Spin correlations and exchange in square-lattice frustrated ferromagnets

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Abstract – The $J_1$-$J_2$ model on a square lattice exhibits a rich variety of different forms of magnetic order that depend sensitively on the ratio of exchange constants $J_2/J_1$. We use bulk magnetometry and polarized neutron scattering to determine $J_1$ and $J_2$ unambiguously for two materials in a new family of vanadium phosphates, Pb$_2$VO(PO$_4$)$_2$ and SrZnVO(PO$_4$)$_2$, and we find that they have ferromagnetic $J_1$. The ordered moment in the collinear antiferromagnetic ground state is reduced, and the diffuse magnetic scattering is enhanced, as the predicted bond-nematic region of the phase diagram is approached.

The square-lattice $S=1/2$ Heisenberg antiferromagnet with nearest-neighbour (NN) exchange constant $J_1$ and next-nearest-neighbour (NNN) exchange $J_2$, has long served as a paradigm for the two-dimensional frustrated magnetism (for a review see ref. [1]). It is described by the following Hamiltonian:

$$\mathcal{H} = J_1 \sum_{\langle i, j \rangle_1} \mathbf{S}_i \cdot \mathbf{S}_j + J_2 \sum_{\langle i, k \rangle_2} \mathbf{S}_i \cdot \mathbf{S}_k$$

where $\langle i, j \rangle_1$ and $\langle i, k \rangle_2$ refer to pairs of NN and NNN, respectively. The so-called $J_1$-$J_2$ model first came to prominence due to its relevance to the high-temperature superconducting cuprates, and the recent discovery of high-$T_c$ superconductivity in pnictides [2,3] has increased interest in this model, since it may play a key role for the magnetism on the square Fe sublattice [4].

The frustrated square-lattice model is characterized by the frustration ratio $\alpha = J_2/J_1$, and the energy scale is given by $J_\alpha = \sqrt{J_1^2 + J_2^2}$. When the exchange constants are antiferromagnetic (AF) and $\alpha \approx 0.5$ the ground state is believed to be a valence bond solid (VBS) in which spins form tightly bound singlets on nearest-neighbour bonds [5]. On the other hand, recent calculations for ferromagnetic (FM) $J_1$ and AF $J_2$ predict $d$-wave bond-nematic order for $\alpha \approx 0.5$ [6,7]. The calculated phase diagram is shown schematically in fig. 1.

There are now several experimental realizations of spin-$1/2$ magnets on a square-lattice where both $J_1$ and $J_2$ interactions play an important role. The first examples, Li$_2$VOO$_4$ (X = Si, Ge), are collinear antiferromagnets (CAF) with AF exchange $J_2 \gg J_1$ [8–15], whereas VOMoO$_4$ [16] and PbVO$_3$ are Néel antiferromagnets (NAF) with AF exchange $J_2 \ll J_1$ [17,18]. In contrast, the new family of vanadium phosphates AA’VO(PO$_4$)$_2$ (A, A’= Pb, Zn, Sr, Ba, Cd) [19–22] and (CuX)LaNb$_2$O$_7$ (X = Cl, Br) [23,24] have been argued to be frustrated ferromagnets with FM $J_1$ and AF $J_2$.

In order to explore this phase diagram, accurate control of $\alpha$ is required. Until now it has proved difficult to determine the exchange constants accurately using bulk thermodynamic properties, and this is reflected by the wide variation reported for $\alpha$ for individual compounds in the

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Fig. 1: (Colour on-line) Calculated phase diagram for the general $J_1$-$J_2$ model, locating Pb$_2$VO(PO$_4$)$_2$ and SrZnVO(PO$_4$)$_2$. The values of $\alpha$ in parentheses are the phase boundaries determined by exact diagonalization [5,7]. At these values, zero-point fluctuations destroy the relevant order parameter. The yellow area corresponds to the valence bond solid (VBS) regime, the purple zone to the bond-nematic (d-BN) region [6,7,25]. The straight lines are obtained from the Curie-Weiss temperatures, and the circles are obtained from the maxima in susceptibility, as described in the text. The filled circles are the solutions selected using polarized neutrons from the maxima in susceptibility, as described in the text.

The determination of $\alpha$ from thermodynamic quantities alone is undermined by the fact that $J_1 + J_2$ and $|J_1 + J_2|$, but not $J_1$-$J_2$ are well determined.

Here we present combined bulk magnetization and polarized neutron scattering studies of Pb$_2$VO(PO$_4$)$_2$ and SrZnVO(PO$_4$)$_2$. The determination of the magnetic structures in the ground state, and the comparison of the diffuse neutron scattering intensity in the paramagnetic phase with high-temperature series expansions (HTSE) provides an unambiguous determination of the exchange constants $J_1$ and $J_2$. We are also able to explore the consequences for the spin correlations of the approach to a quantum disordered region of the phase diagram.

Large powder samples were synthesized at the Max-Planck Institute for Chemical Physics of Solids in Dresden by the solid-state reaction method, in order to avoid multiphase composition for these compounds. The quasielastic neutron experiments were performed on the D7 diffuse scattering spectrometer at the Institut Laue-Langevin (ILL) in Grenoble, with a fixed incident wavelength of $\lambda = 3.1$ Å corresponding to an energy window of 8.5 meV. XYZ polarization analysis was employed to separate magnetic signal from the coherent structural and incoherent scattering [26]. Polarized inelastic neutron scattering measurements were performed using the IN20 triple-axis spectrometer of the ILL, in order to confirm the energy scale of the system. Scans of energy transfer were performed at various reciprocal lattice points, $Q$, and temperatures, $T$, and in all cases the excitations were found to be within $\pm 4$ meV. Thus the measurements on D7 integrate over the full spectral energy range to yield the structure factor, $S(Q)$. The bulk magnetisations of Pb$_2$VO(PO$_4$)$_2$ and SrZnVO(PO$_4$)$_2$ were measured using a SQUID magnetometer at the University of Liverpool.

Pb$_2$VO(PO$_4$)$_2$ crystallizes in the monoclinic system with spacegroup $P2_1/a$ and lattice parameters $a = 8.747(4)$ Å, $b = 9.016(5)$ Å, $c = 9.863(9)$ Å and $\beta = 100.96(4)^\circ$ [20,27]. Two projections of the Pb$_2$VO(PO$_4$)$_2$ structure are shown in fig. 2. The structure contains corrugated layers formed by VO$_4$ square pyramids oriented in alternating directions in a chessboard fashion. The pyramids are connected by tetrahedral PO$_4$ groups. The layers are buckled along the $b$-axis. The square bases of the similarly oriented pyramids are located approximately at the same level. The magnetic VOPO$_4$ layers are well separated ($\sim 10$ Å) by non-magnetic Pb atoms and isolated PO$_4$ tetrahedra, indicating a quasi-2D character for the system. SrZnVO(PO$_4$)$_2$ shares many characteristics with its relative Pb$_2$VO(PO$_4$)$_2$ structure. Their structural relationship is the replacement of the two Pb$^{2+}$ cations by Sr$^{2+}$ and Zn$^{2+}$. Again, it forms a two-dimensional square lattice of V$^{4+}$ ions with competing interactions leading to frustration. The profound structural similarities with Pb$_2$VO(PO$_4$)$_2$ attracted our interest since small changes introduced by the cationic substitution can tune the magnetic exchanges $J_1$ and $J_2$ and thus the frustration ratio. SrZnVO(PO$_4$)$_2$ crystallises in the orthorhombic system with spacegroup $Pbca$ and lattice parameters $a = 9.0660$ Å, $b = 9.0117$ Å and $c = 17.5130$ Å [27,28]. The main difference between the two compounds’ space groups arises from the way the VOPO$_4$ layers are stacked along the $c$-axis.

The polycrystalline samples were measured under an applied field of 1000 Oe, giving the results of fig. 3. For $T > 50$ K, $\chi(T)$ is characterised by a paramagnetic
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Fig. 3: (Colour on-line) Magnetic response of polycrystalline (a) Pb$_2$VO(PO$_4$)$_2$ and (b) SrZnVO(PO$_4$)$_2$ as measured at 1000 Oe. The broad peaks of $\chi(T)$ are characteristic for low-dimensional spin systems. The magnetic phase transitions at $T_N$ manifest as a change of slope in $\chi(T)$, while $T_{\text{Max}}$ indicates the energy scale for these systems. Insets show inverse susceptibilities for $T > 50$ K, together with the Curie-Weiss law fits (solid lines), giving $\theta_{\text{CW}} = (4.5 \pm 1)$ K and $\theta_{\text{CW}} = (1.5 \pm 1)$ K for Pb$_2$VO(PO$_4$)$_2$ and SrZnVO(PO$_4$)$_2$, respectively.

Curie-Weiss (CW) behaviour. Below that, $\chi(T)$ passes through a broad maximum that is characteristic of a low-dimensional magnet, peaked at $T_{\text{Max}} \sim 8.5$ K and 6.3 K for Pb$_2$VO(PO$_4$)$_2$ and SrZnVO(PO$_4$)$_2$, respectively. The good quality of the samples is evident by the absence of any trace of impurity tails at the lowest attainable temperatures, which is typical of paramagnetic foreign phases. Kinks in $\chi(T)$ indicate the onset of magnetic ordering at the Néel temperatures $T_N \sim 3.7$ K and 2.6 K for Pb$_2$VO(PO$_4$)$_2$ and SrZnVO(PO$_4$)$_2$, respectively. The fits of the Curie-Weiss law to the high-temperature data ($T > 50$ K) are shown as insets in fig. 3. The effective moments $\mu_{\text{eff}} = (1.72 \pm 0.02)$ are consistent with the predicted value for $S = 1/2$, $\mu_{\text{eff}} = 1.73$. The extrapolated intercepts with the temperature axis give $\theta_{\text{CW}} = J_1 + J_2 = (4.5 \pm 1)$ K and $(1.5 \pm 1)$ K for Pb$_2$VO(PO$_4$)$_2$ and SrZnVO(PO$_4$)$_2$, respectively. The values of $\theta_{\text{CW}}$ are rather small compared to the positions of the maxima in the susceptibilities $T_{\text{Max}}$, which allow the overall energy scales of the systems $J_c$ to be estimated. This suggests that $J_1$ and $J_2$ have opposite signs, providing evidence of mixed FM and AF exchange couplings [6].

The conclusions from the susceptibility measurements for the two compounds are summarized in the phase diagram of fig. 1. The observed value of $\theta_{\text{CW}}$ defines a straight line on this plot, while the relation between $T_{\text{Max}}$ and $J_c$, which has been calculated in ref. [6], enables us to get a pair of solutions on this line. Thus for both compounds, there is one possible solution in the CAF and another in the NAF region of the phase diagram.

The neutron scattering experiment complemented these bulk property results, yielding a unique solution in each case. All of the scattering in fig. 4 is magnetic, and it has been placed on an absolute scale by reference to a standard vanadium sample. At temperatures below the Néel point, the magnetic scattering consists of sharp magnetic Bragg reflections.

Fig. 4: (Colour on-line) (a) Magnetic ground-state diffraction pattern of Pb$_2$VO(PO$_4$)$_2$ measured at 1.5 K. The ordered component of the ions’ moments gives rise to sharp magnetic Bragg reflections, while the disordered component gives a diffuse background. Fits are a CAF model with $Q = (\pi, 0)$ (solid line) as well as a Néel model (dashed line, for comparison only). Part (b) shows short-range spin correlations in the paramagnetic phase of Pb$_2$VO(PO$_4$)$_2$. The solid curve is a first-order HTSE calculation for the CAF solution with FM $J_1 = (-3.2 \pm 1)$ K and AF $J_2 = (7.7 \pm 1)$ K, and the dashed is the NAF solution. The data clearly favor the CAF solution.

(For the diagram, $J_1$ and $J_2$ have opposite signs, providing evidence of mixed FM and AF exchange couplings [6]. The conclusions from the susceptibility measurements for the two compounds are summarized in the phase diagram of fig. 1. The observed value of $\theta_{\text{CW}}$ defines a straight line on this plot, while the relation between $T_{\text{Max}}$ and $J_c$, which has been calculated in ref. [6], enables us to get a pair of solutions on this line. Thus for both compounds, there is one possible solution in the CAF and another in the NAF region of the phase diagram.)
CAF structures are used to reproduce the data. The ordered moments in the ground state for comparison (dashed line that fails to reproduce the data). Note that a similar analysis for Li$_2$VO(PO$_4$)$_2$ shows the magnetic ground-state diffraction pattern of Li$_2$VO(PO$_4$)$_2$, modelled by both a CAF structure with an ordering wave vector of $Q = (\pi, 0)$ (solid line) and a Néel structure for comparison (dashed line that fails to reproduce the data). The ordered moments in the CAF structures are (0.42 ± 0.04$\mu_B$) for SrZnVO(PO$_4$)$_2$, (0.50 ± 0.04$\mu_B$) for Pb$_2$VO(PO$_4$)$_2$, and (0.55 ± 0.04$\mu_B$) for Li$_2$VOPO$_4$. As the ordered moment in the ground state decreases for this series of compounds, the integrated intensity under the diffuse component was found to increase.

Exchange constants are usually determined via the excitations from the ordered phase. However, the large single-crystal samples required for inelastic neutron scattering were not available for any of these compounds. The novelty in our approach was to model $S(Q)$ in polycrystalline materials by using HTSE of the static susceptibility. In the determination of the NN and NNN exchange constants we used the 1st-order HTSE given by

$$S(Q) \sim S(S + 1) \left[ 1 + \frac{S(S + 1)}{3} \frac{J(Q)}{kT} \right] \cdot F^2(Q),$$

where $S$ is the spin of the magnetic ions, $F^2(Q)$ the magnetic form factor of the individual magnetic ions and $J(Q)$ is the Fourier transform of the exchange interactions [29]. Figure 4b shows the diffuse neutron scattering intensity at $T = 20$ K, a temperature well into the paramagnetic phase for this compound. Although magnetic long-range order has been destroyed at this temperature, the $kT$ term has not completely washed out all magnetic interactions. The presence of oscillations in the data indicates the existence of short-range spin correlations. Note that we have measured and fixed $F^2(Q)$ directly at room temperature, where no oscillations are present and these systems are ideal paramagnets. The calculated scattering from the two pairs of J’s in fig. 1 are shown in fig. 4b. Our results again select the unique solution in the CAF region, with FM $J_1 = (-3.2 \pm 1)$ K and AF $J_2 = (7.7 \pm 1)$ K. Similarly, for SrZnVO(PO$_4$)$_2$, the combined neutron and susceptibility measurements yield $J_1 = (-4.6 \pm 1)$ K (FM) and $J_2 = (6.1 \pm 1)$ K (AF). Note that a similar analysis for Li$_2$VOPO$_4$ was not possible due to absorption of neutrons by the sample.

The ordered moments in the ground states are smaller than the nominal value for $S = 1/2$ systems due to quantum fluctuations. The value for Li$_2$VOPO$_4$ is consistent with ref. [15]. However, the values for Pb$_2$VO(PO$_4$)$_2$ and SrZnVO(PO$_4$)$_2$ are significantly lower, indicating an increase in quantum disorder. This is entirely consistent with the fact that values of $J_1$ and $J_2$ determined in this study place them successively closer to the disordered region of the phase diagram.

In summary, we have unambiguously determined the exchange constants that are key to understanding a new region of the $J_1$-$J_2$ phase diagram with FM NN interactions and AF NNN interactions. We are able to tie down the exchange constants using novel polarized neutron scattering techniques from powdered samples. The reduced ordered moment and increased diffuse magnetic signal indicate the approach to a quantum disordered spin-nematic region. It should be possible to tune the exchange to be closer to the quantum disordered region by other chemical substitutions, or by the application of pressure or magnetic field. These low-energy scale systems are particularly well suited for further experimental study, for example in high magnetic fields [30,31], and the polarized neutron scattering techniques described here open new vistas for the exploration of these model magnetic systems.

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