Magnetic properties of frustrated two-dimensional $S = 1/2$ antiferromagnets on a square lattice

Magnetic properties of frustrated two-dimensional $S = 1/2$ antiferromagnets on a square lattice

Pietro Carretta[1,4]**, Nico Papinutto**[1]**, Roberto Melzi**[1]**, Patrice Millet**[2]**,
Sabine Gonthier**[2]**, Philippe Mendels**[3] **and Pawel Wzietek**[3]

[1] Dipartimento di Fisica A Volta and Unitá INFM di Pavia, Via Bassi 6, 27100 Pavia, Italy
[2] Centre d'Elaboration des Matériaux et d'Etudes Structurales, CNRS,
31055 Toulouse Cedex, France
[3] Laboratoire de Physique des Solides (CNRS URA 8502), Bâtiment 510, Université de
Paris-Sud, 91405 Orsay, France

E-mail: carretta@fisicavolta.unipv.it

Abstract
An overview of the basic magnetic properties of vanadates which represent
prototypes of frustrated two-dimensional $S = 1/2$ antiferromagnets on
a square lattice is presented. It will be shown how information on the
ground state sublattice magnetization, on the static uniform susceptibility
and on the frustration driven lattice distortions can be achieved by means of
NMR spectroscopy and magnetization measurements. The low-energy spin
excitations, investigated by means of NMR and μSR relaxation measurements,
will be analysed and the anomalous very-low-frequency dynamics, originating
from the degeneracy of the ground state, discussed. Finally the effects of
hydrostatic pressure on the degree of frustration of the vanadates will be
addressed.

1. Introduction

The study of the phase diagram of low-dimensional transition metal oxides has received
renewed interest after the discovery of high T_c superconductivity in cuprates [1]. In fact, these
compounds have been the subject of intense research activity because they represent almost
ideal prototypes of two-dimensional (2D) $S = 1/2$ (Q) Heisenberg (H) antiferromagnets (AF)
on a square lattice, where the low dimensionality and low spin values gives rise to an
enhancement of quantum fluctuations [2]. In vanadates such as Li_2VOSiO_4, Li_2VOGeO_4
and $VOMoO_4$, where the $S = 1/2$ can be assumed localized at the V^{4+} ($3d^1$) site, quantum
fluctuations can be further enhanced by competing exchange interaction among the next nearest
neighbours spins [3, 4]. As can be seen in figure 1 the structure of these vanadates is formed

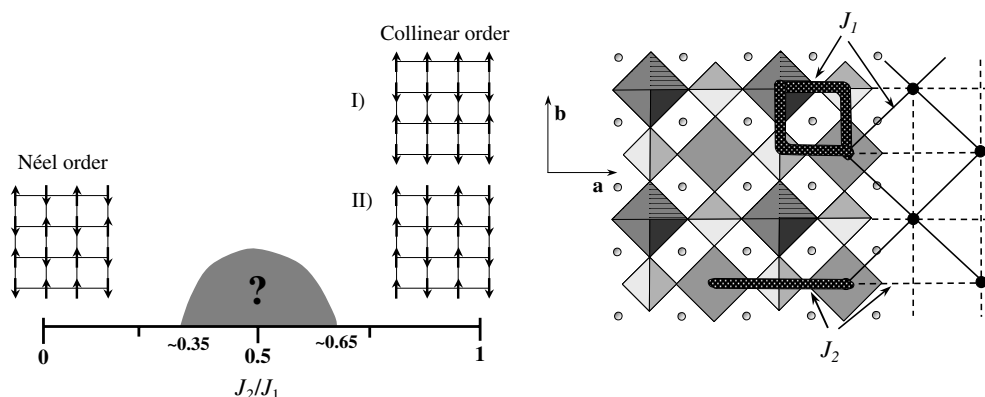[4] Author to whom any correspondence should be addressed.

Figure 1. Left: phase diagram of a frustrated 2D QHAF as a function of the ratio J_2/J_1 between the competing next-nearest neighbour and nearest neighbour exchange couplings. The question mark points out that for $0.35 \leqslant J_2/J_1 \leqslant 0.65$ the nature of the ground state is still not established. Right: structure of Li_2VOSiO_4 projected along the [001]. VO_5 pyramids are in dark grey, SiO_4 tetrahedra in light grey, while Li^+ ions are represented by circles. The thick black lines indicate the superexchange paths for J_1 and J_2 yielding the 2D magnetic lattice sketched on the right-hand side.

by piling up layers of (Si,Ge or Mo)VO_5, where (Si, Ge or Mo)O_4 tetrahedra, placed in the middle of a V^{4+} square lattice [5, 6], yield similar superexchange paths for the nearest (J_1) and next nearest (J_2) V^{4+} neighbours. Therefore these systems can be considered as prototypes of the $S = 1/2 J_1 – J_2$ model on a square lattice. These compounds are particularly attractive since they allow for the first time testing of theoretical predictions put forward several years ago and which have been the subject of an intense debate in recent years [7]. In particular, while it is clearly established which is the nature of the ground state for $J_2/J_1 \ll 1$ and for $J_2/J_1 \gg 1$ (see figure 1) [8], it is not clear if for J_2/J_1 around 0.5 a resonating-valence-bond state is attained or if a dimerized phase is present and not even which are the boundaries of these phases in the $J_1 – J_2$ phase diagram. It has still not been established which is the order of the quantum phase transitions separating the magnetic from the non-magnetic phases. Furthermore, the relevance of the spin–lattice interaction in determining the magnetic ground state needs to be further investigated. In the following a brief overview of the modifications induced by frustration on the static and dynamic properties of 2D QHAF as Li_2VOSiO_4, Li_2VOGeO_4 and $VOMoO_4$ will be presented, based on a series of NMR, μSR, magnetization and specific heat measurements.

2. How frustrated are the vanadates?

One of the first pieces of evidence that frustration is indeed relevant in these vanadates came from the analysis of the static uniform susceptibility (χ) [3]. The temperature dependence of χ in Li_2VOSiO_4, Li_2VOGeO_4 and $VOMoO_4$ is characterized by a high temperature (T) Curie–Weiss behaviour with a Curie–Weiss temperature $\Theta = J_1 + J_2$, a maximum at a temperature T_χ^m arising from the onset of 2D AF correlations and then a kink at T_c, associated with a transition to a long-range ordered phase (figure 2). For a non-frustrated 2D QHAF the susceptibility is expected to show a maximum at $T_\chi^m \simeq 0.93\Theta$, while in these vanadates a reduction of T_χ^m is evident (see table 1) and indicates a decrease of the in-plane correlations due to the competing AF exchange couplings. Also specific heat measurements [4] show a departure from the behaviour expected for the pure 2D QHAF on a square lattice (see figure 2), with a
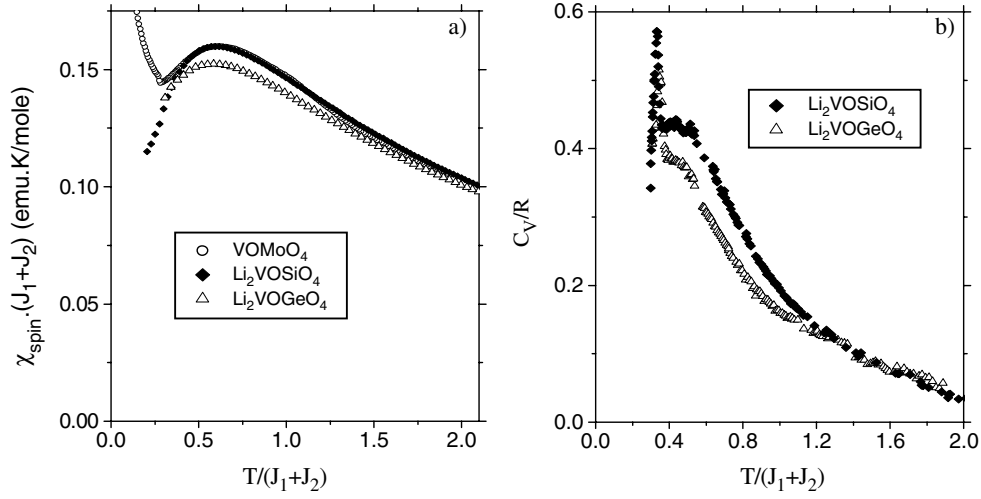
Figure 2. (a) Temperature dependence of the static uniform susceptibility of $VOMoO_4$, Li_2VOSiO_4 and Li_2VOGeO_4 powders measured with a SQUID magnetometer in an external magnetic field of 1 kG. (b) Temperature dependence of the magnetic contribution to the heat capacity of Li_2VOSiO_4 and Li_2VOGeO_4, obtained after subtraction of the high temperature phonon contribution.

Table 1. Characteristic values of $J_1 + J_2$, T_χ^m, T_c and J_2/J_1 for $VOMoO_4$, Li_2VOSiO_4 and Li_2VOGeO_4 derived from susceptibility, specific heat and NMR measurements.

Compound	$J_1 + J_2$	T_χ^m (K)	T_c (K)	J_2/J_1	J_2/J_1 from band structure
$VOMoO_4$	155 ± 10	100	42	—	0.15
Li_2VOSiO_4	9 ± 1	5.35	2.85	1–5	12
Li_2VOGeO_4	6.0 ± 0.3	3.5	1.95	0.9–4	5

broad maximum occurring at lower temperature and decreasing in intensity. These results have been analysed in the light of different theoretical models [3, 9, 10] in order to derive the ratio J_2/J_1. Although none of these models has allowed an accurate estimate of J_2/J_1, due to the limitations inherent in each one of the approaches, all of them indicate that $J_2/J_1 \geqslant 1$ and, on the whole, that $1 \leqslant J_2/J_1 \leqslant 4$, with a slightly lower ratio for Li_2VOGeO_4 than for Li_2VOSiO_4 (see table 1). These results have been also compared to the ones obtained from estimates of the transfer integrals based on band structure calculations and a reasonable agreement was found [9, 11].

3. The collinear phase

At T_c a second order phase transition to a long-range-ordered magnetic phase is observed (see figure 3). The analysis of ^{7}Li and ^{29}Si NMR spectra below T_c showed that the order is collinear [3], as recently confirmed by neutron scattering measurements [12]. This type of order is the one expected for $J_2/J_1 \geqslant 1$ and is thus consistent with the estimates of J_2/J_1 based on the analysis of magnetization and specific heat measurements. The temperature dependence of the sublattice magnetization is characterized by a critical exponent $\beta \simeq 0.236$ (see figure 4), very close to the one expected for a 2D XY model on a finite lattice [13], suggesting that the 3D ordering is triggered by the divergence of the in-plane correlations caused by a small XY
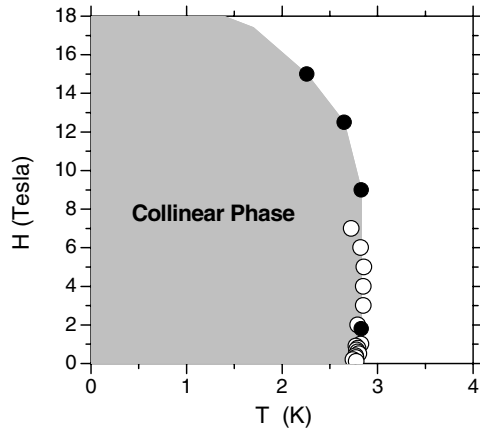
Figure 3. Li$_2$VOSiO$_4$ magnetic field versus temperature phase diagram. The transition temperature T_c to the collinear order was estimated either from susceptibility measurements (open circles) or from NMR relaxation measurements (closed circles).
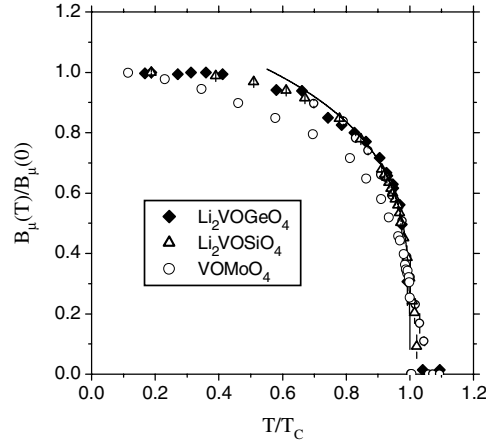
Figure 4. Temperature dependence of the sublattice magnetization below T_c, derived from the temperature dependence of the local field at the muon, in VOMoO$_4$, Li$_2$VOSiO$_4$ and Li$_2$VOGeO$_4$. The dotted curve shows the critical behaviour of the magnetization for a critical exponent $\beta = 0.235$, the one expected for a 2D *XY* system on a finite lattice.

anisotropy. Nevertheless, it has to be pointed out that even for a very small spin anisotropy $\alpha = 10^{-3}$ the critical exponent is still expected to be the one of the 2D *XY* model [14]. At low temperature the V^{4+} magnetic moment saturates at a value of $0.6\,\mu_B$ [12]. This value, very close to the one expected for a non-frustrated system, is consistent with a sharp discontinuous increase and a saturation of the sublattice magnetization for J_2/J_1 above $\simeq 0.65$, recently predicted by Capriotti [15]. The low-temperature dependence of the magnetization can be compared with the behaviour expected for a 2D QHAF with an inter-plane coupling $J_\perp$ [2]. One observes that the T dependence of the magnetization is consistent with $10^{-4} \leqslant J_\perp/J_1 + J_2 \leqslant 10^{-2}$. A reduced value of the interlayer coupling is also consistent with band structure calculations which indicate a negligible hopping integral among adjacent layers [9, 11]. The application of strong magnetic fields is observed to reduce sizeably T_c only for $H \geqslant 10$ T, as shown in figure (figure 3).

4. Frustration driven lattice distortion

Due to the two-fold degeneracy of the collinear ground-state for $J_2/J_1 \geqslant 0.7$ it is not possible to say *a priori* which will be the magnetic wavevector below T_c [16]. On classical grounds it has been demonstrated that for a J_1–J_2 model on a square lattice, an Ising transition is expected to occur at a finite temperature and the system should collapse into one of the two ground states [17]. This transition is expected to vanish on approaching the critical value $J_2/J_1 = 0.5$ and its observation for $J_2/J_1 > 1$ can be difficult due to the decreasing entropy change expected on increasing J_2/J_1. On the other hand, such a scenario can change if the spin–lattice coupling is also considered. In fact, by analogy with the Jahn–Teller effect, a lattice distortion can relieve the degeneracy of the ground-state and lower its energy [18, 19].

In Li$_2$VOSiO$_4$ and VOMoO$_4$ a distortion was revealed by analysing the T dependence of the ^{7}Li and ^{95}Mo NMR shift. The paramagnetic shift of an NMR resonance line can be written as

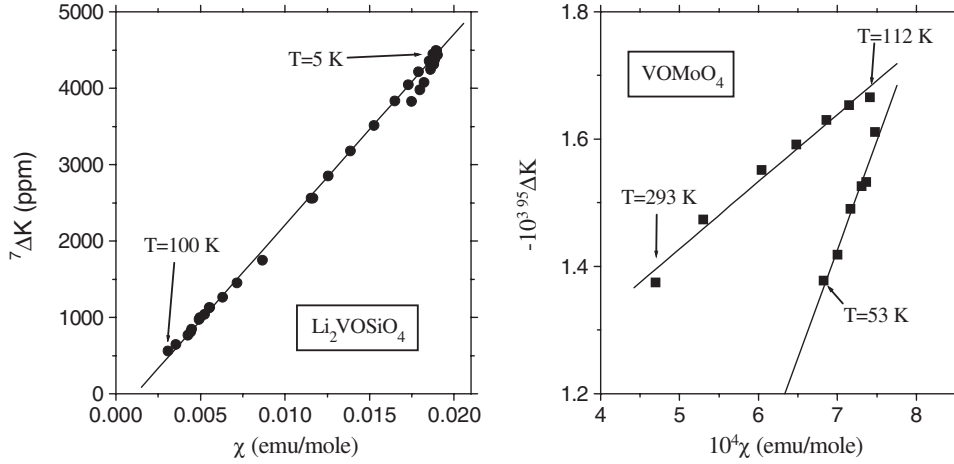$$\Delta K = \frac{A\chi_s}{g\mu_B N_A} + \delta \tag{1}$$

Figure 5. Plot of ^{7}Li NMR shift in Li_2VOSiO_4 (left) and of [95]Mo NMR shift in $VOMoO_4$ (right) versus the static uniform susceptibility. The temperature, which is an implicit parameter, is reported for a few selected points. A clear change of slope, i.e. of hyperfine coupling, is evident for $T \simeq T_\chi^m$. The lines are guides to the eye.

where A is the hyperfine coupling, χ_s the molar spin susceptibility and δ the chemical shift. Hence, the slope of the ΔK versus χ_s plot (see figure 5) directly yields the hyperfine coupling constant which is extremely sensitive to the overlap of the atomic orbitals and hence to the lattice distortions. One observes that in both Li_2VOSiO_4 and $VOMoO_4$ a change in the hyperfine coupling takes place at a temperature close to T_m^χ. It is interesting to note that the temperature at which the distortion takes place in these two compounds, where the exchange couplings change by more than an order of magnitude, roughly scales with $J_1 + J_2$, as expected for a frustration driven distortion in compounds having similar elastic constants [11]. It must be mentioned that while in all $VOMoO_4$ samples investigated a distortion was always present, several Li_2VOSiO_4 samples did not show any distortion. The absence of reproducibility might be associated with different amounts of impurities, which tend to hinder the distortion, in the Li_2VOSiO_4 samples. Furthermore, one has to note that since the distortion increases with the ratio $(J_1 + J_2)/\kappa$, where κ is an effective elastic constant, it is much more likely to be observed in $VOMoO_4$ than in Li_2VOSiO_4 and Li_2VOGeO_4 [18].

5. Very-low-energy excitations in the J_1–J_2 model

NMR spin–lattice relaxation measurements allow us to probe the low-energy spin excitations in these frustrated systems. The spin–lattice relaxation rate $1/T_1$ can be written in terms of the components of the dynamical structure factor $S(\vec{q}, \omega)$ at Larmor frequency as [20]

$$\frac{1}{T_1} = \frac{\gamma^2}{2N} \sum_{\vec{q}} |A_{\vec{q}}|^2 S(\vec{q}, \omega_L) \qquad (2)$$

where γ is the gyromagnetic ratio and $|A_{\vec{q}}|^2$ is the form factor, which describes the hyperfine coupling of the spin excitations at wavevector $\vec{q}$ with the nuclei. In Li_2VOSiO_4, the most investigated among the 2D vanadates, while [7]Li form factor is not sizeably q-dependent, the [29]Si form factor peaks at $(q_x = \pi, q_y = \pi)$ and vanishes at the critical wavevector $\mathbf{Q} = (0, \pi)$ or $(\pi, 0)$. Accordingly, in several Li_2VOSiO_4 samples one can observe that while [7]Li $1/T_1$
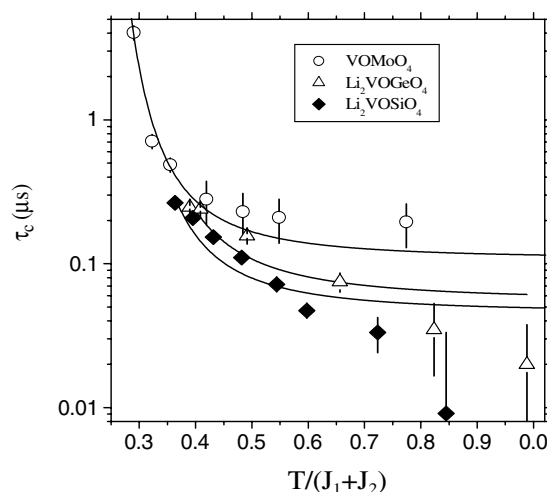
Figure 6. Temperature dependence of the characteristic correlation time for the very-low-frequency spin dynamics evidenced by longitudinal μSR measurements. The solid curves show the theoretical behaviour expected for an activated motion across an energy barrier corresponding to the one separating collinear I and II domains [21].

always shows a neat peak at T_c, ^{29}Si progressively decreases on cooling with no critical anomaly. On the other hand, it was observed that in some Li$_2$VOSiO$_4$ samples a peak is also present in ^{29}Si NMR $1/T_1$. These samples were the ones where a lattice distortion was evident in ^{29}Si and ^{7}Li NMR spectra [3]. Hence, the observation of a peak in ^{29}Si $1/T_1$ in these samples relies on the modifications in the $|A_{\vec{q}}|^2$ factor induced by the lower lattice symmetry.

The temperature dependence of ^{7}Li $1/T_1$ above the critical region can be related to the one of the in-plane correlation length. In fact, in several two-dimensional antiferromagnets it was shown that, on the basis of scaling arguments, one can write $1/T_1$ in terms of the in-plane correlation length ξ [20] and, taking into account the ^{7}Li form factor, one should have $1/T_1 \sim \xi \propto \exp(2\pi\rho_s/T)$, with ρ_s the spin stiffness. Therefore, the weakly T-dependent ^{7}Li $1/T_1$ observed from T_c up to $J_1 + J_2 \simeq 9$ K [4] reveals that either ρ_s is sizeably reduced or that the scaling approach used for $J_2/J_1 \lesssim 0.1$ is no longer valid.

μSR measurements in Li$_2$VOSiO$_4$, Li$_2$VOGeO$_4$ and VOMoO$_4$ have shown that besides a dynamic having characteristic frequencies of the order of the Heisenberg frequency, as the one probed by means of NMR $1/T_1$, an unusual dynamic at frequencies orders of magnitudes lower is present (see figure 6) [21]. These very-low frequency dynamics have been associated with the motions of domain walls separating collinear I and II domains [21] (see figure 1). The fluctuations between these two phases are expected to be characterized by a correlation time $\tau_c = \tau_0 \exp(E(T)/T)$, where $E(T)$ is the energy barrier separating the two phases [16]. At a lower temperature the Ising transition [17] or a lattice distortion will determine the ground state.

6. Spanning the J_1–J_2 phase diagram with pressure

It is quite tempting to explore the phase diagram of a frustrated 2D QHAF continuously from the high to the low J_2/J_1 regime and not to study just a few compounds having well defined values of J_2/J_1. A wide range of the J_1–J_2 phase diagram can be suitably investigated, almost continuously in principle, by applying high hydrostatic pressures (P), which modify
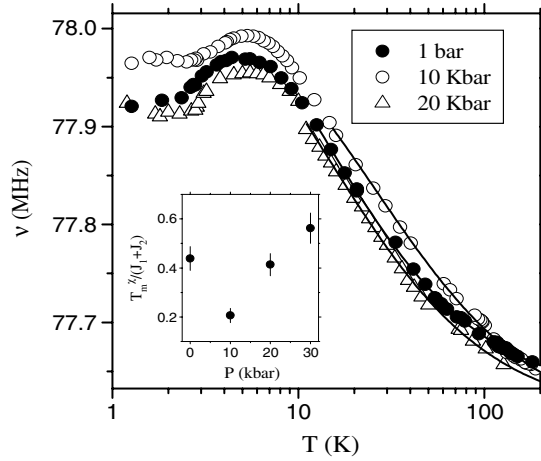
Figure 7. Temperature dependence of ^{7}Li NMR resonance frequency in Li$_2$VOSiO$_4$, for a magnetic field along the c axis, under different hydrostatic pressures. The solid curves above 15 K are the best fit of the data according to Curie–Weiss law. In the inset the pressure dependence of the ratio between T_χ^m and $J_1 + J_2$, i.e. the Curie–Weiss temperature, is reported.

the bonding lengths and angles and, therefore, J_2/J_1. It is not straightforward to say *a priori* if, starting from a certain value of J_2/J_1 at ambient pressure, J_2/J_1 will decrease or increase with pressure. One can measure the effect of pressure on the static uniform susceptibility and from the modifications in T_χ^m and $J_1 + J_2$ establish how the degree of frustration is changing.

The temperature dependence of χ_s can be conveniently derived from NMR paramagnetic shift measurements. The NMR resonance frequency, in the presence of an external field H_0, can be written as

$$\nu(T, P) = \left(1 + \frac{A\chi_s(T, P)}{g\mu_B N_A} + \delta\right)\gamma H_0, \qquad (3)$$

namely one has $\nu(T, P) = a_1(P) + a_2(P)\chi(T, P)$, with a_1 and a_2 two temperature independent constants which may be slightly P-dependent due to possible modifications in the hyperfine coupling induced by pressure. In figure 7 the temperature dependence of $\nu(T, P)$ at different pressures is shown for Li$_2$VOSiO$_4$. One notices first that the high temperature value of the resonance frequency is almost pressure independent, confirming the expected weak pressure dependence of the chemical shift. Upon increasing pressure one observes first a more rapid increase of $\nu(T, P)$ on cooling and then, for $P \to 30$ kbar, a less steep increase. The temperature dependence of $\nu(T, P)$ was analysed, for $T \gg J_1 + J_2$, i.e. above 15 K, by assuming a Curie–Weiss form for the spin susceptibility. The resulting pressure dependence of the ratio $T_\chi^m/(J_1 + J_2)$ is shown in the inset of figure 7. One notices that the ratio first decreases and then increases, as expected if J_2/J_1 was decreasing from the value $J_2/J_1 > 1$ at ambient pressure towards a value $J_2/J_1 \simeq 0.5$ or lower by increasing the pressure up to 30 kbar. On the other hand, it was observed that at low temperature a magnetic ground state was always present and that T_c was left practically unchanged by the application of hydrostatic pressure. This observation appears to be in contrast with the phase diagram depicted in figure 1 and further investigation is required to unravel the origin of this discrepancy.

7. Summarizing remarks

In this brief overview it was shown how the properties of a 2D QHAF are modified by frustration in vanadates characterized by $J_2/J_1 > 1$. Although several static properties, such as the sublattice magnetization, are modified to a lower extent for $J_2/J_1 > 0.7$, the spin dynamics show novel features, not observed in pure 2D QHAF. ^{7}Li $1/T_1$ in Li$_2$VOSiO$_4$ and Li$_2$VOGeO$_4$ is surprisingly almost temperature independent and longitudinal μSR relaxation measurements reveal a very-low-frequency dynamics originating from the degeneracy of the ground state. This degeneracy can be lifted by lattice distortions which manifest themselves in the NMR spectra. Finally, it was shown that although J_2/J_1 can be modified by applying high hydrostatic pressures the ground state is only weakly affected. Future inelastic neutron scattering experiments are required to clarify some of the issues put forward by NMR and μSR in this new field.

References

[1] Dagotto E and Rice T M 1995 *Science* **271** 619
     Dagotto E 1999 *Rep. Prog. Phys.* **62** 1525
[2] Johnston D C 1997 *Handbook of Magnetic Materials* vol 10, ed K H J Buschow (Amsterdam: North-Holland)
        chapter 1, pp 1–237
[3] Melzi R, Carretta P, Lascialfari A, Mambrini M, Troyer M, Millet P and Mila F 2000 *Phys. Rev. Lett.* **85** 1318
[4] Melzi R, Aldrovandi S, Tedoldi F, Carretta P, Millet P and Mila F 2001 *Phys. Rev.* B **64** 024409
[5] Millet P and Satto C 1998 *Mater. Res. Bull.* **33** 1339
[6] Eick H A and Kihlborg L 1966 *Acta Chem. Scand.* **20** 722
[7] see for example Capriotti L 2000 *Int. J. Mod. Phys.* B **14** 3386
     Schulz H J and Ziman T A L 1992 *Europhys. Lett.* **18** 355
     Sorella S 1998 *Phys. Rev. Lett.* **80** 4558
     Capriotti L and Sorella S 2000 *Phys. Rev. Lett.* **84** 3173
     Kotov V N, Zhitomirsky M E and Sushkov O P 2001 *Phys. Rev.* B **63** 064412
     Kotov V N, Oitmaa J, Sushkov O P and Weihong Z 1999 *Phys. Rev.* B **60** 14613
[8] Chandra P and Doucot B 1988 *Phys. Rev.* B **38** 9335
[9] Rosner H, Singh R R P, Zheng W H, Oitmaa J and Pickett W E 2003 *Phys. Rev.* B **67** 014416
[10] Misguich G, Bernu B and Pierre L 2003 *Preprint* cond-mat/0302583
[11] Carretta P, Papinutto N, Azzoni C B, Mozzati M C, Pavarini E, Gonthier S and Millet P 2002 *Phys. Rev.* B **66** 094420
[12] Bombardi L 2004 *J. Magn. Magn. Mater.* at press
[13] Bramwell S T and Holdsworth P C W 1994 *Phys. Rev.* B **49** 8811
     Bramwell S T and Holdsworth P C W 1993 *J. Phys.: Condens. Matter* **5** L53
[14] Cuccoli A, Roscilde T, Tognetti V, Vaia R and Verrucchi P 2003 *Phys. Rev.* B **67** 104414
[15] Capriotti L 2003 *Preprint* cond-mat/0306679
[16] Chandra P, Coleman P and Larkin A I 1990 *Phys. Rev. Lett.* **64** 88
[17] Weber C, Capriotti L, Misguich G, Becca F, Elhajal M and Mila F 2003 *Preprint* cond-mat/0307431
[18] Becca F and Mila F 2002 *Phys. Rev. Lett.* **89** 037204
[19] Tchernyshyov O, Moessner R and Sondhi S L 2002 *Phys. Rev. Lett.* **88** 067203
[20] Rigamonti A, Borsa F and Carretta P 1998 *Rep. Prog. Phys.* **61** 1367
[21] Carretta P, Melzi R, Papinutto N and Millet P 2002 *Phys. Rev. Lett.* **88** 047601