EPR and inelastic neutron scattering in spin-frustrated V$_3$ and Cu$_3$ nanomagnets with Dzialoshinsky-Moriya exchange

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Abstract. The inelastic neutron scattering (INS) and EPR transitions are considered for the spin-frustrated V$_3$ and Cu$_3$ nanomagnets. It is shown that the DM exchange and distortions determine the Q-dependence and redistribution of the intensities of the intra- and inter-doublet INS transitions in the spin-frustrated 2(S=1/2) states as well as the intensities of the EPR transitions. The peculiarities of the INS and EPR spectra of the V$_3$ ring of V$_{15}$ quantum molecular magnet and EPR spectra of the V$_3$ and {Cu$_3$} nanomagnets are described by the isosceles Heisenberg model with the DM exchange.

1. Introduction
Trinuclear Cu$_3$ and V$_3$ clusters have attracted significant interest as molecular magnets [1] and possible components for molecule-based quantum computation [2, 3]. Antiferromagnetic Cu$_3$ and V$_3$ clusters with the spin-frustrated ground state 2(S=1/2) are the simplest systems which allow to investigate the effects of the Dzialoshinsky-Moriya [4, 5] (DM) exchange $H_{DM} = \sum G_{ij}[S_i \times S_j]$, spin-frustration, spin chirality and quantum magnetization. In the Cu$_3$ trimers with large Heisenberg parameter J ($H_{J}=\sum J_{ij}S_i S_j$, J>200K, $G_{z}=7-68$K) [6-8], and in the clusters with small J, such as the [V$_3$] [9] and {Cu$_3$} [10] nanomagnets, and the V$_3$ ring of V$_{15}$ quantum molecular magnet [11-15, 3] (J=2-5K, G=0.05-0.5K), the DM exchange determines the zero-field splitting (ZFS) 2$\Delta$ of the 2(S=1/2) states, magnetic and EPR anisotropy. The effect of quantum magnetization, owing to the spin-frustrated 2(S=1/2) doublets, observed in the V$_3$ ring of V$_{15}$ [11], and in the V$_3$ [9], {Cu$_3$} [10] nanomagnets has been described in the DM exchange model [9-11, 13, 14]. The microscopic origin of the 2$\Delta$-gap in the V$_3$ ring of V$_{15}$ is a subject of discussion [15, 16]. This 2$\Delta$-gap has been described [16] by the isotropic Heisenberg scalene triangle model ($J_{12} \neq J_{13} \neq J_{23}$, $G_{z}=0$) on the basis of the observed inelastic neutron scattering (INS) spectra [16]. On the other hand, the ZFS 2$\Delta$, tunneling gaps, quantum magnetization and EPR spectra of the V$_3$ ring of V$_{15}$ have been described in the equilateral DM exchange model ($J_{12}=J_{13}=J_{23}$, G=0) [11-14, 3]. Recent EPR investigations [15] of the V$_3$ ring of V$_{15}$ show the angle dependence of the resonance fields, which also has been explained in the equilateral DM exchange model [15]. The correlations between the INS and EPR spectra, spin structure and geometry of the V$_3$ clusters require the joint analysis of the INS and EPR spectra in the trimeric DM models. Since the DM exchange has been found in the Cu$_3$ and V$_3$ clusters, the problem of the influence of the DM exchange on the INS and EPR spectra is of interest for the nanomagnetism of these systems and their applications. The influence of the DM exchange on the INS transitions has
not been considered in the Heisenberg spin models for the INS transitions [16, 17]. The aim of the paper is the consideration of the INS and EPR transitions in the V\textsubscript{3} and Cu\textsubscript{3} clusters with the DM exchange for the explanation of the observed INS and EPR spectra.

2. INS in isosceles clusters with DM exchange

The Hamiltonian of the distorted V\textsubscript{3} and Cu\textsubscript{3} clusters (ij=12, 23, 31)

\[ H_1 = \sum (J_i S_i S_j + G_{ij} \langle S_i \times S_j \rangle) + \mu_B S_i g_i H + D_{ij} S_i^z - S(S + 1)/3 \]  

(1)

describes the isotropic Heisenberg exchange \( H_0 \), the DM exchange [4, 5], Zeeman interaction and ZFS of the S=3/2 state. For the equilateral clusters, the DM(z) exchange \( H_{\text{DM}}(z) = G_z \sum [S_i \times S_j]_z \) results in ZFS \( 2\Delta_{0\text{DM}} = G_z \sqrt{3} \) of the 2(S=1/2) ground state (GS), and determines anisotropy of magnetic and spectroscopic characteristics. In the isosceles \( (J_{12} \neq J_{13} = J_{23}) \) clusters with the DM(z) exchange, the ZFS \( 2\Delta = 2(\delta^2 + d_z^2)^{1/2} \) of the 2(S=1/2) states is determined by \( G_z \) and \( \delta \)-distortion: \( \delta = (J_{12} - J_{23})/2 \), \( d_z = G_z \sqrt{3}/2 \) [6]. The Z-components of the pair \( G_{ij} \) DM vector parameters are oriented perpendicular to the plain of the cluster \( G_z = (G_{12z} + G_{23z} + G_{31z})/3 \), \( Z || Z \). The in-plain \( G_x, G_y \) DM exchange [8] results in the mixing of the S=1/2 and S=3/2 states, which plays significant role in the V\textsubscript{3} and \{Cu\textsubscript{3}\} nanomagnets [9-11, 13, 14]. For magnetic fields \( H < 2T \), the INS and EPR transitions can be described in the DM(z) exchange model since the DM exchange mixing does not influence the INS and EPR transitions at low fields. Figure 1 shows the ZFS, the Zeeman splittings in magnetic field \( H_{||Z} \) (solid) and \( H_{\perp Z} \) (dash), calculated INS (I-V) and EPR (\( \tau_{13}, \tau_{14}, \tau_{34}, \tau_{24} \)) transitions for the isosceles V\textsubscript{3} cluster with the exchange parameters \( J_{12} = 226.0 \mu \text{eV}, J_{13} = J_{23} = 205.4 \mu \text{eV}, G_z = G_y = 10.6 \mu \text{eV}, G_x = 0 \). The ZFS \( 2\Delta = 27.4 \mu \text{eV} \) in figure 1 is equal to observed ZFS \( 2\Delta = 0.31 \text{K} \) [16].

Fig. 1 Zeeman splittings, ZFS, INS (I-V) and EPR (\( \tau_{13}, \tau_{14}, \tau_{34}, \tau_{24} \)) transitions for the isosceles V\textsubscript{3} cluster. The exchange parameters and spin structure factors \( S_I, S_{II} \) are presented in text.
The intensities of the INS transitions are described by the spin structure factors $S_{\phi}(Q)$ [16, 17] and the powder averaged structure factors, which depend on the intermediate and total spin quantum numbers of the initial and final states, $Q$ is the scattering vector. The scheme of the calculated low-temperature INS transitions $I_{z}$-$V_{x}$ in magnetic field $H=H_{zz}||z$ for the $V_{3}$ isosceles Heisenberg (G$_{z}$=0) nanomagnet is shown schematically in figure 1 by solid arrows ($H=H_{y}$). The analysis [16] of the experimentally observed INS transitions $I$-$V$ of the $V_{15}$ molecular magnet in the isosceles Heisenberg $V_{3}$ ring model results in the intensity ratios $(III:IV:V)$=3:2:1 for the doublet-quartet transitions III, IV and V (figure 1). The Q-dependence of the transitions II-V in the isosceles Heisenberg trimer is described [16] by the equations $I_{II}=1/3[1-sin(QR)/QR]$, $I_{IV}=1/2[1-sin(QR)/QR]$, $I_{V}=1/3[1-sin(QR)/QR]$, $I_{V}=1/6[1-sin(QR)/QR]$ with the sum $I_{II}+I_{IV}+I_{V}=1-sin(QR)/QR$. For description of the Q-dependent intensity of the intra-doublet INS transition I (figure 1) of a scalene Heisenberg trimer (transition $[\Omega_{a}(-1/2)\rightarrow\Omega_{a}(+1/2)]$ for GS $\Omega_{0}(\pm 1/2)=a\varphi_{0}(\pm 1/2)+b\varphi_{1}(\pm 1/2)$ [16]), the equation $I_{I}=I_{0}F^{2}(Q)[a^{2}+1/3b^{2}(1-sin(QR)/QR)]$ has been proposed [16], where $I_{0}$ is an intensity factor.

The analysis of the INS and EPR spectra of the $V_{3}$ clusters and comparison with the experimental data show that the scalene pure Heisenberg model alone cannot describe the peculiarities of the INS and EPR spectra of $V_{3}$ ring. The joint consideration of the INS and EPR spectra requires the taking DM exchange into account. In the DM($z$) exchange model, the spin structure factors for the INS transitions $I_{z}$-$V_{x}$ of the isosceles trimer in the field $H=H_{zz}||z$ (figure 1, solid arrows) have the form

$$S_{I} = 1/2 + (G_{z}^{2}/8\Delta^{2})[1-4cos(QR_{23})],$$

$$S_{II} = 1/3[1-cos(QR_{12})]- (G_{z}^{2}/8\Delta^{2})[1-4cos(QR_{23})],$$

$$S_{III} = 1/2[1-cos(QR_{12})], S_{IV} = 1/3[1-cos(QR_{12})], S_{V} = 1/6[1-cos(QR_{12})],$$

$R_{k}$ is inter-ion distance. In the transverse field $H_{zz}||z$, the spin structure factors for the transitions I$_{z}$ and II$_{y}$ at fields $H_{y}>>\Delta$ are reduced to their values in the pure Heisenberg model ($G_{z}$=0 in (2)), since high transverse field $H_{zz}$ suppresses the effect of the DM($z$) exchange. In figure 1, the transitions III-V are considered unperturbed. The INS peaks $I_{I}$ and $I_{II}$ in the transverse magnetic field $H_{y}$ are shown schematically in figure 1 by the dash vertical arrows. In the Heisenberg model ($G_{z}$=0), the INS peaks $I_{I}$ and $I_{II}$ are independent of the field $H_{zz}$. Calculated shifts $\Delta H$ of the positions of the INS peaks I and II due to the non-linear magnetic behaviour of the spin levels of the DM trimer in the transverse field (figure 1) have the value $\Delta H_{II}=-7\mu eV$ and $\Delta H_{I}=7\mu eV$. These shifts and corresponding broadening are significantly smaller than the widths of the peaks (17-19 $\mu eV$) and cannot be the origin of the significant broadening of these INS peaks. The powder averaged structure factors $S_{N,av}$ for the INS transitions in the isosceles $V_{3}$ DM trimer have the form:

$$S_{IV,av} = 1/3[1-sin(QR)/QR], S_{IV,av} = 1/3[1-sin(QR)/QR], S_{IV,av} = 1/6[1-sin(QR)/QR].$$

In the absence of the DM exchange ($G_{z}$=0), the averaged structure factor $S_{av}$ (3) of the INS transition I (figure 1) is reduced to the Q-independent term $S_{I,0}=1/2$, the structure factor $S_{II,av}$ for transition II (fig 1) is reduced to the factor $S_{II,0}=1/3[1-sin(QR)/QR]$ of the Heisenberg isosceles model. Eq (3) shows significant influence of the DM exchange on the spin structure factors of the intra-doublet I and doublet-doublet II transitions $S_{I}'=[S_{I}^{A}S_{I}^{B}sin(QR)/QR]$ and $S_{II}'=[S_{II}^{A}S_{II}^{B}sin(QR)/QR]$, respectively, where $S_{I}^{A}=S_{I,0}^{A}+\Delta S_{I}^{A}=1/2+G_{z}^{2}/24\Delta^{2}$, $S_{II}^{A}=S_{II,0}^{A}+\Delta S_{II}^{A}=1/3-G_{z}^{2}/24\Delta^{2}$; $S_{II}^{A}=S_{II,0}^{A}+\Delta S_{II}^{A}=1/3-G_{z}^{2}/24\Delta^{2}$. $S_{II,av}=S_{II,av}^{A}-\Delta S_{II}^{B}=1/3-G_{z}^{2}/24\Delta^{2}$. Thus, the $S_{II}^{B}=G_{z}^{2}/6\Delta^{2}$ term of the DM exchange origin (3) results in the Q-dependence of the transition II. The redistribution of the intensities of the INS transitions I and II, which is governed by the DM exchange and distortions (the $[G_{z}/\Delta]^{2}$ term in (3)), takes place with the...
In the pure Heisenberg isosceles and scalene models, 1) only intra-doublet 1→3. EPR in isosceles clusters with DM exchange conservation rules: S^A_{1,0}+S^A_{II,0} for the Q-independent terms and S^B_{1,0}+S^B_{II,0} for the Q-dependent terms, where S^A_{N,0} and S^B_{N,0} are the averaged spin structure factors in the Heisenberg model.

Calculated values of the Q-independent S^A_{N} and S^B_{N} terms and coefficients S^B_{1,0} and S^B_{II,0} of the Q-dependent terms of the averaged structure factors S_i and S_{II} of the INS transitions I and II of the V_3 ring in figure 1 for the considered set of the exchange parameters are the following: S^A_{I}=0.529, S^A_{II}=0.304; S^B_{I}=0.115, S^B_{II}=0.218.

The Q-dependence of the transitions I and II (3) allows to determine the DM exchange and distortions from the experimental data. Thus, the experimentally observed Q-dependence of the transition I in the V_3 ring of V_{13} has been described [16] by the Q-independent term (a^2+b^2/3=0.6) and Q-dependent term [-0.2sin(QR)/QR] in I. For case, where the Q-dependence of the INS transition I is determined by the DM exchange (3), the comparison with the coefficient [(G_i/Δ)^2/6] in the Q-dependent term in S_i leads to the estimate G_i/2Δ≈0.55, G_i=0.17K, δ=0.17K (2Δ≈0.31K). In this case, the Q-independent term in the structure factor S_i’ (3) of transition I is S^A_{i,0}≈0.55. This value is close to the Q-independent term 0.6 for I in [16]. That allows explaining qualitatively the observation [16] that the overall intensity of peak I is significantly smaller than the sum of (III+I+V).

For the \{Cu_{1}\} nanomagnet [10] with J_{12}=4.52K, J_{13}=J_{23}=4.04K, G_e=G_x=G_y=0.53K, the theory predicts significant redistribution of the intensities of the INS transitions I and II induced by the strong DM exchange coupling: S_{Ix}=0.501 (S_{II,0}=0), and S_{II,0}=−0.168 (S_{II,0}=+0.333).

3. EPR in isosceles clusters with DM exchange

In the pure Heisenberg isosceles and scalene models, 1) only intra-doublet 1→2, τ_{12} (1→3, τ_{13}) and 3→4, τ_{34} (2→4, τ_{24}) EPR transitions in fig 1 are allowed for \hbar<2Δ (\hbar>2Δ) in magnetic field H_{||Z} and H_{⊥Z}, W_{12/13}=W_{34/24}=0.25, W_{14}=W_{23}=0; and 2) the resonance frequencies \nu are characterized by the linear dependence on magnetic field for H_{||Z} and H_{⊥Z}.

For the isosceles trimer with the DM exchange, the relative intensities of the allowed EPR transitions (τ_{13}, τ_{24}, τ_{32}, τ_{14} in figure 1, \hbar>2Δ) for H=H_y are determined by the equation W_{13}=W_{24}=\hbar^2/4Δ^2 = d_{13}^2/4Δ^2, W_{14}=W_{23}=\hbar^2/4Δ^2 = d_{14}^2/4Δ^2. In high transverse magnetic field, g\mu_B H_y \gg Δ, the effect of the DM exchange is suppressed: W_{13}=W_{24}=0.25, W_{14}=W_{23}=0. Figure 2 shows

![Graph](image_url)

Fig. 2 Frequency (υ/γ_{g}) field (H) diagram for EPR transitions τ_{12}, τ_{13}, τ_{24}, τ_{23}, τ_{14} for isosceles cluster with DM exchange, H_{||Z} and H_{⊥Z}.
the calculated frequency-field dependences \((\nu/\gamma) - H\) of the resonance fields of the EPR transitions \(\tau_{12}, \tau_{13}, \tau_{23}, \tau_{14}\) (figure 1) for the \(2(S=1/2)\) states of the isosceles \(V_3\) trimer with the DM exchange, \(\gamma = g\mu_B/h\). The straight A, [B] and (C) curves in figure 2 show the calculated resonance conditions for the allowed EPR transitions \(\tau_{13z}, \tau_{24z}\) for \(H>2\Delta\) \((\tau_{12z}, \tau_{34z}\) for \(H<2\Delta)\), \(\tau_{23}\) and \(\tau_{14}\), respectively, in magnetic field \(H_{||Z}\), figure 1. The \(A\) (\(B\)) (\(C\)) curve in figure 2 shows the resonance conditions for the non-linear frequency-field dependences \(\nu(H)\) \(A\), \(B\) (figure 2) of the resonance fields for \(H=H_z\). The low-frequency EPR spectra [15] of the \(V_{15}\) quantum molecular magnet have been explained [15] in the model of the equilateral \(V_3\) ring with the DM exchange. The non-linear frequency-field dependences \(\nu(H)\) \(A\)' (\(B\)' (figure 2) of the resonance fields \(H=H_z\)) have been observed (figure 2b [15]), as well as the magnetic behavior of the resonance frequencies for \(H_{||Z}\) and non-linear magnetic behavior for \(H_{\perp Z}\) (figure 2a [15]). The observation [15] of the inter-doublet EPR transitions \(\tau_{14z}, \tau_{23z}\) and the intra-doublet \(\tau_{13z}, \tau_{24z}\) transitions (figure 1, \(H=H_z\)) have been observed (figure 2b [15]), as well as the linear magnetic behavior of the resonance frequencies for \(H_{||Z}\) and non-linear magnetic behavior for \(H_{\perp Z}\) (figure 2a [15]). The observation [15] of the inter-doublet EPR transitions \(\tau_{14z}\) and \(\tau_{23z}\) (figure 1) and linear (non-linear) \(\nu(H)\) magnetic behavior of the resonance frequencies \(\nu_{13z}, \nu_{24z}\) for \(H_{||Z}\) \((\nu_{13y}, \nu_{24y}\) for \(H_{\perp Z}\)) cannot be described in the pure Heisenberg scalene or isosceles models and is the evidence of the presence of the DM exchange in the \(V_3\) ring (see curves A, B, C, A' in figure 2), \(W_{14z}=W_{23z}=(\delta^2/4\Delta^2/\gamma^2)\). The intradoublet \(\tau_{13z}, \tau_{24z}\) and \(\tau_{24z}\) transitions are allowed for the isosceles \(V_3\) ring (figure 1, \(W_{13z}=W_{24z}=(\delta^2/4\Delta^2, \delta\neq0)\) and forbidden for the equilateral DM model with \(\delta=0\) \((W_{13z}=W_{24z}=0, W_{14z}=W_{23z}=0.25)\). The observation of the \(\tau_{13z}, \tau_{24z}\), as well as the \(\tau_{14z}, \tau_{23z}\) EPR transitions on the \(V_3\) ring of \(V_{15}\) [15] shows that this \(V_3\) ring has the symmetry of the isosceles triangle (not equilateral) with the DM exchange. The correlations between the intensities of the observed EPR transitions, \(W_{14z}=W_{23z}<W_{13z}=W_{24z}[15]\) correspond to the relation \(\delta<\Delta\). The analysis of the calculated INS and EPR transitions [18] for the equilateral \(V_3\) cluster and comparison with the observed INS [16] and EPR [15] spectra shows that the equilateral DM model, as well as the pure Heisenberg scalene model, cannot describe the INS and EPR spectra of the \(V_3\) ring of \(V_{15}\). The EPR spectra of the \(V_3\) and \(\{Cu_3\}\) nanomagnets also are described in the isosceles DM model.

4. Conclusion

The DM exchange results in the Q-dependence of the structure factor \(S_T\) of the INS intra-doublet transition and the redistribution of the both Q-independent and Q-dependent parts of the spin structure factors of the intensities of the intra-doublet I and doublet-doublet II INS transitions with the conservation of the summary intensities of these two transitions. The changes and redistribution of the intensities of the INS transitions I and II, on the one hand, and the intensities of the intra-doublet and inter-doublet EPR transitions, on the other hand, have the same origin: the DM exchange and distortions. The joint consideration of the INS and EPR transitions in the Heisenberg plus DM exchange models shows that the Q-dependence and peak positions of the INS transitions, and EPR transitions in the \(V_3\) ring of \(V_{15}\) quantum molecular magnet, as well as the EPR transitions in the \(V_3\) and \(\{Cu_3\}\) nanomagnets can be explained in the isosceles triangle model with the DM exchange.

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