We report synthesis and magnetic properties of quasi-one-dimensional spin-\(\frac{1}{2}\) Heisenberg antiferromagnetic chain compound BaNa\(_2\)Cu(VO\(_4\))\(_2\). This orthovanadate has a centrosymmetric crystal structure, \(C2/c\), where the magnetic Cu\(^{2+}\) ions form spin chains. These chains are arranged in layers, with the chain direction changing by 62° between the two successive layers. Alternatively, the spin lattice can be viewed as anisotropic triangular layers upon taking the inter-chain interactions into consideration. Despite this potential structural complexity, temperature-dependent magnetic susceptibility, heat capacity, ESR intensity, and NMR shift agree well with the uniform spin-1/2 Heisenberg chain model with an intrachain coupling of \(J/k_B \approx 5.6\) K. The saturation field obtained from the magnetic isotherm measurement consistently reproduces the value of \(J/k_B\). Further, the \(^{51}\)V NMR spin-lattice relaxation rate mimics the 1D character in the intermediate temperature range, whereas magnetic long-range order sets in below \(T_N \approx 0.25\) K. The effective interchain coupling is estimated to be \(J_{\perp}/k_B \approx 0.1\) K. The theoretical estimation of exchange couplings using band-structure calculations reciprocate our experimental findings and unambiguously establish the 1D character of the compound. Finally, the spin lattice of BaNa\(_2\)Cu(VO\(_4\))\(_2\) is compared with the chemically similar but not isostructural compound BaAg\(_2\)Cu(VO\(_4\))\(_2\).

I. INTRODUCTION

The studies of low-dimensional and frustrated spin systems have contributed substantially in understanding the quantum phase transitions at low temperatures [1, 2]. In one-dimensional (1D) antiferromagnetic (AFM) spin-1/2 uniform Heisenberg chains, magnetic long-range-order (LRO) is forbidden at zero temperature as a result of enhanced quantum fluctuations, thereby exhibiting a gapless excitation spectrum and power-law decay of spin-spin correlations [3]. However, non-zero inter-chain interactions, inherent to real materials, lead to the formation of magnetic LRO at finite temperatures [4, 5]. On the other hand, the inter-chain interactions often create frustrated network between the chains that eventually prevents the system from achieving the conventional LRO but stabilizes different exotic states instead [2, 6–8]. Further, competing interactions as realized in a set of compounds, add magnetic frustration in spin chains which along with quantum fluctuations host a multitude of intriguing magnetic ground states [9–11]. The transition-metal oxides offer nearly endless opportunities for realizing 1D spin chains with different types of exchange couplings, and may harbor wide varieties of exotic phases of matter.

Recently, synthesis and magnetic properties of a series of compounds AA\(^{+}\)M(VO\(_4\))\(_2\) (\(A = Ba\) and Sr, \(A' = Na_2\) and Ag\(_2\), and \(M = Mn, Ni, Co, Fe, and Cu\)) were reported. Despite some variations in their crystal structures, the magnetic model of anisotropic triangular lattice has been generally used to understand their magnetism [12–18]. BaAg\(_2\)Cu(VO\(_4\))\(_2\) stands as an exception in this series, because its crystal structure is triclinic (space group: \(P\overline{1}\)) [12], and indeed microscopic analysis via density-functional band-structure calculations [19] combined with resonance spectroscopy [20] revealed 1D magnetism with two dissimilar types of spin chains, one ferromagnetic and one antiferromagnetic, coexisting in the structure.

Here, we present for the first time the magnetic properties of BaNa\(_2\)Cu(VO\(_4\))\(_2\), another Cu\(^{2+}\) member of the series [21]. Its structure features four equal Cu–Cu distances of 5.507 Å as well as two slightly longer distances of 5.686 Å, all in the ab plane. This interaction geometry is a pre-requisite of the triangular-lattice scenario previously established for other members of the AA\(^{+}\)M(VO\(_4\))\(_2\) series. On the other hand, the square-planar oxygen coordination of Cu\(^{2+}\) and the VO\(_4\) bridges between such CuO\(_4\) plaquette units may lead to one preferred direction for magnetic couplings in the ab plane (Fig. 1). Interestingly, this preferred direction changes from \(\mathbf{a} + \mathbf{b}\) in one plane to \(\mathbf{a} - \mathbf{b}\) in the adjacent plane, thus leading to the formation of crossed spin chains arranged at 62° relative to each other. This geometry resembles the crossed-chain magnetic model, where exotic ground states and potential spin-liquid behavior have been proposed theoretically [22–26].

Here, we use magnetization, heat capacity, electron spin resonance (ESR), and nuclear magnetic resonance
Fig. 1. Left panel: crystal structure of BaNa$_2$Cu(VO$_4$)$_2$ showing corner-shared CuO$_4$ plaquettes and VO$_4$ tetrahedra forming layers of spin chains. The coupling of Na$^{1+}$ ions with the magnetic Cu$^{2+}$ ions is also shown. Middle panel: crystal structure of BaNa$_2$Cu(VO$_4$)$_2$ shown in a different orientation to visualize the spin chains running along the [110] and [1bar10] directions; black spheres show the Ba atoms, the Na atoms are omitted for clarity. Right panel: the structure of the single spin chain with the geometrical parameters $\phi$ and $r$ that control the sign and strength of superexchange through the double bridges of the VO$_4$ tetrahedra.

(NMR) measurements, as well as complementary band-structure calculations to uncover magnetic interactions in BaNa$_2$Cu(VO$_4$)$_2$ and establish its microscopic magnetic model. Our data suggest the formation of uniform AFM spin chains with the exchange coupling $J/k_B \approx 5.6$ K, and the subsequent onset of magnetic LRO below $T_N \approx 0.25$ K. We suggest that this magnetic order can be driven by residual inter-chain couplings of $J_\perp/k_B \approx 0.1$ K that remain non-frustrated despite the crossed-chain structural geometry. Our results establish that the mere presence of spin chains arranged along two different directions is insufficient to reach the interesting physics of the crossed-chain model, and an additional condition for the lateral displacement of these chains has to be met experimentally.

II. METHODS

Polycrystalline sample of BaNa$_2$Cu(VO$_4$)$_2$ was prepared by the usual solid-state reaction method. Initially, the reactants Na$_2$CO$_3$ (Aldrich, 99.995%), BaCO$_3$ (Aldrich, 99.995%), CuO (Aldrich, 99.999%), and V$_2$O$_5$ (Aldrich, 99.995%) were mixed in proper molar ratios, thoroughly ground, and then pressed into pellets. The pellets were sintered in an alumina crucible at 500 °C for three days in air with several intermediate grindings. The phase purity of the sample was confirmed from the powder x-ray diffraction (XRD) performed at room temperature. For the powder XRD experiment, a PANalytical powder diffractometer with CuK$\alpha$ radiation ($\lambda_{\text{avg}} \approx 1.54182$ Å) was used. Le-Bail analysis of the powder XRD pattern was performed using the FullProf software package [27]. Figure 2 displays the room-temperature powder XRD data along with the fit. The structural parameters given in Ref. [21] were used as the initial parameters. The goodness-of-fit was found to be $\chi^2 \approx 3.57$. The obtained lattice parameters are $a = 9.4379(1)$ Å, $b = 5.6926(1)$ Å, $c = 14.0519(1)$ Å, and $\beta = 92.343(8)^\circ$ and the unit cell volume $V_{\text{cell}} \approx 754.34$ Å$^3$, which are in close agreement with the previous report [21].

Magnetization ($M$) measurements were performed as a function of temperature (0.48 K $\leq T \leq 380$ K) and...
magnetic field ($0 \leq H \leq 14$ T) using a Superconducting Quantum Interference Device (SQUID, Quantum Design) magnetometer and a Physical Property Measurement System (PPMS, Quantum Design). The SQUID enabled us to measure magnetization down to 0.48 K with a $^3$He attachment. High-field magnetization up to 14 T were measured using PPMS. Heat capacity ($C_p$) was measured as a function of $T$ (0.4 K $\leq T \leq 200$ K) on a sintered pellet using the thermal relaxation method in PPMS. The temperature down to 0.4 K was achieved using a $^3$He attachment to the PPMS.

The ESR experiments were performed on the powder sample with a standard continuous-wave spectrometer in the temperature range 2.5 K $\leq T \leq 300$ K. As a function of external magnetic field $B$, the resonance shows up as an absorbed power $P$ of a transversal magnetic microwave field ($\nu \simeq 9.4$ GHz, X-band). In order to improve the signal-to-noise ratio, a lock-in technique was used by modulating the applied field, which yields the derivative of power absorption $dP/dB$ as a function of $B$. By using the resonance condition $g = \frac{\hbar \nu}{\mu_B H_{\text{res}}}$, where $\hbar$ is the Planck’s constant, $\mu_B$ is the Bohr magneton, $\nu$ is the resonance frequency, and $H_{\text{res}}$ is the corresponding resonance field, the $g$-value was obtained.

The pulsed NMR measurements were performed on both $^{23}$Na (nuclear spin $I = 3/2$ and gyromagnetic ratio $\gamma = 11.26$ MHz/T) and $^{51}$V ($I = 7/2$ and $\gamma = 11.19$ MHz/T) nuclei in the temperature range 0.044 K $\leq T \leq 200$ K. For measurements above 2 K a $^4$He cryostat (Oxford Instrument) with a field-sweep superconducting magnet was used, while for measurements in the low-temperature range (0.044 K $\leq T \leq 2$ K), a $^3$He/$^4$He dilution refrigerator (Kelvinox, Oxford Instruments) with a field sweep magnet was used. All the NMR measurements were carried out in a radio frequency of 77 MHz. The NMR spectra were measured as a function of temperature $T$ by sweeping the magnetic field at a constant radio frequency of 77 MHz. The NMR shift was calculated for both $^{23}$Na and $^{51}$V nuclei as $K(T) = (H_{\text{ref}} - H(T))/(H(0))$, where $H$ is the resonance field for $^{23}$Na and $^{51}$V and $H_{\text{ref}}$ is the resonance field of the nonmagnetic reference sample. The spin-lattice relaxation rate $1/T_1$ was measured by the conventional single saturation pulse method.

Density-functional (DFT) band-structure calculations were performed in the FPLO code [28] using the structural parameters from Ref. [21] and local-density approximation (LDA) for the exchange-correlation potential [29]. Exchange parameters of the spin Hamiltonian

$$\mathcal{H} = \sum_{i,j} J_{ij} S_i S_j$$

with $S = \frac{1}{2}$ and the summation over atomic pairs $(ij)$, were extracted via two complementary procedures. First, band structure obtained on the LDA level was mapped onto a tight-binding model for the half-filled $d_{x^2-y^2}$ orbitals of Cu$^{2+}$ as the magnetic ion. Squared hopping parameters $t_i$ of this tight-binding model are proportional to AFM contributions to the exchange, $J_{ij}^{\text{AFM}} = 4t_i^2/\epsilon_{\text{eff}}$, where $\epsilon_{\text{eff}}$ is the effective on-site Coulomb repulsion. Alternatively, full exchange couplings $J_i$ comprising both FM and AFM contributions are extracted by a mapping procedure [30] from total energies of magnetically ordered states calculated on the DFT+$U$ level, with correlation effects in the Cu 3$d$ shell modeled by the on-site Coulomb repulsion $U_d = 6$ eV, Hund’s exchange $J_d = 1$ eV, and around-mean-field flavor of the double-counting correction [19, 31]. The $k$ mesh with up to 150 points in the symmetry-irreducible part of the first Brillouin zone was used.

Field-dependent magnetization and magnetic specific heat of a uniform spin-$\frac{1}{2}$ chain were obtained from quantum Monte-Carlo simulations for $L = 32$ finite lattices with periodic boundary conditions. The loop [32] and dirloop sse [33] algorithms of the ALPS simulation package [34] were used.

## III. RESULTS AND DISCUSSION

### A. Magnetization

Temperature-dependent magnetic susceptibility $\chi(T)$($= M/H$) of the polycrystalline Na$_2$BaCu(VO$_4$)$_2$ sample measured in two different applied fields $H = 1$ T and 3 T is depicted in the Fig. 3. The most significant feature in the $\chi(T)$ curve is the presence of a broad maximum at 3 K, signaling a crossover to an AFM short-range ordered state, typical for low-dimensional spin systems [35, 36]. This broad maximum is more pronounced in the 3 T data shown in the lower inset.
of Fig. 3. No anomaly indicative of the potential LRO could be seen down to 0.48 K.

The preliminary analysis was done by fitting the \( \chi(T) \) data using the Curie-Weiss (CW) law, \( \chi(T) = \chi_0 + C/(T + \theta_{\text{CW}}) \), where \( \chi_0 \) is the temperature-independent susceptibility, \( C \) is the Curie constant, and \( \theta_{\text{CW}} \) is the characteristic CW temperature. The fit shown in the upper inset of Fig. 3 in the high-temperature regime \( (T \geq 16 \text{ K}) \) yields the following parameters: \( \chi_0 \approx 7.9288 \times 10^{-5} \text{ cm}^3/\mu\text{mol}, C \approx 0.445 \text{ cm}^3/\text{K}\mu\text{mol}, \) and \( \theta_{\text{CW}} \approx 3 \text{ K} \). In order to estimate the Van-Vleck paramagnetic susceptibility \( \chi_{\text{VV}} \), which arises from the second-order contribution to free energy in the presence of magnetic field, core diamagnetic susceptibility \( \chi_{\text{core}} \) of \( \text{Na}_2\text{BaCu(VO}_4)\text{)}_2 \) was calculated to be \(-1.57 \times 10^{-4} \text{ cm}^3/\mu\text{mol}\) by summing the core diamagnetic susceptibilities of individual ions \( \text{Na}^+ \), \( \text{Ba}^{2+} \), \( \text{Cu}^{2+} \), \( \text{V}^{5+} \), and \( \text{O}^{2-} [37, 38] \). Subsequently, \( \chi_{\text{VV}} \) was obtained by subtracting \( \chi_{\text{core}} \) from \( \chi_0 \) to be \( \approx 2.36 \times 10^{-4} \text{ cm}^3/\mu\text{mol} \), which is close to the values reported for other cuprates [39-41] and consistent with tetragonal crystal-field splitting at the \( \text{Cu}^{2+} \) site with the square-planar oxygen coordination [42].

From the Curie constant \( C \), the effective moment is calculated using the relation \( \mu_{\text{eff}} = \sqrt{3k_B C/N_A} \) to be \( \approx 1.88 \mu_B \), where \( k_B \) is the Boltzmann constant, \( \mu_B \) is the Bohr magneton, and \( N_A \) is the Avogadro’s number. For a spin-\( \frac{1}{2} \) system, the spin-only effective moment is expected to be \( \mu_{\text{eff}} = g\sqrt{S(S + 1)} \mu_B \approx 1.73 \mu_B \), assuming Landé \( g \)-factor \( g = 2 \). However, our experimental value of \( \mu_{\text{eff}} \approx 1.88 \mu_B \) corresponds to a \( g \)-factor of \( g \approx 2.17 \), which is consistent with the ESR experiments discussed later. The positive value of \( \theta_{\text{CW}} \) suggests that the dominant exchange interactions between the \( \text{Cu}^{2+} \) ions are AFM in nature.

In order to estimate the exchange coupling between the \( \text{Cu}^{2+} \) ions, we decomposed \( \chi(T) \) into three components,

\[
\chi(T) = \chi_0 + \frac{C_{\text{imp}}}{T} + \chi_{\text{spin}}(T).
\]

Here, the second term is the Curie law, which accounts for the paramagnetic contributions from impurity spins and/or defects, and \( \chi_{\text{spin}}(T) \) is the intrinsic spin susceptibility. This last term can be chosen in different forms depending on the underlying magnetic model. The best fit was achieved with the spin-chain model, which is further supported by the specific-heat data (Sec. III C) and \textit{ab initio} calculations (Sec. III E).

The susceptibility of a spin-\( \frac{1}{2} \) uniform Heisenberg AFM chain takes the form

\[
\chi_{\text{spin}} = \frac{N_A \mu_B^2 g^2}{k_B T} \left[ 0.25 + 0.0775 x + 0.0752 x^2 \right],
\]

with \( x = |J|/k_B T \) [35]. This is simply a high-temperature series expansion (HTSE) valid in the regime \( k_B T/J \geq 0.5 \). The solid line in Fig. 3 represents the best fit of the \( \chi(T) \) data above 4 K by Eq. (2). The following parameters were obtained: \( \chi_0 \approx 1.44 \times 10^{-5} \text{ cm}^3/\mu\text{mol} \), \( C_{\text{imp}} \approx 0.0258 \text{ cm}^3/\mu\text{mol}, g \approx 2.13 \), and the dominant intra-chain AFM exchange coupling \( J/k_B \approx 5.6 \text{ K} \). From the value of \( C_{\text{imp}} \), the sample was found to contain \( \approx 6\% \) spin-\( \frac{1}{2} \) impurities/defects. At temperatures below 1 K, this impurity contribution becomes dominant and causes the reduction in the susceptibility with the applied field, even though \( \chi_{\text{spin}}(T) \) should increase when the field is applied [43].

The magnetic isotherm at \( T = 2 \text{ K} \) up to 14 T is shown in Fig. 4. \( M \) increases almost linearly with \( H \) but with a small curvature. It develops a tendency of saturation at \( H \approx 9 \text{ T} \). From these values, the average \( g \)-value was calculated as \( g = (g_{\parallel} + 2g_{\perp})/3 \approx 2.17 \) [45]. This value is slightly larger than \( \Delta g/g \approx 0.085 \) compared to the free electron value \( (g = 2) \), typical for \( \text{Cu}^{2+} \) based oxides [46, 47].

The integrated ESR intensity \( (I_{\text{ESR}}) \) obtained from the

![FIG. 4. Magnetization (\( M \)) vs \( H \) measured at \( T = 2 \text{ K} \). Inset: \( dM/dH \) vs \( H \) to highlight the saturation field \( H_s \).](attached image)

\( C_{\text{imp}} \approx 0.0258 \text{ cm}^3/\mu\text{mol}, g \approx 2.13 \), and the dominant intra-chain AFM exchange coupling \( J/k_B \approx 5.6 \text{ K} \). From the value of \( C_{\text{imp}} \), the sample was found to contain \( \approx 6\% \) spin-\( \frac{1}{2} \) impurities/defects. At temperatures below 1 K, this impurity contribution becomes dominant and causes the reduction in the susceptibility with the applied field, even though \( \chi_{\text{spin}}(T) \) should increase when the field is applied [43].

The magnetic isotherm at \( T = 2 \text{ K} \) up to 14 T is shown in Fig. 4. \( M \) increases almost linearly with \( H \) but with a small curvature. It develops a tendency of saturation above 9 T. A more accurate value of the saturation field \( H_s \approx 9 \text{ T} \) was found by drawing tangential at the curvature (see Fig. 4). The field derivative of the \( M \) vs \( H \) plot also implies \( H_s \approx 9 \text{ T} \) (see the inset of Fig. 4). For a spin-1/2 Heisenberg AFM chain, the saturation field is directly proportional to the intra-chain exchange coupling as \( H_s = 2gJ(\frac{1}{g_B} + 2g_{\perp}) \) [44]. Using the value of \( J/k_B \approx 5.6 \text{ K} \), the saturation field is calculated to be \( H_s \approx 8.34 \text{ T} \), which matches well with the experimental value, confirming the dominant 1D character of the compound.

### B. ESR

ESR experiment was performed on the powder sample and the results are shown in Fig. 5. The inset of Fig. 5(a) depicts a typical ESR powder spectrum at 300 K. The uniaxial \( g \)-factor anisotropy was obtained by fitting the spectra using the powder-averaged Lorentzian line. The fit of the spectral at room temperature yields the anisotropic \( g \)-tensor components \( g_{\parallel} \approx 2.315 \) and \( g_{\perp} \approx 2.098 \). From these values, the average \( g \)-value was calculated as \( g = ([g_{\parallel} + 2g_{\perp})/3] \approx 2.17 \) [45]. This value is slightly larger than \( \Delta g/g \approx 0.085 \) compared to the free electron value \( (g = 2) \), typical for \( \text{Cu}^{2+} \) based oxides [46, 47]. The integrated ESR intensity \( (I_{\text{ESR}}) \) obtained from the
In order to estimate the exchange coupling, $I_{\text{ESR}}(T)$ was fitted by

$$I_{\text{ESR}}(T) = A + B \chi_{\text{spin}}(T). \quad (4)$$

Here, $A$ and $B$ are arbitrary constants, and $\chi_{\text{spin}}$ is given by Eq. (3). Our fit (see Fig. 5) in the high-temperature regime ($T \geq 5$ K) produced $J/k_B \approx 5.55$ K. This value of $J/k_B$ is close to the one obtained from the $\chi(T)$ analysis. During the fit, the value of $g$ was kept constant to 2.17, as obtained above. We have also fitted the $1/I_{\text{ESR}}$ data in the high-temperature regime ($T \geq 10$ K) using the relation $I_{\text{ESR}} = M + N/(T + \theta_{\text{CW}})$ where $M$ and $N$ are arbitrary constants. As shown in the lower inset of Fig. 5(a), the fit returns $\theta_{\text{CW}} \approx 3.9$ K, which is in good agreement with the value obtained from the $\chi^{-1}(T)$ analysis.

The temperature-dependent ESR linewidth, or equivalently the half-width at half maximum of the ESR absorption signal, is presented in Fig. 5(c). Both the parallel ($\Delta B_\parallel$) and perpendicular ($\Delta B_\perp$) components of the ESR line width follow the general trend, commonly observed in most of the low-dimensional spin systems [48, 49]. The rapid increase/divergence below $\sim 25$ K indicates the growth of strong spin correlations at low temperatures as the system approaches the magnetic LRO state.

**C. Heat Capacity**

Temperature-dependent heat capacity $C_p$ of the polycrystalline sample is shown in the upper panel of Fig. 6. In magnetic insulators, the two major contributions to $C_p$ are from phonon and magnetic parts. At high temperatures, $C_p(T)$ is dominated by the phonon part, while at low temperatures it is dominated by the magnetic part. Our experimental $C_p$ data exhibit a pronounced broad maximum at $T \approx 1.52$ K indicative of the low-dimensional short-range order and also reflects the dominant magnetic contribution at low temperatures. In order to estimate the magnetic contribution to the heat capacity $C_{\text{mag}}$, we proceed as follows. First we approximate the lattice contribution $C_{\text{ph}}$ by fitting the high-temperature data by a linear combination of one Debye and two Einstein terms (Debye-Einstein model) as [50, 51]

$$C_{\text{ph}}(T) = f_D C_D(\theta_D, T) + \sum_{i=1}^{2} g_i C_{E_i}(\theta_{E_i}, T). \quad (5)$$

The first term in Eq. (5) is the Debye term,

$$C_D(\theta_D, T) = 9nR \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D} \frac{x^4 e^x}{(e^x - 1)^2} dx. \quad (6)$$

Here, $x = \frac{\theta_D}{k_B T}$, $\omega$ is the vibration frequency, $R$ is the universal gas constant, and $\theta_D$ is the characteristic Debye temperature. The second term in Eq. (5) is a combination of the Einstein terms that are usually responsible
atoms and two apical oxygens of the VO$_4$ tetrahedra (altogether 6 atoms per formula unit), whereas $\theta_E$ reflects higher-energy vibrations of the remaining four oxygens that are bound to V and Cu at the same time.

The high-$T$ fit was extrapolated down to low temperatures and $C_{\text{mag}}(T)$ was estimated by subtracting $C_{\text{ph}}(T)$ from $C_p(T)$ [see Fig. 6 (upper panel)]. $C_{\text{mag}}(T)/T$ was plotted as a function of temperature in the lower panel of Fig. 6. The broad maximum corresponding to the short-range order is apparent at $T \approx 1.52$ K. At low temperatures, $C_{\text{mag}}(T)/T$ shows a rapid increase, which could be related to the onset of magnetic LRO below 0.4 K. The magnetic entropy was calculated as $S_{\text{mag}}(T) = \int_0^T \frac{C_{\text{mag}}(T')}{T'} dT'$, which yields $S_{\text{mag}} \approx 5.83$ J/mol K at 20 K (see the lower panel of Fig. 6). This value is close to the expected magnetic entropy for spin-$\frac{1}{2}$: $S_{\text{mag}} = R \ln 2 = 5.76$ J/mol K.

In the inset of the lower panel of Fig. 6, $C_{\text{mag}}/R$ is plotted against $T$. The peak of $C_{\text{mag}}/R$ can be used to discriminate between different microscopic scenarios. Its height depends on the nature of the underlying spin lattice [52]. Our experimental peak value of $C_{\text{mag}}/R$ $\approx 0.323$ fits well to the aforementioned 1D scenario, suggesting that VO$_4$ bridges choose the direction of spin chains. Alternatively, four shortest Cu–Cu contacts of 5.507 Å could cause interactions of equal strength and form a 2D square-lattice interaction topology that should manifest itself by a much higher peak with $C_{\text{mag}}/R \approx 0.47$. On the other hand, the triangular-lattice scenario would reduce the peak value to $C_{\text{mag}}/R \approx 0.22$, lower than seen experimentally. We thus conclude that our specific-heat data favor the spin-chain scenario for BaNa$_2$Cu(VO$_4$)$_2$.

D. $^{23}$Na and $^{51}$V NMR

NMR is a potent tool to study the static and dynamic properties of spin systems. In Na$_2$BaCu(VO$_4$)$_2$, the $^{23}$Na and $^{51}$V nuclei are hyperfine-coupled to the magnetic Cu$^{2+}$ ions along the spin chains. Therefore, the low-lying excitations of Cu$^{2+}$ spins can be probed by means of $^{23}$Na and $^{51}$V NMR measurements.

The quadrupole nuclei $^{23}$Na ($I = 3/2$) and $^{51}$V ($I = 7/2$) are in a non-cubic symmetry that may produce an asymmetric charge distribution and hence electric field gradient (EFG). Therefore, the four-fold and eight-fold degeneracies of the $I = 3/2$ and $I = 7/2$ spins, respectively, are lifted partially due to the interaction between the nuclear quadrupole moment ($Q$) and the surrounding EFG. In this case, the nuclear spin Hamiltonian is a sum of the Zeeman and quadrupole interaction terms [53, 54],

$$\mathcal{H} = -\gamma \hbar \mathbf{I} \mathbf{H} (1 + K) + \frac{\hbar \nu_Q}{6} (3\hat{I}_z^2 - \hat{I}^2) + \eta (\hat{I}_x^2 - \hat{I}_y^2).$$

Here, the nuclear quadrupole resonance (NQR) frequency is defined as $\nu_Q = \frac{3e^2Q}{2\hbar(2I-1)}$, $e$ is the electron charge,
by the parameters are not equally spaced. The EFG is fully characterized by the principal axes of EFG, and \( \eta = |V_{xx} - V_{yy}| / V_{zz} \) is the EFG asymmetry (here, the principal axes of EFG are chosen such that \( |V_{zz}| \geq |V_{yy}| \geq |V_{xx}| \)). Experimentally, the transitions can be observed at the frequency \( \nu_z = \nu_Q \sqrt{1 + \eta^2/3} \).

The principal axes \( \{x, y, z\} \) of the EFG tensor are defined by the local symmetry of the crystal structure. Consequently, the corresponding resonance frequency to any nuclear transition will have strong dependence on the direction of the applied field with respect to the crystallographic axes. For a site with axial symmetry (\( \eta = 0 \)), there will be \( 2I - 1 \) quadrupolar resonances at frequencies \( n \nu_Q \), where \( n = 1, \ldots, 2I - 1 \). When \( \eta > 0 \), the resonances are not equally spaced. The EFG is fully characterized by the parameters \( \nu_z \), \( \eta \), and \( \hat{z} \), where \( \hat{z} \) is the unit vector in the direction of the principal axis of the EFG with the largest eigenvalue. When the Zeeman term dominates over the quadrupole term, first-order perturbation theory is enough for describing the system. In such a scenario, for a quadrupole nucleus, equally spaced satellite peaks should appear on either side of the central peak separated by \( \nu_Q \).

The NMR spectra as a function of temperature measured by sweeping the magnetic field at 77 MHz are presented in Fig. 7. Since \( ^{23}\text{Na} \) and \( ^{51}\text{V} \) nuclei have nearly the same \( \gamma \) values, one expects their spectral lines to appear very close to each other. Further, \( ^{23}\text{Na} \) and \( ^{51}\text{V} \) are quadrupolar nuclei with nuclear spins \( I = 3/2 \) and \( 7/2 \), respectively and the transitions with \( \Delta m = \pm 1 \) are expected between the energy levels. Therefore, one would anticipate three NMR lines for \( ^{23}\text{Na} \): one central line corresponding to \( I_z = +1/2 \leftrightarrow -1/2 \) and two equally spaced satellite lines corresponding to \( I_z = \pm 3/2 \leftrightarrow \pm 1/2 \) and seven NMR lines for \( ^{51}\text{V} \): the central line being \( I_z = +1/2 \leftrightarrow -1/2 \) and the satellite lines \( I_z = \pm 1/2 \leftrightarrow \pm 3/2 \leftrightarrow \pm 5/2 \leftrightarrow \pm 7/2 \). Indeed, at high temperatures, we observed two sharp and prominent peaks at the resonance field position and two satellite peaks on either side of those. The central peak towards the low-field side is identified to be the signal coming from the \( ^{23}\text{Na} \) nuclei, while the one towards the high-field side appears to be the \( ^{51}\text{V} \) peak. In addition to the central peaks, two satellite peaks correspond to the \( ^{23}\text{Na} \) line. At high temperatures, the NMR spectra are found to be narrow and one can distinguish the \( ^{23}\text{Na} \) and \( ^{51}\text{V} \) signals. As the temperature is lowered, the line broadens asymmetrically and the central lines shift weakly with temperature. No abrupt line broadening was noticed down to 44 mK, which may signal the absence of magnetic LRO.

The spectra were fitted assuming the superposition of \( ^{23}\text{Na} \) and \( ^{51}\text{V} \) signals. The spectral fit at \( T = 125 \) K is presented in the upper panel of Fig. 8, where \( ^{23}\text{Na} \) and \( ^{51}\text{V} \) lines and their satellites are marked by arrows. The obtained fitting parameters are \( K \approx 0.0345 \) (isotropic shift), \( \eta = 0 \) (asymmetry parameter), and \( \nu_Q \approx 0.92 \text{ MHz (NQR frequency)} \) for \( ^{23}\text{Na} \) and \( K \approx 0.627 \), \( \eta = 0 \), and \( \nu_Q \approx 0.234 \text{ MHz for } ^{51}\text{V} \). The quadrupole frequency is found to be almost constant with temperature down to 1.5 K, which essentially excludes the possibility of any structural distortion in the studied compound.

The NMR shift \( K(T) \) for both \( ^{23}\text{Na} \) and \( ^{51}\text{V} \) lines obtained from the spectral fits is plotted in the lower panel of Fig. 8. The temperature-dependent \( ^{23}\text{Na} \) shift \( [K(T)] \) is found to have a broad maximum at around 3 K, similar to the \( \chi(T) \) data. As \( K(T) \) in an intrinsic measure of the spin susceptibility \( \chi_{\text{spin}} \), one can write the linear relation

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

where \( K_0 \) is the temperature-independent chemical shift and the proportionality constant \( A_{hf} \) is the hyperfine coupling between the probed nuclei and the electron spins.

From Eq. (9), \( A_{hf} \) can be calculated by taking the slope of the linear \( K \) vs \( \chi \) plot (inset of Fig. 8) with temperature as an implicit parameter. In the case of \( ^{23}\text{Na} \), the data for \( T \geq 5 \) K were fitted well by a linear function,
and the slope of the fit yields $^{23}A_{hf} \simeq 0.021$ T/µB. Similarly, for $^{51}$V the linearity is found over a large temperature range down to 10 K, and the linear fit returns $^{51}A_{hf} \simeq -0.016$ T/µB. To estimate the exchange coupling, $^{23}K(T)$ above 2.5 K was fitted by Eq. (9) taking $\chi_{spin}$ for the 1D $S = 1/2$ Heisenberg chain [Eq. (3)]. The fit returns $J/k_B \simeq 4.22$ K and $^{23}A_{hf} \simeq 0.0194$ T/µB. The value of $g$ was fixed to $g = 2.17$ during the fitting procedure. This value of $J/k_B$ is close to the one obtained from the $\chi(T)$ analysis, whereas $^{23}A_{hf}$ is also in good agreement with the value obtained from the $K$ vs $\chi$ analysis. An anomaly at $\sim 0.3$ K in $^{23}K(T)$ could be due to a magnetic transition.

To study the spin dynamics, spin-lattice relaxation rate ($1/T_1$) was measured by irradiating the central position of the $^{51}$V spectra corresponding to the $1/2 \leftrightarrow -1/2$ transition, choosing an appropriate pulse width. The recovery of the longitudinal magnetization was fitted by the following exponential function relevant for a quadrupole $(I = 7/2)$ nuclei [57, 58]

$$1 - \frac{M(t)}{M(\infty)} = 0.0119 \times e^{(-t/T_1)} + 0.068 \times e^{(-6t/T_1)} + 0.21 \times e^{(-15t/T_1)} + 0.71 \times e^{(-28t/T_1)}$$

Here, $M(t)$ and $M(\infty)$ are the nuclear magnetizations at a time $t$ and $t \rightarrow \infty$, respectively, after the saturation pulse. Temperature dependence of $^{51}$V $1/T_1$ obtained from the above fit is shown in Fig. 9. Our measurements were carried out down to 0.04 K. At high temperatures, $1/T_1$ is almost temperature-independent as expected in the paramagnetic regime [59]. At low temperatures, it exhibits a sharp peak at $T \simeq 0.25$ K due to slowing down of the fluctuating moments and is a direct evidence of the onset of magnetic LRO. In order to highlight the behavior in the intermediate temperature range, $1/T_1$ above 2 K is magnified in the inset of Fig. 9. As the temperature is lowered, $1/T_1$ decreases linearly below about 25 K, remains almost temperature-independent for 4 K $\leq T \leq 10$ K, and then starts increasing for $T \leq 4$ K. This increase below 4 K can be attributed to the growth of AFM correlations as the system approaches the magnetic LRO state.

Further, $1/T_1 T$ is directly proportional to the imaginary part of the dynamic susceptibility $\chi_M(\vec{q}, \omega)$ at the nuclear Larmor frequency $\omega_0$, which is $q$-dependent [59]. In low-dimensional spin systems, temperature-dependent $1/T_1$ often reflects dominant contributions from different $q$ values in different temperature regimes. For instance, for spin-1/2 Heisenberg AFM spin chains, it is theoretically predicted that with the dominant staggered contribution ($q = \pm \pi/a$) the spin-lattice relaxation rate behaves as $1/T_1 \sim T^0$, while the dominant contribution of the uniform component ($q = 0$) results in $1/T_1 \sim T$ [60, 61]. The dominant contributions of $q = \pm \pi/a$ and $q = 0$ are typically observed in the low-temperature ($T < J$) and high-temperature ($T \sim J$)
TABLE I. Exchange parameters of BaNa$_2$Cu(VO$_4$)$_2$ obtained from DFT calculations: Cu–Cu distances $d$ (in Å), electron hoppings $t_i$ (in meV), AFM contributions to the exchange $J_{i}^{\text{AFM}} = 4t_i^2/U_{\text{eff}}$ (in K), and total exchange couplings $J_i$ (in K) from the DFT+$U$ mapping procedure.

| $d_{\text{Cu–Cu}}$ | $t_i$ | $J_{i}^{\text{AFM}}$ | $J_i$ |
|-------------------|------|---------------------|------|
| Cu–Cu             | 5.507| −40                 | 14.9 | 6.8  |
| $J_{ab}$          | 5.507| −5                  | 0.2  | <0.2 |
| $J_{a}^{\prime}$  | 5.686| −1                  | 0.01 | <0.2 |
| $J_c$             | 7.024| 3                   | 0.08 | <0.2 |

regimes, respectively [40, 62]. Thus, our experimentally observed constant and linear behaviors of $1/T_1$ with temperature over 4 K $\leq T \leq 10$ K and 10 K $\leq T \leq 25$ K, respectively (inset of Fig. 9), are compatible with the 1D physics.

In real spin-chain systems, the non-vanishing interchain couplings often leads to the onset of magnetic LRO at very low temperatures. The interchain coupling can be calculated using the expression proposed by Schulz [5]

$$|J_{\perp}| \simeq \frac{T_N}{2.8 \sqrt{\ln(5.8J/T_N)}}.$$  

where $J_{\perp}$ is an effective interchain coupling. Taking $T_N \simeq 0.25$ K and $J/B_0 \simeq 5.6$ K, we arrive at the possible value of $J_{\perp}/k_B \simeq 0.1$ K, which is indeed consistent with the value estimated from the band-structure calculations, as discussed in the following.

E. Microscopic magnetic model

LDA band structure of BaNa$_2$Cu(VO$_4$)$_2$ (Fig. 10) features Cu 3$d$ states below the Fermi level and V 3$d$ states above 2 eV, confirming the non-magnetic state of vanadium. The overall energy spectrum is metallic, as typical for a transition-metal compound when correlation effects in the 3d shell were not taken into account. Nevertheless, this band structure gives an overview of possible exchange interactions, as the hopping parameters $t_i$ are proportional to the LDA bandwidth, whereas $J_{i}^{\text{AFM}} = 4t_i^2/U_{\text{eff}}$. The Fermi level is crossed by two narrow bands formed by the half-filled $d_{x^2−y^2}$ orbitals of Cu$^{2+}$. The width of these bands is less than 0.2 eV, one of the smallest in cuprates, and indicates very weak exchange couplings in BaNa$_2$Cu(VO$_4$)$_2$.

DFT results for the exchange couplings are summarized in Table I. Only one sizable coupling, $J/I_{B_0} \simeq 6.8$ K is found. It corresponds to spin chains running along [110] in one layer and along [110] in the adjacent layer, the direction being chosen by the position of the double VO$_4$ bridges that connect the CuO$_4$ plaquette units (Fig. 1). Such a coupling mechanism is fairly common among the Cu$^{2+}$ compounds and can give rise to both FM and AFM superexchange depending on the orientation of the VO$_4$ tetrahedra relative to the CuO$_4$ planes [19]. Larger rotations of the tetrahedra favor FM couplings.

In BaNa$_2$Cu(VO$_4$)$_2$, we find $\varphi = 99.0^\circ$, which is similar to $\varphi^{(2)} = 102.2^\circ$ for the AFM coupling $J_{a}^{(2)}/k_B = 9.5$ K in BaAg$_2$Cu(VO$_4$)$_2$ and very different from $\varphi^{(1)} = 123.7^\circ$ for the FM coupling $J_{a}^{(1)}/k_B = −19$ K in the same compound [19]. Here, $\varphi$ is the angle between the face of the VO$_4$ tetrahedron and the plane connecting the adjacent CuO$_4$ plaquettes, as shown in Fig. 1. Compared to BaAg$_2$Cu(VO$_4$)$_2$, the AFM coupling weakens from 9.5 K to ~ 6 K, likely because of the longer Cu–Cu distance (5.507 Å vs. 5.448 Å) and the increased lateral displacement $r$ of the CuO$_4$ plaquettes (0.895 Å vs. 0.860 Å).

All couplings beyond the aforementioned spin chains appear to be very weak, below 0.2 K, and unfeasible for the DFT+$U$ mapping analysis. Their relative strengths can be assessed from the hopping parameters that suggest the dominant interchain couplings $J_{ab}$ in the $ab$ plane (along [110] for the spin chains along [110], and vice versa) and $J_c$ along the $c$ direction. The in-plane coupling $J_{a}^{\prime}$ is negligible. The two stronger interchain couplings, $J_{a}^{\prime}$ and $J_c$, form a non-frustrated 3D network. From $4t_i^2/U_{\text{eff}}$ with $U_{\text{eff}} = 5$ eV [41, 63], one expects the coupling strength of 0.2 K or lower, in agreement with the DFT+$U$ results. Altogether, our modeling results establish weak and non-frustrated interchain couplings in BaNa$_2$Cu(VO$_4$)$_2$, with $J_{\perp}/J \simeq 0.02$. The average interchain coupling of $J_{\perp}/k_B \simeq 0.1$ K leads to $T_N/J \simeq 0.22$ K [4] in good agreement with 0.25 K found experimentally. Therefore, we argue that long-range magnetic order in BaNa$_2$Cu(VO$_4$)$_2$ should be driven by weak interchain couplings, and the Néel temperature $T_N/J$ is determined by the $J_{\perp}/J$ ratio.

Above $T_N$, a purely one-dimensional description should hold. Indeed, we were able to fit magnetization curves down to 0.49 K using the spin-chain model with $J/k_B = 5.5$ K and $g = 2.17$ in excellent agreement with 5.6 K from the fit to the magnetic susceptibility and $g = 2.17$ from the ESR experiment (Fig. 11). This confirms that the in-
terchain couplings are very weak and play only marginal role even at $T < J$. Magnetic specific heat is also well described by the spin-chain model showing small deviations below 1 K only. These deviations correspond to the upturn in $C_{\text{mag}}/T$ upon approaching $T_N$ (Fig. 6).

IV. CONCLUSIONS

We have shown that BaNa$_2$Cu(VO$_4$)$_2$ strongly deviates from all of its structural siblings in terms of the magnetic behavior. The majority of these compounds are triangular magnets, while the only Cu$^{2+}$ member studied to date, BaAg$_2$Cu(VO$_4$)$_2$, revealed a very unusual coexistence of different spin chains, one ferromagnetic and one antiferromagnetic [19, 20]. Our present results for BaNa$_2$Cu(VO$_4$)$_2$ corroborate non-trivial magnetostructural correlations in Cu$^{2+}$ vanadates, where the sign of a magnetic coupling strongly depends on the spatial orientation of the VO$_4$ tetrahedra relative to the spin chains and CuO$_4$ plaquette units.

The disparity of spin chains is absent in BaNa$_2$Cu(VO$_4$)$_2$, but now the chains adopt two different directions and form an unusual crossed pattern. Interestingly, this crossed pattern does not cause any magnetic frustration, because the Cu$_{\text{II}}$ ion of one chain sits exactly on top of the Cu$_{\text{II}}$ ion of the adjacent chain (Fig. 1). Then, each magnetic site has only one coupling to a spin chain of another direction, and not two couplings, as expected theoretically [22]. This fact highlights the importance of lateral displacements between the Cu$_{\text{II}}$ ions of the crossed chains to induce the frustration. Such displacements do not occur in BaNa$_2$Cu(VO$_4$)$_2$, but they may potentially appear in sister compounds, because even the substitution of Na$^+$ by Ag$^+$ causes significant structural changes, although the two ions are very similar in size. Alternatively, one may consider structure types with a weaker spatial separation between the crossed chains that, in turn, allows several non-equivalent interactions to form a frustrated topology even in the absence of lateral displacements [64–66].

ACKNOWLEDGMENTS

We would like to acknowledge SERB, India, for financial support bearing sanction Grant No. CRG/2019/000960. Work at the Ames Laboratory was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division. The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. DEAC02-07CH11358. AT was funded by the Federal Ministry for Education and Research through the Sofja Kovalevskaya Award of Alexander von Humboldt Foundation.

[1] S. Sachdev, *Quantum phase transitions* (Wiley Online Library, 2007).
[2] A. P. Ramirez, “Strongly Geometrically Frustrated Magnets,” *Annu. Rev. Mater. Sci.* 24, 453 (1994).
[3] N. D. Mermin and H. Wagner, “Absence of ferromagnetism or antiferromagnetism in one- or two-dimensional isotropic Heisenberg models,” *Phys. Rev. Lett.* 17, 1133–1136 (1966).
[4] C. Yasuda, S. Todo, K. Hokushima, F. Alet, M. Keller, M. Troyer, and H. Takayama, “Néel Temperature of Quasi-Low-Dimensional Heisenberg Antiferromagnets,” *Phys. Rev. Lett.* 94, 217201 (2005).
[5] H. J. Schulz, “Dynamics of Coupled Quantum Spin Chains,” *Phys. Rev. Lett.* 77, 2790 (1996).
[6] Greedan, John E., “Geometrically frustrated magnetic materials,” *J. Mater. Chem.* 11, 37 (2001).
[7] K. M. Kojima, Y. Fudamoto, M. Larkin, G. M. Luke, J. Merrin, B. Nachumi, Y. J. Uemura, N. Motoyama, H. Eisaki, S. Uchida, K. Yamada, Y. Endoh, S. Hosoya, B. J. Sternlieb, and G. Shirane, “Reduction of Ordered Moment and Néel Temperature of Quasi-One-Dimensional Antiferromagnets Sr$_2$CuO$_3$ and Ca$_2$CuO$_3$,” *Phys. Rev. Lett.* 78, 1787 (1997).
[8] T. Lancaster, S. J. Blundell, M. L. Brooks, P. J. Baker, F. L. Pratt, J. L. Manson, C. P. Landee, and C. Baines, “Magnetic order in the quasi-one-dimensional spin-$\frac{1}{2}$ molecular chain compound copper pyrazine dinitrate,” *Phys. Rev. B* 73, 020410 (2006).
[9] S. Furukawa, M. Sato, and S. Onoda, “Chiral order and electromagnetic dynamics in one-dimensional multiferroic cuprates,” *Phys. Rev. Lett.* 105, 257205 (2010).
[10] M. Hase, I. Terasaki, and K. Uchinokura, “Observation of the spin-Peierls transition in linear Cu$^{2+}$ (spin-$\frac{1}{2}$) chains in an inorganic compound CuGeO$_3$,” Phys. Rev. Lett. 70, 3651 (1993).

[11] S.-L. Drechsler, O. Volkova, A. N. Vasiliev, N. Tristam, J. Richter, M. Schmitt, H. Rosner, J. Måle, R. Klingeler, A. A. Zyvagin, and B. Büchner, “Frustrated Cuprate Route from Antiferromagnetic to Ferromagnetic Spin-$\frac{1}{2}$ Heisenberg Chains: Li$_2$ZrCuO$_4$ as a Missing Link near the Quantum Critical Point,” Phys. Rev. Lett. 98, 077202 (2007).

[12] N. E. Amuneke, D. E. Gheorghe, B. Lorenz, and A. Möller, “Synthesis, Crystal Structure, and Physical Properties of Ba$_2$Ag$_2$Cu[VO$_4$]$_2$: A New Member of the S = 1/2 Triangular Lattice,” Inorg. Chem. 50, 2207 (2011).

[13] A. Möller, N. E. Amuneke, P. Daniel, B. Lorenz, C. R. de la Cruz, M. Gooch, and P. C. W. Chu, “A$_2$M$[\text{VO}_4]_2$ (A = Ba, Sr; M = Co, Ni): A series of ferromagnetic insulators,” Phys. Rev. B 85, 214422 (2012).

[14] G. Nakayama, S. Hara, H. Sato, Y. Narumi, and H. Nohjiri, “Synthesis and magnetic properties of a new series of triangular-lattice magnets, Na$_2$BaMV$_2$O$_6$ (M = Ni, Co, and Mn),” J. Phys.: Condens. Matter 25, 116003 (2013).

[15] A. Reuß, V. Ksenofontov, J. Tapp, D. Wulferting, P. Lemmens, M. Panthöfer, and A. Möller, “Screw-Type Motion and Its Impact on Cooperativity in Ba$_2$Na$_2$Fe[VO$_4$]$_2$,” Inorg. Chem. 57, 6300 (2018).

[16] L. D. Sanjeeva, V. O. Garlea, M. A. McGuire, C. D. McMillen, and J. W. Kolis, “Magnetic Ground State Crossover in a Series of Glaserite Systems with Triangular Magnetic Lattices,” Inorg. Chem. 58, 2813 (2019).

[17] N. E. Amuneke, J. Tapp, C. R. de la Cruz, and A. Möller, “Experimental realization of a unique class of compounds: XY-antiferromagnetic triangular lattices, KAg$_2$Fe[VO$_4$]$_2$ and RbAg$_2$Fe[VO$_4$]$_2$, with ferroelectric ground states,” Chem. Mater. 26, 5930–5935 (2014).

[18] S. Lee, R. Klauser, J. Menten, W. Lee, S. Yoon, H. Luetkens, P. Lemmens, A. Möller, and K.-Y. Choi, “Unconventional spin excitations in the $S = \frac{3}{2}$ triangular antiferromagnet RbAg$_2$Cr[VO$_4$]$_2$,” Phys. Rev. B 101, 224420 (2020).

[19] A. A. Tsirlin, A. Möller, B. Lorenz, Y. Skourski, and H. Rosner, “Superposition of ferromagnetic and antiferromagnetic spin chains in the quantum magnet Ba$_2$Ag$_2$Cu[VO$_4$]$_2$,” Phys. Rev. B 85, 014401 (2012).

[20] Y. Krupskaya, M. Schäpers, A.U.B. Wolter, H.-J. Grafe, E. Vavilova, A. Möller, B. Büchner, and V. Kataev, “Magnetic resonance study of the spin-1/2 quantum magnet Ba$_2$Ag$_2$Cu[VO$_4$]$_2$,” Z. Phys. Chem. 231, 759 (2017).

[21] M. von Postel and Hk. Müller-Buschbaum, “Na$_2$BaCu$_2$O$_8$: Ein neuer Strukturtyp der Alkali-Äralkalametall Kupfer-Oxovanadate,” Z. Anorg. Allg. Chem. 618, 107 (1992).

[22] O. A. Starykh, R. R. P. Singh, and G. C. Levine, “Spinons in a crossed-chains model of a 2D spin liquid,” Phys. Rev. Lett. 88, 167203 (2002).

[23] P. Sindzingre, J.-B. Fouet, and C. Lhuillier, “One-dimensional behavior and sliding Luttinger liquid phase in a frustrated spin-1/2 crossed chain model: Contribution of exact diagonalizations,” Phys. Rev. B 66, 174424 (2002).

[24] W. Brenig and M. Grzeschik, “Valence-bond crystal phase of the crossed-chain quantum spin model,” Phys. Rev. B 69, 064420 (2004).

[25] O. A. Starykh, A. Furusaki, and L. Balents, “Anisotropic pyrochlores and the global phase diagram of the checkerboard antiferromagnet,” Phys. Rev. B 72, 094416 (2005).

[26] R. F. Bishop, P. H. Y. Li, D. J. J. Farnell, J. Richter, and C. E. Campbell, “Frustrated Heisenberg antiferromagnet on the checkerboard lattice: $J_1 - J_2$ model,” Phys. Rev. B 85, 205122 (2012).

[27] J. Rodriguez-Carvajal, “Recent advances in magnetic structure determination by neutron powder diffraction,” Physica B: Condensed Matter 192, 55 (1993).

[28] K. Köpferlik and H. Eschrig, “Full-potential nonorthogonal local-orbital minimum-basis band-structure scheme,” Phys. Rev. B 59, 1743 (1999).

[29] J. P. Perdew and Y. Wang, “Accurate and simple analytic representation of the electron-gas correlation energy,” Phys. Rev. B 45, 13244 (1992).

[30] H. J. Xiang, E. J. Kan, S.-H. Wei, M.-H. Whangbo, and X. G. Gong, “Predicting the spin-lattice order of frustrated systems from first principles,” Phys. Rev. B 84, 224429 (2011).

[31] O. Janson, A. A. Tsirlin, E. S. Osipova, P. S. Berdensov, A. V. Olenev, V. A. Dolgikh, and H. Rosner, “CaCu$_2$(SeO$_3$)$_2$Cl$_2$: Spin-$\frac{1}{2}$ Heisenberg chain compound with complex frustrated interchain couplings,” Phys. Rev. B 83, 144423 (2011).

[32] S. Todo and K. Kato, “Cluster algorithms for general-S quantum spin systems,” Phys. Rev. Lett. 87, 047203 (2001).

[33] F. Alet, S. Wessel, and M. Troyer, “Generalized directed loop method for quantum Monte Carlo simulations,” Phys. Rev. E 71, 036706 (2005).

[34] A.F. Albuquerque, F. Alet, P. Corboz, P. Dayal, A. Feiguin, S. Fuchs, L. Gamper, E. Gull, S. Görling, A. Honecker, R. Igarashi, M. Körner, A. Kozhevnikov, A. Läuchli, S.R. Manmana, M. Matsumoto, I.P. McCulloch, F. Michel, R.M. Noack, G. Pawlowski, L. Pollet, T. Pruschke, U. Schollwöck, S. Todo, S. Trebst, M. Troyer, P. Werner, and S. Wessel, “The ALPS project release 1.3: Open-source software for strongly correlated systems,” J. Magn. Magn. Mater. 310, 1187 (2007).

[35] J. C. Bonner and M. E. Fisher, “Linear Magnetic Chains with Anisotropic Coupling,” Phys. Rev. 135, A640 (1964).

[36] S. Eggert, I. Affleck, and M. Takahashi, “Susceptibility of the spin-$\frac{3}{2}$ Heisenberg antiferromagnetic chain,” Phys. Rev. Lett. 73, 332 (1994).

[37] P. W. Selwood, Magnetochemistry (Read Books Ltd, 2013).

[38] Mendelssohn, Biggs, and Mann, “Hartree-fock diamagnetic susceptibilities,” Phys. Rev. A 2, 1130 (1970).

[39] N. Motoyama, H. Eisaki, and S. Uchida, “Magnetic Susceptibility of Ideal Spin-$\frac{3}{2}$ Heisenberg Antiferromagnetic Chain Systems, Sr$_2$CuO$_3$ and SrCu$_2$O,” Phys. Rev. Lett. 76, 3212 (1996).

[40] R. Nath, A. V. Mahajan, N. Büttgen, C. Kegler, A. Loidl, and J. Bobroff, “Study of one-dimensional nature of Spin-$\frac{3}{2}$ (Sr,Ba)Cu$_2$PO$_4$$_2$ and BaCu$_2$P$_2$O$_7$ via 31P NMR,” Phys. Rev. B 7, 174436 (2005).

[41] N. Ahmed, A. A. Tsirlin, and R. Nath, “Multiple magnetic transitions in the spin-$\frac{1}{2}$ chain antiferromagnet...
SrCuTe₂O₆,” Phys. Rev. B 91, 214413 (2015).
[42] M. Takigawa, P. C. Hammel, R. H. Heffner, Z. Fisk, J. L. Smith, and R. B. Schwarz, “Anisotropic Cu Knight shift and magnetic susceptibility in the normal state of YBa₂Cu₃O₇,” Phys. Rev. B 39, 300 (1989).
[43] A. Klümper, “The spin-1/2 Heisenberg chain: thermodynamics, quantum criticality and spin-Peierls exponents,” Eur. Phys. J. B 5, 677–685 (1998).
[44] S. Leberneck, A. A. Tsirlin, O. Janson, R. Nath, J. Sichelschmidt, Yu. Skourski, G. Amthauer, and H. Rosner, “Magnetic model for A₂CuP₂O₇ (A = Na, Li): One-dimensional versus two-dimensional behavior,” Phys. Rev. B 84, 174436 (2011).
[45] A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions (OUP Oxford, 2012).
[46] B. I. Kochelaev, J. Sichelschmidt, B. Elschner, W. Lemor, and A. Loidl, “Intrinsic EPR in La₂₋₋₄Sr₄CuO₆: Manifestation of Three-Spin Polarons,” Phys. Rev. Lett. 79, 4274 (1997).
[47] R. Nath, K. M. Ranjit, J. Sichelschmidt, M. Baenitz, Y. Skourski, F. Alet, I. Roussochatzakis, and A. A. Tsirlin, “Hindered magnetic order from mixed dimensionalities in CuP₂O₇,” Phys. Rev. B 89, 014407 (2014).
[48] V. A. Ivanshin, V. Yushankhai, J. Sichelschmidt, D. V. Zakharov, E. E. Kaul, and C. Geibel, “ESR study of the anisotropic exchange in the quasi-one-dimensional antiferromagnet Sr₂V₃O₉,” Phys. Rev. B 68, 064404 (2003).
[49] J. Sichelschmidt, M. Baenitz, C. Geibel, F. Steglich, A. Loidl, and H. H. Otto, “Quasi-one-dimensional spin chains in CuSiO₃: An EPR study,” Appl. Magn. Reson. 23, 75 (2002).
[50] C. Kittel, Introduction to Solid State Physics (J. Wiley, Hoboken, NJ, c2005) 500317.
[51] K. Caslin, R. K. Kremer, F. S. Razavi, A. Schulz, A. Muñoz, F. Pertlik, J. Liu, M.-H. Whangbo, and J. M. Law, “Characterization of the spin-½ linear-chain ferromagnet Cu₆As₂O₄,” Phys. Rev. B 89, 014412 (2014).
[52] B. Bernu and G. Misguich, “Specific heat and high-temperature series of lattice models: Interpolation scheme and examples on quantum spin systems in one and two dimensions,” Phys. Rev. B 63, 134409 (2001).
[53] N. J. Curro, “Nuclear magnetic resonance in the heavy fermion superconductors,” Rep. Prog. Phys. 72, 026502 (2009).
[54] C. P. Slichter, Principle of Nuclear Magnetic Resonance, 3rd ed. (Springer, New York, 1992).
[55] G. Lang, J. Bobroff, H. Alloul, P. Mendels, N. Blanchard, and G. Collin, “Evidence of a single non-magnetic Co⁺⁺⁺⁺ state in the Na₁CoO₂ cobaltate,” Phys. Rev. B 72, 094404 (2005).
[56] Ranjit, K. M. and Nath, R. and Majumder, M. and Kasinathan, D. and Skoulatsos, M. and Keller, L. and Skourski, Y. and Baenitz, M. and Tsirlin, A. A., “Commensurate and incommensurate magnetic order in spin-1 chains stacked on the triangular lattice in Li₂NiW₂Os,” Phys. Rev. B 94, 014415 (2016).
[57] M. I. Gordon and M. J. R. Hoch, “Quadrupolar spin-lattice relaxation in solids,” J. Phys. C 11, 783 (1978).
[58] W. W. Simmons, W. J. O’Sullivan, and W. A. Robinson, “Nuclear Spin-Lattice Relaxation in Dilute Paramagnetic Sapphire,” Phys. Rev. 127, 1168 (1962).
[59] T. Moriya, “Nuclear Magnetic Relaxation in Antiferromagnetics,” Prog. Theor. Exp. Phys. 16, 23–44 (1956).
[60] A. Sandvik, “NMR relaxation rates for the spin-1/2 Heisenberg chain,” Phys. Rev. B 50, R9831 (1995).
[61] S. Sachdev, “NMR relaxation in half-integer antiferromagnetic spin chains,” Phys. Rev. B 50, 13006 (1994).
[62] R. Nath, D. Kasinathan, H. Rosner, M. Baenitz, and C. Geibel, “Electronic and magnetic properties of K₂CuP₂O₇: A model S = ½ Heisenberg chain system,” Phys. Rev. B 77, 134451 (2008).
[63] S. Leberneck, A. A. Tsirlin, O. Janson, and H. Rosner, “Spin gap in malachite Cu₂(OH)₂CO₃ and its evolution under pressure,” Phys. Rev. B 88, 224406 (2013).
[64] A. A. Tsirlin, R. Nath, J. Sichelschmidt, Y. Skourski, C. Geibel, and H. Rosner, “Frustrated couplings between alternating spin-½ chains in AgVOAs₄,” Phys. Rev. B 83, 144412 (2011).
[65] P. K. Mukharjee, K. M. Ranjit, B. Koo, J. Sichelschmidt, M. Baenitz, Y. Skourski, Y. Inagaki, Y. Furukawa, A. A. Tsirlin, and R. Nath, “Bose-Einstein condensation of tripleons close to the quantum critical point in the quasi-one-dimensional spin-½ antiferromagnet NaVOPO₄,” Phys. Rev. B 100, 144433 (2019).
[66] F. Weickert, A. A. Aczel, M. B. Stone, V. O. Garlea, C. Dong, Y. Kohama, R. Movshovich, A. Demuer, N. Harrison, M. B. Gam za, A. Steppke, M. Brando, H. Rosner, and A. A. Tsirlin, “Field-induced double dome and Bose-Einstein condensation in the crossing quantum spin chain system AgVOAs₄,” Phys. Rev. B 100, 104422 (2019).