High field properties of $S = 1/2$ square lattice $J_1$-$J_2$ magnetic compounds

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Abstract. We discuss the two-dimensional $S = 1/2$ frustrated Heisenberg model on a square lattice. This model provides a good description of two classes of quasi-two-dimensional vanadates, namely the Li$_2$VOXO$_4$ ($X = $ Si, Ge) and AA’VO(PO$_4$)$_2$ ($A, A’ = $ Pb, Zn, Sr, Ba, Cd) compounds. We use the finite-temperature Lanczos method and spin wave analysis to study the high-field properties of this model in the whole $J_1$-$J_2$ plane.

Of particular interest is the saturation field of the low-temperature magnetization. Together with the estimates for the average effective exchange constant $J_c = \sqrt{J_1^2 + J_2^2}$ from the zero-field heat capacity and $\Theta_{CW} = (J_1 + J_2)/k_B$ from the uniform magnetic susceptibility, the saturation field determines the position of a particular compound in the phase diagram uniquely.

We give a summary of the results for the experimentally known compounds and show that our numerical findings agree very well with the experimental data for the magnetic susceptibility and the field dependence of the magnetization of the new compound BaCdVO(PO$_4$)$_2$. This compound is close to the quantum-critical point of the spin-nematic and collinear antiferromagnetic phase of the $J_1$-$J_2$ model as witnessed by a pronounced nonlinear magnetization curve.
of the $J_1$-$J_2$ model for arbitrary values of the exchange energies. We have used spinwave theory and exact diagonalization methods for finite clusters. In this paper, we will summarize the main features of the susceptibility and the magnetization of the model in the parameter range of the experimental compounds. In particular, we will extend the discussion to a new recently synthesized material [1], namely BaCdVO(PO$_4$)$_2$.

Fig. 1 shows the corresponding phase diagram for $H = 0$. The circle corresponds to constant $J_c = 10$ K, the frustration angle $\phi$ is counted counterclockwise beginning at $J_2 = 0$. The $J_1$-$J_2$ model has three main phases, a Néel-type antiferromagnet (NAF) with ordering vector ($\pi, \pi$), a collinear phase (CAF) with ordering vector ($\pi, 0$) or (0, $\pi$), and a ferromagnetic phase (FM). At the edges of the collinear phase, two different types of nonmagnetic phases appear due to strong exchange frustration. These phases were discussed extensively in Refs. [6, 7].

Also shown in the phase diagram are the locations of the known compounds inside the phase diagram. These are marked with black dots and a small circle. The latter denotes the result from a fit to neutron scattering data [4] and differs from the findings in [2, 3]. According to Refs. [1, 2, 3, 4], all compounds except one are believed to have a ground state with collinear antiferromagnetic order. Only for Zn$_2$VO(PO$_4$)$_2$, it is assumed that it has a Néel-type ground state [5].

It is difficult, if not impossible, to distinguish between a location of a particular compound in the collinear and in the Néel phase by zero-field thermodynamics alone [9]. Diffuse neutron scattering would give a definite answer, but to our knowledge only has been published for Pb$_2$VO(PO$_4$)$_2$ [4]. Therefore, the determination of the saturation field $H_{sat}$ of the magnetization at low temperatures can be helpful in determining the correct value for the frustration angle $\phi$. Linear spinwave theory gives [7]

$$g\mu_B H_{sat} = J_1 [2 - (\cos Q_x + \cos Q_y)] + 2 J_2 [1 - \cos Q_x \cos Q_y],$$

where $Q_x$ and $Q_y$ are the components of the respective magnetic ordering vector.

Fig. 2 shows on the left-hand side a plot of the two possible values for $H_{sat}$ for the experimentally known compounds, including the recently published BaCdVO(PO$_4$)$_2$. $H_{sat}$ is
Figure 2. Left: Predicted saturation fields of the experimentally known compounds. $\phi_+$ labels the frustration angle for the collinear phase, and $\phi_-$ for the Néel phase. Their values are determined from the data given in Refs. [1, 2, 3, 5]; for the compound labels see the table in Fig. 1. Right: Field dependence of the magnetization of BaCdVO(PO$_4$)$_2$ for $T \ll T_N$. The open circles denote the experimental data [1]. The filled symbols denote zero-temperature data from our Lanczos calculations using a Bonner-Fisher construction [10]. We used tiles with 16 sites (squares), 20 sites (diamonds), and 24 sites (dots).

given in Tesla using the $J_c$ values of Fig. 1; we have assumed a gyromagnetic ratio $g = 2$ for all substances. All values for $H_{sat}$ are less than 25 T. The two curves correspond to the two possible values $\phi_\pm$ of the frustration angle, where $\phi_+$ labels the collinear phase, and $\phi_-$ the Néel phase.

Measurements of the magnetic susceptibility and the magnetization at low temperatures of the new compound BaCdVO(PO$_4$)$_2$ have been published in Ref. [1]. Fig. 3 shows a plot of the temperature dependence of the magnetic susceptibility (dots). Also shown is a plot of a Curie-Weiss fit to the high-temperature part of the data (dashed line; $20 \, K \leq T \leq 300 \, K$). Additionally, we have made a series of fits using our finite-temperature Lanczos (FTLM) data calculated on a 24-site cluster [7]. The best fit is plotted in Fig. 3 (black line). From this, we get a frustration angle $\phi = 0.77\pi$ and an effective exchange $J_c = 4.8 \, K$. (The latter was used to normalize the experimental data for the plot.) This result is in excellent agreement with Ref. [1], where a high-temperature series expansion was used to determine the exchange constants.

The position of the maximum in $\chi(T)$ is slightly higher, and its value slightly lower for the FTLM data than for the experimental data. This can be regarded as a finite-size effect, since for the lowest temperatures, the finite-size gap influences the temperature dependence of the susceptibility. This gap is of the order of $J_c/N$ where $N$ is the size of the cluster used to tile the lattice.

The right-hand side of Fig. 2 shows a plot of the experimental magnetization data [1], plotted as open circles, and a plot of data derived from exact diagonalization (full symbols). The latter are determined from the zero-temperature field dependence of the magnetization for tiles of $N = 16$ (squares), $N = 20$ (diamonds), and $N = 24$ sites (dots) using a construction introduced by Bonner and Fisher [10]. Except for low magnetic fields, and taking into account the finite-temperature rounding of the experimental data around the saturation field, the agreement with experiment, again, is excellent. From our values for $J_c$ and $\phi$ stated above, we get a saturation field $H_{sat} = 4.1 \, T$, compared to $H_{sat}^{exp} = 4.2 \, T$ from Ref. [1]. The latter value gives a clear
Figure 3. Temperature dependence of the magnetic susceptibility of BaCdVO(PO$_4$)$_2$. Dots denote the experimental result [1], the two curves denote a Curie-Weiss fit to the high-temperature part (dashed line) and a fit using our finite-temperature Lanczos data (solid line).

Indication that BaCdVO(PO$_4$)$_2$, like Pb$_2$VO(PO$_4$)$_2$, is a collinear antiferromagnet, since for the Néel phase, according to Fig. 2, the saturation field would be more than 50% higher, namely $H_{\text{sat}}^{\text{NPF}} \approx 6.5$ T.

Finite-size effects may play a role for the deviations of the two curves at low fields $H \leq 0.4H_{\text{sat}}$: Experimentally, a linear classical field dependence is observed at the lowest fields, whereas the finite-size gap and the corresponding Zeeman splitting of the ground-state doublet determines the nonlinear field dependence of the numerical values. We note that for a value $\phi = 0.77\pi$ (Fig. 2 right) close to the CAF instability a spin wave calculation for $M(H)$ no longer converges for small $H$ [8]. Since the fully polarized state is an eigenstate of the Hamiltonian, finite size effects do not play a crucial role near the saturation field.

To summarize, our study of the $S = 1/2$ frustrated Heisenberg model on a square lattice shows that the thermodynamic and magnetic properties of the Li$_2$VOXO$_4$ ($X = \text{Si, Ge}$) and AA’VO(PO$_4$)$_2$ ($A, A' = \text{Pb, Zn, Sr, Ba, Cd}$) compounds can be well understood. Magnetic susceptibility, heat capacity (not discussed here), and magnetization together provide a unique means to characterize a particular compound. As an example, we applied our findings to the new compound BaCdVO(PO$_4$)$_2$. This compound has a frustration angle $\phi = 0.77\pi$ very close to the spin-nematic region of the phase diagram, an important step towards the synthesis of a compound actually being located inside that region.

References
[1] Nath R, Tsirlin A A, Rosner H and Geibel C 2008 Physical Review B 78 064422
[2] Kaul E, Rosner H, Shannon N, Shpanchenko R and Geibel C 2004 Journal of Magnetism and Magnetic Materials 272-276 922
[3] Kaul E 2005 Ph.D. thesis Technische Universität Dresden
[4] Skoulatos M, Goff J P, Shannon N, Kaul E, Geibel C, Murani A P, Enderle M and Wildes A R 2007 Journal of Magnetism and Magnetic Materials 310 1257–1259
[5] Kini N S, Kaul E and Geibel C 2006 Journal of Physics: Condensed Matter 18 1303
[6] Shannon N, Schmidt B, Pene K and Thalmeier P 2004 European Physical Journal B 38 599
[7] Schmidt B, Thalmeier P and Shannon N 2007 Physical Review B 76 125113
[8] Thalmeier P, Zhitomirsky M E, Schmidt B and Shannon N 2008 Physical Review B 77 104441
[9] Misguich G, Bernu B and Pierre L 2003 Physical Review B 68 113409
[10] Bonner J C and Fisher M E 1964 Physical Review 135 A640