$Li_2VO(Si,Ge)O_4$, a Prototype of a Two-Dimensional Frustrated Quantum Heisenberg Antiferromagnet

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NMR and magnetization measurements in Li_2VOSiO_4 and Li_2VOGeO_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 sizable frustration induced by the competition between the superexchange couplings J_1 along the sides of the square and J_2 along the diagonal. Li_2VOSiO_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 sizable 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 [3–5]. For $J_2/J_1 \ll 0.5$ a Néel order is envisaged [6], while for $J_2/J_1 \gg 0.5$ a collinear order should develop. The collinear order (see Fig. 1a), which is formed by two interpenetrating Néel sublattices with staggered magnetization $\mathbf{n}_1$ and $\mathbf{n}_2$, is characterized by an Ising order parameter $\sigma = \mathbf{n}_1 \cdot \mathbf{n}_2 = \pm 1$ [7]. The two values of σ 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 chooses 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 neighbor coupling [7]. 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_2VOSiO_4 (LSVO for short) and Li_2VOGeO_4 (LGVO) [8], 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) neighbors. Moreover we show that LSVO undergoes a phase transition to a low temperature

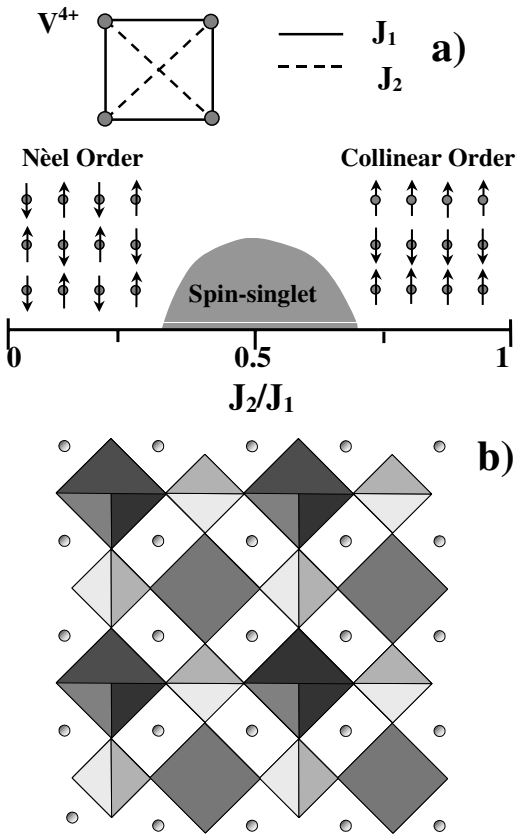

FIG. 1. (a) Schematic phase diagram of a frustrated 2DQHAF on a square lattice as a function of the ratio J_2/J_1 of the superexchange couplings. (b) Structure of LSVO and LGVO projected along [001]. $(Si,Ge)O_4$ tetrahedra are in grey, VO_5 pyramids are in black, while the grey circles indicate Li^+ position. For details see Ref. [8].

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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 [8] suggests that both the couplings between first and second neighbors can be significant. It is, however, difficult *a priori* to decide which one should dominate: first neighbors are connected by two superexchange channels, but they are located in pyramids pointing in opposite directions and are not exactly in the same plane, whereas second neighbors are connected by only one channel, but are located in pyramids pointing 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 [9], and the maximum occurs at $T_{\max} \simeq 0.935J$. Since in that case the Curie-Weiss temperature $\Theta = J$ one has a ratio $T_{\max}/\Theta \simeq 0.935$. Now,

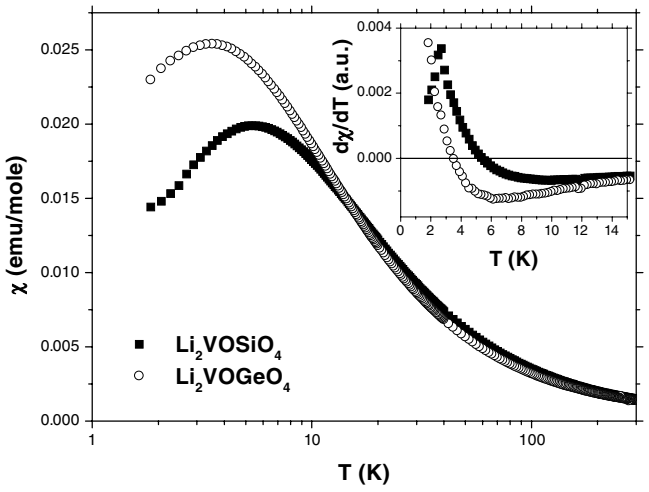

FIG. 2. Temperature dependence of the magnetic susceptibility $\chi = M/H$, for $H = 0.3$ T, in LSVO (closed squares) and LGVO (open circles) powders. In the inset the temperature dependence of the derivative $d\chi/dT$ is reported.

while $T_{\max}$ is known very accurately from our measurements, the precise determination of Θ is more problematic. A simple fit with $\chi(T) = \chi_{VV} + C/(T + \Theta)$, with χ_{VV} 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, Θ depends very weakly on the lowest temperature and a precise estimate of the Curie-Weiss temperature can be achieved. The results are $\Theta \simeq 7.4$ K for LSVO and $\Theta \simeq 5.2$ K for LGVO [10]. Accordingly, the ratios $T_{\max}/\Theta$ 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 sizable 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 $T_{\max}/\Theta$ 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 $J_2/J_1 \simeq 1/2$, but exact diagonalizations with three sizes available (4, 8, and 16 sites) give a reliable estimate for $J_2/J_1 < 0.4$, while quantum Monte Carlo simulations, which suffer from the minus sign problem, provide useful information down to $J_2/J_1 \simeq 2$ 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 $T_{\max}/\Theta = 0.72$ for LSVO then implies that J_2/J_1 is approximately equal to 0.1 or to 3.5, while for LGVO, $T_{\max}/\Theta = 0.67$ implies that J_2/J_1 is close to either 0.25 or 2.5.

A significant difference between the two compounds is discernible if one reports the derivative $d\chi/dT$ vs T (see the inset of Fig. 2). One observes that around $T_c \simeq 2.83$ 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}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 ± 0.15 K (i.e., $\pm 5\%$), up to $H = 7$ T.

In LSVO, for $H = 1.8$ T, one observes that ^{7}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 [11]

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

with A_{ij} $(i = x, y, z,\ j = x, y)$ the components of the hyperfine tensor due to the kth V^{4+}, γ the gyromagnetic

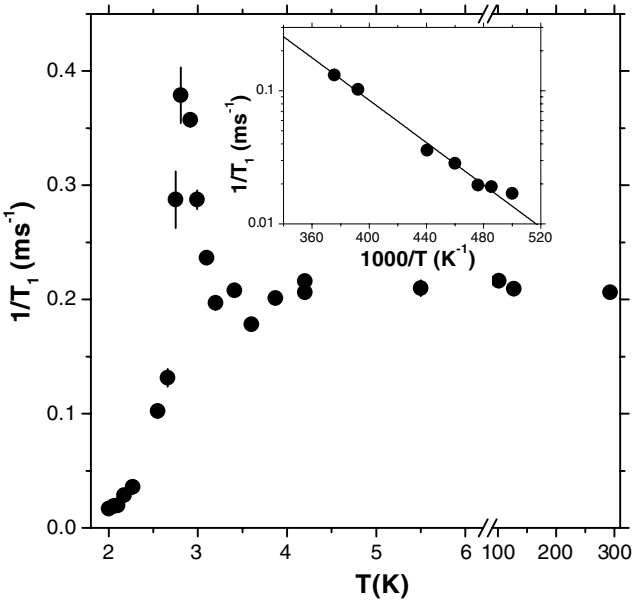

FIG. 3. Temperature dependence of ^{7}Li NMR $1/T_1$ for $H = 1.8$ T along the c axis in a LSVO single crystal. In the inset we report the corresponding Arrhenius plot of the experimental data for $T \leq 2.66$ K. The error bars when not reported are within the circles.

ratio, and $\omega_E = Jk_B\sqrt{2zS(S+1)/3}/\hbar$. $z = 8$ is the number of nearest neighbor spins of a V^{4+} coupled via an effective superexchange coupling J related to J_1 and J_2. ^{7}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}Li nuclei are coupled to V^{4+} ions via both a dipolar and a transferred hyperfine coupling $A_T = 1700$ G [12], which is attributed to the two V^{4+} nearest neighbors. 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 $T < \Theta$, V^{4+} spins are strongly correlated and the behavior of $1/T_1$ depends on which regime LSVO is, as follows: quantum critical, renormalized classical, or quantum disordered [13]. However, one has to notice that the temperature dependence of $1/T_1$ can be strongly influenced by the q-dependent hyperfine form factor [14]. 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 sizable 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 $\simeq 3$ K suggests that LSVO, for $H = 1.8$ T, is in the quantum critical regime [13].

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 [15]. An estimate of the gap amplitude can be done using a simple Arrhenius fit, which yields $\Delta = 18$ K (see the inset of Fig. 3). Although the estimate of Δ 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 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}Si NMR powder spectra below $\simeq 3.4$ K (see Fig. 4a). One observes, just above T_c the appearance of a shifted narrow peak in ^{29}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 noted: (1) ^{29}Si NMR line does not broaden below T_c indicating that the local field at ^{29}Si nuclei is zero; and (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.

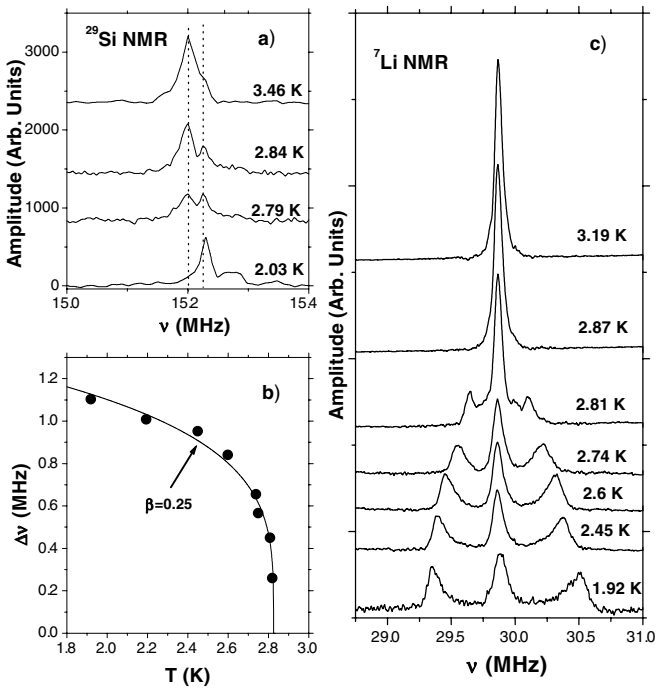

FIG. 4. (a) ^{29}Si NMR powder spectrum in LSVO for $H = 1.8$ T. The dotted lines mark the position of the peak at high and at low temperatures. (b) Temperature dependence of the splitting between the low-frequency and the high-frequency peaks for ^{7}Li NMR spectra in (c). The solid line indicates the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

The absence of a magnetic field at the ^{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 [12]. By considering the same hyperfine coupling tensor determined above T_c [16], 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 [17], 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 co-workers [3,7].* 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 fourfold 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 nonzero (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 β would require a temperature stability better than 5×10^{-3} K which could not be achieved with our cryogenic apparatus. Still an upper limit for β 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_2VOSiO_4 and Li_2VOGeO_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 $J_2/J_1 > 1/2$ [7]. 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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