FRUSTRATION DRIVEN LATTICE DISTORTIONS IN Li₂VOSiO₄ AND VOMoO₄*

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NMR and EPR measurements in the two-dimensional frustrated anti-ferromagnets on a square lattice Li₂VOSiO₄ and VOMoO₄ are presented. It is found that a structural distortion, possibly driven by the frustration, takes place in both compounds. The modifications induced by the distortion in the NMR and EPR spectra on cooling can be accounted for by a progressive growth of the size of the domains where the lattice is distorted.

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1. Introduction

One of the most relevant effects induced by frustration in an antiferro-magnet is the degeneracy of the ground-state. In a two-dimensional $S = 1/2$ frustrated Heisenberg antiferromagnet on a square lattice (2DFQHAF), with competing antiferromagnetic interactions J_1 along the sides of the square and J_2 along the diagonal, for $J_2/J_1 \geq 0.65$ the ground-state is two-fold degenerate and the magnetic wave-vector can be either $\boldsymbol{Q} = (q_x = \pi/a, q_y = 0)$ or $(0, \pi/a)$ [1]. When the temperature is lowered below $J_1 + J_2$, an Ising transition takes place and the 2DFQHAF collapses in either one or the other ground-state [2]. Recently, two prototypes of 2DFQHAF have been identified: Li₂VOSiO₄ and VOMoO₄ , with $J_1 + J_2 \simeq 8.5$ K and $\simeq 155$ K, respectively [3,4]. Both systems are characterized by a similar temperature dependence of the spin susceptibility (see Fig. 1), which is consistent with

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the one expected for a 2DFQHAF with $J_2/J_1 \simeq 1$ [5], where the two-fold degenerate ground state is expected. However, experimentally it was found that Li_2VOSiO_4 ground-state has always $\boldsymbol{Q} = (\pi/a, 0)$ (with x the direction of V^{4+} spins) [3], since the degeneracy is relieved by a lattice distortion occurring above the transition temperature T_c to the collinear ground-state.

Here we will show from NMR and EPR measurements that such a structural distortion starts at a temperature T_{dist} which roughly scales with $J_1 + J_2$ and that it is of diffusive nature, namely the size of the distorted domains progressively grows as the temperature is lowered below T_{dist}.
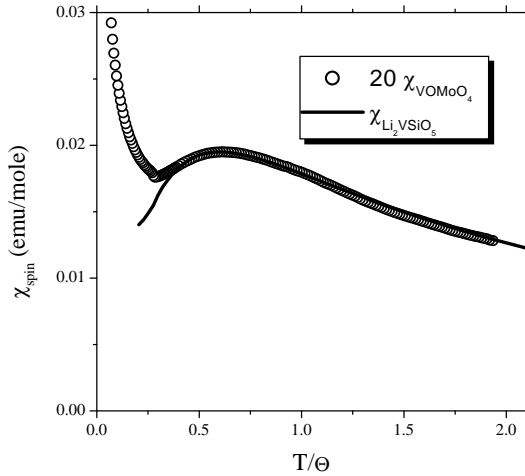

Fig. 1. Spin susceptibility of Li_2VOSiO_4 and $VOMoO_4$ as a function of T/Θ, with $\Theta = J_1 + J_2 = 8.7$ K and 155 K, respectively, the Curie–Weiss temperature. The amplitude of the susceptibility of $VOMoO_4$ has been rescaled by a factor slightly larger than the ratio between the Curie–Weiss temperatures indicating a slightly lower purity of $VOMoO_4$ sample with respect to Li_2VOSiO_4.

2. Experimental results and discussion

The NMR shift ΔK is related to the static uniform susceptibility χ by the equation $\Delta K = A\chi + \delta$, where A is the hyperfine coupling and δ the chemical shift. Hence, the plot of ΔK vs χ, derived from SQUID magnetization measurements, directly yields A. In Fig. 2 we report the corresponding plots for Li_2VOSiO_4 and $VOMoO_4$, with ΔK measured on ^7Li and on ^{95}Mo NMR lines, respectively. It can be noticed that in both compounds around $T_{\text{dist}} \simeq 4.3$ K for Li_2VOSiO_4 and $\simeq 100$ K for $VOMoO_4$, a sizeable change in the hyperfine coupling constant takes place, suggesting the onset of a lattice distortion. It is interesting to observe that, in spite of the huge difference in the exchange couplings, for both compounds $T_{\text{dist}}/(J_1 + J_2) =$

0.57 ± 0.08, suggesting a common origin of the distortion. In fact, one can justify the similarity in the values of $T_{\text{dist}}/(J_1 + J_2)$ for both compounds by considering the magnetoelastic coupling, which leads in first order to $T_{\text{dist}} \simeq C(J_1 + J_2)/k$, where C is a constant related to the crystal structure and k is an effective elastic constant [6]. Taking into account the similarity in the structure of the two compounds [7,8] one can assume that C and k are comparable and, thus, $T_{\text{dist}}/(J_1 + J_2)$ should be the same for Li$_2$VOSiO$_4$ and VOMoO$_4$. Therefore, in these 2DFQHAF a lattice distortion develops since there is a magnetoelastic energy gain and, accordingly, the degeneracy of the ground-state is relieved.
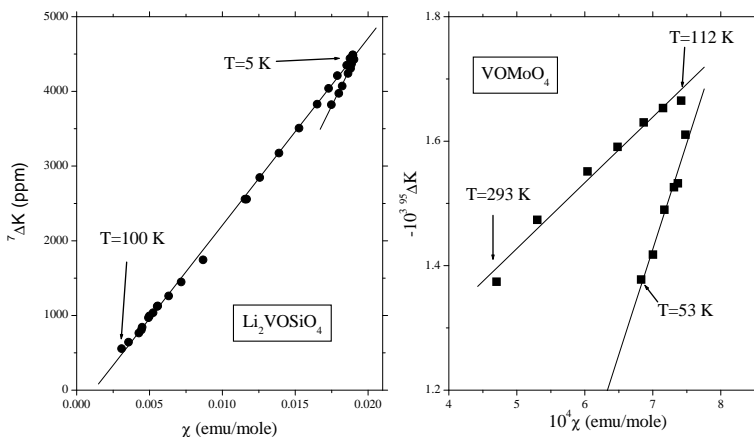

Fig. 2. Left: ^{7}Li NMR shift in Li$_2$VOSiO$_4$ plotted against the spin susceptibility derived from magnetization measurements with the temperature as an implicit parameter. The temperature of a few selected points is shown. The solid lines evidence the change of hyperfine coupling on cooling. Right: ^{95}Mo NMR shift in VOMoO$_4$ *vs* the spin susceptibility derived from magnetization measurements.

^{29}Si NMR spectra in Li$_2$VOSiO$_4$ show for $T \leq T_{\text{dist}}$ a shifted line, associated with ^{29}Si nuclei in distorted domains [3], whose intensity grows on cooling. In VOMoO$_4$ a similar observation can be done on the basis of EPR measurements. Upon cooling below 100 K one notices a decrease of V^{4+} integrated EPR signal, much more pronounced than the one of the static uniform susceptibility (see Fig. 3). This decrease is not due to a saturation of the signal and is not expected if the magnetic ion has a pyramidal coordination as V^{4+}. However, if valence fluctuations take place in the distorted regions so that the magnetic ion becomes Mo^{5+}, the EPR signal might decrease. In fact, when Mo^{5+} is in a regular tetrahedral coordination the EPR signal is canceled out by the selection rules. Hence, the progressive decrease of the EPR signal with decreasing temperature could also be associated with

a corresponding increase of distorted domains in $VOMoO_4$. The occurrence of valence fluctuations is a consequence of the non-negligible hopping integral between V and Mo, via O $2p$ orbitals and could also support the changeover in the resistivity behavior below $T_{dist} \simeq 100$ K [9].
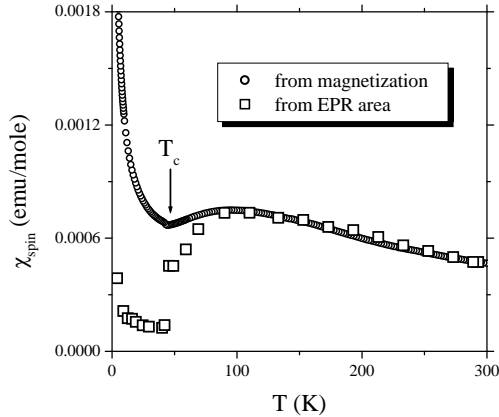

Fig. 3. Temperature dependence of the area of the EPR signal (squares) and of the spin susceptibility (circles) in $VOMoO_4$, measured experimentally with a SQUID magnetometer after subtraction of the Van-Vleck contribution. The area of the EPR signal, which in principle is proportional to the spin susceptibility, was rescaled to match the value of the spin susceptibility at room temperature.

In conclusion, it was shown that in $VOMoO_4$ and Li_2VOSiO_4 a lattice distortion of diffusive character takes place at a temperature which scales with $J_1 + J_2$, suggesting that the distortion is driven by the magnetic frustration.

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