Determination of the exchange energies in Li$_2$VOSiO$_4$ from a high-temperature series analysis of the square lattice $J_1$-$J_2$ Heisenberg model.

G. Misguich
Service de Physique Théorique, CEA/DSM/SPhT – URA 2306 of CNRS.
CEA/Saclay, 91191 Gif-sur-Yvette Cédex, FRANCE

B. Bernu
Laboratoire de Physique Théorique des Liquides,
Université Paris-VI – URA 765 of CNRS.
75252 Paris Cédex, FRANCE.

L. Pierre
Université Paris-X – UMR 7600 of CNRS
92001 Nanterre Cédex, FRANCE.

We present a high-temperature expansion (HTE) of the magnetic susceptibility and specific heat data of Melzi et al. on Li$_2$VOSiO$_4$ [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 $J_1 = 1.25 \pm 0.5$ K and $J_2 = 5.95 \pm 0.2$ K. The maximum of the specific heat $C_v(T_{\text{max}})$ is obtained as a function $J_2/J_1$ from an improved method based on HTE.

PACS numbers: 75.10.Jm 75.50.Ee

I. INTRODUCTION

The vanadium oxide Li$_2$VOSiO$_4$ is a quasi two-dimensional magnet 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:

\[ H = J_1 \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j + J_2 \sum_{\langle\langle i,j \rangle\rangle} \vec{S}_i \cdot \vec{S}_j \] (1)

In their NMR experiments Melzi et al. 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 $J_2 \gtrsim 0.6J_1$. From the high temperature behavior of $\chi(T)$ the Curie-Weiss temperature $\Theta = J_1 + J_2$ was estimated to be $\Theta \approx 8.2 \pm 1$ 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. estimated the ratio of exchange energies to be $J_2/J_1 \approx 1.1$.

In two recent papers, Rosner et al. considered the determination of $J_1$ and $J_2$ in Li$_2$VOSiO$_4$. They performed band-structure calculations (local-density approximation) and found $J_1 + J_2 \approx 9.5 \pm 1.5$ K and $J_2/J_1 \approx 12$. They also computed the high-temperature expansion (HTE) of the magnetic susceptibility and of the specific heat for the Hamiltonian of Eq. (1). The $\chi(T)$ and $C_v(T)$ obtained from these series at $J_2/J_1 \approx 12$ are in reasonable agreement with the experimental data for $\chi(T)$ and $C_v(T)$. Rosner et al. 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.

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 $1/T^3$. Each coefficient is a rational number and is computed exactly (series available upon request). These series were computed independently in Ref. 3 to order $1/T^3$ and our results agree with their.

III. FIT OF THE SUSCEPTIBILITY

In the first step we fit the susceptibility data of Melzi et al. by the following procedure:
• **Temperature range of the fit.** The experimental data are fitted over a fixed temperature range \([T_{\text{min}}, T_{\text{max}}]\) where \(T_{\text{max}} = 300\,\text{K}\) is the highest available temperature available in Ref. \cite{2} and \(T_{\text{min}}\) is determined self-consistently so that the susceptibilities calculated from the HTE are well converged down to \(T_{\text{min}}\) when \(J_1\) and \(J_2\) are close to the optimal parameters. A rather high \(T_{\text{min}} = 8\,\text{K}\) is chosen for the first global scan of Fig. \ref{fig:fig1} this insures 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, \(T_{\text{min}}\) is lowered down to \(T_{\text{min}} = 5.5\,\text{K}\), a temperature still above that where the various approximants approximants (Padé) start to differ from each other.

• **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 \([T_{\text{min}}, T_{\text{max}}]\) are discarded.

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

The figure \ref{fig:fig1} shows that two regions of the parameter space are compatible with the susceptibility of the \(J_1-J_2\) model. The points where \(\Sigma^2\) 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 \(T \approx 5.5\,\text{K}\) in the two “patches” of Fig. \ref{fig:fig1}. For this reason \(T_{\text{min}}\) can be lowered down to \(5.5\,\text{K}\) to refine the scans. Although both regions give fits of comparable quality, the existence of \((\pi, 0)\) magnetic ordering in \(\text{Li}_2\text{VOSiO}_4\) as well as the results of Ref. \cite{5} make the \(J_1 > J_2\) scenario extremely unlikely. For this reason we will only focus on the region \(J_1 \approx 1.25\,\text{K}\) and \(J_2 \approx 6\,\text{K}\) in the following. The refined scan is shown in Fig. 2. The susceptibility obtained from the HTE is compared with the experimental results in Fig. \ref{fig:fig2}.

The Van-Vleck susceptibility and Curie constant are parameters of the fit and the optimal values are in complete agreement with Ref. \cite{2}. 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. \ref{fig:fig2}), the deviation of the Padé approximants from the experimental results remains within experimental error bars.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Quality of the susceptibility fit as a function of \(J_1\) and \(J_2\). The biggest circles correspond best fits. Two regions which give \(r < 0\) are not represented. Dashed circles: \(J^2 = 14.5 \pm 1.5\,\text{K}^2\). The dashed line corresponds to a Curie-Weiss temperature \(J_1 + J_2 = 7\,\text{K}\).}
\end{figure}

\section{IV. Specific Heat}

At high temperature, the specific heat of the \(J_1-J_2\) model behaves as:

\[ C_v/(Nk_B) \sim \left( \frac{J_{C_v}}{T} \right)^2 = \frac{3}{8} \frac{(J_1^2 + J_2^2)}{T^2} \]

(2)

Although the specific heat data are not very accurate at high temperatures due to the subtraction of the phonon contribution, a plot of \(C_vT^2\) shows (see inset of Fig. \ref{fig:fig4}) that \(J_{C_v} \approx 14.5 \pm 1.5\,\text{K}^2\). This constrains the values of \(J_1\) and \(J_2\) to lie between the two large circles in Fig. \ref{fig:fig1} which is compatible with the independent fit performed on the susceptibility.

The specific heat is obtained from the HTE as described in Ref. \cite{2} and will not be reviewed here. In addition to the series itself, this method requires the knowledge of three quantities:

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

• Ground-state energy per site \(e_0\) of the Hamiltonian. Since the energy of Eq. \ref{eq:energy} is zero at infinite temperature we have \(\int_0^\infty C_v(T)\,dT = -Ne_0\).

• The low-temperature behavior of \(C_v(T)\). It behaves as \(\sim T^2\) (resp. \(\sim \exp(-\Delta/T)\)) when the ground-state is Néel long-ranged ordered (resp. gapped).
The ground-state energy of the first-neighbor Heisenberg antiferromagnet on the square lattice is known very accurately from quantum Monte Carlo simulations. $e_0 = -0.6694 J_1$. 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. From these results we constructed a simple ansatz which interpolates between the pure-$J_1$ and pure-$J_2$ models:

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

with $\alpha_1 = -0.3135$, $\alpha_2 = -0.1207$, $\alpha_{11} = 0.1267$, $\alpha_{22} = 0.3011$ and $\alpha_{12} = -0.3762$. 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 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 $T_c \approx 2.8$ K corresponding to the (3D) magnetic ordering of the system), as suggested by Melzi et al. from the analysis of the NMR spectra and by Becca and Milan 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 comp-
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 $\sim T^2$ (resp.
$\sim e^{-\Delta/T}$) specific heat are indicated.

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) 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 the value $C_v^{\text{max}}$ of the maximum of the specific heat and the temperature $T^{\text{max}}$ 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 which develop zeros or poles in the physical energy interval cannot be considered.

The results for $C_v^{\text{max}}$ and $T^{\text{max}}$ 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 $J_2 \simeq 0.5J_1$. The existence of a low $C_v^{\text{max}}$ is indeed compensated by a small $T^{\text{max}}$ to conserve the total entropy. This shift of the entropy to lower temperatures and lowered 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$_2$VOSiO$_4$. 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$_2$VOSiO$_4$ 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. Chandra, Coleman and Larkin 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.

Acknowledgments.— It is a pleasure to thank Roberto Melzi and Philippe Mendels for fruitful discussions concerning the analysis of the experimental data.

* Electronic address: gmisguich@cea.fr
† Electronic address: bernu@lptl.jussieu.fr
‡ Electronic address: ipierre@lptl.jussieu.fr

1 P. Millet and C. Satto, Mater. Res. Bull. 33, 1339 (1998).
2 R. Melzi, P. Carretta, A. Lascialfari, M. Mambrini, M. Troyer, P. Millet, and F. Mila, Phys. Rev. Lett. 85, 1318 (2000).
3 M. P. Gelfand, R. R. P. Singh, and D. A. Huse, Phys. Rev. B 40 10801 (1989); M. P. Gelfand, 42 8206 (1990); J. Oitmaa and Z. Wei, Phys. Rev. B 54, 3022 (1996).
4 R. Melzi, S. Aldrovandi, F. Tedoldi, and P. Carretta, P. Millet, and F. Mila, Phys. Rev. B 64, 024409 (2001).
5 H. Rosner, R. P. Singh, W. H. Zheng, J. Oitmaa, S-L. Drechsler, and W. E. Pickett, Phys. Rev. Lett. 88, 186405 (2002).
6 H. Rosner, R. R. P. Singh, W. H. Zheng, J. Oitmaa, and W. E. Pickett Phys. Rev. B 67, 014416 (2003).
7 B. Bernu and G. Misguich, Phys. Rev. B 63, 134409 (2001).
8 K. J. Runge, Phys. Rev. B 45, 12292 (1992). A. W. Sandvik, Phys. Rev. B 56, 11678 (1997). M. Calandra and S. Sorella, Phys. Rev. B 57, 11446 (1998).
9 R. R. P. Singh, Z. Wei, H. C. J. Hamer, and J. Oitmaa, Phys. Rev. B 60, 7278 (1999).
10 F. Becca and F. Mila, Phys. Rev. Lett. 89, 037204 (2002).
11 P. Chandra, P. Coleman, and A. I. Larkin, Phys. Rev. Lett. 64, 88 (1990).
12 We thank F. Mila for pointing this possibility to us.