Magnetic properties of NaV$_2$O$_5$, a one-dimensional spin 1/2 antiferromagnet with finite chains

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Abstract

We have performed measurements of the magnetic susceptibility of NaV$_2$O$_5$ between 2 and 400 K. The high temperature part is typical of spin 1/2 chains with a nearest–neighbour antiferromagnetic exchange integral $J$ of 529 K. We develop a model for the susceptibility of a system with finite chains to account for the low temperature part of the data, which cannot be fitted by a standard Curie-Weiss term. These results suggest that the next nearest–neighbour exchange integral $J_2$ in CaV$_4$O$_9$ should be of the order of 500 K because, like $J$ in NaV$_2$O$_5$, it corresponds to corner sharing VO$_5$ square pyramids.

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The report by Taniguchi et al. [1] of a spin gap behaviour in the quasi-two dimensional system CaV$_4$O$_9$ has triggered an intensive theoretical activity aimed at understanding the origin of this gap [2–8]. The emerging picture is that there is no spin gap in the model with only exchange integrals $J_1$ between nearest neighbours [3,4,5], and that there is a spin gap if a coupling constant to second neighbours $J_2$ is included as long as $0.2 \leq J_2/J_1 \leq 0.7$ [4,5,7]. To check this theory, one needs information on the value of the exchange integrals. This information turns out to be difficult to extract from the susceptibility. The best calculation of the temperature dependence of the susceptibility of that model is a high temperature expansion due to Gelfand et al. [8]. Assuming $J_2/J_1 = 1/2$, they could reproduce the maximum of the susceptibility around 100 K with $J_1 \approx 200$ K. The fit of the high temperature part is not satisfactory however, and the question of the value of the integrals is still pretty much open.

CaV$_4$O$_9$ is actually a member of a large family of vanadium oxides studied by Galy and coworkers in the mid seventies [10], and a natural idea is to look at other members of the family to try to get information on the exchange integrals. The other 2D compounds that can be synthesized with Ca, CaV$_2$O$_5$ and CaV$_3$O$_7$, lead to a similarly difficult problem because they involve both $J_1$ and $J_2$. This difficulty can be overcome by studying another mixed valence vanadium oxide, NaV$_2$O$_5$. This compound, first synthesized by Hardy et al. [11], is isostructural to CaV$_2$O$_5$. Note however that NaV$_2$O$_5$ crystallizes with the orthorhombic non centro-symmetric space group P2mn, while CaV$_2$O$_5$ crystallizes with the centro-symmetric space group Pmmm. Now, NaV$_2$O$_5$ contains Na$^+$ instead of Ca$^{2+}$, and half the vanadium have to be in the oxydation state V$^{5+}$ (formally one has NaV$^{5+}$V$^{4+}$O$_5$). These ions do not carry a spin, while remaining V$^{4+}$ carry a spin $1/2$ and form a set of well separated chains of corner sharing VO$_5$ square pyramids (SP) (see Fig. 1). The magnetic properties should thus be well described by the one-dimensional spin $1/2$ Heisenberg model:

\[ H = J \sum_i \vec{S}_i \cdot \vec{S}_{i+1} \]  

(1)

Note that the exchange integral $J$ between corner sharing VO$_5$ SP is equivalent to the
next-nearest neighbour exchange integral $J_2$ of CaV$_4$O$_9$.

In this Letter, we present measurements of the magnetic susceptibility of NaV$_2$O$_5$ from 2 to 400 K. The compound was prepared starting from a stoichiometric mixture of NaVO$_3$ (Merck, min 99%), V$_2$O$_3$ (obtained by hydrogen reduction of V$_2$O$_5$ at 800 °C) and V$_2$O$_5$ (Aldrich Chem. Co., 99.9%). The mixture was ground intimately, sealed in an evacuated quartz tube and then heated for 10 hours at 615 °C. The X-ray diffraction pattern of the resulting dark powder indicated the formation of the pure phase NaV$_2$O$_5$. A refinement of the structure of NaV$_2$O$_5$ was proposed by Carpy and Galy [12]. It is orthorhombic and consists, as shown on the perspective view in fig. 1a), of two dimensionnal layers of VO$_5$ SP with the Na atoms between the layers. It is worth mentioning in this structure the ordering of the V$^{4+}$ and V$^{5+}$ atoms in the layers with formation of rows (Fig. 1b)). Magnetic susceptibility measurements were performed using a SQUID susceptometer. The magnetic field intensity was 1kG. The molar susceptibilities were corrected for diamagnetism by using Pascal’s constants.

The raw data are presented in Fig. 2. They agree with the early measurements between 80 and 600 K by Carpy et al [13]. Above 100 K, the susceptibility is consistent with that of a spin 1/2 chain [14][15]. In that temperature range, the best available estimate of the susceptibility due to Eggert et al [15] is actually indistinguishable from the Bonner-Fisher result [14], so it does not matter which theory we use to fit the data. There is a maximum at 350 K which implies an exchange integral $J \simeq 529$ K.

Below that temperature, there is no evidence of a phase transition or of three dimensional ordering, but, as usual, there is an increase of the susceptibility at low temperature due to some kind of defects. The standard procedure is to describe these defects by a Curie-Weiss term $\chi^{CW}(T) = g^2 \mu_B^2 S(S+1)/3k_B(T-\theta)$, so that the spin part of the susceptibility reads:

$$\chi^{tot}(T) = (1-\rho)\chi^\infty(T) + \rho\chi^{CW}(T) + \chi^{VV}$$

(2)

$\chi^{VV}$ is the temperature independent Van Vleck paramagnetic susceptibility, $\rho$ is the concentration of impurities, and $\chi^\infty(T)$ is the susceptibility of the infinite chain. At low tempera-
tured, the difference between the Bonner-Fisher estimate and the recent results of Eggert et al. is not negligible, and we have used the results of Eggert et al for $\chi^\infty(T)$. It turns out that the low temperature part of the susceptibility cannot be fitted satisfactorily along these lines. The best fit one can get using Eq. (2) is depicted as a dashed line in Fig. (2). It considerably overestimates the actual susceptibility around the minimum at 70 K.

The main problem is that the amount of impurities one needs to interpret the low temperature susceptibility gives a much too large contribution at higher temperatures. In other words, the susceptibility behaves as if the impurities were slowly disappearing when the temperature increases. While this clearly cannot be reconciled with extrinsic impurities, such a behaviour actually makes sense if the impurity contribution comes from finite chains with an odd number of sites. The idea is the following: Roughly speaking, a finite-length chain with $N$ spins behaves like an infinite one at temperatures larger than the finite-size gap, and like a finite one below that temperature. Now, the finite size gap is of order $J/N$. So if we have a distribution of finite chains with different lengths, they will progressively disappear from the impurity term to contribute to $\chi^\infty(T)$ as the temperature is increased.

To be more quantitative, we need to know the distribution of length of the finite chains. If we make the reasonable assumption that the finite chains are due to a random distribution of point defects, then elementary statistical mechanics shows that the distribution of length is of the form

$$P(N) = \frac{\exp(-\lambda N)}{Z}$$

where the partition function $Z = (1 - \exp(-\lambda))^{-1}$ while the Lagrange parameter $\lambda$ is fixed by the average number of sites $N_0$ of the chains according to $\lambda = \log(1 + 1/N_0) \simeq 1/N_0$ if $N_0 \gg 1$. The average number of sites of the chains is itself related to the concentration $\rho$ of defects by $N_0 = 1/\rho$. Then the total susceptibility per spin is simply given by $\chi(T) = (1/N_0) \sum_N P(N) \chi_N(T)$ where $\chi_N(T)$ is the susceptibility of a chain of length $N$.

Numerical calculations of $\chi_N(T)$ are indeed possible, but even with today’s numerical facilities, accurate results would be limited to relatively short chains. However, a good
estimate can be obtained in the following way. At low enough temperature, a finite chain with an odd number of sites behaves like a spin 1/2 impurity according to Curie’s law
\[ \chi^{\text{Curie}}(T) = g^2 \mu_B^2 S(S+1)/3k_B T, \]
while the susceptibility of a chain with an even number of sites vanishes exponentially. Averaging the susceptibility according to
\[ \chi_T = \frac{1}{2}(\chi_N + \chi_{N+1}), \]
and neglecting the exponentially small contribution of the even chain, the susceptibility of finite chains is given by
\[ \chi_T(T) = \chi^{\text{Curie}}(T)/2 \]
at low temperature and \( \chi_T(T) = N\chi^\infty(T) \)
at high temperature. So, if we define the cross-over temperature \( T_c(N) \) as the temperature where these two expressions are equal, we can approximate \( \chi(T) \) by \( \chi^{\text{Curie}}(T)/2 \) if \( T < T_c(N) \) and \( N\chi^\infty(T) \) if \( T > T_c(N) \). Equivalently, one can define a length scale \( L(T) \) by
\[ k_B T_c(L(T)/a) = J, \]
where \( a \) is the lattice parameter. Then, for a given temperature \( T \), \( \chi_N(T) \) will be given by \( N\chi^\infty(T) \) if \( N > L(T)/a \) and by \( \chi^{\text{Curie}}(T)/2 \) if \( N < L(T)/a \). Solving
\[ k_B T_c(L(T)/a) = J \]
for \( L(T) \) yields \( L(T)/a = \chi^{\text{Curie}}(T)/2\chi^\infty(T) \). This expression can be cast in a more transparent form if one writes \( \chi^\infty(T) = (g\mu_B^2 J)/(\bar{\chi}(T)) \)
where \( \bar{\chi}(T) \) is the normalized susceptibility that equals \( 1/\pi^2 \) at \( T = 0 \). In terms of this function, one has
\[ L(T)/a = (1/8\bar{\chi}(T))J/k_B T. \]
Note that \( 8\bar{\chi}(T) \) is of order 1 for \( T < J \). The cross-over temperature \( T_c(N) \simeq J/N \) is thus of the order of the finite size gap, as it should.

So, the total susceptibility per site is given by
\[ \chi(T) = (1/N_0) \left( \frac{\chi^{\text{Curie}}(T)}{2} + \sum_{N< L(T)/a} P(N) + \chi^\infty(T) \sum_{N> L(T)/a} N P(N) \right) \]
(4)
This equation is actually valid for any distribution of chain length \( P(N) \). Concentrating on the distribution of Eq. (3), the sums are readily performed: \( \sum_{N< L(T)/a} P(N) = 1 - \exp(-L(T)/a N_0) \) and \( \sum_{N> L(T)/a} N P(N) = N_0 - (N_0 + L(T)/a) \exp(-L(T)/a N_0) \). Including a VanVleck contribution, our final result for the susceptibility reads
\[ \chi^\text{tot}(T) = \frac{1 - \exp(-L(T)/a N_0)}{2 N_0} \chi^{\text{CW}}(T) + \left( 1 + \frac{L(T)}{a N_0} \right) \exp(-L(T)/a N_0) \chi^\infty(T) + \chi^{VV} \]
(5)
with \( L(T)/a = (1/8\bar{\chi}(T))J/k_B T \). We have replaced \( \chi^{\text{Curie}}(T) \) by \( \chi^{\text{CW}}(T) \) to account for possible residual interactions between the finite chains. This can be seen as an extension of Eq. (2). The concentration \( \rho = 1/N_0 \) is still an adjustable parameter. However, the
coefficients in front of $\chi^{CW}(T)$ and $\chi^\infty(T)$ are no longer simply $\rho$ and $1 - \rho$, but functions of temperature. Using Eq. (5), we have been able to obtain a much better fit of the raw experimental data. This fit is shown as a solid line on Fig. (2). The parameters are $J = 529$ K, $g = 2.043$, $\chi^{VV} = 141.10^{-6}$ ccm/mole, $N_0 = 35$ and $\theta = -1.26$ K. This value of $N_0$ corresponds to a concentration of defects $\rho = 2.9$ % which seems to be a reasonable number. The fit was realized with the help of a simplex non-linear least-squares fitting procedure, and the relative deviation defined as $\sum_i(x_i^{obs} - x_i^{calc})^2 / \sum(x_i^{obs})^2$ was equal to $3.10^{-5}$.

Let us come back to CaV$_4$O$_9$ for a moment. Our data for the susceptibility of NaV$_2$O$_5$ are consistent with the model of Eq. (1) with an exchange constant $J = 529$ K. This value should be contrasted with the values proposed for $J_2$ in the case of CaV$_4$O$_9$, which range from 50 to 100 K [3,7,8]. While one cannot exclude some dependence of the exchange integrals on the overall chemical environment, they should essentially depend on the local geometry, which is the same in NaV$_2$O$_5$ and CaV$_4$O$_9$ for corner sharing SP. Besides, the present determination of $J$ is quite unambiguous because this is the only exchange integral involved. So we are led to the conclusion that previous estimates of $J_2$ in CaV$_4$O$_9$ cannot be correct. If we put all the information we have at the moment, a consistent picture of exchange integrals can still be obtained. The presence of a gap of 107 K in CaV$_4$O$_9$, i.e. much smaller than $J_2$, can still be explained by the $J_1 - J_2$ model on the depleted lattice if $J_2/J_1$ is not too far from either of the critical values 0.2 and 0.7 where the gap disappears. Now, according to a recent work of Kontani et al [18], the observation by neutron scattering of stripe order in the compound CaV$_3$O$_7$ [13] implies that $J_2/J_1$ cannot be too small. At a quantitative level, the bound given by the modified spin-wave theory $J_2/J_1 > 0.6932$ cannot be taken too seriously, but a ratio $J_2/J_1$ close to 0.2 can be excluded because CaV$_3$O$_7$ should then exhibit Néel order. So we think that coupling constants $J_1 \simeq 700$ K and $J_2 \simeq 500$ K are the best candidates so far to describe this type of vanadium oxides. A very useful check will be to see if such values are compatible with the temperature dependences of the susceptibility reported for CaV$_3$O$_7$ [20] and CaV$_4$O$_9$ [1].

In conclusion, we have developped a theory to describe the low temperature susceptibility.
of a one-dimensional spin 1/2 antiferromagnetic system with finite chains. This theory leads to a very nice fit of the data we have obtained for NaV$_2$O$_5$. More generally, this theory should provide a much more accurate way of substracting the contribution of finite chains from the experimental data than just adding a Curie-Weiss term. This might help identify in other compounds the remarkable temperature dependence predicted by Eggert et al [15] for the infinite spin 1/2 antiferromagnetic chain and already observed in Sr$_2$CuO$_3$ according to Eggert’s reinterpretation of the experimental data [16]. It would be quite interesting to see how accurate the present theory is by performing Monte Carlo calculations of the temperature dependence of the susceptibility of finite chains. It would also be very interesting to test it on systems where the concentration of non magnetic defects that break chains can be controlled. Work along these lines on various vanadium based oxides is in progress.

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REFERENCES

[1] S. Taniguchi, T. Nishikawa, Y. Yasui, U. Kobayashi, M. Sato, T. Noshioka, M. Kontani and K. Sano, J. Phys. Soc. Jpn. 64, 2758 (1995).

[2] N. Katoh and M. Imada, J. Phys. Soc. Jpn. 64, 4105 (1995).

[3] K. Ueda, H. Kontani, M. Sigrist and P. A. Lee, Phys. Rev. Lett. 76, 1932 (1996).

[4] K. Sano and K. Takano, J. Phys. Soc. Jpn. 65, 46 (1996).

[5] M. Albrecht and F. Mila, Phys. Rev. B 53, R2945 (1996).

[6] M. Troyer, H. Kontani and K. Ueda, unpublished.

[7] O. A. Starykh, M. E. Zhitomirsky, D. I. Khomskii, R. R. P. Singh and K. Ueda, unpublished.

[8] M. Gelfand, Z. Weihong, R. R. P. Singh, J. Oitmaa and C. J. Hamer, unpublished.

[9] M. Albrecht, F. Mila and D. Poilblanc, unpublished.

[10] See J. C. Bouloux and J. Galy, J. Solid State Chem. 16, 385 (1976), and references therein.

[11] A. Hardy, J. Galy, A. Casalot and M. Pouchard, Bull. Soc. Chim. Fr. 4, 1056 (1965); J. Galy, A. Casalot, M. Pouchard, P. Hagenmuller, C. R. Acad. Sc. 262 C, 1055 (1966); M. Pouchard, A. Casalot, J. Galy et P. Hagenmuller, Bull. Soc. Chim. Fr. 11, 4343 (1967).

[12] A. Carpy and J. Galy, Acta Cryst. B31, 1481 (1975).

[13] A. Carpy, A. Casalot, M. Pouchard, J. Galy and P. Hagenmuller, J. Solid State Chem. 5, 229 (1972).

[14] J. C. Bonner and M. E. Fisher, Phys. Rev. 135, A640 (1964).

[15] S. Eggert, I. Affleck and M. Takahashi, Phys. Rev. Lett. 73, 332 (1994).
[16] S. Eggert, unpublished.

[17] For practical purposes, the function $\tilde{\chi}(T)$ can be approximated by the following analytical expression ($x = T/J$): a) $x < 0.022$: $\tilde{\chi}(T) = 1/\pi^2 + 1/(2\pi^2 \log(7.3/x))$; b) $0.022 < x < 0.3$: $\tilde{\chi}(T) = 0.1084232 + 0.0801571x - 0.318277x^2 + 1.56832x^3 - 2.00499x^4$; c) $x > 0.3$: $\tilde{\chi}(T) = 0.10062 + 0.052056x + 0.374768x^2 - 0.997104x^3 + 0.986688x^4 - 0.4912832x^5 + 0.12330496x^6 - 0.0124234x^7$. The expression for $x > 0.3$ is nothing but the fit of the Bonner-Fisher result proposed by Torrance et al (Phys. Rev. B 15, 4738 (1977)) with the appropriate rescaling of $J$ by a factor 2.

[18] H. Kontani, M. E. Zhitomirsky and K. Ueda, unpublished.

[19] H. Harashina, K. Kodama, S. Shamoto, S. Taniguchi, T. Nishikawa, M. Sato, K. Kakurai and M. Nishi, unpublished.

[20] G. Liu and J. E. Greedan, J. Solid State Chem 103, 139 (1993).
FIGURES

FIG. 1. Structure of NaV$_2$O$_5$. a) Perspective view in the [010] direction. The square pyramids occupied by V$^{4+}$ are indicated by an arrow. b) Schematic representation of the (V$_2$O$_5$)$_n$ rows along the Oy axis.

FIG. 2. Thermal variation of the molar magnetic susceptibility of NaV$_2$O$_5$. Diamonds: Experimental data; Broken line: Fit using Eq. (2); Solid line: Fit using the present theory (Eq. 5). Insert: Enlargement of the low temperature region.
