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Crossover of the magnetic sublevels in spin frustrated clusters: The role of static and dynamic deformations

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Abstract

We model the magnetic behavior of spin frustrated trinuclear clusters in the region of field induced crossover of the levels. The emphasis is made on a competitive role of the antisymmetric (AS) exchange and static structural distortions as well as on the consequences of the dynamic pseudo-Jahn–Teller (JT) instability. We employ the three-spin model for the cluster anion present in $K_6[V^{IV}_{15}As_6O_{42}(H_2O)]\cdot 8H_2O$ (V_{15} cluster) and analyze the role of different components of AS in the half step magnetization. Both types of deformations (static and dynamic) are shown to be competitive with the AS exchange and tend to reduce the magnetic anisotropy caused by AS.

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

1. Introduction

The cluster anion present in $K_6[V^{IV}_{15}As_6O_{42}(H_2O)]\cdot 8H_2O$ (hereafter V_{15} cluster) has been discovered more than 15 years ago [1] and since that time this system attracts continuous and increasing attention as an unique molecular magnet exhibiting three magnetic layers, a central spin triangle and two almost spin paired hexagons (Fig. 1). The system contains 15 V^{4+} spins ($S = 1/2$) that are antiferromagnetically coupled via oxo-bridges and the overall structure possesses D_{3d} symmetry. Studies of adiabatic magnetization and quantum dynamics of the V_{15} cluster [2–7] showed that this system exhibits the magnetization hysteresis loop of molecular origin and can be referred to as a mesoscopic system. Low lying spin excitation of this system affects its low-temperature magnetic properties [2] and inelastic neutron scattering (INS) [8,9] and can be treated within the model of spin frustrated triangular unit [10–12] formed by a central magnetic layer weakly coupled to two spin hexagons (Fig. 1b). Spin frustration is inherently related to orbital degeneracy of the system whose ground state is represented by the orbital doublet ^2E [13]. Spin frustration leads to the crucial role of the AS exchange (Dzyaloshinsky–Moriya interaction, [13–15]), especially in the V_{15} cluster ([16–19]), and importance of the even small concurring perturbations like structural deformations and dynamical distortions caused by the spin–vibronic JT interactions. The latter gives rise to a structural instability [20] with spontaneous symmetry lowering. The deviation from the trigonal symmetry in the V_{15} molecule has been assumed in Refs. [8,9] on the basis of inelastic neutron scattering data and attributed to the water molecule located in the center of spherical cavity (Fig. 1a) or to the presence of water in the lattice structure. In this article we study the interplay between the AS exchange, scalene structural and JT distortions with emphasis on the region of the crossing/anticrossing of magnetic sublevels. This region is important for description of half step magnetization in the triangular spin frustrated clusters [2,19,21–23], dynamical behavior of magnetization [2] in a sweeping field and magnetoelastic instability resulting in a field induced cooperative phenomena in molecule based magnets [24].

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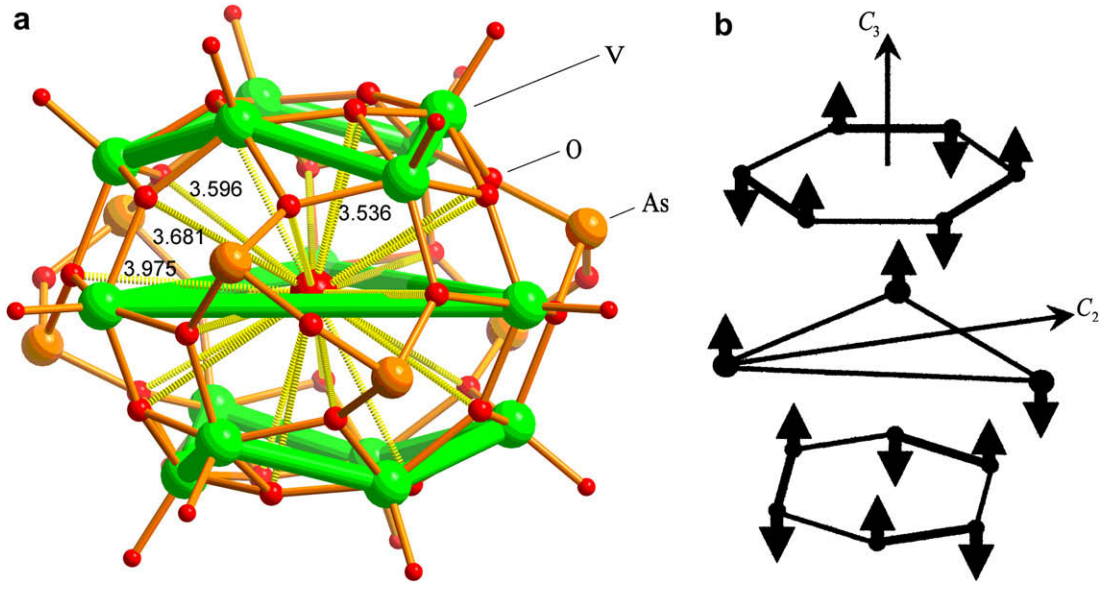

Fig. 1. (a) Structure of the cluster anion of $K_6[V^{IV}_{15}As_6O_{42}(H_2O)]^{6-}$ with D_{3d} symmetry in ball-and-stick representation; central ball – water molecule. The metal network is highlighted by thick green lines. The magnetic layers are formed by the V_3 triangle sandwiched by two distorted V_6 hexagons (interatomic distances in Å). (b) Scheme of spin arrangements in the ground state when the spins of the external hexagons are paired and the spins of the central triangle are frustrated.

2. The Hamiltonian, spin levels in a static model

The full Hamiltonian of a slightly distorted trinuclear system, Eq. (1), includes isotropic exchange (first term, H_0), selected static structural distortion along side 12 (Fig. 2), AS exchange H_{AS}, energy of the free harmonic vibrations of the metal core and spin–vibronic interaction (term H_{sv}) and an isotropic Zeeman term:

$$H = 2J\sum_{i,k=1,2,3} \boldsymbol{S}_i\boldsymbol{S}_k + 2\delta\,\boldsymbol{S}_1\boldsymbol{S}_2 + \sum_{i,k} \boldsymbol{D}_{ij}[\boldsymbol{S}_i \times \boldsymbol{S}_k] + H_{sv} + g\beta\,\boldsymbol{H}\sum_i \boldsymbol{S}_i. \quad (1)$$

The vector parameters $\boldsymbol{D}_{ik}$ have components along and perpendicular to the sides (in-plane of the triangle, see Ref. [19]) and perpendicular to the plane whose absolute values are $D_{ik\,l}$, $D_{ik\,t}$

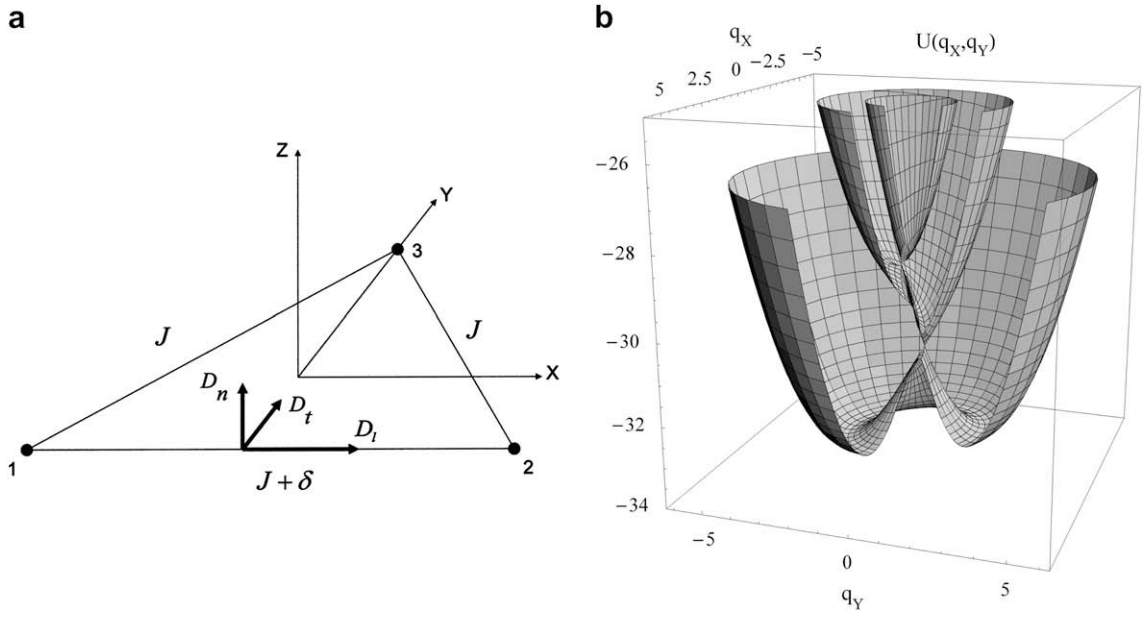

Fig. 2. The model of magnetic exchange interactions acting in the effective triangle of the V_{15} cluster. $J_{13} = J_{23} \equiv J$, $J_{12} = J + \delta$, XYZ – molecular coordinate frame.

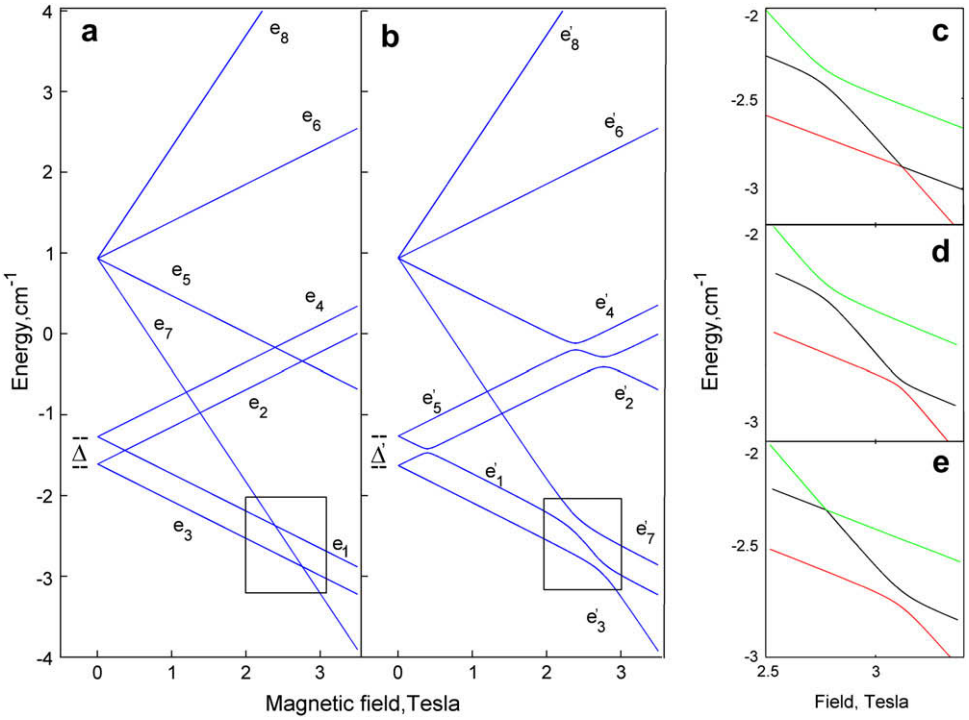

Fig. 3. Energy levels in the perpendicular field (in-plane of the triangle) and influence of the D_t, D_l parameters on the anticrossing region (box). In all the pictures $J = 0.85\ \mathrm{cm}^{-1}$ and $\delta = +0.2J$. (a) $D_n = D_l = D_t = 0$; (b) $D_n = 0.1J$, $D_t = 0.08J$, $D_l = 0.13J$; (c) $D_n = 0.1J$, $D_t = 0$, $D_l = 0.1J$; (d) $D_n = 0.1J$, $D_t = 0.05J$, $D_l = 0.1J$; (e) $D_n = 0.1J$, $D_t = 0.1J$, $D_l = 0$.

and $D_{ik\,n}$ (Fig. 2). Influence of small distortions on the AS exchange is neglected so we assume that in the H_{AS} contribution $D_{ik\,\alpha} = D_\alpha$, $\alpha = l, t, n$ for any side. For the sake of simplicity the g-factor is assumed to be isotropic. For $S_i = 1/2$ one finds two eigen-values of H_0 corresponding to the full spin values $S = 1/2$ (“accidentally” degenerate ground state [13] in the case of antiferromagnetic coupling) and $S = 3/2$ that are crossed at $H_{\mathrm{cr}} = 3J/g\beta$. The main contribution to the vibronic interaction arises from the modulation of the isotropic exchange by the JT displacements of the E-type (double degenerate mode Q_X, Q_Y, see Fig. 3 in Ref. [20]) of spin sites, the corresponding operator is deduced in Ref. [20]. It is worthwhile to consider the Zeeman energy pattern in the crossover from $S = 1/2$ to $S = 3/2$ region within the perturbation theory. To get a more clear insight, the field is assumed to be directed in the plane of the system. Formula (2) gives the matrix of the Hamiltonian (1) in the restricted basis set of three eigenfunctions $|(S_{12})S, M_S\rangle$: $|(1)3/2, M_\perp = -3/2\rangle$,$|(0)1/2, M_\perp = -1/2\rangle$,$|(1)1/2, M_\perp = -1/2\rangle$ of the unperturbed Hamiltonian H_0; these eigenfunctions correspond to the crossing levels (symbol $\perp$ indicates that the field is lying in the triangle plane and quantization axis is along the field):

The first term in Eq. (2) is the elastic energy of nuclei vibrations (ω is the frequency). Within the adiabatic model the kinetic vibrational energy is omitted and the spin–vibronic coupling parameter λ is explicitly defined in Ref. [20].

Let us first focus on the results of the static model ($Q_X = Q_Y = 0$) neglecting vibronic coupling. Fig. 3a shows the energy pattern within the isotropic model ($D_{ij} = 0$). The static distortion removes “accidental” degeneracy of the ground level (separating its states accordingly to the intermediate spin $S_{12} = 0, 1$) and results in the zero-field splitting $\Delta = 2\delta$. Due to isotropy of the system one can observe exact crossing of the magnetic sublevels as shown in Fig. 3a. Fig. 3b shows that combined action of static deformation and AS exchange results in the zero-field splitting that can be approximately presented as $\Delta' = \sqrt{4\delta^2 + 3D_n^2} - (D_l^2 + D_t^2)/8J$, avoided crossing and a peculiar non-linear behavior at low field $\boldsymbol{H}$ whose direction is in-plane of the triangle.

In the avoiding crossing region the behavior of the levels (which influences the dynamic of magnetization) crucially depends on the interrelation between D_t, D_l and δ (Fig. 3, insets). One can see that the combined action of the distortions

$$\frac{\hbar\omega}{2}\left(Q_x^2 + Q_y^2\right) + \begin{pmatrix} (-3J - g\beta H)/2 + \delta - \sqrt{6}\lambda\, Q_X/4 & \sqrt{6}\lambda Q_Y/4 & -3D_l/4\sqrt{2} \\ \sqrt{6}\lambda\, Q_Y/4 & (-3J - g\beta H)/2 - \delta + \sqrt{6}\lambda Q_X/4 & -3D_t/4\sqrt{2} \\ -3D_l/4\sqrt{2} & -3D_t/4\sqrt{2} & 3(J - g\beta H)/2 + \delta \end{pmatrix}. \qquad (2)$$

and AS exchange results in the new pattern in the anticrossing region, in particular, new rules for the crossing, that cannot be described in a symmetric model (see Ref [16]). It is interesting that due to the symmetry lowering the two in-plane components of AS exchange, namely D_t and D_l, act independently and cannot be combined into the only parameter $D_\perp = \sqrt{D_t^2 + D_l^2}$ which has been introduced in Ref. [16] for a strictly trigonal system.

3. Field induced Jahn–Teller instability in the crossing region

In the anticrossing region the Zeeman sublevels along with the structural deformation can be affected by the pseudo-JT effect that appears due to the presence of quasidegenerate levels mixed by the AS exchange. For the sake of clarity the JT distortion will be considered separately from the static one, i.e. in the limit $\delta = 0$. The symmetry adopted vibrational coordinates and the explicit form of the spin–vibronic Hamiltonian is deduced in Ref. [20]. It is convenient to use the dimensionless parameters: vibronic coupling $\upsilon = (\lambda/\hbar\omega)(\hbar/M\omega)^{1/2}$ (M is the effective mass), applied field $\xi = g\beta H/\hbar\omega$, vibrational coordinates $q_\alpha = (M\omega/\hbar)^{1/2}Q_\alpha$ and exchange parameters $j = J/\hbar\omega$, $\gamma_\alpha = (3/4)\sqrt{2}(D_\alpha/\hbar\omega)$, $\alpha = n, l, t$. Fig. 4 illustrates the adiabatic surfaces of the system for a model set of parameters in different regions of the applied field. In the crossing point ($\xi = 3j$) the symmetric (trigonal) system is stable providing weak vibronic coupling (Fig. 4a) or/and relatively strong AS exchange, meanwhile in the case of a relatively strong vibronic coupling and/or weak AS exchange the symmetric configuration of the magnetic sites becomes unstable and the minima of the adiabatic surface are disposed at the ring of the trough (Fig. 4b). Finally, in a high field (beyond the anticrossing region) when the

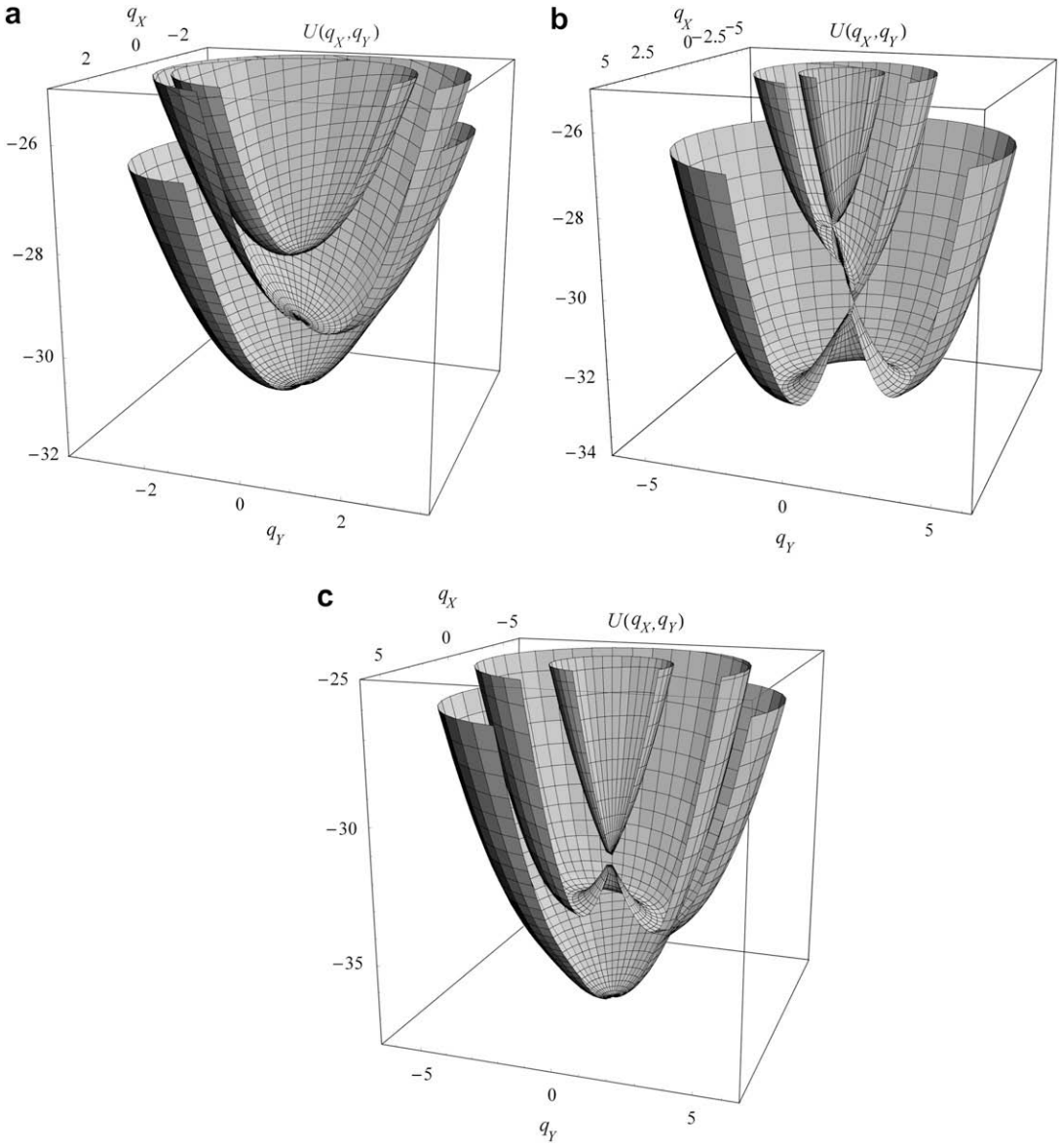

Fig. 4. Adiabatic surfaces of a triangular system, $j = 10$, $\gamma_l = \gamma_t = 0.1j$: (a) weak spin–vibronic coupling, $\upsilon = j$, $\xi = 3j$; (b) strong spin–vibronic coupling, $\upsilon = 4j$, $\xi = 3j$; (c) strong magnetic field $\upsilon = 4j$, $\xi = 3.5j$.

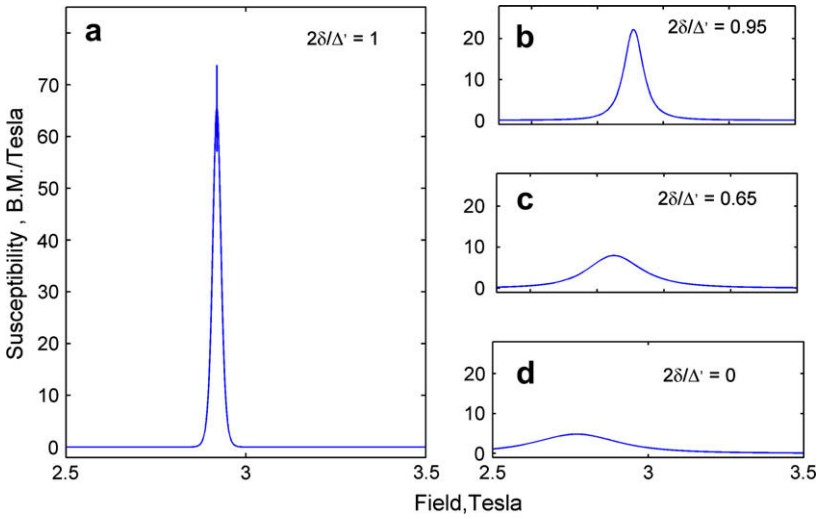

Fig. 5. Magnetic susceptibility in the perpendicular field at $T = 0.01\ K$ for the different ratios between $\delta \geq 0$ and AS provided fixed value of Δ' equal to 0.14 cm^{-1}, $J = 0.85\ cm^{-1}$ and constant ratio $D_n : D_t : D_l = 1 : 2.12 : 2.12$.

degeneracy is removed the symmetric system becomes stable again (Fig. 4c). As distinguished from the static distortion the JT conformations are dynamical in the sense that the motion along the ring of the trough corresponds to a series of isosceles configurations in which the spin frustration is eliminated.

4. Magnetic susceptibility

The influence of structural deformation on the shape of static susceptibility in the anticrossing region is illustrated in Fig. 5. Within the isotropic model the low-temperature susceptibility has a narrow-pulse shape (Fig. 5a) that corresponds to exact crossing of $S = 3/2$, $M_S = -3/2$ and $S = 1/2$, $M_S = -1/2$ levels giving rise to a sharp step of magnetization. Fig. 5a–c shows the effect of AS exchange provided that the zero-field gap Δ' is fixed while the ratio $2\delta/\Delta'$ is varying. With increase of the contribution of AS exchange the peak of χ vs. field becomes smoother. This shows that structural deformation reduces the AS exchange and consequently the magnetic anisotropy. On the other hand, strong AS exchange reduces the effect of structural deformation, so that these two interactions are competitive.

This observation reveals also the role of the spin–vibronic JT coupling. In the case of strong coupling leading to instability of the symmetric configuration the magnetic anisotropy caused by the AS exchange is expected to be reduced and in this limit one can expect sharp step of magnetization (see Ref. [20]). On the contrary, when AS exchange is strong enough the symmetric system remains stable and shows the magnetic anisotropy related to AS.

5. Summary

In conclusion, we have reported the study of the Zeeman energy pattern of trinuclear spin frustrated system in the crossover region and have revealed a crucial role of the interplay between different components of AS exchange, static and dynamical JT distortions of the system. The patterns of adiabatic surfaces were qualitatively studied and the conditions for emerging of field induced JT instability are discussed. AS exchange from one side and structural and dynamical distortions from the other side are shown to be competitive. The discussion of the INS experimental data and magnetization of V_{15} and other spin frustrated trinuclear systems will be given elsewhere.

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