Low temperature specific heat of the molecular cluster Fe₈: 
contribution of the local field

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Abstract

We present low temperature specific heat and ac-susceptibility measurements on Fe₈ powdered sample. Below 1.3 K, superparamagnetic blocking effects as well as an excess specific heat contribution are evident. The latter is attributed to a splitting of the ground state doublet in an inhomogeneous local field of hyperfine and dipolar origin. The local field contributions are evident in the resonances observed in the field dependent ac-susceptibility and specific heat below 0.5 K. The low temperature Schottky contribution allowed us to check the crystal field parameters of effective spin Hamiltonians, recently proposed to simulate EPR and inelastic neutron scattering experiments.

I. INTRODUCTION

Recently nanomagnetic molecular cluster compounds have attracted attention due to the clear demonstration of collective quantum effects and its implications in information storage and quantum devices. Compounds based on organometallic clusters have been studied in physics and chemistry as its magnetic properties can be modified by manipulation of its molecular structure. Some of these clusters present a high spin ground state with
high anisotropy. At low temperatures, it was found that magnetization reversal occurs by quantum tunneling through the anisotropy energy barrier, becoming a prototype system to study macroscopic quantum tunneling (MQT). This was possible as these clusters form a crystal of identical and non-interacting macrospins with magnetic properties easily detected. Although this system cannot be directly related to a macroscopic entity, as its typical size is of a few angstroms, their magnetic properties are governed by the magnetic moment associated to the total spin of the cluster, which is in the borderline of the mesoscopic scale. The most studied molecular cluster of this kind is Mn$_{12}$Ac, which has shown spectacular effects such as steps in magnetic hysteresis due to thermally activated field resonant tunneling.

The crossover temperature to pure quantum regime, where the magnetic relaxation becomes temperature independent is not well established yet. On the other hand, the theory developed explains reasonably most effects found for this material although some features are not yet explained specially the second relaxation process and the excess specific heat found at low temperatures.

The Fe$_8$ molecule was the first nanomagnet to show clear evidence of a pure quantum tunneling regime at low temperatures around 0.4 K. Having a smaller energy barrier, 28-32 K, as compared to $\sim$70 K in Mn$_{12}$Ac, and the considerable transversal anisotropy, it became the most appropriate system to study quantum tunneling of magnetization (QTM). Very recently, this system allowed the experimental observation of spin quantum phase interference effects.

Here, we present absolute measurements of specific heat and ac-susceptibility in this octonuclear iron cluster. The novelty in our studies of this compound is the role played by the interaction of the spins with the internal local fields on the specific heat results at very low temperatures. Our data show that there is a considerable contribution that can be well explained in terms of the already known Hamiltonian and an excess contribution due to a distribution of local internal fields.
II. THE FE$_8$ CLUSTER

The Fe$_8$ molecular cluster was reported to be synthesized for the first time in 1984, its chemical formula is [Fe$_8$O$_2$(OH)$_{12}$(tacn)$_6$]$^{8+}$, where tacn is the tryazacyclononane molecule. The iron atoms are embedded in an organic matrix, where four iron III are bridged by hydroxo groups to central iron atoms. A preliminary study has reported an uncompensated antiferromagnetic ground state with spin $S=10$, presenting a superparamagnetic behavior. The cluster has approximately a $D_2$ symmetry and a proposed structure of six iron III ions $(S=5/2)$ pointing in opposition to the remaining two, recently confirmed by polarized neutron experiments. At low temperatures, the magnetic relaxation of this cluster follows roughly an Arrhenius law with energy barrier of approximately 28 K, in fair agreement with high field EPR spectra experiments showing an easy-axis with strong in-plane (rhombic) anisotropy. The effective spin Hamiltonian (EPR) used to simulate the results is given by:

$$\kappa = D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2) + H',$$

(1)

where $D = -0.27$ K, $E = 0.046$ K and $H'$ is the Zeeman splitting term. The transversal anisotropy term in this cluster is different and considerably larger than in Mn$_{12}$Ac being responsible for the clear observation of quantum tunneling of magnetization in this system.

Recently, inelastic neutron spectroscopy of Fe$_8$ single crystals has shown that a more complex Hamiltonian (INS) is necessary to describe the cluster energy levels:

$$\kappa = D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2) + D'\hat{O}_4^0(S) +$$

$$+E'\hat{O}_4^2(S) + C'\hat{O}_4^4(S) + H',$$

(2)

where the expressions for $\hat{O}_4^0(S)$, $\hat{O}_4^2(S)$, $\hat{O}_4^4(S)$ contain operator in $S_z^n$, $S_x^n$ and $S_y^n$ ($n = 2, 4$). The complete expressions can be found in Ref. 21 with $D = -0.29$ K, $E = 0.047$ K, $D' = 1.00 \times 10^{-6}$K, $E' = 1.16 \times 10^{-7}$ K, and $C' = 8.56 \times 10^{-6}$ K, corresponding to a total energy barrier of 32.8 K. Note that $S_z$ does not commute with $\kappa$, the pairs of $+m_s$ states are splitted and the energy levels are related to a mixture of different $m_s$ states.
Magnetic relaxation curves for this cluster show for temperature above 1.3 K a single exponential relaxation, while for lower temperatures the system presents a more complex behavior described by a stretched exponential. Temperature independent relaxation was observed below 0.4 K indicating that a clear quantum tunneling regime is attained below this temperature. Above 1.5 K ac-susceptibility and Mössbauer spectroscopy experiments show that this system follows a thermal activation law:

\[ \tau = \tau_0 e^{\frac{\Delta E}{k_B T}}, \]

with \( \tau_0 = 3.4 \times 10^{-8} \) s and \( \Delta E/k_B = 24.5 \) K, an energy barrier about three times smaller than in Mn\(_{12}\)Ac. This fact in conjunction with the strong rhombic term allowed the clear observation of magnetic relaxation in the quantum regime in the low temperature limit.

### III. SPECIFIC HEAT MEASUREMENTS

Calorimetric measurements are useful to check the energy levels obtained from Hamiltonians (Eq. 1 and 2), as was recently done for Mn\(_{12}\)Ac. For Fe\(_8\), in contrast with Mn\(_{12}\)Ac, hyperfine contribution should be almost negligible, as natural abundance of \(^{57}\)Fe is 2.2%, allowing an easier separation of the different contributions to the specific heat at very low temperature.

Specific heat measurements between 1.3 and 20 K were made with an automated semi-adiabatic calorimeter in a pumped He\(^4\) refrigerator while measurements below 1.5 K were done in a similar calorimeter within a dilution refrigerator. We measured 293 mg of Fe\(_8\) powder sample mixed with copper powder and Apiezon N grease in order to increase thermal contact. Data is obtained by monitoring the temperature time dependence of the sample assembly before and after a heat pulse of about 4 minutes is applied to the calorimeter. Correction for the addenda was previously obtained representing about 40% of the total heat capacity in the worst case. The whole specific heat curve from 80 mK up to 22 K is shown in the inset of Fig. 1, with an overall experimental error being less than 4%. Results do
not present the unexplained small anomalies reported recently by Fominaya et al. around 2 K. Their results were obtained by a different technique, the ac method, using a unique single crystal. Our data obtained by the two measurement systems are superposed between 1.3 and 1.5 K with a discrepancy smaller than 1%. Data below 2 K (see Fig. 1) reveals two surprising features: the specific heat curve presents an expressive reduction around 1.2 K and an upturn as temperature decreases. At first, this Schottky-like contribution could be thought to be originated from hyperfine and/or superhyperfine interactions with other nuclei in the cluster, but this should be relevant only below 200 mK. A more realistic possibility is due to Zeeman splitting of the ground state by internal dipolar fields. Both hypothesis will be discussed latter in the text.

We analyzed the experimental data calculating the zero field splitting Schottky (ZFS-Schottky) using the two proposed Hamiltonians (EPR and INS), . For zero internal magnetic field \( H' = 0 \), only the crystal field energy levels are calculated by diagonalization of the \((2S+1) \times (2S+1)\) matrix using only \( S = 10 \) multiplet and the \( S_z \) eigenstates. Specific heat contribution is calculated numerically using the eigenvalues \( \varepsilon_i \) of the diagonalized matrix and differentiating the expression for the mean energy of the system:

\[
c = \frac{dE}{dT} = \frac{d}{dT} \left( \frac{\sum_{i=-m_s}^{m_s} \varepsilon_i \exp(-\varepsilon_i/T)}{R \sum_{i=-m_s}^{m_s} \exp(-\varepsilon_i/T)} \right), \quad (4)
\]

where \( R = 8.314 \text{ J} \cdot \text{K}^{-1} \). The calculated curves using both Hamiltonians are shown in Fig. 2. As can be seen, the INS and EPR Hamiltonians produce slightly different results, indicating that the forth-order terms have a small but not negligible influence in the specific heat. Data below 1 K cannot be explained by both Hamiltonians only, the calculated contributions decreases monotonically, becoming zero below 0.5 K, whereas the experimental data show an increase.

Hyperfine contribution due to \(^{57}\text{Fe}\) isotopes should be negligible. This contribution yields a \( T^{-2} \) term that is observable only at very low temperatures. An estimate of the hyperfine term was made for \( \text{Fe}_{10} \) and \( \text{Fe}_6 \) samples by Affronte et al. and could be applied to \( \text{Fe}_8 \).
In this case, the coefficient of the $T^{-2}$ term is of the order of $10^{-6}$ J K mol$^{-1}$ and cannot explain the observed increase of the specific heat at low temperatures.

Measurements with an applied dc-magnetic field were made within a superconducting solenoid in the temperature range between 1.3 and 23 K. The results are shown in Fig. 3 for 0.17 T and 0.32 T being similar though more pronounced than those obtained for Mn$_{12}$Ac. Here, a gradual decrease of the specific heat can be observed for temperatures below 1.6 K. Below 1 K the relaxation times becomes bigger than 1 minute and cease to contribute to the specific heat measurements, being in the blocked regime. The field effect is better seen in the inset, where the data is plotted as $C/T$ versus $T$. The calculation with both Hamiltonians were repeated, including now a Zeeman term $H' = g\mu SH$, and performing a powder average in the mean energy expression, with a discrete sum over $\theta$, the angle between the magnetic field and the easy axis:

$$E = \left( R \sum_{\theta=0}^{\pi} \sum_{i=-m_s}^{m_s} \frac{\epsilon_i \exp(-\epsilon_i/T) \sin \theta}{\sum_{i=-m_s}^{m_s} \exp(-\epsilon_i/T)} \right) / \sum_{\theta=0}^{\pi} \sin \theta , \quad (5)$$

In Fig. 3, the calculated Schottky contribution for 0.17 T is plotted using Eq. 5. In this figure, the lowest temperature of the equipment unfortunately limits the experimental data under external magnetic field, not available in the dilution refrigerator system. Even so, a downturn can be clearly seen below 2 K. This can be explained again as due to superparamagnetic blocking in the time scale of the specific heat measurements. At higher temperatures, above 10 K, the Zeeman contribution, for those small fields, becomes negligible, not affecting the specific heat results.

**IV. AC-SUSCEPTIBILITY AND LOCAL FIELD DISTRIBUTION**

We have performed ac-susceptibility measurements with a Fe$_8$ powder sample from 10 Hz to 10 kHz and temperatures from 2.4 to 15 K. In Fig. 4 is shown the plot of the real and imaginary components of the ac-susceptibility as function of a static external magnetic field.
The oscillating field was of the order of 0.1 mT at 10 kHz. Above the blocking temperature (for 10 kHz, \( T_B = 3.5 \) K) several dips are observed in the imaginary component, while the real one is smooth. At the measured temperatures, \( T = 6.6 \) and \( 7.1 \) K, a large part of the relaxation mechanism is dominated by thermal activation and thermally activated tunneling process near the top of the barrier. The dips occur at the positions where steps were found in the magnetization hysteresis cycles. Below \( T_B \), the real component of the susceptibility also show maxima. These are attributed to level crossing fields and are not regularly spaced in field as indicated in the Fig. 4. The important point here is the width of the dips, which is the same as the width of the maxima observed in the real component at lower temperatures. The expected width of the tunneling resonance (tunnel splitting) was estimated by Prokofe’v and Stamp to be only \( 10^{-8} \) mT for \( \text{Mn}_{12} \text{Ac} \), for \( \text{Fe}_8 \) it is expected also to be very small, not explaining the observed resonance width. This is a clear indication that there is a distribution of local fields mainly of dipolar origin superposed with hyperfine fields from the few \( ^{57}\text{Fe} \), \( \text{N} \), and \( \text{H} \) nuclei present in the molecule. The dipolar local field distribution was also probed recently by Wernsdorfer et al. which found a width \((\sigma_d)\) of the order of \( 50 \) mT, in agreement with estimates for dipolar contribution of the surrounding neighbors. Data in Fig. 4 have a width of \( 0.11 \) T, which is larger than the ones reported in Ref. 23, due to the fact that a powder sample was used.

These internal fields have been already addressed in order to explain the magnetic relaxation process. The spins which are within the narrow resonant condition, at some specific local field, tunnel producing spin flips which in turn change the neighboring dipolar field, bringing up other clusters into resonance resulting in a complex evolution of the internal fields and relaxation. We discuss now the influence of this local field on the specific heat results. For simplicity, we assume that each cluster spin is in a local field with a probability given by the field distribution \( P(H) \) independent of the temperature. The specific heat \((c')\) is obtained by averaging over the distribution \( P(H)\):
\[ c'(T) = \frac{\sum_i c_i(T, H_i) P_i(H_i)}{\sum_i P_i(H_i)}, \] (6)

where \( c_i(T, H_i) \) is the calculated specific heat at a field \( H_i \). We have used both Lorentzian and Gaussian distributions centered at \( H = 0 \) and width \( 0.1 < \sigma_d < 70 \) mT. The calculated specific heat for both distributions present no quantitative difference for temperatures above 2 K. However there is a slight difference between them below 2 K. In Fig. 5 we show in more detail the results below 2 K and the different contributions important in this range.

It is clear that by using a Lorentzian distribution with \( \sigma_d = 10 \) mT, the calculated curve lies well above the experimental results below 1 K, though presenting the same shape. The other important feature is the decrease in the experimental data observed below 1.3 K, which is the superparamagnetic blocking temperature observed in magnetic relaxation experiments. Similar effect was found previously in specific heat measurements on Mn\(_{12}\)Ac powder sample\(^{22}\) under small external magnetic field. This is another evidence that in Fe\(_8\) blocking effects are observed due to a splitting of the ground state by internal fields. Well below this blocking temperature, this contribution should vanish unless part of the clusters may tunnel to the other side of the anisotropy barrier.

Using a field distribution larger than 10 mT produces a specific heat maximum above 0.1 K, being contrary to experimental results. As \( \sigma_d \) increases this maximum shifts to higher temperatures, acquiring a different shape from the experimental data. Thorsten et al.\(^{24}\) had succeeded to describe the fast relaxation process in Fe\(_8\) with a Gaussian distribution of dipolar fields with \( \sigma_d = 40 \) mT. On the other hand, using a phenomenological model that accounts for the evolving distribution of local dipolar fields in time they found \( \sigma_d = 10 \) mT distribution. Both cases do not explain fully our data, and indicate that the hyperfine fields have to be taken into account.

We calculated this hyperfine contribution by assuming that each Spin 10 is subjected to a field following a Lorentzian distribution of width \( \sigma_h = 2 \) mT, shown separately in Fig. 5. This is in fair agreement with estimates made by Wernsdorfer et al.\(^{27}\) which found the
line width of the hyperfine field fluctuations to be about 1.2 mT. Even being much higher than pure $^{57}$Fe hyperfine contribution discussed previously, it is still too small to explain the experimental results. In order to explain the full curve one has to take into account all those contributions and the blocking effect, which reduce them. This is accomplished if we assume that a fraction of the total clusters are unblocked during the course of the experiment. Note that below 0.5 K the magnetic relaxation is in the quantum regime, being temperature independent. The blocked clusters do not contribute to the specific heat in this temperature range, only the clusters that change its magnetic orientation either by thermal activation and/or tunneling, in a time shorter than the measuring time. The data was only well fitted when considering 30% of both dipolar and hyperfine contributions as shown as a full line in Fig. 5.

Finally we now discuss the phonon contribution to the specific heat. This can be found by analyzing the data above 2 K after subtracting the magnetic contributions, as displayed in Fig. 6 in the traditional $c \cdot T^{-1} \times T^2$ plot. Here we also took into account the tail of the local field contribution, which depends on its width. We have found that there is an apparent linear term in the specific heat which depends considerably on the local field distribution width. This was already observed on Mn$_{12}$Ac with no explanation. By using the 10 mT width distribution, the linear term is practically nulled as showed in Fig. 6. From the slope of the fitted straight line the Debye temperature $\theta_D = (33 \pm 1)$ K is determined.

V. CONCLUSIONS

Specific heat of the nanomagnet Fe$_8$ was measured down to 0.1 K. For temperatures above 1 K, the results are dominated by the crystal field Schottky anomaly and lattice contributions and the recently proposed Hamiltonian used to fit inelastic neutron scattering experiments gives the best agreement with our data. Below 1 K an excess contribution associated to a distribution of local fields of dipolar and hyperfine origin is evidenced. The results indicate that dynamical hyperfine and dipolar fields play a significant role to explain
the specific heat below 0.6 K and a good agreement between the calculated contributions and the experimental data is obtained only when we consider a fraction of the spins remain unblocked, due to magnetic tunneling, below the known superparamagnetic blocking temperature.

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FIGURE CAPTIONS

FIG. 1. Experimental specific heat results for Fe₈ between 80 mK < T < 2 K. Data decreases abruptly below 1.5 K and at lower temperatures an excess specific heat is present. Inset: complete specific heat curve up to 18 K.

FIG. 2. Calculated ZFS-Schottky for EPR and INS Hamiltonians. Open circles: experimental data. Dotted line: EPR Hamiltonian. Full line: INS Hamiltonian. Inset: calculated curves up to 20 K.

FIG. 3. Low temperature specific heat in external applied magnetic field of 0.17 T (full circles), and 0.32 T (squares) compared to the experimental data with $H' = 0$ (open circles). Inset: Same data shown in a $c \cdot T^{-1} \times T$ plot where the onset of the superparamagnetic blocking effect in the specific heat can be seen.

FIG. 4. Imaginary component of the ac-susceptibility as function of the external magnetic field for 10 kHz at 7.1 and 6.6 K, full squares and open circles respectively. Resonant fields are identified by a minima in the curves ($H = 0, 0.23, 0.46, 0.67$ and $0.88$ T). Inset: real component which does not show any resonance.

FIG. 5. Experimental data (empty circles) below 0.5 K is fitted by assuming 30% (full line) local dipolar contribution with $\sigma_d = 10$ mT (crosses) and hyperfine distribution with $\sigma_h = 2$ mT (full squares).

FIG. 6. $c \cdot T^{-1} \times T^2$ plot after subtracting the local dipolar field contribution. The Debye temperature, $\theta_D = (33 \pm 1)$ K, is obtained from the straight line fit for data above the blocking temperature.
FIG. 1, A.M. GOMES, PRB
FIG. 2, A.M. GOMES, PRB
FIG. 3, A.M. GOMES, PRB
FIG. 4, A.M. GOMES, PRB
FIG. 5, A.M. GOMES, PRB
$c \frac{T^{-1}}{\text{J mol}^{-1} \text{K}^{-2}}$

$T^2(\text{K}^2)$

FIG. 6, A.M. GOMES, PRB