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Abstract. The spin dynamics of a cluster of four iron (III) ions characterized by a spin ground state of 5 and Ising anisotropy has been investigated by means of Mössbauer spectroscopy from 10 to 80 K. For $T \leqslant 35$ K, spectra display a partially relaxed magnetic structure, while for higher temperatures, spectra are wholly relaxed. The trend of the probabilities of transition per unit time derived from the spectrum fittings is typical of an Orbach process or of a coupling with vibration modes in a narrow frequency range. According to an order-of-magnitude estimate, the relaxation mechanism should consist of modulations of the exchange interaction due to atom vibrations.

1. Introduction

Studies of transition-metal molecular clusters have revealed many interesting features. In particular, they can display bistability of molecular origin [1–6]. Furthermore, the characteristics of their spin dynamics are intermediate between those of bulk magnetic materials and those of single magnetic molecules; therefore, new theoretical approaches are necessary in order to study the magnetic properties of these clusters.

In this paper, we will present a Mössbauer investigation of a tetranuclear iron (III) cluster having the formula $Fe_4(OCH_3)_6(dpm)_6$ (where Hdpm = dipivaloylmethane). Our study will be mainly directed towards the characterization of the spin dynamics in the cluster ground state.

The synthesis, x-ray structure determination (figure 1), magnetic measurements and EPR spectra are reported in reference [7]. The main findings of that work are summarized here as follows.

The Fe atoms lie exactly on a plane. Three bis-bridges (μ-OCH$_3$) connect the central Fe(1) atom with the peripherals Fe(2), Fe(3) and Fe(3′); see figure 1. The symmetry group of the molecule is $\mathcal{C}_2$, with the C$_2$ axis passing through Fe(1) and Fe(2). The peripheral iron atoms form a quasi-equilateral triangle with the Fe(1) at the centre. To be more precise, the Fe(1)–Fe(2) distance (3.146 Å) is only 0.4% larger than the Fe(1)–Fe(3) and Fe(1)–Fe(3′) distances (3.133 Å). However, the symmetry of the oxygen ions around the Fe(2) ion is very different from that around the Fe(3) and Fe(3′) ions.
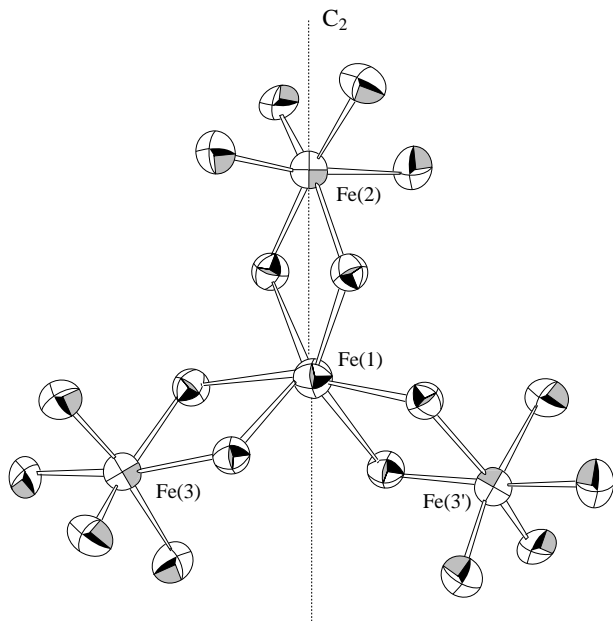
Figure 1. The structure of the tetranuclear iron (III) cluster $Fe_4(OCH_3)_6(dpm)_6$. The C and H atoms are omitted.

The temperature dependence of the susceptibility χ was interpreted in terms of an antiferromagnetic interaction between central and peripheral iron ions and a small ferromagnetic interaction between peripheral ions. By using the Hamiltonian (1), the exchange constants $J = 21.1$ cm$^{-1} = 30.4$ K, $J' = -1.1$ cm$^{-1} = -1.6$ K were obtained.

The cluster ground state has $S = 5$ with $g = 2$. The first excited level is a doubly degenerate $S = 4$ state, and its energy with respect to the ground state is about 60 cm$^{-1} = 86.4$ K.

Information on the cluster ground state was provided by EPR measurements, whose results agreed with a uniaxial anisotropy of $D = -0.20$ cm$^{-1} = -0.29$ K ($E = 0$). The corresponding energy barrier, which is associated with the energy difference between the lowest $M = \pm 5$ states and the highest $M = 0$ state, is given by $\Delta = |D|5^2 = 7.25$ K.

Calculations based on a ligand-field approach showed that the anisotropy for the $S = 5$ ground state has both single-ion and dipolar contributions, with the unique axis quasi-perpendicular to the iron plane.

Alternative susceptibility measurements were also performed in order to study the magnetization dynamics. The relaxation time data were fitted according to an Arrhenius law: $\tau = \tau_0 \exp[-\Delta/T]$, and the values $\tau_0 = 1.1 \times 10^{-6}$ s and $\Delta = 3.5$ K were found. The disagreement between the value of Δ given by the relaxation measurements and the value obtained from EPR could be explained by the fact that both the thermal jump and the quantum tunnelling could contribute to the magnetization inversion. However, the uncertainty in determining the barrier using relaxation measurements leaves the question open.

In section 2, the experimental procedure is described. In section 3, the quantities characterizing the spin dynamics are introduced. In section 4, we discuss the influence of the spin dynamics on the Mössbauer spectra, and the forms of the latter are evaluated. Finally, in section 5, the results obtained are analysed.

2. Experimental procedure and results

A powdered sample was prepared, the effective thickness of which was about 5 mg cm^{-2}. A Gifford–MacMahon cryogenerator was used to cool the sample. The temperature was stabilized within one kelvin by an ITC4 Oxford controller. Spectra were collected in the 12–200 K range. The ^{57}Co source in a Rh matrix with an activity of 25 mCi was kept at room temperature. Spectra collected at temperatures lower than 40 K displayed a partial collapsing of the magnetic hyperfine structure: i.e. an intermediate relaxation rate characterizes this temperature range. Spectra collected at higher temperatures showed no magnetic hyperfine structure, but instead showed collapsed structures which are characteristic of fast relaxation rates.

3. Ground-state spin dynamics

By denoting as s_i the spin operator of the single iron ions i (with $s = 5/2$ and $i = 1, 2, 3, 3'$) and as S the cluster spin operator, the magnetic Hamiltonian of the latter can be written as [7]

$$H = J s_1 \cdot (s_2 + s_3 + s_{3'}) + J'(s_2 \cdot s_3 + s_2 \cdot s_{3'} + s_3 \cdot s_{3'}) + D\left[S_z^2 - \frac{1}{3}S(S+1)\right]$$

$$= J s_1 \cdot S_p + \frac{J'}{2}\left[S_p(S_p+1) - \frac{105}{4}\right] + D\left[S_z^2 - \frac{1}{3}S(S+1)\right] \tag{1}$$

where we have denoted as S_p the total spin of the peripheral ions, namely: $S_p = s_2 + s_3 + s_{3'}$.

Since $J > 0$ and $J' \approx -\frac{1}{10}J$, the ground state of the cluster is obtained to a good approximation by coupling the peripheral spins parallel to each other to give a total spin $S_p = 15/2$ and then by coupling the central spin s_1 with S_p to give the cluster spin $S = 5$.

We note that the Mössbauer probes are the single iron nuclei. According to the symmetry, the cluster spectra will then consist of the superposition of three single-ion spectra. However, the magnetic Hamiltonian is symmetrical with respect to the peripheral-ion indices. Consequently, the hyperfine fields and their dynamics can be assumed to be equal for all of these ions. Similarly, since the stiffnesses of the ion-2 bonds with the ions of their surroundings are similar to those of the ions 3 and 3', we can assume the f-factors of the peripheral ions to be equal to each other. On the other hand, as the structural symmetries are different, the quadrupole splitting relative to site 2 cannot be equal to that relative to sites 3 and 3'.

In a fixed cluster state $|S, M\rangle$, the single-iron-ion spin z-components are not constant in time; only their mean value is definite. The fluctuation rate of these single-ion z-components depends on J, the value of which, in the frequency unit, is of the order of 10^{12} s^{-1}. That is, if the state $|S, M\rangle$ is fixed, one would expect the spin-correlation functions $\langle s_i^z(0)s_i^z(t)\rangle$ to oscillate with a much higher frequency than the nuclear Larmor frequency (about 10^8 s^{-1} for ^{57}Fe^{3+} ions). Consequently, the Mössbauer nucleus should experience the static hyperfine field created by the mean z-component of the electronic spin. Standard techniques [8] provide the projection $\langle m_i\rangle$ of the individual spin s_i on the total spin S as

$$M = c_1\langle m_1\rangle + c_2\langle m_2\rangle + c_3\langle m_3\rangle + c_{3'}\langle m_{3'}\rangle \tag{2}$$

where $c_1 = -0.4167$ and $c_2 = c_3 = c_{3'} = 0.472$. As $\langle m_2\rangle = \langle m_3\rangle = \langle m_{3'}\rangle = \frac{1}{3}(M - \langle m_1\rangle)$, we have

$$\frac{\langle m_1\rangle}{M} = -0.4167 \qquad \text{and} \qquad \frac{1}{3}\frac{(M - \langle m_1\rangle)}{M} = 0.472. \tag{3}$$

The spectra obtained in the range between 12 and 80 K display a strong dependence on the temperature. This means that the relaxation mechanisms involve energy exchanges

between the cluster spins and thermal vibrations. Spectra then have to be evaluated by considering the transition between the $|S, M\rangle$ states induced by the cluster-atom vibrations. Phenomenologically, the interaction Hamiltonian between these interactions and the cluster spin will be assumed to have the form [9]

$$H_I = F G(S_x, S_y, S_z) \tag{4}$$

where F and G are operators, which are functions of the atom vibrations and cluster spin components respectively. The tensor operator G is chosen dimensionless and F has the dimension of energy.

For the sake of simplicity, here we consider only transitions $M \rightarrow M'$ for which $\Delta M = \pm 1$. The probabilities per unit time of transition between the states $|S, M\rangle$ and $|S, M \pm 1\rangle$ are given by [9]

$$W_{M,M-1} = |\langle M|G|M-1\rangle|^2 J(\omega_{\Delta M}) \tag{5}$$

and

$$W_{M-1,M} = W_{M,M-1} \exp(\omega_{\Delta M}/T) \tag{6}$$

where $\omega_{\Delta M}$ is the difference in energy of the states $|S, M-1\rangle$ and $|S, M\rangle$, and $J(\omega)$ is the Fourier transform of the correlation function of F:

$$J(\omega) = \int_{-\infty}^{\infty} \exp(i\omega t)\langle F(0)F(t)\rangle \, dt. \tag{7}$$

Since the energy levels of the cluster ground state $S = 5$ are not equidistant, the transition probabilities depend on the five different parameters $J(\omega_{\Delta M})$, with $\omega_{\Delta M} = 9|D|, 7|D|, 5|D|, 3|D|, |D|$. However, on assuming for the correlation function of F an exponential dependence:

$$\langle F(0)F(t)\rangle = F^2 \exp(|t|/\tau) \tag{8}$$

the two parameters τ and F are sufficient for determining the five $J(\omega)$:

$$J(\omega) = F^2 \tau^{-1}/(\tau^{-2} + \omega^2).$$

In the following, τ and $W_{5,4} = W$ will be assumed as independent parameters instead of τ and F, so for the Hamiltonian (3) we have

$$W_{M,M-1} = \frac{|\langle M|G|M-1\rangle|^2}{|\langle 5|G|4\rangle|^2} \frac{\tau^{-2} + \omega_{5,4}^2}{\tau^{-2} + \omega_{M,M-1}^2} W. \tag{9}$$

On the other hand, τ is correlated with the vibration frequencies of the cluster atoms (in particular, of the oxygen ions) which are of the order of 10^{13} s^{-1}. Then, since $D = 0.29$ K $= 6 \times 10^9$ s^{-1}, we have $\tau^{-1} \gg \omega_{M,M-1}$. Thus, the ratios between the transition probabilities per unit time are practically independent of τ.

4. Low-temperature Mössbauer spectra

Since we want to study the spin dynamics in the cluster ground state, spectra in the $T < 90$ K range have to be considered.

When the cluster spin undergoes transitions between its states, the spin mean z-components of all of the single iron ions change simultaneously between their corresponding values. Consequently, the iron nuclei are subjected to stochastic changes in the hyperfine-field magnitude. According to this picture, the four iron nuclei experience fields that change at the same rate, but which have different magnitudes for central and peripheral ions because of the different values of the spin mean z-components (equation (4)).

Since the environment symmetry of the iron ions is lower than octahedral, the electric quadrupole interaction has to be considered. The electric field gradient (EFG) at the four iron sites was estimated by using point-charge approximation. One of the EFG principal axes was found to be almost perpendicular to the iron plane, i.e. practically parallel to the magnetic anisotropy axis, for all of the sites. It was then convenient to take this principal axis as the z-axis, regardless of whether or not V_{zz} was the maximum component of the EFG. With this assumption, $\eta > 1$ values are possible. In our case, $\eta \approx 0$ resulted for the central ion, $\eta \approx 18$ for the peripheral Fe(2) ion and $\eta \approx 4$ for the other two peripheral ions. As for quadrupole splitting, the values of ≈ 0.5 mm s^{-1} and ≈ -0.5 mm s^{-1} were obtained for the central and peripheral iron ions, respectively.

The nuclear Hamiltonian of an iron ion can then be written as the sum of the time-independent and stochastically changing terms, V_1 and V_2, respectively:

$$V_1 = H_0 + Q\left\{[3I_z^2 - I(I+1)] + \frac{\eta}{2}(I_+^2 + I_-^2)\right\}$$

$$V_2 = g_I \mu_N I_z B_h(t)$$

(10)

where $B_h(t)$ is the hyperfine field which depends on time because of the transitions between cluster spin states of the ground manifold.

The other symbols in equation (9) have the usual meaning [10].

In order to evaluate the spectral forms, Blume's stochastic theory [11, 12] will be used. According to this theory, we consider the operator

$$\mathbf{L} = \left(\frac{\Gamma}{2}I^x - iV_1^x\right)\mathbf{I} - ig_I\mu_N I_z^x \mathbf{F} - \mathbf{W}I^x$$

(11)

where the bold letters denote matrices of the order 11×11. The rows of these matrices are labelled by the M components of the cluster spin. Since M changes stochastically in time because of the transitions between the cluster spin states, the above-mentioned matrices are referred to as stochastic matrices. In particular, $\mathbf{I}$ is the unit matrix and $\mathbf{F}$ is a diagonal matrix, the elements of which are

$$\frac{\langle m_i \rangle_M}{5/2} B_{max}$$

where B_{max} is the hyperfine field corresponding to the maximum z-component ($S_z = 5/2$) of the Fe^{3+} ion. Lastly, $\mathbf{W}$ denotes the matrix whose non-diagonal elements are the probabilities per unit time of transitions between the M states of the cluster. They are given by equations (4) and (5). Moreover, the diagonal elements are given by the negative of the sum of the non-diagonal elements of the same row:

$$W_{ii} = -\sum_j W_{ij}.$$

In the expression for $\mathbf{L}$, the quantities with apex 'x' are the so-called Liouville operators: they act not on the quantum-state space of the nucleus, but on the space whose basis vectors are the initial and final states of the Mössbauer transitions. If the states of the ground and excited nuclear levels are denoted by $|I_0, m_0\rangle$ and $|I_1, m_1\rangle$, the Liouville space is defined by $|I_0, m_0; I_1, m_1\rangle \equiv |m_0, m_1\rangle$. In the case of ^{57}Fe, the Liouville space has a dimension of 8. To an ordinary operator O, acting on the nuclear states, corresponds a Liouville operator O^x, the matrix elements of which are obtained from those of O via the relation (see for example [12])

$$\langle m_0, m_1 | O^x | m_0', m_1' \rangle = \delta_{m_1, m_1'} \langle m_0 | O | m_0' \rangle - \delta_{m_0, m_0'} \langle m_1 | O | m_1' \rangle.$$

(12)

By considering the matrix $\mathbf{L}$ connecting the eight Liouville states, a complex non-Hermitian matrix $\mathcal{L}$ of order $11 \times 8 = 88$ is obtained. Let us denote as U_α the eigenvector

of $\mathcal{L}$ corresponding to the eigenvalue a_α and as V_α the eigenvector of $\mathcal{L}^\dagger$ corresponding to the eigenvalue a_α^*. If $\mathcal{A}$ denotes the vector whose 88 components are

$$[\mathcal{A}(m_0, m_1)]_M = \langle m_0|A|m_1\rangle \tag{13}$$

where A is the multipolar operator of the Mössbauer transitions, the normalized Mössbauer spectrum line-shape can be written in the form [13]

$$I(\omega) = \frac{2}{(2I_0 + 1)\Gamma}\Re\sum_\alpha \frac{(\rho_M \mathcal{A}^\dagger U_\alpha)(V_\alpha^\dagger \mathcal{A})}{i\omega - a_\alpha} \tag{14}$$

where ω denotes the γ-ray Doppler energy and ρ_M the occupation probabilities of the M states.

The normalized line-shape for the whole cluster can be written in the form

$$I(\omega) = \frac{1}{1 + 3\phi}[I^{(c)}(\omega) + \phi I^{(p2)}(\omega) + 2\phi I^{(p3)}(\omega)] \tag{15}$$

where c and p refer to central and peripheral ions, respectively, and the ϕ-parameter takes into account the fact that the absorption areas may be different for the central and peripheral sites. To be more precise, for thin absorbers $\phi = f^{(p)}/f^{(c)}$, where $f^{(p)}$ and $f^{(c)}$ are the Debye–Waller factors of the peripheral and central ions, respectively.

As we have seen, in order to determine the line-shape of a spectrum, two 88×88 complex matrices have to be diagonalized. However, with appropriate exchanges of lines and columns, the $\mathcal{L}$-matrix is transformed into four 22×22 diagonal blocks, so the diagonalization time decreases by about a factor of 4.

5. Results and discussion

The spectra depend on a large number of parameters: the isomer shift, the quadrupolar splitting and the asymmetry parameter are characteristic of each site. Instead, quantities such as the probability per unit time of transitions between the cluster spin states, the correlation time of F (or F'), the ϕ-factor and the characteristic spectrum parameters, such as the baseline and the absorption area, concern the whole cluster. Overall, we have 20 parameters. To fit the spectra, the natural linewidth Γ and the hyperfine field $B_{5/2}$ were kept at the fixed values of 0.21 mm s^{-1} and 54 T [14], respectively. Moreover, the six parameters relating to the quadrupole interaction were first fixed at the values calculated within the framework of the point-charge approximation. Then, they were left free and their values fitted.

The quadrupole splitting was found to be strongly correlated with the isomer shifts, but weakly correlated with W. The explanation for this is that the transition probabilities per unit time are essentially correlated with the wings of the spectra, while the quadrupole parameters, together with the isomer shifts, mainly determine the central part of the line-shape. However, the η-values are also critical to obtaining a good fit for the central part of spectra, but they were fixed at the calculated values. Consequently, the isomer shift and the quadrupole parameters, which were obtained as described above, have to be considered as rough estimates. In contrast, the evaluation of the transition probability is fairly reliable.

In order to choose an expression for the operator G, the nature of the spin–vibration interaction has to be considered. Two relaxation mechanisms are possible in our case. One of these consists of a modulation of the magnetic dipolar intracluster interactions and/or the exchange coupling due to atom vibrations [15]. The effect of these modulations can be phenomenologically described in terms of the action of a fluctuating magnetic field $H(t)$ on the cluster spin. Since $H_z(t)$ does not induce transitions, the interaction Hamiltonian can be written in the form

$$H_I = g\mu_B H_x(t)S_x \tag{16}$$

giving $F = g\mu_B H_x(t)$ and $G = S_x$.

The other mechanism consists of a modulation of the crystal field at the iron-ion sites, due to vibrations of the nearest-neighbouring oxygen ions. This produces a fluctuating electric field which does not interact with the spin, but acts on the orbital motions and through the spin–orbit coupling on the spin. Consequently, we expect this mechanism to make a small contribution when the magnetic ion has $L = 0$ (S states), as in our case (Fe^{3+} has the ground state $^6S_{5/2}$). However, the corresponding G-operator must have a homogeneous form of even order [16] in the spin components; so, to lowest order, we can assume that

$$H_I = F(S_x S_z + S_z S_x)/2. \tag{17}$$

Here, F is obviously correlated with the fluctuating electric field at the iron-ion sites.

As mentioned above, the ratios between the transition probabilities per unit time are independent of τ, so the only parameter relating to the spin dynamics which was obtained from the fitting is $W_{5,4} = W$.

The spectra were fitted by using both of the dynamic Hamiltonians (16) and (17). However, the second of these was unable to reproduce spectra that did not have a completely collapsed magnetic structure, i.e. the spectra in the $T \leqslant 35$ K range. In contrast, with the former Hamiltonian we obtained very good fits throughout the temperature range. We obtained χ^2-values
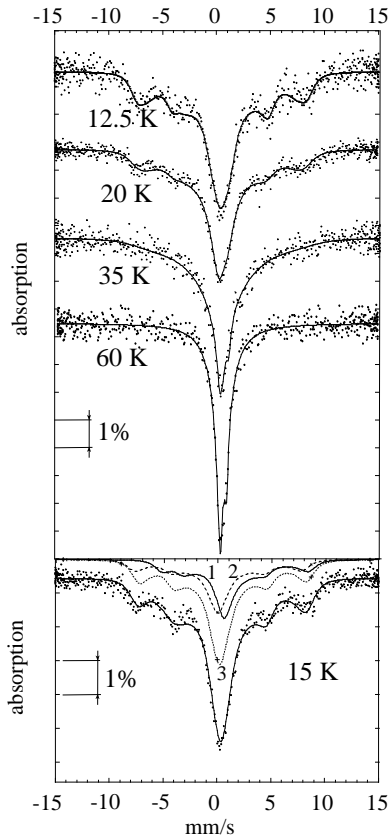

Figure 2. (a) The evolution of the Mössbauer spectrum versus temperature. The magnetic structure of the spectra disappears above 35 K. (b) The spectrum at 15 K: the contributions from the three different cluster sites 1, 2 and 3 are also indicated.

between 984 and 1184 for the 1024-channel spectra. The fact that the second Hamiltonian can fit the spectra corresponding to $T > 35$ K does not necessarily mean that the corresponding mechanism is effective for these temperatures. In fact, in the case of wholly collapsed spectra, the fits are practically independent of the nature of the interaction [17].

Figure 2 shows a series of spectra obtained at the temperatures indicated, together with the theoretical fitted trends. Contributions to the spectra from the three cluster sites are also indicated for the 15 K spectrum.

Figure 3 shows the temperature dependence of W. The temperature dependence of W was fitted with both a polynomial function of the form $a + bT^n$ and the exponential function $a + b\exp(-c/T)$. The best fit was obtained with the latter function (the full curve in figure 3).
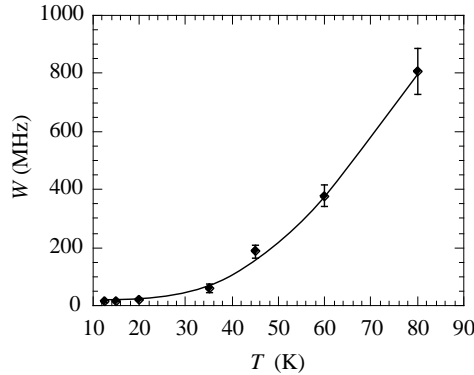

Figure 3. The transition probability per unit time versus temperature.

In fact, we obtained

$$W = (18.7 \pm 9) + (6988 \pm 850)\exp[-(175 \pm 9)/T] \tag{18}$$

where W is expressed in MHz. The first term, which is temperature independent, is probably due to magnetic dipolar interactions. Obviously, the second term describes the effect of the coupling with the thermal bath. Its form is typical of Orbach's effect or of the coupling with vibration modes in a narrow frequency range [18].

In order to establish the nature of the relaxation mechanism, it might be worthwhile to perform a rough comparison of the fluctuating magnetic fields corresponding to modulations of the dipolar and exchange energies. In the first case, when the distance R between two dipoles $\mu = g\mu_B S$ varies in δR, their interaction energy changes by the quantity

$$\Delta U_d \approx \frac{\mu_0}{4\pi} \frac{(g\mu_B S)^2}{R^3} \frac{\delta R}{R}. \tag{19}$$

The corresponding magnetic field is given by

$$H_d(t) \approx \frac{\mu_0}{4\pi} \frac{g\mu_B S}{R^3} \frac{\delta R}{R}. \tag{20}$$

As regards the exchange energy, we note that, in the case of bridged iron (III) dimers (FeO$_2$Fe) theoretical and experimental studies have revealed a J-dependence on the angle $\alpha = \text{Fe}\hat{\text{O}}\text{Fe}$ [19, 20]. In particular, for dimers having α around $110°$, it has been shown that J decreases in a linear fashion as the α-angle decreases [19]. In our case, where the central ion is bridged to the peripheral ones, we can assume that the oscillations of the α-angle determine a large modulation of J. Underestimating the order of magnitude, we have

$$\Delta U_{ex} \approx J\frac{\delta\alpha}{\alpha} \tag{21}$$

and for the corresponding magnetic field

$$H_{ex}(t) \approx \frac{J}{g\mu_B S} \frac{\delta\alpha}{\alpha}. \tag{22}$$

By taking $\delta R/R = \delta\alpha/\alpha$, we obtain

$$\frac{H_d}{H_{ex}} \approx \frac{\mu_0}{4\pi} \frac{(g\mu_B S)^2}{R^3 J} \approx 5 \times 10^{-2}. \tag{23}$$

In agreement with this result, the modulation of the exchange energy would seem to be the main cause of the spin fluctuations. However, our estimate is not definitive; it needs a deeper analysis, which will be carried out in a separate study.

Acknowledgments

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