Li$_2$VO(Si,Ge)O$_4$, a prototype of a two-dimensional frustrated quantum Heisenberg antiferromagnet

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NMR and magnetization measurements in Li$_2$VOSiO$_4$ and Li$_2$VOGeO$_4$ are reported. The analysis of the susceptibility shows that both compounds are two-dimensional $S = 1/2$ Heisenberg antiferromagnets on a square lattice with a sizeable frustration induced by the competition between the superexchange couplings $J_1$ along the sides of the square and $J_2$ along the diagonal. Li$_2$VOSiO$_4$ undergoes a low-temperature phase transition to a collinear order, as theoretically predicted for $J_2/J_1 > 0.5$. Just above the magnetic transition the degeneracy between the two collinear ground states is lifted by the onset of a structural distortion.

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In recent years one has witnessed an extensive investigation of quantum phase transition in low-dimensional $S = 1/2$ Heisenberg antiferromagnets (QHAF) as a function of doping, magnetic field and disorder [1]. For example, two-dimensional QHAF (2DQHAF) have been widely studied to show the occurrence of a phase transition from the renormalized classical to the quantum disordered regime upon charge doping [2]. Another possibility to drive quantum phase transitions in a 2DQHAF is to induce a sizeable frustration. In particular, for a square lattice with an exchange coupling along the diagonal $J_2$ about half of the one along the sides of the square $J_1$ (see Fig. 1a), a crossover to a quantum disordered phase with a finite gap between the singlet ground state and the first excited state is expected [3]. For $J_2/J_1 \ll 0.5$ a Néel order is envisaged, while for $J_2/J_1 \gg 0.5$ a collinear order should develop. The collinear order (see Fig. 1a), which can be considered as formed by two interpenetrating Néel sublattices with staggered magnetization $\mathbf{n}_1$ and $\mathbf{n}_2$, is characterized by an Ising order parameter $\sigma = \mathbf{n}_1 \cdot \mathbf{n}_2 = \pm 1$ [3]. The two values of $\sigma$ correspond to the two collinear configurations, one with spins ferromagnetically aligned along the $x$ axis, with a magnetic wave-vector $\mathbf{Q} = (0, \pi/a)$, the other with spins ferromagnetically aligned along the $y$ axis ($\mathbf{Q} = (\pi/a, 0)$). At a certain temperature an Ising phase transition occurs and the system choses among the $x$ or $y$ collinear configurations. The precise boundaries of the $J_2/J_1$ phase diagram for a frustrated 2DQHAF are unknown and could be modified by the presence of a finite third neighbour coupling [4]. These theoretical predictions have not found an experimental support so far, mainly due to the absence of a system which can be regarded as a prototype of a frustrated 2DQHAF.

In this letter we present NMR and magnetization measurements that prove that the isostructural compounds Li$_2$VOSiO$_4$ (LSVO for short) and Li$_2$VOGeO$_4$ (LGVO) [5], formed by layers of V$^{4+}$ ($S = 1/2$) ions on a square lattice (see Fig. 1b), are prototypes of frustrated 2DQHAF with significant coupling between both first ($J_1$) and second ($J_2$) neighbours. Moreover we show that LSVO undergoes a phase transition to a low temperature collinear order, as expected for $J_2/J_1 > 0.5$. The phase transition is triggered by a lattice distortion which lifts the degeneracy between the two possible collinear ground states and could belong to the Ising universality class.

$^{29}$Si NMR and magnetization measurements have been performed on powder samples while $^7$Li NMR measurements, thanks to $^7$Li sensitivity, have been carried out also on a $\sim 1 \times 1 \times 0.2$ mm$^3$ LSVO single crystal. NMR spectra and nuclear spin-lattice relaxation rate $1/T_1$ have been measured by using standard pulse sequences. The field-cooled magnetization $M$ was measured with a commercial Quantum Design MPMS-XL7 SQUID magnetometer.

The structure of V$^{4+}$ layers [6] suggests that both the couplings between first and second neighbours can be significant. It is however difficult a priori to decide which one should dominate: first neighbours are connected by two superexchange channels, but they are located in pyramids looking in opposite directions and are not exactly in the same plane, whereas second neighbours are connected by only one channel, but they are located in pyramids looking in the same directions and are in the same plane. It would thus be highly desirable to extract information on the relative value of these exchange integrals from the susceptibility ($\chi = M/H$) (see Fig. 2). Although the temperature dependence of the susceptibility of the $J_1 - J_2$ model is not known accurately as a function of $J_1$ and $J_2$, it turned out to be possible to obtain useful information from the following considerations. If the system was not frustrated, i.e. if $J_1 \gg J_2$ or $J_2 \gg J_1$, the susceptibility would be that of a regular Heisenberg AF on the square lattice with coupling $J$. In
that case, Quantum Monte Carlo simulations can be used to determine the temperature dependence of the susceptibility \[ \Theta \approx J \]
and the maximum occurs at \( T_{\text{max}} \approx 0.935 J \).
Since in that case the Curie-Weiss temperature \( \Theta = J \)
one has a ratio \( T_{\text{max}}/\Theta \approx 0.935 \). Now, while \( T_{\text{max}} \)
is known very accurately from our measurements, the precise determination of \( \Theta \) is more problematic. A simple fit with \( \chi(T) = \chi(0) + C/(T + \Theta) \), with \( \chi(0) \) Van-Vleck susceptibility, is not good enough because there is an important dependence of the results on the lowest temperature used in the fit. To overcome this problem, we have performed a fit of the high temperature part of the susceptibility up to third order. The coefficients are then consistent with a \( J_1 - J_2 \) model only in a small window for the lowest temperature. Within this window, \( \Theta \) depends very weakly on the lowest temperature and a precise estimate of the Curie-Weiss temperature can be achieved. The results are \( \Theta \approx 7.4 K \) for LSVO and \( \Theta \approx 5.2 K \) for LGVO. Accordingly, the ratios \( T_{\text{max}}/\Theta \) are equal to 0.72 and 0.67, respectively. In both cases, this ratio is significantly lower than the value 0.935, supporting the presence of a sizeable frustration. Besides, with a smaller ratio, LGVO is expected to be closer to the fully frustrated point \( J_2/J_1 = 1/2 \) than LSVO, in qualitative agreement with the fact that no phase transition was found in that system down to 1.9 K (see below).
What we cannot say however on the basis of this analysis is which of the couplings \( J_1 \) and \( J_2 \) is larger.

To be more quantitative, we need to know the ratio \( T_{\text{max}}/\Theta \) for the \( J_1 - J_2 \) model as a function of \( J_2/J_1 \). It turned out to be impossible to get accurate estimates in the strongly frustrated region \( J_2/J_1 \approx 1/2 \), but exact diagonalizations with 3 sizes available (4, 8 and 16 sites) give a reliable estimate for \( J_2/J_1 < 4 \), while Quantum Monte Carlo simulations, which suffer from the minus sign problem, provide useful information down to \( J_2/J_1 \approx 2 \) on the other side, where only two sizes can be used for exact diagonalizations due to the type of order (8 and 16 sites). The experimental ratio \( T_{\text{max}}/\Theta = 0.72 \) for LSVO then implies that \( J_2/J_1 \) is approximately equal to 1 or to 3.5, while for LGVO, \( T_{\text{max}}/\Theta = 0.67 \) implies that \( J_2/J_1 \) is either close to 0.25 or to 2.5.

A significant difference between the two compounds is discernable if one reports the derivative \( d\chi/dT \) vs. \( T \) (see the inset to Fig. 2). One observes that around \( T_c \approx 2.83 \) K a peak is present for LSVO, while no anomaly in \( d\chi/dT \) is detected for LGVO, down to 1.9 K. The peak occurs at the same temperature where a peak in \( ^7\text{Li NMR} 1/T_1 \) is observed (see Fig. 3), signaling a phase transition to a magnetically ordered state. Remarkably, \( T_c \) was found independent on the magnetic field intensity, within \( \pm 0.15 \) K (i.e. \( \pm 5\% \)), up to \( H = 7 \) Tesla.

In LSVO, for \( H = 1.8 \) Tesla, one observes that \( ^7\text{Li} 1/T_1 \) is constant between 3.5 and 293 K. In the high temperature limit \( (T \gg \Theta) \), by resorting to the usual Gaussian form for the spin correlation function one has

\[
(1/T_1)_{\infty} = \frac{\gamma^2}{2} \frac{S(S+1)}{3} \frac{\sqrt{2\pi}}{\omega_E} \times \sum_{k,i,j} (A_{ij}^k)^2
\]  

with \( A_{ij} \) \( (i = x, y, z, j = x, y, z) \) the components of the hyperfine tensor due to the \( k^{th} \) \(^{4+}\) \( V \) the gyromagnetic ratio and \( \omega_E = g B \sqrt{2zS(S+1)/3}/h \). \( z = 8 \) is the number of nearest neighbour spins of a \(^{4+}\) coupled via an effective superexchange coupling \( J \) related to \( J_1 \) and \( J_2 \). \(^7\text{Li} \) hyperfine coupling constants in LSVO have been estimated by reporting the temperature dependence of the paramagnetic shift, both for the single crystal and for the powders, as a function of the susceptibility. It turned out that \(^{7}\text{Li} \) nuclei are coupled to \(^{4+}\) ions both via a dipolar and a transferred hyperfine coupling \( A_T = 1700 \) Gauss \([1]\), which is attributed to the two \(^{4+}\) nearest neighbours. The dipolar term is close to the one estimated on the basis of lattice sums. From Eq. 1, by using the high temperature value of \( 1/T_1 \), one finds \( J = 6.4 \) K, a value consistent with the Curie-Weiss temperature derived from the analysis of the susceptibility.

For \( T < \Theta \), \(^{4+}\) spins are strongly correlated and the behaviour of \( 1/T_1 \) depends on which regime LSVO is: quantum critical, renormalized classical or quantum disordered \([2]\). However, one has to notice that the temperature dependence of \( 1/T_1 \) can be strongly influenced by the \( q \)-dependent hyperfine form factor \([3]\). Hence, in order to make significant statements on the correlated spin dynamics of this frustrated 2DQHAF we have first calculated the hyperfine form factor, which was found only weakly \( q \)-dependent in view of the sizeable transferred coupling. Therefore, the temperature dependence of \( 1/T_1 \) is fully determined by the one of the correlation length and the fact that \( 1/T_1 \) is constant down to \( \sim 3\) K suggests that LSVO, for \( H = 1.8 \) Tesla, is in the quantum critical regime \([4]\).

Below \( T_c \) one observes an activated decrease of \( 1/T_1 \) which is typical of a magnetically ordered system with a gap in the spin wave spectrum \([4]\). An estimate of the gap amplitude can be done using a simple Arrhenius fit, which yields \( \Delta = 18 \) K (see the inset to Fig. 3). Although the estimate of \( \Delta \) might not be very accurate in view of a certain proximity to the phase transition it should be noticed that the estimated value is considerably larger than what one would expect for a magnetic system with a coupling constant of a few degrees kelvin, as deduced from susceptibility and \( 1/T_1 \) measurements for \( T \gg \Theta \). This fact could suggest a modification of the superexchange coupling at low temperatures, possibly involving a lattice distortion. The occurrence of a lattice distortion is, in fact, corroborated by the modifications in \(^{29}\text{Si NMR} \) powder spectra below \( \sim 3.4 \) K (see Fig. 4a). One observes, just above \( T_c \), the appearance of a shifted narrow peak in \(^{29}\text{Si NMR} \) powder spectrum. On decreasing temperature the low-frequency peak progressively disappears while the intensity of the high frequency one increases. Two aspects should be remarked:
1) $^{29}$Si NMR line does not broaden below $T_c$ indicating that the local field at $^{29}$Si nuclei is zero; 2) the modification in the shift has to be associated with a modification in the chemical shift or hyperfine coupling, suggesting the occurrence of a structural distortion. The absence of a magnetic field at $^{29}$Si site can be accounted for either by an AF order with the spins parallel to the c axis or by a collinear order with $V^{4+}$ spins along the sides of the square lattice. In order to exclude the presence of an AF order we studied the angular dependence of the magnetic field at $^{7}$Li nuclei below $T_c$. [1]. By considering the same hyperfine coupling tensor determined above $T_c$ [15] we found that for the AF order the magnetic field intensity should always increase on turning the magnetic field from parallel to the c-axis to parallel to the ab plane, at variance with the experimental findings. Moreover, the fact that the spins are parallel to the ab plane below $T_c$ is supported by a recent EPR analysis of the g tensor [16], showing that there is a larger in-plane magnetic anisotropy. Therefore, we conclude that the magnetic order is collinear with the spins in the ab plane. This is the first evidence of a collinear order in a frustrated 2DQHAF, whose existence has been theoretically put forward long ago by Chandra and coworkers [3,6]. It should be observed that only one of the two possible collinear orders, with $\sigma = \pm 1$, is compatible with zero magnetic field at $^{29}$Si, the one with the spins parallel to the staggered modulation, i.e. for spins along the x-axis the one with magnetic vector $\mathbf{Q} = (\pi/a, 0)$. The fact that in LSVO always one type of collinear order develops indicates that the four-fold symmetry of the square lattice was broken, possibly by the lattice distortion occurring just above $T_c$.

Further information on the collinear phase in LSVO can be derived from the temperature dependence of $^{7}$Li NMR spectra below $T_c$ (see Fig. 4c). The temperature dependence of the order parameter, proportional to $V^{4+}$ average magnetic moment, is obtained from the splitting of the satellites of $^{7}$Li NMR spectrum. The central peak and the two satellites do not correspond to the $1/2 \rightarrow -1/2$ and $\pm 3/2 \rightarrow \pm 1/2$ transitions, respectively, but correspond to Li sites where the local field is either zero or non-zero (parallel or antiparallel to the external one). We have ruled out the possibility of a quadrupolar splitting by checking that both the length of the RF pulse yielding a $\pi/2$ rotation and the recovery curve of nuclear magnetization were the same for all lines. Moreover the observed splitting is nearly an order of magnitude larger than the quadrupolar one calculated on the basis of a point charge approximation. One notices (see Fig. 4b) a rather sharp, but continuous, decrease of the order parameter close to $T_c$. An accurate determination of the critical exponent $\beta$ would require a temperature stability better than $5 \times 10^{-3}$ K which could not be achieved with our cryogenic apparatus. Still an upper limit for $\beta$ can be estimated from our measurements which are carried out in steps of $10^{-2}$ K for $T \rightarrow T_c$. We find that $\beta \leq 0.25$, a value compatible with a 2D Ising phase transition, where $\beta = 1/8$. It should be observed that the relative amplitude of the central and satellite lines varies with decreasing temperature. This could be due to a modification of the interplanar correlation, to which $^{7}$Li spectrum is sensitive. To elucidate this aspect further investigation of the collinear order is demanded.

In conclusion, we have presented for the first time susceptibility measurements showing that Li$_2$VOSiO$_4$ and Li$_2$VOGeO$_4$ can be considered as prototypes of frustrated 2DQHAF and NMR spectra demonstrating that in the former a collinear phase is established at low-temperature, as predicted for $J_2/J_1 > 1/2$ [2]. Finally $^{29}$Si NMR spectra suggest the occurrence of a structural distortion, just above the magnetic transition, which lifts the degeneracy between the two collinear ground states.

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FIG. 1. a) Schematic phase diagram of a frustrated 2DQHAF on a square lattice as a function of the ratio $J_2/J_1$ of the superexchange couplings. b) Structure of LSVO and LGVO projected along [001]. (Si,Ge)O$_4$ tetrahedra are in grey, VO$_5$ pyramids are in black while the grey circles indicate Li$^+$ position. For details see Ref. 8.

FIG. 2. Temperature dependence of the magnetic susceptibility $\chi = M/H$, for $H = 0.3$ Tesla, in LSVO (closed squares) and LGVO (open circles) powders. In the inset the corresponding temperature dependence of the derivative $d\chi/dT$ is reported.

FIG. 3. Temperature dependence of $^7$Li NMR $1/T_1$ for $H = 1.8$ Tesla along the $c$ axis in a LSVO single crystal. In the inset we report the corresponding Arrhenius plot of the experimental data for $T \leq 2.66$ K. The error bars when not reported are within the circles.

FIG. 4. a) $^{29}$Si NMR powder spectrum in LSVO for $H = 1.8$ Tesla. The dotted lines mark the position of the peak at high and at low temperatures. b) Temperature dependence of the splitting between the low-frequency and the high frequency peak for $^7$Li NMR spectra in c). The solid line indicates the behaviour expected for an order parameter with a critical exponent $\beta = 0.25$. c) $^7$Li NMR spectra for $H = 1.8$ Tesla along the $c$ axis of a LSVO single crystal, in the proximity of $T_c = 2.83 \pm 0.005$ K.
Fig. 1 (R. Melzi et al.)

(a) 

Néel Order 

Collinear Order 

Spin-singlet 

(b)
Fig. 2 (R. Melzi et al.)
Fig. 3 (R. Melzi et al.)
Fig. 4 (R. Melzi et al.)