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## Superparamagnetic-like behavior in an octanuclear iron cluster

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**Abstract.** – Using high-frequency EPR spectroscopy we have found that a cluster comprising eight iron(III) ions, Fe<sub>8</sub>, which is essentially flat, has a ground  $S = 10$  state and an Ising-type anisotropy. For the first time both ac susceptibility and Mössbauer spectroscopy could be used in order to monitor the relaxation time of the magnetization, which was found to follow a thermally activated behavior, as in a superparamagnet, with  $\tau_0 = 1.9 \times 10^{-7}$  s and an energy barrier of 22.2 K. The set of data allowed us to conclude that the origin of the anisotropy in nanosize molecular clusters is associated with the single ion contributions and not with the shape of the clusters.

Molecular magnetic clusters comprising large numbers of coupled metal ions have been extensively investigated in the last few years in order to understand the mechanism associated with the transition from simple paramagnetic to bulk magnetic behavior [1]. In fact large clusters of interacting magnetic centers can be seen as an ideal model of nanometric single-domain magnetic particles as no distribution in size and shape is present and inter-cluster interactions can be reduced to zero by dissolving the clusters in the appropriate solvent. The reorientation of the magnetization of single-domain particles requires the crossing of a large energy barrier proportional to the volume of the particle, and the relaxation time of the magnetization,  $\tau$ , is expected to follow an exponential dependence on temperature:

$$\tau = \tau_0 \exp[KV/kT], \quad (1)$$

where  $\tau_0$  is the relaxation time at infinite temperature,  $K$  is the magnetic anisotropy per volume, and  $V$  is the volume of the particle.

Some of us reported for the first time evidences of superparamagnetic-like behavior in a molecular cluster of formula [Mn<sub>12</sub>O<sub>12</sub>(CH<sub>3</sub>COO)<sub>16</sub>], Mn<sub>12</sub>, characterized by a ground

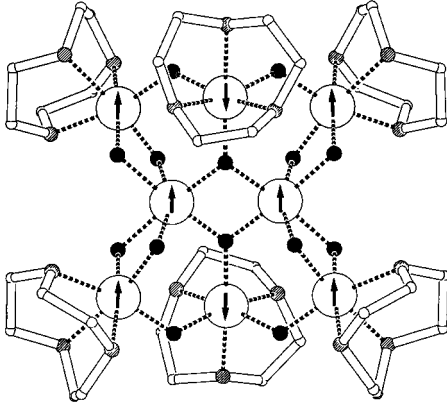


Fig. 1.

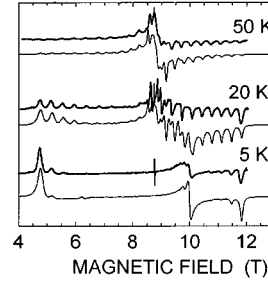


Fig. 2.

Fig. 1. – View of the structure of  $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]^{8+}$ . The large open empty circles represent iron atoms; full, hatched, and empty small ones stand, respectively, for oxygen, nitrogen, and carbon atoms. The spin structure of the  $S = 10$  ground state is schematized by the arrows.

Fig. 2. – Polycrystalline powder EPR spectra at 245 GHz at three temperatures ( $g = 2.0$  resonates at 8.75 T). The upper curve for each temperature corresponds to the experimental spectrum while the lower curve is the simulated spectrum using  $S = 10$ ,  $D = -0.191 \text{ cm}^{-1}$ , and  $E/|D| = 0.169$ .

$S = 10$  state [2]. The relaxation time of the magnetization follows eq. (1) below 10 K, with  $\tau_0 = 2.1 \cdot 10^{-7} \text{ s}$ ,  $KV/k = 61 \text{ K}$ .  $\tau$  at 2 K is of the order of two months, and magnetic hysteresis effects of molecular origin are observed [3]. Such a long relaxation time for the magnetization of an isolated molecule is unprecedented and has been attributed to the association of the unusually high value of the spin with the presence of a magnetic-anisotropy barrier originated by the single ion contributions of the Jahn-Teller distorted manganese(III) ions [3], [4].  $\text{Mn}_{12}$  has been the object of many further experiments, which have also shown that, below 2 K,  $\tau$  becomes temperature independent and quantum tunneling has been proposed as a possible origin [5].

Another series of molecular clusters containing iron(III) was examined with Mössbauer spectroscopy and showed relaxation times smaller than  $10^{-8} \text{ s}$  at low temperatures. The author concluded that shape, surface, and strain anisotropy originated the phenomenon as in small particles of classical ferromagnets [6]. Further, since slow relaxation effects were observed only in clusters in which the metal ions are arranged in different planes and not in one plane or in a ring, it was concluded that the superparamagnetic-like behavior is associated with the pseudo-tridimensional structure of the cluster and that it is visible in clusters with 10 or more iron atoms.

We have now discovered slow relaxation effects in an octanuclear iron cluster,  $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]^{8+}$ ,  $\text{Fe}_8$ , whose structure, essentially two-dimensional [7], is shown in fig. 1. The static magnetic properties of  $\text{Fe}_8$  down to 3 K were previously reported [8], and it was concluded that a ferrimagnetic ground state with either  $S = 9$  or 10 is originated by the presence of competing antiferromagnetic interactions between the  $S = 5/2$  spins of the iron(III) centers with some similarity to  $\text{Mn}_{12}$ . With  $\text{Fe}_8$ , however, for the first time the relaxation of the magnetization of a cluster has been monitored by using both Mössbauer spectroscopy and ac susceptibility measurements, and the results, here reported, show that the Arrhenius law is obeyed over a large temperature range. Both axial and in-plane magnetic

anisotropy have been accurately determined by using high-frequency electron paramagnetic resonance, HF-EPR, spectroscopy and the results suggest that the energy barrier is originated by magneto-crystalline single ion and not by shape and surface anisotropy.

Unconventional high-frequency EPR spectroscopy has been found to be well suited to univocally assign the total spin multiplicity of the ground state of large clusters [9]. We have recorded the polycrystalline powder spectra of Fe<sub>8</sub> at 245 GHz in the temperature range 5–50 K <sup>(1)</sup>. In the high-field approximation, *i.e.* assuming that the Zeeman energy is larger than the zero-field splitting defined by the Hamiltonian  $H = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}$ , an  $S$  multiplet gives  $2S$  equally spaced lines corresponding to the allowed  $\Delta M = \pm 1$  transitions, with the separation depending on the orientation of the magnetic field with respect to the  $\mathbf{D}$  tensor. The energy of the  $M$  components along the principal axes of the zero-field splitting tensor is given by

$$W_i(M) = g_i \mu_B M H + 3/2 M^2 D_i, \quad (2)$$

where  $i = x, y, z$  and  $\mathbf{g}$  and  $\mathbf{D}$  are assumed parallel to each other. The resonance conditions for the transition  $E(M) - E(M - 1)$  is given by

$$H_i(M - 1 \rightarrow M) = g_e/g_i [H_0 - 3/2 (2M - 1) D'_i], \quad (3)$$

where  $D'_i = D_i/(g\mu_B)$ . In a random oriented polycrystalline sample the three features corresponding to the principal directions of  $\mathbf{D}$  are observable, however the spectra at low temperature simplify because the Zeeman energy is large compared to  $kT$ , and the transitions between the lowest components,  $-S \rightarrow -S + 1$ , which fall at the extremes of the spectrum, dominate. Three prominent features at 4.9 T, 10 T, and 11.8 T are indeed observed in the spectrum of Fe<sub>8</sub> at 5 K, shown in fig. 2, and we attribute them to the  $z, x$ , and  $y$  components of the  $M = -10$  to  $M = -9$  transition. On increasing the temperature also the states with  $M = -9, -8, -7$ , etc. become populated and the regular structure of the signals appears, with the larger intensity that moves from the extremes toward the center of the spectrum on increasing the temperature.

For iron(III), an  ${}^6S$  ion, the  $g$ -factor is expected to be almost isotropic and close to  $g_e$ . The spectra are well reproduced <sup>(2)</sup>, as shown in fig. 2, assuming  $S = 10$  with  $D_z = -0.1275 \text{ cm}^{-1}$ ,  $D_x = +0.0315 \text{ cm}^{-1}$ ,  $D_y = 0.096 \text{ cm}^{-1}$ , which correspond to the axial parameter  $D = (3/2)D_z = -0.191 \text{ cm}^{-1}$ , and the rhombic term  $E = (D_y - D_x)/2 = 0.032 \text{ cm}^{-1}$ . No reasonable simulation was possible for  $S = 9$ .

The relative intensity of the exchange interactions suggests that the ground  $S = 10$  state corresponds to the spin scheme shown in fig. 1. The zero-field splitting tensor of such an  $S = 10$  state is expected to be given by

$$\mathbf{D} = a\mathbf{D}_1 + b\mathbf{D}_2, \quad (4)$$

where  $\mathbf{D}_1$  and  $\mathbf{D}_2$  correspond to the single ion contributions of the centers with spin up and spin down, respectively. Using standard projection techniques [11] it is found that:  $a = 6 \times 0.047977$ ,  $b = 2 \times 0.03953$ . By assuming for simplicity that  $\mathbf{D}_1 = \mathbf{D}_2$  and substituting in (4) the observed

<sup>(1)</sup> The spectra of polycrystalline powders of Fe<sub>8</sub> pressed in a pellet to prevent orientation of the grains in the strong field were recorded using a laboratory-made spectrometer based on an optically pumped far-infrared laser and an In-Sb bolometer. See also [10].

<sup>(2)</sup> The EPR spectra have been simulated by assuming  $g_x = g_y = 2.00$  and  $g_z = 2.04$  with an anisotropic linewidth,  $\Delta H_x = \Delta H_y = 60 \text{ mT}$ ,  $\Delta H_z = 140 \text{ mT}$ . The zfs term of the spin Hamiltonian has been treated as a second-order perturbation to the Zeeman term and the thermal population of the different  $M$  levels of the  $S = 10$  multiplet, as a function of the applied magnetic field, has been taken into account.

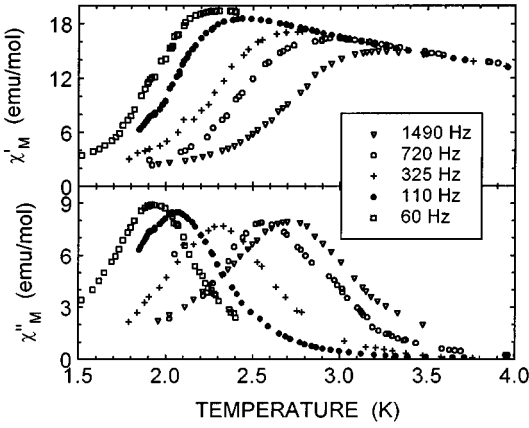


Fig. 3.

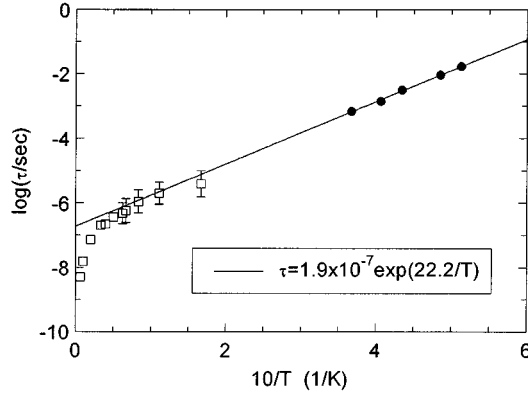


Fig. 4.

Fig. 3. – Temperature dependence of the real (top) and imaginary (bottom) component of the magnetic susceptibility measured at five frequencies of the oscillating magnetic field of 0.1 mT.

Fig. 4. – Temperature dependence of the relaxation time of the magnetization: (●) estimated from the maximum in the imaginary component of the ac susceptibility, (□) estimated from the Mössbauer spectra. The solid line represents the best fit of the ac susceptibility data assuming a thermally activated process described by the Arrhenius law.

value of  $D$  for the cluster, we evaluate  $D_1 = -0.522 \text{ cm}^{-1}$ , which is compatible with an iron(III) ion in a low-symmetry environment.

The EPR spectra also provide other information. Since we do not see any evidence of other multiplets we can conclude that  $S = 10$  is the ground state for  $\text{Fe}_8$ . The spectra suggest that the clusters are at best weakly coupled, because the transitions can be justified on the basis of isolated clusters. Therefore the slow relaxation observed at low temperature has a molecular origin. The negative sign of the  $D$  parameter of the  $S = 10$  multiplet or, in other words, the fact that the states with  $M = \pm 10$  are the lowest in energy in zero field is unambiguously determined by the low-field position of the transitions that correspond to the crystallites with the  $z$ -axis parallel to the field, easily recognized as the farthest from the resonance of  $g = 2$ . The system has therefore an Ising-type anisotropy, which at 0 K is calculated to be 27.4 K. If it is assumed that the relaxation time of magnetization of  $\text{Fe}_8$  follows eq. (1), with  $\tau_0$  similar to that observed for  $\text{Mn}_{12}$ , we should observe a blocking temperature  $T_B$  of ca. 2 K for ac susceptibility and a much higher  $T_B$  in the Mössbauer spectra.

Ac susceptibility measurements without applied magnetic field below 4 K, shown in fig. 3, clearly indicate slow relaxation of magnetization with the decrease of  $\chi'$  and the appearance of a maximum in the out-of-phase component  $\chi''$ . The position of the maximum is frequency dependent and occurs at increasing temperature on increasing frequency. This is the behavior usually observed for the blocking of the relaxation of superparamagnets. The relaxation time  $\tau$  can be extracted from the curves of fig. 3, being  $\tau = \nu_{ac}^{-1}$  at the temperature of the maximum in  $\chi''$ , and it is found to follow eq. (1), as shown in fig. 4, with  $KV = 22.2 \text{ K}$  and  $\tau_0 = 1.9 \cdot 10^{-7} \text{ s}$ . The calculated anisotropy barrier compares well with that obtained from the EPR spectra. As in the case of  $\text{Mn}_{12}$ ,  $\tau_0$  is about three orders of magnitude shorter than usually found in classic ferro- and ferri-magnets. Its value was justified within a model which extends to large clusters the Orbach model of relaxation for simple paramagnets [4]. Since both  $\text{Mn}_{12}$  and  $\text{Fe}_8$  have a ground  $S = 10$  state and an Ising-type anisotropy, it may be assumed that the relaxation mechanism is the same in both cases.

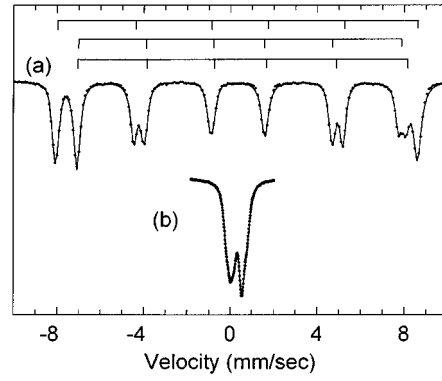


Fig. 5. – Mössbauer spectra of  $\text{Fe}_8$  *a*) at 2 K in a field of 0.22 T perpendicular to the gamma-beam and *b*) at 300 K in zero field. The solid line is given by the superposition of the three six-line patterns, as shown by the bar graph, attributed to the iron sites A, B, and C with the overall splittings  $S$  and isomer shifts  $\delta_{\text{Fe}}$  assigned as follows:  $S_A = 15.13$ ,  $S_B = 14.79$ ,  $S_C = 16.67$ ;  $\delta_A = 0.54$ ,  $\delta_B = 0.42$ ,  $\delta_C = 0.40$ , all in mm/s. In *b*) the solid line represents a constrained fit by three pairs of Lorentzians with area ratios 1:1:2 and the following isomer shifts  $\delta_{\text{Fe}}$  and quadrupole splittings  $A$ , all in mm/s:  $\delta_A = 0.40$ ,  $\delta_B = 0.32$ ,  $\delta_C = 0.28$ ,  $A_A = 0.41$ ,  $A_B = 0.96$ ,  $A_C = 0.50$ .

As shown in fig. 5*a*), for  $T = 2$  K the Mössbauer spectrum of  $\text{Fe}_8$  consists of three superimposed six-line patterns that are resolved on the far right. These patterns are indicated by the bar graph on top of the spectrum and can plausibly be assigned on the basis of the intensities and isomer shifts [12] to the three types of iron sites with different ligand coordination,  $[\text{FeO}_2(\text{OH})_4]_2$  (A),  $[\text{FeO}(\text{OH})_2\text{N}_3]_2$  (B), and  $[\text{Fe}(\text{OH})_3\text{N}_3]_4$  (C).

The spectrum shows some characteristics typically found in magnetically ordered materials rather than in paramagnetic complexes. Firstly, the magnetic hyperfine pattern appears in zero field and is not affected by the presence and direction of an external field of 0.22 T. Secondly, the lines are rather narrow indicating that all irons of a given type are subject to the same Hamiltonian and that the spin fluctuation rate is slow.

The magnetic hyperfine splitting collapses gradually as  $T$  rises, displaying the line shapes characteristic of increasing spin fluctuation rates, and there is no evidence of a phase transition with an abrupt change in line shape. At 50 K a single, very broad line is seen, and at 300 K the spin fluctuation rate is sufficiently fast to reveal the three partially resolved quadrupole doublets shown in fig. 5*b*). Again, the three doublets can be assigned to the (A), (B), and (C) sites on the basis of the intensities and isomer shifts [12].

We have tried to match the Mössbauer spectra with a simplified line shape model to estimate the temperature dependence of the spin fluctuation time,  $\tau_M(T)$ , and to compare it with the relaxation of the magnetization as deduced from ac susceptibility data. In the line shape model adopted the internal fields at each  $^{57}\text{Fe}$  nucleus jump stochastically between  $\pm \mathbf{B}_{\text{int}}$ , the fields observed at 2 K, and the fluctuation time  $\tau_M(T)$  is the same for all sites. The model is implemented in a fictitious spin-(1/2) basis with  $g_z \gg g_x, g_y$  and  $A_z \gg A_x, A_y$  so as to simulate  $\mathbf{B}_{\text{int}}$ ; most of the code is taken from a more general model [13]. While this simple model does not match individual spectra quantitatively, hence the large error bars, it reproduces the general trend quite well.

The results are plotted in fig. 4 as  $\ln(\tau_M)$  vs.  $10/T$ . For  $T \approx 20$  K the plot is reasonably linear, suggesting a dominant thermally activated process with activation energy  $E/k \approx 20$  K, whereas at higher temperatures other processes may dominate. The same figure also shows, in

the same representation, the relaxation time  $\tau_{ac}(T)$  deduced from ac susceptibility discussed above. It is evident that for  $T \leq 20$  K  $\tau_M$  matches  $\tau_{ac}$  within experimental uncertainty. We therefore conclude that the dynamics of the net spin, as measured by the relaxation of the magnetization, also controls the fluctuations of the individual iron spins, as observed by the Mössbauer line shape and modeled crudely by a fictitious spin doublet.

To conclude, we can say that  $Fe_8$  is a new fascinating example of slow relaxing molecule for which the thermally activated regime has been observed over a large temperature range.  $Fe_8$  is therefore the ideal candidate for investigations at lower temperature to detect deviations from (1) due to the presence of quantum tunneling effects [14]. The crossover temperature from the thermally activated to the quantum tunneling regime in the relaxation of the magnetization is expected to be related to the axial and in-plane magnetic anisotropies. While for  $Mn_{12}$  the amplitude of the transverse anisotropy remains unknown, for  $Fe_8$  both components have been accurately provided by the EPR spectra. The experimentally determined energy barrier is in good agreement with the magnetic anisotropy evaluated from the EPR spectra, thus suggesting that the superparamagnetic-like behavior is associated with the magnetic anisotropy of the ground state essentially given by the single ion contribution, and not with the shape of the cluster or the number of interacting spins, as previously suggested [6].

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