Determination of the exchange energies in Li_2VOSiO_4 from a high-temperature series analysis of the square-lattice J_1-J_2 Heisenberg model

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We present a high-temperature expansion (HTE) of the magnetic susceptibility and specific heat data of Melzi *et al.* on Li_2VOSiO_4 [Phys. Rev. B **64**, 024409 (2001)]. The data are very well reproduced by the J_1-J_2 Heisenberg model on the square lattice with exchange energies $J_1=1.25\pm0.5$ K and $J_2=5.95\pm0.2$ K. The maximum of the specific heat $C_v^{\max}$ ($T_{\max}$) is obtained as a function of J_2/J_1 from an improved method based on HTE.

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I. INTRODUCTION

The vanadium oxide Li_2VOSiO_4 is a quasi-two-dimensional magnet,[1] which is well described by the spin-$\frac{1}{2}$ Heisenberg model on the square lattice with first (J_1) and second (J_2) neighbors interactions:

$$H=J_1\sum_{<i,j>}\vec{S}_i\cdot\vec{S}_j+J_2\sum_{\ll i,j\gg}\vec{S}_i\cdot\vec{S}_j. \qquad (1)$$

In their nuclear magnetic resonance (NMR) experiments Melzi *et al.*[2] found evidence for a $Q=(\pi,0)$ or $(0,\pi)$ ordering in this system, as expected in the classical spin model for $J_2>0.5J_1$ (order from disorder) and also as expected in the spin-$\frac{1}{2}$ case for $J_2\gtrsim0.6J_1$.[3] From the high temperature behavior of $\chi(T)$ the Curie-Weiss temperature $\Theta=J_1+J_2$ was estimated[4] to be $\Theta\simeq8.2\pm1$ K. Combining this information with the position of the maximum of the specific heat of the system (and comparing it to exact diagonalization data for 16 spins), Melzi *et al.*[4] estimated the ratio of exchange energies to be $J_2/J_1\simeq1.1$.

In two recent papers, Rosner *et al.*[5,6] considered the determination of J_1 and J_2 in Li_2VOSiO_4. They performed band-structure calculations (local-density approximation) and found $J_1+J_2\simeq9.5\pm1.5$ K and $J_2/J_1\simeq12$. They also computed the high-temperature expansion (HTE) of the magnetic susceptibility and of the specific heat for the Hamiltonian of Eq. (1). $\chi(T)$ and $C_v(T)$ obtained from these series at $J_2/J_1\simeq12$ are in reasonable agreement with the experimental data for $\chi(T)$ and $C_v(T)$. Rosner *et al.*[5] did not use the HTE to fit the data in the high-temperature region ($T>20$ K) because they could not find a Curie law behavior. Melzi *et al.* indeed had to subtract a temperature-independent constant to recover a $1/T$ behavior at high temperature. This term is due to the Van-Vleck paramagnetism (spin-orbit coupling effect) and its magnitude is typical for a V^{4+} ion in a pyramidal environment.[4] It is of course crucial to exploit the high-temperature region of the experimental data in order to take full advantage of the HTE. In this work we show that the HTE for the susceptibility allows us to determine the exchange energies in Li_2VOSiO_4. We show that this method is an unbiased way of determining the microscopic parameters of this model. As a result we find a ratio $J_2/J_1\simeq5$, which is significantly different from the value 12 predicted previously.[5,6] We checked this result by a calculation of the specific heat. For this purpose we employed a recent technique[7] that extends the convergence of the series to low temperatures by using two constraints related to the total entropy of the system and to its ground-state energy.

II. HIGH-TEMPERATURE SERIES AND EXTRAPOLATION

The series for $\chi(T)$ and $C_v(T)$ are computed in the standard way by a cluster expansion method to order $1/T^{11}$. Each coefficient is a rational number and is computed exactly (series available upon request). These series were computed independently in Ref. 6 to order $1/T^{10}$ and our results agree with their results.

III. FIT OF THE SUSCEPTIBILITY

In the first step we fit the susceptibility data of Melzi *et al.*[2] by the following procedure.

(1) *Temperature range of the fit*. The experimental data are fitted over a fixed temperature range $[T_{\min},T_{\max}]$ where $T_{\max}=300$ K is the highest available temperature available in Ref. 2 and $T_{\min}$ is determined self-consistently so that the susceptibilities calculated from the HTE are well converged down to $T_{\min}$ when J_1 and J_2 are close to the optimal parameters. A rather high $T_{\min}=8$ K is chosen for the first global scan of Fig. 1; this ensures that the calculated $\chi(T)$ is well converged in the whole interval whatever (J_1,J_2). Once the relevant region in J_1-J_2 space is identified, $T_{\min}$ is lowered down to $T_{\min}=5.5$ K, a temperature still above that where

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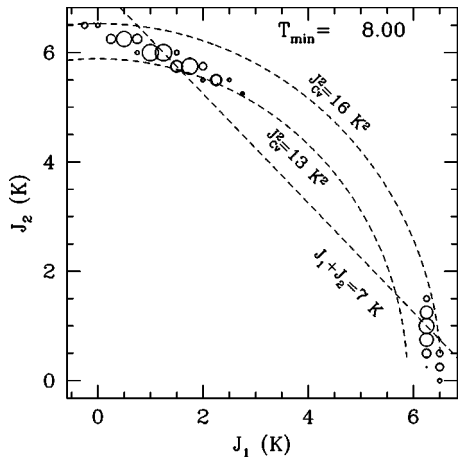

FIG. 1. Quality of the susceptibility fit as a function of J_1 and J_2. The biggest circles correspond best fits. Two regions around $J_2 \sim 6$ K and $J_1 \sim 1$ K (resp. $J_2 \sim 1$ K and $J_1 \sim 6$ K) appear to be compatible with the data on Li_2VOSiO_4. The radius of the circles are proportional to $r = 8\Sigma^2_{\min} - \Sigma^2$, where Σ^2 is the mean square difference between the theoretical curve and experimental data and $\Sigma^2_{\min}$ corresponds to the optimal (smallest value of Σ^2). Parameters that give $r<0$ are not represented. Dashed circles : $J^2_{C_v} = 14.5 \pm 1.5$ K^2. The dashed line corresponds to a Curie-Weiss temperature $J_1 + J_2 = 7$ K.

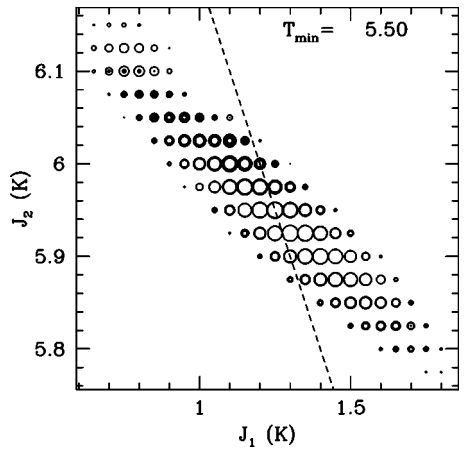

FIG. 2. Quality of the susceptibility fit as a function of J_1 and J_2. Same as Fig. 1. When several concentric circles are visible, some Padé approximants are significantly different from the others at low temperature. The points fall in the rectangle defined by $J_1 + 3.25J_2 = 20.59 \pm 0.11$ K and $J_2 - 3.25J_1 = 1.9 \pm 1.8$ K.

the various approximants (Padé) start to differ from each other.

(2) *Scan over J_1 and J_2*. For each set of couplings, the HTE for $\chi(T)$ (including $1/T^{11}$ order) is extrapolated by all possible Padé approximants. The rational fractions which have (spurious) poles in the interval $[T_{\min}, T_{\max}]$ are discarded.

(3) *Measure of the error*. The experimental data χ^{exp} are compared with $\chi_{VV} + C_0\chi^{th}(T)$, where χ_{VV} is a temperature-independent Van-Vleck term and C_0 is the Curie constant. For each value of (J_1, J_2) and for each Padé the parameters χ_{VV} and C_0 are determined to ensure the best possible fit. The quality of the fit is measured in a standard way through $\Sigma^2 = \Sigma_{T_{\min} \leq T_i \leq T_{\max}} [C_0\chi(T_i) + \chi_{VV} - \chi^{exp}(T_i)]^2$.

Figure 1 shows that two regions of the parameter space are compatible with the susceptibility of the J_1-J_2 model. The points where Σ^2 is larger than eight times its smallest value (fit of poor quality) are not displayed. It turns out that the Padé approximants to the susceptibility converge down to $T \simeq 5.5$ K in the two "patches" of Fig. 1. For this reason $T_{\min}$ can be lowered down to 5.5 K to refine the scans. Although both regions give fits of comparable quality, the existence of $(\pi, 0)$ magnetic ordering in Li_2VOSiO_4 as well as the results of Ref. 5 make the $J_1 > J_2$ scenario extremely unlikely. For this reason we will only focus on the region $J_1 \simeq 1.25$ K and $J_2 \simeq 6$ K in the following.[8] The refined scan is shown in Fig. 2. The susceptibility obtained from the HTE is compared with the experimental results in Fig. 3. The Van-Vleck susceptibility and the Curie constant are parameters of the fit and the optimal values ($\chi_{VV} = 4.014\ 10^{-4}$ emu/mol, $C_0 = 0.333$ emu/mol) are in complete agreement with Ref. 4. In order to estimate the quality of the fit in the high-temperature region where the HTE is almost exact, we subtracted the $1/T$ Curie term from the theoretical curve as well as from the experimental data. Even when the leading Curie term is subtracted (bottom of Fig. 3), the deviation of the Padé approximants from the experimental results remains within experimental error bars.

IV. SPECIFIC HEAT

At high temperature, the specific heat of the J_1-J_2 model behaves as[6]

$$C_v/(Nk_B) \sim \left(\frac{J_{C_v}}{T}\right)^2 = \frac{3}{8}(J_1^2 + J_2^2)\frac{1}{T^2}. \qquad (2)$$

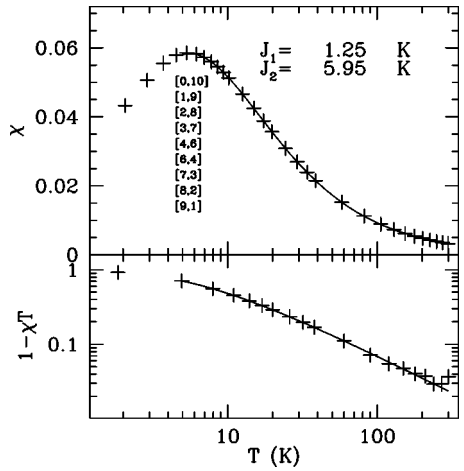

FIG. 3. Top: Experimental susceptibility (crosses) compared to the HTE calculation (full lines). The different Padé approximants (degrees $[u,d]$ indicated) are not distinguishable at the scale of the figure for $T > 7$ K. The best fit is obtained for Curie constant $C_0 = 0.333$ emu/mol, Van Vleck susceptibility $\chi_{VV} = 4.014 \times 10^{-4}$ emu/mol. Bottom: Deviation from the Curie law (same data as top panel).

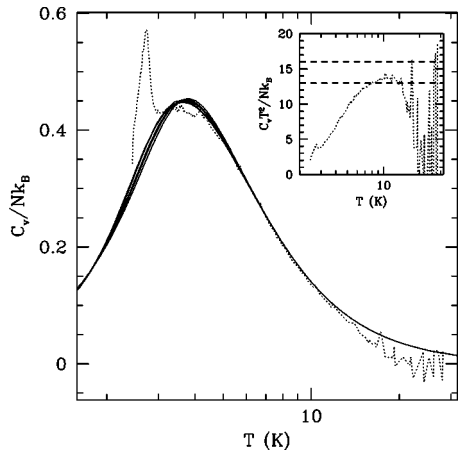

FIG. 4. Specific heat. Full lines: Theoretical prediction for $J_1 = 1.25$ K and $J_2 = 5.95$ K. The different lines correspond to different Padés approximants. Their dispersion is a measure of the error bars. Dotted line: Experimental data. Inset: Experimental specific heat multiplied by T^2. We estimate that $C_v T^2/Nk_B \rightarrow 14.5 \pm 1.5$ K^2 (horizontal lines). The agreement between the calculated C_v and the experimental data can easily be improved (data not shown) at high temperatures by changing slightly the T^3 contribution (phonons) that was subtracted from the raw data (Ref. 4).

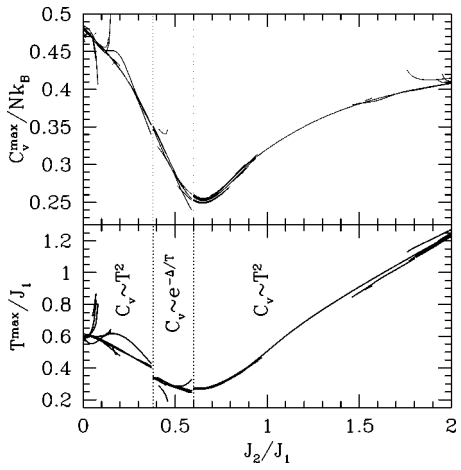

FIG. 5. Maximum of the specific heat and temperature of that maximum as functions of J_2/J_1. The different curves correspond to the different Padé approximants at order $1/T^{11}$. The regions where the model is assumed to have a $\sim T^2$ or $\sim e^{-\Delta/T}$ specific heat are indicated.

Although the specific heat data are not very accurate at high temperatures due to the subtraction of the phonon contribution, a plot of $C_v T^2$ shows (see inset of Fig. 4) that $J^2_{C_v} \simeq 14.5 \pm 1.5$ K^2. This constrains the values of J_1 and J_2 to lie between the two large circles in Fig. 1, which is compatible with the independent fit performed on the susceptibility.

The specific heat is obtained from the HTE, as described in Ref. 7, and will not be reviewed here. In addition to the series itself, this method requires the knowledge of three quantities.

(1) The total entropy, that is ln(2) per site. This means $\int_0^\infty C_v(T)/T dT = Nk_B \ln(2)$.

(2) Ground-state energy per site e_0 of the Hamiltonian. Since the energy of Eq. (1) is zero at infinite temperature we have $\int_0^\infty C_v(T) dT = -Ne_0$.

(3) The low-temperature behavior of $C_v(T)$. It behaves as $\sim T^2$ when the ground-state is Néel long-ranged ordered and as $\sim \exp(-\Delta/T)$ when the spectrum is gapped.

The ground-state energy of the first-neighbor Heisenberg antiferromagnet on the square lattice is known very accurately from quantum Monte Carlo simulations:[9] $e_0 = -0.6694 J_1$. This result also applies to the infinite J_2 limit of the J_1-J_2 model. In the frustrated case the ground-state energy has been computed by different numerical techniques, such as zero-temperature series expansion.[10] From these results we constructed a simple ansatz which interpolates between the pure-J_1 and pure-J_2 models:

$$e_0 = \alpha_1 J_1 + \alpha_2 J_2 - \sqrt{(\alpha_{11} J_1^2 + \alpha_{22} J_2^2 + \alpha_{12} J_1 J_2)}, \qquad (3)$$

with $\alpha_1 = -0.3135$, $\alpha_2 = -0.1207$, $\alpha_{11} = 0.1267$, $\alpha_{22} = 0.3011$, and $\alpha_{12} = -0.3722$. The comparison between the different approximants for the specific heat (with $C_v \sim T^2$) at $J_1 = 1.25$ K and $J_2 = 5.95$ K and the experimental data is shown in Fig. 4. Unlike usual Padé approximants directly constructed on the HTE of the specific heat, our procedure[7] leads to accurate results (with a relative error smaller than a few percents) down to zero temperature. The agreement with the experimental data is very good for $T > 4.5$ K (no adjustable parameter). On the other hand, we checked that the flat maximum observed in the experiment between 3 K and 4 K can hardly be accounted for by the J_1-J_2 Heisenberg model, whatever the couplings. This is a serious indication of a structural distortion (above $T_c \simeq 2.8$ K corresponding to the three-dimensional magnetic ordering of the system), as suggested by Melzi *et al.*[4] from the analysis of the NMR spectra and by Becca and Mila[11] from the theoretical point of view.

When one of the J's is much larger than the other, the specific heat and the magnetic susceptibility are found to be nearly symmetric under the exchange $J_1 \leftrightarrow J_2$ (at least at no too low temperatures). Thus, this analysis cannot strictly discriminate between the two patches of Fig. 1. Nevertheless, $J_2 > J_1$ gives slightly better fits.

$C_v(T)$ for arbitrary J_2/J_1. The specific heat is computed by the method above in a large range of coupling J_2/J_1. The behavior of C_v at low temperatures is assumed to be (i) $C_v \sim T^2$ for $J_2/J_1 \lesssim 0.38$ (corresponding to an ordered antiferromagnet) (ii) $C_v \sim \exp(-\Delta/T)$ for $0.38 \lesssim J_2/J_1 \lesssim 0.6$ (gapped region[3]) and (iii) $C_v \sim T^2$ for $0.6 \lesssim J_2/J_1$ (ordered antiferromagnet). The ground-state energy is approximated by Eq. (3). The results are summarized in Fig. 5 where the value $C_v^{\max}$ of the maximum of the specific heat and the temperature $T^{\max}$ at which C_v reaches its maximum are displayed. The dispersion of the different approximants is again an estimate of the error. The discontinuities in the curves are due to the fact that the Padé approximants that develop zeros or poles in the physical energy interval cannot be considered.[7] The results for $C_v^{\max}$ and $T^{\max}$ represent a significant improvement over the estimate made in Ref. 4. The shape of the specific heat appears to be relatively independent of J_2/J_1 when $J_2 \gtrsim 2J_1$ but some interesting structure

appear in the strongly frustrated region around $J_2 \simeq 0.5 J_1$. The existence of a low $C_v^{\max}$ is indeed compensated by a small $T^{\max}$ to conserve the total entropy. This shift of the entropy to lower temperatures and lower energies is indeed expected close to quantum phase transitions and in frustrated systems in general.

V. CONCLUSIONS

We have computed the HTE for the uniform susceptibility of the J_1-J_2 Heisenberg model on the square lattice up to order $1/T^{11}$ and obtained $J_1 = 1.25 \pm 0.5$ K and $J_2 = 5.95 \pm 0.2$ K by fitting the experimental data of Li_2VOSiO_4. The HTE for the specific heat to the same order and an improved method allowed us to extrapolate $C_v(T)$ down to $T=0$. A good agreement is found with the experimental data of Li_2VOSiO_4 for $T \gtrsim 4.5$ K. Below that temperature the specific heat slightly differs from our results on J_1-J_2 Heisenberg model, which is consistent with the lattice distortion transition observed by Melzi *et al.*;[4] Chandra, Coleman, and Larkin[12] predicted an Ising-like finite temperature phase transition in the classical and quantum J_1-J_2 Heisenberg models. We could not find such a transition in the present calculations on the quantum model but some work is in progress to investigate thoroughly this question.[13]

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