



Review

Magnetic properties of atomic clusters and endohedral metallofullerenes

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ABSTRACT

Magnetic clusters are aggregates of a few to thousands of atoms or molecules that exhibit magnetism. Understanding the evolution of magnetism from individual atom to bulk solid is fundamentally important, and combining different types and number of atoms would lead to many opportunities in tuning magnetic properties of an alloy cluster. The magnetic behaviors of a cluster can be measured by the Stern–Gerlach deflections or the X-ray magnetic circular dichroism spectroscopy in a molecular beam and calculated by *ab initio* methods. Herein we present a comprehensive review on the experimental and theoretical progresses on the magnetic properties of the ligand-free gas-phase clusters up to a few hundred atoms, including elemental metal clusters, alloy clusters, metal-doped semiconductor clusters, magnetic superatom clusters. Endohedral metallofullerenes, a special kind of magnetic clusters, are also briefly illustrated.

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1. Introduction

Since the foundation of quantum mechanics, the magnetism of atoms and solids has been extensively investigated and well understood. It is known that the macroscopic magnetic behavior of a solid is not a simple superposition of the magnetic moments of every constituting atom. Without external magnetic field, the orientations of the magnetic moments in an aggregate of atoms usually align in a random way that does not induce a permanent macroscopic moment. Only with the exchange interaction (which is a quantum mechanical effect related to the Pauli exclusion principle), the magnetic moments of neighboring atoms in a solid may exhibit some long-range ordering (i.e., ferromagnetic, antiferromagnetic, ferrimagnetic, see Fig. 1), leading to various fascinating magnetic materials.

Clusters, as the aggregates of a few to thousands of atoms or molecules, constitute an important intermediate state between microscopic atoms/molecules and macroscopic condensed matters. Since 1980s, clusters have been intensively investigated due to their importance in physics, chemistry, materials science, energy and environmental science, and life science, as well as their potential applications as building blocks for novel nanoscale materials and devices [1–6].

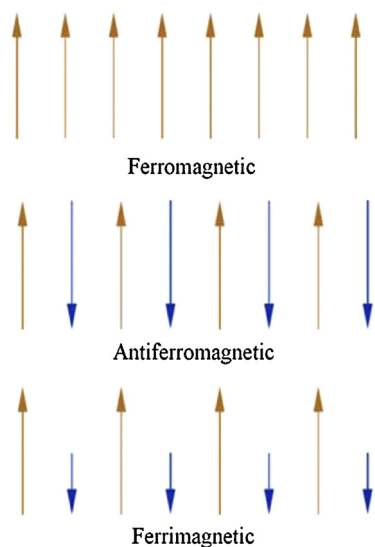


Fig. 1. Schematic plot of the ferromagnetic, antiferromagnetic, ferrimagnetic ordering (local magnetic moments are illustrated by up and down arrows).

In the past three decades, we have witnessed increasing interest in the magnetic properties of clusters from both basic science and technological applications. First of all, it is fundamentally interesting to understand the evolution of magnetism from individual atoms (which obeys the Hund's rule) to solids (which is determined by spin-polarized band structure of the itinerant electrons). For example, many open-shell transition metal (TM) atoms possess certain magnetic moments, whereas only a few of them (like Fe, Co, Ni) exhibit ferromagnetism in their crystalline state. Moreover, the combination of different types and number of atoms would lead to tunable magnetism in the alloy clusters, which may even go beyond the current magnetic alloy of solid phase. Finally and most importantly, as a kind of novel nanoscale magnetic materials, magnetic clusters (including endohedral fullerenes) are rather promising in many fields, such as high-density information storage [7], spintronic devices [8], quantum computing [9], and magnetic resonance imaging (MRI) [10].

Experimentally, a collection of gas-phase clusters can be produced in a molecular beam and their magnetic behaviors can be measured by the well-known Stern–Gerlach deflections apparatus, as schematically shown in Fig. 2. First, the clusters are generated in a laser vaporization source cavity with helium as carrier gas. The cluster/gas mixture exits the source cavity through two nozzles into vacuum to produce a supersonic molecular beam, passing through two skimmers. After laser ionization, the clusters are mass-selected

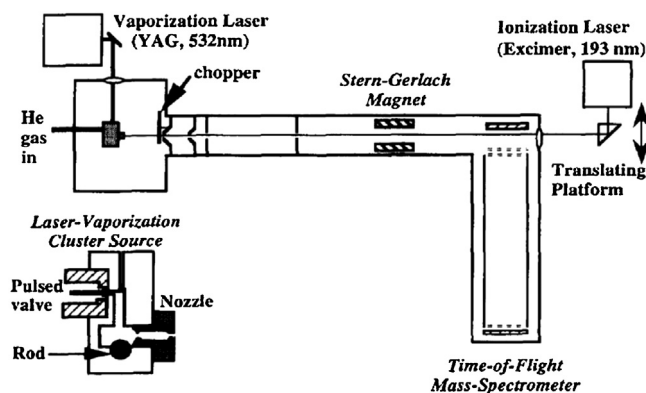


Fig. 2. Schematic illustration of the cluster beam apparatus including the laser vaporization cluster source (which is shown in more details on the bottom left of the figure), the Stern–Gerlach magnet and the time-of-flight mass spectrometer.

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