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# Magnetic molecular nanoclusters in strong magnetic fields

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## 1. Introduction

We have studied, both experimentally and theoretically, the dependence of the magnetic susceptibility of magnetic molecular nanoclusters, which are characterized by complex chemical formulas and are usually denoted $Mn_6R_6$, $V_{15}$, and $Mn_{12}$ ac, on an external magnetic field in strong fields. Comparison of the results of theoretical calculations with the experimental data makes it possible to substantially clarify the nature of the exchange interactions between the magnetic ions in these molecular clusters.

Magnetic molecular nanoclusters are molecular crystals containing ions of rare-earth and transition metals [1–3]. The molecules comprising these crystals have a complex structure. Their molecular weight is on the order of $10^3$. Each molecule contains nonzero-spin ions of rare-earth or transition metals (usual 10 to 20 such ions) coupled by strong exchange interaction. Thus, magnetic molecular nanoclusters occupy the intermediate position between microscopic magnetic objects (individual magnetic ions) and macroscopic magnetic materials, which contain large numbers of interacting magnetic ions. Hence, they are often called mesoscopic magnetic materials.

The energy of the interaction between the magnetic ions inside a nanocluster is on the order $10^2$ K, while the energy of the magnetic interaction between molecular nanoclusters is lower than 0.1 K. Hence, a crystal consisting of magnetic molecular nanoclusters can be regarded as an ensemble of noninteracting mesoscopic magnets. This is an entirely new class of magnetic materials, which have attracted a lot of interest in connection with studies of such phenomena as macroscopic quantum coherence, macroscopic quantum tunneling, and the magnetocaloric effect, to name but a few (e.g., see Ref. [4]). More than that, these materials have attracted much interest because of the bright prospect of their practical applications in magnetic memory devices with high data-recording density, quantum computers, and other devices for processing information (e.g., see Refs [5, 6]).

In the present report, we examine magnetic molecular nanoclusters from a somewhat different angle, not from the traditional viewpoint, as objects convenient for studying exchange interactions. In most magnetic nanoclusters, there is observed an antiferromagnetic exchange interaction between the magnetic ions. Then, in a zero external magnetic field, the ground state of a nanocluster has a ferrimagnetic structure. As the strength of the external magnetic field grows, the ferrimagnetic state changes to ferromagnetic through a series of jumps in the total spin of the magnetic molecule when the Zeeman energy exceeds the exchange energy. These jumps in the magnetic moment of a molecular nanocluster correspond to peaks in the curve representing the dependence of the magnetic susceptibility on the external field. Since the number of spins involved in the exchange interaction is comparatively small, we can, using the spin Hamiltonian, calculate the positions of the peaks and, by comparing the results of the calculations with the experimental data, determine the coupling constants of the exchange interaction between the magnetic ions of the molecular nanocluster. We have studied, both experimentally and theoretically, the magnetic susceptibility of magnetic molecular nanoclusters $Mn_6R_6$, $V_{15}$, and $Mn_{12}$ac, which made it possible to substantially clarify the magnitude and nature of the exchange interactions in these molecular nanoclusters.

## 2. Experiment

Magnetic susceptibility was measured at liquid-helium temperatures in megagauss fields. An MK-1 magnetic cumulation generator was used to generate the magnetic field. The operation of this generator is based on the compression produced by an implosion of a conducting shell inside which an initial magnetic field has been generated. This initial field ($B = 16$ T) is generated in a thin-wall multilayer multiturn solenoid by a discharge from a capacitor bank ($W = 2$ MJ). In our experiments we used single-cascade generators with an initial cascade diameter of 139 mm. The magnetic flux trapped by the conducting cylinder was compressed by the explosion products to a diameter of 20 mm, with the magnetic field compression time amounting to 16 μs. Each experiment involved 4 to 8 samples. The magnetic field was measured by a set of single-turn variable-reluctance pickups whose diameters varied from 0.6 to 14.0 mm. The signals were registered by Tektronix 784 and Tektronix 744 four-channel oscilloscopes with a resolution of 2 ns per point. Measurements of the magnetic susceptibility were made with a four-balance transducer consisting of two well-compensated induction coils connected in opposition. The degree of coil compensation was tested in a high-frequency magnet. The total area of the coils, $NS$, where $S$ is the area of one turn, differed by no greater than 2%. The sample was placed in a bore 1.6 mm in diameter drilled in one of the coil forms. Placing a sample inside one of the coils generates a signal proportional to the time derivative of the magnetic moment of the sample, $V(H) \propto \mathrm{d}M/\mathrm{d}t + K\,\mathrm{d}B/\mathrm{d}t$, where $K$ depends on the accuracy of coil compensation. It is impossible to achieve ideal compensation, especially when the rate of variation of the magnetic field $\mathrm{d}B/\mathrm{d}t$ becomes as high as $10^6$ T s$^{-1}$. However, if the rate of variation of the magnetic field is a smooth function, the observed discontinuities in the $V(B)$ curve may be caused only by variations in the magnetic moment of the sample.

## 3. Theory and discussion

**$Mn_6R_6$.** The magnetic molecular cluster $Mn_6R_6$ is a ring of six Mn ions with spins $S_{Mn} = 5/2$ with radicals with spins $S_R = 1/2$ between them. According to the experimental data on the magnetic susceptibility of the $Mn_6R_6$ nanocluster gathered by Caneschi et al. [7], at $H = 0$ the nanocluster in the ground state has a total spin $S_\Sigma = 12$, which can be explained by the presence of an antiferromagnetic exchange interaction between the Mn ions and the radicals R.

Figure 1 shows the curve representing the experimental dependence of the magnetic susceptibility on the external magnetic field, $\chi(H)$. A characteristic feature of this dependence is greatly varying distances between adjacent peaks. Analytical estimates based on the spin-wave approximation and numerical calculations have shown that this feature cannot be explained by the presence of two-spin exchange interactions (Heisenberg and biquadratic) exclusively [8].

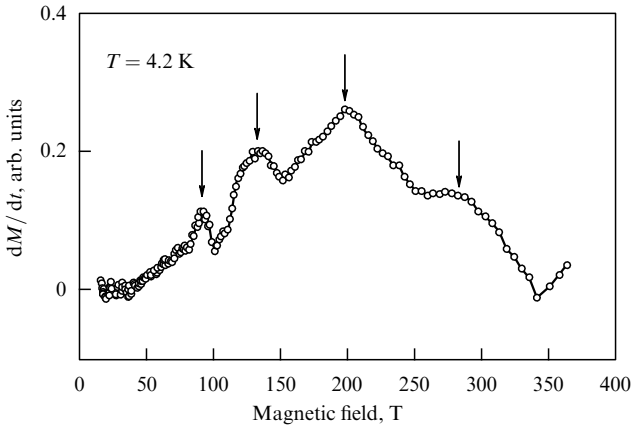


**Figure 1.** Dependence of the magnetic susceptibility of the molecular nanocluster $Mn_6R_6$ on the external magnetic field.

Only by incorporating three-spin interaction into the picture does it become possible to arrive at a satisfactory agreement between the experimental data and the results of theoretical calculations.

To calculate the spin structure and the energy of the ground state of the molecular nanocluster $Mn_6R_6$ using the spin Hamiltonian

$$\mathcal{H} = J\sum_{i=1}^{12}\mathbf{S}_i\mathbf{S}_{i+1} + g\mu_B H\sum_{i=1}^{12}S_i^z + J_3\sum_{j=1}^{6}\Big[\big(\mathbf{S}_{2j-1}\mathbf{S}_{2j}\big)\big(\mathbf{S}_{2j}\mathbf{S}_{2j+1}\big) + \big(\mathbf{S}_{2j}\mathbf{S}_{2j+1}\big)\big(\mathbf{S}_{2j-1}\mathbf{S}_{2j}\big)\Big], \tag{1}$$

we employed a modified Lanczos method (e.g., see Refs [9, 10]). In Eqn (1) we assume that even-valued subscripts correspond to Mn ions, and odd-valued subscripts to radicals, and that $\mathbf{S}_{i+12} \equiv \mathbf{S}_i$. The first term on the right-hand side describes the Heisenberg exchange interaction; the second term, the Zeeman energy in an external field; and the third term, the three-spin interaction.

The positions of the peaks in the susceptibility were found from the condition that the minimum energies for states with different total-spin values are equal for different values of the exchange-parameter ratio $J_3/J$. Then, the results of these calculations were compared with the experimental data. Each peak in the curve representing the dependence of the magnetic susceptibility on the external field corresponds to an increase of one unit in the total spin of the molecular cluster $Mn_6R_6$. The variation of total spin from $S_\Sigma = 12$ to $S_\Sigma = 18$ should be reflected by six peaks in the experimental $\chi(H)$ curve. Due to the lower resolving power of the measuring instruments in fields higher than 250 T, the last three peaks in the curve merge into one broad peak, which makes precise comparison of the theoretical and experimental data more difficult. Calculations have shown that better agreement with the experimental data is achieved when the fourth peak is associated with the transition $S_\Sigma = 15 \to S_\Sigma = 16$. In this case, the calculated values of the exchange coupling constants are $J = 40$ cm$^{-1}$ and $J_3/J = 0.14$, with a variance of about 10%.

**$V_{15}$.** The magnetic molecular cluster $V_{15}$ contains 15 magnetic ions $V^{4+}$, each with spin 1/2. These ions are located at the vertices of two flat hexagons and one triangle between the hexagons. The diagram of exchange interactions between the cluster ions is shown in Fig. 2. All the exchange interactions are antiferromagnetic, with the result that in the ground state the total spin of the cluster is 1/2. The spin Hamiltonian of the molecular cluster $V_{15}$ is written as

$$\begin{aligned}\mathcal{H} = {} & \sum_{i=1} g\mu H S_i^z + J_0\Big(\mathbf{S}_a\mathbf{S}_b + \mathbf{S}_b\mathbf{S}_c + \mathbf{S}_c\mathbf{S}_a\Big) \\ & + J\big[(\mathbf{S}_1\mathbf{S}_2 + \mathbf{S}_3\mathbf{S}_4 + \mathbf{S}_5\mathbf{S}_6) + ()'\big] \\ & + J'\big[(\mathbf{S}_2\mathbf{S}_3 + \mathbf{S}_4\mathbf{S}_5 + \mathbf{S}_6\mathbf{S}_1) + ()'\big] \\ & + J''\big[(\mathbf{S}_2\mathbf{S}_4 + \mathbf{S}_4\mathbf{S}_6 + \mathbf{S}_6\mathbf{S}_2 + \mathbf{S}_1\mathbf{S}_3 + \mathbf{S}_3\mathbf{S}_5 + \mathbf{S}_5\mathbf{S}_1) + ()'\big] \\ & + J_1\big(\mathbf{S}_a\mathbf{S}_1 + \mathbf{S}_b\mathbf{S}_3 + \mathbf{S}_c\mathbf{S}_5 + \mathbf{S}_a\mathbf{S}_{2'} + \mathbf{S}_b\mathbf{S}_{4'} + \mathbf{S}_c\mathbf{S}_{6'}\big) \\ & + J_2\big(\mathbf{S}_a\mathbf{S}_2 + \mathbf{S}_b\mathbf{S}_4 + \mathbf{S}_c\mathbf{S}_6 + \mathbf{S}_a\mathbf{S}_{1'} + \mathbf{S}_b\mathbf{S}_{3'} + \mathbf{S}_c\mathbf{S}_{5'}\big)\,. \end{aligned} \tag{2}$$

Here $()'$ stands for a term similar to the preceding term in parentheses but incorporating spins belonging to the upper hexagon (see Fig. 2).

As shown by Chiorescu et al. [11], at $H = 3$ T the spin structure of the cluster changes (the projections of the spins of the ions located at the triangle's vertices become equal, $S_a^z = S_b^z = S_c^z = 1/2$), with the result that the total spin of the cluster becomes 3/2. It has also been found (see Ref. [12]) that in strong magnetic fields the spin structure of the nanocluster undergoes further transformation in three jumps of equal amplitude $\Delta S = 2$ from a ferrimagnetic ($S_\Sigma = 3/2$) to a ferromagnetic ($S_\Sigma = 15/2$) state. For the values of the exchange parameters given in Ref. [11] (they are only useful as rough estimates), the magnitudes of the fields corresponding to these jumps are 371, 650, and 929 T,

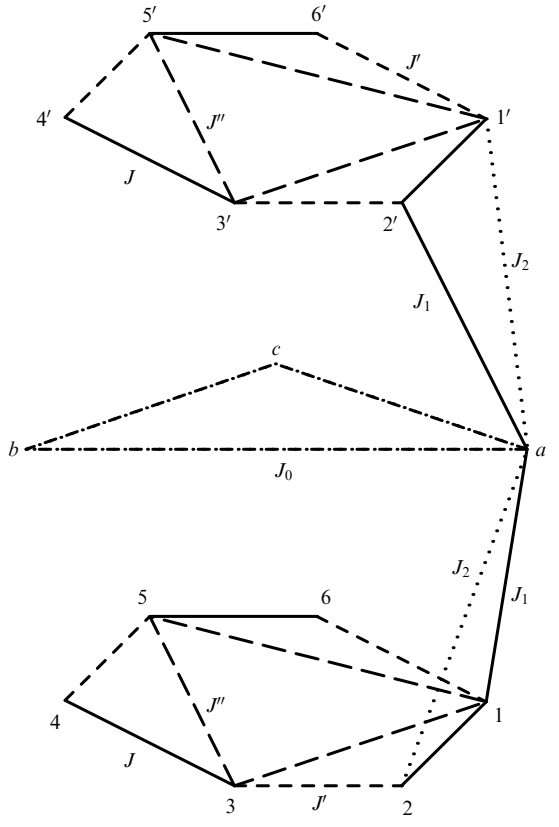


**Figure 2.** Structure of exchange interactions between the ions of the molecular nanocluster $V_{15}$.

respectively. Experimental investigations in magnetic fields of up to 450 T indicate the presence of peaks in the magnetic susceptibility vs. external field diagram at 200 and 350 T [13]. For example, the following values of the exchange integrals correspond to the experimentally observed heights of the peaks: $J = 490$ K, $J' = J_1 = 80$ K, and $J'' = J_2 = 161$ K [13]. However, at present there are insufficient experimental data to reliably determine the exchange constants.

**$Mn_{12}$-acetate.** The spin structure of the magnetic molecular cluster $Mn_{12}$ac is represented by a tetrahedron of $Mn^{4+}$ ions with spin 3/2 surrounded by eight $Mn^{3+}$ ions with spin 2. The spins of the $Mn^{4+}$ and $Mn^{3+}$ ions are antiparallel, and in the ground state the molecular cluster has a total spin $S = 10$. Figure 3 shows the diagram of the exchange interactions inside the cluster. The spin Hamiltonian of the molecular cluster $Mn_{12}$ac is written as

$$\begin{aligned}\mathcal{H} = {} & g\mu H \sum_{i=1}^{12} S_i^z + J_1(\mathbf{S}_1\mathbf{S}_9 + \mathbf{S}_3\mathbf{S}_{10} + \mathbf{S}_5\mathbf{S}_{11} + \mathbf{S}_7\mathbf{S}_{12}) \\ & + J_2(\mathbf{S}_2\mathbf{S}_9 + \mathbf{S}_2\mathbf{S}_{10} + \mathbf{S}_4\mathbf{S}_{10} + \mathbf{S}_4\mathbf{S}_{11} \\ & + \mathbf{S}_6\mathbf{S}_{11} + \mathbf{S}_6\mathbf{S}_{12} + \mathbf{S}_8\mathbf{S}_{12} + \mathbf{S}_8\mathbf{S}_9) \\ & + J_3(\mathbf{S}_9\mathbf{S}_{10} + \mathbf{S}_{10}\mathbf{S}_{11} + \mathbf{S}_{11}\mathbf{S}_{12} + \mathbf{S}_9\mathbf{S}_{12} \\ & + \mathbf{S}_9\mathbf{S}_{11} + \mathbf{S}_{10}\mathbf{S}_{12}) + J_4(\mathbf{S}_1\mathbf{S}_2 + \mathbf{S}_2\mathbf{S}_3 + \mathbf{S}_3\mathbf{S}_4 \\ & + \mathbf{S}_4\mathbf{S}_5 + \mathbf{S}_5\mathbf{S}_6 + \mathbf{S}_6\mathbf{S}_7 + \mathbf{S}_7\mathbf{S}_8 + \mathbf{S}_1\mathbf{S}_8)\,. \end{aligned} \tag{3}$$

According to Sessoli et al. [14], in the ground state the molecular cluster $Mn_{12}$ac has spin $S_\Sigma = 10$, which is the result of predominantly antiferromagnetic interaction $J_1$ (see Fig. 3) between the $Mn^{3+}$ and $Mn^{4+}$ ions. These data agree with the results of computations carried out within the local-density approximation (LDA) [15]. Using these data as a basis, we developed (see Ref. [16]) a perturbation scheme that made it possible to analytically calculate the positions of the peaks in the magnetic susceptibility vs. external magnetic field curve for $Mn_{12}$ac. At $J_2 = J_3 = J_4 = 0$, the transition in an external field from the ferrimagnetic to the ferromagnetic state proceeds in three quantum jumps, and in each such jump the spin changes by four units. Allowance for the exchange interactions $J_2$, $J_3$, and $J_4$ leads to splitting of each peak into four peaks. According to the experimental data of Ref. [17], the splitting of the central peak is extremely small. Based on this condition, the values of the exchange constants were determined in Ref. [17] to be $J_1 = 122$ cm$^{-1}$, $J_2 = 60$ cm$^{-1}$, $J_3 = -11.2$ cm$^{-1}$, and $J_4 = 30$ cm$^{-1}$, which are close to those obtained in Refs. [14, 18] but lie outside the scope of perturbation theory. Our numerical calculations have shown that all the sets of exchange constants calculated so far do not provide the necessary agreement with the experimental data, and further theoretical investigations are required.

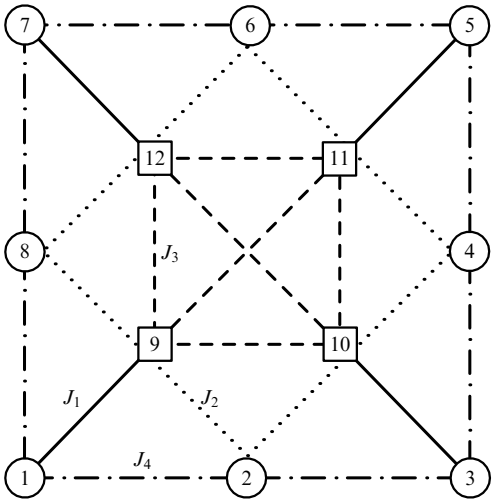


**Figure 3.** Structure of exchange interactions between the ions of the molecular nanocluster $Mn_{12}$ac. □ $Mn^{4+}$ ($S = 3/2$) and ○ $Mn^{3+}$ ($S = 2$).

## 4. Conclusion

Our theoretical and experimental studies of the transformation of the spin structure in strong magnetic fields have substantially clarified the ideas about the nature of exchange interactions in molecular magnetic clusters.

The experimental data on the magnetic susceptibility of the $Mn_6R_6$ nanocluster cannot be explained on the basis of two-spin interaction. Allowance for three-spin interaction yields satisfactory agreement between the experimental data and the results of theoretical calculations.

The proposed set of values of the exchange parameters provides quantitative agreement with the experimental data on the magnetic susceptibility of the $V_{15}$ molecular cluster, but there is insufficient experimental data to unambiguously select the exchange interaction constants.

The experimental data on the magnetic susceptibility of the nanocluster $Mn_{12}$ac agree with the predictions of the theory qualitatively but not quantitatively. Further theoretical studies are needed.

## References


1. Sessoli R et al. *Nature* **365** 141 (1993)
2. Thomas L et al. *Nature* **383** 145 (1996)
3. Wernsdorfer W, Sessoli R *Science* **284** 133 (1999)
4. Chudnovsky E M, Tejada J *Macroscopic Quantum Tunneling of the Magnetic Moment* (Cambridge: Cambridge Univ. Press, 1998)
5. Kahn O, Martinez C J *Science* **279** 44 (1998)
6. Tejada J et al. *Nanotechnology* **12** 181 (2001)
7. Caneschi A et al. *J. Am. Chem. Soc.* **110** 2795 (1988)
8. Kostyuchenko V V et al. (submitted to *Phys. Rev. B*)
9. Gagliano E R et al. *Phys. Rev. B* **34** 1677 (1986)
10. Dagotto E *Rev. Mod. Phys.* **66** 763 (1994)
11. Chiorescu I et al. *Phys. Rev. Lett.* **84** 3454 (2000)
12. Zvezdin A K et al. *Fiz. Tverd. Tela* **43** 177 (2001) [*Phys. Solid State* **43** 185 (2001)]
13. Platonov V V et al. *Fiz. Tverd. Tela* **44** 2010 (2002) [*Phys. Solid State* **44** 2104 (2002)]
14. Sessoli R et al. *J. Am. Chem. Soc.* **115** 1804 (1993)
15. Boukhvalov D W et al., cond-mat/0110488
16. Zvezdin A K, Popov A I *Zh. Eksp. Teor. Fiz.* **109** 2115 (1996) [*JETP* **82** 1140 (1996)]
17. Platonov V V et al. (submitted to *Phys. Rev. B*)
18. Raghu C et al. *Phys. Rev. B* **64** 064419 (2001)