3 Single-Molecule Magnets

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Summary. Single-molecule magnets (SMMs) are among the best materials for studies of nano-scale magnets. SMMs are located in the boundary region between the discrete atoms and the bulk magnets, and exhibit unusual classical and quantum magnetic properties such as meso-scale magnets. In this chapter, we will review the chemistry and physics of 12-nucleus Mn clusters (Mn12) as a SMM. After explaining the magnetization process and the quantum tunneling or coherence in Mn12, we will describe the magneto-structural correlation in Mn12, referring to the Jahn–Teller isomers of Mn12; a slight difference in structure at the Mn(III) site gives rise to a significant difference in magnetic relaxation. The possible application of SMMs is also described.

3.1 Single-Domain Magnets

Magnetic materials usually exhibit magnetic ordering below a certain critical temperature; this ordering arises from interactions between neighboring spins. In ferromagnets, the magnetic energy favors a parallel spin alignment, while the lowest-energy state is achieved with an antiparallel alignment in antiferromagnets and ferrimagnets. Ferro- and ferrimagnets, which have a spontaneous magnetization, contain magnetic domains. While the atomic (or molecular) magnetizations are all parallel in one domain, the domains have different magnetization orientations so as to reduce the magnetostatic energy. The domains are separated by domain walls in which the magnetization gradually rotates from one direction to another. Domain-wall motion is very important in the technology of magnetic information storage, because it governs the strength of permanent magnets.

If an isolated magnetic particle is smaller than \( \sim 100 \) Å in diameter, it becomes a single-domain magnet, because it is hard to include domain walls whose widths are \( \sim 50 \) Å [1,2]. Recently, the magnetic properties of single-domain magnets have been investigated extensively, making use of the rapid advances in nanostructure fabrication techniques and of highly-sensitive magnetic measurements.

The magnetic dynamics of single-domain particles are simpler than those of bulk magnets. The energy of a single-domain particle depends only on the direction of the magnetization vector. If there is a magnetocrystalline
anisotropy in this particle, the two stable states, “up” and “down”, are separated by a potential barrier, $\Delta E$ (see Fig. 3.1). This results in the generation of a hysteresis loop in the magnetization curve, similar to those of bulk ferromagnets. While the hysteresis loops of bulk ferromagnets originate from the motion of domain walls, those of single-domain magnets result from the potential barriers. Figure 3.1 schematically illustrates the field dependence of the double-minimum potential well: (a) the particle stays in the “up” state, exhibiting the saturation magnetization $M_s$ in a large external field applied parallel to the magnetic easy axis; (b) the particle persists in the “up” state because of the barrier, even when the field is reduced to zero; and (c) the magnetization changes its direction from metastable “up” to stable “down” in a field that is opposite to the original direction and is larger than the coercive field $H_c$.

The relaxation rate $1/T$ is governed by the Arrhenius thermal-activation law; the rate is proportional to $\exp(-\Delta E/k_B T)$ at a finite temperature, where $k_B$ is the Boltzmann constant. At high temperatures ($k_B T \geq \Delta E$) the magnetization flips easily because the thermal energy is large enough to overcome the barrier, while the magnetization rotation gradually becomes frozen with a decrease in temperature. We usually define the blocking temperature, $T_B$, as the point at which $\tau = 100$ s. Hysteresis loops become observable below $T_B$ in conventional magnetic measurements. The value of $\Delta E$ is roughly proportional to the product of the magnetic anisotropy and the volume of the particle. There is a dilemma that the smaller volume of the particle, the smaller the values of $\Delta E$ and $T_B$.

Another reason for interest in single-domain magnets is concerned with quantum phenomena [3]. Even below $T_B$, the magnetization of the particle can rotate by macroscopic quantum tunneling through the barrier. These quantum effects are classified into quantum coherence of magnetization (QCM) [4-8] and quantum tunneling of magnetization (QTM) [9-12]. The former is coherent, while the latter is incoherent. QCM occurs between degenerate states in a symmetric potential well at zero field (Fig. 3.2a); the magnetization rotates coherently between the “up” and “down” states. QTM occurs in an asymmetric potential well. A state on the unstable side makes a transition to an energetically degenerate state on the stable side, going through the barrier, and then relaxes to the ground state (Fig. 3.2b). These