"Phase" diagram of Izing and Heisenberg cubic clusters

Yu. A. Koksharov
Faculty of Physics, M.V.Lomonosov Moscow State University, 119899, Moscow, Russia
(November 15, 2018)

We have studied the ground state of a simple cubic magnetic cluster, which contains a spin $s$ at each corner site. The ground state of such cluster depends on the competition between nearest, next-nearest and next-next-nearest-neighbor exchange interactions. We have calculated "phase" diagrams for the Izing clusters with $s = \frac{1}{2}; 1; 3; \frac{5}{2}; \infty$ and for the Heisenberg cluster with $s = \frac{1}{2}; 1$.

We have found that the "phase" diagram is remarkably independent on the $s$ value. It is important also that the Izing "phase" diagram can be used as a rough approximation for the Heisenberg model.

In recent years much attention has been given to magnetic properties of molecular magnets - clusters, each containing relatively small number of paramagnetic ions. The best known examples of such clusters are Mn$_{12}$ and Fe$_8$, which have been intensively studied due to quantum tunneling magnetization phenomena. The number of transition metal ions in molecular paramagnetic clusters extends from 2 (in dimers) up to 30, as in polyoxometalate Mo$_{72}$Fe$_{30}$.[3] A spin quantum number $s$ varies from 1/2, e.g. for polylolate-bridged copper clusters,[4] up to 5/2 for iron and manganese clusters.

It appears that the majority molecular magnets can be described by a model of single-particle localized magnetic moments ("spins") coupled by the Heisenberg exchange interactions.[5] In spite of smallness of molecular magnets, a numerical calculation of the energy spectrum could be a nontrivial task, since the dimension of the Hilbert space for a system of $N$ spins $s$, given by $(2s + 1)^N$, grows rapidly with $N$ and $s$. For example, in the case of Mn$_{12}$ the exact calculation of energies of all spin states arising from the coupling of eight $s_a = 2$ spins and four $s_b = 3/2$, whose number is $(2s_a + 1)^8(2s_b + 1)^4 = 10^6$, is practically outside the capability of the most powerful computers.[6]

In magnetic clusters each of spin has a few neighbors, resulting in a frustration of exchange interactions. Because of complexity of exchange pathways, both a sign and a magnitude of exchange constants are difficult to predict a priori. A cluster becomes magnetic, if it has a non-zero-spin ground state. It is interesting to study effects of competing interactions on the ground state of a relatively small and highly symmetrical spin cluster, for which a wide range of exchange parameters can be relatively easily examined. In this paper we continue our examination of zero-temperature magnetic properties of cubic clusters[1] and present results of an investigation of ground-state properties of a cubic cluster of eight spins $s$, coupled by Izing or Heisenberg interactions. There are enough examples of real molecular clusters, containing metal ions at corner sites of a simple cube. Unfortunately, these ions often have "non-magnetic" valence (e.g. copper-dithiolato species and related compounds,[5] cobalt cyanide clusters[6]). However, many potentially
for the Heisenberg Hamiltonian, and 

$$D$$ by noting that the spin states of 

singlet $$S_0$$ states, 28 triplets with 

$$J$$ combinations of basis functions 

$$S$$ each of which can be described by quantum 

Therefore, the energy level scheme consists of a number 

important that the Heisenberg Hamiltonian (1) commutes 

NNN and NNNN interactions, correspondingly. It is im-

A sketch of the cluster is shown in Fig. 1. The model 

Heisenberg Hamiltonian of the system takes the form 

$$H = J_1 H_{nn} + J_2 H_{nnn} + J_3 H_{nnnn}$$  \(1\) 

with 

$$H_{nn} = S_0 S_1 + S_0 S_3 + S_0 S_4 + S_1 S_2 + S_1 S_5 + S_2 S_3 +$$ 

$$+ S_2 S_6 + S_3 S_7 + S_4 S_5 + S_4 S_7 + S_5 S_6 + S_6 S_7;$$ \(1a\) 

$$H_{nnn} = S_0 S_2 + S_0 S_5 + S_0 S_7 + S_1 S_3 + S_1 S_4 + S_1 S_6 +$$ 

$$+ S_2 S_5 + S_2 S_7 + S_3 S_4 + S_3 S_6 + S_4 S_6 + S_5 S_7;$$ \(1b\) 

$$H_{nnnn} = S_0 S_6 + S_1 S_7 + S_2 S_4 + S_3 S_5;$$ \(1c\) 

for the Heisenberg Hamiltonian, and 

$$H_{nn} = S_0^z S_1^z + S_0^z S_3^z + S_0^z S_4^z + S_1^z S_2^z + S_1^z S_5^z + S_2^z S_3^z +$$ 

$$+ S_2^z S_6^z + S_3^z S_7^z + S_4^z S_5^z + S_4^z S_7^z + S_5^z S_6^z + S_6^z S_7^z;$$ \(1d\) 

$$H_{nnn} = S_0^z S_2^z + S_0^z S_5^z + S_0^z S_7^z + S_1^z S_3^z + S_1^z S_4^z + S_1^z S_6^z +$$ 

$$+ S_2^z S_5^z + S_2^z S_7^z + S_3^z S_4^z + S_3^z S_6^z + S_4^z S_6^z + S_5^z S_7^z;$$ \(1e\) 

$$H_{nnnn} = S_0^z S_6^z + S_1^z S_7^z + S_2^z S_4^z + S_3^z S_5^z;$$ \(1f\) 

for the Ising Hamiltonian. Here $$\vec{S}_i$$ is the spin operator 

located at lattice site $$i$$, and $$S_i^z$$ denotes its z component. 

Terms $$J_1 H_{nn}$$, $$J_2 H_{nnn}$$ and $$J_3 H_{nnnn}$$ describes the NN, 

NNN and NNNN interactions, correspondingly. It is im-

portant that the Heisenberg Hamiltonian (1) commutes 

with the operator of the total spin $$\vec{S}^2$$ as well as its z com-

ponent $$S_z$$, where $$\vec{S} = S_0 + S_1 + S_2 + S_3 + S_4 + S_5 + S_6 + S_7$$. 

Therefore, the energy level scheme consists of a number 

multiplets each of which can be described by quantum 

numbers $$S$$ and $$S_z$$. The number of states is easily derived 

by noting that the spin states of $$S_i$$ form a basis for the 

irreducible representation $$D_S$$. For example, in case 

of $$s = 1/2$$ the 256 states must form a basis for the repre-

sentation $$D_{1/2} \times D_{1/2} \times D_{1/2} \times D_{1/2} \times D_{1/2} \times D_{1/2} \times D_{1/2}$$. This 

yields 14 singlet $$S = 0$$ states, 28 triplet with $$S = 1$$ and so on. 

The eigenfunctions of (1) can be expressed as linear combi-

nations of basis functions $$\varphi_m = \ldots \uparrow \downarrow \ldots \downarrow \ldots \rangle$$, 

where $$m = \sum_{i=0}^{7} a_i 2^i$$, $$a_i = 1$$ or 0 according as the i-

th spin is up ($$\uparrow$$) or down ($$\downarrow$$). All the eigenvalues $$\epsilon_n$$
and the corresponding eigenfunctions \( \varphi_n \) of the Hamiltonian (1) can be found by the exact diagonalization of a 256\( \times \)256 matrix (for example, using the standard Householder method\(^{[2]} \)). It should be noted that the functions \( \varphi_m \) are exactly equal to the eigenfunctions of the Izing Hamiltonian (Eqs.(1d-1f)), which commutes with the \( S_z \) operator. Hence, the eigenvalues for the Izing model can be easily calculated without the energy matrix diagonalization.

Let us consider the Izing cubic cluster in the case of \( s = 1/2 \). For each eigenfunction \( \varphi_m \) we have found the average values \( \langle H_{nn} \rangle, \langle H_{nnn} \rangle \) and \( \langle H_{nnnn} \rangle \) (see Table 1).

**TABLE 1. Matrix elements for the Izing model.**

|\( (H_{nn}) \)|\( (H_{nnn}) \)|\( (H_{nnnn}) \)\( (S_z) \)|\( N \) |
|---|---|---|---|---|
|1.0| -1.0| -1.0| 0| 6 |
|-1.0| 0.0| 0.0| 0| 24 |
|0.0| -1.0| 0.0| 0| 24 |
|0.0| 0.0| -1.0| 0| 8 |
|-1.0| -1.0| 1.0| 0| 6 |
|-3.0| 3.0| -1.0| 0| 2 |
|0.5| -0.5| -0.5| 1| 24 |
|-0.5| -0.5| 0.5| 1| 24 |
|-1.5| 1.5| -0.5| 1| 8 |
|1.0| 0.0| 0.0| 2| 12 |
|0.0| 1.0| 0.0| 2| 12 |
|0.0| 0.0| 1.0| 2| 4 |
|1.5| 1.5| 0.5| 3| 8 |
|3.0| 3.0| 1.0| 4| 1 |

Here \( \langle H_{nn} \rangle = \langle \varphi_m | H_{nn} | \varphi_m \rangle \), \( \langle H_{nnn} \rangle = \langle \varphi_m | H_{nnn} | \varphi_m \rangle \), \( \langle H_{nnnn} \rangle = \langle \varphi_m | H_{nnnn} | \varphi_m \rangle \), \( N \) is the number of the wavefunctions \( \varphi_m \) with the equal values of \( \langle H_{nn} \rangle, \langle H_{nnn} \rangle \) and \( \langle H_{nnnn} \rangle \). Fortunately, the number of different sets of \( \langle H_{nn} \rangle, \langle H_{nnn} \rangle, \langle H_{nnnn} \rangle \) is much less than the total number of the wavefunctions. For example, we have seventy functions \( \varphi_m \) with \( S_z = 0 \) and only six different sets of corresponding \( \langle H_{nn} \rangle, \langle H_{nnn} \rangle, \langle H_{nnnn} \rangle \) (Table 1).

Using data from Table 1 we can write analitical expression for all Izing eigenvalues \( \varepsilon_m \):

\[
\varepsilon_m = J_1 \langle H_{nn} \rangle + J_2 \langle H_{nnn} \rangle + J_3 \langle H_{nnnn} \rangle. \tag{2}
\]

Complete set of different \( \varepsilon_m \) can be written as follows:

\[
\varepsilon_1^{(0)} = J_1 - J_2 - J_3;
\]
\[
\varepsilon_2^{(0)} = -J_1; \quad \varepsilon_3^{(0)} = -J_2; \quad \varepsilon_4^{(0)} = -J_3; \tag{3}
\]
\[
\varepsilon_5^{(0)} = -J_1 - J_2 + J_3; \quad \varepsilon_6^{(0)} = -3J_1 + 3J_2 - J_3.
\]
\[
\varepsilon_1^{(1)} = 0.5(J_1 - J_2 - J_3);
\]
\[
\varepsilon_2^{(1)} = 0.5(-J_1 - J_2 + J_3); \tag{4}
\]

3
\[ \varepsilon^{(1)}_3 = 0.5(-3J_1 + 3J_2 - J_3). \]

\[ \varepsilon^{(2)}_1 = J_1; \quad \varepsilon^{(2)}_2 = J_2; \quad \varepsilon^{(2)}_3 = J_3. \] (5)

\[ \varepsilon^{(3)}_1 = 0.5(3J_1 + 3J_2 + J_3). \] (6)

\[ \varepsilon^{(4)}_1 = 3J_1 + 3J_2 + J_3. \] (7)

In Eqs.(2-6) the upper index shows $S_z$ absolute value, the lower index numerates energy levels with the same $S_z$.

The comparative analysis of Eqs.(3,4) as well as Eqs.(6,7) immediately shows that eigenstates with $S_z = \pm 1$ or $S_z = \pm 3$ can not be the ground states. It results from Eqs.(3,5,7) that the eigenstates with $S_z = \pm 2$ can not be the ground states either.

Indeed, $\varepsilon^{(2)}_1 > \varepsilon^{(0)}_2$, if $J_1 > 0$. Further, if $J_1 < 0$, there is a competition between $\varepsilon^{(2)}_1$, $\varepsilon^{(0)}_i$ ($i = 1,6$) and $\varepsilon^{(4)}_1$. Assuming $J_1 = -1$ and writing the system of inequalities

\[
\begin{cases}
\varepsilon^{(0)}_i \geq -1 \quad (i = 1,6); \\
\varepsilon^{(4)}_1 \geq -1;
\end{cases}
\]

we get

\[
\begin{cases}
J_2 \in \emptyset; \\
J_3 \in \emptyset.
\end{cases}
\]

Hence, the energy levels with $\varepsilon^{(2)}_1$ can not be lowest.

Analogously, we have from Eqs.(3,5,7) the relations for $\varepsilon^{(2)}_2$ and $\varepsilon^{(2)}_3$,

- $\varepsilon^{(2)}_2 > \varepsilon^{(0)}_3$, if $J_2 > 0$, and $\varepsilon^{(2)}_2 > \varepsilon^{(0)}_6$ or $\varepsilon^{(2)}_2 > \varepsilon^{(4)}_1$, if $J_2 < 0$;

- $\varepsilon^{(2)}_3 > \varepsilon^{(0)}_4$, if $J_3 > 0$; and $\varepsilon^{(2)}_3 > \varepsilon^{(0)}_5$ or $\varepsilon^{(2)}_3 > \varepsilon^{(4)}_1$, if $J_3 < 0$.

Using Eqs.(3,7) we can find the "phase" boundaries between the ground states with $S_z = 0$ and $S_z = \pm 4$:

\[
J_3 = -J_1 - 2J_2; \quad J_3 = -3J_1 - 4J_2; \quad J_3 = -4J_1 - 3J_2;
\]

\[
J_3 = -1.5J_1 - 1.5J_2; \quad J_2 = -J_1; \quad J_3 = -3J_1. \] (8)

"Phase" diagram for the Ising cubic cluster with $s = 1/2$ is shown in Fig.2. We use the word "phase" for convenience to distinguish between regions with different ground states.

Now we consider the Ising cubic clusters with $s > 1/2$. The analysis for the classical spins ($s = \infty$) is the same as for the $s = 1/2$ since there are only two spin projections in both cases. The analytical examination of clusters with $s = 1, \frac{3}{2}, \frac{5}{2}$ is simple but cumbersome since there are much more unique sets of parameters $\langle H_{nn} \rangle$, $\langle H_{nnn} \rangle$, $\langle H_{nnnn} \rangle$ (66, 129 and 999 for the eigenstates with $S_z = 0$ and $s = 1, \frac{3}{2}, \frac{5}{2}$, correspondingly). So, we have performed
numerical calculations and found that for all values $s$ the "phase" diagram is exactly the same as shown in Fig.2.

It is interesting to compare the ground state properties of the Izing and Heisenberg cubic clusters. Below the case of $s = 1/2$ is described. For the Heisenberg cluster the zero-temperature two-spin correlation functions have been calculated using the relation $\omega_{ij} = \langle \phi_0 | \vec{S}_i \vec{S}_j | \phi_0 \rangle$, where $\phi_0$ is the ground-state eigenfunction. The cubic symmetry allows us to take into account only three correlation functions: $\omega_{01}$, $\omega_{02}$ and $\omega_{06}$.

First we assume $J_3 = 0$ in Eq.(1). There are four different cases to be considered: (a) all the interactions are ferromagnetic ($J_1 < 0$; $J_2/J_1 = \alpha > 0$); (b) all the interactions are antiferromagnetic ($J_1 > 0$; $\alpha > 0$); (c) the NN interactions are antiferromagnetic, the NNN interactions are ferromagnetic ($J_1 > 0$; $\alpha < 0$); (d) the NN interactions are ferromagnetic, the NNN interactions are antiferromagnetic ($J_1 < 0$; $\alpha < 0$).

The case (a) is trivial: the ground-state has $S = 4$, all correlation functions are equal to 0.25 irrespective of $\alpha$. In the case (b) for all values of $\alpha$ the ground state is non-magnetic ($S = 0$), but both signs and magnitudes of the correlation functions are sensitive to the $\alpha$ variation (Fig.3). For example, $\omega_{06}$ changes the sign at $\alpha = 0.50$ and has the highest value 0.25 at $\alpha = 1$. The latter point corresponds to the triplet dimerized state with the eigenfunction $\phi = (06)(17)(24)(35)$, where $(ij) = \frac{|i\downarrow j\uparrow + i\uparrow j\downarrow|}{\sqrt{2}}$. With $\alpha \to +\infty$, $\omega_{02}$ tends to $-0.25$, $\omega_{01}$ and $\omega_{06}$ approach zero (Fig.3).

In the case (c) the ground state is always non-magnetic ($S = 0$), NN and NNN interactions do not really compete (Fig.1), since the opposite direction of NN spins (0 and 1, 1 and 2, etc) is favorable for the identical direction of NNN spins (0 and 2, 1 and 3, etc). As a result, $\omega_{02}$ is always positive ($\approx 0.25$), $\omega_{01}$ and $\omega_{06}$ are negative and depend only slightly on $\alpha$.

The case (d) is the most interesting. Fig.4 shows the $\alpha$-dependence of the correlation functions. If $\alpha$ is small, all spins correlate ferromagnetically ($\omega_{01} = \omega_{02} = \omega_{06} = 0.25$). At $\alpha_4 = -0.33$ the correlation functions change suddenly, so that $\omega_{02}$ and $\omega_{06}$ become negative and $\omega_{01}$ is lowered by a factor 2.5. It should be noted that $|\alpha_4| = 1/3$ with an accuracy of $10^{-16}$. We found that if $|\alpha| < 1/3$ the ground state has $S = 4$. In the case of $|\alpha| > 1/3$ the ground state becomes non-magnetic ($S = 0$).

So far it has been assumed that $J_3 = 0$. If the NNNN interactions exist, an analysis becomes more intricate since two degrees of freedom appear ($\alpha$ and $\beta = J_3/J_1$). Fig.5a shows a "phase" diagram in the case of ferromagnetic NN interactions ($J_1 = -1$) for $-3 < \alpha < 3$, $-3 < \beta < 3$. The line AG separate regions with magnetic ($S = 4$) and non-magnetic ($S = 0$) ground states. The curve AG tends asymptotically to lines $J_2 = |J_1|$ and $J_3 = 3|J_1|$ (Fig.5a). Hence, if either $J_2 \geq |J_1|$ or $J_3 \geq 3|J_1|$ the ground state is always non-magnetic. Ferromagnetic correlations between spins, which exist in the magnetic "phase" in the case of $J_2 < 0$ and $J_3 < 0$, can be
destroyed by means of a gradual increasing of \( J_2 \) and/or \( J_3 \). Let us consider, for example, the case \( J_1 = J_2 < 0, \beta < 0 \). If \(|\beta| < 1.5\), the ground state is magnetic \((S = 4)\) and \(\omega_{01} = \omega_{02} = \omega_{06} = 0.25\). When \(|\beta| \) exceeds 1.5 the ground state becomes non-magnetic \((S=0)\). We found that the straight line \( BC \) (Fig.4a), which satisfies \( J_1 = J_2 = -(2/3) J_3 < 0, \) corresponds to a dimer ground state with the eigenfunction \( \phi_{0,d} = [06][17][24][35], \) where \( \{km\} = \frac{1}{\sqrt{s}}( \hat{t}_k \hat{v}_m - \hat{v}_m \hat{t}_k ) \). For the dimer ground state the correlation between the NN and NNN spins reduces to zero \((\omega_{01} = \omega_{02} = 0)\), the NNNN spins are coupled antiferromagnetically \((\omega_{06} = -0.75)\). An another specific non-magnetic ground state, corresponding to the line \( DE \) (Fig.4a), appears when \( J_1 = J_3 < 0 \). If \( \alpha < -0.66 \) the tetramerization takes place. Namely, the non-zero correlation exists between only the NNNN spins: \( \omega_{01} = \omega_{06} = 0; \omega_{02} \neq 0 \). The average value of \( \omega_{02} \) is equal to \(-0.25\) for the four-fold degenerate tetramerized ground state (see details below). Obviously, the non-magnetic tetramer or dimer ground states can be achieved also in a different way, simply in limiting cases \( J_2 \to +\infty \) or \( J_3 \to +\infty \).

The "phase" diagram for \( J_1 = +1 \) is shown in Fig.5b. The ground state has always \( S = 0 \) if \( \alpha > -1 \) or \( \beta > -3 \). The line \( KM \) tends asymptotically to lines \( J_2 = -J_1 \) and \( J_3 = -3 J_1 \) (Fig.5b) and serves as the boundary between magnetic \((S=4, \omega_{01} = \omega_{02} = \omega_{06} = 0.25)\) and non-magnetic \((S=0)\) ground states. The dimer ground state with the eigenfunction \( \phi_{0,d} \) occurs in case of \( \alpha = 1, \beta > 1 \). The tetramer ground state \((\omega_{01} = \omega_{06} = 0; \omega_{02} \neq 0)\) takes place if \( \beta = 1, \alpha > 1 \).

Now we can compare the "phase" diagrams for the Heisenberg and Izing models. "Phase" boundaries for the cubic \( s=1/2 \) Izing cluster are shown in Fig.5 by dotted lines. It is important that the Izing "phase" diagram can be used as a rough approximation for the Heisenberg model (Fig.5). In particular, the asymptotic straight lines for the curves \( AG \) and \( KM \) (Fig.5) coincide with the Izing "phase" boundaries. The same situation takes place in the case of \( s = 1/2 \).

We have found that the dimer or tetramer ground state appears only if \( \alpha = 1 \) or \( \beta = 1 \), respectively. This regularity can be explained in the following way. It is straightforward to show that \( H_{nn} = \hat{S}_{0257} \hat{S}_{1346} - H_{nmm} \) and \( H_{nnn} = 0.5( \hat{S}_{0257}^2 + \hat{S}_{1346}^2 ) - 4s(s+1) \), where \( \hat{S}_{0257} = \hat{S}_0 + \hat{S}_2 + \hat{S}_5 + \hat{S}_7, \hat{S}_{1346} = \hat{S}_1 + \hat{S}_3 + \hat{S}_4 + \hat{S}_6 \), \( s = 1/2 \).

Since \( \hat{S} = \hat{S}_{0257} + \hat{S}_{1346} \), we get for \( \alpha = 1 \)

\[
H = J_1[0.5S^2 - 3 + (\beta - 1)H_{nmm}].
\]  
(9)

We present Eq.(9) for \( s = 1/2 \), in the case of \( s > 1/2 \) the numerical parameters should be modified, but the structure of the the equation is universal.

Assuming \( J_1 > 0 \), it is evident from Eq.(9) that the dimerization can be favorable only for \( \beta > 1 \), because of \( \langle \phi_{0,d} | H_{nmm} | \phi_{0,d} \rangle = -3 < 0 \) and \( S = 0 \). If \( J_1 < 0 \), we have to compare \( \langle \phi_f | H | \phi_f \rangle \) and \( \langle \phi_{0,d} | H | \phi_{0,d} \rangle \), where \( \phi_f = \varphi_{255} \), and \( H \) is given by Eq.(9). Taking into account that \( \langle \phi_f | H_{nmm} | \phi_f \rangle = 1 \), we have the simple equation.
\[(0.5 \cdot 20 - 3) + 1 \cdot (\beta - 1) = -3 - 3(\beta - 1), \text{ which results to } \beta = -1.5.\]

In the case of \(\beta = 1\), Eq.(1) transforms to

\[H = J_1[S_{1346} + 0.5(\alpha - 1)] =\]

\[= J_1[0.5S^2 + 0.5(\alpha - 1)(S_{1346}^2 + S_{1346}^2) - 3\alpha].\]  \((10)\)

For all four eigenfunctions \(\phi_{t,i} (i = 1, 4)\) of the tetramerized ground state we have got

\[\langle \phi_{t,i}|S_{1346}^2|\phi_{t,i}\rangle = \langle \phi_{t,i}|S_{1346}^2|\phi_{t,i}\rangle = 0.\]

Since \(\langle \phi_f|S_{1346}^2|\phi_f\rangle = \langle \phi_f|S_{1346}^2|\phi_f\rangle = 6\), in the case of

\[J_1 < 0\]

the tetramer state has the lowest energy if \((0.5 \cdot 20) + 6 \cdot (\alpha - 1) - 3\alpha < -3\alpha\), which leads to \(\alpha < -\frac{3}{2}\).

Assuming \(J_1 > 0\), it is easily seen from Eq.(10) that the tetramer ground state is energetically preferable if \(\alpha > 1\). Otherwise, states with the non-zero averages of \(S_{0257}^2\) and \(S_{1346}^2\) are lowest.

The Hamiltonian in (10) commutes with \(S_{0257}^2\) and \(S_{1346}^2\). Hence \(\phi_{t,i}\) are the eigenfunctions of these operators with the eigenvalues \(S_{0257} = S_{1346} = 0\). To get more information about the tetramer ground state we have to introduce the dimer spin operator \(\vec{S}_{02} = \vec{S}_0 + \vec{S}_2\) with eigenfunctions \(\phi_{02}(S_{02}, M)\), which are defined by the equations

\[\vec{S}_{02}^2|\phi_{02}(S_{02}, M)\rangle = S_{02}(S_{02} + 1)|\phi_{02}(S_{02}, M)\rangle\]

and \(S_{02,z}|\phi_{02}(S_{02}, M)\rangle = M|\phi_{02}(S_{02}, M)\rangle\) \((S_{02} = 0; 1; M = 0; \pm 1)\). The similar relations are valid for the \(\vec{S}_{57}, \vec{S}_{13}\) and \(\vec{S}_{46}\) operators. We have found that

\[\langle \phi_{t,i}|S_{02,z}|\phi_{t,i}\rangle = \langle \phi_{t,i}|S_{57,z}|\phi_{t,i}\rangle = 0; i = 1, 4\]

\[\langle \phi_{t,i}|S_{02}^2|\phi_{t,i}\rangle = \langle \phi_{t,i}|S_{57}^2|\phi_{t,i}\rangle = \]

\[= \langle \phi_{t,i}|S_{13}^2|\phi_{t,i}\rangle = \langle \phi_{t,i}|S_{46}^2|\phi_{t,i}\rangle = 0;\]

\[\langle \phi_{t,1}|S_{02}^2|\phi_{t,1}\rangle = \langle \phi_{t,1}|S_{57}^2|\phi_{t,1}\rangle = 0;\]

\[\langle \phi_{t,2}|S_{02}^2|\phi_{t,2}\rangle = \langle \phi_{t,2}|S_{57}^2|\phi_{t,2}\rangle = 2;\]

\[\langle \phi_{t,3}|S_{02}^2|\phi_{t,3}\rangle = \langle \phi_{t,3}|S_{57}^2|\phi_{t,3}\rangle = 2 - \kappa;\]

\[\langle \phi_{t,4}|S_{02}^2|\phi_{t,4}\rangle = \langle \phi_{t,4}|S_{57}^2|\phi_{t,4}\rangle = 2 - \kappa,\]

\[\langle \phi_{t,3}|S_{02}^2|\phi_{t,3}\rangle = \langle \phi_{t,3}|S_{57}^2|\phi_{t,3}\rangle = 2 - \kappa,\]
where the factor $\kappa$ is fractional and $\alpha$-dependent. Explicit forms for $\phi_{t,3}$ and $\phi_{t,4}$ also depend on the $\alpha$ value. The functions $\phi_{t,1}$ and $\phi_{t,2}$ can be always written as

$$\phi_{t,1} = \phi_{02}(0,0)\phi_{57}(0,0)\phi_{13}(0,0)\phi_{46}(0,0);$$

$$\phi_{t,2} = \frac{1}{3}\left\{\phi_{02}(1,1)\phi_{57}(1,-1) + \phi_{02}(1,-1)\phi_{57}(1,1) - \phi_{02}(1,0)\phi_{57}(1,0)\right\} \times \left\{-\phi_{13}(1,0)\phi_{46}(1,0) + \phi_{13}(1,1)\phi_{46}(1,-1) + \phi_{46}(1,1)\phi_{13}(1,-1)\right\}.$$  

It is easy to check that $\langle \phi_{t,1} | \vec{S}_0 \vec{S}_2 | \phi_{t,1} \rangle = -0.75$; $\langle \phi_{t,2} | \vec{S}_0 \vec{S}_2 | \phi_{t,2} \rangle = 0.25$. Our calculations have showed also that always $\sum_{i=1}^{4} \langle \phi_{t,i} | \vec{S}_0 \vec{S}_2 | \phi_{t,i} \rangle = -1$, and the average value of $\omega_{02}$ for the tetramer state is equal to $-0.25$.

In conclusion, we have studied effects of competing exchange interactions on the ground state of the cubic Izing clusters with $s = \frac{1}{2}; 1; 3; \frac{5}{2}; \infty$. The “phase” diagram for all Izing clusters is universal. In case of $s = 1/2$ and $s = 1$ we have studied both Izing and Heisenberg clusters. For the Heisenberg $s = 1/2$ cluster it has been found that the ground state can be either magnetic with $S = 4$ or non-magnetic with $S = 0$. Intermediate values of the total spin $S$ are not realized for the ground state. For $s = 1/2$ the non-magnetic dimer ground state appears in two cases: if $J_1 = J_2 < 0$; $\beta < -\frac{3}{2}$ and if $J_1 = J_2 > 0$; $\beta > 1$. The tetramer four-fold degenerate ground state takes place if $J_1 = J_3 < 0$; $\alpha < -\frac{2}{3}$ and $J_1 = J_3 > 0$; $\alpha > 1$. The two-spin correlation functions are much more sensitive to $\alpha$ and $\beta$ changes than the total spin $S$ of the ground state. It is important that for $s = 1/2$ and $s = 1$ (and, probably, for higher spin values) the Izing “phase” diagram can be used as a rough approximation for the Heisenberg model.

1. L.Thomas, F.Lionti, R.Ballou, D.Gatteschi, R.Sessoli, and B.Barbara, Nature 383, 145 (1996), and references therein.
2. A.Muller, S.Sarkar, S.Q.N.Shah, H.Bogge, M.Schmidtmann, Sh.Sarkar, P.Kogerler, B.Hauptfleisch, A.X.Trautwein, and V.Schunemann, Angew.Chem.Int.Ed. 38 3238 (1999).
3. B.Pilawa and J.Schuhmacher, J.Phys.: Condensed Mater. 8 1539 (1996).
4. A.Bencini and D.Gatteschi, Electron Paramagnetic Resonance of exchange coupled systems (Springer, Berlin, Heidelberg), 1990.
FIG. 1. A sketch of a cubic cluster with eight spins.

FIG. 2. The Izing cubic cluster. Dotted lines show "phase" boundaries between the ground states with $S_{z,\text{max}} = \pm 8$ for $s = 1/2$, $\pm 8$ for $s = 1$, etc.) and $S_z = 0$.

FIG. 3. The Heisenberg cluster with $s = 1/2$. The $\alpha$-dependence of the two-spin correlation functions: $J_1 > 0$; $J_3 = 0$.

FIG. 4. The Heisenberg cluster with $s = 1/2$. The $\alpha$-dependence of the two-spin correlation functions: $J_1 < 0$; $J_3 = 0$.

FIG. 5. The Heisenberg cluster with $s = 1/2$. "Phase" diagrams for (a) $J_1 < 0$; $-3 < \alpha < 3$; $-3.5 < \beta < 3$, and (b) $J_1 > 0$; $-3.5 < \alpha < 2$; $-5.5 < \beta < 2$. Dotted lines show boundaries between the ground states with $S_z = \pm 4$ and $S_z = 0$ for the Izing model.
\[ J_3 = -3J_1 \]

\[ S_z, \text{max} \]

\[ J_1 = -1 \]

\[ J_3 = -2J_2 - J_1 \]

\[ J_2 = -J_1 \]

\[ S_z = 0 \]

\[ J_1 = 1 \]

\[ J_3 = -3J_1 \]

\[ J_2 = -J_1 \]

\[ S_z, \text{max} \]
two-spin correlation functions

$J_1 > 0$
$\alpha > 0$
$J_3 = 0$

$\omega_{01}$
$\omega_{02}$
$\omega_{06}$
two-spin correlation functions

\[ J_1 < -1 \]
\[ \alpha < 0 \]
\[ J_3 = 0 \]
dimmerization line
($\omega_{06} = -0.75, \omega_{01}=\omega_{02} = 0$)

non-magnetic ground state
($S=0$)

tetramerization line
($\omega_{02} \neq 0, \omega_{01}=\omega_{06} = 0$)
magnetic ground state
($S=4, \omega_{01}=\omega_{02}=\omega_{06} =0.25$)

$J_1 < 0$

$J_1 > 0$

(a)

(b)