ESR Intensity and Anisotropy of the Nanoscale Molecular Magnet V_{15}

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Abstract. The low temperature ESR intensity of the nanoscale molecular magnet V_{15} is studied theoretically. First we numerically obtain the temperature dependence of the intensity. Then we analytically explore the effect of the Dzyaloshinsky-Moriya interaction on the intensity at zero temperature using the triangle model.

Keywords: ESR, molecular magnets, ultra-cold temperature
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INTRODUCTION

The nanoscale molecular magnet V_{15} is the complex of formula $K_6\left[V^{IV}_{15}As_6O_{42}(H_2O)\right]\cdot 8H_2O$. In the molecule, fifteen vanadium ions of spin $1/2$ are placed almost forming a sphere: three ions in the middle are sandwiched by two hexagons formed by the upper and lower twelve ions [1].

In this paper, we theoretically study the ESR of V_{15} at low temperatures. Using the triangle model, we study the effect of the Dzyaloshinsky-Moriya (DM) interaction [2, 3, 4] on the intensity ratio (intensity divided by that of a single isolated spin 1/2) at zero temperature. In particular, we reveal how the intensity ratio deviates from 1 due to the DM interaction when the ground state magnetization is $1/2$. The results of this analysis explain the behavior of the numerically obtained ESR intensity of V_{15} quite well.

In experiments, the magnetization changes smoothly at zero field from $-1/2$ to $1/2$, and around 2.8T from $1/2$ to $3/2$, when the field is swept adiabatically at low temperatures. These facts imply that gaps open between the ground state and the lowest excited state at 0T and 2.8T, and the origin of the gaps may be attributed to the DM interaction [5, 6, 7, 8, 9]. However, the details of the DM interaction in V_{15} are not yet fully understood.

ESR INTENSITY RATIO OF V_{15}

The V_{15} molecule is modeled by the following spin Hamiltonian [10, 11].

$$\mathscr{H} = -\sum_{\langle i,j\rangle} J_{ij}\boldsymbol{S}_i\cdot\boldsymbol{S}_j + \sum_{\langle i,j\rangle}\boldsymbol{D}_{ij}\cdot[\boldsymbol{S}_i\times\boldsymbol{S}_j] - \sum_i \boldsymbol{H}_\mathrm{S}\cdot\boldsymbol{S}_i. \quad (1)$$

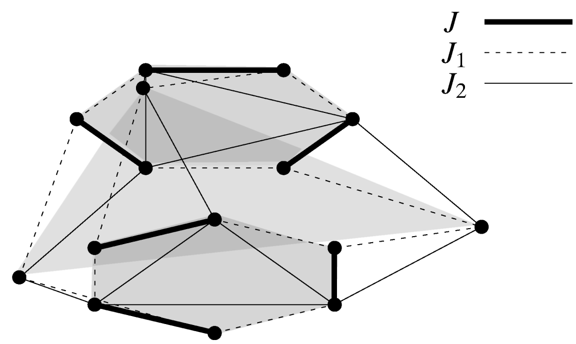

FIGURE 1. Schematic picture of V_{15} showing the magnetic interactions J, J_1, and J_2.

For J_{ij}, we have three different values J, J_1, and J_2 ($|J| > |J_2| > |J_1|$), as shown in Fig. 1. Here we take $J = -800$K, $J_2 = -350$K, and $J_1 = -225$K [12]. The second term on the right-hand side in (1) describes the DM interaction. DM vectors are considered to exist on the two hexagons along the bonds with J. We take the reference DM vector $\boldsymbol{D}_{1,2}$ to be $D^x_{1,2} = D^y_{1,2} = D^z_{1,2} =$ 40K. The other DM vectors are determined from the D_3 symmetry of V_{15} [13]. We assume the static magnetic field is applied parallel to the c-axis of the molecule (z-axis) and put $\boldsymbol{H}_\mathrm{S} = (0,0,H_\mathrm{S})$.

At low temperatures, the ESR absorption occurs only from transitions among low-lying energy levels because only these states are populated. Hence, we calculate the ESR absorption of V_{15} by taking a small subspace of the total Hilbert space which concerns the lowest eight levels [13]. Within this subspace, the ESR absorption is obtained by the explicit formulation [14] of the Kubo

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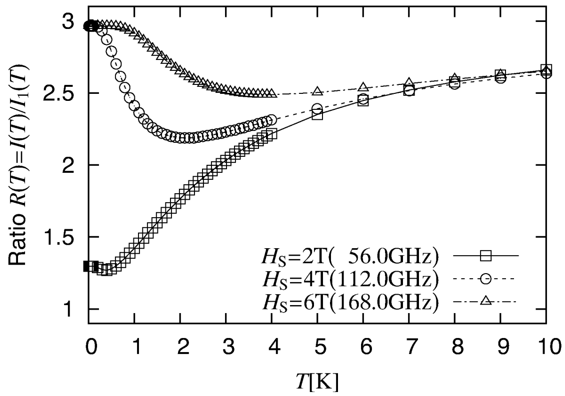

FIGURE 2. Temperature dependence of the intensity ratio $R(T)$.

formula. That is, we obtain the imaginary part of the susceptibility $\chi''(\omega;T)$ by direct diagonalization of the small Hamiltonian. The intensity $I(T)$ and the average energy absorption per unit time $I(\omega;T)$ are given by

$$I(T) = \int_0^\infty I(\omega;T)\,\mathrm{d}\omega, \quad I(\omega;T) = \frac{\omega H_R^2}{2}\chi''(\omega;T), \tag{2}$$

where T is temperature, and ω and H_R are the frequency and amplitude of the radiation field $\boldsymbol{H}_R$, respectively. We note that $\boldsymbol{H}_R$ is perpendicular to the static field $\boldsymbol{H}_S$. We define the intensity ratio as

$$R(T) = I(T)/I_1(T), \tag{3}$$

where $I_1(T)$ is the intensity of an isolated spin 1/2: $I_1(T) = \frac{\pi H_R^2 H_S}{8}\tanh\left(\frac{\beta H_S}{2}\right)$. In Fig. 2, we plot $R(T)$ for $H_S = 2\mathrm{T}(56.0\mathrm{GHz})$, $H_S = 4\mathrm{T}(112.0\mathrm{GHz})$, and $H_S = 6\mathrm{T}(168.0\mathrm{GHz})$. The behavior of $R(T)$ is consistent with experiment [15, 16]. We note that, for $H_S = 2\mathrm{T}$, $R(T=0)$ deviates from 1.

TRIANGLE MODEL ANALYSIS FOR WEAK DM INTERACTION

The triangle model is given by considering only three spins in (1) with $J_{12} = J_{23} = J_{31} \equiv J < 0$. Assuming C_3 symmetry, we determine the DM vectors as $D_{12}^x = D_x$, $D_{12}^y = D_y$, $D_{23}^x = (-D_x + \sqrt{3}D_y)/2$, $D_{23}^y = (-\sqrt{3}D_x - D_y)/2$, $D_{31}^x = (-D_x - \sqrt{3}D_y)/2$, $D_{31}^y = (\sqrt{3}D_x - D_y)/2$, and $D_{12}^z = D_{23}^z = D_{31}^z = D_z$. Let us further assume $D_x = D_y = D_z \equiv D > 0$. If we put $J = -2.5\mathrm{K}$ and $D = 0.25\mathrm{K}$, the energy levels of the triangle model reproduce the lowest eight levels of V_{15} quite well [11].

We analytically obtain the ESR intensity ratio $R_{\mathrm{tri}}(T)$ of this triangle model. In the calculation, we assume $D \ll 2|H_S - H_S^c|$, $H_S^c \equiv -\frac{3}{2}J$, and ignore terms smaller than $O(D)$. Note that the ground state magnetization changes from 1/2 to 3/2 as the field H_S increases across $H_S = H_S^c$. In the ultra-cold limit, $R_{\mathrm{tri}}(T)$ near H_S^c is obtained as [17]

$$R_{\mathrm{tri}}(T) \simeq \begin{cases} 1 + \frac{\sqrt{3}D}{H_S} & (H_S < H_S^c) \\ 3 & (H_S^c < H_S). \end{cases} \tag{4}$$

This behavior of $R_{\mathrm{tri}}(T)$ gives a qualitative understanding of $R(T)$ in Fig. 2 at zero temperature.

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