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Crossover of the magnetic levels and adiabatic magnetization of the mesoscopic cluster V_{15}

Boris Tsukerblat [a,*], Alex Tarantul [a], Achim Müller [b]

[a] *Department of Chemistry, Ben-Gurion University of the Negev, 84105 Beer-Sheva, Israel*
[b] *Fakultät für Chemie, Universität Bielefeld, 33501 Bielefeld, Germany*

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Abstract

The magnetic three spin-1/2 model for nanometer-scale molecular cluster V_{15} is analyzed with the emphasis on the origin of the mixing of different spin levels in the resonance fields that is generally important for the problem of single molecular magnets. The zero-field splitting in the ground quadruplet (two $S = 1/2$ levels) is shown to depend mainly on the normal component of AS exchange meanwhile the zero-field splitting in the excited $S = 3/2$ multiplet is a second order effect with respect to in-plane components of AS exchange. The normal component of the AS exchange is shown to lead to the exact crossing of the magnetic sublevels at the arbitrary direction of the field. The positions of two crossing/anticrossing points in the ground manifold depend mainly on the isotropic exchange and normal component of AS exchange meanwhile the gap in the avoided crossing point in parallel field is affected only by the in-plane component. We discuss the role of AS exchange in the field and temperature dependence of the adiabatic magnetization. We predict a specific field dependence of the magnetization vs. field caused by AS exchange.

Keywords: Molecular magnets; Antisymmetric exchange; Magnetic anisotropy; V_{15} cluster

1. Introduction

The discovery of the phenomenon of single molecular magnetism [1–7] has given a strong impact to the study of the magnetic anisotropy [8–15] and relaxation processes [6,16,17] in large magnetic clusters, objects of "zero-dimensional" magnetism. High-spin molecules such as a classical single molecule magnet, so-called Mn_{12}-acetate ($Mn_{12}O_{12}(OAc)_{16}(H_2O)_4$) (see review article [6]) possess high spin ($S = 10$) ground state and negative anisotropy that give rise to a significant barrier for spin-reorientation. During the past decade much attention has been attracted by a large low spin molecule $K_6[V^{IV}_{15}As_6O_{42}(H_2O)]\cdot 8H_2O$ (hereafter V_{15}) containing 15 ions V^{IV} ($S_i = 1/2$) that are strongly coupled through antiferromagnetic exchange interaction to give total ground state spin $S = 1/2$ [18–20]. Detailed experimental and theoretical studies of the adiabatic magnetization and quantum dynamics show that despite the absence of the barrier for the spin reversal the V_{15} molecule exhibits the hysteresis loop of magnetization [21–29] of molecular origin and can be referred to as a mesoscopic system.

Extensive studies of the static magnetic susceptibility [19,20], ab-initio [31–34] and spin-Hamiltonian [19,35–39] energy pattern, inelastic neutron scattering [40,41] and EPR [42,43] showed that the low lying part of the energy spectrum is well isolated from the remaining spin levels. This part of the spectrum involves two spin doublet states and a spin quadruplet that 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, so that the V_{15} molecule entire can be

* Corresponding author.
E-mail addresses: tsuker@bgumail.bgu.ac.il, tsuker@bgu.ac.il (B. Tsukerblat).

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represented as the cluster of three spins $S_i = 1/2$ located on the corner of the equilateral triangle. The three-spin model of V_{15} substantiated in [19,20] and developed in the subsequent studies [30,35–39] well explains stepwise behavior of the adiabatic magnetization vs. applied field and the dynamic behavior.

The magnetic model for V_{15} so far suggested [19,24,35,38,39] includes isotropic Heisenberg–Dirac–Van Vleck (HDVV) exchange interaction and antisymmetric (AS) exchange. This interaction arises from the combined action of spin–orbital coupling and isotropic exchange and introduced by Dzyaloshinsky [44] by using phenomenological symmetry conditions and Moria [45] from the microscopic point of view by the inclusion of spin–orbit coupling in the Anderson's theory of superexchange. AS exchange that is called Dzyaloshinsky–Moria interaction was shown to give rise to the avoided crossings of the magnetic sublevels in resonant fields affecting thus the adiabatic magnetization, the energy gap in the Landau–Zener–Stückelberg transitions and the hysteresis loop in alternate fields.

The understanding of role of the AS exchange in the spin frustrated systems (particularly in trinuclear metal clusters) dates back to the seventies (see review article [46]). In the first papers dealing with the analysis of the exchange coupling in the trinuclear clusters [47–50] the group-theoretical classification of the exchange multiplets and "accidental degeneracies" in the HDVV scheme is proposed. The AS exchange was shown to be responsible for the zero-field splitting of the frustrated ground state of the half-integer triangular spin systems in view of the Kramers theorem [46,51,52]. Anisotropic Zeeman splitting has been discovered and the manifestations of the AS exchange (as well as of the symmetry breaking) in magnetic anisotropy have been studied [53,54]. AS exchange in the triangular systems was shown to result in the essential peculiarities of the EPR spectra in single crystals, shape of the lines in powder, hyperfine structure of EPR spectra and relaxation processes [55–62]. AS exchange proved to be crucially important for the description of the wide range of the phenomena related to the hyperfine interactions such as Mössbauer spectra, hyperfine magnetic fields on the nuclei [63,64] and inelastic neutron scattering [46,65,66].

In this Letter we study in detail the three-spin magnetic model for V_{15} cluster with the emphasis on the manifestations of different kinds of AS exchange and reveal the set of the independent effective AS parameters allowed by the symmetry conditions. We analyze the magnetic anisotropy induced by the AS exchange, crossover and anticrossover of the magnetic sublevels belonging to different spin states and field and temperature dependence of the adiabatic magnetization (slow sweeping velocity field).

2. Model of isotropic exchange interaction

Molecular cluster V_{15} has a distinct layered quasispherical structure within which fifteen V^{IV} ions ($s_i = 1/2$) placed in a large central triangle sandwiched by two hexagons [18] (Fig. 1). Five different pathways for the antiferromagnetic isotropic superexchange can be distinguished as schematically shown in Fig. 1 where the corresponding exchange parameters are also indicated. Isotropic exchange interactions can be described by

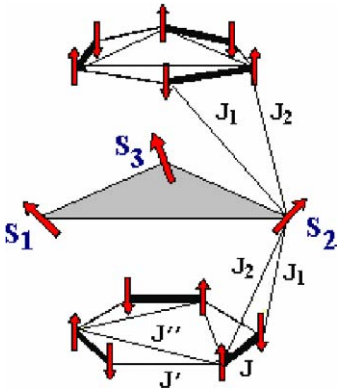


Fig. 1. Schematic structure of the metal network of V_{15} cluster, dominant exchange pathways and pictorial representation of spin arrangement and frustration effect in the central triangle.

Table 1
Isotropic exchange parameters (in cm^{-1}) in V_{15} molecule

Sets of parameters	Reference	J	J'	J''
I	[19]	−262	−10	−62
II	[20]	−278	−52	−104
III	[30]	−170	−28	−56

Heisenberg–Dirac–Van Vleck (HDVV) Hamiltonian:

$$H_0 = -2\sum_{\langle i,j\rangle} J_{ij}\boldsymbol{S}_i\boldsymbol{S}_j, \tag{1}$$

where the summation is extended over all pairs of the magnetic ions and J_{ij} are the exchange parameters. First calculation of the spin pattern within the isotropic exchange model was given in [19] with the aid of the irreducible tensor operators technique and the exchange parameters J, J_1, $J_2 J'$, J'' have been estimated. Later on a new set of these parameters was deduced from the adiabatic magnetization measurements in superhigh fields [30]. Using the package Magpack [67] we have recalculated the energy levels with the three sets (I, II, III) of these five parameters so far suggested (Table 1) assuming also that $J_1 \approx J'$ and $J_2 \approx J''$ as suggested in [19] (Fig. 2). One can see that two low lying levels corresponding to the full spins $S = 1/2$ and $S = 3/2$ are very close in all three cases, the corresponding gaps were proved to be 3.2 cm^{-1} (set I), 3.54 cm^{-1} (set II) and 1.5 cm^{-1} (set III). The next excited level is found to be a spin doublet at 621.07 cm^{-1}, 528.72 cm^{-1} and 345.04 cm^{-1}, correspondingly, that shows that in all cases the two low lying levels are well separated from the excited ones and can be viewed as an energy pattern of an isolated spin-1/2 triangular unit as was proposed in [19] and substantiated within the perturbation theory.

The full Hilbert space for 15 spins involves $2^{15} = 32\,768$ states and although the exchange problem is tractable even if anisotropic contributions are taken into account [19,20,34,38,39] a simplified model of a spin triangle [19,20] gives accurate and descriptive results for the low lying set of the levels. In fact, the parameter J is the leading one and the parameters J_1, J', J'' are significantly smaller and seem to be of the same

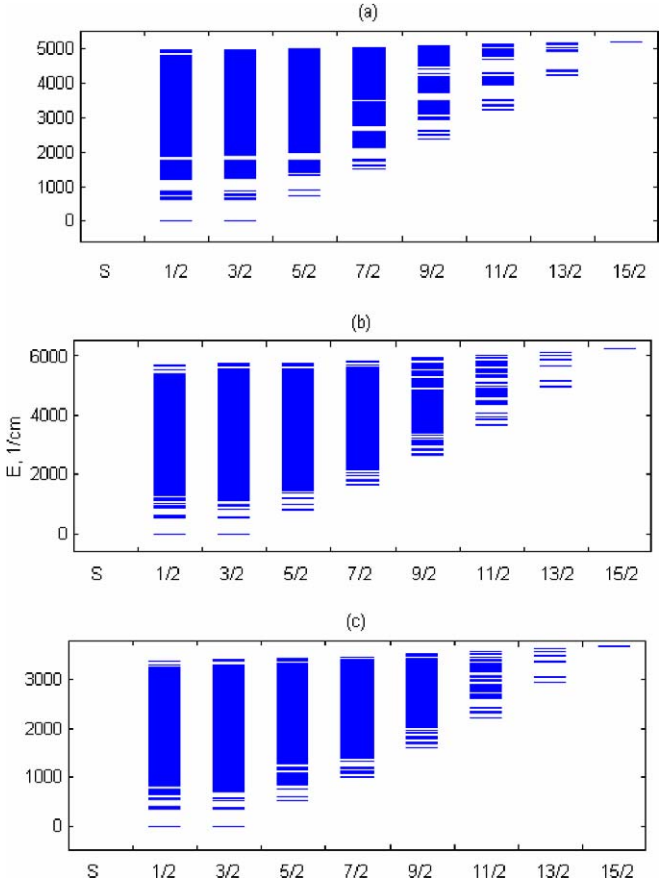


Fig. 2. Energy patterns of V_{15} molecule evaluated with three sets of the isotropic exchange parameters: (a) set I, (b) set II, (c) set III.

order so that each spin of the central triangle is coupled to a pair of strongly coupled spins belonging to the lower and upper hexagons as shown in Fig. 1. Each pentanuclear subunit consisting of two dimers (marked in bold in Fig. 1) and a spin of the triangle can be considered as an effective spin $s = 1/2$ placed in the central layer so that the low lying part of the energy pattern of the system entire can be viewed as the result of spin coupling within the triangular cluster.

We will focus on the three-spin model of V_{15} within which the isotropic superexchange can be described by the HDVV Hamiltonian reflecting trigonal symmetry of the system:

$$H_0 = -2J_0(\boldsymbol{S}_1\boldsymbol{S}_2 + \boldsymbol{S}_2\boldsymbol{S}_3 + \boldsymbol{S}_3\boldsymbol{S}_1), \tag{2}$$

where $\boldsymbol{S}_1$, $\boldsymbol{S}_2$ and $\boldsymbol{S}_3$ denote the spin operators on the sites 1, 2 and 3 ($S_1 = S_2 = S_3 = 1/2$) each associated with five strongly coupled spins as indicated in Fig. 1 and J_0 is the isotropic exchange parameter ($J_0 < 0$). Hereunder for the sake of convenience a positive parameter $J = -J_0$ will be used. As usually the following spin coupling scheme $S_1S_2(S_{12})S_3S \equiv (S_{12})S$ is assumed with S_{12} being the intermediate spin ($\boldsymbol{S}_{12} = \boldsymbol{S}_1 + \boldsymbol{S}_2$) so that in our case $(S_{12})S = (0)1/2$, $(1)1/2$ and $(1)3/2$. Accordingly, the basis functions will be labeled as $|S_1S_2(S_{12})S_3SM\rangle \equiv |(S_{12})SM\rangle$. The energy levels $\varepsilon_0(S)$ are expressed as:

$$\varepsilon_0(S) = -J_0\big[S(S+1) - 9/4\big]. \tag{3}$$

They do depend upon the full spin S and are independent of S_{12}. This leads to the problem of the four-fold "accidental" degeneracy of two $S = 1/2$ doublets that is in a seeming contradiction with the Kramers theorem and over the last years this issue became a subject of the discussion regarding the model for V_{15}. More deep insight on the problem of degeneracy and consequently, zero-field splitting of spin multiplets (in particular, in view of the Kramers theorem) can be made on the basis of the group-theoretical consideration of the exchange coupling scheme that sheds light on the nature of the excessive degeneracies in the energy pattern of the exchange coupled systems [46,51,52]. The analysis of the HDVV Hamiltonian (see review article [46]) revealed that the "degeneracy doubling" is related to the unitary symmetry of the spin-Hamiltonian, Eq. (2). In particular, the degeneracy with respect to the intermediate spin within the spin coupling scheme in the ground manifold $(S_{12})S = (0)1/2$, $(1)1/2$ is associated with the exact orbital degeneracy in the multielectron triangular system so that the ground term is the orbital doublet ^2E of the trigonal point group meanwhile the excited one is the orbital singlet $^4A_2$. The orbital degeneracy of two $S = 1/2$ levels is closely related to spin-frustration in the ground state (leading to a special triangular spin arrangement and spin density distribution) and is peculiar to all symmetric triangular spin-systems with half-integer spins [46].

It was concluded that the AS exchange acts within the $(S_{12})S = (0)1/2$, $(1)1/2$ manifold like a first order spin–orbital interaction within the ^2E term that is allowed by the symmetry rules in trigonal point groups [52] and gives rise to two Kramers doublets in full agreement with the Kramers theorem as it was pointed out in [46]. For $\boldsymbol{D}_3$ symmetry two Kramers doublets can be specified as a pair of complex conjugated double-valued irreps $\bar{A}_1 + \bar{A}_2 = 2\bar{A}$ and $\bar{E}$ [52]. It was also demonstrated that AS exchange in trimeric systems removes the degeneracy with respect to intermediate spin values and produces first order splitting in $(S_{12})S = (0)1/2$, $(1)1/2$ quadruplet resulting at the same time in an essential axial magnetic anisotropy. Hereafter we will analyze the effects of AS exchange in a more general form allowed by the trigonal symmetry with the emphasis on the behavior of the magnetic sublevels near the crossing points at high fields.

3. Antisymmetric exchange

AS exchange terms within the full Hilbert space are considered in Refs. [35,38,39] on the base of the developed numerical procedures that allow to relate the original AS exchange parameters in the strongly coupled dimeric units of the hexagons to the ground state splitting in the ground manifold of the V_{15} system entire. AS exchange in a triangular cluster can be described by the Hamiltonian:

$$H_{\mathrm{AS}} = \boldsymbol{D}_{12}[\boldsymbol{S}_1 \times \boldsymbol{S}_2] + \boldsymbol{D}_{23}[\boldsymbol{S}_2 \times \boldsymbol{S}_3] + \boldsymbol{D}_{31}[\boldsymbol{S}_3 \times \boldsymbol{S}_1], \tag{4}$$

where $[\boldsymbol{S}_i \times \boldsymbol{S}_j]$ are the vector products and $\boldsymbol{D}_{ij}$ are the antisymmetric vector parameters ($\boldsymbol{D}_{ij} = -\boldsymbol{D}_{ij}$). Site symmetry of the V^{IV}–V^{IV} pair in the molecule implies a set of Moria's conditions [45] that determine possible directions of each vector

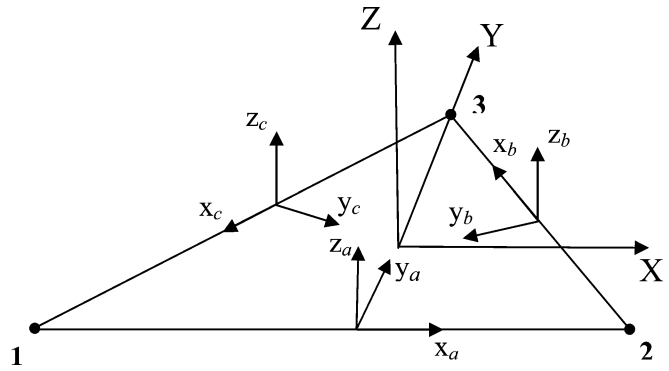


Fig. 3. Local $(x_i\, y_i\, z_i)$ and molecular (XYZ) coordinate systems for the vanadium triangle in V_{15}.

$\boldsymbol{D}_{ij}$, these conditions should be combined with the conditions of the overall symmetry present in V_{15} molecule. In the isolated equilateral metal triangle (symmetry $\boldsymbol{D}_{3h}$) each pair possesses C_2 symmetry axis and two symmetry planes (C^a_{2y}, $\sigma_h = \sigma^a_{xy}$, $\sigma_\upsilon = \sigma^a_{yz}$, etc.) so that accordingly to Moria's conditions [45] all vectors $\boldsymbol{D}_{ij}$ in this idealized structure have to be perpendicular to the triangle plane and due to overall trigonal symmetry they should be equal $D^z_{12} = D^z_{23} = D^z_{31} = D_n$ with z being the common Z-direction of the local (a, b and c) and global coordinate systems (Fig. 3) and D_n is the only AS exchange parameter.

Actual symmetry $\boldsymbol{D}_3$ of the V_{15} molecule includes C_3 axis and three C_2 axes in the plane of the triangle. Each pair of the triangle possesses only C_2 axis and accordingly to the Moria's conditions vectors $\boldsymbol{D}_{ij}$ should be perpendicular to these C_2 axes. Therefore, we conclude that each vector $\boldsymbol{D}_{ij}$ has two components in the local coordinate frames, $D_n = D^z_{12} = D^z_{23} = D^z_{31}$ and $D_l \equiv D_{12x_a} = D_{23x_b} = D_{31x_c}$ (Fig. 2), these values can be considered as two independent parameters of AS exchange compatible with the overall $\boldsymbol{D}_3$ symmetry. In the case of $\boldsymbol{C}_{3v}$ point group each pair has only vertical symmetry plane perpendicular metal–metal bond so that the vectors $\boldsymbol{D}_{ij}$ should be situated in these planes so that the nonzero components of $\boldsymbol{D}_{ij}$ are: $D_n = D^z_{12} = D^z_{23} = D^z_{31}$ and $D_t \equiv D_{12y_a} = D_{23y_b} = D_{31y_c}$. Finally, under the condition of $\boldsymbol{C}_3$ symmetry all components of $\boldsymbol{D}_{ij}$ are nonzero (D_n, D_t, $D_l \neq 0$). In general, the actual symmetry of the triangle in the model should be compatible with the overall symmetry of the molecule entire to ensure the invariance of the full Hamiltonian with respect to point group operations.

The Hamiltonian of AS exchange for the three spin model with a trigonal symmetry in a common form can be represented as a sum of pairwise interactions H^{ij}_{AS}. For the pair 12 one finds

$$H^{12}_{\mathrm{AS}} = D_n[\boldsymbol{S}_{1a} \times \boldsymbol{S}_{2a}]_{za} + D_l[\boldsymbol{S}_{1a} \times \boldsymbol{S}_{2a}]_{xa} + D_t[\boldsymbol{S}_{1a} \times \boldsymbol{S}_{2a}]_{ya}, \tag{5}$$

where the symbol a indicates that the spin-operators and the components of the vector products are related to the local frame a. The remaining terms H^{23}_{AS} and H^{31}_{AS} can be obtained by the cyclic permutations of the symbols in Eq. (5).

4. Zero-field splitting

By rotating the local coordinate frames one can pass to the global coordinate system in each pairwise contribution, Eq. (5), to the AS exchange. In this way one can find the following expression for the full AS exchange Hamiltonian in which all operators are related to the common frame (Fig. 2):

$$\begin{aligned} H_{\mathrm{AS}} = {} & D_n\big([\boldsymbol{S}_1 \times \boldsymbol{S}_2]_Z + [\boldsymbol{S}_2 \times \boldsymbol{S}_3]_Z + [\boldsymbol{S}_3 \times \boldsymbol{S}_1]_Z\big) \\ & + D_l\bigg([\boldsymbol{S}_1 \times \boldsymbol{S}_2]_X - \frac{1}{2}[\boldsymbol{S}_2 \times \boldsymbol{S}_3]_X + \frac{\sqrt{3}}{2}[\boldsymbol{S}_2 \times \boldsymbol{S}_3]_Y \\ & - \frac{1}{2}[\boldsymbol{S}_3 \times \boldsymbol{S}_1]_X - \frac{\sqrt{3}}{2}[\boldsymbol{S}_3 \times \boldsymbol{S}_1]_Y\bigg) \\ & + D_t\bigg([\boldsymbol{S}_1 \times \boldsymbol{S}_2]_Y - \frac{\sqrt{3}}{2}[\boldsymbol{S}_2 \times \boldsymbol{S}_3]_X - \frac{1}{2}[\boldsymbol{S}_2 \times \boldsymbol{S}_3]_Y \\ & + \frac{\sqrt{3}}{2}[\boldsymbol{S}_3 \times \boldsymbol{S}_1]_X - \frac{1}{2}[\boldsymbol{S}_3 \times \boldsymbol{S}_1]_Y\bigg). \end{aligned} \tag{6}$$

It is convenient to express the Hamiltonian in terms of the irreducible tensor operators (ITO) with the aid of well known [68] interrelations between the spherical components ($q = 0, \pm 1$) of the vector product and the first rank irreducible tensor product

$$[\boldsymbol{S}_i \times \boldsymbol{S}_j]_q = -i\sqrt{2}\big\{S^i_1 \times S^j_1\big\}_{1,q}, \tag{7}$$

where S^i_{1q} ($i = 1, 2, 3$) is the spin tensor relating to the site i and $\{S^i_1 \times S^j_1\}_{k,q}$ is the component q of the tensor product of the rank k. Straightforward calculation leads to the following Hamiltonian expressed in terms of ITO:

$$\begin{aligned} H_{\mathrm{AS}} = {} & -i\sqrt{2}D_n \\ & \times \big(\big\{S^1_1 \times S^2_1\big\}_{1,0} + \big\{S^2_1 \times S^3_1\big\}_{1,0} + \big\{S^3_1 \times S^1_1\big\}_{1,0}\big) \\ & + (D_t + iD_l)\big\{S^1_1 \times S^2_1\big\}_{1,1} \\ & + (D_t - iD_l)\big\{S^1_1 \times S^2_1\big\}_{1,-1} \\ & + \omega^*(D_t + iD_l)\big\{S^2_1 \times S^3_1\big\}_{1,1} \\ & + \omega(D_t - iD_l)\big\{S^2_1 \times S^3_1\big\}_{1,-1} \\ & + \omega(D_t + iD_l)\big\{S^3_1 \times S^1_1\big\}_{1,1} \\ & + \omega^*(D_t - iD_l)\big\{S^3_1 \times S^1_1\big\}_{1,-1}, \end{aligned} \tag{8}$$

where $\omega = \exp(2\pi i/3)$. This is the most common expression for the AS exchange Hamiltonian compatible with the trigonal symmetry. The matrix elements of the pairwise AS exchange interactions in the triangle within the $|(S_{12})SM\rangle$ basis can be calculated for an arbitrary set of S_1, S_2, S_3 in a general way with the use of the ITO approach [51, 52,69,70]. Omitting the details of calculation we give here the final result for the matrix elements of $S_i = 1/2$ triangle:

$$\begin{aligned} & \big\langle (S_{12})SM\big|\big\{S^1_1 \times S^2_1\big\}_{1,q}\big|(S'_{12})S'M'\big\rangle \\ & = -\frac{3\sqrt{3}}{2}(-1)^{\frac{1}{2}+S+S'+2S_{12}-M}\begin{pmatrix} S & 1 & S' \\ -M & q & M' \end{pmatrix} \\ & \times \sqrt{[S][S'][S_{12}]\big[S'_{12}\big]}\big(S'_{12} - S_{12}\big)\big(S_{12} + S'_{12} + 1\big) \\ & \times \begin{Bmatrix} S & S_{12} & 1/2 \\ S'_{12} & S' & 1 \end{Bmatrix}\begin{Bmatrix} 1/2 & S_{12} & 1/2 \\ S'_{12} & 1/2 & 1 \end{Bmatrix}, \end{aligned}$$

$$\begin{aligned}
&\langle (S_{12})SM|\{S_1^2\times S_1^3\}_{1,q}|(S'_{12})S'M'\rangle\\
&\quad=\frac{\sqrt{3}}{4}(-1)^{3S+S'+2S_{12}+2S'_{12}+\frac{3}{2}-M}\begin{pmatrix} S & 1 & S'\\ -M & q & M'\end{pmatrix}\\
&\qquad\times\sqrt{[S][S'][S_{12}][S'_{12}]}\\
&\qquad\times\big[(S_{12}-S'_{12})(S_{12}+S'_{12}+1)-(S-S')(S+S'+1)\big]\\
&\qquad\times\begin{Bmatrix} S'_{12} & 1/2 & 1/2\\ 1/2 & S_{12} & 1\end{Bmatrix}\begin{Bmatrix} S_{12} & S & 1/2\\ S' & S'_{12} & 1\end{Bmatrix},\\
&\langle (S_{12})SM|\{S_1^3\times S_1^1\}_{1,q}|(S'_{12})S'M'\rangle\\
&\quad=\frac{\sqrt{3}}{4}(-1)^{3S+S'+S_{12}+3S'_{12}+\frac{3}{2}-M}\begin{pmatrix} S & 1 & S'\\ -M & q & M'\end{pmatrix}\\
&\qquad\times\sqrt{[S][S'][S_{12}][S'_{12}]}\\
&\qquad\times\big[(S_{12}-S'_{12})(S_{12}+S'_{12}+1)-(S-S')(S+S'+1)\big]\\
&\qquad\times\begin{Bmatrix} S_{12} & 1/2 & 1/2\\ 1/2 & S'_{12} & 1\end{Bmatrix}\begin{Bmatrix} S_{12} & S & 1/2\\ S' & S'_{12} & 1\end{Bmatrix},
\end{aligned}\tag{9}$$

where the conventionally accepted notations for the $3j$- and $6j$-symbols are used and $[S]=2S+1$.

By analyzing Eqs. (9) one can arrive to a conclusion that the "normal" part of the AS exchange (term associated with the parameter D_n) operates only within the basis of two "accidentally" degenerate doublets $(S_{12})S=(0)1/2$, $(1)1/2$, meanwhile two "in-plane" contributions (terms of the Hamiltonian associated with the parameters D_l and D_t) lead only to a mixing of the ground spin doublets $(0)1/2$, $(1)1/2$ with the excited spin quadruplet $(1)3/2$. This conclusion is useful for the understanding of the role of different components of AS exchange at low magnetic fields as well as at high fields in the vicinity of the crossover of the magnetic sublevels of $S=1/2$ and $S=3/2$.

The matrix of the AS exchange has the following analytical solutions defining the zero-field spectrum at the arbitrary interrelation between all involved parameters:

$$\begin{aligned}
\varepsilon_1=\varepsilon_2&=\frac{\sqrt{3}}{4}\Big(-D_n-\sqrt{D_\perp^2+\big(D_n+2\sqrt{3}J\big)^2}\Big),\\
\varepsilon_3=\varepsilon_4&=\frac{\sqrt{3}}{4}\Big(D_n-\sqrt{3D_\perp^2+\big(D_n-2\sqrt{3}J\big)^2}\Big),\\
\varepsilon_5=\varepsilon_6&=\frac{\sqrt{3}}{4}\Big(-D_n+\sqrt{D_\perp^2+\big(D_n+2\sqrt{3}J\big)^2}\Big),\\
\varepsilon_7=\varepsilon_8&=\frac{\sqrt{3}}{4}\Big(D_n+\sqrt{3D_\perp^2+\big(D_n-2\sqrt{3}J\big)^2}\Big).
\end{aligned}\tag{10}$$

Here the notation $D_\perp^2=D_t^2+D_l^2$ is introduced. Due to axial symmetry so far mentioned the matrix of AS exchange is blocked into four (2×2)-matrices according to the definite $|M_J|$ so that the analytical solutions, Eqs. (10), are achieved. The energy pattern consists of four Kramers doublets in agreement with the Kramers theorem (see Ref. [46]), the levels $\varepsilon_{1,2}(\bar{E})$ and $\varepsilon_{3,4}(\bar{A}_1+\bar{A}_2)$ can be attributed to the ground manifold $(0)1/2$, $(1)1/2$, the pairs $\varepsilon_{5,6}$ and $\varepsilon_{7,8}$ originate from the excited level $(1)3/2$ (in Fig. 4 they are shown in a weak magnetic field). One can see that the energy levels do depend upon two effective parameters of AS exchange that are not interrelated by the symmetry conditions, namely, D_n and $D_\perp$ but not from three initially introduced parameters D_n, D_l and D_t. This conclusion is valid for all systems possessing C_3 axis and important for the meaningful definition of the set of independent parameters within the semiempirical approach. Usually isotropic exchange is the leading interaction so that in the case of strong isotropic exchange one can find the following approximate expressions for the energies that are accurate to the terms of the order of D_i^2/J:

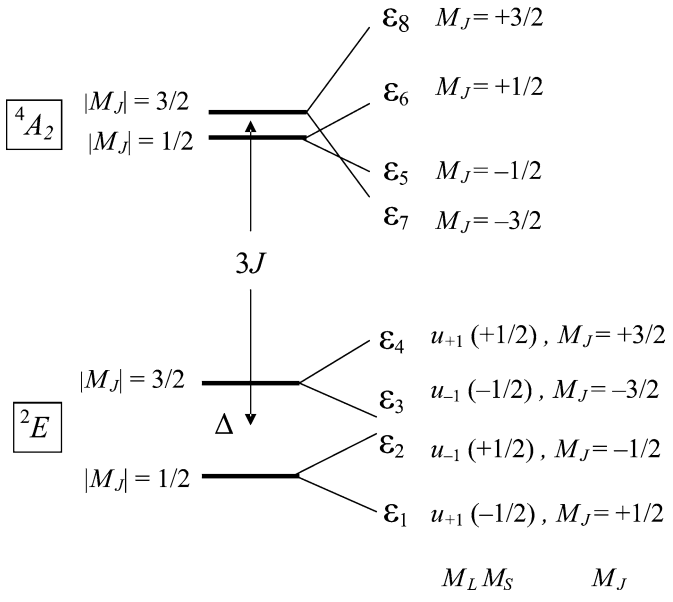


Fig. 4. Labeling of the Kramers doublets and Zeeman sublevels in parallel magnetic field ($\boldsymbol{H}\parallel C_3$), $D_n>0$.

$$\begin{aligned}
\varepsilon_1=\varepsilon_2&=-\frac{3}{2}J-\frac{\sqrt{3}D_n}{2}-\frac{D_\perp^2}{16J},\\
\varepsilon_3=\varepsilon_4&=-\frac{3}{2}J+\frac{\sqrt{3}D_n}{2}-\frac{3D_\perp^2}{16J},\\
\varepsilon_5=\varepsilon_6&=\frac{3}{2}J+\frac{D_\perp^2}{16J},\qquad \varepsilon_7=\varepsilon_8=\frac{3}{2}J+\frac{3D_\perp^2}{16J}.
\end{aligned}\tag{11}$$

One can see that the normal component of the AS exchange leads to a first order splitting of the accidentally degenerate ground state $(0)1/2$, $(1)1/2$ of HDVV model, this was substantiated in [46,50]. On the contrary, the perpendicular part of AS exchange does not contribute to the first order splitting of the ground $S=1/2$ manifold and leads to the second order shifts. The corresponding gap between two $S=1/2$ levels

$$\varepsilon_{3,4}-\varepsilon_{1,2}=\Delta\equiv\sqrt{3}D_n-\frac{D_\perp^2}{8J}\tag{12}$$

shows the first order effect with respect to normal component of AS exchange and contains also second order corrections arising from the mixing of $(S_{12})1/2$ and $(1)3/2$ states through in-plane components of AS exchange. It can be said that in-plane components of the AS exchange are reduced by the isotropic exchange so that under the realistic conditions $|D_n|$, $|D_\perp|\gg J$ the parameter $D_\perp$ is effectively small. Due to second order effects the splitting Δ is always decreased.

The mixing results also in a zero-field splitting of the excited $S=3/2$ level, the splitting $D_\perp^2/8J$ being a second order effect

with respect to in-plane part of AS exchange and for this reason is expected to be much smaller than the splitting in the ground state. It should be noted that D_n component in zero-field splitting of $S = 3/2$ level appears in the high order terms. Regarding the symmetry condition for the AS exchange one should note that the zero field splitting in $S = 3/2$ level is allowed in the cases when $D_\perp \neq 0$. This conclusion is compatible also from the fact the $S = 3/2$ level is an orbital singlet $^4A_2$ that shows zero field splitting due to mixing with the ground term through perpendicular components of spin–orbital interaction.

Alternative labeling [46,51] of the eigen-states based on the pseudoangular momentum representation seems to be useful, in particular, for the study of the crossing points of the magnetic sublevels. Let us employ the pseudoangular momentum representation and take into account that four states $|(0)1/2, \pm 1/2\rangle$, $|(1)1/2, \pm 1/2\rangle$ can be associated with the basis set of the orbital doublet ^2E of the relevant trigonal group. Within the pseudoangular momentum representation the basis of the irrep E in trigonal groups can be associated with two components $M_L = +1$ and $M_L = -1$ belonging to the effective $L = 1$. In the limit $D_\perp = 0$ the eigen-vectors of AS exchange matrix within the $(0)1/2$, $(1)1/2$ basis can be found as

$$u_{\pm 1}(\pm 1/2) = \mp\frac{1}{\sqrt{2}}\big(\big|(0)1/2, \pm 1/2\big\rangle \pm i\big|(1)1/2, \pm 1/2\big\rangle\big),$$
$$u_{\pm 1}(\mp 1/2) = \mp\frac{1}{\sqrt{2}}\big(\big|(0)1/2, \mp 1/2\big\rangle \pm i\big|(1)1/2, \mp 1/2\big\rangle\big), \quad (13)$$

where the functions $u_{LM_L}(SM_S) \equiv u_{M_L}(M_S)$ with $L = 1$ (fictitious orbital angular momentum) and $S = 1/2$ are introduced. The functions defined by Eq. (13) are just the states with $M_L = +1$ and $M_L = -1$ due to the fact that $|(0)1/2, M_S\rangle$ and $|(1)1/2, M_S\rangle$ are transformed like x and y basis under the rotations around C_3 axis of the triangle. Using this conception one can introduce the functions $U(M_J)$ belonging to a definite projection $M_J = M_L + M_S$ of the full pseudoangular momentum, so that $U(\pm 3/2) = u_{\pm 1}(\pm 1/2)$ and $U(\pm 1/2) = u_{\pm 1}(\mp 1/2)$. The Kramers doublets ε_1, ε_2 and ε_3, ε_4 can be thus associated with the pairs $M_J = \pm 1/2$ and $M_J = \pm 3/2$ and can be alternatively labeled by the double valued irreducible representations of the point group: irrep $\bar{E}$ and complex conjugated pair $\bar{A}_1 + \bar{A}_2 = 2\bar{A}$ in $\boldsymbol{C}_{3v}$ and $\boldsymbol{D}_3$ [52,72]. Providing $D_n > 0$ the $M_J = \pm 1/2$ doublet proves to be the ground state, in the opposite case $D_n < 0$ the doublet $M_J = \pm 3/2$ is lower in energy as shown in Fig. 4 where the assignation of the levels to the definite $M_L M_S$ and M_J is also indicated.

The excited spin level with $S = 3/2$ is also split into two pairs $M_J = \pm 1/2$ and $M_J = \pm 3/2$ ($\bar{E}$ and pair $\bar{A}_1 + \bar{A}_2 = 2\bar{A}$ correspondingly [52,71]). Small second order zero-field splitting $D_\perp^2/8J$ in the excited spin level $S = 3/2$ arises from the mixing of two $M_J = \pm 1/2$ levels (from $S = 3/2$ and from $S = 1/2$) and two $M_J = \pm 3/2$ pairs, the splitting vanishes providing $D_\perp = 0$. The gap $D_\perp^2/8J$ can be assigned to the AS exchange splitting of the $S = 3/2$ level reduced by the isotropic exchange to a second order effect, the $M_J = \pm 3/2$ sublevel is higher in energy providing $J > 0$. The zero-field splitting of $S = 3/2$ level is to be taken into account in the analysis of the EPR data on V_{15} molecular magnet [42].

5. Zeeman splitting, crossover points

We shall assume the axial form of the Zeeman term

$$W_Z = g_\parallel \beta(S_{1Z} + S_{2Z} + S_{3Z})H_Z + g_\perp \beta\big[(S_{1X} + S_{2X} + S_{3X})H_X + (S_{1Y} + S_{2Y} + S_{3Y})H_Y\big], \quad (14)$$

related to the molecular coordinate system. In order to reveal the role of different interactions let us consider the following particular cases:

(a) Model of the "normal" AS exchange, $D_n \neq 0$, $D_\perp = 0$. In this case both AS exchange and Zeeman interaction do not mix the ground and excited multiplets and the analytical expressions for the energy levels can be found for an arbitrary direction of the field. For the four sublevels belonging to $S = 1/2$ one finds:

$$\varepsilon_{1,2} = -\frac{3}{2}J - \frac{1}{2}\big[(g_\parallel \beta H\cos\vartheta)^2 + \big(\sqrt{3}D_n \pm g_\perp \beta H\sin\vartheta\big)^2\big]^{1/2},$$
$$\varepsilon_{3,4} = -\frac{3}{2}J + \frac{1}{2}\big[(g_\parallel \beta H\cos\vartheta)^2 + \big(\sqrt{3}D_n \pm g_\perp \beta H\sin\vartheta\big)^2\big]^{1/2}. \quad (15)$$

For the four $S = 3/2$ levels one gets a standard expression that exhibits axial anisotropy implied solely by the angular dependence of the g-factor, $\varepsilon_M = g(\vartheta)\beta HM$ ($M = \pm 3/2, \pm 1/2$) with $g^2(\vartheta) = g_\parallel^2\cos^2\vartheta + g_\perp^2\sin^2\vartheta$.

Figs. 5 and 6 represent the energy diagram for the magnetic sublevels that are the eigen-states of the Hamiltonian $H_0 + H_{AS} + W_Z$. To illustrate the consequences of the AS exchange the g-factors are assumed to be isotropic and we put $g = 2$ and $J = 0.847\ \text{cm}^{-1}$ [72], we use also rather large values for the AS exchange parameters in order to make its influence clearly visible. Fig. 5 shows the case when only the normal part of the AS exchange is taken into account. The low-lying levels vs. in a relatively weak field ($g\beta H < 3J$) in this case and the magnetic anisotropy were considered in detail a long time ago (see [46,49,50,64]). From the inset 1 in Fig. 5 one can see that the AS exchange introduces strong magnetic anisotropy related to the angular dependence of the magnetic splitting of the two $S = 1/2$ doublets. In parallel field both low lying levels exhibit linear field dependence, increase of the angle ϑ leads to the mixing of the levels and finally at $\vartheta = \pi/2$ they become degenerate (inset 1 in Fig. 5). The magnetic moments are specific for $S = 1/2$ in parallel field and fully suppressed in a weak ($g\beta H \ll |D_n|$) perpendicular field $\boldsymbol{H} \perp C_3$ (inset 1), in this case the system behaves like a Van Vleck paramagnet. On the contrary, behavior of the levels vs. field shows that strong perpendicular field $g\beta H \gg |D_n|$ (but at the same time $g\beta H \ll J$) fully reduces the AS exchange [46]. Since the normal part of the AS exchange does not mix different spin levels the magnetic splitting of the excited $S = 3/2$ level is insensitive to the AS exchange and therefore proves to be isotropic (not shown in Fig. 5).

In the HDVV model the step of the magnetization corresponding to the transition from $S = 1/2$ to $S = 3/2$ is expected at the field $H_{res} = 3J/g\beta$. Due to zero-field splitting

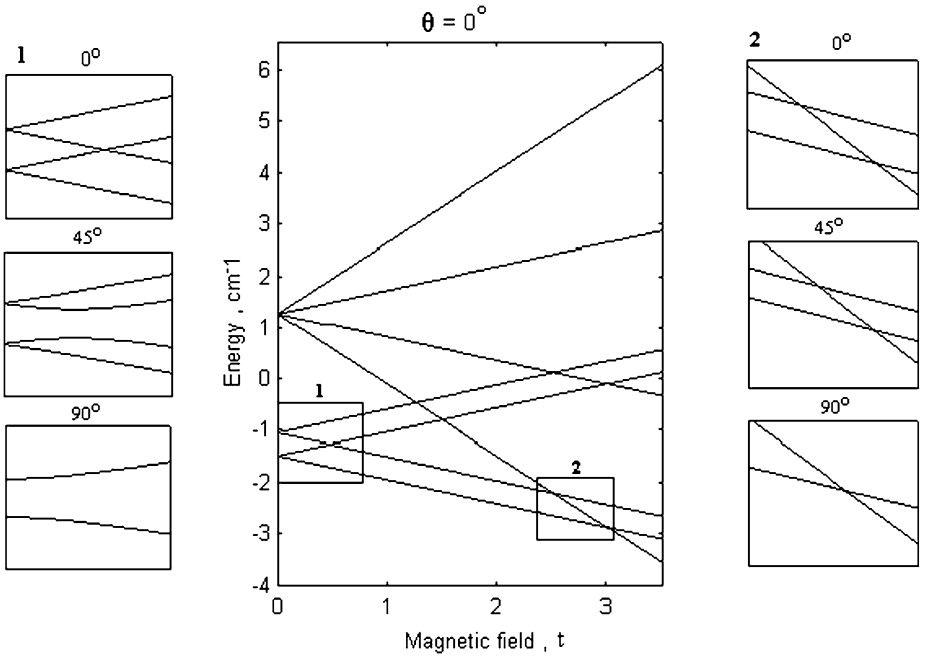


Fig. 5. Diagram of the angular dependence of the magnetic sublevels (magnetic field in tesla) in the case of $D_\perp = 0$ and $D_n = 0.1J$. $J = 0.847\ \mathrm{cm}^{-1}$ [72].

of in $S = 1/2$ levels there are two crossing points (Fig. 5). In the case under consideration there are no avoided crossing points of the magnetic sublevels at any angles ϑ, in particular, the lowest magnetic sublevel ε_7 ($M_S = -3/2$) of $S = 3/2$ crosses all magnetic sublevels belonging to the ground $S = 1/2$ levels. Inset 2 in Fig. 5 shows strict crossings of E_7 with two lowest levels of $S = 1/2$. The positions (fields) and the energies corresponding to these points do depend on the angle ϑ that is a consequence of the anisotropy of AS exchange. Since J considerably exceeds all AS exchange parameters, these points can be determined from the high field expansion of the energy levels. Assuming isotropic Zeeman interaction ($g_\parallel = g_\perp = g$) one can find with the accuracy to $D_n/g\beta H$:

$$\varepsilon_{1,2} = -\frac{3}{2}J - \frac{\sqrt{3}}{2}D_n\cos\vartheta \pm \frac{3D_n^2\sin^2\vartheta}{g\beta H} \pm \frac{1}{2}g\beta H,$$
$$\varepsilon_{3,4} = -\frac{3}{2}J + \frac{\sqrt{3}}{2}D_n\cos\vartheta \pm \frac{3D_n^2\sin^2\vartheta}{g\beta H} \pm \frac{1}{2}g\beta H. \qquad (16)$$

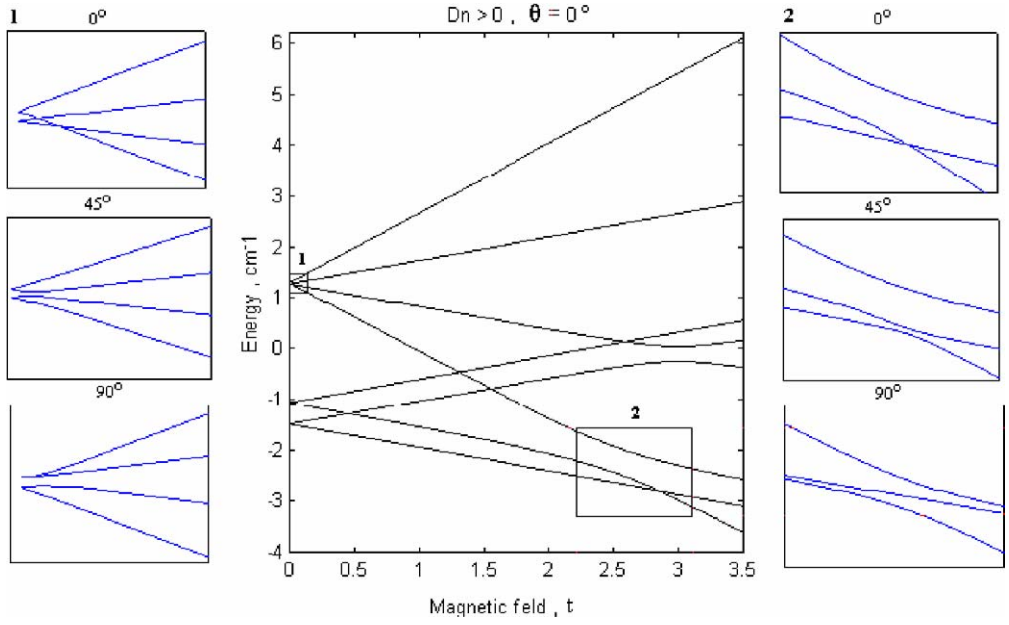
Eqs. (16) illustrate the reduction of the normal part of the AS exchange by the perpendicular component of the magnetic field (see [46]). In fact, as it follows from Eqs. (16), in strong field ($g\beta H \gg |D_n|$) only the projection of the vector $\boldsymbol{D}_n$ on the field direction ($D_n\cos\vartheta$) survives. The component of $\boldsymbol{D}_n$ perpendicular to field ($D_n\sin\vartheta$) decreases linearly with the increase of the field so that in strong field effective splitting of (0)1/2, (1)1/2 becomes $\Delta(\vartheta) = \sqrt{3}|D_n|\cos\vartheta$ that is decreased, respectively, zero-field splitting $\Delta = \sqrt{3}|D_n|$. Two fields, H_1 and H_2, correspond to two crossing points of the lowest magnetic sublevel E_7 of $S = 3/2$ with magnetic sublevels belonging of the ground $S = 1/2$ levels (Fig. 5). Since usually $J \gg |D_n|$ they can be calculated with a good accuracy as:

$$H_{1,2} = \frac{3J}{g\beta} \mp \frac{\sqrt{3}D_n\cos\vartheta}{2g\beta}. \qquad (17)$$

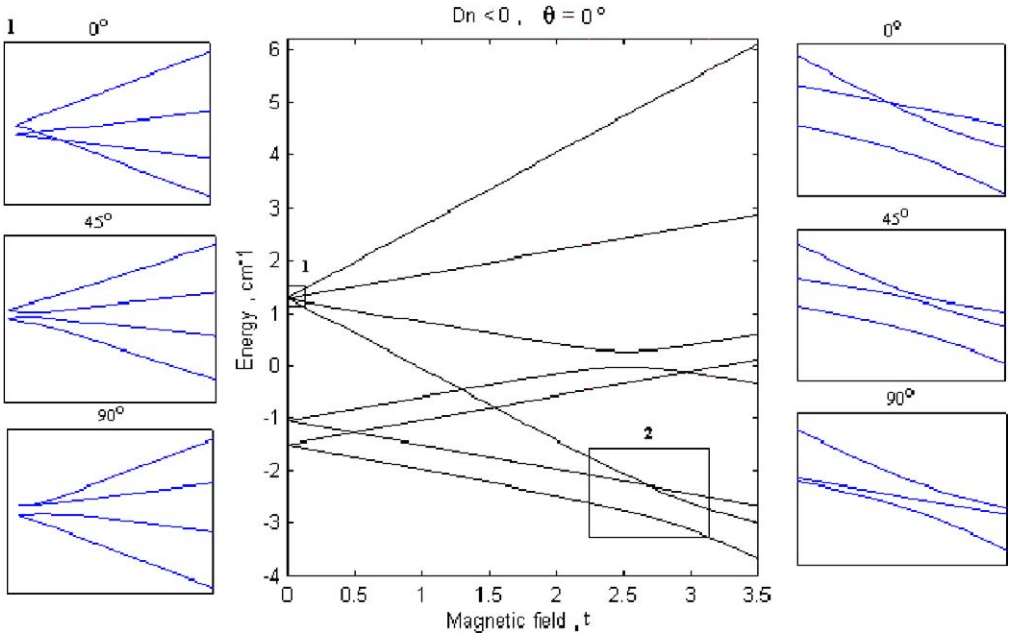
In perpendicular field the two crossing points are transformed into one (Fig. 5, inset 2) due to degeneracy of magnetic sublevels, $H_1 = H_2 = 3J/g\beta$ as expected from the HDVV model. This illustrates so far mentioned quenching of the AS exchange in perpendicular field. Low temperature stepwise magnetic moments vs. field and T strongly depend on the position of these crossing points as well as on the field dependence of the magnetic sublevels in the vicinity of these points.

(b) General case, $D_n \neq 0$, $D_\perp \neq 0$. In this case the analytical results can be obtained in the case of parallel field ($\boldsymbol{H} \parallel C_3$) which leads to a simple conclusion about the role of different components of AS exchange. In fact, in this case the projection of the pseudoangular momentum M_J is still a good quantum number due to the fact that the parallel part of the Zeeman interaction $g_\parallel\beta S_Z H_Z$ preserves the axial symmetry, so that the full matrix is blocked into four second order matrices each corresponding to a definite value of M_J (Eq. (13) and Fig. 4). The results for the energies of the eight Zeeman levels are the following:

$$\varepsilon_{1,2} = -\frac{1}{4}\sqrt{\left(\sqrt{3}D_n \pm 2g_\parallel\beta H + 6J\right)^2 + 3D_\perp^2} - \frac{\sqrt{3}}{4}D_n,$$
$$\varepsilon_{3,4} = -\frac{1}{4}\sqrt{\left(\sqrt{3}D_n \pm 2g_\parallel\beta H - 6J\right)^2 + 9D_\perp^2} + \frac{\sqrt{3}}{4}D_n \mp g_\parallel\beta H,$$
$$\varepsilon_{5,6} = \frac{1}{4}\sqrt{\left(\sqrt{3}D_n \mp 2g_\parallel\beta H + 6J\right)^2 + 3D_\perp^2} - \frac{\sqrt{3}}{4}D_n,$$



(a)



(b)

Fig. 6. Diagram of the angular dependence of the magnetic sublevels in the case of positive D_n ($D_n = 0.1J$) (a) and negative D_n ($D_n = -0.1J$) (b); $D_\perp = 0.4J$, $J = 0.847\ \mathrm{cm}^{-1}$ [72].

$$\varepsilon_{7,8} = \frac{1}{4}\sqrt{\left(\sqrt{3}D_n \pm 2g_\parallel \beta H - 6J\right)^2 + 9D_\perp^2} + \frac{\sqrt{3}}{4}D_n \mp g_\parallel \beta H, \tag{18}$$

where the numeration of the zero-field and Zeeman sublevels is shown in Fig. 4 in the case of $D_n > 0$ and low fields that are far from the crossing points.

In a strong field limit ($g\beta H \gg J$) with the accuracy to the terms $\propto H^{-1}$ one can find:

$$\begin{aligned}
\varepsilon_{1,2} &= -\frac{3}{2}J - \frac{\sqrt{3}D_n}{2} \pm \frac{3D_\perp^2}{16g\beta H} \pm \frac{1}{2}g\beta H,\\
\varepsilon_{3,4} &= -\frac{3}{2}J + \frac{\sqrt{3}D_n}{2} \mp \frac{3D_\perp^2}{16g\beta H} \pm \frac{1}{2}g\beta H,\\
\varepsilon_{5,6} &= +\frac{3}{2}J \pm \frac{3D_\perp^2}{16g\beta H} \pm \frac{1}{2}g\beta H,\\
\varepsilon_{7,8} &= -\frac{3}{2}J \pm \frac{9D_\perp^2}{16g\beta H} \pm \frac{3}{2}g\beta H.
\end{aligned} \tag{19}$$

These expressions (note the alteration of the labeling due to crossing points) illustrate that strong magnetic field affects the normal and tangential parts of the AS exchange in different ways. While the normal part has the same form as in the case of low field, the parallel field reduces the tangential part of the AS exchange. As a result the terms containing $D_\perp^2$ disappear in strong field limit so that the zero field splitting in the ground state (that can be measured in a high field limit) becomes $\sqrt{3}|D_n|$, just as in the case of $D_\perp = 0$. Note that under the condition of strong field exceeding the crossing fields between different spin levels ($g_\parallel \beta H \gg J$) the zero-field splitting in the excited level is reduced. In strong field limit the anisotropic contribution to anisotropy in the $S = 3/2$ (arising from second order mixing) is fully reduced and the direction of the field becomes the axis of spin quantizaton.

Fig. 6 shows the diagram of the magnetic splitting at different angles ϑ in the general case $D_n, D_\perp \neq 0$. The picture of the energy levels is strongly dependent on the field direction. One can see that one of the two crossing points (H_1 or H_2) that are found at $D_n \neq 0$, $D_\perp = 0$ is avoided in parallel field when $D_\perp \neq 0$. In this respect the cases of positive and negative D_n (Fig. 6) exhibit different qualitative features. In the case $D_n > 0$ (Fig. 6(a)) the right (low lying) point shows exact crossing in the ground state meanwhile the left point (excited levels) is avoided. On the contrary, in the case of $D_n < 0$ (Fig. 6(b)) the avoided crossing occurs in the ground level meanwhile the exact crossing is observed in the excited levels. Two intersections in the inset 2 (Fig. 4) can be assigned to crossing of $M_J = -3/2$ ($S = 3/2$) level with the levels $M_J = -3/2$ ($S = 1/2$) and $M_J = -1/2$ ($S = 1/2$). The first one is avoided (the same symmetry) meanwhile the second one is avoided (different symmetries).

To estimate the gap in the avoided crossing one can use as a zero-order approximation the fields H_1 (H_2) evaluated at $D_\perp = 0$, Eq. (17). For example, in the case of $D_n > 0$, the avoided crossing is expected at $H = H_2$ so the gap will be $E_7(H_1) - E_3(H_1)$. The gap is found to be $3D_\perp/2$ and proves to be independent on D_n. One can conclude that the splitting is the first order effect with respect to in-plane AS exchange meanwhile the difference in the fields H_1 and H_2 depends on the parameter D_n solely. First order splitting in the crossing point can be regarded as the effect of suppression of the antiferromagnetic isotropic exchange resulting in the restoration of the AS exchange that initially (in zero magnetic field) was reduced to a second order correction. Summarizing this section one has to conclude that the two parts of the AS exchange have different physical consequences: while the normal part of AS exchange mainly determines the positions of the crossing points (resonance fields) in the ground manifold as the functions of the angle ϑ, the in-plane components lead to a splitting in the avoided crossing points and determine the corresponding gap.

6. Adiabatic magnetization

As it follows from the low-field experiments on magnetization [24] the ground state n changes from $S = 1/2$ value to $S = 3/2$ around 2.8 T and this change occurs smoothly even at low temperature. The AS exchange was proposed as an origin of the broadening of the step in the magnetization vs. field [72]. Figs. 7 and 8 modelize the influence of AS exchange on the shape of the step in low temperature magnetization. Fig. 7 shows static magnetization $M(H, \vartheta, T)$ vs. applied field at different angles ϑ in the model that takes into account AS exchange with a negative D_n (first row) and in the isotropic HDVV model (second row), to illustrate the influence of the AS exchange the parameters are increased. The static magnetization exhibits a stepwise behavior as a function of applied field at low temperatures [21] with saturation values $1\mu_B$ and $3\mu_B$ that correspond to $S = 1/2$ and $S = 3/2$. By comparing the results obtained within the HDVV model and those with the regard for the AS exchange one can see that the AS exchange gives rise to the angular dependence $M(H, \vartheta, T)$. The shape of the step in M vs. H function does depend on the direction of the field and the broadening increases with the increase of ϑ. Influence of the AS exchange is essential in both ranges: at low fields and in the high fields corresponding to the range of crossing points. The shape of the smoothed step $M(H, \vartheta, T)$ vs. H is closely related to the anisotropy of Zeeman splitting due to AS exchange so far discussed. One can see that the angular dependence of the magnetization is most pronounced at low temperature, on the contrary, when all levels in the crossing/anticrossing point are well populated the anisotropy becomes negligible and HDVV model gives accurate results.

Since the pattern of the low lying levels in the vicinity of the crossing range depends on the sign of D_n (Fig. 6) the shape of the step of magnetization is also sensitive to this sign. The influence of the sign of D_n in parallel field and at fixed temperature and D_t is illustrated in Fig. 8. One can see that in the case of negative D_n, the broadening and shape of the step in M vs. H at low temperature depends weakly upon the parameter D_n. In fact, the broadening of the step depends on the area (in the scale of the field) of the efficient mixing of the $S = 1/2$ and $S = 3/2$ levels (Fig. 6(b)). Since the mixing is produced only by the in-plane component of AS exchange this area proves to be almost independent of D_n. On the contrary, in the case of positive D_n the shape of the step depends significantly on D_n, the increase of D_n resulting in the sharpening of the step. This unusual dependence looks like being in a contradiction with the general belief about the role of AS exchange. Actually, providing positive D_n the exact crossing occurs in parallel field (Fig. 6(a)) and one can easily see that of the efficient mixing in this area decreases with the increase of D_n (Fig. 6).

7. Conclusion

We have considered AS exchange in the three-spin model of the exchange interactions in V_{15} molecule. The AS exchange gives rise to a strong magnetic anisotropy and acts as a source for the zero-field splitting of the accidentally degenerate levels possessing $S = 1/2$. The different role of the normal and in-plane components of the AS exchange are underlined. The zero-field splitting in the ground manifold is mostly determined by the normal component of the AS exchange (first order effect), meanwhile the zero-field splitting in the excited $S = 3/2$

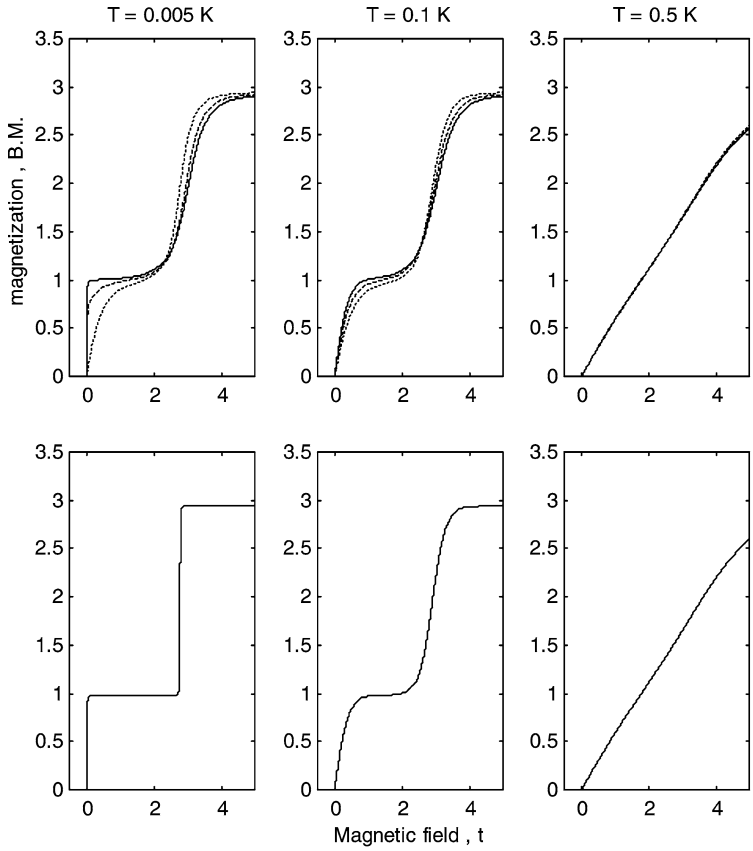


Fig. 7. Static magnetization vs. applied field (in tesla) at different temperatures and angles ϑ ($\vartheta = 0$ solid line, $\vartheta = \pi/4$ dashed line, $\vartheta = \pi/2$ dotted line), $J = 0.847\ \mathrm{cm}^{-1}$ [72]; $D_n = -0.3J$, $D_\perp = 0.4J$ (first row), $D_n = 0$, $D_\perp = 0$ (second row).

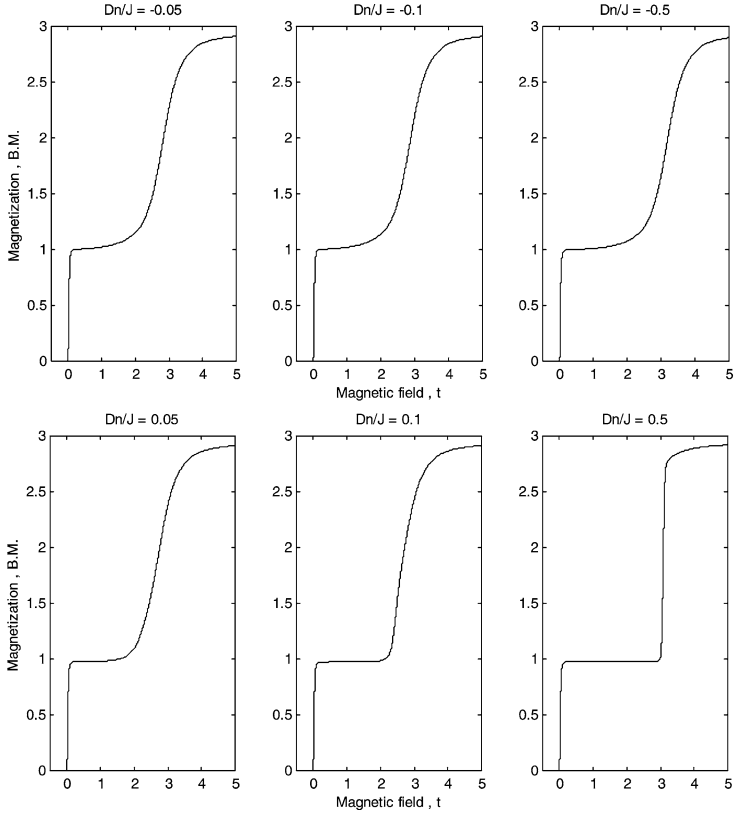


Fig. 8. Magnetization vs. parallel field ($\vartheta = 0$): influence of the sign of the AS exchange, $J = 0.847\ \mathrm{cm}^{-1}$, $D_\perp = 0.4J$, $T = 0.01$ K.

proves to be a second order effect with respect to in-plane component of the AS exchange. Normal component of the AS exchange is reduced by perpendicular component of the magnetic field meanwhile the in-plane component is reduced by the field of an arbitrary direction. We have revealed the origin of the energy gap at the crossing points, the detailed structure of the magnetic sublevels closely related to the orientation of the magnetic field and interrelation between different components of AS exchange. We have studied also the dependence of the magnetization vs. field and temperature, the shape of the step in magnetization is affected by the temperature and direction of the field and reflect the magnetic anisotropy caused by the AS exchange. The experimental data on magnetization will be discussed in the forthcoming publications devoted to the consideration of the EPR spectra of V_{15} system that contain additional spectroscopic information about the exchange parameters of the system

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