Magnetic susceptibility and spin dynamics of polyoxovanadate cluster {V12}: a proton NMR study of a model spin tetramer

D. Procissi[a], A. Shastri[b], I. Rousochatzakis, M. Al Rifai[b], P. Kögerler, M. Luban

Department of Physics and Astronomy and Ames Laboratory, Iowa State University, Ames, Iowa, USA, 50011

B. J. Suh

Department of Physics, The Catholic University of Korea, Puchon, 420-743, Korea

F. Borsa

Department of Physics and Astronomy and Ames Laboratory, Iowa State University, Ames, Iowa, USA, 50011 and

Dip. Fisica "A. Volta" e Unita' INFM di PAvia, Via Bassi 6, Pavia. I27100, Italia

 Abstract

  We report susceptibility and nuclear magnetic resonance (NMR) measurements in a polyoxovanadate compound with formula $(NHEt)_3[V^{IV}_8V^V_4As_8O_{40}(H_2O)] \cdot H_2O \equiv \{V12\}$. The magnetic properties can be described by considering only the central square of localized V^{4+} ions and treated by an isotropic Heisenberg Hamiltonian of four intrinsic spins 1/2 coupled by nearest-neighbor antiferromagnetic interaction with $J \sim 17.6 K$. In this

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[a] procissi@ameslab.gov

[b] Permanent Address: Department of Physics and Astronomy, Minnesota State University-Moorhead, MN

simplified description the ground state is nonmagnetic with S_T=0. The ^{1}H NMR line width (FWHM) data depends on both the magnetic field and temperature, and is explained by the dipolar interaction between proton nuclei and V^{4+} ion spins. The behavior of the nuclear spin-lattice relaxation rate T_1^{-1} (NSLR) in the temperature range (4.2-300K) is similar to that of χT vs. T and it does not show any peak at low temperatures contrary to previous observations in AFM rings with larger intrinsic spins. The results are explained by using the general features of the Moriya formula and by introducing a single T-independent broadening parameter for the electronic spin system. From the exponential T dependence of T_1^{-1} at low T (2.5K $< T<$4.2K) we have obtained a field dependent gap following the linear relation $\Delta_{NMR} = \Delta_0 - g\mu_B H$, with the gap $\Delta_0 \sim$17.6K in agreement with the susceptibility data. Below 2.5K the proton T_1^{-1} deviates from the exponential decrease indicating the presence of a small, almost temperature independent, but strongly field dependent, nuclear relaxation contribution, which we will investigate in detail in the near future.

(I) Introduction

Magnetic polyoxovanadate clusters are a very interesting class of spin systems in which a few magnetic moments are strongly coupled by exchange interaction and are arranged in a vast variety of both geometrical and spin structures[1]. Within this class of molecules the (NHEt)$_3$[$V^{IV}_8V^V_4$As$_8$O$_{40}$(H$_2$O)]·H$_2$O $\equiv$ {V12} cluster is comprised of 12 vanadium atoms arranged in a stack of three V squares as shown in Fig1(a). The top and bottom squares form strongly antiferromagnetically (AFM) coupled singlet states at room temperature and below and thus do not contribute significantly to the magnetic properties of the cluster at $T\leq$300K [2]. The central square of V^{4+} ions, on the other hand, forms a square of s=1/2 localized

moments coupled by an almost isotropic AFM nearest-neighbor exchange interaction $J/k_B = 17.6 K$. Thus {V12} behaves as a prototype of a spin 1/2 Heisenberg tetramer. The investigation of the spin dynamics of this molecule over the whole temperature range and for different values of the external magnetic field is of interest because one can follow the evolution from the high temperature regime of uncorrelated paramagnetic spins ($k_B T \gg J$) to the low temperature regime with a ground state of total spin S_T=0. The nuclear magnetic resonance (NMR) of protons probes the spin dynamics of the system since the protons in the molecule are coupled to the V^{4+} electron spins via nuclear-electron dipolar interactions. In particular the proton spin-lattice relaxation rate T_1^{-1} is proportional to the low frequency part of the spectral density of the electron spin fluctuations[3]. As pointed out in a preliminary report on {V12}[4], the low spin value (s=1/2) of each magnetic moment makes this system a good quantum counterpart of several other investigated AFM rings with high intrinsic spin value (s=5/2), i.e. nearly classical spins[5,6]. Unfortunately, no "bonafide" AFM ring system, with S_T=0 ground state, composed of spins s=1/2 is presently available except for Cu8 ring which, however, has an exchange interaction constant (J) so large that the spin system is in the S_T=0 ground state at room temperature and below [7]. Thus V12 appears to be the only s=1/2 single quantum system whose results can be compared with the s=1/2 classical AFM rings.

In the present paper we report a detailed proton NMR investigation of the spin dynamics of the model spin tetramer aimed at testing the following issues: (i) the behavior of the electronic spin correlation function in the high temperature regime ($k_B T > J$); (ii) the evolution of the spin correlations when the temperature becomes of the order of the exchange coupling J ($k_B T \sim J$); (iii) the spin fluctuations at very low temperature when the

molecular magnet is mostly in its singlet ground state ($k_B T < J$). In Sec. (II) we describe the experimental details of the NMR measurements. In Sec. (III) we present the experimental results including magnetic susceptibility results which will guide us in the interpretation of the NMR data. In Sec. (IV) we analyze the data by using the general features of the Moriya formula and exact first-principles results based on the isotropic Heisenberg model. Finally, in Sec. (V) we give a summary and conclusions of the paper.

(II) Experimental details

Measurements of magnetization versus temperature were performed at 0.5T using Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometers. The NMR measurements were performed on polycrystalline powder samples synthesized as described in the Ref. [2], by using a standard Fourier transform (FT) pulse spectrometer. The proton NMR line was sufficiently narrow (<70kHz) to be irradiated by a single radio frequency (rf) pulse of duration between 2-4 μsec. The proton nuclear spin-lattice relaxation rate T_1^{-1} was measured by monitoring the recovery of the nuclear magnetization following a short sequence of saturating radio frequency pulses. The recovery of the nuclear magnetization was found to be exponential in most cases over more than one decade. Each molecule contains many non equivalent protons with different dipolar coupling to the four V^{4+} magnetic moments, namely 24×5 protons belonging to the C_2H_5 groups attached on the outside of the vanadium cluster and the remaining four belonging to the two water molecules. Thus the observation of an exponential recovery law implies the presence of a common spin temperature [8,9]. The common spin temperature is established if $T_1 >> T_2$ where T_2 is the spin-spin relaxation time. Under these circumstances the measured

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T_I^{-1} is the weighted average of the relaxation rate for the different protons in the molecule. At high temperature and high magnetic field we observed non-exponential behavior due to the breakdown of the common spin temperature approximation and the T_I^{-1} quantity was derived from the initial part of the nuclear magnetization recovery curve (i.e. tangent to the origin). In this case also the measured T_I^{-1} is a weighted average of the different relaxation rates [5,6]. The spin-lattice relaxation rate in the rotating frame was measured by using an initial $\pi/2$ rf pulse immediately followed by a lock-in RF pulse of intensity $H_1 \sim 0.001$T and of variable duration τ. The $T_{1\rho}^{-1}$ parameter was obtained from monitoring the amplitude of the free precession decay as a function of the duration τ of the lock-in pulse [9].

(III) Experimental Results

The results for the magnetic susceptibility χ measured in our {V12} sample at 0.5T are plotted in Fig. 2 as χT vs. T. The rapid drop of χT for $T \leq 100$ K is indicative of the non-magnetic ground state ($S_T=0$). The inset in Fig. 2 shows χ vs. T. The proton NMR line was found to be a single symmetric line whose full width at half maximum (FWHM) is plotted in Fig. 3 as a function of temperature at two different external magnetic fields (0.5T and 4.7T). The low temperature limit (i.e. ~ 50 kHz) of the low field line width T-dependence, can be ascribed almost entirely to the nuclear dipole-dipole interaction among the 124 protons in the molecule. The partial line narrowing from 50kHz to 28kHz occurring on increasing temperature is due to the averaging of the nuclear dipolar interaction by the onset of molecular hindered rotation of the C_2H_5 groups. This can be inferred by the fact that a similar line narrowing is commonly observed in the same temperature range as here in many compounds containing the same radical group[8,9]. From the comparison of the line width

data for the two fields there appears to be only a slight inhomogeneous field dependent broadening. The inhomogeneous broadening is due to the relatively small dipolar coupling of the protons with the for V^{4+} magnetic moments. The nuclear spin-lattice relaxation rate T_1^{-1} is shown as a function of temperature in Fig. 4 for an external field of 0.5T and 4.7T respectively. In the temperature range (4.2-300K) the behavior of T_1^{-1} vs. T is similar to the behavior χT vs. T. It is of particular importance to note that there is no enhancement of T_1^{-1} at temperatures close to $J/k_B \sim 17K$, contrary to what has been reported in other AFM rings and clusters with intrinsic spins s>1/2 [5,6]. The T_1^{-1} results in the low temperature range (1.5-4.2K) are shown separately in Fig. 5(a) and 5(b). It is noted that below 4K the majority of the molecules are in the nonmagnetic ground state and therefore the T_1^{-1} data in this low-T regime are of particular interest and will be analyzed separately. A detailed field dependent study of T_1^{-1} was performed at 300K and the results are shown in Fig. 6. We have included two points which refer to $T_{1\rho}^{-1}$ measurements at 4.7T. In this case the relaxation rate in the rotating frame probes the spectral density at $\omega_1 = \gamma_N H_1$ and thus the points have been plotted in the graph at the magnetic field in the rotating frame $H_1 = \dfrac{\omega_1}{\gamma_N} \sim 0.001T$. The strong field dependence of T_1^{-1} indicates that the spectral density of the magnetic fluctuations is peaked at low frequency, a characteristic feature of low dimensional Heisenberg systems[5,6,10].

(IV) Analysis of experimental results

(i) Magnetic susceptibility

The magnetic susceptibility data in Fig. 2 can be fitted well by a theoretical calculation based on the exact solution of the Heisenberg Hamiltonian. In Ref. [2] the starting Hamiltonian is an empirical anisotropic Heisenberg Hamiltonian with four exchange parameters, i.e. J_{12}^{xy}/k_B = -9.28K, J_{12}^{zz}/k_B = -9.516K, J_{23}^{xy}/k_B = -7.77K, J_{23}^{zz}/k_B = -8K (with $J_{12}= J_{34}$ and $J_{23}= J_{14}$) [c] as shown in the schematic depiction of Fig. 1(b). The choice of the Hamiltonian with these parameters was dictated by the need to reproduce the energy level scheme (shown in Fig. 7(a)) obtained directly from inelastic neutron scattering (INS) experiments [2]. However, an almost identical fit of the susceptibility can be obtained by using a far simpler isotropic Heisenberg Hamiltonian[d] with a single exchange parameter J. The eigenstates of H are of the form $|S_T$ M S_{13} $S_{24}>$, where $\vec{S}_{13} = \vec{S}_1 + \vec{S}_3$, $\vec{S}_{24} = \vec{S}_2 + \vec{S}_4$, $\vec{S}_T = \vec{S}_{13} + \vec{S}_{24}$. Thus we have a singlet S_T=0 ground state ($|$ 0 0 1 1>) with E=0, a triplet S_T=1 ($|$1 M 1 1>) with E=J, a singlet ($|$0 0 0 0>) and two triplets ($|$1 M 0 1>, $|$1 M 1 0>) with E=2J and finally a quintet S_T=2 state ($|$2 M 1 1>) with E=3J, for a total number of $(2s+1)^N=2^4$=16 states (see Fig. 7(b)). It is then straightforward to obtain the field-free partition function Z [11]. Moreover the zero field molar susceptibility χ_0(T) is given by the fluctuation formula $\chi_0(T) = N_A [(g \mu_B)^2 /(3k_B T)] < S_T^2 >$. One then finds

$$\chi_0 T = \frac{2N_A(g\mu_B)^2}{Zk_B}\left(e^{-J/k_BT} + 2e^{-2J/k_BT} + 5e^{-3J/k_BT}\right),$$ (1)

where N_A is Avogadro's number. We found that Eq. (1) provides a very good fit to the experimental data upon choosing g=1.97 and $J/k_B = 17.6K$. The theoretical susceptibility

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[c] In Ref. 2 the convention $H = - 2\Sigma_{ij} J_{ij}^{\alpha\beta}$ ($s_i^{\alpha}s_j^{\beta}$) was used (α and β take on the values x, y, z).

[d] Here we have used the convention $H =+ J (S_1 \cdot S_2 + S_2 \cdot S_{3+} S_3 \cdot S_4 + S_4 \cdot S_1) +2J$.

curve is given by the solid line in Fig. 2. This agreement is further evidence of the fact that the overall magnetic properties can be associated with the four central spins s=1/2.

(ii) ^{1}H NMR line width (FWHM) vs T

The ^{1}H NMR line width Δv (full width at half maximum FWHM) as a function of temperature and for two different fields is shown in Fig. 3. The dependence of Δv on both the magnetic field and the temperature is ascribed to magnetic dipolar broadening via the dipolar interaction of the ^{1}H with the V^{4+} magnetic moments. For the dipolar magnetic broadening, the inhomogeneous line width Δv for a given susceptibility per spin χ, is given

by $\dfrac{\Delta v}{v_N} = \dfrac{\Delta v}{\dfrac{\gamma_N}{2\pi}H} = A_z \chi \sim \dfrac{\langle \mu \rangle}{r^3 H}$, where v_N is the proton Larmor frequency, A_z is the

component of the dipolar hyperfine coupling constant along the direction of the external magnetic field H, and r is the average distance between the ^{1}H and the vanadium ions[8]. From the field dependence at room temperature (not shown here) and the susceptibility in Fig. 2 one can estimate the component A_z of the dipolar coupling constant by considering the

slope $\dfrac{\Delta v(H_{02}) - \Delta v(H_{01})}{\dfrac{\gamma_N}{2\pi}(H_{02} - H_{01})} = A_z \chi \sim \dfrac{\langle \mu \rangle}{r^3 H}$. We obtained a value of $A_z \sim 10^{22}$ cm^{-3} which

corresponds to the field generated by a V^{4+} magnetic moment at an average distance of about 3 Å. This agrees with the results for V15 and V6 given in Ref. [12]. The result demonstrates that ^{1}H NMR is a direct probe of the magnetic properties of the V ions in the {V12} compound.

(iii) ^{1}H spin-lattice relaxation rate $T_1{}^{-1}$

One can obtain a general expression for the spin-lattice relaxation rate $T_1{}^{-1}$ through a method based on a perturbative treatment ("weak collision approach") of the dipolar coupling between nuclear and paramagnetic spins [3,8,9]. The major features of the spin-lattice relaxation rate can be easily seen in the following formula

$$T_1^{-1} = \left(\gamma_e \gamma_N \hbar^2\right)^2 \sum_{ij,aa'} C_{ij}^{aa'} \int_{-\infty}^{+\infty} dt\, e^{i\omega_N t} \left\langle S_i^a(0) S_j^{a'}(t) \right\rangle , \qquad (2)$$

where the coefficients $C_{ij}^{aa'}$ contain all the detailed geometrical coefficients of the dipolar interactions, $\{i,j\}$ are paramagnetic spin sites and $\{a,a'\}$ cartesian coordinates. It can be easily seen that the difficulty in evaluating T_1^{-1} in (2) arises firstly from the calculation of $C_{ij}^{aa'}$ and secondly from the calculation of all the spin-spin correlation functions. The following simplifications have been made in order to get the major features:

(1) We use the isotropic Heisenberg Hamiltonian[d] that we used for the susceptibility;

(2) We replace the delta functions that arise from (2) by Lorentzian functions with a single temperature independent broadening parameter ω_0 whose physical interpretation is in terms of a cut-off frequency of the spin-spin correlation functions due to couplings that don't commute with the Heisenberg isotropic exchange[10];

(3) The difference in the dipolar interactions of the inequivalent protons (different $C_{ij}^{aa'}$ for different protons) in the molecule is treated by averaging out the geometrical details of the system, i.e. we deal with a single, average T_1^{-1};

(4) Since the energies of the electronic spin system are of the order of $J/k_B \sim 17.6K$, we keep only terms that correspond to zero transition frequencies. This simplification is valid for fields far below the first level crossing (~13.3 T);

By using the total spin symmetries of the Hamiltonian, i.e. $[H, S_T^2] = [H, S_T^z] = 0$ and the resulting selection rules, we get the following general form for the spin lattice relaxation rate[3,13]

$$T_1^{-1} = F_L(T,H)\frac{\omega_0}{{\omega_0}^2 + {\omega_N}^2} + F_T(T,H)\frac{\omega_0}{{\omega_0}^2 + {\omega_e}^2} \ , \qquad (3)$$

where the first term comes from the (auto and pair) longitudinal correlation functions and the second comes from the transverse terms. The temperature and field dependence of F_L, F_T arises from the various Boltzmann factors of the electronic spin levels. There is no need for a further simplification of setting F_L and F_T equal [13].

In the expressions for F_L, F_T in Eq. (3), the contribution from the ground state vanishes since the ground state is a non-degenerate $S_T=0$ state. We will use this additional feature in writing Eq. (4), and also in the low-T behavior of T_1^{-1} (Eq. 6).

We are ready now to discuss our experimental results using the above general features of T_1^{-1}.

(a) T_1^{-1} vs. field at T=300K

In the high temperature regime (T=300K) the Boltzmann factors in F_L, F_T in (3) are all close to unity. Hence one should be able to reproduce the field dependence of T_1^{-1} at T=300K with the relation

$$T_1^{-1} = P\frac{\omega_0}{\omega_0^2 + \omega_N^2} + Q\frac{\omega_0}{\omega_0^2 + \omega_e^2} \quad , \tag{4a}$$

where P and Q are constants. Indeed, the field dependence of T_1^{-1} at T=300K, can be well described by the relation

$$T_1^{-1} = K\frac{H_0^{-1}}{1 + (H/H_0)^2} \quad , \tag{4b}$$

where K and H_0 are fitting parameters. From the fit in Fig. 6 one obtains $K/H_0 = 8.9 m\sec^{-1}$ and $H_0 = 1.3T$. Eq. 4(b) arises from Eq. 4(a) in two limiting cases: (i) if $P<<Q$ and $\omega_0 \sim \omega_e$ in which case one would have $\omega_0 = \gamma_e H_0 \sim 2.3 \times 10^{11} Hz$ and (ii) if $P\sim Q$ and $\omega_0 \sim \omega_N << \omega_e$ in which case one would have $\omega_0 = \gamma_N H_0 \sim 3.5 \times 10^8 Hz$. Both choices are consistent with the fact that $T_{1\rho}^{-1}$ value is of the order of the zero field extrapolated T_1^{-1} since the spin-lattice relaxation in the rotating frame is proportional to the spectral density of the fluctuations at very low frequency, i.e. $\omega_1 \sim 250kHz$. One could argue that there is no physical reason why $P<<Q$ since the constants are both related to the components of dipolar coupling tensor, and therefore the second choice is the relevant one. One way to determine this experimentally would be to perform a T_1^{-1} measurement using a different (other than proton) nuclei. Unfortunately, an attempt to detect the ^{51}V NMR signal was unsuccessful most likely due to the very short T_1^{-1} and/or T_2^{-1}. Furthermore ^{13}C NMR in natural abundance yields a signal which is too weak for the required low field measurements.

(b) T_1^{-1} vs. temperature at *H=0.5T* for *T>4.2K*

For H=0.5T, we have $\hbar\omega_e \ll k_B J$, and therefore we can neglect the field dependence in

the Boltzmann factors in F_L and F_T. Hence, the temperature dependence of T_1^{-1} in Fig. 4 can

be reproduced reasonably well by the following relation

$$T_1^{-1} = \frac{1}{Z}\left(\alpha(H)\exp(-J/k_B T) + \beta(H)\exp(-2J/k_B T) + \gamma(H)\exp(-3J/k_B T)\right), \qquad (5)$$

where the field dependence in the fitting parameters α, β and γ arises from the Lorentzian

broadening as in equation (3). There is no contribution in (5) from the ground state, as

indicated previously. The data of T_1^{-1} for H=0.5T can be fitted by Eq. (5), for $T > 4$K, with

the proper choice of fitting parameters α, β, γ (solid black curve in Fig. 4 with $\alpha = 5.6$

msec^{-1}, β=76.8 msec^{-1}, γ= 28 msec^{-1}). One can see a deviation from the behavior given in

Eq. (5) below T=4.2K in Fig. 4 which will be treated separately.

(c) T_1^{-1} vs. temperature at *H*=4.7T and for *T*>4.2K

If one assumes that the constants α, β and γ in Eq. (5) have the same field dependence as

in Eq. 4(b) and that the parameter ω_0, which defines the width of the Lorentzian function, is

T-independent, one can try to fit the T_1^{-1} data at *H*= 4.7T(O) with the same set of parameters

as for the fit at 0.5T simply by rescaling by the field dependence given by Eq. 4(b). We

would expect that at 4.7T, which is approximately 1/3 of the first level crossing field, the

Boltzmann factors that enter F_L, F_T would be affected significantly especially at low *T*.

Indeed, there is a deviation below 10K (see the dotted line in Fig. 4). It is noteworthy that

one finds good qualitative agreement over a wide temperature range and this implies that the

broadening parameter ω_0 is *T*-independent at these temperatures. The above result suggest

that the *T* and *H* dependence of T_1^{-1} can be expressed in first approximation as the product

of a temperature dependent function *f(T)* and a field dependent function *g(H)*. This approximation obviously breaks down at high fields and low temperatures.

(d) T_1^{-1} vs. temperature for T<4.2K

For temperatures below the ^{4}He boiling temperature only the ground state ($|0000\rangle$) and the first excited state ($|1-111\rangle$) are of importance. Then, for given field, the temperature dependence of T_1^{-1}, assuming again no *T*-dependence in ω_0 in Eq. (3), follows the relation

$$T_1^{-1} \sim \frac{A(H)}{Z}\exp(-\Delta_{NMR}(H)/k_BT), \qquad (6)$$

where $\Delta_{NMR}(H) = \Delta_0 - \Delta E(H)$, with $\Delta_0 = J$, is the gap between the ground state S_T=0 and S_T=1 excited state and *A(H)* is a fitting parameter for each field coming from the Lorentzian broadening. One can easily see that $A(H)\exp(-\Delta_{NMR}(H)/k_BT)$ in Eq. (6) corresponds to $\alpha(H)$ in (5) when $k_BT \gg J$.

The initial part of the curve (2.5K<*T*< 4.2K) in Fig. 5(a) and 5(b) can indeed be fit with Eq.(6) (dotted curves in Fig. 5(a) and 5(b)) with *A*(0.4T)=5.8msec^{-1}, *A*(1.34T) = 1.3msec^{-1}, *A*(4.7T) = 0.3msec^{-1}, and Δ_{NMR}(0.4T)/k_B = 17.1K, Δ_{NMR}(1.34T)/k_B = 15.8K, and finally Δ_{NMR}(4.7T)/k_B = 11.4K. The obtained gap values Δ_{NMR} vs. *H* are plotted in the inset of Fig. 5(b), the dashed curve represents the Zeeman field dependence of the gap given by $\Delta_{NMR}(H)=\Delta_0$-$g\mu_B H$, with Δ_0 /k_B =17.6K.

For the case of the low field data (0.4T and 1.34T) one must note the deviation from the exponential thermally activated behavior given in Eq. 6 with $\Delta_0/k_B \sim$ 17.6K for *T*<2.5K (Fig. 5(a)), while in the case of the high field data (4.7T) the fit given by Eq. (6) reproduces

the data also below 2.5K as shown in Fig 5(b). The weak temperature dependence below 2.5K suggests that we fit the data in this regime by simply adding a T-independent but H-dependent term in Eq. (6) (see Fig. 5). It is noted that in the octanuclear Cu8 antiferromagnetic ring, of $S_T=0$ ground state, a similar deviation at low temperatures was observed [7]. In Cu8 the [63,65]Cu NMR and NQR indicated the presence of non equivalent Cu sites suggesting a deviation from the exact isotropic Heisenberg Hamiltonian. Moreover, inelasting neutron scattering [2] in the present system, indicated the presence of anisotropic exchange. However, no contribution to T_1^{-1} can arise in Moriya's formula from a non-degenerate $S_T=0$ ground state, whatever the form of the Hamiltonian, and in particular whether *H* includes anisotropic exchange and non-equivalent sites. Therefore we are lead to conclude that the very low-T contribution to T_1^{-1} is coming either from paramagnetic "defects" or from a relaxation mechanism other than proton-vanadium dipolar coupling terms of Moriya's theory.

(V) Summary and conclusions

In this work we have presented comprehensive susceptibility and ^{1}H nuclear magnetic resonance experimental results of the polyoxovanadate cluster {V12}. The susceptibility experimental data were well fitted using results from exact calculations based on an isotropic Heisenberg Hamiltonian for the spin 1/2 tetramer. From the NMR spectral measurements and the temperature and field dependence of the NMR line width we have established that the inhomogeneous broadening is due to the dipolar coupling of the protons

with the localized vanadium ions. The spin dynamics of the tetramer has been characterized through the proton spin-lattice relaxation rate, T_1^{-1}, in different temperature regimes and for different fields and we used general arguments (based on Moriya's first-principles treatment) to reproduce the results. At high temperature ($k_B T \gg J$) T_1^{-1} exhibits a strong and well defined field dependence which is well reproduced by a Lorentzian spectral density of the spin fluctuations. This field behavior is similar to that observed in one-dimensional magnetic systems[10]. In the intermediate temperature range ($10K < T < 300K$) the temperature behavior of T_1^{-1} is similar to the T-dependence of χT indicating that the proton T_1^{-1} is dominated by the amplitude of the local spin fluctuations. Particularly relevant is the absence of an enhancement of the relaxation rate T_1^{-1} for $k_B T \sim J$ which is found in other similar molecular magnetic rings comprised of spins with s>1/2 [6]. The fact that we were able to roughly reproduce the high and low field data simply by means of a rescaling factor is evidence of the fact that the T and H dependence of T_1^{-1} can be expressed in first approximation as the product of two independent functions $f(T)$ and $g(H)$ and most importantly that the broadening parameter ω_0 is weakly temperature dependent down to at least 10K. Finally, in the low T regime ($2.5K < T < 4.2K$), and for both high and low fields, T_1^{-1} decreases exponentially as the temperature is lowered. The value of the gap Δ obtained from the fit of the data is consistent with the simple linear field dependence $\Delta_{NMR}(H) = \Delta_0 - g\mu_B H$ with $\Delta_0 = 17.6K$ in excellent agreement with the susceptibility results and with INS and dynamic magnetization measurements [14]. For $T < 2.5K$ the temperature dependence of T_1^{-1} deviates from the thermally activated exponential behavior and this is most evident in the low field data (0.4T and 1.34T). This deviation will be explored in detail in the near future.

The most remarkable conclusion of the present work is found by comparing the behavior of the present s=1/2 tetramer with the s>1/2 AFM rings. Although in both cases the proton T_1^{-1} can be well described by Moriya's theory, the characteristic frequency ω_0 defining the broadening of the magnetic levels of the molecule and thus the spin fluctuations is quite different for the s=1/2 quantum case and the s>1/2 classical case. In V12, ω_0 appears to be almost T-independent and thus it does not give rise to the peak in T_1^{-1} observed in AFM rings[4,6] where ω_0 is strongly T-dependent becoming of the order of the nuclear Larmor frequency at the peak[15]. Another important finding is the existence of a residual nuclear relaxation mechanism at very low temperatures. It will be noted that similar results were obtained in half-integer isotropic high-spin ground state molecules of different spin values[16].

Acknowledgements

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Figures

Fig 1

(a) Schematic representation of the $[V^{IV}_8 V^V_4 As_8 O_{40}(H_2O)]^{4-}$ cluster anion. The three planes formed by the vanadium ions (black spheres) are depicted in dark gray. (b) Schematic view of the central tetramer with definition of the superexchange and parameter pathways through the diarsenite ligands: (!) As; (O) O [1,2]

Fig 2

Temperature dependence of χT in {V12} at 0.5T. The solid curve is the theoretical result (Eq.(1)) with g=1.97 and J=17.6K. Also shown in the inset is the susceptibility χ vs. T at 0.5T.

Fig 3

Temperature dependence of the proton line width (FWHM) in {V12} at two different external fields (O) H_o=0.5T ; (,) H_o=4.7T.

Fig 4

Temperature dependence of the proton spin-lattice relaxation rate in {V12}: (,) data at H=0.5T. The solid curve is the best fit according to Eq. (5), with $\alpha = 5.6$ msec^{-1}, β =76.8 msec^{-1}, $\gamma = 28$ msec^{-1}; (O) data at 4.7T. The dotted curve is the same curve as for the 0.5T

data but with a rescaling factor which takes into account the field dependence in Eq. 4(b) with H_0=1.3T.

Fig 5

(a) Semilog plot of T_1^{-1} vs. 1000/T for the low-T range (1.5K –4.2K) for different magnetic fields: (O) 0.4T; (,) 1.34T data. The dotted curves are fits according to Eq. (6) with Z=1, $A(0.4T)$=7msec^{-1}, $A(1.34T)$=1.3 msec^{-1} and with $\Delta_{NMR}(0.4T)$=17.1 K, $\Delta_{NMR}(1.34T)$=15.8 K. The solid curve corresponds to the addition in Eq. (6) of a constant, field-dependent term $G(H)$, with G(0.4T)=3.9×10^{-3}msec^{-1}, G(1.34T)=7.3×10^{-4}msec^{-1}.

 (b) (8) 4.7T data. The dotted curve corresponds to Eq. (6) with Z=1, $A(4.7T)$ =0.3 msec^{-1} and $\Delta_{NMR}(4.7T)$=11.3 K. The solid curve corresponds to the addition in Eq. (6) of the constant $G(H)$, with G(4.7T)=1.7×10^{-4}msec^{-1}. The inset shows the obtained values of Δ_{NMR} vs. H, and the solid black line is the linear dependent expected behavior $\Delta_{NMR}(H)$=Δ_0 - $g\mu_B$ H_0 with Δ_0=17.6 K and $g\mu_B$ = 1.33 K/T.

Fig 6

T_1^{-1} vs. H at T=300K. The solid black curve represents the best fit to the data according to Eq. 4(b) with H_0 = 1.3T and K/H_0 = 8.9 msec^{-1}. The two points plotted at very low fields are $T_{1\rho}^{-1}$ measurements at 4.7T (see text).
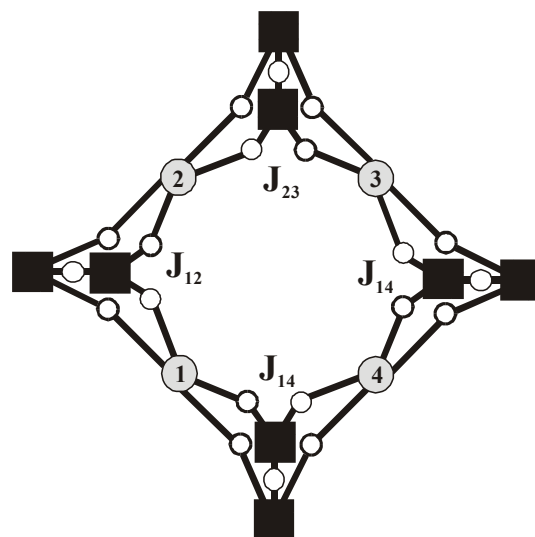
Fig 7

(a) Level scheme as obtained from INS [2] (depicted are the observed inelastic neutron scattering transitions).

(b) Level scheme as obtained from the isotropic Heisenberg model for four spin s=1/2.
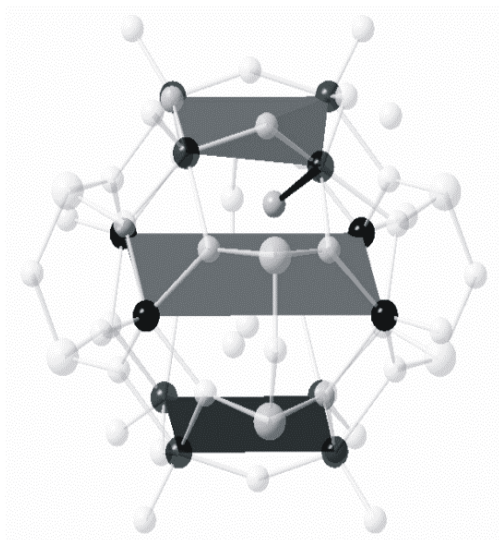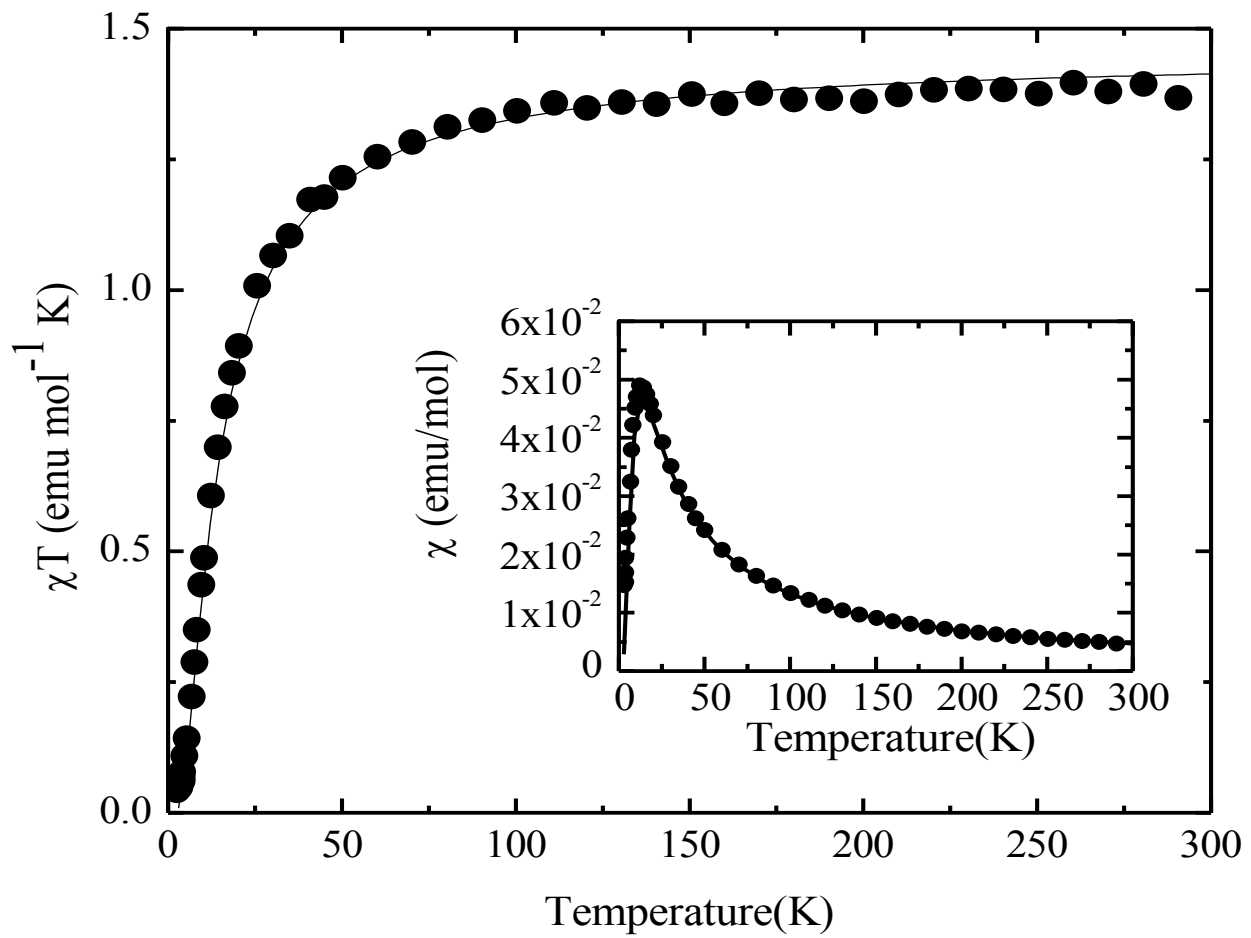

(a)

(b)

Fig 1 Procissi et al, Phys Rev B
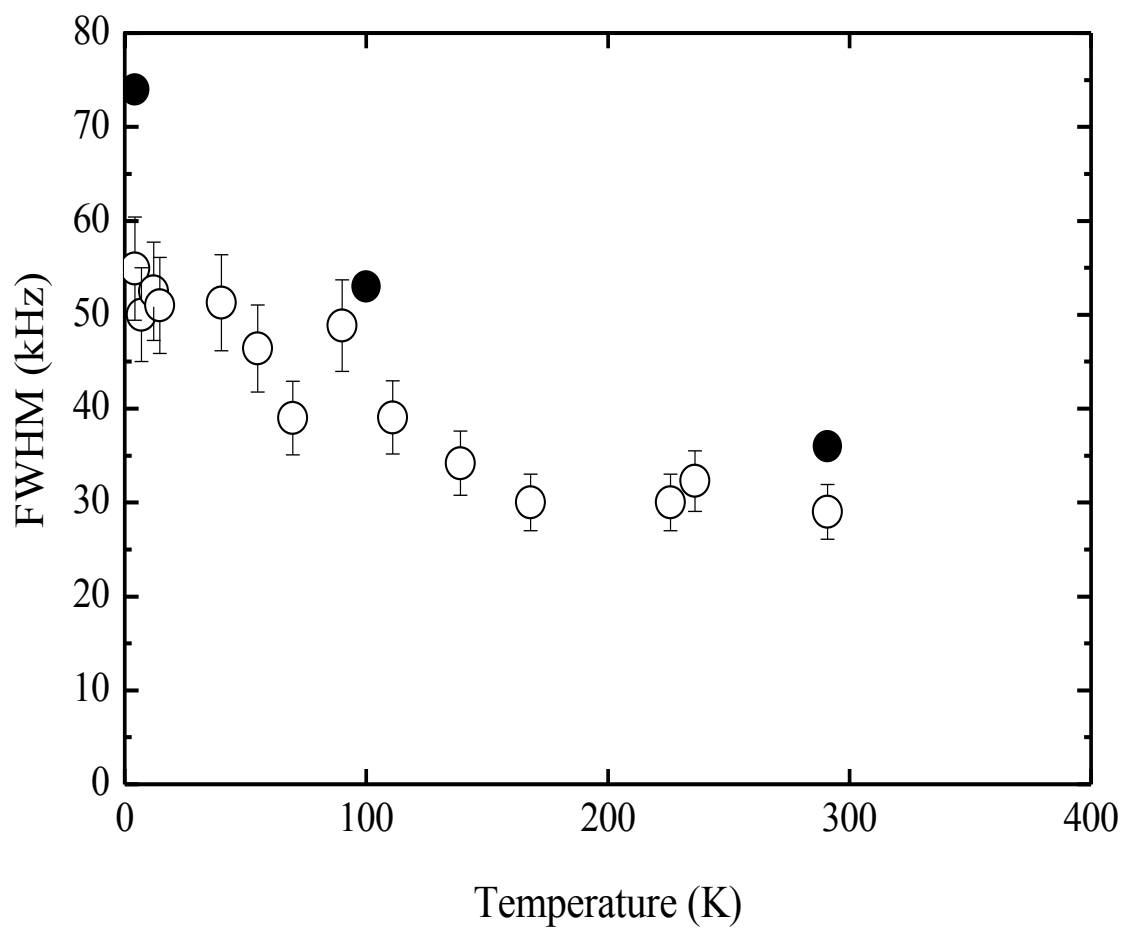
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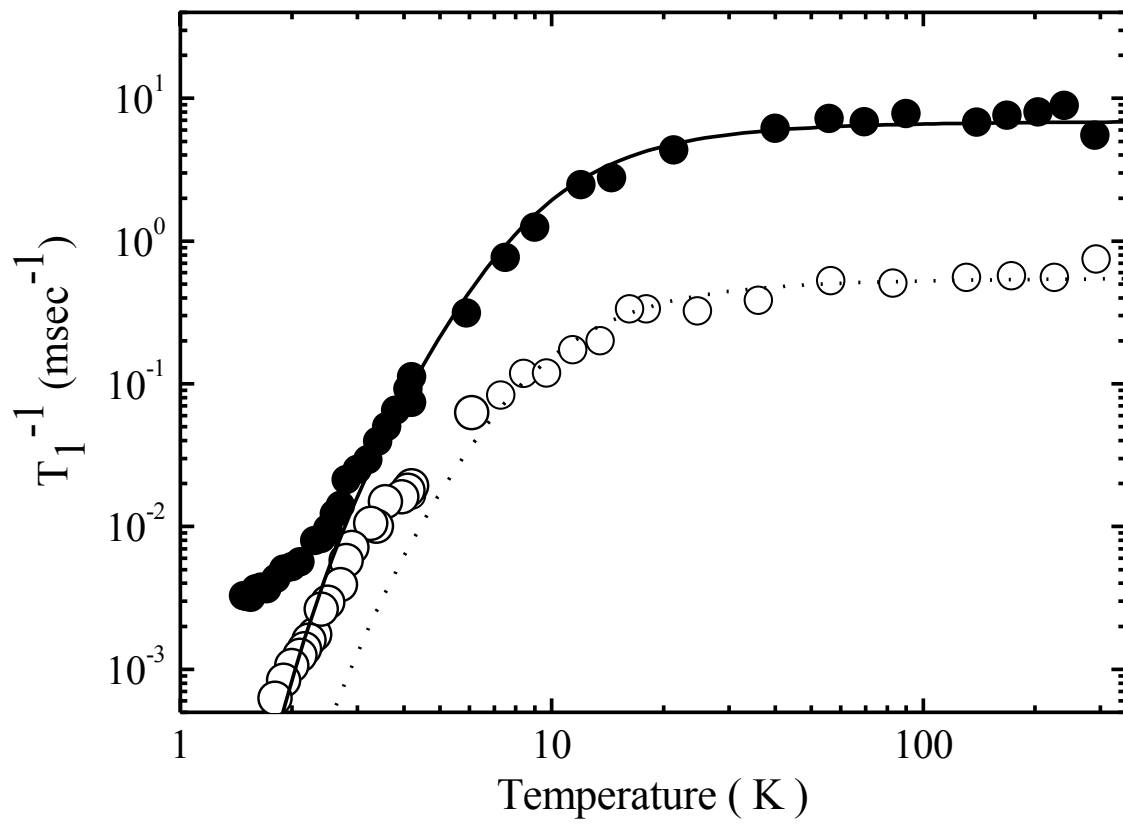
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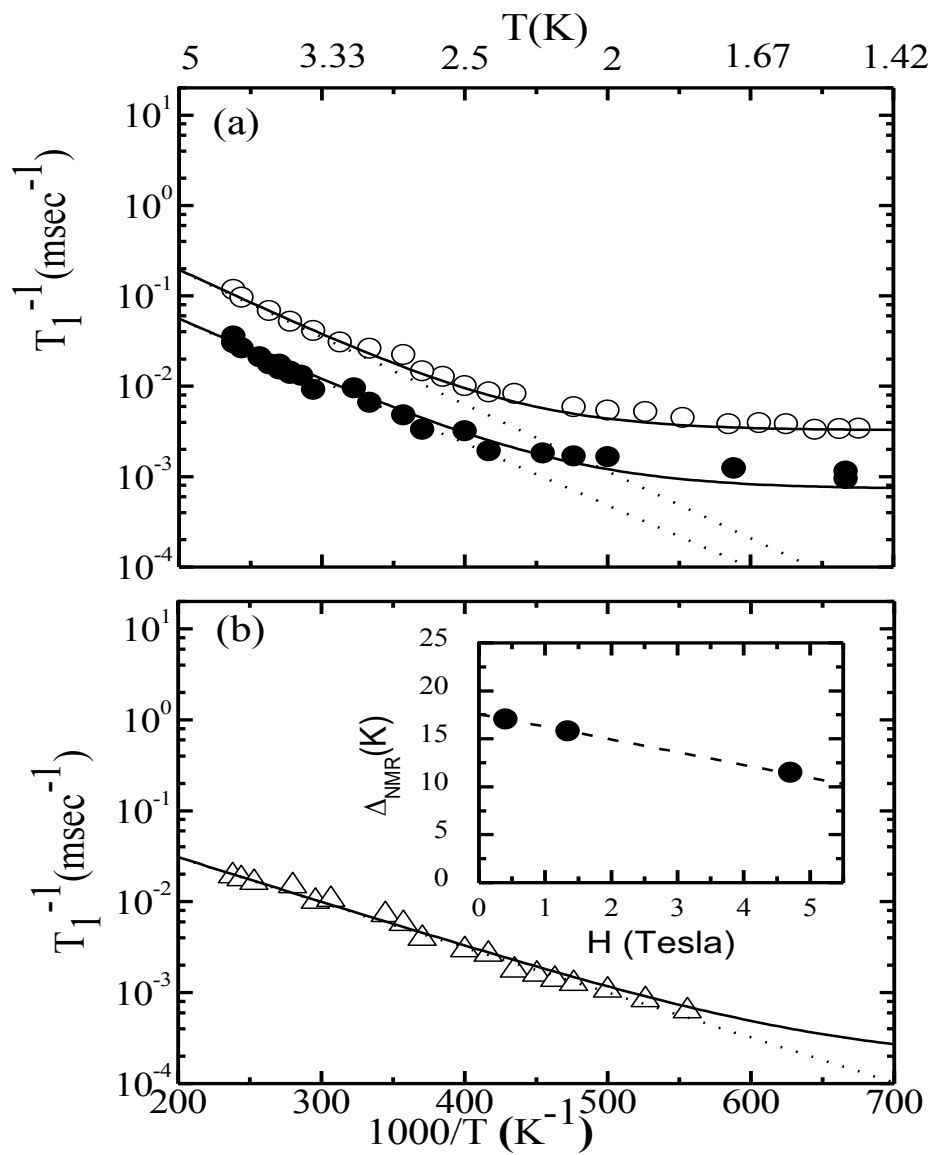
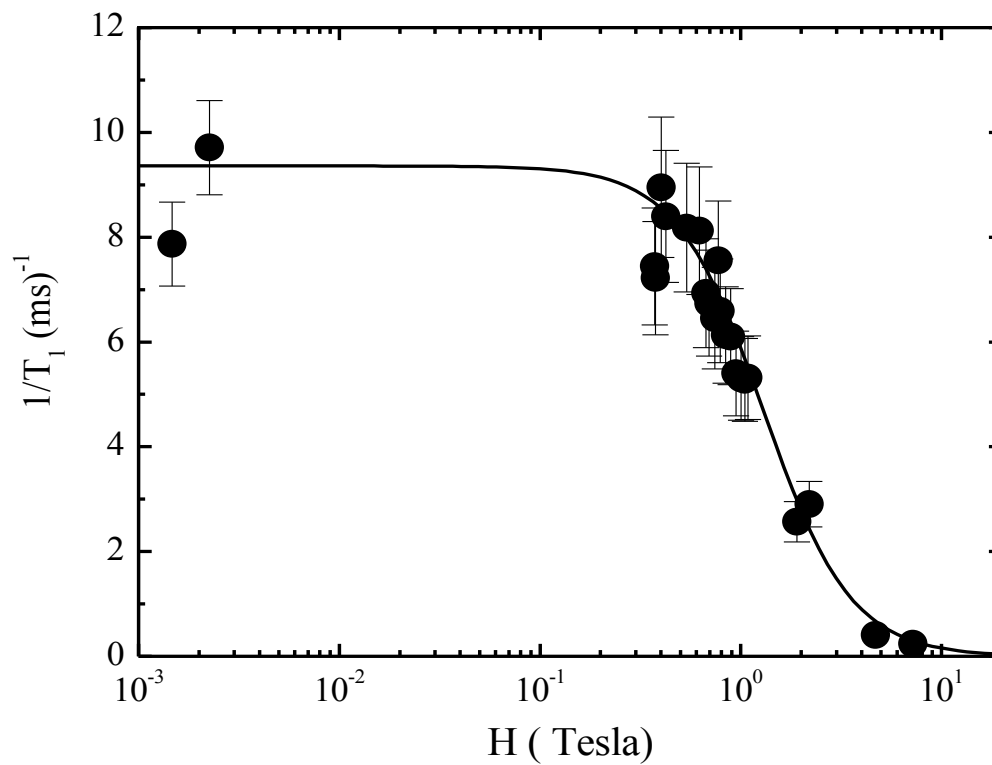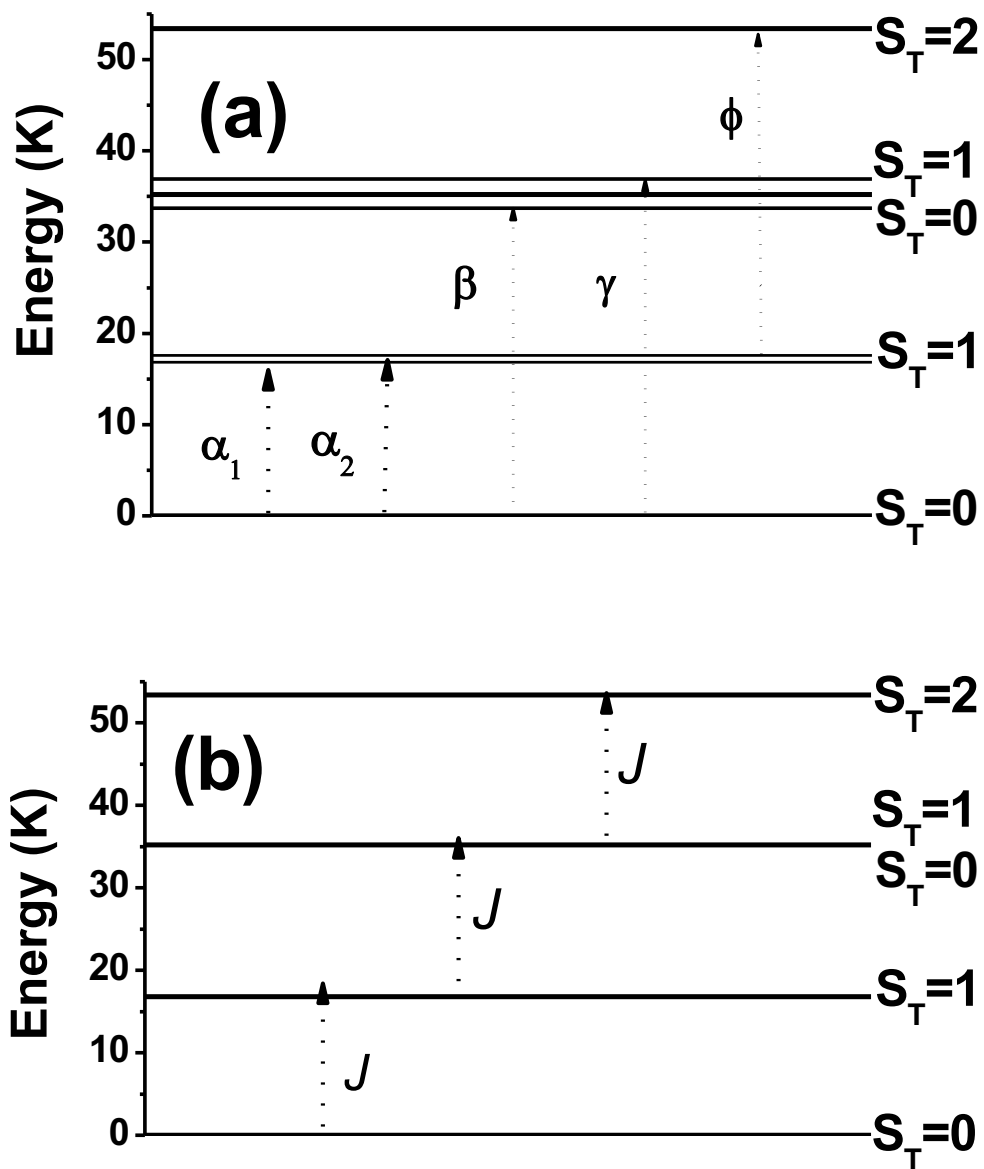**Fig 4 Procissi et al Phys Rev B**

Fig 5 Procissi et al Phys Rev B

Fig 6 Procissi et al Phys Rev B

Fig 7 Procissi et al Phys Rev B