Effects in Molecular Nanomagnets

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single-molecule magnet (SMM)   single-chain magnet (SCM)   molecular nanomagnet

molecular structure   information storage

1. Introduction

When thinking about nanomagnets from a physicist's point of view, usually zero-dimensional (0D) or one-dimensional (1D) magnets will come to mind. Such nanomagnets may be formed, e.g., from the ferromagnets iron, nickel, cobalt, or permalloy, or from the ferrimagnets of magnetite or nickel ferrite, to name just a few [1][2][3][4][5]. Ferromagnetic materials contain elementary magnets for which a parallel orientation is energetically favored, while ferrimagnets can be imagined as containing two antiparallely oriented ferromagnetic sub-lattices with different magnitudes of magnetization, in this way also resulting in a net magnetization. Diverse shapes can be thought of, from square or round nanodots [6][7] to magnetic nanowires, e.g., those used in the so-called Racetrack memory [8][9][10], to more complicated shapes, including 3D particles [11][12][13]. Combining different magnetic materials, e.g., a ferromagnetic and an antiferromagnetic one, can result in additional effects as a result of the surface interactions, such as the exchange bias [14][15][16][17].

Molecular magnets, in principle, have a similar hierarchy. Starting from single-molecule magnets (SMM) [18][19][20] and single-chain magnets (SCM) [21][22][23] , more complex structures are also possible [24][25][26]. In general, molecular nanomagnets can be built without the aforementioned magnetic elements [27]; however, highly interesting molecular nanomagnets can be created by adding Mn 12, Fe 8, Mn 4, or other metallic elements [28][29][30].

2. Magnetic Interactions via a Ligand

Generally, magnetic interactions via ligands can be assumed to be similar to those found in inorganic materials. As organic molecules are usually isolating, the magnetic interactions are more localized. In the easiest approach, singly occupied molecular orbitals (i.e., unpaired electrons) inside a molecule are regarded as magnetic orbitals,

with their relative orientation being responsible for ferromagnetic or antiferromagnetic coupling [31][32]. This exchange interaction works directly between unpaired electrons or via a ligand, in this case usually described as a super-exchange interaction. This interaction is depicted in more detail in **Figure 1** [33].
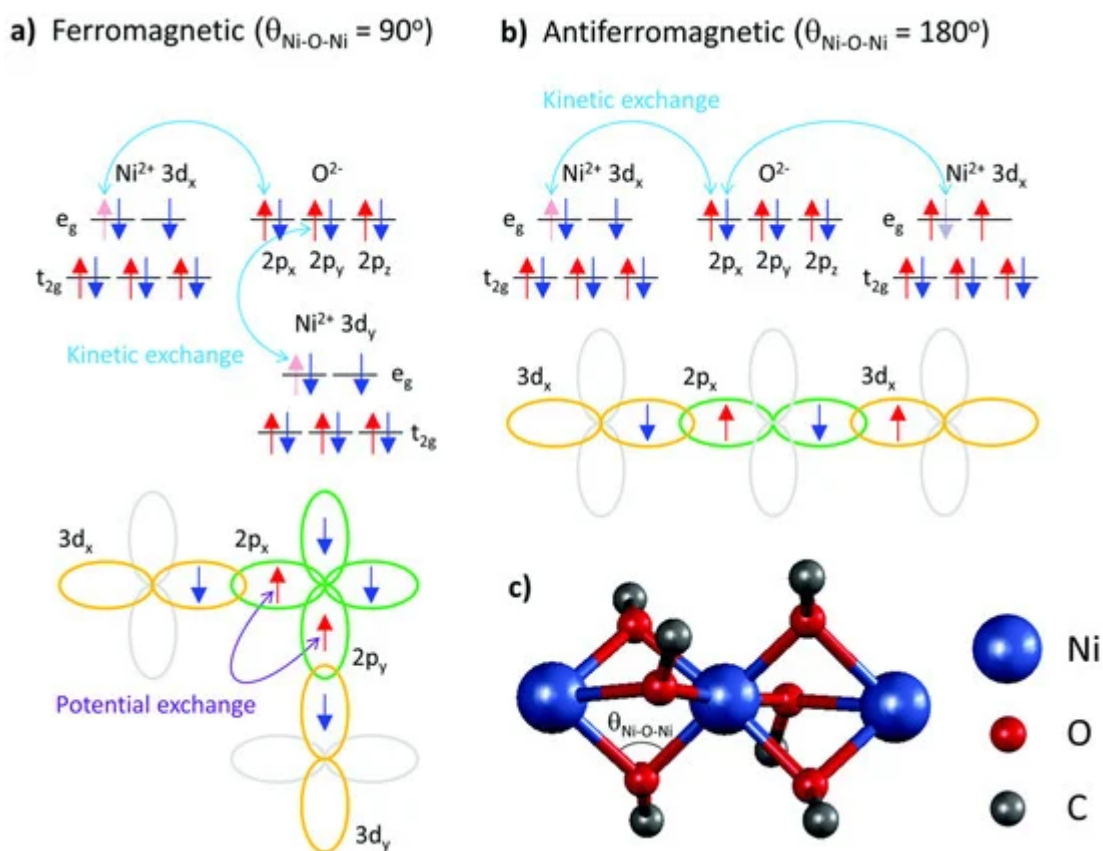
Figure 1. Super-exchange coupling between nearest-neighbor 3d orbitals of Ni via the ligands of O^{2-} (2p orbitals). (**a**) In the case of a 90° angle between Ni-O-Ni, super-exchange results in a ferromagnetic coupling between the orthogonal oxygen 2p orbitals; (**b**) for an angle of 180° between Ni-O-Ni, an antiferromagnetic coupling occurs due to the nickel and oxygen orbitals overlapping; and (**c**) geometry of nickel(II) acetylacetonate (Ni(acac)$_2$) molecular magnets. From ref. [33], originally published under a CC-BY license.

In addition, a double exchange can occur in mixed valence systems (e.g., metal ions in different oxidation states, such as Mn III and Mn IV), describing the fast hopping of unpaired electron between the ions, i.e., delocalization of the valences. This results in a ferromagnetic coupling, as the transferred spin must be parallel to the other Mn 4+ spins because of the Pauli principle [34][35].

3. Single-Molecule Magnets

One disadvantage of the aforementioned single-molecule magnets is their very small blocking temperature, typically below the temperature of liquid helium. Ideally, magnetic properties should be reached above the temperature of liquid nitrogen , i.e., 77 K. This is one of the challenges diverse research groups have been working on during the last decades [36].

Much higher values were observed by Gould et al. who compared the divalent linear metallocenes Ln(Cp iPr5) 2 (with Ln = Tb, Dy) with the trivalent ones [Ln(Cp iPr5) 2][B(C 6F 5) 4], and found longer relaxation times in Tb II than in TB III and longer relaxation times in Dy III than in Dy II , and a similar behavior for Tb II and Dy III , as could be expected from the identical number of unpaired electrons in the latter. Most importantly, in Tb(Cp iPr5) 2 they found a high blocking temperature of 52 K [37].

For spin-based devices based on SMMs, controlling the spin relaxation is of the utmost importance. Sorensen et al. reported on the effect of a non-linear to pseudo-linear change in the crystal field symmetry in a dysprosium complex, leaving the residual chemistry unaltered, and found a strong reduction in the tunnel splitting at very low temperatures in the milliKelvin range [38]. Switching the magnetic anisotropy reversibly was enabled in lanthanide complexes as a function of external magnetic field and temperature [39][40].

Redox-active tetrathiafulvalene (TTF)-based ligands, on the other hand, allowed for designing coordination lanthanide complexes in different oxidation states, resulting in different magnetic properties for such SMMs [41]. An overview of such TTF-based ligands is given in [42].

4. Recent Trends in Molecular Nanomagnets

Besides the aforementioned topics, which are often related to basic research, some recent trends should be mentioned that are currently in the focus of research in this area, often aiming at multifunctional molecular magnets.

One of these topics is related to luminescent SMMs based on lanthanides for possible application in quantum computing, bio-labeling, or LEDs. Jia et al. recently reviewed the design strategies for such luminescent lanthanide-based SMMs, pointing out the necessary combination of a strongly UV absorbing ligand environment that efficiently populates excited states in the metal ion, with a filled-up coordination sphere of the Ln(III) ions to reduce radiation-less deactivation processes [43]. Yi et al. investigated the isostructural dimers [Ln(hfac) 3(PyNO)] 2 (with the lanthanides Eu, Gd, Tb, and Dy) and found luminescence for Eu, Tb, and Dy [44]. For Yb III , Er III , and Eu III , Jiménez et al. found luminescence in different mononuclear Ln III complexes [45]. Wang et al. suggested using a near-infrared emissive SMM as a highly sensitive luminescent thermometer [46]. A review of luminescent Schiff-base lanthanide SMMs can be found in [47].

Even ferroelectricity was found in SMMs [48][49] and SCMs [50][51].

As this short entry shows, multifunctional molecular nanomagnets enable combining magnetic with different optical or electrical properties, making them highly useful for diverse recent applications.

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