PHYSICAL REVIEW B VOLUME 54, NUMBER 17 1 NOVEMBER 1996-I

Exchange integrals of vanadates as revealed by magnetic-susceptibility measurements of NaV_2O_5

Frédéric Mila
Laboratoire de Physique Quantique, Université Paul Sabatier, 31062 Toulouse, France

Patrice Millet and Jacques Bonvoisin
Centre d'Elaboration des Matériaux et d'Etudes Structurales, Centre National de la Recherche Scientifique, 29, rue J. Marvig, 31055 Toulouse Cedex, France

(Received 3 July 1996)

In order to get information on the exchange integrals in vanadates having V^{4+} ions in a square pyramid geometry, like CaV_4O_9, we have performed measurements of the magnetic susceptibility of a one-dimensional member of the family, NaV_2O_5, whose spin dynamics is controlled by a single exchange integral J between corner-sharing VO_5 square pyramids. The high-temperature part is typical of spin-1/2 chains with a nearest-neighbor antiferromagnetic exchange integral J of 529 K. Under the reasonable assumption that the exchange between corner-sharing VO_5 square pyramids arises mainly from superexchange through O $2p$ orbitals in all vanadates, this result indicates that the next-nearest-neighbor exchange integrals in CaV_4O_9 have to be larger than 440 and 275 K for inter- and intraplaquette bonds, respectively. [S0163-1829(96)08741-3]

The report by Taniguchi *et al.*[1] of a spin-gap behavior in the quasi-two-dimensional (2D) system CaV_4O_9 (see Fig. 1) has triggered an intensive theoretical activity aimed at understanding the origin of this gap.[2–9] The emerging picture is that there is no spin gap in the model with only exchange integrals J_1 between nearest neighbors,[5,6,8] and that there is a spin gap if a coupling constant to second neighbors J_2 is included as long as $0.05 \leqslant J_2/J_1 \leqslant 0.7$.[7,4,9,10] This picture might be slightly modified if exchange integrals are allowed to take different values inside the plaquettes, say J_1 and J_2, and between the plaquettes, say J_1' and J_2' (see Fig. 2). The problem is now to get 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 $J_1'=J_1$, $J_2'=J_2$, and $J_2/J_1=1/2$, they could reproduce the maximum of the susceptibility around 100 K with $J_1 \simeq 200$ 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_4O_9 is actually a member of a large family of vanadium oxides studied by Galy and co-workers in the mid 1970's,[11] 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_2O_5, and CaV_3O_7, lead to a similarly difficult problem as far as the interpretation of the temperature dependence of the susceptibility is concerned because they involve both J_1 and J_2. This difficulty can be overcome by studying another mixed-valence vanadium oxide, NaV_2O_5. This compound, synthesized by Hardy *et al.*,[12] is isostructural to CaV_2O_5.[13] However, NaV_2O_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 the 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:

$$H = J \sum_i \vec{S}_i \cdot \vec{S}_{i+1}. \tag{1}$$

Note that the exchange integral J between corner-sharing VO_5 SP is the analog of the next-nearest-neighbor exchange integrals J_2 and J_2' of CaV_4O_9 (see Fig. 2).

In this paper, we present measurements of the magnetic susceptibility of NaV_2O_5 from 2 to 400 K. The compound was prepared starting from a stoichiometric mixture of $NaVO_3$ (Merck, min 99%), V_2O_3 (obtained by hydrogen reduction of V_2O_5 at 800 °C) and V_2O_5 (Aldrich Chem. Co.,99.9%). The mixture was ground intimately, sealed in an evacuated quartz tube and then heated for 10 h at 615 °C. The x-ray diffraction pattern of the resulting dark powder indicated the formation of the pure phase NaV_2O_5. A refinement of the structure of NaV_2O_5 was proposed by Carpy and Galy.[14] It is orthorhombic and consists, as shown on the perspective view in Fig. 1(a), of two-dimensional 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. 1(b)]. Magnetic-susceptibility measurements were performed using a superconducting quantum interference device susceptometer. The magnetic-field intensity was 1 kG. The molar susceptibilities were corrected for diamagnetism by using Pascal's constants.

The raw data are presented in Fig. 3. They agree with the early measurements between 80 and 600 K by Carpy *et al.*[15] Above 100 K, the susceptibility is consistent with that of a spin-1/2 chain.[16,17] In that temperature range, the best available estimate of the susceptibility due to Eggert *et al.*[17] is

0163-1829/96/54(17)/11925(4)/$10.00

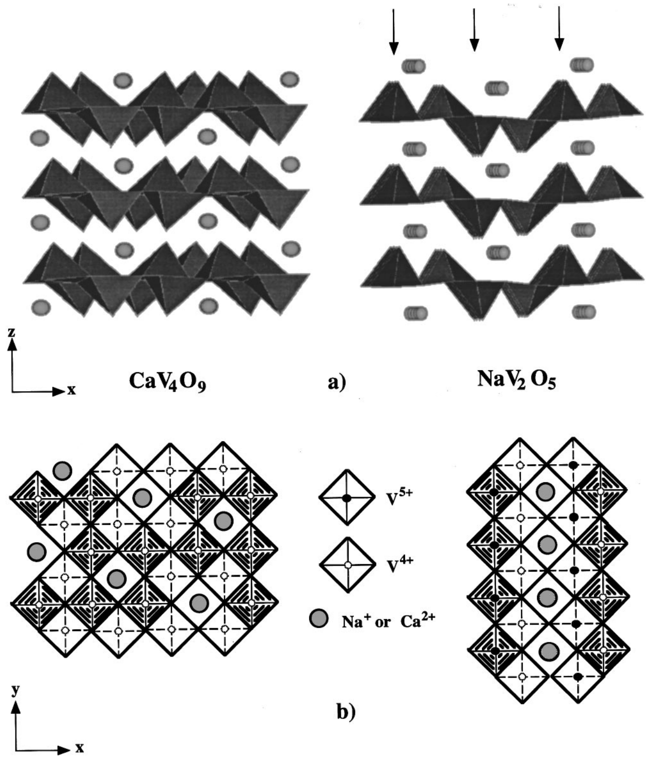

FIG. 1. Structure of CaV_4O_9 and NaV_2O_5. (a) Perspective view in the [010] direction. For NaV_2O_5, the square pyramids occupied by V^{4+} are indicated by an arrow. (b) Schematic representation of both structures in the [001] direction.

actually indistinguishable from the Bonner-Fisher result,[16] and the maximum at 350 K implies an exchange integral $J \simeq 529$ K.

Although, for our present purpose, we are mainly interested in the position of the maximum of the susceptibility, which lies in the high-temperature domain, we have tried to understand the low-temperature part as well. At low temperature, there is no evidence of a phase transition or of three-dimensional ordering, but, as usual, there is an increase of the susceptibility due to some kind of defects. The standard procedure is to describe these defects by a Curie-Weiss term $\chi^{\mathrm{CW}}(T)=g^2\mu_B^2 S(S+1)/3k_B(T-\theta)$, so that the spin part of the susceptibility reads

$$\chi^{\mathrm{tot}}(T)=(1-\rho)\chi^{\infty}(T)+\rho\chi^{\mathrm{CW}}(T)+\chi^{\mathrm{VV}}. \tag{2}$$

χ^{VV} is the temperature-independent Van Vleck paramagnetic susceptibility, ρ is the concentration of impurities, and $\chi^{\infty}(T)$ is the susceptibility of the infinite chain. At low temperature, the difference between the Bonner-Fisher estimate and the recent results of Eggert *et al.*[17] is not negligible,[18] 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 main problem is that the amount of impurities one needs to interpret the low temperature susceptibility gives too large a contribution at higher temperatures. To illustrate this, we have depicted as a dashed line in Fig. 3 the fit one gets if one tries to reproduce the low-temperature part by a Curie law ($\theta=0$, $\rho=0.0075$) and the high-temperature part by a spin-1/2 chain ($J=529$ K, $g=2$, $\chi^{\mathrm{VV}}=1.5610^{-4}$ emu/mole). This fit clearly overestimates the actual susceptibility around the minimum at 70 K. Taking all the parameters as free, independent parameters does not yield any significant improvement. So 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 behavior 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.

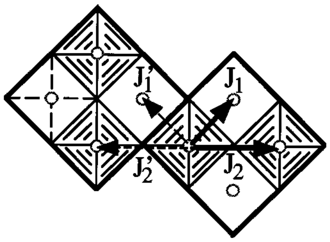

FIG. 2. Exchange integrals in CaV_4O_9.

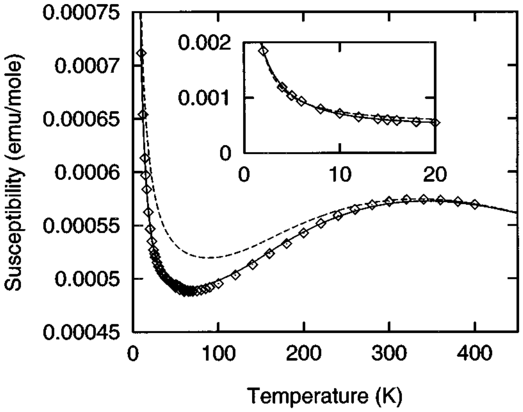

FIG. 3. Thermal variation of the molar magnetic susceptibility of NaV_2O_5. Diamonds: Experimental data; Broken line: Fit using Eq. (2); Solid line: Fit using the present theory [Eq. (3)]. Inset: Enlargement of the low-temperature region.

Assuming that the finite chains are due to a random distribution of point defects, we have derived the following expression for the temperature dependence of the susceptibility:

$$\chi^{\mathrm{tot}}(T)=\frac{1-\exp[-L(T)/aN_0]}{2N_0}\chi^{\mathrm{CW}}(T)+\left(1+\frac{L(T)}{aN_0}\right)\times\exp[-L(T)/aN_0]\chi^{\infty}(T)+\chi^{\mathrm{VV}}. \tag{3}$$

The details of this calculation, together with further experimental data that support it, will be presented elsewhere.[19] In this expression, N_0 is the average length of the finite chains.

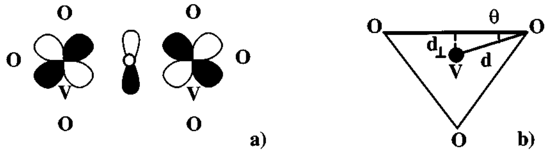

FIG. 4. (a) V $3d$ and O $2p$ orbitals involved in superexchange between corner-sharing VO_5 square pyramids; (b) Basic parameters of a VO_5 square pyramid.

It is related to the defect concentration by $N_0=1/\rho$. The length scale $L(T)$ corresponds to the length above which finite segments contribute to the susceptibility as if they were infinite. It is given by $L(T)/a=(g\mu_B)^2/[8k_BT\chi^\infty(T)]$, where a is the lattice constant along the chains. This expression 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 ρ and $1-\rho$, but functions of temperature. Using Eq. (3), we have been able to obtain a much better fit of the raw experimental data. This fit is shown as a solid line in Fig. 3. The parameters are $J=529$ K, $g=2.043$, $\chi^{VV}=141.10^{-6}$ cm^3/mole, $N_0=35$ and $\theta=-1.26$ K. This value of N_0 corresponds to a concentration of defects $\rho=2.9\%$. The fit was realized with the help of a simplex nonlinear least-squares fitting procedure, and the relative deviation defined as $\Sigma_i(\chi_i^{obs}-\chi^{calc})^2/\Sigma(\chi_i^{obs})^2$ was equal to 3×10^{-5}. Note that the number of adjustable parameters is exactly the same as for the usual ansatz of Eq. (2). So the dramatic improvement of the fit is an indication that this might be the correct explanation of the low-temperature susceptibility of NaV_2O_5, although more work is needed before this can be firmly established.

Let us now discuss the implication for CaV_4O_9 of an exchange integral $J=529$ K in NaV_2O_5. In a square-pyramid environment, the $3d$ electron of V^{4+} is in the $3d_{xy}$ orbital to avoid the negatively charged oxygens[20] (x and y are the directions of the in plane V-O bonds). The exchange will then be dominated by the superexchange mechanism through O $2p$ orbitals [see Fig. 4(a)]. The size of the exchange integral depends mostly on the hopping integral t_{pd} between the $3d_{xy}$ orbital of vanadium and the $2p_y$ orbital of oxygen. According to semiempirical laws,[21] t_{pd} is related to the local geometry by

$$t_{pd}=\eta_{pd\pi}\frac{\hbar^2}{m}\frac{r_d^{3/2}}{d^{7/2}}\cos\theta, \qquad (4)$$

where $\eta_{pd\pi}=1.36$, $\hbar^2/m=7.62$ eV Å^2, $r_d=0.98$ Å for vanadium, while d and θ are defined in Fig. 4(b). Besides, fourth-order perturbation theory in t_{pd} leads to the following expression for J:

$$J=\frac{4t_{pd}^4}{(\epsilon_p-\epsilon_d)^2}\left(\frac{1}{U_d}+\frac{1}{(\epsilon_p-\epsilon_d)+U_p/2}\right), \qquad (5)$$

where ϵ_d and ϵ_p are the on-site energies on vanadium and oxygen, respectively, while U_d and U_p are the on-site Coulomb repulsions between two electrons sitting on the same vanadium or oxygen orbital. Using the structural parameters deduced from x-ray measurements (see Table I), estimates of the ratios J_2/J and J_2'/J can be obtained from Eqs. (4) and (5). With $J=529$ K, they lead to $J_2=275$ K and $J_2'=440$ K.

TABLE I. Average distance between vanadium and neighboring oxygen (d), distance between vanadium and oxygen plane ($d_\perp$), and estimated exchange integral for three vanadium-vanadium bonds corresponding to corner-sharing VO_5 pyramids: intraplaquette next-nearest-neighbor bonds of CaV_4O_9 (J_2), interplaquette next-nearest-neighbor bonds of CaV_4O_9 (J_2'), and nearest-neighbor bonds in NaV_2O_5.

	d (Å)	$d_\perp$ (Å)	Exchange integral (K)
CaV_4O_9 (J_2)	2.035	0.685	$>$ 275
CaV_4O_9 (J_2')	1.955	0.685	$>$ 440
NaV_2O_5 (J)	1.961	0.364	529

How reliable are these estimates of J_2 and J_2' in CaV_4O_9? In their careful analysis of superexchange in copper oxides, Eskes and Jefferson[22] showed that hopping between oxygen orbitals lead to a weaker dependence of J upon t_{pd} than predicted by Eq. (5) ($J\propto t_{pd}^{2.3}$ for La_2CuO_4, in reasonable agreement with the experimental result $J\propto d^{-6.4}$ obtained by Aronson *et al.*[23] in their study of the pressure dependence of J). In the present case, we do not have enough information on the other parameters to reproduce Eskes and Jefferson's analysis. But one point seems to be clear: Eq. (5) overestimates the dependence of J on t_{pd}. So the actual ratios J_2/J and J_2'/J are presumably closer to 1 than the estimates obtained from Eqs. (4)–(5), and the values $J_2=275$ K and $J_2'=440$ K should be considered as lower bounds to the actual exchange integrals in CaV_4O_9.

These values are much bigger than the numbers assumed in most theoretical studies so far, namely $J_2\simeq J_2'\simeq 50-100$ K. If we put together all the information we have at the moment, a consistent picture of exchange integrals can nevertheless be obtained. For clarity, let us neglect the difference between J_1 (resp. J_2) and J_1' (resp. J_2') for a moment. The presence of a gap of 107 K in CaV_4O_9, i.e., considerably 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 (0.05 and 0.7) where the gap disappears. Now, according to a recent work of Kontani *et al.*,[24] the observation by neutron scattering of stripe order in the compound CaV_3O_7 (Ref. 25) 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 0.05 can be excluded because CaV_3O_7 should then exhibit Néel order. Under the assumption that exchange integrals have the same origin in all vanadates, this implies that J_2/J_1 cannot be too small in CaV_4O_9 as well. So exchange integrals $J_2>440$ K and $J_2'>275$ K are possible if the exchange integrals between first neighbors J_1 and J_1' are only slightly larger. A very useful check will be to see if such values are compatible with the temperature dependences of the susceptibility reported for CaV_3O_7 (Ref. 26) and CaV_4O_9.[1]

To summarize, we have measured the magnetic susceptibility of a one-dimensional vanadate, NaV_2O_5, between 2 and 400 K. The high temperature data are typical of a spin-1/2 chain with an exchange integral of 529 K. The increase at low temperature is not well accounted for by assuming that it comes from extrinsic paramagnetic impurities. We have proposed an alternative explanation in terms of finite chain effects which provides a much better fit in all the temperature range. Assuming that superexchange is the leading exchange mechanism between vanadium in corner-sharing square pyramids, we have shown that the present results imply that the next-nearest-neighbor exchange integrals in CaV_4O_9 are much larger than usually assumed. We believe that this information will prove very useful in understanding the magnetic properties of CaV_4O_9.

Note added in proof. We have been informed that NaV_2O_5 has recently and independently been studied by M. Isobe and Y. Ueda [J. Phys. Soc. Jpn. **65**, 1178 (1996)]. Their high temperature data for the susceptibility are in good agreement with ours as well as their estimate of the exchange integral *J*. Thus, the main point of the present paper concerning the value of the exchange integrals in vanadates is confirmed by their results. The presence of a spin Peierls transition at 34 K in their data not seen in our sample is presumably due to the presence of defects in our sample, in agreement with our interpretation of our low temperature data.

We acknowledge useful discussions with M. Albrecht, J. P. Daudey, M. Luchini, D. Poilblanc, J.-P. Renard, and J. M. Savariault. We are especially grateful to J. Galy for sharing with us his expertise on vanadium oxides. We are also grateful to S. Eggert for sending us his numerical estimates of the susceptibility of Ref. 17.

---

[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] S. White (unpublished).

[10] M. Albrecht, F. Mila, and D. Poilblanc (unpublished).

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

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

[13] Note, however, that NaV_2O_5 crystallizes with the orthorhombic non-centro-symmetric space group $P2_1mn$, while CaV_2O_5 crystallizes with the centro-symmetric space group $Pmmn$.

[14] A. Carpy and J. Galy, Acta Crystallogr. Sect. B **31**, 1481 (1975).

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

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

[17] S. Eggert, I. Affleck, and M. Takahashi, Phys. Rev. Lett. **73**, 332 (1994).

[18] S. Eggert (unpublished).

[19] F. Mila, P. Millet, J. Bonvoisin, and J. Galy (unpublished).

[20] J.-P. Daudey (private communication).

[21] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).

[22] H. Eskes and J. Jefferson, Phys. Rev. B **48**, 9788 (1993).

[23] M. C. Aronson *et al.*, Phys. Rev. B **44**, 4657 (1991).

[24] H. Kontani, M. E. Zhitomirsky, and K. Ueda (unpublished).

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

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