Antiferromagnetic square lattice in Zn$_2$VO(PO$_4$)$_2$ and its dilution with Ti$^{4+}$

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We report static and dynamic properties of the antiferromagnetic square-lattice compound Zn$_2$(VO)(PO$_4$)$_2$, and the consequences of non-magnetic Ti$^{4+}$ doping at the V$^{4+}$ site. $^{31}$P nuclear magnetic resonance (NMR) spectra and spin-lattice relaxation rate ($1/T_1$) consistently show the formation of the long-range antiferromagnetic order below $T_N \approx 3.75$K. The critical exponent $\beta = 0.33 \pm 0.02$ estimated from the temperature dependence of the sublattice magnetization measured by $^{31}$P NMR at 9.4 MHz is consistent with universality classes of three-dimensional spin models. The isotropic and axial hyperfine couplings between the $^{31}$P nuclei and V$^{4+}$ spins are $A_{31}^{iso} = (9221 \pm 100)$ Oe/$\mu_B$ and $A_{31}^{ax} = (1010 \pm 50)$ Oe/$\mu_B$, respectively. Magnetic susceptibility and heat capacity data are well described by quantum Monte-Carlo simulations for the Heisenberg model on the square lattice with $J \approx 7.7$K. This value of $J$ is consistent with the values obtained from the NMR shift, $1/T_1$, and electron spin resonance (ESR) intensity analysis. Doping Zn$_2$VO(PO$_4$)$_2$ with non-magnetic Ti$^{4+}$ leads to a marginal increase in the $J$ value and the overall dilution of the spin lattice. In contrast to the recent ab initio results, we find neither evidence for the monoclinic structural distortion nor signatures of the magnetic one-dimensionality for doped samples with up to 15% of Ti$^{4+}$. The Néel temperature $T_N$ decreases linearly with increasing the amount of the non-magnetic dopant.

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I. INTRODUCTION

Square lattice of antiferromagnetically coupled Heisenberg spins is the simplest spin model in two dimensions (2D). Its properties are nowadays well established by extensive numerical studies. The case of spin-$\frac{1}{2}$ entails strong quantum effects that reduce the sublattice magnetization and have an impact on the correlation length and spin dynamics. The ideal 2D model lacks long-range order (LRO) above zero temperature, following the Mermin-Wagner theorem. However, any real material features a non-negligible interplane coupling that triggers the LRO at a non-zero temperature $T_N$. When interplane couplings are frustrated and inactive, the LRO is driven by anisotropy terms in the spin Hamiltonian.

Suppression of the LRO in square-lattice-based magnets is possible via two mechanisms, frustration of in-plane couplings or dilution of the spin lattice. The former mechanism is revealed by the model of the $J_1 - J_2$ frustrated square lattice, where the competition between nearest-neighbor couplings $J_1$ and second-neighbor couplings $J_2$ destroys the magnetic order in the vicinity of the quantum critical point at $J_2/J_1 = 0.5$ for spin-$\frac{1}{2}$. This is the well-established theoretically but hitherto never observed experimentally case of the spin-liquid ground state in 2D. The majority of the $J_1 - J_2$ systems, mostly layered V$^{4+}$ phosphates, feature columnar antiferromagnetic (AFM) order induced by $J_2 > J_1$. Materials with $J_2/J_1 < 0.5$ developing Néel AFM order remain low in number and sometimes challenging to investigate.

The second mechanism is the dilution of the spin lattice with non-magnetic impurity atoms. Diluted systems are largely classical even for spin-$\frac{1}{2}$. The LRO vanishes at the classical percolation threshold of $x_c = 0.41$ where $x$ is the doping level. The doping leads to a gradual suppression of the Néel temperature $T_N$ but in many spin-$\frac{1}{2}$ materials the $T_N$ drops much faster than expected, because non-magnetic impurity atoms introduce magnetic frustration that contributes to the suppression of the LRO. On the other hand, Li$_2$VOSiO$_4$, which is a frustrated square-lattice antiferromagnet even without dilution, exhibits a weaker effect on the sublattice magnetization and $T_N$ when diluted with non-magnetic Ti$^{4+}$. Apparently, the dilution of real materials never follows the idealized models and entails a modification of individual exchange couplings.

Here, we address magnetic properties and dilution behavior of the square-lattice antiferromagnet Zn$_2$VO(PO$_4$)$_2$, where spin-$\frac{1}{2}$ V$^{4+}$ ions can be replaced...
FIG. 1. Left panel: crystal structure of $\text{Zn}_2\text{VO(PO}_4\text{)}_2$. Right panel: magnetic layer in the $ab$ plane. Dotted lines show hyperfine couplings between the P atom and the neighboring V$^{4+}$ spins; each P atom is coupled to two magnetic ions with opposite spin directions. The spins are along the $c$ direction.

by the non-magnetic Ti$^{4+}$. The crystal structure of $\text{Zn}_2\text{VO(PO}_4\text{)}_2$ features V$^{4+}$O$_5$ pyramids that are linked into layers via PO$_4$ tetrahedra in the $ab$ plane (Fig. 1). Given the small size of the interlayer Zn$^{2+}$ cations, the interplane V–V distance ($4.52\,\text{Å}$) is shorter than the distance in the $ab$ plane ($6.31\,\text{Å}$). This led earlier studies to conclude that $\text{Zn}_2\text{VO(PO}_4\text{)}_2$ is a quasi-one-dimensional (1D) magnet with $J || J_{\perp}$, where $J$ and $J_{\perp}$ stand for the in-plane and interplane couplings, respectively (Fig. 1). A careful evaluation of thermodynamic data put forward the opposite, quasi-2D scenario with $J > J_{\perp}$. Magnetic order observed below $T_N \approx 3.7\,\text{K}$ is AFM in the $ab$ plane and ferromagnetic (FM) along the $c$ direction. It is consistent with $ab\,\text{initio}$ results by Kanungo et al., who also addressed the diluted, Ti-doped case and proposed that the 25% Ti doping should induce a monoclinic distortion reinstating the 1D physics, but this time in the $ab$ plane and not along the $c$ direction.

In this study, we attempt to verify the prediction concerning the Ti-doped $\text{Zn}_2\text{VO(PO}_4\text{)}_2$ experimentally, and show that within the feasible doping levels, neither the monoclinic distortion nor the 1D physics are observed. Instead, thermodynamics of Ti-doped $\text{Zn}_2\text{VO(PO}_4\text{)}_2$ is largely consistent with expectations for the diluted square lattice of Heisenberg spins. The Néel temperature is systematically suppressed upon the dilution, and the rate of suppression is similar to that in Li$_2$VOSiO$_4$. We provide accurate estimates of the in-plane exchange coupling in order to assess this effect quantitatively, and discuss our results in the light of available experimental data on diluted AFM square lattices. We also report additional characterization for thermodynamic properties, ground state and spin dynamics of the parent $\text{Zn}_2\text{VO(PO}_4\text{)}_2$ compound. These data will serve as a starting point for detailed studies of the doped material.

II. METHODS

Polycrystalline samples of $\text{Zn}_2(\text{V}_{1-x}\text{Ti}_x)\text{O(PO}_4\text{)}_2$ ($x = 0\%$, 5\%, 10\%, and 15\%) were prepared by a conventional solid-state reaction route. In the first step, $\text{Zn}_2\text{P}_2\text{O}_7$ was synthesized using ZnO (Aldrich, 99.999\%) and NH$_4$H$_2$PO$_4$ (Aldrich, 99.999\%) as starting materials. The stoichiometric mixtures were fired at 600°C in air with one intermediate grinding. In the second step, $\text{Zn}_2\text{P}_2\text{O}_7$ was mixed with VO$_2$ (Aldrich, 99.999\%) and TiO$_2$ (Aldrich, 99.999\%) and then the stoichiometric mixtures were fired in flowing Ar-gas atmosphere with several intermediate grindings and palletizations at 850°C.

To check the sample purity, powder x-ray diffraction (XRD, PANalytical powder diffractometer and CuK$_\alpha$ radiation, $\lambda_{ave} = 1.54182\,\text{Å}$) was performed at room temperature. The samples with $x = 0\%$, 5\%, and 10\%, were single-phase, but at higher doping concentrations several impurity phases including TiO$_3$(PO$_4$_3) emerged. Our repeated attempts to achieve higher doping levels by increasing or lowering the firing temperature were unsuccessful. Therefore, we focus on studying the samples with $x \leq 15\%$, where a minor amount of non-magnetic Ti-containing impurities does not hinder the data analysis.

Le Bail fit of the powder XRD data was performed using the FullProf software package based on the tetragonal structure with space group $I4cm$ to determine the lattice parameters. No indications of a symmetry lowering were observed. All the data sets could be fitted using structural data of the parent compound as the initial parameters. The refined lattice parameters and the goodness of fit ($\chi^2$) are listed in Table I. No significant change in lattice constants ($a$ and $c$) and unit cell volume ($V$) was observed with increasing $x$. Given the fact that Ti$^{4+}$ features nearly the same ionic radius (0.51 Å) as V$^{4+}$ (0.53 Å), we do not expect any substantial changes in the cell volume. Thus our experimental observation is consistent with expectations based on the ionic radii.

Magnetic susceptibility $\chi(T)$ and heat capacity $C_p(T)$ measurements were performed using a commercial Physical Property Measurement System (PPMS, Quantum Design). For the $\chi(T)$ measurement, the VSM attachment to the PPMS was used.

Electron spin resonance (ESR) experiments were carried out on a fine-powdered sample with a standard continuous-wave spectrometer between 5 K and 300 K.

| $x$  | $a$ (Å) | $c$ (Å) | $V$ (Å$^3$) | $\chi^2$ (%) |
|------|---------|---------|-------------|--------------|
| 0.00 | 8.9221(2) | 9.0376(2) | 719.44(2) | 1.83 |
| 0.05 | 8.9218(2) | 9.0326(2) | 718.99(2) | 2.11 |
| 0.10 | 8.9243(3) | 9.0287(3) | 719.07(4) | 4.75 |
| 0.15 | 8.9251(3) | 9.0292(3) | 719.24(4) | 5.49 |
We measured the power $P$ absorbed by the sample from a transverse magnetic microwave field ($X$-band, $\nu \approx 9.4$ GHz) as a function of an external, static magnetic field $H$. A lock-in technique was used to improve the signal-to-noise ratio which yields the derivative of the resonance signal $dP/dB$.

The NMR measurements were carried out using pulsed NMR techniques on $^{31}$P (nuclear spin $I = 1/2$ and gyromagnetic ratio $\gamma_N/2\pi = 17.237$ MHz/T) nuclei in the temperature range $1.5 \, \text{K} \leq T \leq 250 \, \text{K}$. We have carried out the NMR measurements at two different radio frequencies of 75.5 MHz and 9.4 MHz that correspond to applied fields of about 4.38 T and 0.545 T, respectively. Spectra were obtained either by Fourier transform of the NMR echo signals or by sweeping the field at a fixed frequency. The NMR shift $K(T) = (H_{\text{ref}} - H(T))/H(T)$ was determined by measuring the resonance field of the sample $[H(T)]$ with respect to nonmagnetic reference $\text{H}_2\text{PO}_4$ (resonance field $H_{\text{ref}}$). The $^{31}$P spin-lattice relaxation rate $1/T_1$ was measured by the conventional single saturation pulse method.

Magnetic susceptibility and specific heat of the pristine and diluted AFM square lattice of Heisenberg spins was obtained from quantum Monte-Carlo (QMC) simulations performed by the $\text{1-loop}$ algorithm$^{12}$ of the $\text{ALPS}$ simulation package$^{12}$ Simulations were performed on $L \times L$ finite lattices with periodic boundary conditions and $L$ up to 80. For the three-dimensional (3D) model of coupled square planes, the $16 \times 16 \times 8$ finite lattice was used. Finite-size effects are negligible in the temperature range considered.

III. PURE Zn$_2$VO(PO$_4$)$_2$

A. Thermodynamic properties

In order to analyze the effect of doping on the exchange couplings, we first consider thermodynamic properties of the parent compound. Our $\chi$ and $C_p$ data are similar to those reported by Kini et al.$^{23}$ Magnetic susceptibility (Fig. 2) shows a broad maximum around 6.9 K corresponding to the short-range order in 2D. The LRO transition manifests itself by a kink at $T_N \simeq 3.75$ K in the susceptibility data measured at 1 T and 2 T. This effect is due to the spin-flop transition that increases the susceptibility below $T_N$.

Specific heat reveals a $\lambda$-type anomaly at $T_N$ (Fig. 3). The hump above $T_N$ is a signature of the broad maximum related to the 2D short-range order. The $C_p(T)$ flattens out around 10 K and increases at higher temperatures because of the growing phonon contribution. Applied magnetic field suppresses the hump and shifts the entropy to the transition anomaly at $T_N$. However, the value of $T_N \simeq 3.75$ K remains unchanged.

Magnetic susceptibility of Zn$_2$VO(PO$_4$)$_2$ is well described by the AFM square-lattice model. The susceptibility simulated by QMC was fitted to the experimental curve using the expression:

$$\chi = \chi^* \left( \frac{N_A k_B g^2}{J} \right),$$

where $\chi^*$ is the reduced susceptibility calculated by QMC, $N_A$ is Avogadro’s number, $k_B$ is Boltzmann constant, and $g$ is the $g$-factor. We fit the data with $J = 7.7$ K and $g = 1.95$ down to 6.5 K (Fig. 2). At lower temperatures, experimental susceptibility lies above the simulated curve. This deviation can be mitigated by decreasing the $J$ value to 7.4 K. However, the description of the high-temperature part is deteriorated, and the $g$-value drops to 1.91, which is below our ESR estimate (Sec. III B) and below the typical range of

![Figure 2](image1.png)

![Figure 3](image2.png)
powder-averaged $\bar{g} = 1.94 - 1.98$ reported for V$^{4+}$ oxide compounds. A Curie-like impurity contribution also improves the fit in the low-temperature region, but introduces discrepancies at higher temperatures. Moreover, the low-field data measured at 0.5 T do not show any signatures of a Curie-like upturn down to 2 K (Fig. 2).

Specific heat above $T_N$ is also consistent with the predictions of the square-lattice model. For a proper comparison magnetic ($C_{\text{mag}}$) and phon ($C_{\text{phon}}$) contributions to the specific heat should be separated. Unfortunately, a non-magnetic reference compound for our case is not available, because not more than 15% of Ti$^{4+}$ can be doped into Zn$_2$TiO(PO$_4$)$_2$, and the hypothetic end member Zn$_2$VO(PO$_4$)$_2$ does not exist. Kini et al. approximated $C_{\text{phon}}$ with a series of Debye functions and demonstrated that $C_{\text{phon}} < C_{\text{mag}}$ below 10 K. By using the data from Ref. 28, we verified that in this temperature range of our interest $C_{\text{phon}}$ follows the $T^3$ behavior. Therefore, we fitted our data as:

$$C_p^{\text{exp}} = C_p^{\text{QMC}} R + \beta T^3,$$

where $R$ is the gas constant, and $\beta$ is treated as an adjustable parameter, because in doped samples it may change following the change in the atomic masses and the formation of defects having influence on phonons. This way, we compare specific heat of Zn$_2$VO(PO$_4$)$_2$ to the QMC result and find best agreement for $J = 7.8$ K (Fig. 3) that is nearly equal to $J = 7.7$ K from the susceptibility fit.

For the sake of completeness, let us discuss possible deviations from the idealized square-lattice model. The ratio $T_N/J \approx 0.51$ implies $|J_\perp|/J \approx 0.1$ [10]. This weak $J_\perp$ has no visible effect on the magnetic susceptibility above 5 K, as verified by a direct QMC simulation for the 3D model (Fig. 2).

The square lattice in Zn$_2$VO(PO$_4$)$_2$ can be weakly frustrated by the second-neighbor coupling $J_2$. Frustrated spin models are not amenable to QMC simulations because of the notorious sign problem. Therefore, we resort to the high-temperature series expansion (HTSE) of the frustrated square lattice model [24] for the magnetic susceptibility that is generally valid at temperatures exceeding individual magnetic couplings $J_i$. The data above 10 K yield $J \approx 7.8$ K, $J_2 \approx 0.3$ K, and $g \approx 1.96$ in excellent agreement with Ref. 28. Therefore, the frustration of the square lattice in Zn$_2$VO(PO$_4$)$_2$ is extremely weak, $J_2/J \approx 0.04$ to be compared with the $ab$ initio result $J_2/J = (t_2/t_1)^2 \approx 0.03$ from Ref. 30. We do not expect that this weak frustration affects thermodynamic properties.

The remaining source of the marginal discrepancy between the square-lattice model and the experimental magnetic susceptibility is the magnetic anisotropy. However, we do not find any strong signatures of the anisotropy in the NMR data reported below.

FIG. 4. (Color online) Temperature dependent ESR intensity, $I_{\text{ESR}}(T)$, obtained by double integration of the ESR spectra of powdered Zn$_2$VO(PO$_4$)$_2$ sample; solid line represents the fit described in the text. Upper right inset shows a typical spectrum (symbols) together with a Lorentzian shape bottom left inset shows the relation between $I_{\text{ESR}}$ and $\chi(\parallel)$, where $\chi(\parallel)$ is the gas constant, and $\beta$ is treated as an adjustable parameter (2) powder-averaged $\bar{g} = 1.94 - 1.98$ reported for V$^{4+}$ oxide compounds. A Curie-like impurity contribution also improves the fit in the low-temperature region, but introduces discrepancies at higher temperatures. Moreover, the low-field data measured at 0.5 T do not show any signatures of a Curie-like upturn down to 2 K (Fig. 2).

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B. ESR

Results of the ESR experiment are presented in Fig. 4. In the right inset of Fig. 4 a typical ESR spectrum at room temperature is shown. The shape of the spectra can be well described by a powder-averaged Lorentzian line for the case of an easy-axis anisotropy of the $g$-tensor, as shown by the solid line, yielding the parallel $g_{\parallel} = 1.94(6)$ and perpendicular $g_{\perp} = 1.98(7)$ components at $T = 295$ K. The isotropic $g = \sqrt{(g_{\parallel}^2 + 2g_{\perp}^2)/3}$ was calculated to be $\sim 1.97$. Regardless of $g_{\parallel} = g_{\perp}$ (as expected for an easy-axis anisotropy), these V$^{4+} g$-factors are similar to those reported for Pb$_2$VO(PO$_4$)$_2$ (Ref. 33) or SrZnVO(PO$_4$)$_2$ (Ref. 30).

The integrated ESR intensity $I_{\text{ESR}}(T)$ increases with decreasing temperature and then exhibits a broad maximum at about 7 K as observed in $\chi(T)$ (Fig. 2) and $K(T)$ (Fig. 6). Below $T_N$, it decreases rapidly towards zero. $I_{\text{ESR}}(T)$, as obtained by integrating the whole spectrum, linearly depends on the uniform static susceptibility $\chi(T)$ of the V$^{4+}$ spins probed by ESR. Hence, one can get an estimate of the exchange couplings by fitting $I_{\text{ESR}}(T)$ data to the HTSE of the square lattice model. We fitted the data above 8 K to $I_{\text{ESR}}(T) = A + B \chi_{\text{spin}}$, where $A$ and $B$ are arbitrary constants and $\chi_{\text{spin}}$ is the expression for HTSE (valid over $k_B T > 0.1$) of $\chi(T)$ for the 2D $S = 1/2$ HAF square lattice given by Rushbrooke and
Wood\textsuperscript{22} which can be written as

\[
\chi_{\text{spin}}(T) = \frac{N\mu_B^2 g^2}{J} \times \left[ (4x + 4 + 2.00025x^{-1} + 0.66656x^{-2} + 0.06286x^{-3} - 0.06043x^{-4} + 0.000237x^{-5})^{-1}, \right.
\]

where \( x = \frac{k_BT}{J} \). By fitting the data in the high-\( T \) regime \((T > 8 \text{ K})\), the exchange coupling was estimated to be \( J = (8.7 \pm 0.2) \text{ K} \) which agrees with the values estimated from \( \chi \) and NMR shift (discussed later) analysis. In an attempt to see how \( I_{\text{ESR}} \) scales with \( \chi \), we plotted \( I_{\text{ESR}} \) vs. \( \chi \) with temperature as an implicit parameter (see bottom left inset of Fig. 1). A nearly linear behavior down to 9 K reflects that \( I_{\text{ESR}}(T) \) tracks \( \chi(T) \) of the \( V^{4+} \) spins very well.

The influence of critical spin fluctuations on the temperature dependencies of linewidth and resonance field become noticeable below 30 K. However, we refrained from using these temperature dependencies to obtain information on the critical spin dynamics for which an accurate determination of the parallel and perpendicular line components is needed. For this purpose, our powder spectra are too broad compared to the difference between \( g_\parallel \) and \( g_z \). Investigations of single crystals would certainly provide the required accuracy as the ESR results on \( \text{Pb}_2\text{VO}(\text{PO}_4)_2 \) have shown in Ref. \textsuperscript{23}.

C. \( ^{31}\text{P} \) NMR Shift

According to Ref. \textsuperscript{20}, the structure of \( \text{Zn}_2\text{VO}(\text{PO}_4)_2 \) features one \( \text{P} \) site. We observed a narrow spectral line above \( T_N \) as is expected for an \( I = 1/2 \) nucleus.\textsuperscript{25} Figure 3 shows the \( ^{31}\text{P} \) NMR spectra measured at different temperatures. The line shape was found to be asymmetric because of the anisotropy in \( \chi \) (T) and/or in the hyperfine coupling constant between the \( \text{P} \) nucleus and the \( V^{4+} \) spins.

The line position was found to shift with temperature. Temperature dependence of the NMR shift \( K \) extracted by fitting the spectra (see inset of Fig. 3) are presented in Fig. 6(a), which shows a strong anisotropy along different directions. At high temperatures, both isotropic \( (K_{\text{iso}}) \) and axial \( (K_{\text{ax}}) \) parts of the NMR shift vary in a Curie-Weiss manner and then pass through a broad maximum at around 9 K reflecting the 2D short-range order, similar to the \( \chi(T) \) data (Fig. 2).

The NMR shift \( K(T) \) is related to the spin susceptibility \( \chi_{\text{spin}}(T) \) by the relation

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

where \( K_0 \) is the temperature-independent chemical shift, and \( A_{\text{hf}} \) is the hyperfine coupling constant between the \( \text{P} \) nuclei and the \( V^{4+} \) electronic spins. The \( K \) vs. \( \chi \) plot with \( T \) as an implicit parameter is fitted very well by a straight line [Fig. 6(b)] over the whole temperature range \((T > T_N)\) yielding the isotropic and axial parts of the hyperfine coupling \( A_{\text{hf}}^{\text{iso}} = (9221 \pm 100) \text{ Oe}/\mu_B \) and \( A_{\text{hf}}^{\text{ax}} = (1010 \pm 50) \text{ Oe}/\mu_B \), respectively. Since the NMR shift is a direct measure of \( \chi_{\text{spin}} \) and is free from extrinsic impurities, it serves as an independent test for the bulk susceptibility \( \chi(T) \). We fitted the temperature dependence of \( K_{\text{iso}} \) above 6 K by Eq. (4), where the expression for \( \chi_{\text{spin}} \) is given in Eq. (3). During the fitting process, \( A_{\text{hf}}^{\text{iso}} \) and \( g \) were fixed to the values \( g \approx 1.97 \) and \( A_{\text{hf}}^{\text{iso}} \approx 9221 \text{ Oe}/\mu_B \), obtained from the ESR experiments and \( K_{\text{iso}} \) vs. \( \chi \) analysis, respectively. In this way, we obtained \( K_0 = (0.025 \pm 0.001) \% \) and \( J/k_B = (8.4 \pm 0.3) \text{ K} \). The fit is shown in Fig. 6(a) as a solid line. The resulting \( J \) value is close to the values estimated from the \( \chi(T) \) analysis\textsuperscript{23} and neutron diffraction experiments\textsuperscript{29}.

D. NMR spectra below \( T_N \)

Below \( T_N \), the \( ^{31}\text{P} \) spectra measured at 75.5 MHz were found to broaden abruptly. In order to precisely probe the intrinsic line shape, we remeasured the \( ^{31}\text{P} \) spectra at a lower frequency of 9.4 MHz. As shown in Fig. 7, the \( ^{31}\text{P} \) line above \( T_N \) remains narrow and immediately below \( T_N \) it starts broadening indicating that the \( \text{P} \) site
is experiencing the static internal field in the ordered state through the hyperfine field between the P nuclei and the ordered V$^{4+}$ moments. With decrease in temperature, the spectrum takes a nearly rectangular shape but the central peak still persists down to the lowest measured temperature. As discussed later, this central peak is found to be intrinsic to the sample.

The internal field $H_{\text{int}}$, which is proportional to the V$^{4+}$ sublattice magnetization, was determined from the fit of the experimental spectra following the procedure adopted recently for BiMn$_2$PO$_6$ (Ref. 39). The temperature dependence of $H_{\text{int}}$ is plotted in Fig. 8. In order to extract the critical exponent ($\beta$) of the order parameter (sublattice magnetization), $H_{\text{int}}(T)$ was fitted by the power law:

$$H_{\text{int}}(T) = H_0 \left(1 - \frac{T}{T_N}\right)^\beta.$$  (5)

One can notice that $H_{\text{int}}$ decreases sharply on approaching $T_N$. We have estimated $\beta$ by fitting the data points as close as possible to $T_N$ (i.e., in the critical region) as shown in Fig. 8. The maximum value of $\beta = 0.33 \pm 0.02$ with $T_N \approx 3.9(1)$ K was obtained by fitting the data points in the $T$-range 3.7 K to 3.95 K close to $T_N$. By increasing the number of fitting points toward low-$T$s, the $\beta$ value was found to decrease. At low-$T$s, $H_{\text{int}}$ develops the tendency of saturation and it saturates faster than expected from the mean-field theory [see the deviation of fits in Fig. 8 at low-$T$s].
The solid and dashed lines represent $T_1^N$ and $T_2^N$ behaviors, respectively. (b) $1/(\chi T)$ is plotted as a function of $T$.

### E. Nuclear spin-lattice relaxation rate $1/T_1$

The $^{31}$P nuclear spin-lattice relaxation rate $1/T_1$ above $T_N$ was measured at the field corresponding to the central peak position. For $T \leq T_N$, the measurements were performed at both the central peak position as well as at the right-hand side (RHS) edge position (see Fig. 7). For an $I = 1/2$ nucleus, the recovery of the longitudinal magnetization is expected to follow a single-exponential behavior. In Zn$_2$VO(PO$_4$)$_2$, the recovery of the longitudinal nuclear magnetization was indeed fitted well by the exponential function $1 - \frac{M(t)}{M_0} = A e^{-t/T_1}$, where $M(t)$ is the nuclear magnetization at a time $t$ after the saturation pulse and $M_0$ is the equilibrium magnetization. The temperature dependence of $1/T_1$ extracted from the fit is presented in Fig. 9(a).

The $1/T_1$ data measured at two different frequencies (75.5 MHz and 9.4 MHz) almost resemble each other at low temperatures. At high temperatures ($T \gtrsim 10$ K), $1/T_1$ is temperature-independent. In the high temperature limit $T \gg J/k_B$, a temperature-independent $1/T_1$ behavior is typical due to random fluctuation of paramagnetic moments. With decrease in temperature, $1/T_1$ decreases slowly for $T < 10$ K and then shows a weak anomaly around $T_N \approx 3.8$ K. This decrease is very similar to that observed previously in the cases of the antiferromagnetic square lattices Pb$_2$VO(PO$_4$)$_2$ (Ref. 10), SrZnVO(PO$_4$)$_2$ (Ref. 42), VOMoO$_3$ (Ref. 13), and [Cu(HCO$_2$)$_2$.4D$_2$O]$_2$, where the decrease of $1/T_1$ above $T_N$ is explained by cancellation of the antiferromagnetic spin fluctuations at the probed nuclei.

Below the peak, $1/T_1$ again decreases smoothly towards zero. As shown in Fig. 9(a) no difference in $1/T_1$ below $T_N$ was observed between the data measured at the central peak and RHS edge positions at 9.4 MHz.

### IV. Ti-DOPED Zn$_2$VO(PO$_4$)$_2$

As mentioned in Sec. II, all Ti-doped samples revealed tetragonal symmetry, similar to the parent compound. The sample with $x = 0.15$ contained trace amounts of impurity phases, so its doping level may be slightly below 15%, but this minor deviation had no visible effect on the results.

Magnetic susceptibility of doped samples normalized to one mole of V$^{4+}$ spins is shown in Fig. 10. The susceptibility maximum is systematically shifted to higher values of $\chi$ and to lower temperatures. For the sake of better presentation, we use a different scaling for the specific heat and normalize the data to one mole of the compound. Fig. 11 presents the systematic reduction in the specific heat maximum around 4.5 K following the reduced amount of the magnetic V$^{4+}$ ions. The position of the maximum is roughly unchanged up to $x = 0.15$.

Magnetic order persists in all Ti-doped samples. The magnetic transition is seen by a change in the slope of $\chi(T)$ (Fig. 10). The precise value of $T_N$ is better tracked by the $\lambda$-type anomaly in the specific heat (Fig. 11). The Néel temperature determined with the 0.05 K uncertainty from the maximum of the transition anomaly, displays a systematic reduction from 3.75 K in the parent compound to 2.9 K at $x = 0.15$. This corresponds to the slope of $-dT_N(x)/dx = CT_N(0)$ with $C = 1.5(2)$, which is reminiscent of $C \approx 2$ in Li$_2$VOSiO$_4$ and well below $C \approx 2.7$ or $C \approx 3.5$ for La$_2$CuO$_4$ doped with Mg and Zn, respectively.

![Fig. 9](image-url)

![Fig. 10](image-url)

FIG. 9. (Color online) (a) Spin-lattice relaxation rate $1/T_1$ vs. temperature $T$ measured at 75.5 and 9.4 MHz. Two data sets at 9.4 MHz correspond to the measurements at both the central peak and RHS edge positions below $T_N$ [see Fig. 7]. The solid and dashed lines represent $T_1^N$ and $T_2^N$ behaviors, respectively. (b) $1/(\chi T)$ is plotted as a function of $T$.
TABLE II. Parameters obtained from fitting the susceptibility and specific heat data for \( \text{Zn}_2\text{V}_{1-x}\text{Ti}_x\text{O(PO}_4)_2 \) with QMC results for the ideal \( (x = 0) \) and diluted \( (x > 0) \) square-lattice models. \( g \) stands for the \( g \)-factor, \( \chi_0 \) is the temperature-independent contribution to the susceptibility (in \( 10^{-5} \text{ emu/mol} \)), and \( J \) is the exchange coupling (in K).

| \( x \) | Susceptibility | Specific heat |
|-------|----------------|---------------|
| \( g \) | \( \chi_0 \) | \( J \) | \( \tilde{J} \) |
| 0.00  | 1.95           | -5            | 7.7 | 7.8 |
| 0.05  | 1.95           | -6            | 7.7 | 7.8 |
| 0.10  | 1.97           | -4            | 7.8 | 7.9 |
| 0.15  | 1.97           | -6            | 8.1 | 8.0 |

FIG. 11. (Color online) Specific heat of Ti-doped \( \text{Zn}_2\text{VO(PO}_4)_2 \) measured in zero magnetic field. The dashed lines are QMC fits, and the arrows mark Néel temperatures \( T_N \) depicted in the inset as a function of the doping level \( x \). The solid line in the inset is the tentative linear fit \( T_N = (1 - Cx)T_N(0) \) with \( C = 1.5 \).

Néel temperature of an antiferromagnet depends on its exchange couplings. Therefore, for a proper interpretation of \( T_N(x) \) and its slope, one has to evaluate the change in \( J \) upon doping. To this end, we fitted magnetic susceptibility and specific heat of Ti-doped samples in the same manner as we did in Sec. III A for the parent compound. Model curves were obtained by QMC simulations for the diluted square lattice of spins-\( \frac{1}{2} \). Fitted parameters are listed in Table II and show a good match between the susceptibility and specific heat data. The error bar for the values of \( J \) is somewhat difficult to define, because statistical errors largely depend on the temperature range of the fitting. However, even with a very optimistic error bar of 0.1 K for the susceptibility fits above 7 K, the change in \( J \) between \( x = 0 \) and \( x = 0.15 \) is only marginal. Moreover, \( T_N \) depends on \( \ln J \) so the 4% change in the \( J \) value should have negligible effect on the \( T_N \). Its reduction is, therefore, solely due to the dilution, and the slope of \( T_N(x) \) reflects the dilution effect on the spin-\( \frac{1}{2} \) AFM square lattice in \( \text{Zn}_2\text{VO(PO}_4)_2 \).

V. DISCUSSION

A. Static Properties

The exchange couplings extracted from \( \chi(T) \), \( I_{\text{ESR}}(T) \), and \( K_{\text{iso}}(T) \) data for \( \text{Zn}_2\text{VO(PO}_4)_2 \) are consistent with the values reported before from the \( \chi(T) \) analysis and neutron scattering experiments within the error bar. According to the \( J_2/J \approx 0.03 \) ratio, \( \text{Zn}_2\text{VO(PO}_4)_2 \) features the Néel antiferromagnetic ground state with antiparallel spins on nearest neighbors in the \( ab \) plane (Fig. 1 right). In the crystal structure, squares are formed via V−O−P−O−V superexchange interaction paths. In contrast to \( \text{Pb}_2\text{VO(PO}_4)_2 \) where each P atom is coupled to four \( V^{4+} \) spins in \( \text{Zn}_2\text{VO(PO}_4)_2 \) each P atom is coupled to two \( V^{4+} \) spins only (Fig. 1 right).

The total hyperfine coupling constant at the P site is the sum of transferred hyperfine (\( A_{\text{trans}} \)) and dipolar (\( A_{\text{dip}} \)) couplings produced by \( V^{4+} \) spins, i.e., \( A_{\text{hf}} = z A_{\text{trans}} + A_{\text{dip}} \), where \( z = 2 \) is the number of nearest-neighbor \( V^{4+} \) spins of the P site. The anisotropic dipolar couplings were calculated using lattice sums to be \( A_a = 210 \text{ Oe/}\mu_B \), \( A_b = 210 \text{ Oe/}\mu_B \), and \( A_c = -420 \text{ Oe/}\mu_B \) along the \( a-, b-, \) and \( c- \) directions, respectively. Clearly, the value of dipolar coupling is almost negligible compared to the total hyperfine coupling \( [A_{\text{hf}}] = (9221 \pm 100) \text{ Oe/}\mu_B \) suggesting that the dominant contribution to the total hyperfine coupling is due to the transferred hyperfine coupling at the P site. The magnitude of this coupling depends on the relative orientation and the extent of overlap between the V(3d\( \ell \)), P(2p), and O(2s) orbitals.

As shown in Fig. 7 the P line in the magnetically ordered state takes a typical rectangular shape, reflecting that the magnetic ordering is commensurate in nature. If the magnetic structure were incommensurate with the lattice, the internal field would be distributed and the spectrum would not exhibit the rectangular shape seen in Fig. 7. Our spectra are, therefore, consistent with the collinear magnetic order determined from the neutron diffraction experiments.

The central line does not disappear from the experimental spectra completely even at the lowest measured temperature. NMR experiments on many other compounds, especially on powder samples, are reported to show similar coexistence of the high-\( T \) and low-\( T \) phases, e.g., in \( \text{BaCuP}_2\text{O}_7 \) (Ref. 38), (Li,Na)\text{VGe}_2\text{O}_6 (Refs. 40, 44) and 15, (\text{Ca}_3\text{Al}_2\text{O}_6)\text{Fe}_2(\text{As}_{1-x}\text{P}_x)_2 \) (Ref. 10), and \( \text{BiMn}_2\text{PO}_4 \) (Ref. 39). One could argue that the coexistence of two phases is due to a spread of the transition temperatures within the polycrystalline sample, but in such a case it is quite unlikely to observe a distinct peak in the temperature dependence of 1/\( T_1 \), as seen in Fig. 9. One possible origin of the central line is the impurity phases. In order to check that, we measured 1/\( T_1 \) below \( T_N \) at the positions corresponding to the central peak and the RHS edge of the spectra. The magnitude and the temperature dependence of 1/\( T_1 \) at both positions are the same, which clearly suggests that the central peak is
an intrinsic feature of the sample and completely rules out the contribution of impurity phases. Another possible origin of the central line could be the presence of crystal defects or local dislocations in the polycrystalline sample.

The temperature dependence of $H_{\text{int}}$ in the critical region provides the critical exponent $\beta$ reflecting the universality class of the spin system. The $\beta$ values expected for different spin- and lattice-dimensionalities are listed in Table II of Ref. [16]. The value of $\beta$ obtained from the experiment is $\approx 0.33$, which would be consistent with any of the 3D spin models (Heisenberg, Ising, or XY). Given the fact that below $T_N$ spins are aligned with the $c$ direction, we may expect a weak Ising anisotropy, but it is impossible to quantify this putative anisotropy using the data at hand. Interestingly, the critical behavior of Zn$_2$VO(PO$_4$)$_2$ deviates from that of other square-lattice $V^{4+}$ antiferromagnets, where $\beta \approx 0.25$ (2D XY universality class) was systematically observed in Li$_2$VOSiO$_4$ and Li$_2$VOGeO$_4$ (Refs. 23 and 47), Pb$_2$VO(PO$_4$)$_2$ (Refs. 16, 35, and 48), SrZnVO(PO$_4$)$_2$ (Refs. 36 and 49), and other compounds. The origin of this difference should be addressed in future studies.

B. Dynamic Properties

As shown in Fig. 9(b), $1/(\chi T_1 T)$ above $\approx 10$ K is $T$-independent and increases slowly below 10 K where the system begins to show antiferromagnetic short-range order. The general expression for $1/T_1 T$ in terms of the dynamic susceptibility $\chi_M(\vec{q}, \omega_0)$ is

$$\frac{1}{T_1 T} = \frac{2\gamma^2_k B}{N_A} \sum_{\vec{q}} |A(\vec{q})|^2 \frac{\chi_M''(\vec{q}, \omega_0)}{\omega_0},$$

where the sum is over wave vectors $\vec{q}$ within the first Brillouin zone, $A(\vec{q})$ is the form factor of the hyperfine interactions as a function of $\vec{q}$, and $\chi''_M(\vec{q}, \omega_0)$ is the imaginary part of the dynamic susceptibility at the nuclear Larmor frequency $\omega_0$. For $q = 0$ and $\omega_0 = 0$, the real component of $\chi_M(\vec{q}, \omega_0)$ corresponds to the uniform static susceptibility $\chi$. Thus the temperature-independent $1/(\chi T_1 T)$ above 10 K in Fig. 9(b) demonstrates the dominant contribution of $\chi$ to $1/T_1 T$. On the other hand, a slight increase of $1/(\chi T_1 T)$ below 10 K indicates the growth of antiferromagnetic correlations with decreasing $T$.

The symmetric location of phosphorochromes between the two $V^{4+}$ spins implies that Néel type AFM spin fluctuations $[\vec{q} = (\pm \pi/a, \pm \pi/b)]$ from neighboring spins should be largely filtered out $(|A(\vec{q})|^2 = 0)$ because the P nuclei interact with $V^{4+}$ spins having opposite directions (Fig. 1 right). When the coupling to the two $V^{4+}$ spins is equivalent, the AFM fluctuations do not contribute to $1/(\chi T_1 T)$. The residual enhancement of $1/(\chi T_1 T)$ below 10 K reflects the asymmetry of the hyperfine couplings. This asymmetry is consistent with the crystal structure of Zn$_2$VO(PO$_4$)$_2$, where the P atoms are located on mirror planes running perpendicular to the $(a + b)$ or $(a - b)$ crystallographic directions. The tensor of hyperfine couplings may change its orientation upon the reflection in the mirror plane, thus leading to non-equivalent interactions between P and the up- and down-spins on the neighboring $V^{4+}$ ions.

In the AFM ordered state, $1/T_1$ is mainly driven by scattering of magnons, leading to a power-law temperature dependence. For $T \gg \Delta/k_B$, where $\Delta/k_B$ is the gap in the spin-wave spectrum, $1/T_1$ either follows a $T^\beta$ behavior due to a two-magnon Raman process or a $T^5$ behavior due to a three-magnon process, while for $T \ll \Delta/k_B$, it follows an activated behavior $1/T_1 \propto T^2 \exp(-\Delta/k_B T)$. As shown from Fig. 9(a), our $^{31}P$ $1/T_1$ data in the lowest temperature regime (1.5 K $\leq T \leq 3.25$ K) follow the $T^5$ behavior rather than the $T^3$ behavior suggesting that the relaxation is mainly governed by the three-magnon process. The lack of activated behavior down to 15 K indicates that the upper limit of $\Delta/k_B$ is 1.5 K.

At sufficiently high temperatures, $1/T_1$ due to local moments is $T$-independent and can be expressed within the Gaussian approximation of the auto-correlation function of the electronic spin as

$$\left( \frac{1}{T_1} \right)_{T \to \infty} = \frac{(\gamma_N g \mu_B)^2 \sqrt{2\pi z'} S(S + 1)}{3 \omega_{ex}} \left( \frac{A_{hf}}{z'} \right)^2,$$

where $\omega_{ex} = (|J_{\text{max}}|k_B/h) \sqrt{2zS(S + 1)/3}$ is the Heisenberg exchange frequency, $z$ is the number of nearest-neighbor spins of each $V^{4+}$ ion, and $z'$ is the number of nearest-neighbor $V^{4+}$ spins for a given P site. The $z'$ in the numerator takes into account the number of nearest-neighbor $V^{4+}$ spins responsible for producing fluctuations at the P site. Using the relevant parameters, $A_{hf} \approx 9221$ Oe/$\mu_B$, $\gamma_N = 1.08 \times 10^8$ rad s$^{-1}$ T$^{-1}$, $z = 4$, $z' = 2$, $g = 2$, $S = \frac{1}{2}$, and the high-temperature (150 K) relaxation rate of $\left( \frac{1}{T_1} \right)_{T \to \infty}$ is $\approx 7270.6$ s$^{-1}$ for the P site in Eq. (7), the magnitude of the exchange coupling is calculated to be $J \approx 9$ K in good agreement with $J \approx 7.7$ K determined from the thermodynamic data (Sec. III.A).

One can see in Fig. 9(a) that for $T > 10$ K a slight increase in $1/T_1$ was observed at 9.4 MHz compared to the data measured at 75.5 MHz. In order to check whether this difference is due to the effect of spin diffusion, we measured $1/T_1$ at different applied fields at $T = 15$ K. Long-wavelength ($q \sim 0$) spin fluctuations in a Heisenberg magnet show diffusive dynamics. In 1D compounds, such spin diffusion results in a $1/\sqrt{T}$ magnetic field dependence of $1/T_1$, which has been observed in $(\text{CH}_3)_4\text{NMnCl}_3$, CuCl$_2$ 2NC$_2$H$_5$ and Sr$_2$CuO$_2$. On the other hand, in 2D materials $1/T_1$ varies as $\log(1/H)$. In Fig. 12, $1/T_1$ is plotted against $-\log H$. A weak field dependence is observed. It can be fitted by the form $1/T_1 = a + \log(1/H)$ where $a$ is a constant. The linearity
of the $1/T_1$ vs. $\log(1/H)$ dependence supports the 2D nature of the compound.

C. Effect of doping

At first glance, $\text{Zn}_2\text{VO}(\text{PO}_4)_2$ reveals an ideal case of the dilution of a spin-$\frac{1}{2}$ AFM square lattice. We have shown that the change in the nearest-neighbor coupling $J$ is marginal (Table I), and the frustration by second-neighbor couplings $J_2$ is negligible in the parent compound. Therefore, it is surprising that the Néel temperature of $\text{Zn}_2\text{VO}(\text{PO}_4)_2$ drops much slower than expected for the diluted AFM square lattice of spins-$\frac{1}{2}$. In a diluted system, the $T_N$ can be written as follows:

$$k_B T_N(x) = J_1(1-x)^2 \xi(x,T_N)^2 \left( \frac{M(x)}{M(0)} \right)^2,$$  \hspace{1cm} (8)

where $J_1(1-x)^2$ reflects the reduction in the interlayer coupling (the probability to find two coupled spins in the adjacent layers), $\xi(x,T_N)$ is the in-plane correlation length, and $M(x)$ is the staggered magnetization at a given value of $x$. All these factors taken together should yield the slope $C \approx 3.2$ (Ref. 38) for the linear dependence of $T_N(x)$ and spin-$\frac{1}{2}$. Experimentally, Carretta et al.\textsuperscript{(22)} report $C \approx 2.7$ and 3.5 for Mg- and Zn-doped $\text{La}_2\text{CuO}_4$, respectively.\textsuperscript{(59)} This finding can be rationalized by assuming that Zn atoms introduce additional frustration, whereas Mg atoms do not.\textsuperscript{(23,24)}

In Ti-doped $\text{Li}_2\text{VOSiO}_4$, the slope of $T_N(x)$ is $C \approx 2$, only. Papinutto et al.\textsuperscript{(25)} proposed that this slope is solely due to the first term $J_1(1-x)^2$, while $M(x)$ is only weakly influenced by doping because the effect of dilution is counteracted by the change in the frustration ratio. This explanation looks plausible for $\text{Li}_2\text{VOSiO}_4$ indeed, because the physics of this compound is determined by the competing nearest-neighbor and second-neighbor couplings on the square lattice.\textsuperscript{(23,24)} Ti-doped $\text{Zn}_2\text{VO}(\text{PO}_4)_2$ reveals an even lower $C \approx 1.5$, and in this compound frustration is clearly inactive. We have shown that it is vanishingly small ($J_2/J \approx 0.03$) in the pristine $\text{Zn}_2\text{VO}(\text{PO}_4)_2$, while its increase (if any) will have an opposite effect on the system and increase $C$ above 3.2 instead of decreasing it to the experimental $C \approx 1.5$ value.

This raises an interesting question to what extent the $T_N(x)$ dependence is influenced by the physics of the diluted Heisenberg square lattice, and whether anisotropy could play a more significant role. Magnetic order in quasi-2D magnets is often stabilized by anisotropy terms.\textsuperscript{(11)} While this may not be the case in the undoped $\text{Zn}_2\text{VO}(\text{PO}_4)_2$ with its well-defined and seemingly non-frustrated FM order along the $c$-direction\textsuperscript{(26)} the presence of magnetic anisotropy may influence the $T_N$ values in doped samples. We note in passing that the crystal structure of $\text{Zn}_2\text{VO}(\text{PO}_4)_2$ is non-centrosymmetric, so that anisotropic magnetic interactions are allowed. Our NMR data provide the upper estimate of the anisotropy gap $\Delta \lesssim 1.5$K, which is, however, about 15% of $J$ and exceeds the typical values of the Dzyaloshinsky-Moriya (DM) anisotropy in $\text{V}^{4+}$ compounds.	extsuperscript{(60,61)} A further study of the anisotropy effects on single crystals of $\text{Zn}_2\text{VO}(\text{PO}_4)_2$ will be certainly insightful. It is also interesting to evaluate $M(x)$ for Ti-doped samples, and our extensive NMR study of the parent compound provides solid basis for this work.

VI. SUMMARY AND CONCLUSIONS

$\text{Zn}_2\text{VO}(\text{PO}_4)_2$ is a quasi-2D AFM square-lattice compound with $J \approx 7.7$K, negligible in-plane frustration, and long-range magnetic order below $T_N \approx 3.75$K. Thermodynamic properties are well described by the Heisenberg model on the AFM square lattice. However, we detect subtle deviations in the low-temperature magnetic susceptibility. NMR results confirm the commensurate nature of the magnetic order. The spin-lattice relaxation rate $1/T_1$ below $T_K$ follows the $T^5$ behaviour reflecting that the relaxation is governed by the three-magnon process. $1/T_1$ at 15 K varies as $\log(1/H)$ and supports the 2D nature of the compound. The critical exponent for the sublattice magnetization is consistent with any of the 3D universality classes. $\text{Ti}^{4+}$ doping with up to 15% of $\text{Ti}^{4+}$ leads to a uniform dilution of the spin lattice and only a marginal change in the in-plane exchange coupling. $T_N$ goes down in a linear manner, but its slope is well below theoretical expectations for the diluted Heisenberg antiferromagnet on the square lattice of spins-$\frac{1}{2}$.
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ibid. 78, 024418 (2008).

39. R. Nath, K. M. Ranjith, B. Roy, D. C. Johnston, Y. Furukawa, and A. A. Tsirlin, Phys. Rev. B 90, 024431 (2014).

40. P. Vonlanthen, K. B. Tanaka, A. Goto, W. G. Clark, P. Millet, J. Y. Henry, J. L. Gavilano, H. R. Ott, F. Mila, C. Berthier, M. Horvatic, Y. Tokunaga, P. Kuhns, A. P. Reyes, and W. G. Moulton, Phys. Rev. B 65, 214413 (2002).

41. T. Moriya, Prog. Theor. Phys. 16, 23 (1956).

42. L. Bossoni, P. Carretta, R. Nath, M. Moscardini, M. Baenitz, and C. Geibel, Phys. Rev. B 83, 014412 (2011).

43. P. Carretta, N. Papinutto, C. B. Azzoni, M. C. Mozzati, E. Pavarini, S. Gonthier, and P. Millet, Phys. Rev. B 66, 094420 (2002).

44. J. L. Gavilano, S. Mushkolaj, H. R. Ott, P. Millet, and F. Mila, Phys. Rev. Lett. 85, 409 (2000).

45. B. Pedrini, J. L. Gavilano, D. Rau, H. R. Ott, S. M. Kazaakov, J. Karpinski, and S. Wessel, Phys. Rev. B 70, 024421 (2004).

46. H. Kinouchi, H. Mukuda, Y. K. P. M. Shirage, H. Fujihisa, Y. Gotoh, H. Eisaki, and A. Iyo, Phys. Rev. B 87, 121101 (2013).

47. P. Carretta, R. Melzi, N. Papinutto, and P. Millet, Phys. Rev. Lett. 88, 047601 (2002).

48. P. Carretta, M. Filibian, R. Nath, C. Geibel, and P. J. C. King, Phys. Rev. B 79, 224432 (2009).

49. T. Moriya, J. Phys. Soc. Jpn. 18, 516 (1963).

50. A. V. Mahajan, R. Sala, E. Lee, F. Borsa, S. Kondo, and D. C. Johnston, Phys. Rev. B 57, 8890 (1998).

51. D. Beeman and P. Pincus, Phys. Rev. 166, 359 (1968).

52. M. Belesi, F. Borsa, and A. K. Powell, Phys. Rev. B 74, 184408 (2006).

53. D. Hone, C. Scherer, and F. Borsa, Phys. Rev. B 9, 2215 (1974).

54. Y. Ajiro, Y. Nakajima, Y. Furukawa, and H. Kiriyama, J. Phys. Soc. Jpn. 44, 420 (1978).

55. M. Takigawa, N. Motoyama, H. Eisaki, and S. Uchida, Phys. Rev. Lett. 76, 2173 (1996).

56. Y. Furukawa, A. Iwai, K. Kumagai, and A. Yakubovsky, J. Phys. Soc. Jpn. 65, 2393 (1996).

57. Y.-C. Chen and A. H. Castro Neto, Phys. Rev. B 61, R3772 (2000).

58. A. L. Chernyshev, Y. C. Chen, and A. H. Castro Neto, Phys. Rev. B 65, 104407 (2002).

59. J.-Y. P. Delannoy, A. G. Del Maestro, M. J. P. Gingras, and P. C. W. Holdsworth, Phys. Rev. B 79, 224414 (2009).

60. M. D. Lumsden, B. C. Sales, D. Mandrus, S. E. Nagler, and J. R. Thompson, Phys. Rev. Lett. 86, 159 (2001).

61. V. A. Ivanshin, V. Yushankhai, J. Sichelschmidt, D. V. Zakharov, E. E. Kaul, and C. Geibel, Phys. Rev. B 68, 064404 (2003).

62. K. Momma and F. Izumi, J. Appl. Crystallogr. 44, 1272 (2011).