A spin Hamiltonian for BaCdVO(PO$_4$)$_2$

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Single crystal inelastic neutron scattering is used to study spin wave excitations in the fully polarized state of the frustrated quantum ferro-antiferromagnet BaCdVO(PO$_4$)$_2$. The data analysis is based on a Heisenberg spin Hamiltonian that includes as many distinct nearest-neighbor and next-nearest neighbor interactions as allowed by crystal symmetry. All 8 such exchange constants are obtained in a simultaneous fit to over 150 scans across the dispersion manifold. This establishes a definitive quantitative model of this material. It turns out to be substantially different from the one assumed in numerous previous studies based on powder experiments.

I. INTRODUCTION

Despite its simplicity, the square lattice $S = 1/2$ Heisenberg model with ferromagnetic (FM) nearest-neighbor (NN) coupling $J_1$ and frustrating antiferromagnetic (AF) next nearest neighbor (NNN) interaction $J_2$ is among the most important models in magnetism. It is famous for supporting an exotic spin-nematic phase for sufficiently strong frustration ratios $|J_2/J_1| > 1.73$ or in applied magnetic fields for moderate frustration $|J_2/J_1| > 1$. Unfortunately, no perfect experimental realizations of this model have been discovered to date. The closest approximations are found among layered vanadyl phosphates with the general formula AA VO(PO$_4$)$_2$ (A, A$'$ = Ba, Cd, Pb, Sr, Zn) [6,8]. Of these the most frustrated and the most promising spin nematic candidate is BaCdVO(PO$_4$)$_2$ [7,8]. Indeed, recent studies have produced compelling thermodynamic and neutron diffraction evidence that this material may have a novel exotic quantum phase in a wide range of applied magnetic fields below saturation [9,10].

All initial estimates of the coupling constants and frustration strengths in AA VO(PO$_4$)$_2$ materials were based on powder sample experiments analyzed with the assumption that the underlying model is indeed a perfect $J_1$-$J_2$ square lattice [6]. However, the latter is incompatible with the crystal symmetries of any compound in the family. All evidence points to that NN interactions stay FM, NNN remain AFM, but beyond that the deviations from simple square lattice symmetry are substantial. For example, single crystal experiments on Pb$_2$VO(PO$_4$)$_2$ revealed that it has as many as 5 distinct exchange constants and a weaker frustration than suggested by previous powder studies [11,12]. The situation is even more complicated for BaCdVO(PO$_4$)$_2$, where the powder/perfect square lattice estimate is $J_2/J_1 = -0.9$ [9]. Already the room temperature crystal structure [13] allow for 4 distinct exchange constants. A recently discovered structural transition [10] at 240 K lowers the symmetry even further. As many as 4 nearest-neighbor and 4 next nearest neighbor coupling constants are allowed.

The main question is whether the rather complex interactions in BaCdVO(PO$_4$)$_2$ are compatible with the presence of a high-field nematic state? To answer it one has to know the exact values of exchange parameters. A first step in this direction was made in our preliminary inelastic neutron scattering study of the spin wave spectrum in the fully saturated phase [10]. Due to the limited amount of data that could be collected on a unique but small $^{114}$Cd enriched crystalline sample, it was not possible to determine all 8 relevant parameters unambiguously. Nonetheless, the data were enough to demystify the peculiar “up-up-down-down” zero field magnetic structure previously detected in powder experiment [13].

As far as the field-induced nematic phase, recent theoretical calculations made use of our preliminary estimates to demonstrate its robustness [15]. Still, the exact Hamiltonian remains undetermined.

In the present work we report the results of a full-scale continuation of the preliminary neutron measurement. We utilize the extremely high efficiency MACS spectrometer at NIST to map out the spin wave dispersion in the entire Brillouin zone. We then analyze the combination of new and previously collected data in a single global model fit. In doing so we fully take into account the complex mosaicity of the sample and the energy-momentum resolution of the spectrometers. The result is a definitive spin Hamiltonian for BaCdVO(PO$_4$)$_2$.

II. MATERIAL AND EXPERIMENTAL DETAILS

The room temperature crystal structure of BaCdVO(PO$_4$)$_2$ is orthorhombic (space group $P_{bcm}$ No. 61) with lattice parameters $a = 8.84$ Å, $b = 8.92$ Å, and $c = 19.37$ Å [13]. Magnetism is due to $S = 1/2$ V$^{4+}$ ions that form layers parallel to the $(a,b)$ plane. There are 8 magnetic ions per crystallographic unit cell, four in each layer within a single cell. Intra-layer NN and NNN interactions are expected to dominate while inter-layer coupling is negligible [8]. However, even at...
room temperature there are two distinct NN and two NNN superexchange pathways, as illustrated in Fig. 1(b), which shows a single magnetic layer. As mentioned above, the crystal symmetry is further lowered upon cooling through a structural transition at about 250 K. At \( T = 120 \) K the space group is \( P_{\text{ca}21} (C_{2h}^{2}, \text{No. 29}) \) with lattice parameters \( a = 8.8621(4) \) Å, \( b = 8.8911(4) \) Å, and \( c = 18.8581(9) \) Å [10]. There are two \( V^{4+} \) symmetry-inequivalent sites represented now by two different colors in each layer and 8 distinct superexchange paths as shown in Fig. 1(b). Magnetic order sets in at \( T_N \approx 1.05 \) K [9]. Its “up-up-down-down” character [14] is enabled by the alternation of NN interaction strengths along the crystallographic \( a \) axis [9]. As mentioned, the magnetic phase diagram includes an extensive pre-saturated spin-nematic candidate phase, as discussed in detail in Refs. [9, 10]. Full saturation is reached at \( \mu_0 H_{\text{sat}} \approx 6.5 \) T.

The present measurement of the spin Hamiltonian is based on the method pioneered by Coldea et al. in Ref. [16]. Inelastic neutron scattering is used to measure the spin wave dispersion in the fully saturated phase. It is then analyzed in the framework of spin wave theory, which for the Heisenberg model becomes exact above saturation. We made use of the same \( \sim 320 \) mg 98% \( ^{114}\text{Cd} \)-enriched sample as in the experiments reported in Ref. [10]. All neutron measurements were carried out with momentum transfers in the \((h,k,0)\) reciprocal space plane. The mosaic of the crystal was characterized by mapping out the distributions of the \((200)\) and \((020)\) Bragg peaks both within and out of the scattering plane using a series of rocking curves. The survey revealed 7 distinct crystallites of individual mosaic spreads < 1°, but distributed over about 12° in the \((a,b)\) plane and within \( \pm 5^\circ \) out of the plane. A tilt-integrated rocking curve of the \((020)\) Bragg peak is shown in Fig. 2.

An analysis of the measured integrated peak intensities yielded the rotations of individual crystallites in the \((a,b)\) plane relative to the mean setting \((-6.74^\circ, -5.96^\circ, -5.19^\circ, -4.18^\circ, -1.8^\circ, 0.34^\circ, 4.8^\circ)\), as well as their relative masses \((0.13, 0.3, 0.5, 0.65, 0.7, 0.15, 1)\) normalized to the largest crystallite, correspondingly.

New inelastic data were collected with the Multi-Axis Crystal Spectrometer (MACS) at NIST [17]. All measurements were done in a 9 T magnetic field applied along the crystallographic \( c \) axis. Due to high neutron flux at the neutron absorbing sample the stable temperature was \( \sim 700 \) mK in a \(^3\text{He}-\text{He} \) dilution refrigerator. With it’s 20 detectors positioned at different scattering angles but tuned to the same energy, MACS is optimized for measuring two-dimensional intensity maps at a constant energy transfer, as was done, for example, in
The energy step was 0.025 meV with counting time of angles below $±$<sup>0</sup> and energy. Data points collected with scattering detectors performed “oblique” scans in both momentum 3 meV with an energy. The measured energy width of the incoherent constant-netic field [10]. The latter were all taken in conventional at the IN12 3-axis spectrometer at ILL in a 10 T magnetic field [10]. The energy was scanned from 0.55 meV to 0.15 meV. Concentric arcs represent the magnetic form factor squared of V$^{4+}$.

III. DATA ANALYSIS

The analysis of the measured magnetic scattering intensities was based on the Heisenberg model for V$^{4+}$ spin in each layer. Interactions between layers were assumed negligible. Unlike the constrained model used in Ref. [10], we allowed for 8 distinct exchange constants connecting nearest-neighbor and next-nearest neighbor spins as shown in Fig. 5. The spin wave dispersion relation for the fully saturated phase has been worked out in Ref. [15]. It contains two distinct dispersion branches corresponding to two crystallographically inequivalent V$^{4+}$ sites:

$$\hbar\omega_q = \frac{A_q + A'_q}{2} \pm \sqrt{\left(\frac{A_q - A'_q}{2}\right)^2 + |B_q|^2}.$$

Here

$$A'_q = \tilde{h} - J_1^a (1 - \cos qa)$$
$$A_q = \tilde{h} - J_1^a (1 - \cos qa)$$
$$2B_q = (J_1^b e^{i qb} + J_1^b e^{-i qb}) + (J_2^e e^{-i(qa-qb)} + J_2^e e^{i(qa+qb)})$$
$$+ (J_2^i e^{i(qa+qb)} + J_2^i e^{-i(qa+qb)})$$
$$\tilde{h} = g\mu_B\mu_0H - \frac{1}{2}(J_1^b + J_1^b + J_2^i + J_2^i + J_2^i + J_2^i).$$

Due to the corrugated character of the V$^{4+}$ layers, each of these branches will give rise to three additional “replicas”, similarly to what was seen for zig-zag spin chains.
FIG. 4. Left panels: Representative neutron scattering data collected by individual detectors in the course of energy scans on the MACS spectrometer (symbols) and the error bars represent one standard deviation. The solid red line is a result of a global model fit to the entire collected data set, as explained in the text. The shaded peaks are individual contributions of each of the 7 crystallites in the sample. Right panels: reciprocal space trajectories of the corresponding scans.
The relative strength of ferromagnetic interactions is estimated to be no more than 10 % between different data points.

The model was fit to the bulk of experimental data from MACS and IN12 using a Levenberg-Marquardt least squares procedure. Randomly sampling the initial parameter values consistently produced the same final fit result with good convergence. In the best fit we obtain $\chi^2 = 3.05$. Considering the numerous experimental complications and the global nature of the fit, the degree of agreement is very good. The fitted exchange constants with 95% confidence interval are listed in Table I. Once again we note that these values are valid only to within the above-mentioned permutations that leave the dispersion intact.

The magnon dispersion relation computed from the obtained exchange constants is represented by white lines in Fig. 6. Blue lines are contributions of each individual crystallite. In Fig. 4 solid red lines show results of the global fit and shaded areas are again contributions of individual crystallites. Considering the global nature of the fit, the complex measured scans profiles are very well reproduced.

### IV. DISCUSSION AND CONCLUSION

As expected, BaCdVO(PO$_4$)$_2$ is not the simple $J_1 - J_2$ square lattice material that it was initially believed to be. Instead, it has significantly alternating interactions along both $a$ and $b$ directions, and also along the diagonals. Despite that, NN and NNN interactions are all ferromagnetic and antiferromagnetic, respectively. A quantitative correspondence with the square lattice model can be made by computing the ratio of mean values:

$$\frac{\langle J_2 \rangle}{\langle J_1 \rangle} = \frac{J_2^+ + J_2^- + J_2^{+'} + J_2^{-'}}{J_1^+ + J_1^{+'} + J_1^- + J_1^{-'}} = -0.63. \quad (2)$$

The relative strength of ferromagnetic interactions is actually larger than the $J_2/J_1 = -0.9$ estimate from powder studies [9], suggesting the system may be more frus-
FIG. 6. False color intensity plot of magnetic scattering in BaCdVO(PO$_4$)$_2$ shown for several representative slices of energy-momentum space. In all cases the integration range along $h$ or $x$ is $\pm 0.1$ (r. l. u.). The white line is the dispersion relation obtained in a global fit to all collected data, as described in the text. Semi-transparent blue lines are the contributions of individual crystallites. The solid black lines separate data from two different parts of the reciprocal space.

trated than originally thought. It is also considerably larger than in the sister compound Pb$_2$VO(PO$_4$)$_2$ where $\langle J_2 \rangle / \langle J_1 \rangle = -2.74$ [11].

The minimum of the magnon dispersion computed using the exchange constants listed in Table I is located at $q_{\text{min}} = (0, 1/2, 0)$. This exactly corresponds to the propagation vector of the zero-field magnetic structure in BaCdVO(PO$_4$)$_2$, which can thus be seen as a magnon condensate. Correspondingly, the computed critical field of single-magnon instability is $\mu_0H_c = 3.92(3)$ T. This is consistent with the experimentally measured field $\mu_0H_c = 4.08(5)$ T, at which the $q = (0, 1/2, 0)$ structure collapses [10]. We conclude that the previously observed presaturation phase between $\mu_0H_c$ and $\mu_0H_{\text{sat}} \simeq 6.5$ T is an exotic state from beyond the single-magnon BEC paradigm. A spin nematic phase remains a strong candidate. We hope that the newly obtained model Hamiltonian for BaCdVO(PO$_4$)$_2$ will help further refine the calculations such as those in Ref. [15], confirming this expectation.

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[1] N. Shannon, T. Momoi, and P. Sindzingre, Nematic order in square lattice frustrated ferromagnets, Phys. Rev. Lett. 96, 027213 (2006)

[2] R. Shindou and T. Momoi, $SU(2)$ slave-boson formulation of spin nematic states in $S = \frac{1}{2}$ frustrated ferromagnets, Phys. Rev. B 80, 064410 (2009)
A. Smerald, H. T. Ueda, and N. Shannon, Theory of inelastic neutron scattering in a field-induced spin-nematic state, Phys. Rev. B 91, 174402 (2015).

H. T. Ueda and T. Momoi, Nematic phase and phase separation near saturation field in frustrated ferromagnets, Phys. Rev. B 87, 144417 (2013).

H. T. Ueda, Magnetic Phase Diagram Slightly below the Saturation Field in the Stacked $J_1 - J_2$ Model in the Square Lattice with the $J_C$ Interlayer Coupling, J. Phys. Soc. Jpn. 84, 023601 (2015).

R. Nath, A. A. Tsirlin, H. Rosner, and C. Geibel, Magnetic properties of BaCdVO(PO$_4$)$_2$: A strongly frustrated spin-$\frac{1}{2}$ square lattice close to the quantum critical regime, Phys. Rev. B 78, 064422 (2008).

A. A. Tsirlin, B. Schmidt, Y. Skourski, R. Nath, C. Geibel, and H. Rosner, Exploring the spin-$\frac{1}{2}$ frustrated square lattice model with high-field magnetization studies, Phys. Rev. B 80, 132407 (2009).

K. Y. Povarov, V. K. Bhartiya, Z. Yan, and A. Zheludev, Thermodynamics of a frustrated quantum magnet on a square lattice, Phys. Rev. B 99, 024413 (2019).

V. K. Bhartiya, K. Y. Povarov, D. Blosser, S. Better, Z. Yan, S. Gvasaliya, S. Raymond, E. Ressouche, K. Beauvois, J. Xu, F. Yokaichiya, and A. Zheludev, Pre-saturation phase with no dipolar order in a quantum ferro-antiferromagnet, Phys. Rev. Research 1, 033078 (2019).

S. Better, F. Landolt, O. M. Aksoy, Z. Yan, S. Gvasaliya, Y. Qiu, E. Ressouche, K. Beauvois, S. Raymond, A. N. Ponomaryov, S. A. Zyyagin, and A. Zheludev, Magnetic structure and spin waves in the frustrated ferro-antiferromagnet Pb$_2$VO(PO$_4$)$_2$, Phys. Rev. B 99, 184437 (2019).

F. Landolt, S. Better, Z. Yan, S. Gvasaliya, A. Zheludev, S. Mishra, I. Sheikin, S. Krämer, M. Horvatić, A. Gazizulina, and O. Prokhnenko, Presaturation phase in the frustrated ferro-antiferromagnet Pb$_2$VO(PO$_4$)$_2$, Phys. Rev. B 102, 094414 (2020).

S. Meyer, B. Mertens, and H. Müller-Buschbaum, SrZnVO(PO$_4$)$_2$ and BaCdVO(PO$_4$)$_2$: Vanadylphosphates Related to but not Isotypic with the BaZnVO(PO$_4$)$_2$ Type., Z. Naturforsch. 52b, 985 (1997).

M. Skoulatos, F. Rucker, G. J. Nilsen, A. Bertin, E. Pompjakushina, J. Ollivier, A. Schneiderwind, R. Georgii, O. Zaharko, L. Keller, C. Riegg, C. Pfeiferer, B. Schmidt, N. Shannon, A. Kriele, A. Senyshyn, and A. Smerald, Putative spin-nematic phase in BaCdVO(PO$_4$)$_2$, Phys. Rev. B 100, 014405 (2019).

A. Smerald, Magnon binding in BaCdVO(PO$_4$)$_2$ arXiv:2003.12747 (2020).

S. Toth and B. Lake, Linear spin wave theory for single-Q incommensurate magnetic structures, J. Phys.: Condens. Matter 27, 166002 (2015).

M. Popovici, On the resolution of slow-neutron spectrometers. IV. The triple-axis spectrometer resolution function, spatial effects included, Acta Crystallographica Section A 31, 507 (1975).

A. Zheludev, Reslib: Resolution library for 3-axis neutron spectroscopy, https://neutron.ethz.ch/Methods/reslib.html