          | 2.08(6)          |                 |
| P(1)–O11         | 1.29(8)          | O12–P1–O11      | 161(3)  |
| P(1)–O12         | 1.56(7)          | O11–P1–O13      | 160(3)  |
| P(1)–O13         | 1.55(5)          | O13–P1–O12      | 82(20)  |
| P(1)–O14         | 1.54(8)          | O11–P1–O14      | 97(5)   |
|                  |                  | O13–P1–O14      | 120(5)  |
|                  |                  | O14–P1–O12      | 144(3)  |
| P(2)–O21         | 1.53(6)          | O24–P2–O21      | 118(4)  |
| P(2)–O22         | 1.51(7)          | O21–P2–O23      | 135(17) |
| P(2)–O23         | 1.40(7)          | O23–P2–O22      | 165(3)  |
| P(2)–O24         | 1.71(7)          | O22–P2–O24      | 161(3)  |
|                  |                  | O23–P2–O24      | 170(6)  |
|                  |                  | O22–P2–O21      | 160(2)  |
Figure 4: (a) The magnetic susceptibility $\chi$ of $\gamma$-SrCo$_2$(PO$_4$)$_2$ versus $T$ measured in a field $H = 1$ T. Inset of (a) shows the $d(\chi(T))/dT$ versus $T$ for the applied field at $H = 1$ T in the low-$T$ regime. In this inset, the arrow indicates magnetic transition at 8.5 K. (b) The inverse magnetic susceptibility ($\chi^{-1}$) of $\gamma$-SrCo$_2$(PO$_4$)$_2$. The straight solid red line is a CW fit of $\chi^{-1}(T)$ from 55 to 300 K and the blue line is extrapolated CW fit down to 0 K. Inset of (b) shows the behaviour of $T_N$ at different applied fields in the low-$T$ regime.

Fig. 4(b): using Curie-Weiss fitting we obtained the Curie constant $C$ and the Weiss constant $\theta$. To fit the uniform magnetic susceptibility data at high temperatures, we used the
expression

\[ \chi = \chi_0 + \frac{C}{T - \theta_{CW}} , \]  

where \( \chi_0 \) is the temperature-independent contribution that accounts for core electron diamagnetism and Van Vleck (VV) paramagnetism. The second term is the Curie-Weiss (CW) law with Curie constant \( C = N_A \mu_{\text{eff}}^2 / 3k_B \), where \( N_A \) is Avogadro’s number, \( \mu_{\text{eff}} \) is the effective magnetic moment, and \( k_B \) is Boltzmann’s constant) and Weiss temperature \( \theta_{CW} \). The data above 55 K were fitted with the parameters \( \chi_0 = -5.268(2) \times 10^{-4} \text{ cm}^3/\text{mol Co} \), \( C = 2.825(8) \text{ cm}^3 \text{ K/mol Co} \), and \( \theta_{CW} = -9.969(5) \text{ K} \). The effective magnetic moment \( \mu_{\text{eff}} \) is calculated to be 4.753(2) \( \mu_B \), which is larger than the value of 3.87 \( \mu_B \) for \( S = \frac{3}{2} \) with a \( g \) value of 2 (free-electron \( g \)-value). This higher value of \( \mu_{\text{eff}} \) is attributed to the presence of some orbital contribution which have been observed in other Co\(^{2+} \) compounds and it agrees well with the earlier reports.\(^{48,49} \) Also, the negative Weiss constant suggests that the dominant interactions between Co\(^{2+} \) ions are AFM. The temperature-dependent magnetic susceptibility \( \chi(T) \) data for \( \gamma \)-SrCo\(_2\)(PO\(_4\))\(_2\) measured as a function of temperature at different applied fields are shown in inset of Fig. 4(b).

We also measured the low temperature Zero Field Cooled (ZFC) and Field Cooled (FC) susceptibilities in a small applied field. No significant splitting between ZFC and FC susceptibilities was observed. This confirms the absence of any glassy component in the ordered state. In order to further confirm the AFM correlation and also to check about the existence of any field induced effect at low temperature, we measured \( M(H) \) at \( T = 2 \) K for \( \gamma \)-SrCo\(_2\)(PO\(_4\))\(_2\).

The isothermal magnetization curve \( M(H) \) measured over all four quadrants at 2 K is shown in Fig. 5. The linear change of magnetization with increasing and decreasing field, indicative of a characteristic AFM ground state. The \( M(H) \) curve shows some interesting behaviors with (i) a very weak hysteresis between \(~ 6 \) T to \(~ 9 \) T, (ii) a change of slope at \(~ 4.5 \) T indicating field induced transition, and then (iii) another change of slope observed above \(~ 10 \) T, also related to field induced transition. The change of slope at the applied magnetic
field of $\sim 4.5$ T is clearly evident in the derivative curve [inset (b) of Fig. 5] which indicates a field induced transition (may be a spin-flop transition) to another antiferromagnetic state. However, another field induced transition around 10 T is possibly originated due to the spin reorientation effect occurring just before the saturation, this transition suggests that large magnetocrystalline anisotropy is present in $\gamma$-SrCo$_2$(PO$_4$)$_2$. Above $\sim 13$ T, the onset of $M(H)$ curve tends to saturate ($H_s \sim 13$ T), however, the value of magnetization at 16 T ($M_{16T} \sim 2.70 \mu_B/\text{Co}^{2+}$) is smaller than the theoretically expected saturation magnetic moment of $M_s = gS \mu_B = 3 \mu_B/\text{Co}^{2+}$ ($S = \frac{3}{2}$); this indicates that the saturation field $H_s$ is probably higher than 16 T to see the expected saturation $M_s$. However, there is a slow linear increase in $M(H)$ curve is attributed to the temperature-independent Van-Vleck paramagnetic contribution, typical for a Co$^{2+}$ ion in an octahedral environment.

Figure 5: Magnetization ($M$) measured as a function of applied field ($H$) over four quadrants measured at 2 K for $\gamma$-SrCo$_2$(PO$_4$)$_2$. Inset (a) and (b) shows the zoomed behaviour of $M(H)$ and derivative curve, respectively. Arrows indicate the field induced transition (spin-flop type).
Heat Capacity

Specific heat for $\gamma$-SrCo$_2$(PO$_4$)$_2$ was measured on a small pressed pellet using the thermal relaxation technique. Specific heat $C_p$ measurement at zero field as well as at different applied fields for $\gamma$-SrCo$_2$(PO$_4$)$_2$ are shown in Fig. 6 in the low temperature range (1.8 - 19 K). At high temperatures, $C_p$ is completely dominated by phonon excitations. Below 8.5 K, an increase of $C_p$ with decreasing temperature indicates that the magnetic contribution of specific heat is dominant in this temperature region. Here, $C_p(T)$ shows a $\lambda$-type anomaly at $T_N \simeq 8.5$ K associated with the long-range magnetic ordering (see Fig. 6) which is in good agreement with the magnetization results.

To gain further information about the nature of magnetic ordering with field, we measured $C_p(T)$ in different applied magnetic fields as shown in Fig. 6. With increasing $H$ from 0 $T$ to 14 $T$, the $\lambda$-type anomaly becomes remarkably broadened after certain applied field ($H \geq 2$ $T$) and clearly split into two shoulders which strongly indicates the presence of two orderings at applied field $H \geq 4.5$ $T$. The two magnetic-field-induced transitions at $T_{N1} = 3.6$ K and $T_{N2} = 7.4$ K are clearly visible at applied field of $H \approx 7$ $T$ (see Fig. 6). At higher fields this double transition is suppressed further. This splitting is related to the expected large magnetic anisotropy for the Co$^{2+}$ ions, analogous heat-capacity behavior is also observed in GeCo$_2$O$_4$. Similar to GeCo$_2$O$_4$, the magnetic-field-induced behavior observed in our magnetization data at around $H \approx 4.5$ $T$ (shown by arrows in Fig. 5), which is a possible spin flop transition; has been also confirmed further by magnetic-field dependent heat capacity results for $\gamma$-SrCo$_2$(PO$_4$)$_2$. At further higher applied field $H \geq 14$ $T$, the $\lambda$-type anomaly almost disappears from heat capacity data and shows only a broad anomaly whose maximum occurs at $C_{\text{max}} \sim 4.4$ K (see Fig. 6). This indicates that LRO is substantially suppressed because of higher magnetic-field, which strongly influenced by the disordered spin state. We emphasize that the microscopic nature of the disordered spin state could be resolved further by neutron diffraction experiments.
Figure 6: Heat capacity of \( \gamma \)-SrCo\(_2\)(PO\(_4\))\(_2\) measured in different applied magnetic fields. The zero field data shows \( \lambda \)-type anomaly at \( T_N \approx 8.5 \) K. The two transitions at \( T_{N1} = 3.6 \) K and \( T_{N2} = 7.4 \) K are shown by down arrows respectively at an applied field \( H \approx 7 \) T. The broad maximum (\( C_{\text{max}} \)) in the heat capacity data at higher field \( H \geq 14 \) T occurring at \( \sim 4.4 \) K is shown by an up arrow.

\[31\]P NMR Shift

The field sweep of the \( ^{31}\)P NMR spectra measured at different temperatures is shown in Fig. 7. Since the crystal structure of \( \gamma \)-SrCo\(_2\)(PO\(_4\))\(_2\) has two inequivalent P site,\(^{47}\) we observed two spectral lines above \( T_N \) as expected for an \( I = 1/2 \) nucleus for each P site.\(^{57}\) Below 10 K there is a long range magnetic ordering and due to that below 10 K nuclear spin relaxations become so fast that the \( ^{31}\)P NMR signal itself is not detected. This phenomenon of fast relaxation pursued even in lower temperatures and the signal is not detected as well.

We observed a significant negative shift of the \( ^{31}\)P NMR line and the Knight shift follows the trend observed in \( \chi(T) \) [see Fig. 8]. At room temperature the \( ^{31}\)P NMR signal is a nice Gaussian-line which is expected for the \( \frac{1}{2} \rightarrow -\frac{1}{2} \) transition of a \( I = \frac{1}{2} \) nucleus. However, at 80 K the single Gaussian NMR line splits into two Gaussian peaks (see Fig. 7). The two Gaussian peaks corresponding to two different P sites, were also observed in Pb\(_2\)Ni(PO\(_4\))\(_2\).
Figure 7: Field-sweep $^{31}$P NMR spectra at different temperatures ($T > T_N$) for polycrystalline $\gamma$-SrCo$_2$(PO$_4$)$_2$ measured at 27 MHz down to 10 K. The spectra clearly shows that below 80 K the single Gaussian pattern of the spectra splits into two lines and they shift at different rates. At 10 K (close to the LRO temperature) they again merge into a single line.

This is quite a surprising aspect considering the SrNi$_2$(PO$_4$)$_2$ compound within this AM$_2$(PO$_4$)$_2$ family where despite having two crystallographic phosphorus sites two different $^{31}$P NMR signals were not observed.\cite{34}

It is important to point in this regard that the amount of shift observed in $\gamma$-SrCo$_2$(PO$_4$)$_2$ is much larger compared to SrNi$_2$(PO$_4$)$_2$, the nearest compound in the AM$_2$(PO$_4$)$_2$ family,\cite{34} which indicates that there might be stronger hyperfine coupling in $\gamma$-SrCo$_2$(PO$_4$)$_2$ compared to the other members in the AM$_2$(PO$_4$)$_2$ family,\cite{34,60,65} which causes the larger shift and also results in the splitting of the $^{31}$P NMR signal from the two structurally different phosphorus. Out of these two Gaussian peaks, one is comparatively broader than the other (see Fig. 9).

For the convenience in discussion, now onwards we call the broader peak as $P_b$ and the other one as $P_s$. From the structural point of view, we can say that there are two different $^{31}$P nucleus in this compound and these two Gaussian peaks are originating from these $^{31}$P nuclei. The relative weight of these two peaks are close to 50% and it is maintained
throughout the whole temperature regime where these two peaks have been observed (see Fig. 10), which is expected since the two structurally different phosphorus sites are present in equal proportion. The interesting fact is that the shifts of these two peaks are unequal, and the shift of \( P_b \) is more than \( P_s \). This suggests that the internal magnetic field is more for the phosphorus atom associated with \( P_b \) compared to \( P_s \) (see Fig. 8). The shift of both the components manifest linear behavior in K-\( \chi \) but the sharp component shows some change of slope around 80 K which might be due to the fact that about 80 K the \( ^{31}\text{P} \) NMR signal starts splitting into two and at this temperature they are also almost overlapping which leads to some errors in the estimation of the sharper one. However, at 10 K (just above the magnetic long range ordering temperature) these two \( ^{31}\text{P} \) NMR lines again merge into a single line.

With the decrease in temperature \( ^{31}\text{P} \) NMR linewidth broadens but as the line splits into two and they are shifting in different rates which makes the calculation of temperature dependence of linewidth complicated.
Figure 9: The two Gaussian fit of the $^{31}$P NMR spectra for $\gamma$-SrCo$_2$(PO$_4$)$_2$ at 15 K.

Figure 10: The variation of the weight percentage of the broad component is shown for $\gamma$-SrCo$_2$(PO$_4$)$_2$. It projects that both the components have nearly similar relative weight which is also expected from the crystal structure.

**Nuclear spin-lattice relaxation rate $1/T_1$**

The $^{31}$P nuclear spin-lattice relaxation rate $(1/T_1)$ above $T_N$ for $\gamma$-SrCo$_2$(PO$_4$)$_2$ was measured at the field corresponding to the central peak position for both components $P_b$ and $P_s$. 

respectively. The features observed in the spectra measurement is also reflected in the measurement of the spin-lattice relaxation of the $^{31}$P NMR nucleus. Above 80 K we found a single-exponential $T_1$-relaxation of the $^{31}$P nucleus. Whereas below 80 K we found two relaxing components. We performed two $T_1$-measurements at the two corresponding peaks resulting from the two phosphorus nuclei.

![Figure 11: The temperature dependence of the spin-lattice relaxation rate ($1/T_1$) vs. $T$ measured at 27 MHz of the broad component of the $^{31}$P NMR spectra for $\gamma$-SrCo$_2$(PO$_4$)$_2$.](image)

Since the two phosphorus lines are overlapping on each other; apart from the phosphorous nucleus which we are probing, we also received contribution from the other phosphorous nucleus. However, $T_1$ measurement at P$_b$ is less effected due to the interference from the other component because due to its broadness when $T_1$ is measured at the center of P$_b$ it is less affected from the contribution from P$_s$ compared to the $T_1$ measured at P$_s$. For analysing $T_1$ measured at P$_b$, if we just consider the longer component which also has more relative weight and we attribute this as the contribution coming from the phosphorous at P$_b$, we find that $1/T_1$ increases slowly down to 80 K, then it slightly drops off constructing a local maximum at 80 K, (this is the temperature where the single Gaussian NMR line splits into two) after that below 40 K it falls off sharply and finally close to the magnetic LRO
(8.5 K) it kicks off again (see Fig. 11) which is commonly observed in long range ordered antiferromagnetic systems. The sharp decrease of $1/T_1$ below 40 K might be attributed to the formation of some spin-gap due to dimerization, as the Co$^{2+}$ ions are structurally forming dimer among themselves. However, to comment in further details about this aspect, further study of the magnetic-structure of this compound is required.

**Summary and Conclusions**

We have synthesized a new HT-phase of SrCo$_2$(PO$_4$)$_2$ and presented the evidence for $\gamma$-phase of SrCo$_2$(PO$_4$)$_2$ through differential thermal analysis and x-ray diffraction analysis. The $\gamma$-SrCo$_2$(PO$_4$)$_2$ phase is found to have the triclinic symmetry with space group $P\bar{1}$, isostructural to $\alpha$-phase. The bulk measurements clearly shows 3D long range magnetic interaction between the magnetic Co$^{2+}$ ions. However, the magnetic susceptibility and specific heat measurements confirm bulk magnetic ordering at $T_N \simeq 8.5$ K which is significantly lower than that of $\alpha$- and $\beta$-phases. $\gamma$-SrCo$_2$(PO$_4$)$_2$ shows sequence of field-induced magnetic transitions in an applied external magnetic field possibly due to magnetocrystalline anisotropy. Both temperature dependence of Knight shift and the spin-lattice relaxation rate of $^{31}$P NMR measurements confirm the LRO at 8.5 K for the $\gamma$-SrCo$_2$(PO$_4$)$_2$ phase. Additionally, we were able to discriminate the two structurally different phosphorus sites via NMR knight shifts. Both the knight shifts follow the trend of the magnetic susceptibility data, but below 80 K, the two Knight shifts corresponding to the two different P-sites split apart. They merge together again at 9.5 K close to the magnetic LRO temperature. Below 80 K, as the spectra splits into two we observe two components (one comparatively broader than the other) in the spin-lattice relaxation. The measurement of the spin-lattice relaxation of the sharper component is interfered by the other one and hence are not very reliable to make any distinct conclusion.

However, in comparison to the sharper component the broader spin-lattice component is
more pristine (due to having more relative weight, it suffered less percentage of interference from the other component). The spin-lattice relaxation rate for the broader component drops around 40 K but close to the ordering temperature it increases sharply which is a characteristic feature for a conventional LRO. Thermograms results of SrCo₂(PO₄)₂ shows additional new intermediate phase around at 860 °C which is sandwiched in between the α- and γ-phase. This new phase might be interesting for future studies to explore the chemistry of this interesting material.

**Associated Content**

**Supporting Information**

Detailed analysis of NMR spectra, such as NMR shift, additional NMR spectra, and Gaussian fitting for NMR spectra (PDF file)

**Author Information**

**Corresponding Authors** *E-mail: yogi.arvind2003@gmail.com (A.Y.)** ORCID Arvind Yogi: 0000-0003-3055-4592

*Notes* The authors declare no competing financial interest.

**Acknowledgement**

AY would like to acknowledge TIFR, Mumbai for financial support. AT would like to acknowledge DAE India for financial support. Fruitful discussions with Juan Rodríguez-Carvajal and Vaclav Petricek⁶⁰⁰ are kindly acknowledged. Figure 1-2 was prepared using the VESTA software.⁶⁰¹
References

(1) He, Z.; Taniyama, T.; Kyomen, T.; Itoh, M. Field-induced order-disorder transition in the quasi-one-dimensional anisotropic antiferromagnet BaCo$_2$V$_2$O$_8$. Phys. Rev. B 2005, 72, 172403:1-4.

(2) He, Z.; Taniyama, T.; Itoh, M. Antiferromagnetic-paramagnetic transitions in longitudinal and transverse magnetic fields in a SrCo$_2$V$_2$O$_8$ crystal. Phys. Rev. B 2006, 73, 212406:1-4.

(3) He, Z.; Yamaura, J. I.; Ueda, Y.; Cheng, W. Temperature and Concentration Control over Interpenetration in a Metal Organic Material. J. Am. Chem. Soc. 2009, 131, 17040–17041.

(4) Yokota, K.; Kurita, N.; Tanaka, H. Magnetic phase diagram of the $S = \frac{1}{2}$ triangular-lattice Heisenberg antiferromagnet Ba$_3$CoNb$_2$O$_9$. Phys. Rev. B 2014, 90, 014403:1-6.

(5) Susuki, T.; Kurita, N.; Tanaka, T.; Nojiri, H.; Matsuo, A.; Kindo, K.; Tanaka, H. Magnetization Process and Collective Excitations in the $S$=1/2 Triangular-Lattice Heisenberg Antiferromagnet Ba$_3$CoSb$_2$O$_9$. Phys. Rev. Lett. 2013, 110, 267201:1-5.

(6) De Joungh, L. J.; Kluwer, Ed. Magnetic Properties of Layered Transition Metal Compounds. Academic Publishers: Dordrecht 1990, 1.

(7) Wichmann, R.; Müller-Buschbaum, Hk. New Compounds of the SrNi$_2$V$_2$O$_8$-Type: BaCo$_2$V$_2$O$_8$ and BaMg$_2$V$_2$O$_8$. Z. Anorg. Allg. Chem. 1986, 534, 153–158.

(8) Vogt, R.; Müller-Buschbaum, Hk. BaCu$_2$V$_2$O$_8$: A Variant of the SrNi$_2$V$_2$O$_8$ Type with Cu$^{2+}$ in 4+1+1 Coordination. Z. Anorg. Allg. Chem. 1990, 591, 167–173.

(9) Osterloh, D.; Müller-Buschbaum, Hk. On SrCo$_2$V$_2$O$_8$ and SrCo$_2$(AsO$_4$)$_2$. Z. Naturforsch., B: Chem Sci. 1994, 49, 923–926.
(10) Uchiyama, Y.; Sasago, Y.; Tsukada, I.; Uchinokura, K.; Zheludev, A.; Hayashi, T.; Miura, N.; Boni, P. Spin-Vacancy-Induced Long-Range Order in a New Haldane-Gap Antiferromagnet. *Phys. Rev. Lett.* **1999**, *83*, 632-635.

(11) von Postel, M.; Müller-Buschbaum, Hk. Na$_2$BaCuV$_2$O$_8$: A New Structure Type of the Alkaline-Alkaline Earth Copper Oxovanadates. *Z. Anorg. Allg. Chem.* **1992**, *618*, 107-110.

(12) Tsujii, N.; Suzuki, O.; Suzuki, H.; Kitazawa, H.; Kido, G. Field-induced magnetic ordering in the Haldane system PbNi$_2$V$_2$O$_8$. *Phys. Rev. B* **2005**, *72*, 104402:1-5.

(13) Oosawa, A.; Ishii, M.; Tanaka, H. Field-induced three-dimensional magnetic ordering in the spin-gap system TlCuCl$_3$. *J. Phys.: Condens. Matter* **1999**, *11*, 265-271.

(14) Kimura, S. (Private Communication).

(15) He, Z.; Ueda, Y.; Itoh, M. Magnetic properties of the quasi-one-dimensional system BaMn$_2$V$_2$O$_8$. *Solid State Commun.* **2007**, *141*, 2924-2926.

(16) He, Z.; Fu, D.; Kyomen, T.; Taniyama, T.; Itoh, M. Crystal Growth and Magnetic Properties of BaCo$_2$V$_2$O$_8$. *Chem. Mater.* **2005**, *17*, 22-24.

(17) He, Z.; Taniyama, T.; Itoh, M. *Appl. Phys. Lett.* Large magnetic anisotropy in the quasi-one-dimensional system BaCo$_2$V$_2$O$_8$. **2006**, *88*, 132504:1-3.

(18) He, Z.; Taniyama, T.; Itoh, M.; Yamaura, J-I.; Ueda, Y. Two magnetic phase transitions in quasi-one-dimensional system SrCo$_2$V$_2$O$_8$. *Solid State Commun.* **2007**, *141*, 667-670.

(19) He, Z.; Ueda, Y.; Itoh, M. Field-induced order disorder transition in quasi-one-dimensional spin system PbCo$_2$V$_2$O$_8$. *Solid State Commun.* **2007**, *141*, 404-406.

(20) Kimura, S.; Yashiro, H.; Okunishi, K.; Hagiwara, M.; He, Z.; Kindo, K.; Taniyama, T.; Itoh, M. Field-Induced Order-Disorder Transition in Antiferromagnetic BaCo$_2$V$_2$O$_8$ Driven by a Softening of Spinon Excitation. *Phys. Rev. Lett.* **2007**, *99*, 087602:1-4.
(21) Maass, K.; Glaum, R.; Gruehn, R. New Orthophosphates of Divalent Chromium
Mg$_3$Cr$_3$(PO$_4$)$_4$, Mg$_{3.75}$Cr$_2.25$(PO$_4$)$_4$, Ca$_3$Cr$_3$(PO$_4$)$_4$, and Ca$_2$Cr$_4$(PO$_4$)$_4$. Z. Anorg.
Allg. Chem. 2002, 628, 1663–1672.

(22) Elbali, B.; Boukhari, A.; Glaum, R.; Gerkm, M.; Maass, K. Preparation and Structure
Determination of SrMn$_2$(PO$_4$)$_2$ and Redetermination of $\beta$-Mn$_3$(PO$_4$)$_2$. Z. Anorg. Allg.
Chem. 2000, 626, 2557–2562.

(23) Elbali, B.; Boukhari, A.; Holt, E.M.; Aride, J. Distrontium Nickel Orthophosphate. Acta
Crystallogr. Sect. C 1993, 49, 1131-1133.

(24) Elbali, B.; Boukhari, A.; Aride, J.; Abraham, F. The Crystal Structure of SrNi$_2$(PO$_4$)$_2$.
J. Solid State Chem. 1993, 104, 453–459.

(25) Hemon, A.; Courbion, G. The crystal structure of $\alpha$-SrZn$_2$(PO$_4$)$_2$: A hurlbutite type.
J. Solid State Chem. 1990, 85, 164–168.

(26) Bircsak, Z.; Harrison, W.T. Barium Cobalt Phosphate, BaCo$_2$(PO$_4$)$_2$. Acta Crystallogr.
Sect. C 1998, 54, 1554-1556.

(27) Moqine, A.; Boukhari, A.; Darriet, J. Crystal Structure and Magnetic Properties of
BaCu$_2$(PO$_4$)$_2$ Phosphate. J. Solid State Chem. 1993, 107, 362–367.

(28) Sarver, J.F.; Hoffman, M.V.; Hummel, F.A. Phase Equilibria and Tin-Activated Lu-
minescence in Strontium Orthophosphate Systems. J. Electrochem. Soc. 1961, 108,
1103-1110.

(29) Looney, J.R.; Brown, J.J. Phase Equilibria in the Sr$_3$(PO$_4$)$_2$-Cd$_3$(PO$_4$)$_2$ System and
Eu$^{2+}$-Activated Luminescence of Sr$_3$(PO$_4$)$_2$ and Related Phases. J. Electrochem. Soc.
1971, 118, 470-473.

(30) Faza, N.; Treutmann, W.; Babel, D. Structural and Magnetochemical Studies at the
Ternary Phosphates Ba$_2$M$^{II}$\textit{(PO}_4\textit{)}$_2$(M$^{II}$ = Mn, Co) and Refinement of the Crystal Structure of BaNi$_2$(PO$_4$)$_2$. \textit{Z. Anorg. Allg. Chem.} \textbf{2001}, 627, 687-692.

(31) Belik, A.A.; Azuma, M.; Matsuo, A.; Whangbo, M.H.; Koo, H.J.; Kikuchi, J.; Kaji, T.; Okubo, S.; Ohta, H.; Kindo, K.; Takano, M. Investigation of the Crystal Structure and the Structural and Magnetic Properties of SrCu$_2$(PO$_4$)$_2$. \textit{Inorg. Chem.} \textbf{2005}, 44, 6632–6640.

(32) Belik, A.A.; Azuma, M.; Matsuo, A.; Kaji, T.; Okubo, S.; Ohta, H.; Kindo, K. Takano, M. Crystal structure and properties of phosphate PbCu$_2$(PO$_4$)$_2$ with spin-singlet ground state. \textit{Phys. Rev. B} \textbf{2006}, 73, 024429:1–7.

(33) Koo, H.J.; Kang, M.H. Comparison of the spin exchange interactions in PbCu$_2$(PO$_4$)$_2$ and SrCu$_2$(PO$_4$)$_2$ on the basis of spin dimer analysis. \textit{Solid State Sci.} \textbf{2007}, 9, 955–960.

(34) He, Z.; Chen, S. C.; Lue, C. S.; Cheng, W.; Ueda, Y. Two magnetic orderings and a spin-flop transition in spin-1 system SrNi$_2$(PO$_4$)$_2$. \textit{Phys. Rev. B} \textbf{2008}, 78, 212410:1–4.

(35) He, Z.; Ueda, Y. Magnetic properties of a structurally four-spin system SrCo$_2$(PO$_4$)$_2$. \textit{Solid State Commun.} \textbf{2008}, 147, 24–26.

(36) Yang, Ming; Zhang, Suyun; Guo, Wenbin; and He, Zhangzhen Hydrothermal synthesis and magnetic properties of a new phase of SrCo$_2$(PO$_4$)$_2$. \textit{Solid State Commun.} \textbf{2016}, 52, 72–77.

(37) Hunault, M.; Robert, J. L.; Newville, M.; Galoisy, L.; Calas, G. Spectroscopic properties of five-coordinated Co$^{3+}$ in phosphates. \textit{Spectro. Acta Part A: Mole. and Biomole. Spectro.} \textbf{2014}, 117, 406-412.

(38) Blochl, P. E. Projector augmented-wave method. \textit{Phys. Rev. B} \textbf{1994}, 50, 17953–17979.

(39) Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. \textit{Phys. Rev. B} \textbf{1964}, 136, B864–B871.
(40) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. Phys. Rev. 1965, 140, A1133–A1138.

(41) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput. Mater. Sci. 1996, 6, 15-50.

(42) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B 1999, 59, 1758–1775.

(43) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865–3868.

(44) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple [Phys. Rev. Lett. 77, 3865 (1996)]. Phys. Rev. Lett. 1997, 78, 1396–1396.

(45) Monkhorst, H. J.; Pack, J. D. Special points for Brillouin-zone integrations. Phys. Rev. B 1976, 13, 5188–5192.

(46) Rodriguez-Carvajal, J. Recent advances in magnetic structure determination by neutron powder diffraction. Physica B: Condensed Matter 1993, 192, 55–69.

(47) ElBali, B.; Boukhari, A.; Holt, E. M.; Aride, J. Strontium dicobalt orthophosphate. J. Spect. Cry. Res. 1993, 12, 1001-1004.

(48) Yu, C.; Ma, S.; Pechan, M. J.; Zhou, H. Magnetic Properties of a Noninterpenetrating Chiral Porous Cobalt Metal-Organic Framewok. J. Appl. Phys. 2007, 101, 09E108.

(49) Shirata, Y. Tanaka, H. Matsuo, A. Kindo, K. Experimental Realization of a Spin-1/2 Triangular-Lattice Heisenberg Antiferromagnet. Phys. Rev. Lett. 2012, 108, 057205:1–5.

(50) Lines, M. E. Magnetic Properties of CoCl₂ and and NiCl₂. Phys. Rev. 1963, 131, 546–555.
(51) Kittel, C. Introduction to Solid State Physics 38 4th ed. Wiley, New York 1966.

(52) Goetsch, R. J.; Anand, V. K.; Pandey, A.; Johnston, D. C. Structural, thermal, magnetic, and electronic transport properties of the LaNi$_2$(Ge$_{1-x}$P$_x$)$_2$ system. Phys. Rev. B 2012, 85, 054517:1–20.

(53) Yogi, A.; Bera, A. K.; Maurya, A.; Kulkarni, R.; Yusuf, S. M.; Hoser, A.; Tsirlin, A. A.; Thamizhavel, A. Stripe order on the spin-1 stacked honeycomb lattice in Ba$_2$Ni(PO$_4$)$_2$. Phys. Rev. B 2017, 95, 024401:1–11.

(54) Cheng, J. G.; Li, G.; Balicas, L.; Zhou, J. S.; Goodenough, J. B.; Xu, C.; and Zhou, H. D. High-Pressure Sequence of Ba$_3$NiSb$_2$O$_8$ Structural Phases: New S = 1 Quantum Spin Liquids Based on Ni$^{2+}$. Phys. Rev. Lett. 2011, 107, 197204:1–4.

(55) Lashley, J. C.; Stevens, R.; Crawford, M. K.; Boerio-Goates, J.; Woodfield, B. F.; Qiu, Y.; Lynn, J. W.; Goddard, P. A.; Fisher, R. A. Specific heat and magnetic susceptibility of the spinels GeNi$_2$O$_4$ and GeCo$_2$O$_4$. Phys. Rev. B 2008, 78, 104406:1–18.

(56) He, Z.; Zhang, W.; Xia, T.; Yub, W.; Cheng, W. Crystal structure and magnetic properties of Pb$_2$Ni(PO$_4$)$_2$. Dalton Trans. 2013, 42, 5480-5484.

(57) Yogi, A.; Ahmed, N.; Nath, R.; Tsirlin, A. A.; Kundu, S.; Mahajan, A. V.; Sichelschmidt, J.; Roy, B.; Furukawa, Y. Antiferromagnetism of Zn$_2$VO(PO$_4$)$_2$ and the dilution with Ti$^{4+}$. Phys. Rev. B 2015, 91, 024413:1–12.

(58) Nath, R.; Mahajan, A. V.; Büttgen, N.; Kegler, C.; Loidl, A.; Bobroff, J. Study of one-dimensional nature of $S = 12$ (Sr,Ba)$_2$Cu(PO$_4$)$_2$ and BaCuP$_2$O$_7$ via $^{31}$P NMR. Phys. Rev. B 2005, 71, 174436:1–11.

(59) Petricek, V.; Dusek, M.; Palatinus, L. Crystallographic Computing System JANA2006: General features. Z. Kristallogr. 2006, 229, 345-352.
(60) Momma, K.; Izumi, F. *VESTA* 3 for three-dimensional visualization of crystal, volumetric and morphology data *J. Appl. Crystallogr.* **2011**, *44*, 1272-1276.