Giant Keplerate molecule Fe$_{30}$ - the first octopole magnet

A. S. Mischenko$^1$($^*$), A. S. Chernyshov$^1$ and A. K. Zvezdin$^2$

$^1$Physics Department, Moscow Lomonosov State University, 119889, Moscow, Russia
$^2$General Physics Institute of RAS, 119991, Moscow, Russia

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Abstract. – The multipole expansion technique is applied to one of the largest magnetic molecules, Fe$_{30}$. The molecule’s dipole, toroid and quadrupole magnetic moments are equal to zero (in the absence of magnetic field) so the multipole expansion starts from the octopole moment. Probably the Fe$_{30}$ molecule is the most symmetrical magnetic body synthesized so far. The magnetization process is considered theoretically in different geometries. Some components of the octopole moment experience a jump while the magnetization rises linearly up to its saturation value. An elementary octopole moment consisting of four magnetic dipoles is proposed as a hint for designing of an experiment for measurement of octopole magnetic moment components.

Introduction. – Multipole expansion of the electrical field generated by a number of electrical charges has been widely used in theoretical physics. However, multipole expansion of magnetic fields generated by a system of permanent currents is less known. The starting point of such an expansion is a well known formula for the vector potential of the magnetic field:

$$\vec{A} = \frac{1}{c} \sum_i \frac{e_i \vec{v}_i}{R - \vec{r}_i},$$

where $e_i$ and $\vec{v}_i$ stand for a charge and velocity of the $i$-th charge. The vector potential $\vec{A}$ can be expanded in a power series of the $|\vec{r}|/|\vec{R}|$ ratio if an interesting point is rather distant from the system of charges, i.e. $|\vec{r}|/|\vec{R}| \ll 1$. The first term of the expansion in question is $\vec{A}' = |\vec{M}\vec{R}|/R^3$ where $\vec{M} = \frac{1}{\hbar} \sum_i e_i [\vec{r}_i \vec{v}_i] = \frac{1}{\hbar} \sum_i \frac{m_i}{2} \vec{l}_i$ is the magnetic dipole moment of the system, $\vec{l}_i$ are orbital moments of the electrons/ions and $m_i$ are their masses. The spin $\vec{s}_i$ degrees of freedom can be taken into account by the substitution $\vec{l}_i \rightarrow \vec{l}_i + g_i \vec{s}_i$. In this paper we will be concerned with the spin magnetism only. A distinctive feature of the magnetic field potential’s multipole expansion is that it is subdivided into two families: magnetic and toroid moments, unlike the expansion of the scalar electrical potential. The first and easiest representative of the toroid family is the anapole moment – a torus with electric currents flowing along its meridians. Magnetic multipole moments are defined by transverse currents (currents flowing along the torus’ parallels for instance). The necessity of the subdivision is

($^*$) E-mail: smischenko@yahoo.com

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quite obvious since we can decompose the current density into the following terms according to a well known theorem of the vector analysis \[2]: \[ \vec{j}(\vec{r}) = \text{grad}(\eta) + \text{rot}(\vec{f}), \] where the first term corresponds to the toroid moments and the second to the "usual" magnetic multipole moments. Spin systems of finite sizes and magnetic molecules (Mn$_{12}$Ac, V$_{15}$, Fe$_8$, Fe$_{10}$, Fe$_{30}$, etc.) in particular are natural objects for application of the multipole expansion technique.

The magnetic molecules have attracted great attention from the point of view of fundamental problems of quantum mechanics in general and the theory of magnetism in particular \[3\] as well as nanotechnology and microelectron applications (as model systems for quantum informatics for example) \[4,5,6,7\] in recent years. The molecules are large organic molecular complexes with the weight of approximately $10^3$ atomic mass units. The magnetic ions, such as Fe, Mn, V, etc. embedded within the molecule cause their interesting magnetic properties. There is a strong exchange interaction between magnetic ions (in the order of $10^6$ Oe) within the molecule.

**Magnetic multipole expansion.** – The lowest magnetic multipole moments of spin systems (dipole 1, quadrupole 2, octopole 4 and toroid 1) can be defined as follows \[8,9,10\]:

\[
\vec{M}_1 = \mu_B \sum_i g_i \vec{s}_i, \quad (M_2)_{\alpha\beta} = \mu_B \sum_i g_i (r_i \beta s_{i\alpha} + s_i \beta r_{i\alpha}),
\]

\[
(M_3)_{\alpha\beta\gamma} = 3\mu_B \sum_i g_i s_{i\alpha} r_{i\beta} r_{i\gamma},
\]

\[
M_{n,m} = -\mu_B \sum_i g_i [\nabla_i (r_i n C_n^m(\theta_i, \varphi_i)) \times \vec{s}_i], \quad \vec{T}_1 = \mu_B \sum_i g_i [\vec{s}_i \vec{r}_i],
\]

where $M_{n,m}$ are magnetic multipole moment’s components in spherical coordinates ($n$ defines the order of a moment: $n = 1$ - dipole, $n = 2$ - quadrupole, $n = 3$ - octopole, etc., $m$ ranges from $-n$ to $n$ by 1). It is a well-known fact that each multipole moment interacts with the corresponding magnetic field spatial variation. For the sake of brevity we present here the formula for the octopole moment only: $W = -(1/6)(M_3)_{\alpha\beta\gamma} B_{\gamma\beta\alpha}$, \quad $B_{\gamma\beta\alpha} = \nabla_\gamma \nabla_\beta B_{\alpha}$, where $W$ is the energy of interaction between an octopole and external magnetic field in Cartesian coordinates, $\nabla_\gamma$ and $\nabla_\beta$ are Laplace operators for the spatial derivatives and $B_{\alpha}$ stands for the three components of the external magnetic field.

Octopolar electric fields have already been well examined in connection with non-linear optical properties \[11\]. Quadrupole moment of the rare earth ions, their dependence on external magnetic field and connection with magnetic birefringence and magnetostriction have been investigated in \[12,13,14\]. The spin toroid moment $T_1$ has been experimentally found in bulk magnets (GaFeO$_3$, Cr$_2$O$_3$, etc.) recently \[15\]. Molecular complexes with the spin density that can be described by means of the toroid moment $T_1$ have been analyzed theoretically in \[16\] but an experimental realization of the proposed idea still remains unknown. Quadrupole magnetic fields generated by antiferromagnetic crystals have been analyzed in \[17\]. Antiferromagnetic nanoclusters, e.g. Fe$_{10}$, Fe$_{6}$ can be characterized by the quadrupole moment $M_2$ and moments of higher orders.

**Highly symmetrical Keplerate molecule Fe$_{30}$.** – However, no one magnetic object has been characterized by the octopole moment so far. The first object of this kind is a magnetic nanocluster Fe$_{30}$ with the chemical formula [M$_{72}$Fe$_{30}$O$_{252}$ (Mo$_{20}$O$_7$(H$_2$O))$_2$(Mo$_2$O$_8$H$_2$(H$_2$O))(CH$_3$COO)$_{12}$(H$_2$O)$_{91}]*150$H$_2$O.

This molecule has the largest number of magnetic Fe$^{3+}$ ions among all the known molecular magnets synthesized so far \[4\]. The molecule Fe$_{30}$ as well as the other nanoclusters discussed above occupies an intermediate position among the bulk materials and localized magnetic
ions, that is the reason these objects are called "mesoscopic magnets". Toroid \((T_1)\), dipole \((M_1)\) and quadrupole \((M_2)\) moments of this molecule are equal to zero, i.e. the multipole expansion starts from the octopole moment. In other words, probably the \(\text{Fe}_{30}\) molecule with a highly symmetrical spin density is the most symmetrical magnetic body synthesized so far.

The investigated molecular complex consists of 30 \(\text{Fe}^{3+}\) ions each of which has a spin \(s = 5/2\). The magnetic ions are situated in the vertices of the icosidodecahedron, one of the regular Archimedean polytopes (see fig.1). The icosidodecahedron has \(v = 30\) vertices, \(f = 32\) faces and \(e = 60\) edges in accordance with the so-called Euler theorem \([1]\), connecting a number of vertices, faces and edges of a convex polyhedron of O genus \((v + f - e = 2)\). The faces of the icosidodecahedron consist of 20 triangles and 12 pentagons. Neighbouring \(\text{Fe}^{3+}\) ions interact with each other antiferromagnetically by means of the indirect exchange interaction which results in zero total spin of the molecule in the absence of magnetic field \([7]\).

The exact ground state energy and the corresponding ground state of the \(\text{Fe}_{30}\) molecule has been found in \([7]\) basing on graph-theoretical technique and a special geometrical property of the icosidodecahedron, its three-colorability (a graph is called three-colorable if we can color all its vertices with three colors and no neighboring vertices with the same color - see fig.1). In the framework of the proposed model all spins are coplanar and the relative angle between nearest-neighbor spins is 120\(^\circ\). In other words, each of the three colors is assigned to one of three coplanar spin directions (fig.1). It is important to note that \(\textit{ab-initio}\) calculations of the molecule in question have not been performed yet and we have no experimental evidence on how the plane coplanar to the spins is aligned - it can be parallel either to one of the pentagons or to one of the triangles. However, our calculations show that the result is approximately the same in the both cases. The octopole moment components in the spherical system can be found from \([1]\) by substituting \(n = 3; m\) changes from -3 to 3 by 1, thus yielding seven complex components of the moment. Our calculations show that the octopole moment components both in Cartesian and spherical systems are finite but we do not present here the particular values for the sake of brevity.

Magnetic field with octopolar symmetry at least is required to measure the octopole magnetic moment components. Such a field can be generated by an elementary magnetic octopole presented on fig.2. The field will create a torque on the Keplerate molecule(s) placed in the
origin of the coordinate system with the value determined by corresponding octopole moment components. The estimation of particular torques is beyond the scope of this article. This approach can be used to study a wide number of mesoscopic magnets. Neutron spectroscopy can be used to measure the octopole moment as well and further work in this direction is required.

"Deoctopolization" in external magnetic field. – Magnetic properties of the Fe$_{30}$ molecule and its multipole moments are discussed in the following. However, the dependence of the magnetic dipole moment of the magnet in question on external magnetic field has been quantitatively described in [7] in the framework of the classical statistical physics (namely, the magnetic moment rises linearly with magnetic field till the saturation at the critical field value $B_C = 17.7 T$, what is in perfect agreement with experimental results). The consideration was based on a study of a three spin system with antiferromagnetic interactions between the closest neighbour spins placed in external magnetic field in accordance with the following Hamiltonian [18]:

$$H = \vec{S}_1 \cdot \vec{S}_2 + \vec{S}_2 \cdot \vec{S}_3 + \vec{S}_3 \cdot \vec{S}_1 - \beta (\vec{S}_1 + \vec{S}_2 + \vec{S}_3),$$

(5)

where $\beta = g \mu_B / 2 JS$ is a dimensionless magnetic field, $J > 0$ stands for antiferromagnetic exchange integral and all spins are of the same length $S$. The Hamiltonian represents a classical model, i.e. the projections of the spins are not quantized and can take all intermediate values. The exact solution for the ground state energy has been found in [18] and it was shown that the ground state energy depended on the total spin only (or magnetic field, as they are connected linearly), namely $E_{GS}(\beta) = -3/2 - \beta^2 / 2$. At the magnetic field value corresponding to $\beta = 3$ all the three spins are aligned with the magnetic field. The dimension of the Hilbert space for Fe$_{30}$ molecule in the framework of the quantum model is $6^{30}$ which is far beyond calculation possibilities of any modern computer. However, an approximate quantum model based on the isotropic nearest-neighbour antiferromagnetic Heisenberg exchange is presented in [19] and finally results in appearance of special small quantum steps on magnetization typical for molecular magnets. Analogous consideration would lead to the steppes of the same kind on the octopole moment components as well but they would not change the general picture and would be an unnecessary complication. This is the reason we use classical model here.

However, due to the antiferromagnetic interactions the three spin system is highly frustrated and the magnetization process can be carried out in many ways. The three easiest of them are: A) the three spins simultaneously leave the plane where they lied before in the case of magnetic field directed perpendicularly to the spin plane (fig 3 a); B) the field is directed along one of the spins, then the remaining two spins turn in the field’s direction uniformly (fig 3 b); C) the field is opposite to one of the spins (\vec{S}_1), then the magnetization process involves two phases separated by the $S_1$ spin jump at magnetic field $\beta = 1$ (fig 4).

There is one parameter describing each of the first two magnetization processes: the angle of each spin’s declination from the initial state $\vartheta_\perp(\beta)$ in case (A); the angle of the $\vec{S}_2$ and $\vec{S}_3$ spins’ declination $\vartheta_{\parallel}(\beta)$ in case (B) and two parameters in the third case (C) - $\vartheta_a(\beta)$ and $\vartheta_b(\beta)$ (fig 4). The parameters can be found from minimization of the system’s energy in external magnetic field. This can be done by projecting the Hamiltonian [18] on subspaces containing one or two variables in the first two (A) and (B) and the last case (C), respectively. Due to simplicity of the considered cases below we give the answers only:

$$\vartheta_\perp(\beta) = \frac{\pi}{2} \beta, \quad \vartheta_{\parallel}(\beta) = \arcsin \left( \frac{\beta - 1}{2} + \frac{\pi}{6} \right), \quad \vartheta_a(\beta) = \arcsin \left( \frac{\beta + 1}{2} - \frac{\pi}{6} \right),$$

(6)

where $\beta$ changes from 0 up to its saturation (critical) value 3. Note that the second formula describes two parameters - $\vartheta_{\parallel}(\beta)$ and $\vartheta_a(\beta)$.
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Fig. 3 – Two considered geometries of the Fe$_{30}$ molecule magnetization process: (a) - $\vec{B}$ is perpendicular to the spin plane (case A); (b) - $\vec{B}$ is parallel to one of the three spins (cases B, C).

In order to calculate the dependence of high multipole magnetic moments on the magnetic field we have made an assumption that the Fe$_{30}$ molecule can be divided into 20 triangles of antiferromagnetically interacting spins \(5\) \(\&\) \(7\). This assumption can be partially justified by the fact that the icosidodecahedron is three-colorable without any visible anisotropy and that this model’s results are in perfect agreement with experiments. Besides, according to recent calculations with the Density Matrix Renormalization Group technique (DMRG) reported in \(20\), the low lying energy levels of the Fe$_{30}$ molecule form a rotational band, i.e. they depend approximately quadratically on the total spin quantum number \(S\). Actually \(\hat{\beta}\) in \(5\) should be multiplied by a factor of \(1/2\) when writing the Hamiltonian for all 20 triangles to take into account that each spin is shared by two neighbouring triangles. Hence, having the magnetization parameters \(6\) we obtain the spin distribution over the molecule at finite magnetic field and can calculate its multipole moments for any field value. As we have already noted, the magnetic dipole moment rises linearly with the field. Surprisingly, the quadrupole magnetic moment remains equal to zero in all cases (A, B, C) at any fields up to saturation, and further.

The two basic types of the octopole moment components’ behavior in the out-of-plane case (A) are plotted on fig. \(\&\) a. As you can see, almost all the components vanish with the field. There are only three linearly raising components. It can be understood by a simple mathematical consideration. Indeed, at the saturation all the spins are aligned parallel to the magnetic field (and \(Oz\) axis, see fig. \(\&\) a), i.e. their \(x\) - and \(y\) - components are equal to zero as well as 18 octopole magnetic moment components \((M_3)_{1ij},(M_3)_{2ij}, i = 1..3, j = 1..3\) \(3\).

Fig. 4 – A simple scheme of the magnetization process involving the \(S_1\) spin jump (case C).
Moreover, all components of the kind \((M_3)_{3ij}\) with \(i \neq j\) are equal to zero as the contributions from different spins cancel each other out when we perform the summation in \((\text{B})\). The only three surviving components are \((M_3)_{311}\), \((M_3)_{322}\) and \((M_3)_{333}\) as they are the sums of squared coordinates of all spins multiplied by the \(z\) component of the saturated spin and it is obvious that these three components raise with the field.

However, the in-plane magnetization cases (B, C) are more interesting. Their general geometry is shown on fig. 3, b. Note that the magnetic field can have any sign so we cover both B and C cases with this picture. Nevertheless, the octopole moment behaves in different ways and we will consider these cases separately. Take a look at the fig. 5, b. It differs from fig. 5, a with the curvature of \(M_{212}\), \(M_{213}\) components and appearance of dependencies of a new type \(M_{121}\), \(M_{123}\). These facts are connected with the way the spin projections change during the magnetization process (see \((\text{A})\) and fig. 3, b). And just like in the (A) case we have three linearly growing components - \(M_{111}\), \(M_{122}\), \(M_{133}\). The third case (C) is the most interesting as one of the spins, \(\vec{S}_1\) for clarity, abruptly changes its direction for the opposite one at the magnetic field \(\beta = 1\) (see fig. 4). At the same time, the total spin (and magnetization) do not experience a jump or even a kink, what follows from the general solution for the considered problem given in \((\text{C})\). The octopole moment’s components vs. magnetic field are shown on figs. 6, a, b. Quite obviously, all the dependencies have jumps at the field \(\beta = 1\) showing the abrupt changes of symmetry at this point.

It is important to point out that the three considered cases do not exhaust all possible ways the magnetization can be realized. They rather reveal basic features of the "deoctopolization" process and can be a ground for its future classification.

**Conclusion.** – The results of the theoretical investigation of the Fe\(_{30}\) molecule let us make some important conclusions. First of all it is shown that dipole, toroid and quadrupole moments of the Fe\(_{30}\) molecule are equal to zero. Probably the considered system has the most symmetric distribution of spin density of all the mesoscopic magnets synthesized so far. The magnetic octopole moment is calculated in both Cartesian and spherical coordinates. A model of an elementary magnetic octopole as a possible experimental unit for octopole magnetic moment component measurement is proposed. Toroid and quadrupole moments are shown to remain equal to zero at any magnetic fields while components of the octopole moment are changed substantially. Different geometries of the magnetization process are considered...
Fig. 6 – Four basic types of magnetic field dependence of the components of the octopole moment components, in-plane magnetization with the transition (case C).

and discussed.

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