Magnetic relaxation in V$_{15}$ cluster: Direct spin-phonon transitions

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Dedicated to Professor Achim Müller-to highlight his exceptional achievements.

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ABSTRACT

In this article we propose a model of spin-vibronic relaxation in K$_6$[V$_{15}$As$_6$O$_{42}$(H$_2$O)$_8$]·8H$_2$O, the so-called V$_{15}$ cluster exhibiting the unique layered structure. The work is motivated by the recent observation of the Rabi oscillation [1] in this system and aimed to elucidate the nature of the relaxation processes. The model assumes that the spin-phonon coupling arises as a result of modulation of the isotropic and antisymmetric (Dzyaloshinsky–Moriya) exchange interactions in the central triangular layer of vanadium ions by the acoustic lattice vibrations. Within the pseudo-angular momentum representation the selection rules for the direct (one-phonon) transitions between Zeeman levels are derived and a special role of the antisymmetric exchange is underlined. The relaxation times related to one-phonon transitions in different ranges of the field are estimated within the Debye model for the lattice vibrations.

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1. Introduction

During last two decades the fundamental discoveries of Achim Müller in polyoxometalate chemistry led to unprecedented progress in this field including fascinating applications to single molecule magnetism, biophysics and nanomaterials science. Design and study of new nanoscopic objects possessing both beauty and intriguing properties facilitated a new development of fundamental issues of nanophysics (see a comprehensive book [2]). About 20 years ago one of us (B.Ts.) started to collaborate with Achim Müller on magnetic mixed valence polyoxometalates [3,4]. Last years this fruitful and pleasant collaboration got a new impact under the auspices of the German-Israel Science foundation [1,5–13] and was focused mainly on the study of famous V$_{15}$ cluster synthesized in Bielefeld. In this article written in honor of Achim Müller we propose a model of spin-phonon relaxation and evaluate the probability of one-phonon processes in the low lying magnetic sublevels in V$_{15}$. The work is motivated by the recent observation of the Rabi oscillations in this system [1] and aimed to elucidate the role of spin-phonon relaxation as a possible mechanism of decoherence.

The unique cluster anion present in K$_6$[V$_{15}$As$_6$O$_{42}$(H$_2$O)$_8$]·8H$_2$O containing fifteen V$^{5+}$ ions ($S_i = 1/2$) and exhibiting the unique layered structure was discovered two decades ago [14] and pioneer studies of this system dates back to this period [14–17]. The synthesis of this fascinating spin frustrated cluster opened a new trend in molecular magnetism closely related to the promising field of single molecule magnets that is expected to give a revolutionary impact on the design of new memory storage devices of molecular size and quantum computing [2].

The molecular cluster V$_{15}$ has a distinct layered quasi-spherical structure [14,15]. Fifteen V$^{5+}$ ions ($S_i = 1/2$) are placed in a large central triangle sandwiched by two distorted hexagons possessing overall D$_3$ symmetry (Fig. 1).

Studies of the adiabatic magnetization and quantum dynamics show that the V$_{15}$ cluster exhibits the hysteresis loop of magnetization [18–23] and can be referred to as a mesoscopic system on the border line between the classical and quantum world. The studies of the static magnetic susceptibility [16,17], energy pattern [24–32], ab initio electronic structure calculations [33–37] and inelastic neutron scattering (INS) [38,39] showed that the low lying part of the energy spectrum is well isolated from the remaining spin levels and can be understood as a result of interaction between three moieties consisting of five strongly coupled spins giving rise to spin $S_i = 1/2$ of each moiety. The studies of V$_{15}$ cluster are reviewed in Ref. [40].

A novel route to employ the properties of molecular magnets is a spin-based implementation of quantum information processing that is expected to provide a development in the problem of quantum computing [1,41–53]. The key question formulated in Ref. [41] is: “will decoherence times in molecular magnets permit quantum information processing?” First prediction of the coherent states in V$_{15}$ has been made in Ref. [54] where it was explicitly stated: “...quantum coherence in a V$_{15}$ molecule is not suppressed and, in principle, can be detected experimentally.” In fact, recent observation and interpretation of the Rabi oscillation in V$_{15}$ have been reported in Ref. [1]. In Ref. [54] different mechanisms of decoherence have been discussed and in particular a general estimation

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of the order of magnitude of spin-phonon relaxation times has been made. In this article we propose a microscopic approach to the evaluation of the rates of the direct (one-phonon) spin lattice relaxation based on the accurate consideration of the spin states and Zeeman levels of \( V_{15} \), and a simple Debye model for the lattice vibrations. In the subsequent studies this model will be extended and employed for a more general studies of phonon-assisted processes in molecular magnets, including two-phonon and Orbach-type transitions.

2. Triangle model for \( V_{15} \) cluster

The model of spin-triangle for the low-lying spin excitations suggested in Refs. [16,20] includes isotropic Heisenberg–Dirac–Van Vleck (HDVV) exchange interaction and antisymmetric (AS) exchange proposed by Dzyaloshinsky [55] and Moriya [56] as an origin of spin canting in magnetic materials (see Refs. [18–20]). The last interaction was shown [57,58] to be especially important due to relatively strong antiferromagnetic interactions while the in-plane part is responsible for the doublet–quadruplet mixing. This mixing leads to a second order zero-field splitting of the \( S = 3/2 \) level (that is \( D_J^2 + D_h^2 / 8J \)). It was shown [5] that \( D_J \) and \( D_h \) are combined into an effective parameter \( D_\perp = \sqrt{D_J^2 + D_h^2} \) so the model is fully specified by the three parameters \( J, D_J \) and \( D_h \). The parameter \( J \) is found to be about 0.85 cm\(^{-1}\) [4] and recent estimation based on the low temperature magnetization data [19] provides the following AS exchange constants: \( D_J = 0.24 \) cm\(^{-1}\), \( D_h = 0.08 \) cm\(^{-1}\) [57,58].

3. Spin-phonon interaction

The interaction of spins with the lattice vibrations (heat reservoir) arises from the modulation of the isotropic and AS exchange interactions by the molecular displacements \( X, Y, Z \) \((i = 1, 2, 3)\) that provides an adequate description of the whole system at low temperatures when the spin of hexagons are paired \((S > 1/2)\) that provides an adequate description of the whole system at low temperatures when the spin of hexagons are paired. The full Hamiltonian of the system looks as:

\[
H_{\text{AS}}(\perp) = D_h [S_x S_y + S_y S_x + S_y S_z] + \sum_{ij} D_{ij} [S_i \times S_j]
\]

The eigen-values of the Hamiltonian \( H_0 \) with the antiferromagnetic \((J > 0)\) coupling includes two levels, namely “accidentally” degenerate spin doublets (ground level) and excited spin quadruplet separated by the gap \( 3J \). According to the overall point symmetry \( D_3 \) the vector constants \( D_{ij} \) \((i = 1, 2, 3)\) numerate the sides of the AS exchange have, in general, three independent components, namely, along and perpendicular to the side (in plane of the triangle) and perpendicular to the plane component whose absolute values are respectively \( D_x, D_y \) and \( D_z \). Consequently the Hamiltonian \( H_{\text{AS}} \) can be divided into two parts, \( H_{\text{AS}}(||) \) (“normal”) and \( H_{\text{AS}}(\perp) \) (“in-plane”) which are defined as:

\[
H_{\text{AS}}(||) = D_{\perp} [S_x S_y + S_y S_x + S_y S_z] + \sum_{ij} D_{ij} [S_i \times S_j]
\]

where the axes \( X \) and \( Y \) of the global coordinates system are directed as shown in Fig. 2 while the axis \( Z \) is perpendicular to the plane (right-hand coordinate system). These two parts of the AS exchange are explicitly separated as they play quite different physical roles. The normal part of AS exchange splits the ground doublets (the “normal”) and \( (jj) \) levels and the in-plane part is responsible for the doublet–quadruplet mixing. This mixing leads to a second order zero-field splitting of the \( S = 3/2 \) level (that is \( D_J^2 + D_h^2 / 8J \)). It was shown [5] that \( D_J \) and \( D_h \) are combined into an effective parameter \( D_\perp = \sqrt{D_J^2 + D_h^2} \) so the model is fully specified by the three parameters \( J, D_J \) and \( D_h \). The parameter \( J \) is found to be about 0.85 cm\(^{-1}\) [4] and recent estimation based on the low temperature magnetization data [19] provides the following AS exchange constants: \( D_J = 0.24 \) cm\(^{-1}\), \( D_h = 0.08 \) cm\(^{-1}\) [57,58].

\[
H_{\text{AS}}(\perp) = D_h [S_x S_y + S_y S_x + S_y S_z] + \sum_{ij} D_{ij} [S_i \times S_j]
\]

**Fig. 1.** Ball-and-stick representation the cluster anion \( [\text{V}_{15}\text{AsO}_{42}]^+\) emphasizing the \( V_{15} \) triangle (the central water molecule is not indicated) [14].

**Fig. 2.** Vibrational coordinates of a symmetric triangular unit exchange.
ions as shown in Fig. 2. Within this mechanism of spin-phonon (vibrionic) interaction the exchange parameters are assumed to be the functions of the metal-metal distances $R_{ij}$ so that the linear (with respect to the displacements) terms of the vibrionic Hamiltonian $H_{ee}$ can be represented as a sum of two contributions $H_{ee} = H_{ee}^I + H_{ee}^R$, where $H_{ee}^I$ and $H_{ee}^R$ are the contributions of the isotropic and AS parts of the exchange Hamiltonian respectively. They can be written as:

$$H_{ee}^I = \sum_{x=AXY} \left( \frac{\partial H_0}{\partial Q_x} \right)_{Q_x=0} Q_x,$$

(4)

$$H_{ee}^R = \sum_{x=AXY} \left( \frac{\partial H_0}{\partial Q_x} \right)_{Q_x=0} Q_x.$$

(5)

After substitution of the corresponding parts of the exchange Hamiltonian one obtains the following expressions for the spin-phonon coupling operators:

$$H_{ee}^I = \sum_{y=x=AXY} 2S_0 \left( \frac{\partial H_0}{\partial R_{ij}} \right)_{R_{ij}=0} \frac{\partial H_0}{\partial Q_x} Q_x,$$

(6)

$$H_{ee}^R = \sum_{y=x=AXY} S_0 \times S_0 \left( \frac{\partial H_0}{\partial R_{ij}} \right)_{R_{ij}=0} \frac{\partial H_0}{\partial Q_x} Q_x,$$

(7)

where $R_{ij}$ are the instant metal-metal distances in course of the vibrations while $R_{ij}=0$ corresponds to the equilibrium trigonal configuration and symmetric network with the sides $R_0$. Modulation of the isotropic exchange can be described by the parameter $\lambda$ which is defined as $\lambda \equiv \sqrt{b} \left( \frac{\partial H_0}{\partial R_{ij}} \right)_{R_{ij}=0}$. For each side of the triangle there is also a vector coupling parameter which is related to the AS exchange and defined as $\rho_{ij} = \left( \frac{\partial H_0}{\partial R_{ij}} \right)_{R_{ij}=0}$. Due to the trigonal symmetry of the system the absolute values of these three vector parameters have the same value $\beta$ for each side of the triangle. One can also define three components of $\rho_{ij}$ namely, normal part $\rho_n = \rho_{ij}$ and two perpendicular contributions $\rho_{l} = \rho_{ij}$ and $\rho_{t} = \rho_{ij}$ where the symbols $l$ and $t$ have the same meaning as in the definition of the AS exchange Hamiltonian. One can also define a combined vibronic parameter $\beta_{ij} = \sqrt{\beta_l^2 + \beta_t^2}$ that appears in the final results. Eq. (3) contains contributions related to the isotropic and AS exchange interactions to the overall vibronic coupling. After calculation of the derivatives $\partial R_{ij}/\partial Q_x$ (using the relations between the Cartesian displacements $X_i, Y_i, Z_i$ and normal coordinates $Q_x$, Fig. 2) one arrives at the following form of the spin-vibronic Hamiltonian:

$$H_{es} = \sum_{\Gamma \gamma} \alpha \tilde{V}_{\Gamma \gamma} Q_{\Gamma \gamma},$$

$$H_{es}^I = \sum_{\gamma} \beta W_{\Gamma \gamma} Q_{\Gamma \gamma}$$

(8)

$$H_{es}^R = \sum_{\gamma} \alpha \tilde{V}_{\Gamma \gamma} Q_{\Gamma \gamma}.$$

$$H_{es} = \sum_{\Gamma \gamma} \alpha \tilde{V}_{\Gamma \gamma} Q_{\Gamma \gamma},$$

$$\tilde{G}_{\Gamma \gamma} = \alpha \tilde{V}_{\Gamma \gamma} + \beta W_{\Gamma \gamma}.$$ 

Here $\Gamma \gamma = A_1, E_1, E_2$ label the irreducible representations and basis functions of the $D_3$ symmetry group and the operators $\tilde{V}_{\Gamma \gamma}$ and $W_{\Gamma \gamma}$ are expressed in terms of the scalar and vector products of spin operators (Appendix I). The evaluation of the vibronic Hamiltonian is performed with the aid of the irreducible tensor operators approach [2,60–64].

The vibronic term arising from the modulation of the AS exchange ($H_{ee}^R$) can be divided into two parts $H_{ee}^R = H_{ee}^R(||) + H_{ee}^R(\bot)$, namely, the part arising from the modulation of $H_{00}(||)$ and that emerging from the modulation of $H_{00}(\bot)$. These two parts are denoted as $H_{ee}^R(||)$ and $H_{ee}^R(\bot)$ respectively:

$$H_{ee}^R(||) = \sum_{x=AXY} \left( \frac{\partial H_0}{\partial Q_x} \right)_{Q_x=0} Q_x,$$

$$H_{ee}^R(\bot) = \sum_{x=AXY} \left( \frac{\partial H_0}{\partial Q_x} \right)_{Q_x=0} Q_x.$$

(9)

In order to include the interaction of spins with the acoustic lattice vibrations, the symmetry adapted molecular displacement should be expanded into series of the longitudinal $(l)$ and transverse $(t)$ lattice vibrational modes $q_{\lambda v}$ specified by the wave vector $\kappa$ and polarization $v = l, t$ as suggested in ref. [65]:

$$Q_{\Gamma \gamma}(v) = \sum_{\lambda=0}^{\infty} \left( \frac{h}{M_{\text{MOCV}}} \right)^{1/2} a_{\lambda v}(\Gamma \gamma) q_{\lambda v}, \quad v = l, t,$$

(10)

In Eq. (10) $q_{\lambda v}$ are the dimensionless normal coordinates of the lattice, $M$ is a mass of crystal and $a_{\lambda v}(\Gamma \gamma)$ are the so called Van Vleck coefficients [65] introduced in his underlying theory of paramagnetic relaxation; their exact expressions for a triangular molecule are given in Appendix II. The final expression for the spin-phonon interaction is the following:

$$H_{es} = \sum_{\Gamma \gamma} \sum_{\lambda=0}^{\infty} \left( \frac{h}{M_{\text{MOCV}}} \right)^{1/2} a_{\lambda v}(\Gamma \gamma) q_{\lambda v},$$

(11)

It should be noted that the spin-phonon Hamiltonian in Eq. (11), is adapted to the triangle model for $V_{15}$. In fact, by definition the matrices $G_{\Gamma \gamma}$ in this Hamiltonian act within the set of eight spin functions (two $S = 1/2$ doublets and quadruplet $S = 3/2$) of the vanadium triangle.

4. One-phonon spin-lattice relaxation

Let us consider the case of two non-degenerate electronic states $\mid l \rangle$ and $\mid f \rangle$ separated by the energy gap $\Delta E = E_l - E_f > 0$ and a transition $\mid l \rangle \rightarrow \mid f \rangle$ accompanied by the release of a phonon with the energy $\hbar \omega_{\lambda v} = \Delta E$. According to the perturbation theory the probability of this transition is the following:

$$w_{\lambda v} = \frac{2\pi}{\hbar} \left( \sum_{\Gamma \gamma} \left( \frac{h}{M_{\text{MOCV}}} \right)^{1/2} \left( \frac{h}{\hbar \omega_{\lambda v}} \right)^{1/2} \left( \left( \frac{\Delta E}{h} \right)^{1/2} \delta(\hbar \omega_{\lambda v} - \Delta E) \right) \right),$$

(12)

where $\delta(\chi)$ is the Dirac $\delta$ – function. After summation over the vibrational modes (including thermal averaging) one arrives at the following expression:

$$w_{l-v} = \frac{1}{\pi \hbar \rho} \left( \frac{\Delta E}{h} \right)^{3} \frac{L_{df}}{1 - \exp(-\Delta E/2kT)} \left( \frac{\Delta E}{h} \right)^{3},$$

(13)

where $L_{df}$ is the Debye model for the lattice vibrations the averaged (over all directions of the phonon propagation vector but with the fixed specified frequency $\omega$) squared Van Vleck coefficients are given in Appendix II. Substitution of these equations into Eq. (13) leads the following result

$$w_{l-v} = \frac{R_{df}^2}{\pi \hbar \rho} \left( \frac{L_{df}}{1 - \exp(-\Delta E/2kT)} \right) \left( \frac{\Delta E}{h} \right)^{3},$$

(14)

$$L_{df} = \left| F(\Gamma \gamma) \right|^2 \left( \frac{1}{15 \nu_1^2} + \frac{4}{15 \nu_1^2} \right) + \left| F(\Gamma \gamma) \right|^2 \left( \frac{1}{15 \nu_1^2} + \frac{2}{15 \nu_1^2} \right) + \frac{L_{df}}{\pi \hbar \rho} \left( \frac{\Delta E}{h} \right)^{3} \frac{L_{df}}{1 - \exp(-\Delta E/2kT)} \left( \frac{\Delta E}{h} \right)^{3},$$

(15)
where $v_t$ and $v_l$ are the transverse and longitudinal sound velocities in the crystal correspondingly. The long-wave approximation for the acoustic phonons is assumed ($k R_0 << 1$). The results for the specific transitions are obtained by the due substitutions of the elements of the matrices $C_{ij}$. They can be found with the use of the irreducible tensor operators technique [2,60–63].

### 5. Selection rules for one-phonon transitions in pseudo-angular momentum representation

The selection rules for the spin-phonon transitions can be analyzed in terms of the pseudo-angular momentum representation employed for the analysis of the HDVV Hamiltonian and selection rules in EPR transitions reported in $V_{15}$ [8]. It was revealed that the degeneracy doubling ("accidental" degeneracy) in the ground spin-frustrated state $(S_{12})S = (0)1/2, (1)1/2$ is related to the exact orbital degeneracy so that the ground term is the orbital doublet $^2E$ in the trigonal ($D_3$) symmetry while the excited spin level $S = 3/2$ corresponds to the orbital singlet $^4A_2$. This can be symbolically indicated as: $2D^{(1/2)} \Rightarrow ^2E, 2D^{(3/2)} \Rightarrow ^4A_2$, where $D^{2S}$ are the irreducible representations of the rotation group $R_3$ numerating spin states of the system. It was concluded [61] that the AS exchange acts within the manifold $(S_{12})S = (0)1/2, (1)1/2$ like first order spin-orbital interaction within the $^2E$ term and gives rise to the two doublets in agreement with the Kramers theorem [66].

By applying the symmetry operations of the $D_3$ point group to the basis functions $|0)1/2 \pm 1/2 \rangle$ and $|1)1/2 \pm 1/2 \rangle$ (that generate permutations of spins in the triangle) one can find that they are related to the $xy$ basis of the irreducible representation $E$. Therefore their circular components [67] correspond to the projections $M_t = +1$ and $M_t = -1$ of the pseudo-angular momentum (pseudo-angular momentum representation). We will use a short notation $|M_s, S, M_t \rangle = u_{0t}(S, M_t)$. The spin functions of the ground manifold can be represented as:

$$\begin{align*}
u_{+1}(1/2, \pm 1/2) &= \mp 1/\sqrt{2}(|0)1/2, \pm 1/2 \rangle \pm i(|1)1/2, \pm 1/2 \rangle), \\
u_{+1}(1/2, \mp 1/2) &= \mp i/\sqrt{2}(|0)1/2, \mp 1/2 \rangle \mp i(|1)1/2, \mp 1/2 \rangle).
\end{align*}$$

Using the concept of Russell-Sauders coupling (LS) one can introduce the functions $U_1(M_t)$ belonging to a definite full spin $S$ and projections $M_t = M_s + M_t$ of the full pseudo-angular moment, so that $U_{12}(\pm 3/2) = U_{12}(1,1/2) \pm 1/2$ and $U_{12}(\pm 1/2) = U_{12}(1,1/2) \pm 1/2$ (LS scheme). The orbital singlet $^4A_2$ corresponds to $M_t = 0$, and the components $M_t$ are labeled as $u_{0t}(3/2, M_t)$ or $U_{12}(M_t)$ with $M_t = \pm 1/2$ and $M_t = \pm 3/2$, so that $M_t = \pm 1/2$ and $\pm 3/2$. This labeling is valid for the case of parallel field $\{H|C_3\}$ that retains the effective axial symmetry of the system. Fig. 3 illustrates the pseudo-angular momentum labels for the Zeeman levels of the system at relatively low field (far enough from the crossing/anticrossing area) and the selection rules for one-phonon transitions.

The one-phonon transitions have special selection rules that can be illustrated in terms of the pseudo-angular momentum representations providing $H|C_3$. Although the evaluation of the relaxation times are made (Section 7) in the framework of the general model so far suggested it is worth to underline the specific consequences of different terms in spin-phonon coupling Hamiltonian. Since the isotropic exchange is the main part of exchange interaction, the vibronic coupling related to the modulation of this part of the exchange seems to be dominant. Let us consider different transitions caused by the operator $H_{\text{AS}}(1)$ when magnetic field is parallel to the $C_3$ axis of the cluster. At low fields the normal component $H_{\text{AS}}(1)$ gives rise to a zero field splitting of two $S = 1/2$ levels and there are two allowed transitions which obey the selection rules $\Delta M_t = \pm 2$. $\Delta M_t = 0$. $\Delta M_t = \pm 2$ exist in the $S = 1/2$ manifold (solid lines in Fig. 3). When the in-plane part of the AS exchange is taken into account, it triggers additional transitions since both $M_t$ and $M_t$ are no longer "good" quantum numbers and the only selection rule $\Delta M_t = \pm 2$ remains valid. As one can see there are eight transitions obeying this rule (Fig. 3). It also turns out that the in-plane AS exchange gives rise to the transitions with $\Delta M_t = 0$. These additional transitions are important in the region of level anticrossing where the role of the in-plane AS exchange is most pronounced [5]. In order to find some additional transitions that are forbidden in the framework of the model so far discussed, let us consider transitions caused by the operator $H_{\text{AS}}(2)$ that represents a phonon modulation of the parallel part of AS exchange. The parallel component $H_{\text{AS}}(2)$ itself is well pronounced at low fields and in this case there are four transitions between the doublet $S = 1/2$ and quadruplet $S = 3/2$ with the rules $\Delta M_t = \pm 1$. $\Delta M_t = 0$. $\Delta M_t = \pm 1$ (Fig. 4).

The numerical calculations based on the full vibronic Hamiltonian will be given in Section 7.

### 6. Estimation of spin-vibronic coupling parameters

Approximate estimation of spin-vibronic coupling parameters for $V_{15}$ may be done from the available data regarding another

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**Fig. 3.** Zeeman pattern of $V_{15}$, $H|C_3$, and transitions caused by the phonon modulation of the isotropic exchange in the presence of the parallel $H_{\text{AS}}(1)$ term (solid) or in-plane $H_{\text{AS}}(2)$ term (dashed) in the Hamiltonian.

**Fig. 4.** Transitions caused by the operator $H_{\text{AS}}(2)$, $H|C_3$. 

compounds. According to Ref. [68] the dependence of $J$ on the interatomic distance $R$ for MnO and MnF$_2$ is well approximated by the law

$$J = AR^{-3.0} \approx AR^{-10}, \quad (17)$$

where $\gamma_m$ $\approx$ 10/3 is Grüneisen constant and factor $A$ is specific for a given compound. For the V$_{15}$ cluster one can estimate $A = J_0 R_0^{10}$ ($R_0$ is the equilibrium metal-metal distances equal to 7Å in the V$_{15}$ triangle, $J_0$ = 0.85cm$^{-1}$ is the equilibrium value of $J$) and thus the spin-vibronic coupling $\lambda$ can be found as:

$$\lambda = \sqrt{6} \left( \frac{\partial J}{\partial R}_0 \right)_0 \approx -10\sqrt{6}AR_0^{11} \approx -3 \text{ cm}^{-1}/\text{Å} \quad (18)$$

Assuming that for the components of AS exchange ($\alpha = n, t, l$) the relation

$$\frac{1}{D_{\alpha}} \left( \frac{\partial D_{\alpha}}{\partial R}_0 \right)_0 \approx \frac{1}{J_0} \left( \frac{\partial J}{\partial R}_0 \right)_0 \quad (19)$$

is valid, one can deduce the following estimation: $\beta_n \approx -0.11 \text{ cm}^{-1}/\text{Å}, \beta_t \approx -0.34 \text{ cm}^{-1}/\text{Å}.$

Alternative estimation of $\lambda$ is given in ref. [59] where the ratio $(\partial J/\partial R)_0/J$ was found to be in the range 10 – 30Å$^{-1}$ for the Ir:ammonium chloroplatinate and ruby with different doping concentration. This estimation gives one order higher values for $\lambda, \beta_n, \beta_t$ then provided by Eq. (17) but even with this newer estimation spin-vibronic interaction turns out to be very weak.

7. Estimation of the spin-phonon relaxation rates

7.1. The case of weak field

We use the values of the exchange parameters $J_0$, $D_n$ and $D_l$ that are given in Section 2, the spin-phonon coupling parameters $\beta_n \approx -0.34 \text{ cm}^{-1}/\text{Å}, \beta_t \approx -0.11 \text{ cm}^{-1}/\text{Å}$ $R_0 = 7 \text{ Å}$ for the side of the inner triangle in V$_{15}$, $\rho = 3 \times 10^3 \text{ kg/m}^3$ for the density of V$_{15}$ [69]. Due to the lack of the reliable information regarding the velocities of the sound velocities it is assumed the same values for the transversal and longitudinal velocities $v = 2 \times 10^3 \text{ m/s}.$ The relaxation times for the low lying levels at 5K are found to be $\tau_{3-1} = \tau_{4-2} = 1.6 \times 10^{-3} \text{ s}$. These estimations are in agreement with the results of Ref. [54] although the estimation presented here gives shorter relaxation times for a definite set of the levels. Of course, the accuracy of these estimations is restricted by the uncertainty of the parameters like sound velocity and spin-vibronic constants. One can see that the modulation of the isotropic exchange gives much faster (two orders of magnitude) transitions than that arising from the modulation of the normal part of AS exchange. But it should be noted that these two mechanisms of spin-phonon transitions obey different selection rules that are expected to give essentially different phonon broadening of EPR lines.

Table 1

<table>
<thead>
<tr>
<th>Transition</th>
<th>2</th>
<th>3</th>
<th>12</th>
<th>4</th>
<th>5</th>
<th>1</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relaxation time (s)</td>
<td>$1.9 \times 10^{-2}$</td>
<td>$2.4 \times 10^{-3}$</td>
<td>$2.15 \times 10^{-2}$</td>
<td>$6.6 \times 10^{-3}$</td>
<td>$1.1 \times 10^{-2}$</td>
<td>$1.7 \times 10^{-2}$</td>
<td>$7.1 \times 10^{-3}$</td>
</tr>
<tr>
<td>Linewidth (Tesla)</td>
<td>$1.9 \times 10^{-9}$</td>
<td>$1.5 \times 10^{-8}$</td>
<td>$1.7 \times 10^{-9}$</td>
<td>$5.5 \times 10^{-9}$</td>
<td>$4.3 \times 10^{-9}$</td>
<td>$2.1 \times 10^{-9}$</td>
<td>$3.4 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

7.2. The case of high field

The numerical estimations based on the full spin Hamiltonian $(H_0 + H_{AS})$ and full spin-phonon Hamiltonian $(H_{sp} + H_{sp})$ with the values of parameters defined in Section 6. Fig. 5a and b shows the scheme of EPR transitions (labeled as in Ref. [8]) and their calculated intensities for temperature 0.5K and frequency of 57.9GHz that was used for the low-temperature EPR experiments reported in [70]. The estimated relaxation times and linewidths for the transitions at $v = 57.9 \text{GHz}$ for which the spin-phonon relaxation is allowed by symmetry rules are given in Table 1. Although

![Fig. 5. (a) EPR transitions for the EPR frequency of 57.9 GHz at the temperature of 0.5 K, $\mathbf{H}_{ext}$. Transitions 4 and 12 occur at the same resonant field. (b) Calculated intensities of the lines.](image-url)
8. Conclusion

To summarize the results of this article, the following key points are to be mentioned: (1) the model for the spin-phonon coupling for the V15 cluster is proposed. The model takes into consideration the modulation of the isotropic and AS exchange interactions within the central $V^{10}$ triangular spin frustrated layer by the acoustic lattice vibrations (heat reservoir) for which the Debye law of dispersion is assumed; (2) within the pseudo-angular momentum representation the selection rules for the direct (one-phonon) transitions between Zeeman levels are established and the specific role of different contributions to the spin-phonon coupling is elucidated. An important role of the AS exchange in the selection rule for spin-phonon transitions in spin-frustrated systems is underlined; (3) the numerical results are obtained for different of the field corresponding to the available experimental data on EPR of V15 (57.9, 108 GHz). As distinguished from the general estimations, the microscopic approach developed here has allowed to get a detailed information regarding the different direct spin-phonon processes within the Zeeman pattern of the low lying spin excitations in V15. In fact, the relaxation times for one-phonon transitions proved to be specific for the different transitions and ranges of the field. These times for different transitions are estimated as $10^{-2} \div 10^{-3}$ s. The present calculations show that one-phonon processes are less important than the thermal fluctuations of the dipolar interactions between the molecules as a source of decoherence in agreement with the first prediction of coherent states in V15 [54].

It should be noted that along with the one-phonon processes another mechanisms of spin-phonon relaxation can play significant (or even dominant) role. These are the two-phonon (Raman type) processes for which the probability can be high due to participation of the two phonons whose frequencies (and consequently phonon densities) are not small as in the case of one-phonon relaxation. Additionally the quadratic (with respect to the atomic displacements) terms of spin-phonon coupling are able to give a significant contribution to the rate of relaxation. The Raman processes in V15 are expected to be especially important due to the high density of the excited spin states (dimension of the Hilbert space is $10^{15}$) virtually involved in the second order processes. The Orbach type relaxation should also be taken in consideration with due account for the excited spin states and their detailed Zeeman structure. We plan to extend the presented model in future paying special attention to the problem of decoherence in molecular magnets.

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Appendix I

The operators $V_{ij}$ in terms of the scalar products of spin operators:

$$V_A = \sqrt{3}(S_1 S_2 + S_3 S_5 + S_1 S_3),$$

$$V_X = \frac{1}{\sqrt{6}}(S_1 S_3 + S_3 S_1 - 2S_3 S),$$

$$V_Y = \frac{1}{\sqrt{2}}(S_1 S_3 - S_3 S_1).$$

The operators $W_{ij}$ in terms of the vector products of spin operators:

$$W_A = e_{12}[S_1 \times S_2] + e_{23}[S_2 \times S_3] + e_{31}[S_3 \times S_1],$$

$$W_X = \frac{1}{\sqrt{2}}[e_{12}[S_1 \times S_2] + e_{23}[S_2 \times S_3] - 2e_{31}[S_3 \times S_1]],$$

$$W_Y = \sqrt{6}e_{23}[S_3 \times S_3] - e_{31}[S_3 \times S_1])$$

where $e_\theta$ denotes the unit vector in direction of the vector $\theta$. The accuracy in the numerical estimations is restricted by the uncertainty of some parameters (like sound velocity) and approximations so far employed, the interrelations between the relaxation times seem to be reliable for different EPR transitions at different frequencies. Fig. 6 shows the transitions and their comparative intensities at frequency $\nu = 108$ GHz, Table 2 shows relaxation times and linewidths (at the same frequency) for the allowed spin-phonon transitions.

Let us compare the results for different frequencies. Accordingly to the Tables 1 and 2 the relaxation rates decrease with increase of the EPR frequency (due to dependence of the probability as a function of the energy gap) and, consequently, the width of the lines is also increasing. At the frequency 108 GHz these lines are on average four times broader then at 58 GHz. This result is in a reasonable agreement with the broadening observed in Ref. [70], so spin-phonon interaction seems to be a significant factor. It should be noted that the linewidths reported in [70] refer to the absorption line that, constitutes a superposition of the transition lines shown in Figs. 5 and 6.
Appendix II

The Van Vleck coefficients $a_\kappa(\Gamma)$ for the equilateral triangular unit are given by the following equations [59]:

$$a_0(A_1) = (1/2)(\kappa R_0)(l' + m'M'),$$

$$a_0(E_X) = -(1/2)(l' - m'M'),$$

$$a_0(E_Y) = -(1/2)(\kappa R_0)(l'M' - l'l').$$

where $R_0$ is the side of a triangle, $l', m', n'$ are the direction cosines of the wave-vector in the coordinate system defined in Fig. 2, and $l', m', n'$ are direction cosines of polarization vector. In the long-wave Debye approximation $\kappa = \omega /\nu$, in this approximation the coefficients $a_\kappa(\Gamma)$ can be averaged over all propagation and polarization directions. The result is the following:

$$\langle a_0^2(A_1) \rangle = \frac{2}{15} \frac{\omega^2 R_0^2}{\nu^2},$$

$$\langle a_0^2(E_X) \rangle = \frac{1}{15} \frac{\omega^2 R_0^2}{\nu^2},$$

$$\langle a_0^2(E_Y) \rangle = \frac{1}{15} \frac{\omega^2 R_0^2}{\nu^2}.$$

References


