A Possible Origin of the Low-Temperature Curie Law of the Spin Doughnut Mo\textsubscript{75}V\textsubscript{20}

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Abstract. We study a spin-1/2 frustrated magnetic cluster Mo\textsubscript{75}V\textsubscript{20}, whose possible Hamiltonian is

\[ H_{SD} = J \sum_{i=1}^{10} S_{2i-1} \cdot S_{2i+1} + J' \sum_{i=1}^{20} S_i \cdot S_{i+1} + J'' \sum_{i=1}^{10} S_{2i} \cdot S_{2i+4}. \]

The \( J \)- and \( J'' \)-bonds, respectively, form a ten-spin ring and two five-spin rings, and the five-spin rings are coupled to the ten-spin ring by the \( J' \)-bonds so as to form isosceles triangles of one \( J \)-bond and two \( J' \)-bonds. It is shown that experimental susceptibility, accompanied by low-temperature Curie law, is well reproduced by \( J = 388 \text{ K}, J' = 163 \text{ K} \) and \( J'' = 81 \text{ K} \).

We develop a perturbation theory to understand why the stronger \( J' \)-bonds does not wash out the low-temperature Curie law due to the doublet behavior of five-spin rings constructed by the weaker \( J'' \)-bonds. Calculated results of temperature dependence of specific heat under small magnetic fields are also presented.

1. Introduction

A type of giant molybdenum-oxide-based spherical clusters has provided a new direction to investigation of frustrated spin systems [1-3]. Typical examples are Mo\textsubscript{72}Fe\textsubscript{30} [1] and Mo\textsubscript{72}V\textsubscript{30} [2,3], which are called quantum-spin icosidodecahedrons or spin balls.

Müller \textit{et al.} synthesized a frustrated magnetic cluster Mo\textsubscript{75}V\textsubscript{20} [2], whose structure is obtained by replacing ten V\textsuperscript{4+} ions at the top and bottom of the spin ball Mo\textsubscript{72}V\textsubscript{30} with neutrality ions. The term \textit{spin doughnut} is often used to express Mo\textsubscript{75}V\textsubscript{20} (see Figure 1). Two of present authors calculated the susceptibility for \( H_{SD} (= H_{L=20}) \) to reproduce the experimental susceptibility [4], by using the finite-temperature Lanczos method [5]. Assuming the Landé factor of \( g = 2 \), they obtained \( J = 388 \text{ K}, J' = 0.42J \) and \( J'' = 0.21J \). The estimated impurity concentrations were 1.3% for the fresh sample and 4.0% for the aged sample. As seen in Figure 2(a), the agreement
between the calculated and experimental results is rather satisfactory. They also found that the calculated result of specific heat \(C\) was approximately given by the sum of one ten-spin ring formed by \(J\)-bonds and two five-spin rings formed by \(J''\)-bonds except for very low temperatures (see Figure 2(b)), which indicates the low-temperature Curie law originates from the doublet behavior of the five-spin rings. It is interesting to note that the stronger \(J'\)-bonds do not prevent the five-spin rings constructed by weaker \(J''\)-bonds from showing the doublet behavior. In this work, we develop a perturbation theory to understand why the effect of \(J'\)-bonds is so small in this system. Also, we present calculated results of specific heat under magnetic fields, which may be useful to check our theory experimentally.

2. Perturbation Theory

At \(J'' = 0\) the ground states has sixteen-fold degeneration, in which there are four singlet states and four triplet states. When \(J' > 0\), this degeneration is resolved and we have an unique singlet ground state. The energy splitting by \(J'\)-bonds is expected so small that there appears the low-temperature Curie law due to doublet behavior of the five-spin rings. In Ref. [4], the energy splitting as functions of \(a \equiv J' / J\) was studied by using the numerical diagonalization method and it was confirmed that the width of the splitting does not grows even if \(J'\) becomes to be larger than \(J''\).

It is interesting to calculate the energies of those 16 states by using the perturbation expansion method. In order to perform analytic perturbation calculations, we use a 12-site counterpart \(H_{L=12}\), which contains one six-spin ring and two three-spin rings, instead of \(H_{L=20}\). First, we calculate the energies of the 16 states as functions of \(a \equiv J' / J\) to check the validity of the use of \(H_{L=12}\), where we set \(b \equiv J'' / J = 0.21\). The results in Figure 3(a) show that the energy splitting is very small even for \(J' > J''\), which is qualitatively same as that for \(H_{L=20}\) in Ref. [4]. We plot \((E_a - E_0) / J a^2\) against \(a\) in Figure 3(b), where the data for \(a > 0\) are obtained by numerical diagonalization and the values at \(a = 0\) are calculated by the perturbation expansion described below. This result shows that the width of energy splitting is dominated by the second order terms in \(a\).

Now, we turn to the second order perturbation calculation. Our unperturbed Hamiltonian is \(H_{L=12}^0 = H_c + H_t + H_b\), where \(H_c \equiv J \sum_{i=1}^{6} S_{2i-1} \cdot S_{2i+1}\) represents the six-spin ring at the center of spin doughnut and \(H_t \equiv J'' \sum_{i=1,3,5} S_{2i} \cdot S_{2i+4}\), \(H_b \equiv J'' \sum_{i=2,4,6} S_{2i} \cdot S_{2i+4}\) represent the three-spin rings at the top and bottom of spin doughnut. The perturbation Hamiltonian is
\[ H'_{L=12} = J' \sum_{i=1}^{12} S_i \cdot S_{i+1}. \]

We denote the doublet ground states of \( H_t \) (\( H_b \)) as \( |\phi_k^{(m,k)}\rangle \) (\( |\phi_k^{(m,k)}\rangle \)) with total \( S^z \) of \( m = \pm 1/2 \) and crystal momentum of \( k = \pm 2\pi/3 \), whose energy eigenvalue is \(-3J''/4\). Also, the singlet ground state of \( H_c \) is denoted by \( |\phi_c\rangle \), whose energy eigenvalue is \(-(2 + \sqrt{13})J/2 \) and crystal momentum of the rotation by \( 2\pi/3 \) is given by \( k = 0 \). Ground states of \( H'_{L=12} \) can be written as \( |\tilde{\Psi}_{k,k'}^{(m,m')}\rangle = |\phi_k^{(m,k)}\rangle \otimes |\phi_k^{(m',k')}\rangle \otimes |\phi_c\rangle \), whose total crystal momentum \( K \) is given by \( K = k + k' \). Setting \( m = m' \), we have triplet states, \( |\Psi_{k,k'}^{(m,m)}\rangle \). We write these triplet states as \( |\Psi_{k,k'}^{(1/2,1/2)}_{\pm 2\pi/3,\pm 2\pi/3}\rangle \equiv |t_{\pm 2\pi/3}\rangle \) and \( |\Psi_{k,k'}^{(1/2,1/2)}_{\pm 2\pi/3,\mp 2\pi/3}\rangle \equiv |t_{0\pm}\rangle \), where the suffixes in \( |t_{\pm 2\pi/3}\rangle \) and \( |t_{0\pm}\rangle \) represent values of total crystal momentum \( K \). Singlet states can be constructed by \( [[|\Psi_{k,k'}^{(1/2,-1/2)}_{\mp 2\pi/3,\pm 2\pi/3}\rangle - |\Psi_{k,k'}^{(-1/2,1/2)}_{\pm 2\pi/3,\mp 2\pi/3}\rangle]/\sqrt{2} \equiv |\tilde{\Psi}_{k,k'}\rangle \), and we define \( |\tilde{\Psi}_{\pm 2\pi/3,\pm 2\pi/3}\rangle \equiv |s_{\pm 2\pi/3}\rangle \) and \( |\tilde{\Psi}_{\pm 2\pi/3,\mp 2\pi/3}\rangle \equiv |s_{0\pm}\rangle \).

The diagonal element of the effective Hamiltonian \( H_{\text{eff}} \) is calculated as follows:

\[
\langle \varphi | H_{\text{eff}} | \varphi \rangle \simeq \frac{2 + \sqrt{13} + 3b}{2} - \frac{3[F(b) + F(0)]}{13 - 2\sqrt{13}} Ja^2 \quad \text{for} \quad \varphi = s_{0\pm}, s_{\pm 2\pi/3}, t_{0\pm}, t_{\pm 2\pi/3},
\]

(2)

where

\[
F(b) = \frac{1}{\sqrt{13} + 3b} + \frac{c_1}{3 + 2\sqrt{13} - \sqrt{17} + 6b} + \frac{c_2}{3 + 2\sqrt{13} + \sqrt{17} + 6b}
\]

(3)

with \( c_1 = (-13 + 3\sqrt{13} + 3\sqrt{17} - 2\sqrt{22})/2(17 - 3\sqrt{17}) \) and \( c_2 = (13 - 3\sqrt{13} + 3\sqrt{17} - \sqrt{22})/2(17 + 3\sqrt{17}) \). Equation (2) with \( b = 0.21 \) gives \( \lim_{a \to 0} (E_a - E_0)/Ja^2 = -0.634 \) for \( |s_{\pm 2\pi/3}\rangle \) and \( |t_{0\pm}\rangle \). The off-diagonal element for the singlet sector is

\[
\langle s_{0\pm} | H_{\text{eff}} | s_{0\mp} \rangle \simeq \frac{3Ja^2}{2(13 - 2\sqrt{13})} \left[ \frac{2}{\sqrt{13}} - \frac{c_1}{3 + 2\sqrt{13} - \sqrt{17}} - \frac{c_2}{3 + 2\sqrt{13} + \sqrt{17}} \right],
\]

(4)

which leads to \( \lim_{a \to 0} (E_a - E_0)/Ja^2 = -0.577 \) and \( -0.692 \) at \( b = 0.21 \). For the triplet sector, we have

\[
\langle t_{0\pm} | H_{\text{eff}} | t_{0\mp} \rangle \simeq \frac{Ja^2}{13 - 2\sqrt{13}} \left[ \frac{1}{\sqrt{13}} + \frac{c_1}{3 + 2\sqrt{13} - \sqrt{17}} + \frac{c_2}{3 + 2\sqrt{13} + \sqrt{17}} \right],
\]

(5)

which gives \( \lim_{a \to 0} (E_a - E_0)/Ja^2 = -0.615 \) and \( -0.654 \).
Our results of perturbation expansion give the plotted points at $a = 0$ in Figure 3(b), and they are consistent with the results of numerical diagonalization for $a > 0$. The smallness of energy splitting is coming from the fact that the off-diagonal elements of the effective Hamiltonian are so small, i.e., $\langle s_0^+ | H_{\text{eff}} | s_0^- \rangle / J a^2 \approx 0.058$ and $\langle t_0^+ | H_{\text{eff}} | t_0^- \rangle / J a^2 \approx 0.019$. The detail of the perturbation calculation will be published elsewhere.

3. Specific Heat under Small Magnetic Fields

It is also interesting to calculate the low-temperature specific heat under magnetic fields, because both the singlet and triplet states contribute the lowest temperature peak of the specific heat and the energy differences are so small that modest values of the magnetic field can get the specific heat to change. The calculated specific heat, $C(T)$, under magnetic field below than 5 T are shown in Figure 4, where we find visible magnetic field dependence as expected. Unfortunately, experimental studies on the low-temperature specific heat of Mo$_{75}$V$_{20}$ have not done yet. We hope our calculated results serve as a guide to such experimental studies.

![Figure 4](image-url)

Figure 4. Specific heat under magnetic fields $H = 0 \sim 5$ T for $\mathcal{H}_{L=20}$ with $J = 388$ K, $J' = 163$ K and $J'' = 81$ K.

4. Summary

We have proposed a scenario to understand the low-temperature Curie law in the susceptibility of Mo$_{75}$V$_{20}$. In our theory, the doublet behavior of the five-spin ring is ascribed as the cause of the low-temperature Curie law. Our theory predicts that the low-temperature Curie law ends around $T = 1$ K together with the lowest temperature peak of the specific heat, and the form of the lowest temperature peak of the specific heat can be affected by modest values of magnetic field. It is desirable that these predictions be verified experimentally, thereby validating of our theory.

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