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Antisymmetric exchange and pseudo Jahn–Teller instability in spin-frustrated metal clusters

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Abstract

In this article, we analyze the interplay between the antisymmetric (AS) exchange interaction and Jahn–Teller (JT) vibronic coupling in spin-frustrated systems with triangular units. AS exchange in these systems creates a strong first order magnetic anisotropy related to the orbitally degenerate frustrated ground state that is analyzed for the unique structure of the cluster anion present in $K_6[V^{IV}_{15}As_6O_{42}(H_2O)] \cdot 8H_2O$ (V_{15} cluster) exhibiting layers of different magnetization. Spin-frustration inherently related to the orbital degeneracy creates a structural instability that is shown to be competitive to the AS exchange. The vibronic pseudo JT coupling arising from the modulation of the exchange interaction by the double degenerate molecular vibrations is shown to reduce AS exchange giving rise to a restoration of magnetization quenched by AS exchange. This leads to an essential reduction of the magnetic anisotropy in spin-frustrated triangular clusters so that in the limit of strong JT coupling the isotropic exchange model becomes adequate.

Keywords: Molecular magnets; Jahn–Teller effect; Spin–vibronic interaction; Antisymmetric exchange; Magnetic anisotropy; V_{15} cluster

1. Introduction

In this article we address the study of the manifestations of vibronic JT and pseudo JT coupling in the magnetic anisotropy of the exchange coupled frustrated systems in which AS exchange interaction plays a significant role. Magnetic anisotropy is one of the key questions in the field of single molecule magnetism [1,2]. Single molecular magnets based on large metal clusters possessing high spin ground state and barrier for spin reorientation are promising in the design of the new memory storages at the molecular level and at the same time open a new interesting area of physics within the nanoscopic scale [2].

The aim of this paper is to demonstrate the role of AS exchange [3,4] in the magnetic anisotropy of spin-frustrated system and to reveal how the vibronic JT interaction affects the magnetic anisotropy caused by the AS exchange. The understanding of a special role of the AS exchange in spin frustrated systems, particularly, in trinuclear transition metal clusters, dates back to the seventies (see review article [5] and refs [6–12]).

The plan of the paper is the following. First, we shortly summarize the manifestations of the AS exchange in the cluster anion present in $K_6[V^{IV}_{15}As_6O_{42}(H_2O)] \cdot 8H_2O$ (hereafter V_{15} cluster). This system was discovered more than 15 years ago [13] and since that time attracts continuous and increasing attention as an unique molecular magnet based on an unique structure exhibiting layers of different magnetization [14–16] (see also [17–22]). Magnetic properties of the V_{15} cluster are inherently related to spin frustration effect in the layered quasispherical arrangement of vanadium ions and from this point of view V_{15} represents a system for which the manifestations of the AS exchange are especially interesting and the experimental data do allow to find out precisely the key parameters.

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Then we discuss the manifestations of the vibronic coupling arising from the modulation of the exchange interactions by the displacements of the metal ions in spin-frustrated systems. As far as the magnetic anisotropy caused by the AS exchange is related to the orbital degeneracy (or more commonly, to the orbital contributions) the role of the JT effect (JTE) [23–25] becomes crucially important if the vibronic interaction is significant [12] We show that the manifestations of the magnetic anisotropy are strongly influenced by a complicated interplay between AS exchange and pseudo JT coupling. Although the JTE play an universal role in molecular and solid state physics [25] the influence of the JTE on the molecular magnetic anisotropy still remains open.

2. Exchange interactions

The molecular cluster V_{15} has a distinctly layered quasi-spherical structure within which fifteen V^{IV} ions ($s_i = 1/2$) are placed in an arrangement of a central triangle sandwiched by two hexagons [3]. At low temperatures two hexanuclear V_6^{IV} are spin-paired so that only the excitations within the frustrated antiferromagnetic V_3^{IV} triangle affect the magnetic properties [4–7]. We will focus on the three-spin model of V_{15} within which the isotropic superexchange can be described by the Heisenberg-Dirac-van Vleck (HDVV) exchange Hamiltonian:

$$H_0 = 2J(\boldsymbol{S}_1\boldsymbol{S}_2 + \boldsymbol{S}_2\boldsymbol{S}_3 + \boldsymbol{S}_3\boldsymbol{S}_1), \tag{1}$$

where $\boldsymbol{S}_1$, $\boldsymbol{S}_2$ and $\boldsymbol{S}_3$ denote the spin operators on the sites 1, 2 and 3 and $S_i = 1/2$ and for the antiferromagnetic case $J > 0$. 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. An equilateral spin triangle with the antiferromagnetic exchange represents an example in which exchange coupling in the ground state forces spins to be aligned antiparallel in each pair while this condition can not be satisfied. This situation is usually referred to as spin frustration. The analysis of the HDVV Hamiltonian (see review article [5]) revealed that the "degeneracy doubling" of $S = 1/2$ levels with respect to the intermediate spin in the ground manifold $(S_{12})S = (0)1/2,(1)1/2$ is associated with the exact orbital degeneracy in the triangular system so that the ground term is the orbital doublet ^2E of the trigonal point group while the excited one is the orbital singlet $^4A_2$. One can see that spin-frustration is inherently related to the orbital degeneracy and therefore leads to the JT instabilities. At the same time the ground state is split by spin–orbital interaction that appears as AS exchange term in the spin-Hamiltonian. In this Section, we will consider AS exchange and then (Sections 3–5) show how the JT instability affects the magnetic properties and coexists with the AS exchange.

AS exchange in a triangular cluster referred to the molecular coordinate system(see Fig. 3 in Ref. [26]) can be described by the Hamiltonian:

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

where $[\boldsymbol{S}_i\times\boldsymbol{S}_j]$ are the vector products, the parameter D_n is associated with the "normal" to the plane (along Z axis) component of AS exchange and D_l and D_t are those for the "in-plane" (XY) contributions (along and perpendicular to a side of the triangle, see [26]).

As it is well-known the AS exchange is responsible for the magnetic anisotropy of the system [5–11,26–28]. The main consequences of the AS exchange are the following: (1) first order zero-field splitting of two spin doublets $(S_{12})S = (0)1/2,(1)1/2$; (2) zero-field splitting of the $S = 3/2$ state that is a second order effect arising from the mixing of different spin states through "in-plane" contributions; (3) magnetic anisotropy resulting in a strong reduction of the magnetic moments in a weak perpendicular field; (4) restoration of the pure spin magnetic moments in a strong field due to the reduction of the AS exchange under; (5) special rules for the crossing/anticrossing Zeeman levels based on the pseudoangular momentum representation; (6) special selection rules in EPR including peculiar ratio of intensities.

The influence of the AS exchange on the Zeeman pattern for the field $\boldsymbol{H}\perp C_3$ is illustrated in Fig. 1 [28]. The levels $\varepsilon_i(H)$ with $i = 1, 2, 3, 4$ are related to $S = 1/2$ while $i = 5, 6, 7, 8$ are the numbers of Zeeman sublevels for $S = 3/2$

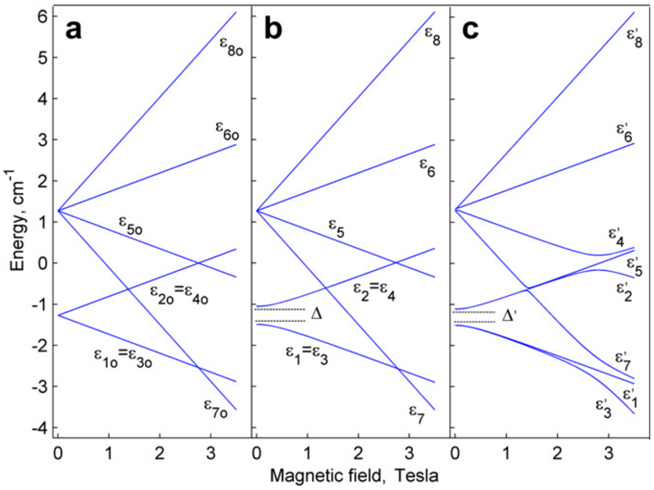

Fig. 1. Energy pattern of the triangular vanadium unit in the magnetic field applied in the plane ($\boldsymbol{H}\perp C_3$), $J = 0.847\ \mathrm{cm}^{-1}$, $g = 2$. (a) $D_n = 0$, $D_\perp = 0$; (b) $D_n = 0.3J$, $D_\perp = 0$; (c) $D_n = 0.3J$, $D_\perp = 0.6\ J$.

(with $M = \mp 1/2$ and $M = \mp 1/2$) as shown in Fig. 1a in which the simplest case of the isotropic model is illustrated. The energy pattern for the case $D_n \neq 0$, $D_l = D_t = 0$ is shown in Fig. 1b. Three peculiarities of the energy pattern that are closely related to the magnetic behavior should be noticed: (1) the ground state involving two degenerate $S = 1/2$ levels shows zero-field splitting into two Kramers doublets separated by the gap $\Delta = \sqrt{3}D_n$; (2) at low fields $g\beta H \leqslant \Delta$ the Zeeman energies are double degenerate and show quadratic dependence on the field like in a van Vleck paramagnet:

$$\begin{aligned}\varepsilon_{1,3}(H) - \sqrt{3}|D_n|/2 - (g\beta H)^2/4\sqrt{3}|D_n|, \varepsilon_{2,4}(H)\\ = +\sqrt{3}|D_n|/2 + (g\beta H)^2/4\sqrt{3}|D_n|.\end{aligned} \tag{3}$$

It is evident that the magnetic moments associated with the ground state are strongly reduced at low fields [5,9]; (3) the magnetic sublevels arising from $S = 3/2$ ($M = -1/2$ and $M = -3/2$) cross the sublevels belonging to $S = 1/2$ spin levels, no avoided crossing points are observed. At high perpendicular field the levels $\varepsilon_{1,3}$ and $\varepsilon_{2,4}$ exhibit again linear magnetic dependence [5]:

$$\begin{aligned}\varepsilon_{1,3}(H) &= -3J/2 - 3D_n^2/g\beta H - g\beta H/2,\\ \varepsilon_{2,4}(H) &= -3J/2 + 3D_n^2/g\beta H + g\beta H/2.\end{aligned} \tag{4}$$

One can see that a strong perpendicular field restores linear Zeeman splitting but without zero-field splitting so that the perpendicular field reduces the normal part of AS coupling.

When the AS exchange in the most general form compatible with the trigonal symmetry is involved ($D_n \neq 0$, $D_l \neq 0$, $D_t \neq 0$) the energy pattern shows new peculiarities (Fig. 1c). The low field part of the spectrum is not affected by the in-plane part of AS exchange and qualitatively as well as quantitatively is very close to that in Fig. 1b. At the same time in the vicinity of the crossing points the effect of the normal AS exchange is negligible but the in-plane part of AS exchange $D_\perp = \sqrt{D_t^2 + D_n^2}$ acts as a first order perturbation giving rise to the avoided crossings of the ground and excited states as shown in Fig. 1c. [26].

In the framework of the isotropic model the magnetization exhibits two sharp non-broadened steps, one at zero-field and the second one at the field $H = 3J/g\beta$. As one can see the normal part of AS exchange results in the broadening of the low field step in $\mu(H)$ meanwhile the high field step remains non-broadened. At the same time the normal AS exchange leaves the exact crossing of $S = 3/2$, $M = -3/2$ level with the lowest component of $S = 1/2$ that results in absence of the broadening of the high field step. Finally when both parts of the AS exchange are taken into account we obtain broadening of both steps.

Fig. 2 shows that the model that includes AS exchange interaction gives perfect fit of the field dependence of magnetization to the experimental data [29] in the whole range of fields for all temperatures including extremely low temperature. The best fit procedure gives the following set of parameters: $J = -0.855\ \text{cm}^{-1}$, $g = 1.94$, $D_\perp = 0.238\ \text{cm}^{-1}$, $D_n = 0.054\ \text{cm}^{-1}$. It should be noted that the in-plane parameter $D_\perp$ brings the main contribution to the overall AS exchange. This parameter is just responsible for the behavior of the levels in the anticrossing region $H \approx 2.8\,Tesla$. The V_{15} cluster represents a system with small exchange and consequently weak vibronic coupling (Section 4). Later on we will consider the case of sufficiently strong vibronic coupling.

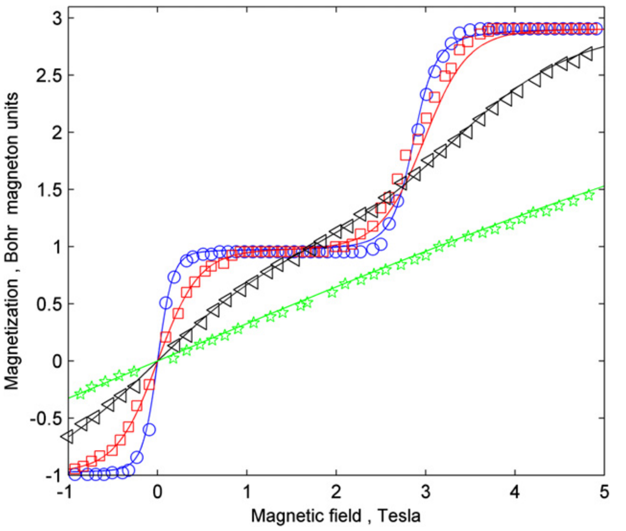

Fig. 2. Experimental data (from ref. [29]) and theoretical curves of static magnetization calculated with account for the isotropic and AS exchange interactions ($\boldsymbol{H} \perp C_3$). Experimental data: circles – $T = 0.1$ K, squares – $T = 0.3\ K$, triangles – $T = 0.9$ K, stars – $T = 4.2\ K$. Solid lines – calculated curves with the best fit parameters (see text).

3. Vibronic interaction

The symmetry adapted vibrations $A_1(Q_{A_1} \equiv Q_1)$ and double degenerate E type ($Q_{Ex} \equiv Q_x, Q_{Ey} \equiv Q_y$) of an equilateral triangular unit can be expressed as (Fig. 3):

$$\begin{aligned}Q_1 &= \frac{1}{\sqrt{3}}\left[-\frac{1}{2}\left(\sqrt{3}X_1 + Y_1\right) + \frac{1}{2}\left(\sqrt{3}X_2 - Y_2\right)\right],\\ Q_x &= \frac{1}{\sqrt{3}}\left[-\frac{1}{2}\left(\sqrt{3}X_1 - Y_1\right) - \frac{1}{2}\left(\sqrt{3}X_2 + Y_2\right)\right],\\ Q_y &= \frac{1}{\sqrt{3}}\left[\frac{1}{2}\left(X_1 + \sqrt{3}Y_1\right) + \frac{1}{2}\left(X_2 - \sqrt{3}Y_2\right) - X_3\right].\end{aligned} \tag{5}$$

The vibronic interaction arises from the modulation of the isotropic and AS exchange interactions by the molecular displacements.

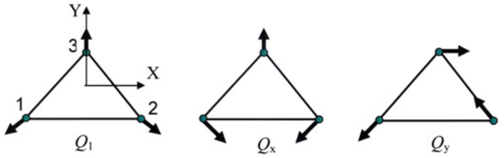

Fig. 3. Full symmetric (A_1) and double degenerate (E) modes of a triangular unit.

In fact, the exchange parameters are the functions of the interatomic distances so the linear terms of the vibronic Hamiltonian can be represented as:

$$H_{ev} = 2\sum_{ij} \boldsymbol{S}_i\boldsymbol{S}_j \sum_{\alpha=1,x\cdot y}\left(\frac{\partial J_{ij}(R_{ij})}{\partial R_{ij}}\right)_{\Delta R_{ij}=0} \times \frac{\partial R_{ij}}{\partial Q_\alpha}Q_\alpha, \qquad (6)$$

$$H'_{ev} = \sum_{ij}\left[\boldsymbol{S}_i \times \boldsymbol{S}_j\right] \sum_{\alpha=1,x\cdot y}\left(\frac{\partial \boldsymbol{D}_{ij}(R_{ij})}{\partial R_{ij}}\right)_{\Delta R_{ij}=0} \times \frac{\partial R_{ij}}{\partial Q_\alpha}Q_\alpha. \qquad (7)$$

Here, the summation is extended over all pairwise spin–spin interactions ($ij = 12$, 23, 31). Eqs. (6) and (7) are the contributions of the overall vibronic coupling relating to the isotropic and AS exchange interactions, respectively. After all required transformations with the use of Eq. (5) one can arrive at the following vibronic Hamiltonian H_{ev}:

$$H_{ev} = \lambda\left(\hat{V}_1Q_1 + \hat{V}_xQ_x + \hat{V}_yQ_y\right), \qquad (8)$$

where $\lambda \equiv \sqrt{6}(\partial J_{ij}(R_{ij})/\partial R_{ij})_0$ is the vibronic coupling parameter associated with the isotropic exchange and the operators $\hat{V}_\alpha$ are the following [30] (see [5,9] and references cited therein):

$$\hat{V}_1 = \sqrt{\frac{2}{3}}(\boldsymbol{S}_1\boldsymbol{S}_2 + \boldsymbol{S}_2\boldsymbol{S}_3 + \boldsymbol{S}_3\boldsymbol{S}_1),$$
$$\hat{V}_x = \frac{1}{\sqrt{6}}(\boldsymbol{S}_2\boldsymbol{S}_3 + \boldsymbol{S}_3\boldsymbol{S}_1 - 2\boldsymbol{S}_1\boldsymbol{S}), \quad \hat{V}_y = \frac{1}{\sqrt{2}}(\boldsymbol{S}_2\boldsymbol{S}_3 - \boldsymbol{S}_3\boldsymbol{S}_1). \qquad (9)$$

By applying a similar procedure one can obtain the vibronic contribution associated with the AS exchange. The final expression is the following:

$$H'_{ev} = \hat{W}_1Q_1 + \hat{W}_xQ_x + \hat{W}_yQ_y. \qquad (10)$$

The operators $\hat{\mathrm{W}}_\alpha$ are expressed in terms of the vector products of spin operators as follows:

$$\hat{W}_1 = \boldsymbol{\lambda}_{12}[\boldsymbol{S}_1 \times \boldsymbol{S}_2] + \boldsymbol{\lambda}_{23}[\boldsymbol{S}_2 \times \boldsymbol{S}_3] + \boldsymbol{\lambda}_{31}[\boldsymbol{S}_3 \times \boldsymbol{S}_1],$$
$$\hat{W}_x = \frac{1}{2}(\boldsymbol{\lambda}_{12}[\boldsymbol{S}_1 \times \boldsymbol{S}_2] + \boldsymbol{\lambda}_{23}[\boldsymbol{S}_2 \times \boldsymbol{S}_3] - 2\boldsymbol{\lambda}_{31}[\boldsymbol{S}_3 \times \boldsymbol{S}_1]),$$
$$W_y = \frac{\sqrt{3}}{2}(\boldsymbol{\lambda}_{23}[\boldsymbol{S}_2 \times \boldsymbol{S}_3] - \boldsymbol{\lambda}_{31}[\boldsymbol{S}_3 \times \boldsymbol{S}_1]). \qquad (11)$$

In Eq. (11) the values $\boldsymbol{\lambda}_{ij}$ are the vector coupling parameters defined as $\boldsymbol{\lambda}_{ij} = (\partial\ \boldsymbol{D}_{ij}\ (R_{ij})/\partial\ R_{ij})_0$. Under the condition of trigonal symmetry there are three parameters, namely, normal part $\lambda_n = \lambda_{ijn}$ and two perpendicular contributions $\lambda_t = \lambda_{ijt}$ and $\lambda_l = \lambda_{ijl}$ where the symbols l and t have the same meaning as in the definition of the AS exchange.

The evaluation of the vibronic matrices can be performed with the aid of the irreducible tensor operators (ITO) approach [31,32]. With this aim each pairwise interaction can be expressed in terms of the zeroth order and first order tensorial products of ITOs as:

$$(\boldsymbol{S}_i\boldsymbol{S}_j) = -\sqrt{3}\left\{\boldsymbol{S}_i^{(1)} \times \boldsymbol{S}_j^{(1)}\right\}^{(0)},$$
$$\boldsymbol{\lambda}_{ij}[\boldsymbol{S}_i \times \boldsymbol{S}_j] = i\sqrt{2}\lambda_- e^{-i\phi}\left\{\boldsymbol{S}_i^{(1)} \times \boldsymbol{S}_j^{(1)}\right\}^{(1)}_1$$
$$- i\sqrt{2}\lambda_+ e^{i\phi}\left\{\boldsymbol{S}_i^{(1)} \times \boldsymbol{S}_j^{(1)}\right\}^{(1)}_{-1} - i\sqrt{2}\lambda_n\left\{\boldsymbol{S}_i^{(1)} \times \boldsymbol{S}_j^{(1)}\right\}^{(1)}_0, \qquad (12)$$

where $\{\boldsymbol{S}_i^{(1)} \times \boldsymbol{S}_j^{(1)}\}^{(k)}_m$ is the symbol of the tensor product [33] (rank κ, component m) of two spin ITOs $\boldsymbol{S}_i^{(1)}$ and $\boldsymbol{S}_j^{(1)}$ relating to the sites i and j and $\phi = 0$, $2\pi/3$, $2\pi/3$ for the sides 12, 23, and 31 of the triangle correspondingly, $\lambda_\pm = \mp(1/\sqrt{2})(\lambda_l \pm i\lambda_t)$.

4. Vibronic matrix for the ground state adiabatic surfaces

In order to simplify our consideration and to get clear insight on the influence of the JT interaction on the magnetic properties we assume that the gap $3J$ exceeds considerably the vibronic coupling and AS exchange and therefore we include in the basis set only four low lying spin 1/2 states and exclude the full symmetric mode Q_1. In this view one should note that the role of A_1 mode is not a simple shift of Q_1 coordinate. In fact, A_1 vibration is active in the pseudo JTE when a relatively small vibronic contribution of AS exchange is taken into account (a more detailed description will be given elsewhere). In the approximation so far assumed the matrix of the full Hamiltonian $H_{\mathrm{AS}} + H_{ev} + H'_{ev} + H_{\mathrm{Zeeman}}$ is obtained as:

$$\begin{pmatrix} \frac{1}{2}g_\parallel\beta H_z + \frac{1}{2}\sqrt{\frac{3}{2}}\lambda Q_x & \frac{1}{2}g_\perp\beta H_x & \frac{\sqrt{3}}{2}\left(-iD_n + \frac{1}{\sqrt{2}}\lambda Q_y\right) & \frac{i}{2}\sqrt{\frac{3}{2}}\lambda_-(Q_x + iQ_y) \\ \frac{1}{2}g_\perp\beta H_x & -\frac{1}{2}g_\parallel\beta H_z + \frac{1}{2}\sqrt{\frac{3}{2}}\lambda Q_x & -\frac{i}{2}\sqrt{\frac{3}{2}}\lambda_+(Q_x - iQ_y) & \frac{\sqrt{3}}{2}\left(iD_n + \frac{1}{\sqrt{2}}\lambda Q_y\right) \\ \frac{\sqrt{3}}{2}\left(iD_n + \frac{1}{\sqrt{2}}\lambda Q_y\right) & -\frac{i}{2}\sqrt{\frac{3}{2}}\lambda_-(Q_x + iQ_y) & \frac{1}{2}g_\parallel\beta H_z - \frac{1}{2}\sqrt{\frac{3}{2}}\lambda Q_x & \frac{1}{2}g_\perp\beta H_x \\ -\frac{i}{2}\sqrt{\frac{3}{2}}\lambda_+(Q_x - iQ_y) & \frac{\sqrt{3}}{2}\left(-iD_n + \frac{1}{\sqrt{2}}\lambda Q_y\right) & \frac{1}{2}g_\perp\beta H_x & -\frac{1}{2}g_\parallel\beta H_z - \frac{1}{2}\sqrt{\frac{3}{2}}\lambda Q_x \end{pmatrix} \qquad (13)$$

In the matrix representation of the full Hamiltonian the basis $|(S_{12})SM\rangle$ is used with the following order of the basis spin functions: $|(0)\frac{1}{2},\frac{1}{2}\rangle, |(0)\frac{1}{2},-\frac{1}{2}\rangle, |(1)\frac{1}{2},\frac{1}{2}\rangle, |(1)\frac{1}{2},-\frac{1}{2}\rangle$.

Since the system has axial magnetic anisotropy one can that the field is applied in a ZX plane ($H_y = 0$). One sees that the vibronic interaction leads to a complicated combined JT and pseudo JT problem. The modulation of the isotropic exchange is expected to provide the dominant contribution to the vibronic interaction. To further simplify the solution of the problem and make it more obvious we put $\lambda_+ = \lambda_- = 0$ and $g_\parallel = g_\perp = g$ (although the eigenvalues of the vibronic matrix (13) are found without these simplifying assumptions). The four eigen-values of the matrix (13) are found as:

$$\varepsilon_{1,4}(\rho,\xi) = \mp\frac{1}{2\sqrt{2}}\hbar\omega\sqrt{2\xi^2+2\delta^2+3\upsilon^2\rho^2-2\sqrt{2}\xi\sqrt{3\upsilon^2\rho^2+2\delta^2\cos^2\theta}}$$
$$\varepsilon_{2,3}(\rho,\xi) = \pm\frac{1}{2\sqrt{2}}\hbar\omega\sqrt{2\xi^2+2\delta^2+3\upsilon^2\rho^2+2\sqrt{2}\xi\sqrt{3\upsilon^2\rho^2+2\delta^2\cos^2\theta}} \quad (14)$$

The following dimensionless parameters are introduced: vibronic coupling parameter $\upsilon = (\lambda/\hbar\omega)(\hbar/M\omega)^{1/2}$, zero-field splitting of the ground state $\delta = \sqrt{3}D_n/\hbar\omega \equiv \Delta/\hbar\omega$, applied field $\xi = g\beta H/\hbar\omega$ and coordinates $q_\alpha = (M\omega/\hbar)^{1/2}Q_\alpha$, $H_z = H\cos\theta$. Finally, ρ is the radial component in the plane q_xq_y defined as usually: $q_x = \rho\cos\varphi$, $q_y = \rho\sin\varphi$.

The adiabatic surfaces are axially symmetric (at an arbitrary direction of the applied field) respectively the C_3 axis complying with the symmetry of the AS exchange.

In the case of $\delta = 0$ and $\xi = 0$ one faces a two mode pseudo JT problem and one obtains simple expressions for a pair of the double degenerate surfaces that are quite similar to that in the pseudo JT $^2E\otimes e$ problem taking the spin–orbital interaction into account.

$$U_\pm(\rho)/\hbar\omega = \rho^2/2 \pm (1/2)\sqrt{\delta^2+3\upsilon^2\rho^2/2}. \quad (15)$$

One can see that in the limit of the isotropic exchange model the surface represents a “Mexican hat” (Fig. 4a) with the conical intersection at $\rho = 0$ that corresponds to the basic JT $E\otimes e$ problem [23–25]: $U_\pm(\rho)/\hbar\omega = \rho^2/2 \pm (\sqrt{3}/2\sqrt{2})|\upsilon|\rho$. This limiting case corresponding to the well-known spin-phonon coupling Hamiltonian [30] (see for details [5,9] and references cited therein) has recently been considered again in [34]. In general, the shape of the surfaces depends on the interrelation between the AS exchange and vibronic coupling that proved to be competitive. In the case of weak vibronic coupling and/or strong AS exchange $\upsilon^2 < 4|\delta|/3$ the lower surface possesses the only minimum at $q_x = q_y = 0 (\rho = 0)$ so that the symmetric (trigonal) configuration of the system proves to be stable. In the opposite case of strong vibronic interaction and/or weak AS exchange, $\upsilon^2 > 4|\delta|/3$, symmetric configuration of the cluster is unstable and the minima are disposed at the ring of the trough of the radius ρ_0:

$$\rho_0 = (1/2)\sqrt{3\upsilon^2/2 - 8\delta^2/3\upsilon^2}. \quad (16)$$

The radius ρ_0 decreases with the increase of AS exchange and vanishes at $|\delta| = 3\upsilon^2/4$. These two types of the pseudo JT surfaces are shown in Fig. 4b and c. The depth of the minima ring in the second type (respectively, to the top in the low surface) depends on the interrelation between the JT constant and AS exchange and is found to be $\varepsilon_0 = (3\upsilon^2 - 4\delta^2)^2/48\upsilon^2$ while the gap between the surfaces in the minima points $3\upsilon^2/4$ is independent of the AS exchange.

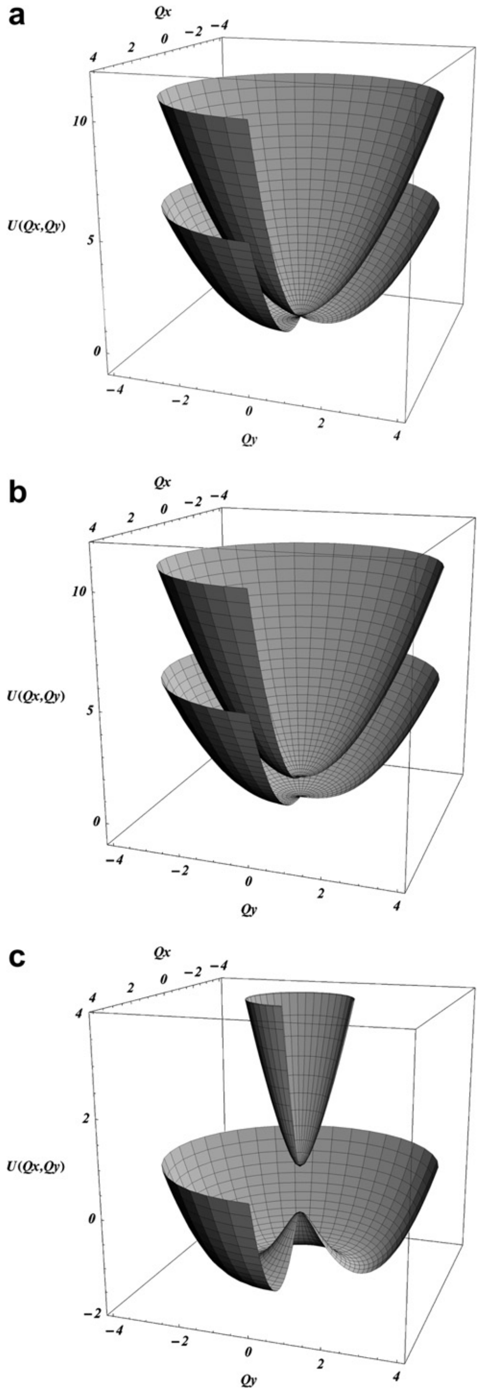

Fig. 4. Adiabatic potentials for the ground state of a triangular exchange system in the space of the double degenerate vibrations: (a) $\delta = 0$, $\upsilon = 2.0$; (b) weak vibronic interaction and/or strong AS exchange ($\delta = 1.0$, $\upsilon = 1.0$); (c) weak AS exchange and/or strong vibronic interaction ($\delta = 1.0$, $\upsilon = 3.0$).

The nuclear motion in the bottom of the trough for the JT $E\otimes e$ problem is described in [24,25]. The metal sites of a distorted triangle move along the circles so that the phases of the ions 2 and 3 are shifted by the angles $2\pi/3$

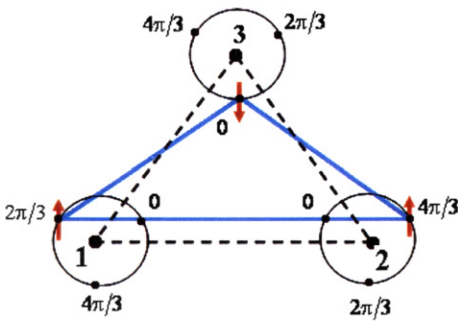

Fig. 5. Rotation of the distorted configurations (solid triangle) in the bottom of the trough-illustration for the elimination of spin frustration through the JT instability. The symmetric configuration is shown by the dashed line.

and $4\pi/3$, respectively, to the phase of the ion 1. Fig. 5 shows an instant nuclear configuration in course of this motion in which the side 12 is elongated while the sides 13 and 23 are compressed taking advantage from the new exchange network. In this geometry of the system two antiferromagnetic pathways 13 and 23 are energetically favorable while the connection 12 is ferromagnetic. One can see that the system possesses a definite spin alignment so that spin frustration is eliminated by the JT distortion with the instant isosceles configuration corresponding to $S_{12} = 1$ in the ground state.

5. Influence of the Jahn–Teller interaction on the magnetization

In order to reveal the effects of the JT vibronic interaction one can employ the adiabatic approximation that was proved to provide a quite good accuracy in the description of the magnetic properties of mixed-valence clusters [35] and allowed to avoid numerical solutions of the dynamic problem. According to the semiclassical adiabatic approach the expressions $U_i(\rho, H) = \hbar\omega\rho^2/2 + \varepsilon_i(\rho, H)$ in which the exact eigen-values of the vibronic matrix are substituted play the role of full energies and the magnetization can be obtained by averaging the derivatives $-\partial U_i(\rho, H)/\partial H_\alpha$ (Z_p is the partition function):

$$M_\alpha(H, T) = Z_p^{-1} \sum_i \int_0^\infty \exp(-U_i(\rho, H)/kT) \times (-\partial U_i(\rho, H)/\partial H_\alpha)\rho d\rho. \tag{17}$$

Integration in Eq. (17) includes all possible nuclear configurations regarding the thermal populations of the levels. To clarify the physical situation let us consider a selected configuration ρ in which the system is instantly distorted. In the case of an arbitrary $\rho \neq 0$ the gap between spin 1/2 levels is increased and at $H = 0$ the zero-field is $\delta(\rho) = \sqrt{3\upsilon^2\rho^2/2 + \delta^2}$ as illustrated in Fig. 6. The Zeeman sublevels in an arbitrary nuclear configuration ρ in the weak field range up to the second order terms with respect to the field ξ defined by the angle θ can be found as:

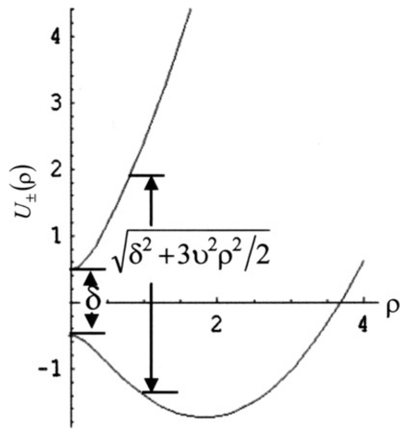

Fig. 6. Section of the adiabatic potentials in the case of JT instability, illustration for the zero-field splitting of the ground state in the vibronically distorted configurations.

$$\frac{\varepsilon_{1,3}(\rho, \xi)}{\hbar\omega} = -\frac{1}{2}\delta(\rho) \pm \frac{1}{2}\kappa_1(\theta)\xi - \kappa_2(\theta)\xi^2,$$
$$\frac{\varepsilon_{2,4}(\rho, \xi)}{\hbar\omega} = +\frac{1}{2}\delta(\rho) \pm \frac{1}{2}\kappa_1(\theta)\xi + \kappa_2(\theta)\xi^2, \tag{18}$$

where the first and second order van Vleck coefficients [36] $\kappa_1(\theta)$ and $\kappa_2(\theta)$ in the Zeeman energies are the functions of the angle θ and JT coupling parameter:

$$\kappa_1(\theta) = \frac{\sqrt{3\upsilon^2\rho^2/2 + \delta^2\cos^2\theta}}{\sqrt{3\upsilon^2\rho^2/2 + \delta^2}}, \quad \kappa_2(\theta) = \frac{\delta^2\sin^2\theta}{4\left(3\upsilon^2\rho^2/2 + \delta^2\right)^{3/2}}. \tag{19}$$

Let us assume that the motion of the system is confined to the bottom of the trough. Strictly speaking this is valid providing strong JT coupling but in all cases it gives clear qualitative results and transparent key expressions. Providing $\rho = \rho_0' \equiv \sqrt{3/8}|\upsilon|$ (radius of the minima ring) the value $\sqrt{3\upsilon^2\rho^2/2}$ is simply the JT splitting $E_{JT} = 3\upsilon^2/4$ (gap between the surfaces in the minima points of the lower surface) and the van Vleck coefficients $\kappa_1(\theta)$ and $\kappa_2(\theta)$ can be directly related to the JT splitting and AS exchange:

$$\kappa_1(\theta) = \sqrt{\frac{E_{JT}^2 + \delta^2\cos^2\theta}{E_{JT}^2 + \delta^2}}, \quad \kappa_2(\theta) = \frac{\delta^2\sin^2\theta}{4(E_{JT}^2 + \delta^2)^{3/2}}. \tag{20}$$

One can see that with the increase of the JT interaction the coefficient $\kappa_1(\theta)$ becomes independent of the angle $\theta(\kappa_1(\theta) \approx 1 - \delta^2\sin^2\theta/2E_{JT}^2)$ and tends to unit while $\kappa_2(\theta)$ disappears $(\kappa_2(\theta) = \delta^2\sin^2\theta/4E_{JT}^3)$ so that in the limit of strong vibronic coupling we arrive at the isotropic linear Zeeman splitting that is obtained within the HDVV model. This is similar to the role of static distortions in the triangular metal clusters in which AS exchange splits the ground state [5,9]. Suppression of the exchange magnetic anisotropy is a quite general conclusion that is closely related to the reduction of the physical quantities of the orbital nature by the JT interaction (Ham effect) [23–25].

In order to reveal the influence of the JT coupling on the anisotropic properties of the AS exchange in more detail let

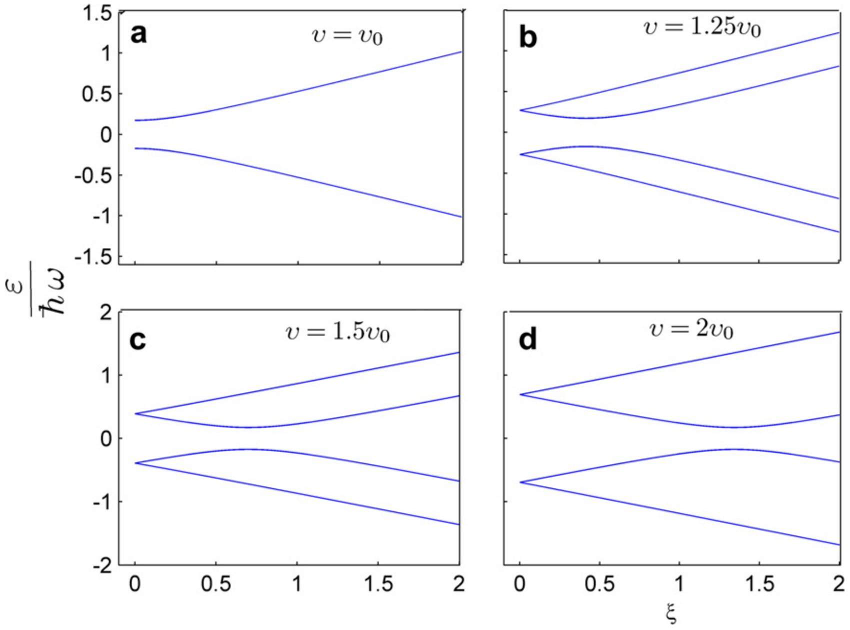

Fig. 7. Influence of the JT interaction (defined by the vibronic coupling parameter υ) on the Zeeman energy pattern in a perpendicular magnetic field ($\boldsymbol{H}\perp C_3$).

us consider the effects of JT coupling in the two principal directions of the magnetic field. In the case of parallel field ($\boldsymbol{H}\|\mathrm{C}_3$) one finds that $\kappa_1(0)=1$ and $\kappa_2\,(0)=0$ so that one obtains the following Zeeman pattern:

$$\frac{\varepsilon_{1,3}(\xi)}{\hbar\omega}=-\frac{1}{2}\sqrt{E_{JT}^2+\delta^2}\pm\frac{1}{2}\xi,$$
$$\frac{\varepsilon_{2,4}(\xi)}{\hbar\omega}=+\frac{1}{2}\sqrt{E_{JT}^2+\delta^2}\pm\frac{1}{2}\xi. \tag{21}$$

Eq. (21) exhibits linear Zeeman splitting in a pair of spin doublets in the parallel field but the role of the zero-field splitting plays now the combined effective gap $\sqrt{E_{JT}^2+\delta^2}$ instead of the initial one $|\delta|$ related to the AS exchange. This does not affect the magnetic moments of the ground manifold so that neither JT interaction nor the AS exchange do not manifest themselves in the magnetic characteristics in the case of $\boldsymbol{H}\|\mathrm{C}_3$.

In the case of perpendicular field $\boldsymbol{H}\perp C_3$ one obtains that $\kappa_1(\pi/2)=E_{JT}/\sqrt{E_{JT}^2+\delta^2}$, $\kappa_2(\pi/2)=\delta^2/4(E_{JT}^2+\delta^2)^{3/2}$ and therefore the Zeeman energy in this case is given by:

$$\frac{\varepsilon_{1,3}(\xi)}{\hbar\omega}=-\frac{1}{2}\sqrt{E_{JT}^2+\delta^2}\pm\frac{E_{JT}}{\sqrt{E_{JT}^2+\delta^2}}\frac{1}{2}\xi-\frac{\delta^2}{4(E_{JT}^2+\delta^2)^{3/2}}\xi^2,$$
$$\frac{\varepsilon_{2,4}(\xi)}{\hbar\omega}=+\frac{1}{2}\sqrt{E_{JT}^2+\delta^2}\pm\frac{E_{JT}}{\sqrt{E_{JT}^2+\delta^2}}\frac{1}{2}\xi+\frac{\delta^2}{4(E_{JT}^2+\delta^2)^{3/2}}\xi^2, \tag{22}$$

where the eigen-values are denoted as $\varepsilon_i(\xi)\equiv\varepsilon_i(\rho_0',\xi)$. Eq. (22) show that the Zeeman pattern contains both linear and quadratic contributions. The role of the JT coupling can be understood by comparing the Zeeman picture so far obtained with that at $\upsilon=0$. It is important that in the absence of the JT coupling the linear Zeeman terms disappear and the Zeeman energies contain only quadratic terms (with respect to the field) as follows from Eq. (3). Thus Fig. 7a illustrates two degenerate pairs of the Zeeman levels in perpendicular field in the symmetric nuclear configuration. In a weak field range they are given by:

$$\varepsilon_1(\xi)/\hbar\omega=\varepsilon_3(\xi)/\hbar\omega=-|\delta|/2-\xi^2/4|\delta|,$$
$$\varepsilon_2(\xi)/\hbar\omega=\varepsilon_4(\xi)/\hbar\omega=+|\delta|/2+\xi^2/4|\delta|. \tag{23}$$

This can be referred to as the effect of the reduction of the magnetization in low magnetic field that is perpendicular to the axis of AS exchange [5,9]. The reduction of the Zeeman energy by the AS exchange gives rise to a small van Vleck type contribution to the magnetic susceptibility at low field $g\beta H\ll D_n$. An essential effect is that the JT interaction leads to the occurrence of the linear terms for the Zeeman energies at low field (see Eq. (22)). This is shown in Fig. 7b–d that illustrate transformation of the Zeeman levels under the influence of the vibronic coupling obtained by the aid of general Eq. (14). As a result the JT coupling essentially increases the magnetic moments of the system at low perpendicular fields when magnetization in symmetric configuration is reduced by the AS exchange. The range of the linear Zeeman splitting increases with the increase of the JT coupling and the crossing point moves in the high field region. This can be considered as the effect of the reduction of the AS exchange by the JT distortions (that are, in fact, dynamic) accompanied by the restoration of

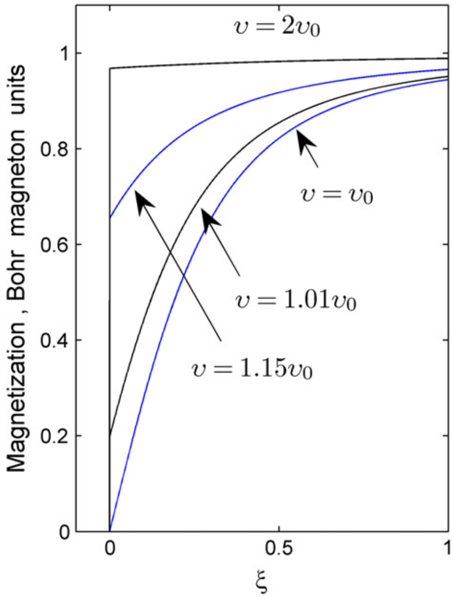

Fig. 8. Influence of the JT interaction on dependence magnetization vs. perpendicular field (***H***⊥C_3).

the magnetic moments to the value specific for a $S = 1/2$ system.

Fig. 8 illustrates the influence of the JTE on the field dependence of the magnetization of a triangular unit that is closely related to the influence of the vibronic coupling on the Zeeman pattern (Fig. 7). The magnetization vs. perpendicular field at $T = 0$ is presented as a function of the vibronic coupling parameter υ that is assumed to satisfy the condition of instability $\upsilon^2 > \upsilon_0^2 \equiv 4|\delta|/3$ (see Eq. (16)). One can see that providing $\upsilon = \upsilon_0$ (and of course $\upsilon < \upsilon_0$ that corresponds to a symmetric stable configuration) the magnetization slowly increases with the increase of the field (due to reduction of the Zeeman interaction in the low field) then reaches saturation when the magnetic field is strong enough to break the AS exchange. Increase of the JT coupling leads to the fast increase of the magnetic moments in the region of low field and formation of the step in magnetization caused by the reduction of the magnetic anisotropy (appearance of the linear terms in the Zeeman levels). The height of the step depends on the interrelation between AS exchange and vibronic coupling and can be expressed as:

$$M(H = 0) = \frac{g\beta}{2} \frac{E_{JT}}{\sqrt{E_{JT}^2 + \delta^2}}. \tag{24}$$

The height of the step increases with the increase of the vibronic coupling. Finally, when the JT coupling is strong enough ($\upsilon = 2\upsilon_0$) one can observe staircase like behavior of magnetization with the sharp step in which $M(H)$ jumps from zero to $M(H = 0) = g\beta/2$ at zero-field (and T = 0) that is expected for a magnetically isotropic system. The influence of the distortions caused by JT instability is very pronounced so that the step starts to appear even when $\upsilon = 1.01\upsilon_0$. Although, the semiclassical description in this range of parameters loses its accuracy the qualitative results are able to draw an adequate physical picture. More accurate quantitative results in this area of vibronic coupling can be obtained by solving the dynamic pseudo JT problem.

Let consider separately the case of a strong magnetic field $g\beta H \gg D_n$. In this limit one can find the following approximate expressions based on the high field expansion in Eq. (14):

$$\begin{aligned} \frac{\varepsilon_{1,3}(\rho, \xi)}{\hbar\omega} &= -\frac{1}{2}\sqrt{E_{JT}^2 + \delta^2\cos^2\theta} \pm \frac{1}{2}\xi. \\ \frac{\varepsilon_{2,4}(\rho, \xi)}{\hbar\omega} &= +\frac{1}{2}\sqrt{E_{JT}^2 + \delta^2\cos^2\theta} \pm \frac{1}{2}\xi \end{aligned} \tag{25}$$

One can see that in a strong magnetic field the system behaves like two $S = 1/2$ levels but the AS exchange contribution to the full zero-field splitting is reduced by the applied field to the value $|\delta\cos\theta|$. At the same time – as one can see from Eq. (21) – the vibronic contribution is not affected by the field so that in the limiting case of strong perpendicular field the zero-field splitting is simply E_{JT} as can be expected for the magnetically isotropic vibronic coupling.

6. Conclusion

In this article, we have analyzed the main manifestations of the AS exchange and JT instability in spin-frustrated systems exhibiting non-collinear spin structure. We employed the three-spin model of the V_{15} cluster that includes isotropic and AS exchange interactions. AS exchange plays a crucial role in the understanding of the field and temperature dependence of the adiabatic magnetization of V_{15} single crystals in which the vibronic interaction is small. It was demonstrated that the orientation of the AS exchange vector, but not only its absolute value, plays a special physical role in the magnetic behavior of spin-frustrated systems. In fact, the normal part of the AS exchange affects the low field part of the magnetization curve when the field is applied in the plane of the vanadium triangle. At the same time the in-plane components of AS exchange give rise to a peculiar shape of magnetization vs. field in the vicinity of the crossing point of the magnetic sublevels belonging to $S = 1/2$ and $S = 3/2$ levels. It is possible to reach a perfect fit to the experimental data on the adiabatic magnetization vs. applied in-plane and for the first time to precisely estimate two components of the AS vector.

Then we considered the pseudo JT vibronic problem for the spin-frustrated ground state of the triangular system with half-integer spins and in context of significant vibronic interaction. The vibronic Hamiltonian matrix is deduced in a general form. Is the case of a weak JT coupling and/or strong AS exchange the adiabatic surface in the space of E- vibrations has the only minimum in the full symmetry point while in the opposite case the system proves to be unstable and has a ring of minima at the bottom of the trough. JT instability is shown to eliminate spin frustration due to removal of "accidental" degeneracy. The influence of the vibronic interaction on the magnetization is revealed with the aid of the semiclassical adiabatic approach that provides qualitatively transparent results. The first and second van Vleck coefficients in the Zeeman energies are deduced as the functions of the direction of the field, AS exchange and vibronic coupling. The JT coupling is shown to be competitive to the AS exchange so that the increase of the vibronic coupling decrease the magnetic anisotropy of the system. On the other hand AS exchange tends to suppress to JTE. This is demonstrated by the theoretical modeling of the field dependence of the magnetization that clearly exhibits crucial role of the pseudo JT coupling in spin-frustrated systems.

The present study is considered to be part of a more extended future investigation regarding multicenter JTE and structure-related magnetism in nanoscopic polyoxometalates/vanadates showing frustration from one-triangle (present paper) via two- (in case of M_6Mo_{57} [37]) to 20-triangle spin-arrays (in case of $M_{30}Mo_{72}$; $M = V^{IV}$, Fe^{III} [38]).

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References

[1] D. Gatteschi, R. Sessoli, Angew. Chem. Int. Ed. 42 (2003) 269.

[2] D. Gatteschi, R. Sessoli, J. Villain, Molecular Nanomagnets, Oxford University Press, Oxford, 2006.

[3] (a) I.E. Dzyaloshinsky, Zh. Exp. Teor. Fiz. 32 (1957) 1547;
(b) Sov. Phys. JETP. 5 (1957) 1259.

[4] T. Moria, Phys. Rev. 120 (1960) 91.

[5] B.S. Tsukerblat, M.I. Belinskii, V.E. Fainzilberg, Magnetochemistry and spectroscopy of transition metal exchange clusters, in: M. Vol'pin (Ed.), Soviet Sci. Rev. B, Harwood Academic Publisher, Chur, London, Paris, Newyork, 1987, pp. 337–482.

[6] B.S. Tsukerblat, M.I. Belinsky, A.V. Ablov, Phys. Stat. Solidi (b) 51 (1972) K71.

[7] M.I. Belinskii, B.S. Tsukerblat, Fizika. Tverdogo Tela (Russian) 15 (1973) 29.

[8] B.S. Tsukerblat, M.I. Belinskii, A.V. Ablov, Fizika. Tverdogo Tela (Rus) 16 (1974) 989.

[9] B.S. Tsukerblat, M.I. Belinskii, Magnetochemistry and Radiospectroscopy of Exchange Clusters, Pub. Stiintsa, Kishinev, 1983 (Russian).

[10] B.S. Tsukerblat, B.Ya. Kuavskaya, M.I. Belinskii, A.V. Ablov, V.M. Novotortsev, V.T. Kalinnikov, Theor. Chim. Acta. 38 (1975) 131.

[11] V.E. Fainzilberg, M.I. Belinskii, B.S. Tsukerblat, Mol. Phys. 44 (1981) 1177, 44 (1981) 1195, 45 (1982) 807.

[12] J. Yoon, L.M. Mirica, T.D.P. Stack, E.I. Solomon, J. Am. Chem. Soc. 126 (2004) 12586.

[13] A. Müller, J. Döring, Angew. Chem. Int. Ed. Engl. 27 (1988) 1721.

[14] D. Gatteschi, L. Pardi, A.-L. Barra, A. Müller, J. Döring, Nature 354 (1991) 465.

[15] A.-L. Barra, D. Gatteschi, L. Pardi, A. Müller, J. Döring, J. Am. Chem. Soc. 114 (1992) 8509.

[16] D. Gatteschi, L. Pardi, A.-L. Barra, A. Müller, Mol. Eng. 3 (1993) 157.

[17] B.J. Barbara, J. Mol. Struct. 656 (2003) 135.

[18] I. Chiorescu, W. Wernsdorfer, A. Müller, H. Bögge, B. Barbara, Phys. Rev. Lett. 84 (2000) 3454.

[19] I. Chiorescu, W. Wernsdorfer, A. Müller, S. Miyashita, B. Barbara, Phys. Rev.B. 67 (2003) 020402(R).

[20] S. Miyashita, J. Phys. Soc. Japan. 65 (1996) 2734.

[21] H. Nojiria, T. Taniguchia, Y. Ajiro, A. Müller, B. Barbara, Physica B. 346-347 (2004) 216.

[22] S. Miyashita, J. Phys. Soc. Japan 64 (1995) 3207.

[23] R. Englman, The Jahn–Teller Effect in Molecules and Crystals, Wiley, London, 1972.

[24] I.B. Bersuker, V.Z. Polinger, Vibronic Interactions in Molecules and Crystals, Springer-Verlag, Berlin, 1989.

[25] I.B. Bersuker, The Jahn-Teller Effect, Cambridge University Press, New York, 2006.

[26] B. Tsukerblat, A. Tarantul, A. Müller, Phys. Lett. A. 353 (2006) 48.

[27] A. Tarantul, B. Tsukerblat, A. Müller, Chem. Phys. Lett. 428 (2006) 361.

[28] B. Tsukerblat, A. Tarantul, A. Müller, J. Chem. Phys. 125 (2006) 054714.

[29] I. Chiorescu, W. Wernsdorfer, A. Müller, H. Bögge, B. Barbara, J. Magn. Magn. Mater. 221 (2000) 103.

[30] C.A. Bates, R.F. Jasper, J. Phys. C: Sol. State Phys. 4 (1971) 2341.

[31] A. Bencini, D. Gatteschi, Electron Paramagnetic Resonance of Exchange Coupled Systems, Springer-Verlag, New York, 1990.

[32] B.S. Tsukerblat, Group Theory in Chemistry and Spectroscopy, Dover Publications, Inc, Mineola, NewYork, 1994.

[33] D.A. Varshalovich, A.N. Moskalev, V.K. Khersonskii, Quantum Theory of Angular Momentum, World Scientific, Singapore, 1988.

[34] A.I. Popov, V.I. Plis, A.F. Popkov, A.K. Zvezdin, Phys. Rev. B 69 (2004) 104418.

[35] J.J. Borras-Almenar, E. Coronado, H.M. Kishinevsky, B.S. Tsukerblat, Chem. Phys. Lett. 217 (1994) 525.

[36] O. Kahn, Molecular Magnetism, VCH, NY, 1993.

[37] D. Gatteschi, R. Sessoli, W. Plass, A. Müller, E. Krickemeyer, J. Meyer, D. Sölter, P. Adler, Inorg. Chem. 35 (1996) 1926.

[38] A. Müller, A.M. Todea, J. van Slageren, M. Dressel, H. Bögge, M. Schmidtmann, M. Luban, L. Engelhardt, M. Rusu, Angew. Chem. Int. Ed. 44 (2005) 3857.