Theoretical Study of Quantum Spin Icosidodecahedron \((S = 1/2)\) with Next-Nearest Neighbor Interactions and Analysis of Experimental Susceptibility for \(\text{Mo}_{72}\text{V}_{30}\)

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Abstract. We study integrated density of states (DOS) and thermodynamic properties for the \(S = 1/2\) quantum spin icosidodecahedron, using a numerical method for calculating an eigenvalue distribution function. For the ideal quantum spin icosidodecahedron with next-nearest neighbor interactions, we find that there exist many singlet states before the first triplet state, which is an evidence of the resonating valence bond (RVB) state, and the experimental susceptibilities of \(\text{Mo}_{72}\text{V}_{30}\) measured by Müller et al. and Botar et al. can not be reproduced within the ideal model. Because \(\text{V}^{4+}\) ions are on vertices of a slightly distorted icosidodecahedron in \(\text{Mo}_{72}\text{V}_{30}\), we study the distorted version of the model and find that agreement between theoretical and experimental susceptibilities is improved. For this distorted model, there exist about ten singlet states before the first triplet state.

1. Introduction

Quantum spin icosidodecahedrons have attracted great attentions, since experimental systems were synthesized recently. The icosidodecahedron is a polygon which is formed by 20 triangles and 12 pentagons (see the inset in Figure 1(a)). The \(S = 5/2\) icosidodecahedron \(\text{Mo}_{72}\text{Fe}_{30}\) has been studied both theoretically and experimentally. Exler and Schnack studied the low-lying energy spectrum for this molecule using the density-matrix renormalization group technique [1]. The \(\text{Mo}_{72}\text{Fe}_{30}\) features 30 \(\text{Fe}^{3+}\) ions on the vertices of an icosidodecahedron that interact via ideal nearest-neighbor antiferromagnetic (AF) exchange \((J = 1.57 \text{ K})\) [2]. We here focus on the case of \(S = 1/2\) quantum spin icosidodecahedron, because the lattice structure of corner-sharing triangles, which is similar to the Kagomé lattice, may lead to the short-range RVB states [3]. Mambrini and Mila studied the low-lying energy spectrum for the \(S = 1/2\) Kagomé lattice by the variational technique, and obtained that the number of singlet states in the spin gap is \(\alpha N\) for \(N\)-site Kagomé lattice, where \(\alpha = 1.15 \sim 1.18\) [3].

In this paper, to study the integrated DOS and thermodynamic property of the 30 spin system, we use a numerical method for calculating the eigenvalue distribution function, \(\rho(\omega) = -\frac{1}{\pi} \sum_n \text{Im}(n|G(\omega + i0)|n)\), where \(G(z) = (z - \mathcal{H})^{-1}\) is Green’s function and \(\{|n\}\) is a set of basis vectors [4]. In the present method, the sum over \(\{|n\}\) is estimated by sampling random vectors \(\{|\phi\}\) in the corresponding Hilbert space, and \(\langle \phi | G(z) | \phi \rangle\) is calculated by using its continued...
fraction form with Lanczos coefficients of $\mathcal{H}$ obtained via the Lanczos procedure starting from an initial vector $|\phi\rangle$.

We study the ideal icosidodecahedron model with next-nearest neighbor interactions in §2, and show that this model has the RVB states. Recently, Müller et al. and Botar et al. measured independently the susceptibility of Mo$_72$V$_{30}$ [5, 6]. Müller et al. evaluated the nearest-neighbor AF exchange from the high-temperature susceptibility data by using the quantum Monte Carlo method and obtained $J = 245$ K. Our calculated results show that the ideal icosidodecahedron model does not reproduce the experimental data at low temperatures. To analyze experimental susceptibility, we introduce the distorted nearest-neighbor icosidodecahedron model in §3. We summarize our results obtained in this paper in the final section.

2. Ideal Icosidodecahedron Model

We first consider the Heisenberg antiferromagnet on the icosidodecahedron with next-nearest neighbor interactions. We can write the Hamiltonian as

$$\mathcal{H} = J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + J' \sum_{\langle\langle i,j \rangle\rangle} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1)$$

where the first and second sums run over nearest and next-nearest neighbor pairs. A schematic representation of this Hamiltonian is given in the inset of Figure 1(a). Note that there are five next-nearest neighbor bonds, which form shape of a star, on each pentagon. In Figure 1(a), we show the integrated DOS as a function of excitation energy normalized by the triplet-excitation gap $\Delta_t$. The value of the triplet-excitation gap is calculated as $\Delta_t \simeq 0.218J$ for $J' = 0$, and this result is consistent with the recent exact-diagonalization study [7]. The triplet-excitation gap is enlarged to $\Delta_t \simeq 0.291J$ at $J' = 0.1J$. We find in Figure 1(a) that the integrated DOS shows a step-like feature and there exist many singlet states before the first triplet state. It has been known that the existence of many singlet states before the first triplet excitation is characteristic behavior of RVB state. For $J' = 0$, we have about 80 singlet states, which is comparable to $1.16^{30} \simeq 86$ for the 30-site $S = 1/2$ Kagomé lattice [3]. The number of singlet states is decreasing from 80 to 50 as $J'$ is increasing from 0 to 0.1J.

Müller et al. measured the experimental susceptibility for Mo$_72$V$_{30}$ and used the quantum Monte Carlo method to evaluate $J$ and the Landé $g$-factor as $J = 245$ K and $g = 1.95$ on the basis of the present model with $J' = 0$ [5]. However, due to the negative sign problem, their

![Figure 1](image.png)

**Figure 1.** Calculated results of (a) integrated DOS and (b) magnetic susceptibility for the ideal icosidodecahedron model.
susceptibility calculation is limited only at $T > 120$ K. Our calculation method, the finite-temperature Lanczos method [4], has been known to give reliable result for thermodynamic quantities at all temperatures. The calculated susceptibility are shown in Figure 1(b), together with the experimental result by Müller et al. We set $g = 1.95$ for all $J'$, and choose the value of $J$ to reproduce the experimental susceptibility at high temperatures. We find in Figure 1(b) that the ideal icosidodecahedron model with next-nearest neighbor couplings does not reproduce the experimental data at low temperatures. The experimental data have a lower peak-temperature ($\approx 10$ K) and a smaller spin gap, compared to the ideal icosidodecahedron model.

Before closing this section, we consider the classical counterpart of eq. (1) and study how the classical grand-state degeneracy at $J' = 0$ is affected by the next-nearest neighbor interactions. For the case of $J' = 0$ Rousoschatzakis et al. pointed out that the classical grand-state manifold consists of coplanar configurations with each of the triangles being in a 120$^\circ$ structure [7]. The grand-state degeneracy at $J' = 0$ comes from way of vertex three-colorings, whose number is sixty [7], in addition to the global O(3) rotations. (An example of the vertex three-colorings is given in Figure 2 of Reference 8.) Color of three vertices on a triangle must be different from each other to achieve a 120$^\circ$ structure, so two vertices on any edges of icosidodecahedron have different colors. When we turn to a pentagon, it is noticed that two of the five bonds forming the star on the pentagon connect vertices with the same color and the other three connect those with different colors, which leads to $\sum_{(i,j)} S_i \cdot S_j = \text{constant}$ in the classical grand-state manifold. Therefore, when we introduce the next-nearest neighbor coupling term as a perturbation, it does not affect the classical grand-state degeneracy at $J' = 0$.

3. Distorted Icosidodecahedron Model for Mo$\text{7}_2\text{V}_{30}$

In the previous section we have found that the ideal icosidodecahedron model does not reproduce the experimental susceptibility of Mo$\text{7}_2\text{V}_{30}$. In this section, taking into account the $C_{5v}$ symmetry of Mo$\text{7}_2\text{V}_{30}$, we introduce the distorted icosidodecahedron model which has the four kinds nearest-neighbor interactions (see Figure 2(a)). Because the length of the $J_1$-bond is shorter than the other bonds, we assume $J_1$ is the largest exchange coupling. As for this extension of model Hamiltonian, we refer a theoretical work on a related material Mo$\text{7}_2\text{V}_{20}$ [9]. This material is obtained by replacing ten $V^{4+}$ ions at the top and bottom of Mo$\text{7}_2\text{V}_{30}$ with neutrality ions [10], and is often called spin doughnut. We have a model of the spin doughnut by omitting the $J_2$- and $J_4$-bonds from the present model. In the above mentioned work [9], the authors presented a theoretical explanation of the low-temperature Curie law in the experimental susceptibility, and discussed that $J_2 < 0.6J_1$ is necessary to get the low-temperature Curie law.

We turn to susceptibility calculations of the distorted icosidodecahedron model. Two typical examples of our calculated susceptibilities are shown in Figure 2(b), where dashed and dash-dotted lines denote our theoretical results for (i) $J_2 = 0.7J_1$, $J_3 = 0.4J_1$, $J_4 = 0.7J_1$ and (ii) $J_2 = 0.6J_1$, $J_3 = 0.5J_1$, $J_4 = 0.3J_1$, where we set $g = 1.95$. As seen in the low-temperature behavior of calculated susceptibilities, the spin gaps are so small: $\Delta_6 \simeq 0.004J_1$ for case (i) and $\Delta_1 \simeq 0.005J_1$ for case (ii). We also found that case (i) reproduces the overall behavior of the experimental result by Müller et al. and case (ii) fails in reproducing the experiment at low-temperatures like the ideal icosidodecahedron model. Therefore, we concentrate on case (i) below. There exist about ten low-energy singlet states before the first triplet excitation in case (i) of the distorted model. However, in our opinion, it may be difficult to ascribe the RVB state as the cause of the low-energy singlet states, because the distorted model is not uniform so singlet bonds are expected to favor specific bonds.

Botar et al. independently synthesized another sample of Mo$\text{7}_2\text{V}_{30}$ with somewhat different building blocks from the sample synthesized by Müller et al. They measured the experimental susceptibility [6], which is shown in Figure 2(b) as small white circles. Their experimental susceptibility has a maximum peak at $T \simeq 11$ K similar to the data measured by Müller et al.
and shows spin gap as small as that of Müller et al. However, there is a serious discrepancy in magnitude of susceptibility between the results of two groups. One of the reasons is ambiguity in correction of inherent diamagnetism and temperature-independent paramagnetism [11]. In order to understand the magnetism of Mo$_{72}$V$_{30}$, microscopic measurements are desired to clarify the low-energy level structure. We hope the finding of low-energy singlet states in this paper stimulate experimental studies along this line.

4. Summary
In this paper, we have found the characteristic behavior of RVB states for the $S = 1/2$ ideal icosidodecahedron model. It has been shown that the ideal icosidodecahedron model does not reproduce the experimental susceptibilities of Mo$_{72}$V$_{30}$. As a more realistic model of Mo$_{72}$V$_{30}$ we have introduced the distorted icosidodecahedron model. Agreement between theoretical and experimental susceptibilities is improved, but it is not conclusive. It is also found that the susceptibility of the distorted icosidodecahedron model is sensitive to exchange parameters. To understand magnetic properties of Mo$_{72}$V$_{30}$, in any case, we have to make detail examinations from both experimental and theoretical sides.

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