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High-Frequency EPR Spectra for the Analysis of Magnetic Anisotropy in Large Magnetic Clusters

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Large clusters of paramagnetic centers are attracting increasing interest among physicists and chemists due to their unusual magnetic properties that resemble those of nanosize magnetically ordered materials,[1,2] which are very important for applications in the field of magnetism.[3] From the point of view of fundamental science, high nuclearity spin clusters are extremely appealing for the possibility of establishing the location of the threshold between simple paramagnetism and bulk magnetism. Superparamagnetic-like behavior was observed in iron−oxo clusters using Mössbauer spectroscopy and was attributed to the 3-dimensional structure of the clusters.[4,5]

Recently we have shown that in a dodecanuclear manganese cluster of formula $[Mn_{12}O_{12}(RCOO)_{16}(H_2O)_4]$, Mn_{12},[6] characterized by an $S = 10$ ground state and by a negative value of the zero-field splitting parameter, $D = -0.5$ cm^{-1}, the relaxation time of the magnetization follows an exponential law below 10 K, becoming as long as 2 months at 2 K. The material behaves like a superparamagnet and shows magnetic hysteresis effects of molecular origin.

We have rationalized the properties of Mn_{12}, which has an essentially two-dimensional structure, as the result of the association of a large-spin ground state with a large Ising type magnetic anisotropy associated with negative zero-field splitting.[7] We are currently trying to find new clusters showing superparamagnetic-like behavior, using as guidelines large spin and large anisotropy.

Some of us have recently reported that, in a class of mixed-valent Mn(III)−Mn(II) decanuclear clusters of formula $[Mn_{10}O_4(Biphen)_4X_{12}]^{4-}$ (with Biphen = biphenolate and X^- = Cl^-), Mn_{10}, consisting of four manganese(III) ions and six manganese(II) arranged in a three-dimensional complex structure due to the presence of four μ_4 oxo bridges, the ground state has an even larger spin, $S \geq 12$.[8,9] However, no unusual relaxation effects of the magnetization were observed down to 1.5 K, presumably because the anisotropy is smaller than in Mn_{12}.

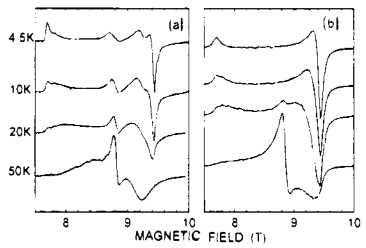

Figure 1. (a) EPR spectra of a polycrystalline powder of Mn_{10} pressed in a pellet recorded at 245 GHz and at variable temperature ($g = 2.0$ resonates at 8.75 T). (b) Calculated spectra assuming $S = 12$, $D = -0.047$ cm^{-1}, and $E/D = 0$.

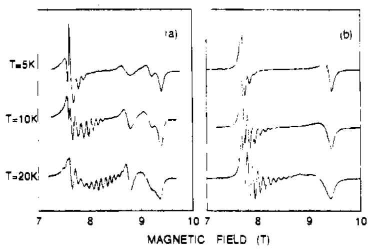

Figure 2. (a) EPR spectra of a polycrystalline sample of Mn_{10} left loose in the sample holder recorded at 245 GHz ($g = 2.0$ resonates at 8.75 T). (b) Calculated spectra assuming $S = 12$, $D = -0.047$ cm^{-1}, and a prefererential orientation of the crystallites with the unique axis of zfs parallel to the field (see text).

The direct measurement of the magnetic anisotropy is often hampered by the impossibility of growing suitable large single crystals. We want to show here that the use of high-frequency EPR spectroscopy, HF-EPR, which is becoming available in several laboratories throughout the world, working with frequencies above 200 GHz, represents a powerful tool for the study of the magnetic anisotropy of high-nuclearity spin clusters, even on polycrystalline samples. There are several advantages in the use of a high-frequency spectrometer, which can be summarized as follows: (i) high fields strongly simplify the spectra as the zero-field splitting can be treated as a perturbation to the Zeeman term of the spin Hamiltonian; (ii) they allow the direct measurement of the sign of the zero-field splitting, thus providing information on the nature of the anisotropy (Ising or XY); (iii) if all the allowed transitions are observed, the spin of the ground state can be unambiguously determined by simply counting the number of transitions. Further, in the presence of magnetic anisotropy the strong field can orient microcrystalline powders left free to move in the sample holder, thus providing the possibility of observing quasi-single-crystal spectra.

We report here the microcrystalline powder EPR spectra obtained at 245 GHz on Mn_{10} which has led to the determination of the nature of the ground multiplet and of the magnitude and sign of its zero-field splitting.

The X band spectrum (9.25 GHz) of a polycrystalline powder of Mn_{10} at liquid helium temperature shows absorptions spread over the entire field scan from 0 to 1 T. It is poorly informative, providing only an indication of the presence of a fine structure.

Figures 1a and 2a show the HF-EPR spectra recorded at 245 GHz for several temperatures ranging from 4.2 to 50 K.[10,11] The two sets of spectra differ in the fact that in Figure 1a are shown those recorded on a sample that has been pressed in a pellet to prevent movement of the crystallites while for the

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(10) The sample of formula $(N(CH_3)_4)_4[Mn_{10}O_4(Biphen)_4Cl_{12}]{\cdot}nCH_2Cl_2$ was prepared according to ref 8 using CH_2Cl_2 for vapor diffusion.

(11) The spectra have been recorded on a laboratory-made spectrometer. An optically pumped far-infrared laser is used as the radiation source. The derivative of the absorption of the far-radiation is recorded by a In−Sb bolometer. See also: Barra, A. L.; Brunel, L. C.; Robert, J. B. *Chem. Phys. Lett.* **1990**, *165*, 107.

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spectra in Figure 2a the powder has been left loose in the Teflon sample holder. From the differences between the two sets of spectra we immediately realize that the microcrystallites are oriented by the large magnetic field, and the spectra of Figure 2a are pseudo-single-crystal spectra. An isotropic signal is present at $g = 2$ whose intensity seems to increase on raising the temperature, which we attribute to an impurity.

A simple qualitative analysis of the spectra evidences a few features: (i) the spectra are extended to the low-field region (referring to $H_0 = 8.75$ T for $g = 2$) about two times as much compared to the high-field region, as well shown by the 4.5 K spectrum of Figure 1a, where a parallel-type resonance is observed at 7.7 T (1.05 T downfield) and a perpendicular type at 9.40 T (0.65 T upfield); (ii) at least 12 transitions are observed in the low-field region in the 20 K spectra of Figure 2a; (iii) at low temperature most of the intensity is located on the extremes of the spectrum, and the intensity gradually moves to the center as the temperature is increased; (iv) in both sets of spectra, but particularly in those of loose powders, a regular structure is present in the low-field region with a peak to peak separation of about 0.1 T.

For an S ground state the powder EPR spectrum in the assumption of axial zero-field splitting much smaller than the energy of the exciting frequency should show $2S$ transitions separated by $2D$ for the parallel, S above and S below the resonance field in the absence of zfs, and $2S$ transition spaced by D for the perpendicular orientation. Therefore the spectra confirm a state with at least $S = 12$.

An important feature of the HF-EPR spectra is that the Zeeman energy, $g_B B_0$, is comparable to kT at low temperature. In fact at 250 GHz the Zeeman energy is ca. 12 K; therefore large depopulation effects must be expected in the ground multiplet at low temperature, especially for large spin S. For $S = 12$ the energy difference between $M_s = +12$ and $M_s = -12$ can be as large as 270 K. As a consequence the EPR spectra, which monitor the difference in the level population by the different intensities of the $M_i \rightarrow M_{i\pm1}$ transitions, provide direct information on the sign of the zero-field splitting. At very low temperature only the $-S \rightarrow -S + 1$ transition will be observed. The resonance fields, in the strong-field approximation, are

$$H_{\parallel} = (g_e/g_{\parallel})[H_0 + (2S - 1)D]$$

$$H_{\perp} = (g_e/g_{\perp})[H_0 - (2S - 1)D/2]$$

where $g_e = 2.0023$ and $\parallel$ and $\perp$ refer to parallel and perpendicular to the unique axis of the zero-field splitting, respectively. The transition will be observed at low field, compared to H_0, when H is parallel to the z axis of the zero-field splitting and at low field when H is perpendicular if $D < 0$. The reverse pattern will be observed for $D > 0$.

The HF-EPR spectrum at 4.5 K of Figure 1a clearly shows the parallel transition at low field and the perpendicular transition at high field, immediately suggesting $D < 0$. From the better resolved spectra of Figure 2a, neglecting some narrow features, we can easily extract the separation between the lines of the fine structure which in our simple model should correspond to $2D$. To simulate the spectra we assumed $D = -0.047$ cm^{-1}, as evaluated from Figure 2a, considering the zero-field splitting as a second-order perturbation to the Zeeman term. For the spectra of Figure 1a recorded on the pellet we have calculated the powder average assuming Lorentzian lines and also taking into account the Boltzmann distribution of the population. We have tried to reproduce the spectra of Figure 1a by assuming $S = 13$, but a good simulation can be achieved only employing an anisotropic **g** tensor with $g_{\parallel} = 1.90$ and $g_{\perp} = 2.03$. These values are, however, rather unreasonable for a system containing Mn(II) and Mn(III) ions, whose individual spins are expected to be very close to 2.[12] A good simulation of the spectra assuming $S = 12$ is shown in Figure 1b. The parameters are $g_{\parallel} = 1.974$, $g_{\perp} = 1.983$, $D = -0.047$ cm^{-1}, and $E = 0$.[13] The g values, slightly smaller than the free electron value especially in the parallel component, are in agreement with the presence of elongated octahedrally coordinated manganese(III).[12] The feature at ca. 9.2 T could originate from the rhombic component in the zero-field splitting tensor. We have tried to introduce an E parameter in the spin Hamiltonian, but the results are rather poor, and no better results are obtained by allowing for a splitting of $g_{\perp}$. The contribution of other spin states could be the origin of the feature. The temperature evolution of the spectra is, however, in agreement with the proposed model.

We have reproduced the partially oriented spectra assuming a Gaussian distribution of the orientation of the crystallites in the field, which has its maximum when the unique axis z is parallel to the field, and superimposing the spectra of the randomly oriented powder with a population ratio of 3:1 for the two species. The spectra reported in Figure 2b have been obtained by using the same parameters $g_{\parallel}$, $g_{\perp}$, and D employed in the simulation of Figure 1b and using as adjustable parameter for the oriented species the percentage (90%) of the crystallites which have the z axis forming an angle $\leq 3°$ with the field direction. Also in this case the general trend of the spectra and their temperature evolution is satisfactorily reproduced.

The present results strongly suggest an $S = 12$ ground state, or at least a significantly populated $S = 12$ state over a wide temperature range, while a previous interpretation gave $S \geq 12$.[8,9] The unambiguous attribution of the spin value to the ground state has been in fact hampered by the presence of a variable number of CH_2Cl_2 solvent molecules of crystallization. The magnetic susceptibility of a microcrystalline powder heated under vacuum to remove all the solvent of crystallization has been measured, and χT was found to approach 100 emu K mol^{-1} at 2 K, a value larger than that expected for $S = 13$, 91 emu K mol^{-1} for $g = 2$. However, a careful analysis of the data suggests that weak intercluster ferromagnetic interactions are active, $\theta = 0.40$ K, and the Curie constant, $C = 82$ emu K mol^{-1}, is closer to that expected for $S = 12$, 78 emu K mol^{-1}, than for $S = 13$.

Beyond the problems encountered in the simulation of the spectra, we believe that the present results clearly show the potentiality of HF-EPR spectroscopy. Its use allowed us to extract from powder measurements precise information on the magnitude and nature of the magnetic anisotropy in a molecular system of great complexity. The results are moreover very promising because the presence of Ising type anisotropy and a large-spin ground state corresponds to the presence of a barrier for the reversal of the magnetization.[14]

A comparison of the zfs observed for Mn_{10} with that of Mn_{12} immediately explains why the latter has slow relaxation below 10 K, while the former is still relaxing faster than 10^{-2} s at 2 K. In fact the barrier for the reorientation of the magnetization of Mn_{10} is ca. 13 K, while for Mn_{12} it is 65 K. Mn_{12} has a blocking temperature of 5.6 K, while for Mn_{10} it is expected to be 1.1 K, if we assume that its relaxation time follows an exponential law, with τ_0 equal to that observed for Mn_{12}.

The origin of the zero-field splitting in Mn_{10} is presumably to be attributed to the single ion contribution of manganese(III). It seems probable therefore that possible examples of superparamagnetic-like behavior can be found in large clusters comprising manganese(III). Mn_{10} itself is a candidate, and we plan to measure the relaxation below 1 K.

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[13] In the simulations of Figures 1b and 2b the line width was assumed isotropic and equal to 60 mT for temperatures up to 10 K and 80 mT for higher temperatures.

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