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# Heisenberg model of an {Fe8}-cubane cluster

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An analysis of the measured magnetic susceptibility of the recently synthesized magnetic molecule $\{Fe_8\}$-cubane ($[Fe_8^{III}O_4(sao)_8(py)_4]$) leads to a detailed proposal based on an isotropic Heisenberg model for the interactions between the eight $Fe^{III}$ ions. In the theoretical model, the magnetic ions are situated on the vertices of a cube with one exchange constant linking nearest neighbors and a second exchange constant (appearing as a single diagonal across each of the six faces of the cube) linking four of the eight ions on alternate sites. Excellent agreement between the experimental and theoretical susceptibility data is achieved, thereby providing estimates for the numerical values of the two exchange constants. Independent tests of the theoretical model are proposed in terms of inelastic neutron scattering and high-field magnetic susceptibility measurements at low temperatures that would probe the predicted low-lying magnetic energy levels of the system.

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## I. INTRODUCTION

Since the early 1990s, the field of molecular nanomagnets has blossomed, and the number of different species that have been synthesized is large and increasing rapidly.[1–6] Magnetic molecules are of great interest since they provide a very convenient platform for exploring fundamental issues in nanomagnetism. Heisenberg exchange interactions between the spins of magnetic ions that are embedded in each molecule give rise to a discrete spectrum of magnetic energy levels. Moreover, because the magnetic interactions (dipole-dipole) between molecules is generally very small as compared to intramolecular exchange interactions, a crystal sample may be regarded as a macroscopic assembly of independent identical quantum nanomagnets.

Recently,[7] it has been demonstrated that, by a new approach based on microwave heating, it is possible to synthesize large polymetallic transition-metal cluster compounds that are impossible to produce under ambient reaction conditions. A successful product of this process is the compound given by the chemical formula $[Fe_8^{III}O_4(sao)_8(py)_4]$, which we abbreviate as $\{Fe_8\}$ cubane. In bulk samples, the dominant magnetic interactions are expected to be intracluster exchange interactions between the eight $Fe^{III}$ ions (spin 5/2). The major goal of this Brief Report is to develop a microscopic model for this system that is based on isotropic intracluster interactions. Using such a model, we find that we can indeed accurately reproduce our experimental data for the temperature-dependent weak-field magnetic susceptibility. Furthermore, as part of the theoretical procedure of calculating the susceptibility, we also calculate the magnetic energy levels of the system. The spacings of these energy levels can be probed by inelastic neutron scattering and high-field magnetic susceptibility measurements at low temperatures. Such future measurements would provide additional quantitative tests of our present theoretical model.

The ligand used for the preparation of the $\{Fe_8\}$ cubane is salicylaldoxime ($saoH_2$; IUPAC name: 2-hydroxybenzaldehyde oxime). This ligand belongs to the family of phenolic oximes which have been used extensively for the preparation of polymetallic cluster compounds and as anticorrosive additives in protective coatings.[8] Molecular clusters of $Fe^{III}$ ranging in nuclearity from 2 to 30 have been reported, and the reasons for their synthesis include the following: the need for biological models for the iron-oxo core of the iron storage protein ferritin,[9] the study of biomineralization processes that form iron-oxo minerals,[10] the study of single-molecule magnetism behavior and associated quantum effects,[11] and the study of spin frustration.[12]

## II. EXPERIMENTAL SUSCEPTIBILITY

Our measurements of the weak-field molar susceptibility, $\chi = M/H$, were made using a superconducting quantum interference device magnetometer in the temperature range 1.8–300 K in a fixed magnetic field $H = 0.1$ T. These data are shown in Fig. 1, where the most noteworthy features are a shallow minimum at approximately 7 K and a monotonic increase with increasing $T$ to the highest measured temperature. Two important inferences follow from an inspection of Fig. 2, where the corresponding values of $T\chi$ are shown. First, we note that, on the low-temperature side, the very small limiting value, $T\chi < 0.01$ cm$^3$ K/mol, strongly suggests that the total angular momentum quantum number of

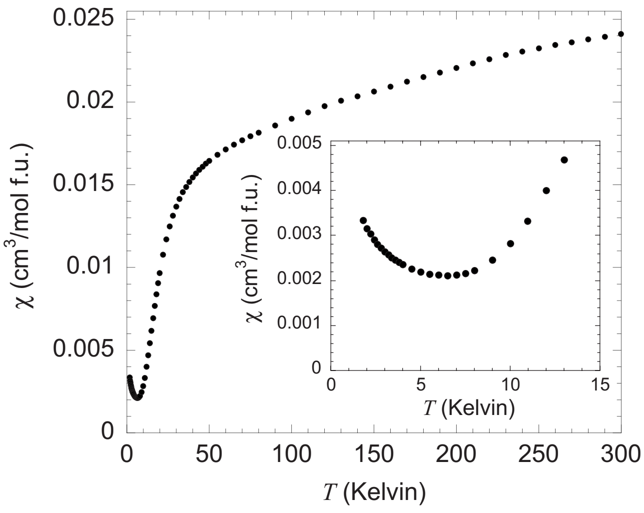

FIG. 1. Experimental values of the molar susceptibility $\chi$ vs temperature $T$ for $H=0.1$ T. The low-temperature data are shown in the inset.

the ground state is given by $S=0$. This follows from the fact that the value of $T\chi$ in the limit $T\to 0$ is given by $N_A g^2\mu_B^2 S(S+1)/(3k_B)$ for a ground state that has total angular momentum $S$, where $N_A$ is Avogadro's number, $g$ is the spectroscopic splitting factor, $\mu_B$ is the Bohr magneton, and $k_B$ is Boltzmann's constant. In particular, for an $S=1$ ground state and with $g=2$,[14] the limiting low-temperature value is $T\chi \approx 1$ cm$^3$ K/mol, which is larger than the observed value by more than 2 orders of magnitude. The second inference from Fig. 2 is that, on the high-temperature side, $T\chi$ has only reached the value of 7.2 cm$^3$ K/mol by 300 K, compared to $8N_A g^2\mu_B^2 s(s+1)/(3k_B)\approx 35$ cm$^3$ K/mol, which is the limiting (Curie law) high-temperature value for eight $s=5/2$ Fe$^{\text{III}}$ ions. This strongly suggests that the dominant interaction strength (all energies henceforth are stated in units of Kelvin) in this system is considerably larger than 10 K. It is thus reasonable to expect that the energy gap between the ground state and the lowest $S=1$ level is of the same order of magnitude, with the consequence that the intrinsic contribution to $\chi(T)$—provided by the {Fe$_8$}-cubane molecules—can be expected to be negligible below about 10 K.

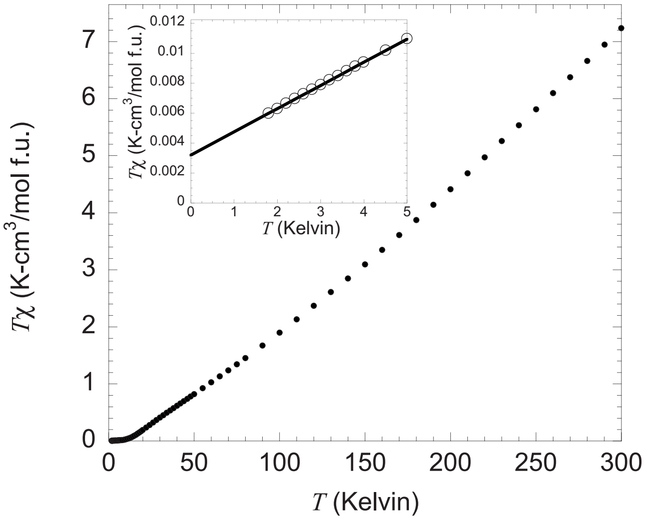

FIG. 2. Temperature dependence of $T\chi$ for the data shown in Fig. 1. The low-temperature data are shown in the inset (symbols), along with the function (solid line) that describes the extrinsic contribution to $\chi$, as described in the text.

Given an $S=0$ ground state, the simplest explanation for the weak rise in the experimental $\chi(T)$ data upon cooling below 7 K is that a small concentration of detached individual Fe$^{\text{III}}$ ions is present in the sample. Such detached ions would provide a contribution to the magnetization $M$ that is proportional to the Brillouin function $B_{5/2}(gs\mu_B H/k_B T)$, which, in turn, is proportional to its argument in the regime $gs\mu_B H/k_B T \ll 1$. In particular, with the weak measuring field of $H=0.1$ T and for the temperature range $T>2$ K, this inequality is satisfied well. Thus, this contribution to the magnetization can be accurately described by the simpler function $cH/T$, where $c$ is proportional to the concentration of detached Fe$^{\text{III}}$ ions. The resulting contribution to $\chi$ is therefore given by $c/T$, so the value of $c$ can be inferred by simply extrapolating the experimental $T\chi$ data to the $T=0$ limit. This is shown in the inset of Fig. 2 and yields the value $c=0.0032$ cm$^3$ K/mol, which corresponds to approximately seven detached Fe$^{\text{III}}$ ions per $10^4$ {Fe$_8$}-cubane molecules.

There is another expected extrinsic contribution to $\chi$ (due to diamagnetism and Van Vleck paramagnetism) that is temperature independent, to be denoted by $\chi_{\text{TI}}$. In fact, we suggest that this is the source of the linear behavior of $T\chi$ that is visible for $T<5$ K (see the inset of Fig. 2) where, as remarked above, the intrinsic contribution to $T\chi$—provided by the {Fe$_8$}-cubane molecules—is expected to be vanishingly small. Using the slope of the low-temperature $T\chi$ versus $T$ data provides the value $\chi_{\text{TI}}=0.001\,55$ cm$^3$/mol. The diamagnetic correction from Pascal's constants is of the order $-10^{-3}$ cm$^3$/mol, implying that the Van Vleck paramagnetism is approximately $2.5\times 10^{-3}$ cm$^3$/mol, which is consistent with the values that have been employed for similar clusters.

Having determined the values of $c$ and $\chi_{\text{TI}}$, which are the two parameters that define the extrinsic contributions to $\chi$, we assume in the following that the experimental susceptibility over the complete temperature range 1.8–300 K is given by

$$\chi(T)=\chi_i(T)+\chi_{\text{TI}}+\frac{c}{T}, \qquad (1)$$

where $\chi_i(T)$ is the intrinsic contribution of the interacting {Fe$_8$}-cubane spin system. The function $\chi_i(T)$ is calculated in the following section using an isotropic Heisenberg model after we introduce a specific scenario for the couplings between the spins. The parameters of the model Hamiltonian will be determined by optimizing the fit between the results for $\chi(T)$ obtained by theory and experiment.

## III. THEORETICAL MODEL

As reported previously in Ref. 7, the geometrical structure of the eight Fe$^{\text{III}}$ ions of the {Fe$_8$}-cubane molecule is as

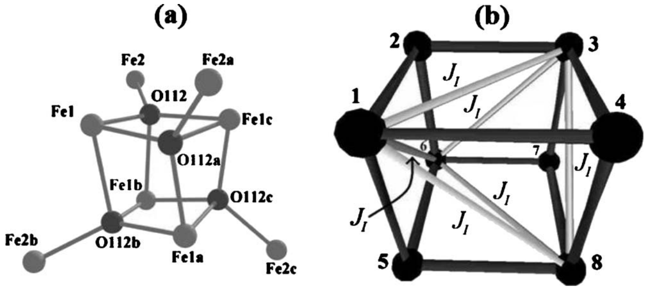

FIG. 3. (a) Crystal structure of the exchange-coupled core of the $\{Fe_8\}$-cubane molecule showing the eight $Fe^{III}$ ions (light gray) and various nonmagnetic oxygen ions (dark gray). (b) Structure of the magnetic interactions for an $\{Fe_8\}$-cubane molecule. The black spheres labeled 1–8 correspond to the $Fe^{III}$ ions of Fig. 3(a) labeled Fe1, Fe2, Fe1c, Fe2a, Fe2b, Fe1b, Fe2c, Fe1a, respectively. The 12 unlabeled black lines [forming the cube in (b)] represent the outer bonds, $J_O$. The six light gray lines, labeled $J_I$, represent the inner bonds.

shown in Fig. 3(a). The interior ions (labeled Fe1, Fe1a, Fe1b, Fe1c) occupy alternate sites of a cube. Each of these interior ions is coordinated to the three other interior $Fe^{III}$ ions, and in each case there are two distinct but presumably identical pathways via intervening oxygen ions. We suppose that each such coordination may be described by isotropic Heisenberg exchange, and we denote the strength of this interaction by $J_I$. Additionally, each of the four exterior $Fe^{III}$ ions (labeled Fe2, Fe2a, Fe2b, Fe2c) are coordinated to three of the four interior $Fe^{III}$ ions via a single oxygen ion. This coordination will also be assumed to be described by isotropic Heisenberg exchange and the strength of this interaction will be denoted by $J_O$. A more convenient way to graphically highlight the various exchange bonds is shown in Fig. 3(b), where the 8 $Fe^{III}$ ions occupy the vertices of a cube and the 12 black edges correspond to interactions of strength $J_O$, while the 6 gray edges correspond to interactions of strength $J_I$. The transcription of the labeling of the $Fe^{III}$ ions from Figs. 3(a) and 3(b) is given in the caption.

Based on the notation of Fig. 3(b), we are, in summary, adopting an isotropic Heisenberg Hamiltonian of the form

$$\begin{aligned}\mathcal{H} = {} & J_O(\vec{s}_1\cdot\vec{s}_2+\vec{s}_2\cdot\vec{s}_3+\vec{s}_3\cdot\vec{s}_4+\vec{s}_4\cdot\vec{s}_1+\vec{s}_5\cdot\vec{s}_6+\vec{s}_6\cdot\vec{s}_7\\ & +\vec{s}_7\cdot\vec{s}_8+\vec{s}_8\cdot\vec{s}_5+\vec{s}_1\cdot\vec{s}_5+\vec{s}_2\cdot\vec{s}_6+\vec{s}_3\cdot\vec{s}_7+\vec{s}_4\cdot\vec{s}_8)\\ & +J_I(\vec{s}_1\cdot\vec{s}_3+\vec{s}_1\cdot\vec{s}_6+\vec{s}_1\cdot\vec{s}_8+\vec{s}_3\cdot\vec{s}_6+\vec{s}_3\cdot\vec{s}_8+\vec{s}_6\cdot\vec{s}_8)\\ & +g\mu_B\vec{H}\cdot\sum_{i=1}^{8}\vec{s}_i,\end{aligned} \tag{2}$$

where each spin operator $\vec{s}_i$ $(1\leqslant i\leqslant 8)$ is in units of $\hbar$. In Fig. 3(b) we show each of these bonds, as well as the numbering scheme for the ions. The dimensionality of this matrix is fairly large $(6^8>10^6)$, but using modern matrix diagonalization methods,[13] we have calculated the intrinsic magnetic susceptibility $\chi_i(T)$ for the Heisenberg Hamiltonian given in Eq. (2) in the weak-field limit as a function of temperature. This calculation was repeated for a very large and representative selection of choices of the two exchange constants, $J_O$ and $J_I$. This process yielded an optimal pair of exchange constants by minimizing the square of the deviation between the experimental $\chi(T)$ data and the theoretical $\chi(T)$ data [calculated from Eqs. (1) and (2)]. As a result, an excellent fit has been achieved over the entire measured temperature range for the values $J_I/k_B=22\pm2$ K and $J_O/k_B=71.5\pm2$ K, which correspond to the ratio $J_O/J_I=3.25$. The intrinsic susceptibility is shown in Fig. 4, where the individual data points represent the inferred experimental data, as obtained by subtracting the extrinsic contributions (diamagnetism, Van Vleck paramagnetism, and detached magnetic ions) from the raw experimental data. The very small values of $\chi_i(T)$ below 10 K is a direct consequence of the relatively large energy gaps, summarized below, of the energy levels with $S>0$ above the ground state level.

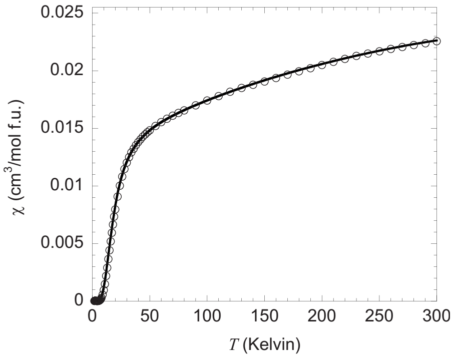

FIG. 4. The intrinsic susceptibility, $\chi_i(T)$, inferred from experiment (circles) and theory (solid curve). The theoretical curve was calculated using the Heisenberg Hamiltonian of Eq. (2), where the numerical values of the exchange constants (given in the text) were chosen so as to provide the best fit to the experimental data.

As part of the matrix diagonalization procedure, we have obtained the full set of energy levels for the $\{Fe_8\}$-cubane spin system. The lowest-lying levels (energies measured from the $S=0$ ground state level, in Kelvin) are 55 K (lowest $S=1$ level, multiplicity=1), 164 K (lowest $S=2$ level, multiplicity=1), and 340 K (first excited $S=1$ level, multiplicity=3). The first excited $S=0$ level has an energy that is higher still: 757 K, with multiplicity=5. A proposal for possible future experiments that could test these specific predictions of our theoretical model is given in the following section.

## IV. SUMMARY AND DISCUSSION

In this Brief Report, we have, first, presented our susceptibility data for the $\{Fe_8\}$-cubane system and, second, provided a quantitative theoretical analysis based on the isotropic Heisenberg model utilizing two relatively large exchange constants. For the optimal choices of the exchange constants, we have achieved excellent agreement between theory and experiment over the full range of measured temperatures (1.8–300 K). In this regard, the present system provides a striking example of where a magnetic molecule is accurately described by the isotropic Heisenberg model. The ground state of the system has total angular momentum $S=0$ and thus the intrinsic susceptibility plummets to zero below approximately 10 K. In addition to the intrinsic contribution to the susceptibility, we have found that there is a small extrinsic contribution which is of some significance below 5 K. Our analysis suggests, apart from standard diamagnetic and temperature-independent Van Vleck contributions, the presence of a small concentration of detached $\mathrm{Fe}^{\mathrm{III}}$ ions.

The most significant remaining open question is whether additional, independent experimental tests of the theoretical model can be provided. In our opinion, successful reproduction of the temperature dependence of the measured susceptibility by a theoretical model is a necessary but perhaps insufficient test of the model. Indeed, we have provided detailed quantitative information on the spectrum of low-lying energy levels in this $\{\mathrm{Fe}_8\}$-cubane system in Sec. III. Inelastic neutron scattering measurements at low temperatures could provide a detailed comparison of the predicted values of these energy levels. Additionally, the large value of the energy gap between the ground state and the lowest $S=1$ level translates to the prediction that the lowest level-crossing field is given by $H_c=41$ T. That is, a measurement at low temperatures of the differential susceptibility, $dM/dH$ (e.g., as obtained using a pulsed-field setup) should not show the characteristic peak associated with a level crossing for fields below $H_c$.

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