MAGNETIC GROUND STATE IN THE FRUSTRATED $S = 1/2$ SQUARE LATTICE OF V^{4+} IN Li_2VOSiO_4

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The phase diagram of two-dimensional (2D) frustrated Heisenberg quantum systems on a square lattice has been the subject of a number of theoretical studies [1]. Thanks to the synthesis of new model compounds theoretical predictions can be explored experimentally. This opportunity has renewed the interest toward the so-called J_1-J_2 model, where J_1 and J_2 are the nearest- and the next-nearest-neighbour antiferromagnetic (AF) exchange integrals. In this model different situations can occur. For $0.35 \leq |J_2/J_1| \leq 0.65$ a spin liquid or dimer ground state is predicted. For $|J_2/J_1| \leq 0.35$ an AF order should develop, whereas for $|J_2/J_1| \geq 0.65$ the ordering by the disorder mechanism [1, 2] is expected to stabilize a twofold degenerate collinear order. Some theoretical studies suggested the possibility that such a twofold residual degeneracy leads to a finite-temperature Ising-like phase transition, with the chosen ground state being collinear or anti-collinear [1]. However, coupling to the lattice may induce, as in the Jahn-Teller effect, a lattice distortion and remove the twofold degeneracy [3].
We have explored such a scenario by making low temperature neutron powder diffraction (using G4.2 and G4.1 at LLB) and single crystal magnetic resonant x-ray scattering (RXS) experiments (ID20, ESRF) on Li_2VOSiO_4, a system that has been proposed as a prototype of frustrated 2D quantum ($S = 1/2$) Heisenberg AF, and one of the most studied among the new J_1-J_2 systems [3–5]. Li_2VOSiO_4 crystallizes in the tetragonal *P4/nmm* space group, with room temperature lattice parameters $a \approx 6.37$Å and $c \approx 4.45$Å. The magnetic sublattices of S=1/2 V^{4+} ions are built up by layers of VO_5 square pyramids sharing corners with SiO_4 tetrahedra. This structure suggests significant super-super-exchange coupling both along the sides (J_1) and the diagonals (J_2) of the distorted V^{4+} square lattice (the ions have different z-coordinates, see Fig. 1). NMR, magnetization, specific heat, and muon spin rotation measurements on Li_2VOSiO_4 [4] indicate that a collinear AF structure is established below T_N=2.8 K, with magnetic moments lying in the *a*-*b* plane. The analysis of these experiments leads to a strongly reduced value for the ordered magnetic moment, $m(T \rightarrow 0) \approx 0.24\mu_B$, which is considerably smaller than that expected [6] on a 2D lattice ($0.65\mu_B$).

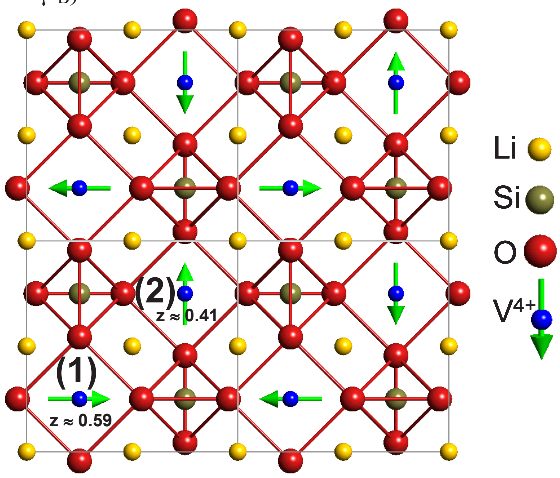

Figure 1. View along [001] of the crystal structure of Li_2VOSiO_4. The apical oxygen atoms of the VO_5 pyramids have not been represented in order to visualize properly the magnetic moments on V^{4+} of one of the non-collinear ground states that are compatible with powder neutron diffraction data.

More recently some doubts were raised [5] concerning the actual value of the ratio J_2/J_1, which was found ≈12 from local density calculations. This result indicates that the system has a large J_2, rather than being close to the border between the collinear and the dimer state. Moreover, it also immediately leads to discrepancy with the reported value of $\approx 0.24\mu_B$, too low for a large J_2 state.
Our study [7] has allowed us to establish the low temperature magnetic structure. The propagation vector is **k**=(1/2,1/2,0) so that the little group is $G_{\mathbf{k}}$= *P4/nmm*. There are four two dimensional

irreducible representations of which only the Γ_4, giving rise to Fourier components of the form $\mathbf{S_k}(1) = (u, v, 0)$ and $\mathbf{S_k}(2) = (v, u, 0)$ (see Fig.1), is compatible with the observations. Neutron powder diffraction data are degenerate with respect to the relative values of *u* and *v*, however RXS, exploiting the fact that the two V^{4+} ions have z(1)≠z(2), is able to confirm that u=v. For instance, in the case of the (±1/2, ±1/2, 3) reflection the π-σ magnetic scattering is strong, whereas the π-π signal is very weak, whatever the value of ϕ ($\tan^{-1}(v/u)$). On the other hand, for the (±1/2, ±1/2, 2) reflection, a negligible π-π magnetic scattering is expected only for ϕ=45° or ϕ=225°. As the experiment shows significant π-σ magnetic scattering for both reflections, with no detectable π-π intensity, we can conclude that the structure is collinear.

The magnetic structure consists then of collinear *a*-*b* AF layers stacked F along the *c* axis (see Fig.2). The refined ordered magnetic moment $m=0.63(3)\mu_B$ is larger than previously reported, and consistent with $|J_2/J_1| \geq 1$, in good agreement with theoretical predictions [5].

High resolution powder neutron (G4.2, LLB) and X-ray diffraction (BM16 at 40 KeV) have also shown the absence of structural phase transition accompanying the magnetic ordering. This work is another example of the complementary use of neutron and synchrotron radiation in the study of magnetism.

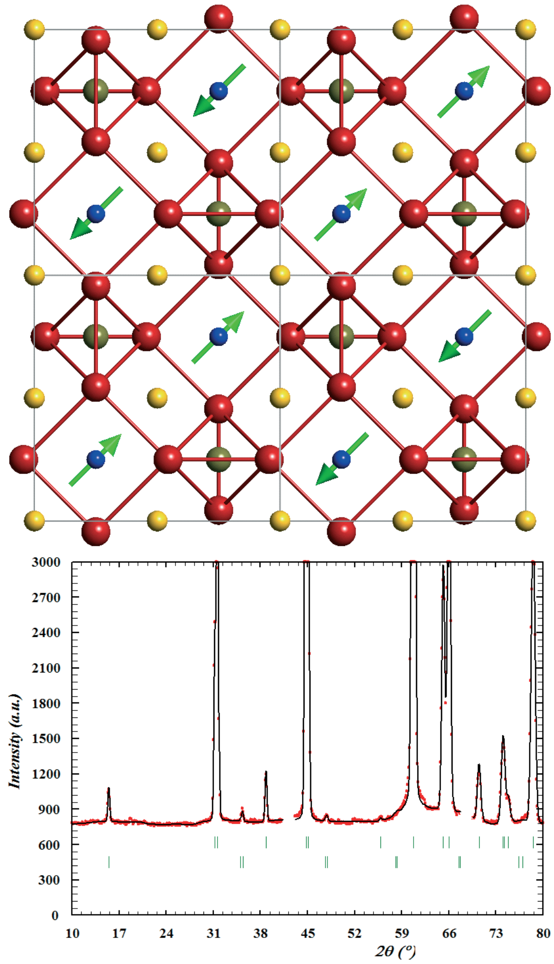

Figure 2. Refinement of the magnetic structure of Li_2VOSiO_4 and picture of its collinear structure. This is compatible with both neutron powder diffraction and resonant X-ray magnetic scattering on a single crystal.

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