Nonlinear magnetic susceptibility of molecular magnets: Tunneling of high-spin molecules

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The magnetic susceptibility of high-spin molecules $CrNi_6$ ($S=15/2$) and $CrMn_6$ ($S=27/2$) has been measured at high frequency (680 MHz), in a magnetic field (up to 5 T), and at low temperature (down to 18 mK). A large decrease of the imaginary part of the susceptibility with increasing electromagnetic power is observed. This nonlinear effect is attributed to tunneling of the high-spin molecules between the two states $|\pm S\rangle$ of the ground doublet across the anisotropy-energy barrier.
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Tunneling of large spins has been treated theoretically for a long time. It has been shown that such spins, if they have a strong anisotropy energy, can be reversed along their anisotropy axis.[1] Symmetry conditions other than the axial one have been also considered.[2] According to all these results, the tunneling rate decreases quite quickly with the magnitude of the quantum number S. Experimentally, some measurements of magnetic susceptibility and relaxation times at low temperature have been explained by macroscopic tunneling of magnetization.[3,4] Tunneling of large spins has been observed in glasses doped with rare-earth ions.[5,6] More recently, steps have been observed in the hysteresis loop of the magnetization of materials containing high-spin molecules,[7,8] and tunneling of these high spins ($S=10$) can explain this effect. In this paper, we report on the observation of a nonlinear magnetic susceptibility of materials containing high-spin molecules: A large decrease of the imaginary part of the magnetic susceptibility with increasing amplitude of the oscillating magnetic field at high frequency and very low temperature is observed. This is a direct evidence for the existence of tunneling.

With intent to make molecular magnets, chemists can obtain magnetic molecules which behave like high spins.[9] For example, $Mn_{12}Ac$ is a manganese cluster of spin $S=10$. The steps in the hysteresis loop above-mentioned[7,8] have been obtained in such molecules. Here we are interested in another kind of molecules: CrR_6 (where R holds for Mn or Ni). These molecules have been very recently synthesized.[10,11] From static-magnetization measurements at low temperature, it has been shown that the fundamental states were $S=15/2$ for $CrNi_6$ and $S=27/2$ for $CrMn_6$.[10,11] We have measured the magnetic susceptibility of these compounds at high frequency ($\nu\sim 680$ MHz) and low temperature (18 mK). The samples studied are powders (red for $CrNi_6$ and yellow for $CrMn_6$). The oscillating field is obtained from a split-ring resonator,[12] which provides a good separation between the region submitted to an ac magnetic field (here called B_1) and the one submitted to an ac electric field. The powder is placed at the center of the ring, where the ac magnetic field B_1 is the most homogeneous. The magnetic susceptibility is obtained as follows: The real part (χ') is proportional to the shift of the resonance frequency and the imaginary part (χ'') is proportional to the line broadening. The relative variations of χ' and χ'' are determined with a good precision, but because of the difficulty to evaluate the filling factor of the resonator, there is an uncertainty on the absolute value of χ' and χ'' of about 20%. To ensure a good thermalization and to avoid any motion of the powder grains, these ones are embedded in a nonmagnetic grease. The orientation of each of the different powder grains is random. The low temperature is obtained with a He^3-He^4 dilution refrigerator. A superconducting coil provides the static magnetic field (called B_0 in the following), up to 5 T and orthogonal to the ac magnetic field B_1. To avoid sample heating, measurements are performed with short electromagnetic pulses. The repetition rate of these pulses is chosen in the range 0.001–10 Hz, depending on the power of the pulses. The duration of the pulses is long enough to reach the steady state of the system.

Figure 1 shows the real and imaginary parts of the magnetic susceptibility of $CrNi_6$ measured at 18 mK as a function of the external magnetic field B_0 (the resonator frequency is around 680 MHz). The real part of the magnetic susceptibility (χ') increases with B_0, up to $B_0=B'_{\max}$

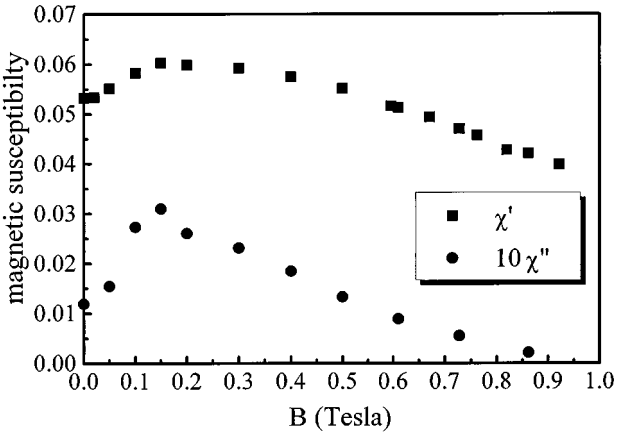

FIG. 1. Real and imaginary parts of the magnetic susceptibility of $CrNi_6$ (in mks units) at 680 MHz and 18 mK as a function of magnetic field.

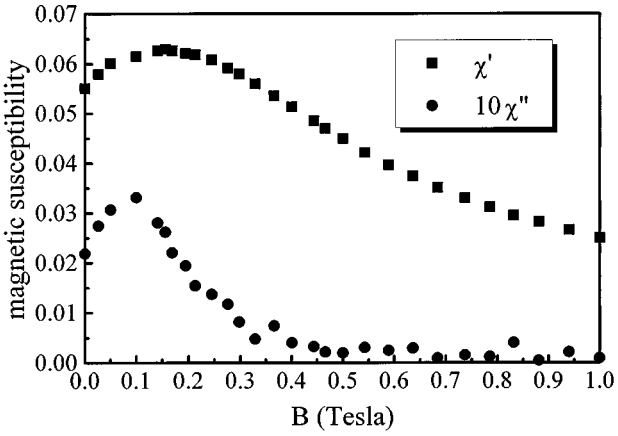

FIG. 2. Real and imaginary parts of the magnetic susceptibility of $CrMn_6$ (in mks units) at 680 MHz and 18 mK as a function of magnetic field.

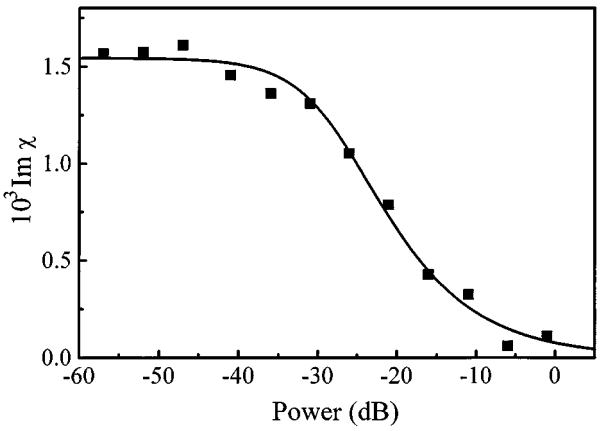

FIG. 3. Imaginary part of the magnetic susceptibility of $CrNi_6$ (in mks units) at 680 MHz and 18 mK in zero magnetic field as a function of electromagnetic power (0 dB corresponds to 3×10^{-2} T).

$=0.23$ T. Then it decreases slowly with increasing field. The behavior of χ'' is similar, except the peak is much sharper and is located at a slightly different field ($B''_{max}=0.15$ T).

Figure 2 shows the results of the same experiment performed in $CrMn_6$ at the same temperature. Again, there are peaks in the two parts of the susceptibility as a function of magnetic field, now located at $B'_{max}=0.15$ T and $B''_{max}=0.10$ T for χ' and χ'', respectively. These peaks look very much like the ones obtained in dysprosium-doped and gadolinium-doped glasses.[5] The shape of $\chi(B_0)$ and the ratio B'_{max}/B''_{max} are the same in every case. Their existence seems to be a general property of high-spin systems having a large anisotropy energy as compared to the temperature. At these low temperatures the activated processes are quenched (see below), and any motion of the high spins can only result from tunneling. However, there is not yet any accounting for these peaks. It is easy to justify the decrease of the susceptibility in high field by taking a density of states proportional to $1/B_0$,[5] but the magnetic field value of the peak location is about 30 times higher than the internal dipolar field. Hence it is difficult to explain this peak with dipolar interactions alone.

To confirm the tunneling motion of these high spins, we have looked for a nonlinearity of χ'' as a function of electromagnetic power. In $CrMn_6$, χ'' is constant in the whole power range (-92 dB, 0 dB), and no nonlinearity is detected. It is not the same in $CrNi_6$ where a nonlinear effect is observed. Figure 3 shows the variation of χ'' in this compound as a function of power or, equivalently, as a function of B_1^2 (0 dB corresponds to $B_1=10^{-3}$ T), in zero external static field and at $T=18$ mK. We have restricted the plot above -60 dB, because the susceptibility is constant between -90 and -60 dB. Here χ'' decreases with increasing power to reach zero at the highest power. We have presented here the results for zero static magnetic field. For $B_0\neq0$, the results are similar, the only change being a slight decrease of the critical power with increasing B_0. The data can be analyzed in the following way: Using the usual expression for χ''(Ref. 13) and integrating it over the distribution of internal magnetic fields, we get the usual expression[5]

$$\chi''=\frac{\chi''_0}{\sqrt{1+\gamma^2B_1^2T_1T_2}}, \tag{1}$$

where χ''_0 is the imaginary part of the low-power magnetic susceptibility. The solid line in Fig. 3 is the theoretical curve obtained from the above equation, giving the best fit with the experimental results. From this fit a critical power (for which $\gamma^2B_1^2T_1T_2=1$) equal to -30 dB and corresponding to $B_1=3\times10^{-5}$ T is obtained. Hence $\gamma^2T_1T_2=1.1\times10^9$. The value of γ is unknown, but taking the value for the free cluster, we get $T_1T_2=3\times10^{-14}$ s^2. The fact that χ'' saturates completely at high power means that the measured χ'' is only due to a resonant effect. So the excitations responsible for χ'' must have a splitting equal to $h\nu$ ($\nu=680$ MHz is the resonator frequency).

We can attempt to describe the tunneling states observed as ground doublets of the clusters. The dipolar interactions between clusters are quite small due to the large distances between each other (16.45 Å), and we can consider them as isolated. It has been shown that one $CrNi_6$ cluster behaves as a spin 15/2 at low temperature and has an anisotropy energy of 4 K.[14] Hence the Hamiltonian of this system can be written[1]

$$H=-DS_z^2+g\mu_B\vec{S}\cdot\vec{B}_0, \tag{2}$$

where $\vec{S}$ is the magnetic moment of the cluster, z is the easy axis, DS^2 is the anisotropy energy, and B_0 is the static magnetic field. This Hamiltonian means that each cluster is in a double-well potential. At 18 mK (much smaller than the anisotropy energy, which is 4 K), only the ground doublet $S_z=\pm15/2$ is populated. We are not dealing with single crystals, but with polycrystals. Hence, the orientation of the anisotropy axis of each cluster is random. The resolution of Eq. (2) shows that the local component $B_\perp$ of the magnetic field perpendicular to the easy axis splits the ground doublet. This term is the tunneling rate between the two states of the dou-

blet. Due to the component $B_{\|}$ of the magnetic field parallel to the easy axis, there is an additional Zeeman splitting. The total splitting of the ground doublet is finally[11]

$$\epsilon = \sqrt{\Delta^2 + 2g\mu_B S B_{\|}}, \tag{3}$$

where g is the Landé factor, μ_B is the Bohr magnetron, and the tunneling rate Δ is given by

$$\Delta \approx DS^2 \left(\frac{2g\mu_B S B_{\perp}}{DS^2} \right)^{2S}. \tag{4}$$

It is important to notice that there can be tunneling inside the doublet only if Δ does not vanish, even if the doublet splitting is different from zero due to the Zeeman term. We assign our nonlinear χ'' to the saturation of this ground doublet. Since the direction of the anisotropy axis is random from cluster to cluster, only those having their axis almost perpendicular to the local magnetic field can tunnel (their splitting must be equal to the energy corresponding to the resonator frequency: $h\nu = 0.032$ K). With increasing magnetic field, the number of satisfactory clusters decreases because the angle between the local field and the anisotropy axis must be closer and closer to 90° to satisfy Eq. (3).[5] It must be pointed out that the tunneling rate obtained from Eq. (4) with the parameters of $CrNi_6$ is quite small: Taking $S=15/2$, $g=2$, $B=0.15$ T, and $DS^2=4$ K, we obtain $\Delta = 10^{-15}$ K. Within this model it remains indeed very small for $B_{\perp}$ less than 0.5 T. Another possibility is to take a tetragonal symmetry instead of an axial one, but also in this case Δ remains small.[15] It has been shown that adding a second constant of anisotropy in Eq. (2) (which means that, instead of an anisotropy axis, there is an easy plane with an easy axis in the latter) leads to a more satisfactory tunneling rate.[6] However, the value of this constant is lacking for $CrNi_6$. Last, the nonobservation of a nonlinear effect in the magnetic susceptibility of $CrMn_6$ could be due to a too high critical power unattainable with our apparatus.

It is important to verify that the effects here reported can be due only to tunneling between $|+S\rangle$ and $|-S\rangle$ states. In $CrNi_6$, for example, the magnetic moment is trapped in one of the two wells we can assume to be the one corresponding to $S_z > 0$. The ground state is $|S_z = 15/2\rangle$ and the first excited level is $|S_z = 13/2\rangle$, which gives according to the Hamiltonian of Eq. (2) a splitting of about 1 K. Hence, at 18 mK, only the ground state is populated, and the allowed transition $|S_z = 15/2\rangle \rightarrow |S_z = 13/2\rangle$ needs an energy gigantic as compared to $h\nu$ (ν is the resonator frequency). So only the transitions $|S_z = -15.2\rangle \rightarrow |S_z = +15/2\rangle$ are energetically possible. The last possibility other than tunneling could be thermal activation between these two states above the energy barrier. In order to test this one, we have measured χ'' as a function of temperature in zero field. Figure 4 shows the results: χ'' decreases slightly with increasing temperature up to 100 mK, then it increases to reach a maximum at 1350 mK, and decreases quickly towards zero. As expected from a double-well potential, there is a thermally activated peak. The maximum of χ'' occurs for $\omega\tau(T) = 1$, where ω is the angular frequency of the resonator and τ is the thermally activated relaxation time. τ depends on the temperature according to Arrhenius law:

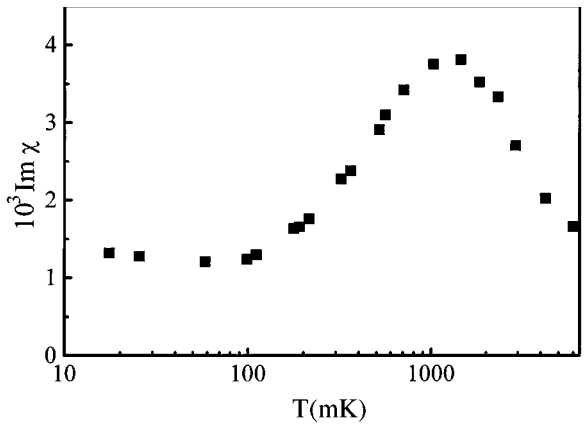

FIG. 4. Imaginary part of the magnetic susceptibility of $CrNi_6$ (in mks units) at 680 MHz in zero magnetic field as a function of temperature.

$$\tau = \tau_0 \exp(E_A / k_B T), \tag{5}$$

where E_A is the height of the energy barrier to overcome to go from one well to the other one. From our peak, we get $\tau(T = 1350\ \text{K}) = 1/\omega = 2.43 \times 10^{-10}$ s. We can add this point (τ,ω) to the ones already obtained by susceptibility measurements at much lower frequency (between 30 and 1000 Hz) by J. L. Tholence at Grenoble.[14] The agreement is very good: Our point is aligned with the former ones in the plot of $\ln(\tau)$ as a function of $1/T$. Fitting again the whole data with Eq. (5), we get $E_A = 4.08$ K and $\tau_0 = 9.3 \times 10^{-12}$ s. Here τ_0 is a quite short value which corresponds to motions of small entities. This agrees with the assumption of activation processes of single clusters. Now we can exclude a thermally activated process at 18 mK. Indeed, at this temperature, Eq. (5) gives $\tau = 0.37 \times 10^{78}$ s. We cannot perform the same calculation for $CrMn_6$, because the susceptibility peak has not been measured at different frequencies. However, we have observed in this material a susceptibility peak similar to Fig. 4 in the same temperature range, and we have verified that below 100 mK, χ'' no longer changes with temperature, which is an evidence for quenching of the activation processes.

In summary, the observation of the saturation of the magnetic susceptibility as a function of electromagnetic power which is a direct evidence of tunneling has been observed in $CrNi_6$. In the case of $CrMn_6$, the test failed, probably because of a too high critical power of these clusters. More generally, the high-frequency susceptibility measurements appears to be a good tool to look for tunneling of high-spin molecules. The existence of χ' and χ'' peaks as a function of magnetic field at very low temperature seems quite general in these systems. However, the explanation of the experiments with tunneling set the problem of the tunneling rate. As we have shown, its smallness is unphysical, using the axial-anisotropy model alone. The same problem arises in the attempt to explain the magnetization curves of $Mn_{12}Ac$.[7,8] Probably, the single-cluster model is too simple, and it will be necessary to take into account some interactions between each other to explain fully the experiments.

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