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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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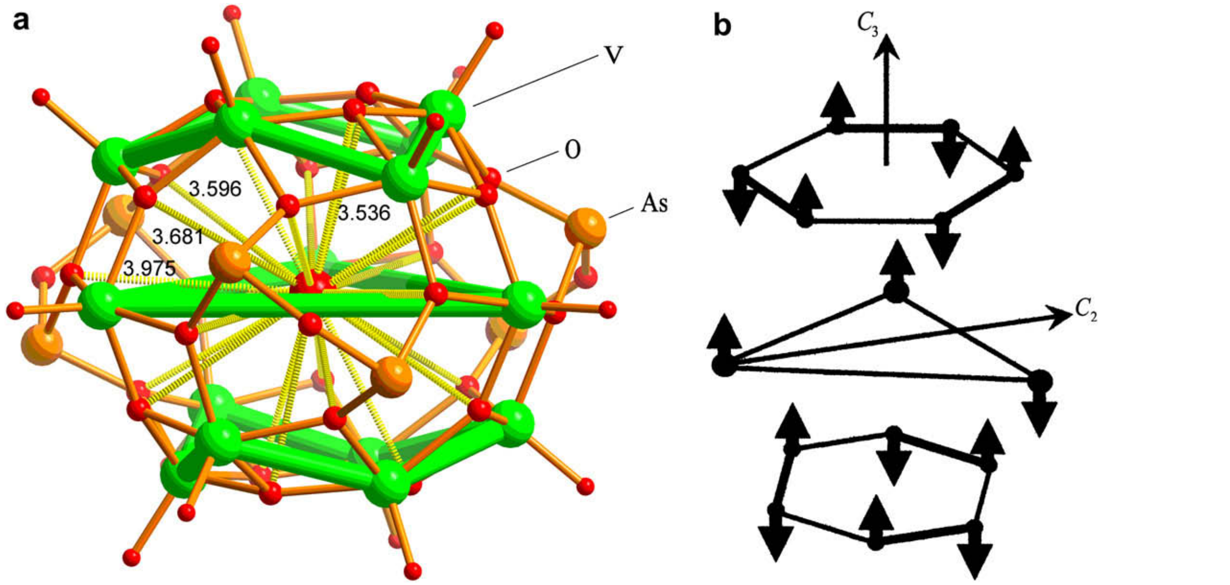

Fig. 1. (a) Structure of the cluster anion of $K_6[V^{IV}_{15}As_6O_{42}(H_2O)]^{6-}$ with D_{3d} symmetry in ball-and-stick representation; central ball − water molecule. The metal network is highlighted by thick green lines. The magnetic layers are formed by the V_3 triangle sandwiched by two distorted 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 $D_{ik\ l}$, $D_{ik\ t}$

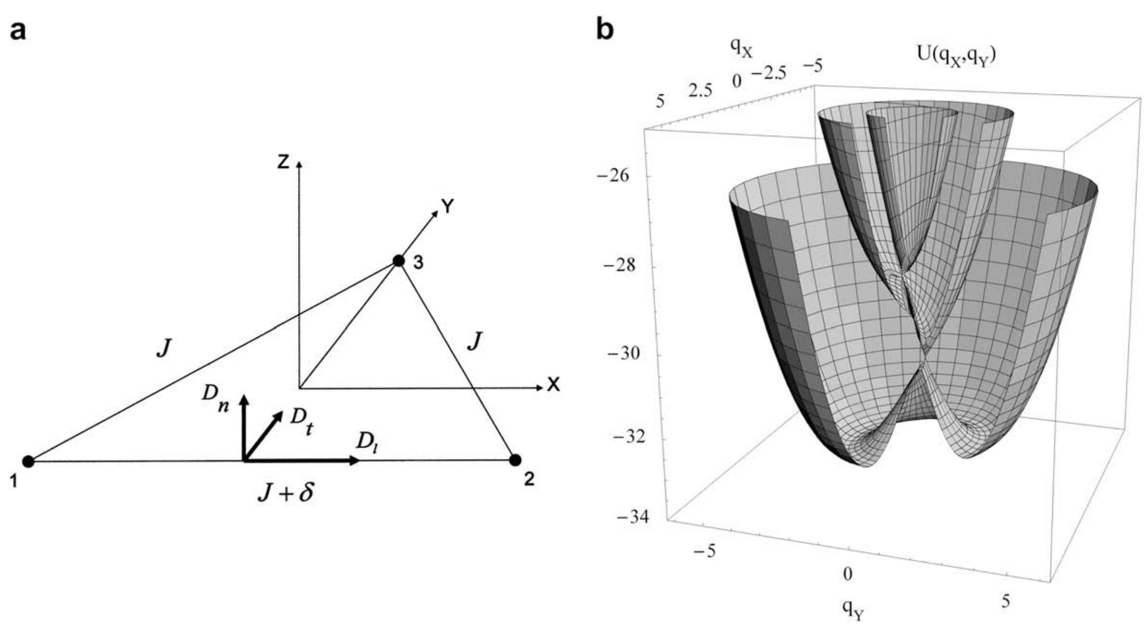

Fig. 2. The model of magnetic exchange interactions acting in the effective triangle of the V_{15} cluster. $J_{13} = J_{23} \equiv J$, $J_{12} = J + \delta$, XYZ − molecular coordinate frame.