Two types of alternating spin-$\frac{1}{2}$ chains and their field-induced transitions in $\varepsilon$-LiVOPO$_4$

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(Dated: March 2, 2020)

Thermodynamic properties, $^{31}$P nuclear magnetic resonance (NMR) measurements, and density-functional band-structure calculations for $\varepsilon$-LiVOPO$_4$ are reported. This quantum magnet features a singlet ground state and comprises two types of alternating spin-$\frac{1}{2}$ chains that manifest themselves by the double maxima in the susceptibility and magnetic specific heat, and by the two-step magnetization process with an intermediate $\frac{3}{2}$-plateau. From thermodynamic data and band-structure calculations, we estimate the leading couplings of $J_1 \simeq 20$ K and $J_2 \simeq 60$ K and the alternation ratios of $\alpha_1 = J'_1/J_1 \simeq 0.6$ and $\alpha_2 = J'_2/J_2 \simeq 0.3$ within the two chains, respectively. The zero-field spin gap $\Delta_0/k_B \simeq 7.3$ K probed by thermodynamic measurements and NMR is caused by the $J_1 - J'_1$ spin chains and can be closed in the applied field of $H_{c1} \simeq 5.6$ T, giving rise to a field-induced long-range order. The corresponding $H - T$ phase boundary follows the universal power law with the critical exponent $\phi = 1.5$, which is consistent with Bose-Einstein condensation of triplons as the origin of the field-induced transition.

I. INTRODUCTION

Field-induced quantum phase transitions (QPT) in magnets set a link between fermionic spin systems and lattice boson gas and have been recognized as Bose-Einstein condensation (BEC) of triplons [1–3]. In this context, spin-dimer compounds possessing a gap in the excitation spectrum are extensively studied [2, 3]. The triplet excitations (triplons) can be considered equivalent to lattice bosons, with their density controlled by the applied magnetic field, which acts as chemical potential. The chemical potential is negligible in the singlet state having no magnetic order, but as the field approaches the critical value $H_{c1}$, the gap is closed and the chemical potential rises resulting in the condensation of triplons (bosons) in a long-range ordered (LRO) state. This phenomenon can either be described as triplon BEC or as a gapless non-Fermi-liquid-type Tomonaga-Luttinger Liquid (TLL) state, depending upon the dimensionality of the spin lattice [4]. The BEC state is typically observed in two-dimensional (2D) and three-dimensional (3D) coupled spin dimers and at very low temperatures where the interchain/interdimer interactions are significant [2, 5, 6]. On the other hand, the TLL phase is expected to be realized at low temperatures but in the one-dimensional (1D) regime [7–10].

In the 2D and 3D regimes, the ground state further depends on the delicate balance between the kinetic energy and repulsive interaction of the triplons or $S_z = +1$ bosons [11]. The dominance of repulsive interaction would lead to the formation of superlattices, which result in magnetization plateaus [12, 13]. This has been experimentally verified in the celebrated Shastry-Sutherland compound SrCu$_2$(BO$_3$)$_2$ [14, 15]. On the other hand, when the kinetic energy dominates over repulsive interactions, the triplons become delocalized, and the ground state is a superposition of singlet-triplon states, which can be approximated as a BEC of triplons. The phenomenon of BEC has been studied in detail for spin-dimer compounds TiCuCl$_3$[16], BaCuSi$_2$O$_6$[17], (Ba,Sr)$_3$C$_2$O$_8$ [18, 19], etc. The crossover from TLL as a 1D quantum critical state to the 3D BEC state has often been observed in quasi-1D spin systems e.g. spin-1/2 ladders (C$_7$H$_{10}$N)$_2$CuBr$_4$ [20–22] and (C$_5$H$_{12}$N)$_2$CuBr$_4$ [7, 10, 23] and spin-1/2 alternating spin chains Cu(NO$_3$)$_2$2.5D$_2$O and F$_2$PNN [8, 9]. Thus, quasi-1D spin-gap materials provide ample opportunities to tune the spin gap and study the field-induced quantum phase transitions.

The V$^{4+}$-based compounds offer an excellent playground to study gapped quantum magnets and related phenomena. Several of these compounds were already reported in the past in the context of spin-gap physics [24–27]. Recently, we studied magnetic properties of the AVOXO$_4$ series ($A =$ Na, Ag; $X =$ P, As), where all compounds were found to host alternating spin-$\frac{1}{2}$ chains not matching the structural chains of the VO$_x$ octahedra [28–31]. In these systems, long-range superexchange couplings via two oxygen atoms play a central role. They are highly tunable and allow the variation of the zero-field spin gap $\Delta_0/k_B$ from 21 K in NaVOAsO$_4$ to $\sim 2$ K in NaVOPO$_4$. External magnetic field closes the gap and leads to a field-induced magnetic transition, which is ex-
TABLE I. Atomic distances and bond angles along the superexchange paths involving P(1) and P(2) in the two alternating spin chains of $\varepsilon$-LiVOPO$_4$ at 300 K to highlight the coupling of P atoms with V atoms.

| Site      | Bond Length (Å) | Angle (deg.) |
|-----------|-----------------|--------------|
| P(1)      |                 |              |
| V(1)-O(3) | 1.96            |              |
| O(1)-P(1) | 1.53            |              |
| P(1)-O(2) | 1.54            | $\angle$V(1)-O(1)-O(2) = 152.16 |
| V(2)-O(7) | 1.98            | $\angle$V(2)-O(8)-O(7) = 140.38 |
| O(7)-P(1) | 1.53            | $\angle$V(2)-O(7)-V(8) = 124.64 |
| P(1)-O(8) | 1.53            | Average value $\simeq$ 131.63 |
| O(8)-V(2) | 2.01            |              |
| P(2)      |                 |              |
| V(1)-O(3) | 1.96            |              |
| O(3)-P(2) | 1.53            |              |
| P(2)-O(4) | 1.55            | $\angle$V(1)-O(4)-O(3) = 118.59 |
| O(4)-V(1) | 2.02            | $\angle$V(1)-O(3)-O(4) = 149.06 |
| V(2)-O(9) | 1.98            | $\angle$V(2)-O(9)-O(10) = 134.87 |
| O(9)-P(2) | 1.53            | $\angle$V(2)-O(10)-O(9) = 132.66 |
| P(2)-O(10)| 1.52            | Average value $\simeq$ 133.79 |
| O(10)-V(2)| 1.94            |              |

plained in terms of the triplon BEC [28, 32].

Herein, we report ground-state properties of the chemically similar, but structurally different LiVOPO$_4$. Unlike the AVOXO$_4$ compounds, which are all monoclinic (P2$_1$/c). LiVOPO$_4$ crystallizes in several polymorphs with different symmetries and atomic arrangements [33, 34]. We shall focus on the triclinic $\varepsilon$-LiVOPO$_4$ (P1) that can be seen as a distorted version of monoclinic AVOXO$_4$ [35]. Each of the Li, V, and P in $\alpha$-LiVOPO$_4$ reside at two nonequivalent sites, whereas the O atoms have ten nonequivalent sites. The magnetic V$^{4+}$ ions form chains of the VO$_6$ octahedra with the alternation of V1 and V2, leading to two alternating V–V distances of 3.599 and 3.629 Å along these structural chains (Fig. 1).

Assuming that strongest magnetic interactions run along the structural chains, one expects the magnetic behavior of alternating spin-$\frac{1}{2}$ chains that was indeed proposed by Onoda and Ikeda [36] who reported magnetic susceptibility of $\varepsilon$-LiVOPO$_4$. On the other hand, our recent results for the monoclinic AVOXO$_4$ compounds suggest that spin chains may not coincide with the structural chains, because leading interactions occur through the double bridges of the XO$_4$ tetrahedra. In this case, $\varepsilon$-LiVOPO$_4$ should feature two types of alternating spin-$\frac{1}{2}$ chains, one formed by V(1) and the other one formed by V(2), each with different interactions and different spin gaps (Fig. 1). Below, we report experimental fingerprints of these two nonequivalent spin chains and thus directly confirm the proposed microscopic scenario. Moreover, we detect a field-induced phase transition, which is reminiscent of triplon BEC.

II. METHODS

Polycrystalline sample of $\varepsilon$-LiVOPO$_4$ was prepared by the conventional solid-state reaction method from stoichiometric mixtures of LiPO$_3$ and VO$_2$ (Aldrich, 99.995%). LiPO$_3$ was obtained by heating LiH$_2$PO$_4$, H$_2$O (Aldrich, 99.995%) for 4 hrs at 400 °C in air. The reactants were ground thoroughly, pelletized, and fired at 740 °C for two days in flowing argon atmosphere with two intermediate grindings. Phase purity of the sample was confirmed by powder x-ray diffraction (XRD) recorded at room temperature using a PANalytical powder diffractometer (CuK$_\alpha$ radiation, $\lambda_{\text{avg}}$ $\simeq$ 1.5418 Å). Rietveld refinement of the acquired data was performed using FULLPROF software package [37] taking the initial cell parameters from Ref. [38]. The low-temperature XRD data down to 15 K were recorded using a low-temperature attachment (Oxford Phoenix) to the x-ray diffractometer.

Magnetization ($M$) was measured as a function of temperature (2 K $\leq T \leq$ 380 K) using the vibrating sample magnetometer (VSM) attachment to the Physical Property Measurement System (PPMS, Quantum Design). A $^3$He attachment to the SQUID [MPMS-7T, Quantum Design] magnetometer was used for magnetization measurements in the low-temperature range (0.5 K $\leq T \leq$ 2 K). Specific heat ($C_p$) as a function of temperature was measured down to 0.35 K using the thermal relaxation technique in PPMS under magnetic fields up to 14 T. For $T \leq$ 2 K, measurements were performed using an additional $^3$He attachment to PPMS. High-field magnetization was measured in pulsed magnetic field up to 60 T at the Dresden High Magnetic Field Laboratory [39, 40].

The NMR experiments on the $^{31}$P nucleus (nuclear spin $I = 1/2$ and gyromagnetic ratio $\gamma/2\pi = 17.235$ MHz/T) were carried out using pulsed NMR technique in the temperature range 1.6 K $\leq T \leq$ 230 K. The $^{31}$P NMR spectra as a function of temperature were obtained either by sweeping the field at a fixed frequency or by taking the Fourier transform (FT) of the echo signal, keeping the magnetic field fixed. The NMR shift $K(T) = [H_{\text{ref}} - H(T)]/H(T)$ was determined by measuring the resonant field $H(T)$ of the sample with respect to the standard H$_3$PO$_4$ sample (resonance frequency $H_{\text{ref}}$). The $^{31}$P nuclear-lattice relaxation rate ($1/T_1$) was measured using the inversion recovery technique at different temperatures.

Density-functional (DFT) band-structure calculations were performed in the FPLO code [41] using experimental crystal structure from Ref. [42] and the Perdew-Burke-Ernzerhof (PBE) flavor of the exchange-correlation potential [43]. Exchange couplings were obtained within superexchange theory or by a mapping procedure [44] using total energies of collinear spin configurations calculated within DFT+$U$, where the on-site Coulomb repulsion $U_d$ = 5 eV and Hund’s coupling $J_d$ = 1 eV [45, 46] were used to account for strong correlations in the V 3d shell. The calculations were performed on a $4 \times 4 \times 4$ k-mesh for several two-fold supercells, which were needed
rise with decreasing temperature. However, the overall a

FIG. 1. (a) Crystal structure of \(\varepsilon\)-LiVOPO\(_4\) projected onto the \(ac\)-plane. The deep blue and light blue solid circles represent the V(1) and V(2) sites, respectively. Chain-1 is formed by V(1) and chain-2 is formed by V(2) atoms via the extended V-O...O-V path. These chains are nearly orthogonal to each other, whereas the structural chains are parallel comprising both V1 and V2 atoms at the same time. These chains run perpendicular to the \(ac\)-plane. (b) A segment of the chain-1 formed by the V(1)O\(_6\) octahedra with the intrachain couplings \(J_1\) and \(J_1'\). (c) A section of the structural chain with the V(1)-O-V(2) paths along the \(b\)-axis. (d) An empirical/qualitative sketch of the spin model with all possible exchange interactions.

to disentangle all relevant exchange couplings.

III. RESULTS

A. X-ray Diffraction

In order to confirm the phase purity and to study the temperature variation of the crystal structure, the powder XRD patterns are analyzed for \(15 \text{ K} \leq T \leq 300 \text{ K}\). The XRD patterns at two end temperatures, \(T = 300 \text{ K}\) and \(15 \text{ K}\), along with the refinement are shown in Fig. 2. At room temperature, all the peaks could be indexed based on the triclinic (space group: \(P\bar{1}\)) structure, implying phase purity of the sample. The refined lattice parameters \(a = 6.729(1) \text{ Å}, b = 7.194(1) \text{ Å}, c = 7.920(2) \text{ Å}, \alpha = 89.82(2)\(^\circ\), \beta = 91.2288(2)\(^\circ\), and \gamma = 116.8799(2)\(^\circ\)\) at room temperature are in good agreement with the previous report [38]. Identical XRD pattern with no extra peaks are observed in the whole measured temperature range, which excludes any structural phase transition or lattice deformation in \(\varepsilon\)-LiVOPO\(_4\), unlike other spin-gap compounds NaTiSi\(_2\)O\(_6\) [47, 48], CuGeO\(_3\) [49], NaV\(_2\)O\(_5\) [50], and K-TCNQ [51].

The variation of both lattice parameters and unit cell volume \((V_{\text{cell}})\) as a function of temperature are shown in Fig. 3. The cell parameters \(b\) and \(c\) decrease systematically, while the rest of the parameters \((a, \alpha, \beta, \text{ and } \gamma)\) rise with decreasing temperature. However, the overall unit cell volume shrinks upon cooling. The temperature variation of \(V_{\text{cell}}\) was fitted by the equation [52]

\[
V_{\text{cell}}(T) = \gamma U(T)/K_0 + V_0,
\]

where \(V_0\) is the unit cell volume at \(T = 0\text{ K}, K_0\) is the bulk modulus, and \(\gamma\) is the Gr"uneisen parameter. The internal energy \(U(T)\) can be expressed in terms of the Debye approximation as

\[
U(T) = 9p\beta B \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} \, dx.
\]

In the above, \(p\) stands for the total number of atoms in the unit cell and \(k_B\) is the Boltzmann constant. The best fit of the data down to 15 K (lower panel of Fig. 3) was obtained with the Debye temperature \(\theta_D \approx 530\text{ K}, \gamma \approx 5.78 \times 10^{-5}\text{ Pa}^{-1}\), and \(V_0 \approx 340.5\text{ Å}^3\).

B. Magnetization

The temperature-dependent bulk magnetic susceptibility \(\chi (\equiv M/H)\) of \(\varepsilon\)-LiVOPO\(_4\) measured in an applied field of \(H = 0.5\text{ T}\) is shown in the upper panel of Fig. 4. It exhibits a very broad maximum with two shoulders at around \(T_{\chi}^{\text{max}1} \approx 11\text{ K}\) and \(T_{\chi}^{\text{max}2} \approx 27\text{ K}\). Such a broad maximum mimics the short-range ordering of a low-dimensional quantum magnet. However, already the fact that two shoulders are observed in the
susceptibility indicates the presence of two nonequivalent spin chains in $\varepsilon$-LiVOPO$_4$. Since peak position is related to the intrachain exchange coupling [53], we can estimate relative strengths of the interactions in the two chains, $J_2/J_1 \simeq 2.45$, where $J_1 = (J_1 + J'_1)/2$ and $J_2 = (J_2 + J'_2)/2$ are average couplings in the chain-1 and chain-2, respectively. The susceptibility alone does not give information on which of the chains features stronger couplings, but our DFT calculations (Sec. III E) suggest that stronger interactions occur within chain-2.

Below $T_{\text{max}}$, $\chi$ decreases rapidly suggesting the opening of a spin gap. However, below 2 K, a large upturn is observed, which can be attributed to the effect of extrinsic paramagnetic contributions. As shown in the inset of the upper panel of Fig. 4, with the application of magnetic field this low-temperature Curie tail get suppressed. Moreover, our powder XRD suggests high purity of the sample. Therefore, this low-temperature upturn in $\chi(T)$ may be due to the uncorrelated V$^{4+}$ free spins or chain-end effects that largely affect $\chi(T)$ at low temperatures [54].

To extract the magnetic parameters, we first fitted the $1/\chi(T)$ data (see the lower panel of Fig. 4) above 150 K by the modified Curie-Weiss (CW) law,

$$\chi(T) = \chi_0 + \frac{C}{T - \theta_{\text{CW}}},$$

where $\chi_0$ represents the temperature-independent susceptibility, which includes the Van-Vleck paramagnetic and core diamagnetic contributions, $C$ is the Curie constant, and $\theta_{\text{CW}}$ is the CW temperature. The resulting fitting parameters are: $\chi_0 \simeq 7.76 \times 10^{-5}$ cm$^3$/mol-V$^{4+}$, $C \simeq 0.383$ cm$^3$/mol-V$^{4+}$, and $\theta_{\text{CW}} \simeq -13.4$ K. Negative value of $\theta_{\text{CW}}$ indicates that the dominant interactions among the V$^{4+}$ spins are AFM in nature. The effective moment was calculated by using the experimental value of $C$ in the relation $\mu_{\text{eff}} = \sqrt{3k_B C/N_A}$, where $N_A$ is the Avogadro's number. The calculated value of $\mu_{\text{eff}} \simeq 1.72\mu_B/V^{4+}$ is very close to the theoretical spin-only value $\mu_{\text{eff}} = g\sqrt{S(S+1)} \simeq 1.73\mu_B$ for
FIG. 4. Upper panel: $\chi(T)$ measured in $H = 0.5$ T. The two shoulders of the broad maximum are indicated by the vertical arrows. Inset: low-$T$ $\chi(T)$ measured in different applied fields. Lower Panel: $1/\chi$ vs $T$ and the solid line is the CW fit using Eq. (3).

The specific-heat ($C_p$) data measured under zero field are shown in the upper panel of Fig. 6. No sharp anomaly/peak was noticed down to $T = 0.35$ K, thus ruling out the possibility of any magnetic or structural transition. A broad hump observed around $T^{\text{max}} \simeq 6$ K moves weakly toward low temperatures with increasing magnetic field, reflecting the closing of the spin gap. The gap was estimated by fitting the data below 4 K with the activated behavior, $C_{\text{mag}} \propto \exp(-\Delta^G/k_B T)$. The fit, as shown in the inset of the upper panel of Fig. 6, returns the zero-field spin gap of $\Delta_0^G/k_B \simeq 7.3$ K that matches nicely the value obtained from the high-field magnetization data.

Typically, in magnetic insulators, the high-temperature part of $C_p$ is dominated by the phonon contribution, whereas the magnetic contribution becomes prominent at low temperatures. To estimate the phonon contribution ($C_{\text{ph}}$), the experimental data at high temperatures ($40$ K $\leq T \leq 100$ K) were fitted by a linear combination of three Debye functions [58],

$$C_{\text{ph}}(T) = 9R \sum_{n=1}^{3} c_n \left( \frac{T}{\theta_{\text{Dn}}} \right)^3 \int_0^{\theta_{\text{Dn}}} \frac{x^4 e^x}{(e^x - 1)^2} dx. \quad (4)$$

In the above, $R$ is the universal gas constant, the coefficients $c_n$ stand for the groups of different atoms present...
in the crystal, and $\theta_D$ are the corresponding Debye temperatures. The $C_{\text{ph}}$ was extrapolated down to low temperatures and subtracted from the total specific heat to obtain the magnetic contribution to the specific heat ($C_{\text{mag}}$). The obtained $C_{\text{mag}}(T)$ is presented in the upper panel of Fig. 6. The accuracy of the above fitting procedure was further verified by calculating the magnetic entropy $S_{\text{mag}}$ obtained by integrating $C_{\text{mag}}/T$ (see the lower panel of Fig. 6). The value of $S_{\text{mag}}$ is calculated to be $\sim 5.9$ J/mol-K at $T \approx 100$ K, which is close to $S_{\text{mag}} = R \ln 2 = 5.76$ J/mol-K expected for spin-$\frac{1}{2}$.

As shown in the upper panel of Fig. 6, $C_{\text{mag}}$ develops two broad maxima at $T_{C\text{mag}}^{\text{max1}} \approx 7$ K and $T_{C\text{mag}}^{\text{max2}} \approx 27$ K, similar to the two shoulders in the $\chi(T)$ data. The clear separation of these maxima indicates the different interaction strength in chain-1 and chain-2.

With the spin gap closed around $H_{c1} \approx 5.6$ T, the system may enter an LRO state. This state is indeed observed in the specific-heat data measured above $H_{c1}$. As shown in Fig. 7, no anomaly in $C_p$ is found down to $T = 0.35$ K and up to $H = 5$ T. However, for $H > 7$ T a clear $\lambda$-type anomaly appears indicating the onset of a field-induced magnetic LRO ($T_N$). This peak shifts toward higher temperature with increasing magnetic field.

D. $^{31}$P NMR

As mentioned previously, $\chi(T)$ does not show an exponential decrease at low temperatures anticipated for a gapped spin system, and may be influenced by extrinsic contributions. To access the intrinsic susceptibility of $\varepsilon$-LiVOPO$_4$, we performed NMR measurements on the $^{31}$P nuclei.

1. NMR Shift

Figure 8 presents the field-sweep $^{31}$P NMR spectra measured over a wide temperature range. At high temperatures, a narrow and symmetric spectral line typical for a $I = 1/2$ nucleus is observed. As the temperature is lowered, the line shape becomes asymmetric, followed by a complete splitting of the two spectral lines below about 120 K. This suggests the existence of two nonequivalent P-sites, P(1) and P(2) with a different crystallographic environment, which is consistent with the structural data. Both lines shift with temperature and merge...
below about 4 K. The absence of drastic line broadening and/or line splitting down to 1.6 K rules out the occurrence of any structural and magnetic transition in this temperature range. The line with a lower intensity shifts much stronger than the one with the higher intensity. The former can be assigned to P(2) and the latter to P(1), because the (P2)O4 tetrahedra mediate stronger exchange interactions, \( J_1 \) in chain-1 and \( J_2 \) in chain-2, whereas the P(1)O4 tetrahedra mediate weaker interactions \( J'_1 \) and \( J'_2 \), respectively (see Sec. IIIE). At \( T = 1.6 \text{ K} \), the position of the peak is very close to the zero shift value suggesting that the ground state of \( \varepsilon \)-LiVOPO4 is non-magnetic.

The temperature-dependent NMR shift \( K(T) \) for both \( ^{31} \)P sites was extracted by fitting each spectrum to a sum of two Gaussian functions. The results are shown in the upper panel of Fig. 9. One advantage of the NMR shift over the bulk \( \chi(T) \) is that the Curie-Weiss term due to foreign phases and/or defects does not appear. The randomly distributed defects/impurities only broaden the NMR line but do not contribute to the NMR shift [59]. Therefore, \( K(T) \) is more favorable than bulk \( \chi(T) \) data for a reliable determination of magnetic parameters.

The Knight shifts corresponding to the P(1) and P(2) sites pass through a very broad maximum, similar to the \( \chi(T) \) data. The overall temperature dependence is similar for P(1) and P(2), but the absolute values differ due to the different hyperfine couplings. The presence of several distinct P sites in the structure is reminiscent of the ambient-pressure polymorph of (VO)PO3O7 with its two non-equivalent alternating spin-1/2 chains. In that case, different phosphorous sites probe the behavior of different spin chains in the structure [25, 60]. In contrast, each of the P sites in \( \varepsilon \)-LiVOPO4 is coupled to both spin chains, so it is not possible to probe \( K(T) \) separately. Two distinct shoulders are observed in \( K(T) \) at \( T \gtrsim 10 \text{ K} \) and \( T_K^{\text{ax}2} \approx 26 \text{ K} \) and closely resemble bulk magnetic susceptibility (Fig. 4).

At low temperatures, both shifts decrease rapidly toward zero suggesting the opening of a spin gap between the singlet \( (S = 0) \) ground state and triplet \( (S = 1) \) excited states. As NMR shift is insensitive to the impurities and defects, one can use it to accurately measure the intrinsic spin susceptibility. In the upper panel of Fig. 9, we show that for both P-sites \( K(T) \) decreases toward zero, which is in contrast to the upturn observed in the low-temperature \( \chi(T) \) data. This confirms the extrinsic nature of the low-temperature upturn observed in \( \chi(T) \).

In powder samples, the defects often break spin chains, with the unpaired spins at the ends of finite chains giving rise to the staggered magnetization, which also appears as the low-temperature Curie tail in \( \chi(T) \).

The direct relation between \( K(T) \) and spin susceptibility \( \chi_{\text{spin}} \) can be written as

\[
K(T) = K_0 + \frac{A_{\text{hf}}}{N_A \mu_B} \chi_{\text{spin}},
\]

where \( K_0 \) is the temperature-independent NMR shift and \( A_{\text{hf}} \) is the total hyperfine coupling constant between the \( ^{31} \)P nuclei and \( V^{4+} \) spins. The \( A_{\text{hf}} \) consists of the contributions due to transferred hyperfine coupling and nuclear dipolar coupling constants. Since both of the aforementioned couplings are temperature-independent, \( K(T) \) is a direct measure of \( \chi_{\text{spin}} \). Using Eq. (5), \( A_{\text{hf}} \) can be calculated from the slope of the linear \( K \) vs \( \chi \) plot with temperature as an implicit parameter. The lower panel of Fig. 9 presents the \( K \) vs \( \chi \) plots for both P sites showing linear behavior at high temperatures. From the linear fit, the hyperfine coupling constants \( A_{\text{hf}}^{(1)} \approx 3290 \text{ Oe}/\mu_B \) and \( A_{\text{hf}}^{(2)} \approx 7068 \text{ Oe}/\mu_B \) are estimated for the P(1) and P(2) sites, respectively. Thus, the P(2) site is coupled with the \( V^{4+} \) ions twice stronger than the P(1) site. These values are comparable to the \( A_{\text{hf}} \) values reported for other spin chains with similar interaction geometry [28, 61, 62].

It is also possible to estimate the value of the spin gap by analyzing the low-temperature \( K(T) \) data. For a gapped spin chain, \( \chi(T) \) can be written as [63, 64]

\[
\chi_{1D} \propto \sqrt{\frac{\Delta K}{k_B T}} \times e^{-\frac{\Delta K}{k_B T}},
\]

assuming quadratic magnon dispersion, \( \epsilon(K) \approx \Delta + \sqrt{\Delta K} \).
The obtained best fit parameters are: $K = K_0 + b \Delta_{1D}^{K_B}/k_B T$, where $b$ is an arbitrary constant. The obtained best fit parameters are: $K_0 \approx 0.053\%$, $b \approx 1.201\%$, and $\Delta_{1D}^{K_B}/k_B \approx 8.7\%$ for the P(1) site and $K_0 \approx 0.043\%$, and $\Delta_{1D}^{K_B}/k_B \approx 8.5\%$ for the P(2) site. The results of the fit are shown in the upper panel of Fig. 10, where $(K - K_0)/T^{1/2}$ is plotted against $1/T$. The $y$-axis is chosen in log scale to highlight the linear behavior in the gapped regime. Since each of the P-sites is coupled to both spin chains, same value of the spin gap should ensue. There is indeed only a minor difference in the $\Delta_{1D}^{K_B}$ values, which may arise from the unequal number of data points for the P(1) and P(2) sites at low temperatures. The average value of the spin gap is 8.6 K.

Our NMR experiments were carried out in the magnetic field of $H = 1.4$ T. Assuming a linear variation of $\delta/k_B$ with $H$, the zero-field spin gap $\Delta_0/k_B \approx 7.3$ K determined from the specific heat and magnetization is expected to be reduced to $\Delta_{1.4\,T}/k_B \approx 5.5$ K at $H = 1.4$ T. The NMR estimate of 8.6 K is therefore well above this value. There could be two reasons for such a discrepancy. First, Eq. (6) is applicable for the data in the low-field limit, whereas our $K(T)$ data are measured in a higher field of $H = 1.4$ T. Second, the non-negligible interchain couplings inevitably present in real materials may cause deviations from Eq. (6).

For a $d$-dimensional system, the susceptibility at $k_BT \ll \Delta$ can be approximated as [65]

$$\chi_d \propto T^{(d/2) - 1} \times e^{-\Delta/k_BT}. \quad (7)$$

Assuming that interchain couplings become significant in this temperature range, the spin-spin correlations should be three-dimensional, and $d = 3$ leads to $\chi_{3D} \sim m T^{1/2} \times e^{-\Delta_{3D}/k_BT}$, where $m$ is a proportionality constant. In the lower panel of Fig. 10, we have plotted $(K - K_0)/T^{-1/2}$ vs $1/T$ that shows a linear behavior for $1/T = 0.22 - 0.5$ K$^{-1}$. The fit in this region returns $K_0 \approx 0.046\%$, $m \approx 0.384\%/K^{1/2}$, and $\Delta_{3D}^{K_B}/k_B \approx 5.2$ K for the P(1) site and $K_0 \approx 0.031\%$, $m \approx 0.824\%/K^{1/2}$, and $\Delta_{3D}^{K_B}/k_B \approx 4.8$ K for the P(2) site. The average value of $\Delta_{3D}^{K_B}/k_B \approx 5$ K is now very close to the value expected for $H = 1.4$ T ($\Delta_{1.4\,T}/k_B \approx 5.5$ K), suggesting the dominant role of 3D correlations at low temperatures. Indeed, we find rather strong interchain couplings from DFT (Sec. III E).
FIG. 11. Upper panel: Recovery of the longitudinal magnetization as a function of waiting time \( t \) at three different temperatures. Solid lines are the fits using Eq. (8). Lower panel: Temperature variation of 1/\( T_1 \) measured in different magnetic fields. For \( H = 1.4 \) T, measurements are done on both P(1) and P(2) sites while for other fields, only P(1) site is probed.

2. Spin-lattice relaxation rate 1/\( T_1 \)

The spin-lattice relaxation rate 1/\( T_1 \) was measured at the central peak position of the spectra at each temperature using an inversion pulse sequence down to \( T = 1.6 \) K. Since \(^{31}\text{P}\) has the nuclear spin \( I = 1/2 \), the value of \( T_1 \) at each temperature was estimated by fitting the recovery curve of the longitudinal magnetization to a single exponential function

\[
\frac{1}{2} \left[ \frac{M(0) - M(t)}{M(0)} \right] = A e^{-t/T_1}.
\]

Here, \( M(t) \) is the nuclear magnetization at a time \( t \) after the inversion pulse and \( M(0) \) is the equilibrium magnetization.

The upper panel of Fig. 11 shows the recovery curves at three different temperatures probed for the P(1) site at \( H = 1.4 \) T. The temperature-dependent 1/\( T_1 \) estimated from the above fit is shown in the lower panel of Fig. 11. Our measurements are done at different field values ranging from 1.4 T to 10 T. For \( H = 1.4 \) T, the measurements are done at both P(1) and P(2) sites and over the whole temperature range, while for other fields only the P(1) site is probed and the measurements are restricted to low temperatures (\( T < 30 \) K). Since there is a large difference in the magnitude of \( A_{hf} \) for the P(1) and P(2) sites, they experience different local magnetic fields induced by the \(^{31}\text{P}\) spins. Therefore, it is expected that the resulting temperature-dependent 1/\( T_1 \) will have different values accordingly. Indeed, for \( H = 1.4 \) T, 1/\( T_1 \) of the P(2) site has larger magnitude than that of the P(1) site, as \( A_{hf} \) of P(2) is larger than that of P(1). For both the P-sites, 1/\( T_1 \) follows a temperature-independent behavior due to the random fluctuation of the paramagnetic moments at high temperatures [66]. At lower temperatures, 1/\( T_1 \) starts to decrease and below about 10 K it drops rapidly towards zero. The 1.6 K value is almost two orders of magnitude lower than the room-temperature one, indicating the opening of a spin gap. In higher fields, the low-temperature values of 1/\( T_1 \) increase and show an upward curvature.

In order to extract the spin gap value, we fitted the 1/\( T_1 \) data below 5 K by an activated behavior of the form [63, 64]

\[
1/T_1 \propto \Delta_{1D}^{T_1} \sqrt{T} e^{-3\Delta_{1D}^{T_1} / 2k_B T},
\]

which leads to \( \Delta_{1D}^{T_1} / k_B \simeq 6.82 \) K and 8.53 K for the P(1) and P(2) sites, respectively. The average value of the spin gap, \( \Delta_{1D}^{T_1} / k_B \simeq 7.7 \) K, is somewhat larger than \( \sim 5.5 \) K expected for \( H = 1.4 \) T and suggests that the above relation may not be an adequate description of the activated behavior.

From the analysis of \( K(T) \) we already inferred that 3D spin-spin correlations caused by the interchain coupling may be relevant. According to Mukhopadhyay et al. [4], in the gapped region (\( H \leq H_{c1} \)) with 3D correlations...
1/T_1 follows an activated behavior of the form,

\[
1/T_1 \propto T^{\alpha_0} \exp \left[ \frac{g\mu_B (H - H_{c1})}{k_B T} \right].
\]

The exponent \(\alpha_0\) in the above equation depends on the effective dimension of the magnon dispersion relation as set by the thermal fluctuations \(k_B T\). With increasing temperature, \(\alpha_0\) slowly decreases from 2 for \(k_B T < J_{1D}\) (3D regime) to 0 for \(J_{1D} < k_B T < J_{1D}\) (1D regime). To obtain the spin gap, we fitted the 1/T_1 data for \(T \leq 5\) K with the fixed value of \(g = 1.95, H = 1.4\) T (experimental NMR field), and \(\alpha_0 = 2\) (for the 3D regime). Figure 12 presents the 1/T_1 vs 1/T plot along with the fit using Eq. (10). The fit yields \(H_{c1} \approx 4.78\) T and 6.36 T for the P(1) and P(2) sites, respectively. The average value of the critical field, \(H_{c1} \approx 5.6\) T, is in good agreement with the zero-field spin-gap of \(\Delta_{1D}/k_B \approx 7.3\) K obtained from the specific heat and magnetization measurements. This further confirms the importance of interchain couplings at low temperatures, where activated behavior is observed.

The spin gap should be closed at \(H_{c1}\) and thereafter an AFM LRO sets in. Therefore, we measured 1/T_1 at different fields above \(H_{c1}\). The increase in the low-temperature values of 1/T_1 confirms the closing of the spin gap and the growth of AFM correlations due to the field-induced LRO. Since our measurements are limited down to 1.6 K, we are unable to detect the field-induced LRO from the 1/T_1 data. Nevertheless, the systematic increase of 1/T_1 with field implies that \(T_N\) shifts toward higher temperatures with increasing \(H\), in good agreement with our \(C_p(T)\) data, where field-induced LRO is detected above \(H_{c1}\).

### E. Microscopic magnetic model

Similar to Refs. [28, 29, 31], we use two complementary computational methods to derive exchange couplings in \(\varepsilon\)-LiVOPO_4. For a single magnetic orbital of \(V^{4+}\), superexchange theory yields antiferromagnetic exchange couplings \(J_i^{AFM} = 4t_i^2/U_{eff}\), where \(t_i\) are V–V hoppings extracted from the uncorrelated (PBE) band structure, and \(U_{eff}\) is an effective Coulomb repulsion in the V 3d bands. On the other hand, exchange couplings \(J_i\) can be obtained from DFT+U by a mapping procedure, where both ferro- and antiferromagnetic contributions are taken into account.

In Table II, we list the \(t_i\) values for the uncorrelated band structure and the exchange couplings \(J_i\) obtained from DFT+U. The two methods are in excellent agreement and consistently show the stronger couplings within chain-2. Moreover, we find that within each spin chain the stronger couplings involve the P(2) bridges and the weaker couplings involve the P(1) bridges. On the structural level, this difference should be traced back to the lateral displacements \(d_i\) of the V\(_6\) octahedra within the spin chain (Fig. 1b), where smaller displacement leads to a stronger coupling [28, 67]. Indeed, we find \(d_1 = 0.71\) Å for \(J_1\) vs. \(d'_1 = 0.97\) Å for \(J'_1\) and \(d_2 = 0.08\) Å for \(J_2\) vs. \(d'_2 = 0.23\) Å for \(J'_2\). The smaller lateral displacements \(d_2\) and \(d'_2\) could also explain the overall stronger couplings in chain-2, although in this case other geometrical parameters [67] are relevant as well, because \(J_1\) is about as strong as \(J'_2\), despite the fact that \(d_1 > d_2\).

Regarding the interchain couplings, the microscopic scenario is very similar to that of monoclinic AVOXO_4 with \(A = Ag, Na\) and \(X = P, As\) [28, 29, 31]. Shorter V–O–V bridges render \(J_{c1}\) and \(J_{c2}\) ferromagnetic, whereas the long-range couplings \(J_{a1}\) and \(J_{a2}\) are weakly antiferromagnetic. These ferromagnetic and antiferromagnetic interactions compete and make the spin lattice of \(\varepsilon\)-LiVOPO_4 frustrated.

Our DFT results suggest that chain-1 shows only a moderate degree of alternation (\(\alpha_1 = J'_1/J_1 \approx 0.6\)) that, together with the lower energy scale of the couplings, leads to a relatively small spin gap closed at \(H_{c1}\). In contrast, the alternation ratio of \(\alpha_2 = J'_2/J_2 \approx 0.3\) renders chain-2 strongly dimerized with a larger spin gap that is closed at the much higher field \(H_{c3}\). The model of two alternating spin-\(\frac{1}{2}\) chains was further used to calculate temperature-dependent magnetic susceptibility and

| TABLE II. Exchange couplings in \(\varepsilon\)-LiVOPO_4. The \(t_i\) values are the V–V hoppings extracted from the uncorrelated band structure, and show relative strengths of the AFM contributions to the exchange couplings, \(J_i^{AFM} \sim t_i^2\). The \(J_i\) are exchange interactions obtained by the mapping procedure within DFT+U. |
|---|---|---|---|
| \(d_{V-V}\) (Å) | \(t_i\) (meV) | \(J_i\) (K) |
| \(J_1\) | 5.250 | V1–V1 | –72 | 33 |
| \(J'_1\) | 5.101 | V1–V1 | –55 | 23 |
| \(J_2\) | 5.275 | V2–V2 | –117 | 63 |
| \(J'_2\) | 5.303 | V2–V2 | –78 | 22 |
| \(J_{c1}\) | 3.599 | V1–V2 | 0 | –15 |
| \(J_{c2}\) | 3.629 | V1–V2 | 0 | –15 |
| \(J_{a1}\) | 6.018 | V1–V2 | –21 | 12 |
| \(J_{a2}\) | 6.070 | V1–V2 | –32 | 7 |

| TABLE III. Exchange couplings (in K) extracted from the \(\chi(T)\) and \(M(H)\) data using the fits shown in Fig. 13. The susceptibility fit using Eq. (11) returns \(\chi_0 = 2.7 \times 10^{-3}\) cm³/mol, \(C_{\text{Cup}} = 0.013\) cm³/mol (3.5% of paramagnetic impurities), \(\theta_{\text{Cup}} = 0.9\) K, and \(g = 2\). This \(g\)-value is slightly higher than 1.98 obtained from the Curie-Weiss fit, probably because the interchain couplings were not taken into account. For magnetization data, \(g = 1.98\) has been used as a fixed parameter. |
|---|---|---|---|
| \(\chi(T)\) | \(J_1\) | \(J'_1\) | \(J_2\) | \(J'_2\) |
| 20 | 12 | 70 | 20 |
| 19 | 12 | 63 | 22 |

\(-LiVOPO_4\)
The fitting results listed in Table III show good agreement between the fits to the susceptibility and magnetic specific heat and in the two-step magnetization process. This unusual microscopic scenario is reminiscent of the ambient-pressure polymorph of (VO)₂P₂O₇ [69], where two spin gaps corresponding to two types of spin chains were directly observed by NMR [25] and inelastic neutron scattering [70]. On the other hand, large size of these gaps (35 K and 68 K, respectively) and high critical fields associated with them preclude experimental access to field-induced transitions, where triplon excitations of the spin chains consecutively condense leading to a long-range magnetic order.

With its lower critical fields, ε-LiVOPO₄ offers a much better platform for studying these transitions experimentally. Indeed, we observed field-induced magnetic order already above \( H_{c1} \approx 5.6 \) T. Transition temperature systematically increases with field and tracks the \( H \sim T \) phase boundary shown in Fig. 14. The field-induced transition in gapped quantum magnets is often understood as Bose-Einstein condensation of triplons. In this case, the phase boundary should follow the universal power law [3, 71, 72],

\[
T_N \propto \left( H - H_{c1} \right)^{\frac{1}{\phi}},
\]

where \( \phi = d/2 \) is the critical exponent reflecting the uni-
versatility class of the quantum phase transition at $H_{c1}$, and $d$ is dimensionality.

In $\varepsilon$-LiVOPO$_4$, three-dimensional spin-spin correlations dominate at low temperatures, owing to the sizable interchain couplings. Therefore, we set $\phi = 1.5$ and compare our data with the behavior expected from Eq. (12). Favorable agreement at low temperatures (Fig. 14) suggests that the field-induced transition in $\varepsilon$-LiVOPO$_4$ can be indeed understood as the Bose-Einstein condensation of tripons.

The fate of this ordered phase in fields above 14 T may be of significant interest. The two-step increase in the magnetization suggests that the transition at $H_{c1}$ corresponds to chain-1 and will lead to a BEC dome between $H_{c1}$ and $H_{c2}$, while chain-2 remains in the singlet state up to $H_{c3}$, where another BEC dome should appear. Phenomenologically, this behavior would be similar to the two-dome $H - T$ phase diagrams of spin-1 dimer magnets [57], although in $\varepsilon$-LiVOPO$_4$ with local spin-$\frac{1}{2}$ it should have a very different microscopic origin. It is also possible that chain-1 and chain-2 are not fully independent. The BEC transition related to chain-1 may lead to a partial polarization of chain-2 via significant interchain couplings. Such an intertwined behavior in gapped quantum magnets with more than one type of spin dimers is unusual critical behavior in BaCuSi$_2$O$_6$ [73, 74]. We believe that $\varepsilon$-LiVOPO$_4$ may be an interesting reference system that clearly deserves further investigation in high magnetic fields, especially with regard to its $H - T$ phase diagram.

In summary, we have shown that $\varepsilon$-LiVOPO$_4$ is a gapped quantum magnet that features singlet ground state in zero field. With two non-equivalent alternating spin-$\frac{1}{2}$ chains, it shows double maxima in the susceptibility and magnetic specific heat and a two-step increase in the magnetization. Chain-1 features weaker couplings and a weaker alternation ($J_1 \simeq 20 \, \text{K}, \alpha_1 \simeq 0.6$), whereas chain-2 reveals stronger couplings and lies closer to the dimer limit ($J_2 \simeq 60 \, \text{K}, \alpha_2 \simeq 0.3$). The zero-field spin gap of $\Delta_0/k_B \simeq 7.3 \, \text{K}$ is closed at $H_{c1} \simeq 5.6 \, \text{T}$. The magnetization increases up to $H_{c2} \simeq 25 \, \text{T}$, flattens out within the $\frac{1}{2}$-plateau, and increases again above $H_{c3} \simeq 35 \, \text{T}$. The gap closing above $H_{c1}$ leads to a field-induced long-range order. The associated $H - T$ phase boundary follows universal power law with the critical exponent $\phi = 1.5$ indicative of tripon Bose-Einstein condensation as the origin of this field-induced transition.

ACKNOWLEDGMENTS

PKM and RN acknowledge BRNS, India for financial support bearing sanction No.37(3)/14/26/2017-BRNS. We also thank C. Klausnitzer (MPI-CPS) for the technical support. A.A.T was funded by the Federal Ministry for Education and Research through the Sofja Kovalevskaya Award of Alexander von Humboldt Foundation. We also acknowledge the support of the HLD at HZDR, member of European Magnetic Field Laboratory (EMFL).

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