MAGNETIC STRUCTURE OF THE LAYERED SQUARE-LATTICE SPIN SYSTEM Zn$_2$VO(PO$_4$)$_2$

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Abstract
The magnetic correlations in the quasi-two dimensional spin-1/2 square-lattice system Zn$_2$VO(PO$_4$)$_2$ have been investigated by neutron diffraction technique. A long-range antiferromagnetic (AFM) ordering below 3.75 K ($T_N$) has been observed with a reduced moment of 0.66(2) $\mu_B$ per V ion at 1.5 K. In a given ab plane, the AFM spin arrangement is Néel type and the AFM layers are coupled ferromagnetically along the c axis. Remarkably, we have observed a pure 2D short-range AFM ordering in the ab plane above $T_N$. Interestingly, the coexistence of diffuse magnetic scattering and three dimensional antiferromagnetic Bragg peaks has been found below $T_N$, indicating the presence of spin-waves as confirmed by our calculation using the linear spin-wave theory. The observed results are discussed in the light of existing theory for a two-dimensional spin-1/2 square-lattice system.

Keywords: Layered material, Low dimensional magnetism, Short-range magnetic ordering

Introduction
Low dimensional magnetism is one of the key areas of interest in the condensed matter physics. The reduced dimensionality of the magnetic ordering and its crossover to a higher dimension can be understood either by strongly anisotropic exchange interactions, or by strongly frustrating topology of the systems. The presence of a long-range magnetic order at a finite temperature in low dimensional systems ($D < 3$) was observed experimentally in presence of non-isotropic exchange constants, single ion anisotropy, and/or infinite-range interactions e.g., the RKKY interactions, classical dipolar interactions, etc.\(^1\)\(^2\) Each of these factors breaks the Mermin-Wagner conditions\(^4\) and may result into a long-range order at $T < JS^2$ and a short-range order above the long-range ordering temperature (retained up to $T = JS^3$), where $J$ is the exchange integral and $S$ is the spin.\(^3\)

The quasi-2D spin-1/2 system Zn$_2$VO(PO$_4$)$_2$ is of particular interest due to its unusual physical properties.\(^5\) Specific heat and dc susceptibility study suggested the presence of a three dimensional antiferromagnetic (3D AFM) ordering below the Néel temperature ($T_N = 3.75$ K) and short-range spin-spin correlations above $T_N$.\(^5\) For a microscopic understanding of the magnetic ground state as well as short-range spin-spin correlations and the crossover to 3D long-range AFM ordering, a neutron diffraction study on this quasi-2D system was necessary.
In this article, we report a detailed neutron powder diffraction study on Zn$_2$VO(PO$_4$)$_2$. The observed results are interpreted in the light of the theoretical predictions for such class of systems.

**Experimental**

The polycrystalline sample of Zn$_2$VO(PO$_4$)$_2$ was prepared by the solid state reaction. The single phase nature of the sample was confirmed by the neutron powder diffraction (NPD) study over 20-300 K at the Dhruva reactor, BARC, INDIA. For the magnetic study, low temperature (1.5-15 K) neutron diffraction measurements were carried out using the G6.1 powder neutron diffractometer at Laboratoire Léon Brillouin (LLB), Saclay, France, covering a limited range of scattering vector length of $-0.12$–$2.5$ Å$^{-1}$. The Rietveld method, by using the FullProf Program, was employed to refine the crystal structure and to determine the magnetic structure.

**Results and Discussion**

The Rietveld refined NPD patterns at 300 and 1.5 K are shown in Figs. 1(a) and 1(b), respectively. The compound crystallizes in the tetragonal symmetry with the space group $I4cm$ with lattice constants $a = 8.9286$ (7) Å and $c = 9.0392$ (1) Å. The crystal structure of Zn$_2$VO(PO$_4$)$_2$ [Fig. 1(c)] consists of a stacking of VO$_5$ square pyramidal layers, separated by a layer of ZnO$_5$ square pyramids, along the crystallographic c-direction. Within a given layer of VO$_5$, the pyramids of VO$_5$ are arranged on a square-lattice and connected through corner sharing PO$_4$ tetrahedra [Fig. 1(c)].
The appearance of extra Bragg peaks at 1.5 K in Fig. 1(b) at the scattering angles (2θ) 30.7, 72.6, 103.9, and 105.1 deg. (Q = 0.70, 1.57, 2.09 and 2.11 Å⁻¹, respectively), where the nuclear Bragg reflections are forbidden for the space group I4cm, confirms a 3D long range (LR) AFM ordering of the V moments. The extra (magnetic) Bragg peaks were indexed as (100), (120), (212), and (300) with respect to the tetragonal chemical unit cell. The size of the magnetic unit cell is found to be same as the chemical unit cell. The temperature dependence of the V magnetic moment, plotted in the inset of Fig. 1(b), indicates that the 3D AFM ordering persists up to a temperature of about 3.75 K (T_N). The analysis of NPD patterns at T < T_N reveals that in a given ab plane, each V moment (aligned along the c axis) is coupled ferromagnetically to its four nearest neighbor V moments (Néel AFM state) [Fig. 1(d)]. Such AFM layers are coupled ferromagnetically along the c axis. At 1.5 K, the effective site-averaged ordered magnetic moment is derived to be 0.66(2) μ_B/V-ion which is almost exactly the moment expected (−0.6 μ_B/V-ion) in a pure 2D antiferromagnetic square lattice with S = 1/2, which is decreased by quantum fluctuations and spin waves. The observed slightly higher value of the ordered moment (0.66 μ_B) may arise from the interlayer ferromagnetic exchange coupling which tends to stiffen the magnetic lattice, reducing the influence of the magnetic fluctuations.

The magnetic diffraction patterns at 10, 7, 4.5, and 4 K, obtained by subtracting a diffraction pattern measured at 15K in the paramagnetic state, are shown in Figs. 2 (i). In the temperature range 4 ≤ T (K) ≤ 7, a broad asymmetric peak appears at the same Q position (~ 0.70 Å⁻¹) where the most intense 3D magnetic Bragg peak (100) is observed below T_N. The observed asymmetric powder diffraction profile is a typical signature of 2D spin-spin correlations. For Zn_2VO(PO_4)_2 with layered structure, when the effective magnetic exchange coupling along the c axis is very weak compared to that in the ab plane, 2D magnetic correlations are expected above T_N. The scattered intensity of a 2D Bragg reflection (hk) can be expressed by the Warren function as,

\[ I_{hk}(2\theta) = C \left( \frac{\xi_{2D}}{\lambda \sqrt{2}} \right)^{1/2} |F_{hk}|^2 \left( 1 + \cos^2 \theta \right) \frac{1}{2(\sin \frac{\pi}{2} \theta)} F(a) \]  

where, C is a scale factor, ξ_{2D} is the 2D spin-spin correlation length, λ is the wavelength of the incident neutrons, |F_{hk}| is the multiplicity of the 2D reflection (hk) with 2D magnetic structure factor F_{hk}, and 2e is the scattering angle. The function F(a) is given by

\[ F(a) = \int_{-\infty}^{\infty} \exp \left[ -\left( x^2 - a^2 \right)^2 \right] dx \]

where,

\[ a = 2\xi_{2D} \sqrt{2/\lambda} (\sin \theta - \sin \theta_{2D}) \]  

and θ_{2D} is the Bragg angle for the 2D (hk) reflection. The expression (1) was calculated numerically to get the best possible agreement with the observed magnetic diffraction patterns in the temperature range of 4-7 K over the Q range of 0.25-1.2 Å⁻¹. The calculation yields ξ_{2D} values of 33(2), 28(2), 25(2) and 21(2) Å at 4, 4.5, 5 and 7 K, respectively. It is, therefore, evident that the in-plane (ab) 2D AFM correlation length is relatively short-ranged and decreases steadily with increasing temperature. At T > 7 K, the Warren scattering becomes too weak to be estimated in the present neutron diffraction study. The observed in-plane (2D) short-range magnetic ordering above T_N is in consistent with the theoretical predictions for quasi-2D systems. This type of 2D magnetic ordering arises due to the anisotropic exchange pathways giving a stronger in-plane exchange coupling.

Now we focus on another important result. Below T_N, an asymmetric broad peak, centred around Q ≈ 0.7 Å⁻¹, has been observed to coexist with the magnetic Bragg peaks down to 1.5 K. The magnetic scattering profiles at two representative temperatures (1.5 and 2 K) are shown in Figs. 2 (ii). Here, a broad asymmetric peak is present along with the 3D magnetic Bragg peak (100). The peak position and peak shape are quite similar to those observed above T_N due to a 2D magnetic ordering. We attribute the observed broad peak (below T_N) to the contribution of spin-waves which are expected to be strongly enhanced for a 2D spin 1/2 system, such as Zn_2VO(PO_4)_2. The influence of spin-waves is also manifested in the reduced value of the ordered moment [0.66(2)μ_B/V ion] at 1.5 K, as discussed earlier.

To confirm this interpretation, we have calculated the spin wave spectrum for the quasi 2D spin 1/2 Heisenberg system Zn_2VO(PO_4)_2, taking into account not only the...
planar near neighbour (NN) interaction $J_1$, but also the planar next nearest neighbour (NNN) interaction $J_2$, the interlayer interaction $J_z$, and the uniaxial anisotropy ($D$) of the $V^{4+}$ ion. All these parameters have different impacts on the spin wave dispersion and ordered moment value. To get a quantitative insight on the influence of all these factors on the spin wave spectrum, we have modelled the spin wave dispersion curves, by writing the energy in a way similar to that done for the compound LiFePO$_4$ by Li et al.$^{13}$ The Hamiltonian for the present spin system has been considered as

$$
H = J_1 \sum_{i,j} (S_i \cdot S_j) + J_2 \sum_{i,j} (S_i \cdot S_{i+j}) + J_z \sum_{i,j} (S_i \cdot S_{i+j}) - D \sum_i (S_i^z)^2
$$

The spin wave dispersion patterns at 10, 7, 4.5, and 4 K, respectively, after subtracting out the nuclear background at 15 K from all patterns. The solid curves [(a)-(d)] are the profiles calculated using the Warren function expected for a purely 2D magnetic ordering. The open circles are the calculated profile of the spin-waves contribution to the scattering. The thick red curves are the sum of the spin-waves and Pseudo-Voigt (3D) peak profiles. (c) The powder averaged spin-wave spectrum. (d) The powder averaged $S(\Omega)$ vs. $T$. (iv) Temperature dependence of FWHM for the 3D magnetic Bragg peak (100) and the 2D spin-spin correlation length ($\zeta_{2D}$). Several magnetic ordering regions, 3D long-range with spin-waves, 3D reduced long-range with 2D short-range, and 2D short-range, are indicated.

Fig. 2: (i) (a)-(d): Magnetic diffraction patterns at 10, 7, 4.5, and 4 K, respectively, after subtracting out the nuclear background at 15 K from all patterns. (ii) Magnetic diffraction patterns at 1.5 K and 2 K, after subtracting out the nuclear background at 15 K. The thin curves are the 3D Bragg peaks calculated by considering a Pseudo-Voigt function for the resolution profile. The open circles are the calculated profile of the spin-waves contribution to the scattering. The thick red curves are the sum of the spin-waves and Pseudo-Voigt (3D) peak profiles. (iii) Calculated spin-wave spectrum along (a) $(h, h, 0)$ and (b) $(0, 0, l)$ directions. The solid curves [(a)-(d)] are the profiles calculated using the Warren function expected for a purely 2D magnetic ordering. (ii) Magnetic diffraction patterns at 1.5 K and 2 K, after subtracting out the nuclear background at 15 K. The thin curves are the 3D Bragg peaks calculated by considering a Pseudo-Voigt (3D) peak profiles. (iii) Calculated spin-wave spectrum along (a) $(h, h, 0)$ and (b) $(0, 0, l)$ directions. The solid curves [(a)-(d)] are the profiles calculated using the Warren function expected for a purely 2D magnetic ordering. The thick red curves are the sum of the spin-waves and Pseudo-Voigt (3D) peak profiles. (iii) Calculated spin-wave spectrum along (a) $(h, h, 0)$ and (b) $(0, 0, l)$ directions. The solid curves [(a)-(d)] are the profiles calculated using the Warren function expected for a purely 2D magnetic ordering. The thick red curves are the sum of the spin-waves and Pseudo-Voigt (3D) peak profiles.
Using the AFM spin wave theory, the lattice with N sites is divided into two sub lattices, namely, spin up (0, 0, z) and spin down (0.5, 0.5, x). The magnon dispersion curves were calculated using the Holstein-Primakoff spin operator transformation in the linear approximation i.e., linear spin-wave theory. The resulting spin-wave dispersion is given by

$$\hbar \omega = \sqrt{A^2 - F^2}$$

(3)

Where, $A = 2J/NZ - 2J/NZ - 2J/NZ + 2J/NZ + J/NZ + 2J/NZ$ and $F = 2J/NZ$ in which Z is the number of the nearest neighbors (Z = 4 for intra-planner interactions and Z = 2 for inter planner interactions) and S is the spin value (S = 1/2 for $V^{+}$). $\gamma_{NN}$, $\gamma_{NNN}$, and $\gamma_{\perp}$ are calculated using the following equation

$$\gamma_{NN, NNN, \perp} = \frac{1}{Z} \sum e^{i\vec{r} \cdot \vec{r}}$$

(4)

Where, $\vec{r} = (r_{NN}, r_{NNN}, r_{\perp})$ are the lattice vectors between a given moment and its intra-plane nearest, next-nearest neighbor and inter-plane nearest-neighbor moments.

A reasonable agreement is obtained [see Fig. 2 (ii)] between experimental spectra at 1.5 and 2 K, and spin wave calculation, by considering the values of $J_1 = 7.9$ K (AFM), $J_2 = 0.2$ K (AFM), $J_\perp = -0.2$ K (FM), and $D = -0.1$, proposed by Kini et al. from their dc susceptibility study. The calculated spin wave spectra along the (hh0) and (00l) directions at $T = 0$ K are shown in Figs. 2 (ii)(a) and 2 (iii)(b), respectively, while Figs. 2(iii)(c) and 2(iii)(d) show the inelastic and integrated powder averaged spectra. Note that the spin wave calculation is done in a semi-classical manner, by reference to an ordered state, and it assumes that the spin waves are only a perturbation of this state. We also plan to carry out an inelastic neutron scattering experiment to confirm the detailed nature of spin-waves in this compound. A phase diagram for the studied quasi-2D compound Zn$_2$VO(PO$_4$)$_2$ is proposed in Fig. 2(iv).

**Summary and Conclusion**

In summary, the quasi 2D compound Zn$_2$VO(PO$_4$)$_2$ shows a rich magnetic phase diagram of pure 2D short-range ordering above $T_{N1}$ (up to 7 K) and, 3D LR ordering along with spin-waves below $T_{N1}$. The observed 3D long-range ordering is Néel type AFM ordering in the $ab$ plane. A reduced value of the ordered moment [0.66(2) $\mu_B$ per V ion at 5 K] is found. The AFM layers are coupled ferromagnetically along the $c$ direction. The observed Néel type long-range AFM ordering (with reduced moment) in the $ab$ plane is in consistent with the theoretically predicted ground state for a frustrated spin-1/2 square-lattice AFM system with a weak next-nearest-neighbor exchange interaction and weak interlayer coupling. The calculation of the magnetic scattering by spin-waves agrees rather well with the observed diffuse neutron scattering below $T_{N1}$. The present study would be useful to understand magnetic properties of low dimensional systems, in general.

**Acknowledgment**

The authors are grateful to S. Petit for his help in the spin-waves calculation.

**References**


