First Experimental Realization of a Frustrated Ferromagnetic Square-Lattice System

Enrique E. Kaul, Christoph Geibel, Nagesh Kini[1], Karlo Penc[2], Nic Shannon[3], and Roman Shpanchenko [4]

Presently, low dimensional or frustrated spin systems are of strong interest due to the fact that low dimensionality and frustration lead to enhanced quantum fluctuations, which results in unusual ground states and unusual low temperature properties. In the past years, one of the most intensively studied examples was the $S = 1/2$ Heisenberg antiferromagnetic (AF) square lattice due to its relevance for high temperature superconductivity in cuprates. In the early days, it was argued, that in such a square lattice quantum fluctuations might lead to the formation of a new kind of disordered spin liquid state [1]. However, it is now widely accepted that a Heisenberg square lattice orders at $T = 0$ K in a Néel antiferromagnetic state (NAF) [2]. Theoretical studies [3] suggest that by introducing an antiferromagnetic exchange J_2 along the diagonal of the square, which frustrates the exchange J_1 along the side of the square, one might recover a spin liquid state at a critical value of the frustration parameter $\alpha = J_2/J_1 \cong 0.5$. The critical region is related to the transition from the NAF state for $\alpha < 0.4$ to a collinear antiferromagnetic state (CAF) for $\alpha > 0.6$. While the corresponding $J_1 - J_2$ model with antiferromagnetic J_1 and J_2 has been the subject of a large number of theoretical papers for more than 15 years, experimental studies have been prevented by the absence of appropriate compounds. The first example for the experimental realization of a frustrated Heisenberg square lattice, $\mathrm{Li_2VOSiO_4}$ (*LVSO*), was found quite recently [4]. The first report suggested *LVSO* to be very close to the critical regime $J_1 = 2 \cdot J_2$, but later studies [5,6] inferred a very weak $J_1 \ll J_2$, placing this compound far away from the critical regime.

In our scientific report 2001/2002, we suggested that a new compound, $\mathrm{Pb_2VO(PO_4)_2}$ *(PbVPO)*, discovered in the context of a cooperation between Moscow State University and our Institute, is likely to be a further experimental realization of a frustrated square lattice system [7]. Meanwhile we have studied this compound in more details, and the results confirm our expectations. A careful analysis of susceptibility and specific heat data revealed *PbVPO* to be first example of a frustrated square lattice system with a ferromagnetic interaction J_1 along the side of the sqare [8]. We further realized that a whole series of compounds with general formula $\mathrm{AA'VO(PO_4)_2}$ *(AA'VPO)*, with *A* and *A'* = Sr, Ba, Zn, crystallizes in closely related structures [9,10]. We synthesized and investigated the compounds $\mathrm{BaZnVO(PO_4)}$ *(BZVPO)* and $\mathrm{SrZnVO(PO_4)_2}$ *(SZVPO)* and found that changing the A and the A' cations allows to tune the ratio between J_1 and J_2. These discoveries initiated a deeper theoretical study of the $J_1 - J_2$ model performed in the theoretical group in our institute, with focus on the region with ferromagnetic exchange J_1 [11]. The results of this theoretical study are also presented in the contribution of B. Schmidt et al. within the present scientific report [12].

The structures of these *AA'VPO* compounds [9,10] are composed of layers of two interpenetrat-

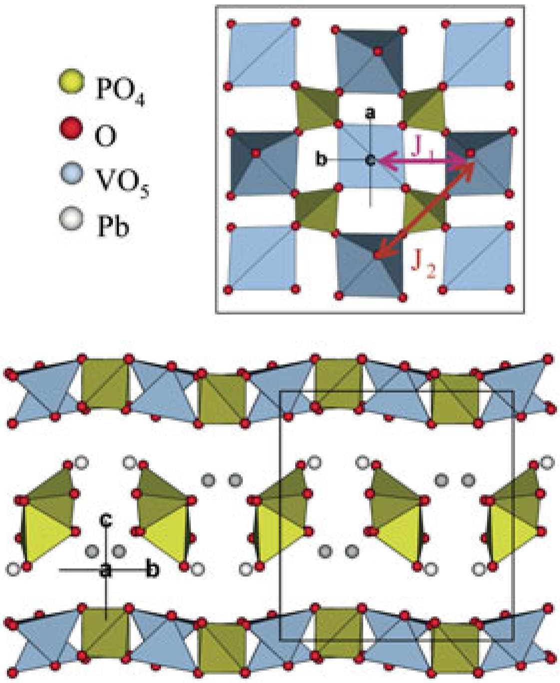

Fig. 1: Structure of $\mathrm{Pb_2VO(PO_4)_2}$. Upper part: top view of the $[\mathrm{VPO_4}]$ layers showing the arrangement of the $\mathrm{VO_5}$ pyramids (blue) and the $\mathrm{PO_4}$ tetrahedra (yellow). The arrows indicate the superexchange paths J_1 and J_2. Lower part: view along a axis showing the large spacing between the layers and the modulation of the $[\mathrm{VPO_4}]$ layers.

ing lattices of VO_5 pyramids connected by one common PO_4 tetrahedron (as an example we show in Fig.1 the structure of *PbVPO*). These layers are separated by large P_2O_7 groups and *AA'* atoms, resulting in a quite large distance between the layers and thus in a very strong two-dimensional character. Within a layer, all VO_5 pyramids pointing to the same direction (up or down) form an almost square lattice with the middle of the square being occupied by a pyramid pointing to the opposite direction. On the basis of basic rules for superexchange, one expect a weak magnetic interaction J_1 between nearest V-neighbors (NN), one V being in an up and one in a down pyramid, while the superexchange J_2 between next-nearest V-neighbors (NNN), which are both either in up or down pyramids, should be stronger. This exchange topology corresponds to a frustrated square lattice.

Polycrystalline samples of *PbVPO*, *BZVPO* and *SZVPO* were synthesized by the solid-state reaction of a stochiometric mixture of $Pb_2P_2O_7$ (or $BaZnP_2O_7$, $SrZnP_2O_7$ respectively) and VO_2 in dynamical high vacuum. We also grow single crystals of *PbVPO* using a Bridgman technique. Magnetic susceptibility $\chi(T)$ measurements were performed in a commercial SQUID magnetometer (Quantum Design MPMS) in the temperature range $2\ K < T < 400\ K$ and for applied fields $\mu_0 H$ up to 5 Tesla. The specific heat $C(T)$ measurements were also performed in an commercial device (Quantum Design PPMS) in the temperature range $0.4\ K < T < 200\ K$, using a relaxation technique on the same samples on which χ(T) was measured. Further on, we synthesized and investigated polycrystals of *LVSO* and of the related compound Li_2VGeO_4 (*LVGO*) in order to resolve the controversy in the literature on the frustration ratio in these compounds and to get a reliable basis for a comparison with the *AA'VPO* compounds. We also synthesized and investigated the compound $Zn_2VO(PO_4)_2$, which crystallizes in a different structure than the other $AA'VO(PO_4)_2$ compounds. Using an analysis procedure similar to that presented in this report, we show that the magnetic lattice of this compound is an unfrustrated square lattice with $J_1 = 7.2$ K [13].

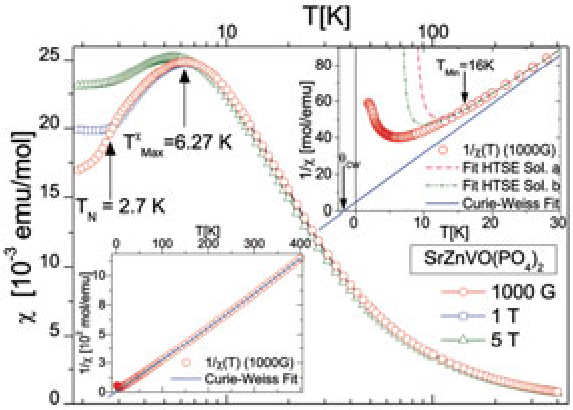

Fig. 2 : Temperature dependence of the susceptibility of $SrZnVO(PO_4)_2$ for different applied fields, showing the broad maximum in $\chi(T)$ corresponding to the onset of AF-fluctuations, and the weak anomaly at T_N marking the onset of long range AF-order. Upper inset: $1/\chi$ vs. T plot below 30 K with the experimental curve and the fit curves calculated for solution a and b using the HTSE (see text). T_{min} marks the lower limit of the fit range. Lower inset: $1/\chi$ vs. T plot up to T = 400 K showing the Curie-Weiss behavior at high temperatures.

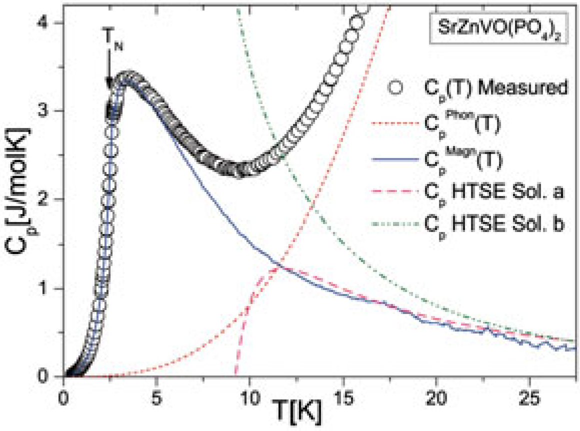

Fig. 3: Specific heat of $SrZnVO(PO_4)_2$ below 20 K, showing the measured specific heat C(T), the phonon contribution C_{phonon} obtained from a fit above 18 K, the magnetic part determined from the difference C(T) - C_{phonon}, and the magnetic part expected for solution a and b as calculated with the HTSE (see text).

Since the properties of all these compounds are quite similar, we only present the raw data of the most interesting one, *SZVPO*, and use these data to illustrate our analysis procedure. The susceptibility $\chi(T)$ follows at high temperatures a Curie-Weiss (CW) law (Fig. 2), with the effective moment $\mu_{eff} = 1.73\ \mu_B$ expected for the spin-only value of V^{4+}, and a very small positive (antiferromagnetic) Weiss temperature $\theta_{CW} = 1.8$ K. Below 20 K, $\chi(T)$ starts to deviate significantly from the CW-law and shows a broad maximum at $T_{\chi max} = 6.3$ K, which is characteristic of low dimensional AF-systems and corresponds to the onset of short range AF-correlations. At lower temperatures, a very weak anomaly at $T_N = 2.7$ K indicates the onset of AF-ordering. Fig. 3 shows the specific heat $C(T)$, which above T = 20 K is completely dominated by the phonon contribution C_{phonon}, while the magnetic part C_{mag} increases with decreasing temperatures and dominates below 10 K. $C_{mag}(T)$ also shows a maximum, but at a temperature T_{Cmax} well below $T_{\chi max}$. A sharp but rather small peak in $C(T)$ at T_N = 2.7 K confirms long range ordering. From these raw data some characteristic parameters can be extracted (table 1), which give preliminary indications on the exchange interactions. Thus the ratio $T_{\chi max}$ /θ_{CW} is strongly increasing from *LVSO* and *LVGO* to *PbVPO* and *BZVPO*, and eventually to *SZVPO*, where θ_{CW} is almost zero. This is a first strong indication that in the *AA'VPO* compounds one of the exchange parameter is ferromagnetic while the other one is antiferromagnetic, because $\theta_{CW} = J_1 + J_2$ while $T_{\chi max}$ reflects the strength of AF-correlations.

For a precise determination of J_1 and J_2, we first fit $\chi(T)$ using the 9th order High Temperature Series Expansion (HTSE) for $\chi(T)$ published by Rosner et al. [5]. The fit was done from 300 K down to 16 K since at lower temperatures the HTSE starts to diverge (see upper inset of Fig. 2). As already noted in the literature [6], because the three first orders in the HTSE of $\chi(T)$ are symmetric in J_1/J_2, this fitting procedure results in two sets of exchange parameters which we called solution *a* ($J_2 > J_1$) and *b* ($J_1 > J_2$), J_1 and J_2 being interchanged between solutions *a* and *b*. The values of J_1 and J_2 were stable against changing the fitting range or reducing the order of the HTSE. Thus these fits gave reliable values for the exchange parameters, but do not allow to discern between the two solutions. For *LVSO* the observation of a CAF state below T_N using NMR implies solution *a* [4]. For the *AA'VPO* compounds a discrimination between the two solutions could be obtained by a careful analysis of the specific heat. In these compounds, because of the different signs of J_1 and J_2, already the second order in the HTSE of the specific heat becomes strongly asymmetric in J_1/J_2, leading to a significant difference in the expected specific heat between solution *a* and *b*. The first step in this analysis was to determine C_{phonon} by fitting $C(T)$ between 18 K and 200 K with a sum of five Debye contributions (in order to take into account the large difference in ionic masses). Since at 18 K the magnetic part cannot be neglected, it was accounted for by adding a term A/T^2, A being a free fitting parameter. Such a term is expected as leading contribution in C_{mag} at high temperatures for any kind of localized spin system. C_{mag} was then determined by subtracting the extrapolated phonon contribution from the measured data (see Fig. 3). In the next step, we used the HTSE for C(T) published by Rosner et al. [5] to calculate the C_{mag} expected for solution *a* and *b* and compared the two calculated curves with the experimental one. Above the temperature $T = 13$ K, below which the HTSE starts to diverge, solution *a* leads to a calculated C_{mag} very close to the experimental results, while C_{mag} for solution *b* exceeds the experimental results significantly (Fig. 3). Thus, the analysis of the specific heat gives rather strong evidence in favor of solution *a*. This solution corresponds to a ferromagnetic exchange J_1 between NN, and a frustrating antiferromagnetic exchange J_2 between NNN along the diagonal of the square. In contrast, solution *b*, with an antiferromagnetic exchange J_1 and a (weaker) ferromagnetic exchange J_2, does not correspond to a frustrated situation, since a ferromagnetic J_2 between NNN supports antiferromagnetic correlations between NN induced by J_1. Further analysis of characteristic properties like e.g. the ratio $T_{\chi max}/\theta_{CW}$, and comparing them with results obtained in our theory group [12], also gave

Tab. 1: Characteristic properties of the compounds presented in this report.

		LVGO	LVSO	BZVPO	PbVPO	SZVPO
θ_{CW}	[K]	5.1	7.4	4.7	4.5	1.8
$T_{\chi max}$	[K]	3.5	5.3	8.6	8.9	6.3
T_N	[K]	2.1	2.7	3.8	3.5	2.7
$T_{\chi max}$ /θ_{CW}		0.69	0.72	1.8	2.0	3.6
T_N /$T_{\chi max}$		0.60	0.51	0.44	0.40	0.43
J_1	K]	0.82	0.56	–5.0	–5.2	–8.2
J_2	[K]	4.1	6.3	9.3	9.4	8.9
$\|J_1\|/J_2$		0.2	0.1	0.54	0.55	0.92

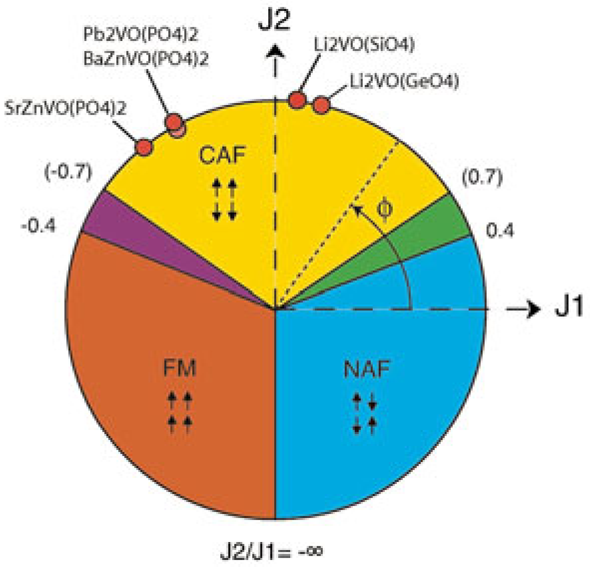

Fig. 4: Phase diagram for the S = 1/2 Heisenberg square lattice with a diagonal exchange J_2 [12], showing the location of the compounds according to the results presented in this report. All compounds are within the region with collinear AF-order (CAF), but SrZnVO(PO_4)$_2$ is rather close to the critical region around $J_1 = -2 \cdot J_2$.

strong support for solution *a*. Independent evidence for solution *a* being the correct one was recently obtained from elastic neutron scattering experiments. We could observe the magnetic Bragg peaks corresponding to the CAF ordered state expected for solution *a*, while one expects a NAF state for solution *b* [14].

In table 1 we summarized the most important characteristic features of the *AA'VPO* compounds and of *LVSO* and *LVGO* as deduced from our experiments, as well as the exchange parameters obtained from our analysis of $\chi(T)$ and $C(T)$. The properties of *LVGO* are similar to those of *LVSO*, those of *BZVPO* are almost identical to those of *PbVPO*, while *SZVPO* is unique. Table 1 reveals a clear systematic from *LVGO* and *LVSO* to *BZVPO* and *PbVPO*, and eventually to *SZVPO*. While J_2 shows only a slight increase from the Li-based compounds to the *AA'VPO* compounds, J_1 strongly decreases, from a very weak antiferromagnetic value in the Li-based compounds, to a sizeable (compared to J_2) negative (ferromagnetic) value for *BZVPO* and *PbVPO*, and eventually to a strong ferromagnetic coupling in *SZVPO*. Accordingly, $T_{\chi max}$ increases slightly from the Li-based compounds to the *AA'VPO* compounds, while θ_{CW} becomes very small in *SZVPO*. In the $J_1 - J_2$ parameter range corresponding to a CAF ground state, which is the case for all compounds considered here, the strength of the frustration is best visualized by the ratio $|J_1|/ J_2$. This ratio increases from a small value in the Li-based compounds to a large value in *SZVPO*, this increase being well reflected in the ratio $T_{\chi max} / \theta_{CW}$, which is directly accessible from the experimental data. In contrast, the ratio $T_N / T_{\chi max}$, which reflects how effectively fluctuations suppress long range order, does not follow the strength of frustration, but is systematically smaller for the *AA'VPO* compounds than for the Li-based compounds. This is in accordance with theoretical considerations where T_N depends logarithmically on the interlayer exchange, which is expected to be much weaker in the *AA'VPO* compound than in the Li-based compounds because of the much larger interlayer spacing.

In Fig. 4 we show the location of the *AA'VPO* compounds and of *LVSO* and *LVGO* within the theoretical phase diagram for the $J_1 - J_2$ model elaborated in our theory group [12]. Our results confirm that *LVSO* and *LVGO* are in the region $|J_1| \ll J_2$. While *PbVPO* and *BZVPO* are still well within the CAF region, *SZVPO* is already rather close to the interesting critical region between the CAF and the FM state. From all compounds which have thus far been suggested to correspond to a frustrated square lattice system, *SZVPO* is presently the system which is closest to one of the critical regions. The evolution of the exchange parameters and their relation to the structure suggest a possibility to get even closer to the critical region $J_1 \approx -2 \cdot J_2$. All three *AA'VPO* compounds have almost the same exchange J_2, while the absolute value of J_1 strongly increases from $|J_1| = 5.0$ K in *BZVPO* to $|J_1| = 8.2$ K in *SZVPO*. Interestingly this increase in $|J_1|$ corresponds to an increase of the modulation of the [VPO_4] layers. This becomes even more evident if the Li-based compounds are included in this comparison. In these compounds the layers are flat, $|J_1|$ is very small and likely antiferromagnetic. This suggest that in this series of compounds one can increase the ratio $-J_1/ J_2$ by increasing the modulation of the layers. In the *AA'VPO* series of compounds, the modulation seems to increase with decreasing size of the *A* and *A'* cations. Thus replacing Sr or Zn by smaller ions could be a way to get a system very close to or in the critical region. That is one of the aim of our further research. The other aim is to study the magnetic excitation spectra using inelastic neutron scattering.

In summary, our results show that the compound series AA'VO(PO$_4$)$_2$ are the first examples for a frustrated Heisenberg square lattice with a ferromagnetic exchange J_1 between nearest neighbors along the side of the square. The frustration can be tuned by the size of the *A* and *A*' cations. The highest yet observed frustration was found in SrZnVO(PO$_4$)$_2$ where our analysis of the susceptibility and specific heat lead to a ratio $J_1/J_2 \cong -1$, locating this compound not too far from the critical region separating the CAF from the FM state. Our results have promoted a new theoretical study of the frustrated Heisenberg square lattice, which evidenced a further spin liquid like critical region at the transition between the collinear antiferromagnetic and the ferromagnetic state [12].

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[1] Hiroshima University, Hiroshima, Japan

[2] Research Institute of Solid State Physics and Optics, Budapest, Hungary

[3] Present address: University of Bristol, Bristol, United Kingdom

[4] Moscow State University, Moscow, Russian Federation