Chapter 1

Introduction

In the last decade, Nanoscience and Nanotechnology has captured immense attention among researchers across the world due to two main reasons. First, the nanotechnology and the underlying nanoscience is expected to affect products and processes over a very wide range, quite unlike the technologies so far which were sector-specific or narrow in their range of applications. And, secondly, the field is truly interdisciplinary - involving overlap which extends through Physics, Chemistry, Biology and Engineering.

The central aim of Nanoscience is to understand, control and manipulate objects of a few nanometers (nm) in size (1-100 nm). The nano-objects are structures which have at least one of its dimension in nanometer. The nanostructures can be classified accordingly to their dimension (D) as 0D, 1D, 2D and 3D structures as shown in Figure 1.1.

![Figure 1.1: Nanostructures of 0D, 1D, 2D and 3D.](image)

The 0D nano-objects have all dimensions very small such as nanoclusters, fullerenes
and quantum dots. The 1D nano-objects are which have linear structure such as nanowires and nanotubes which have diameter in few nm. The 2D nano-objects are planar structures with thickness in nm such as Graphene and thin films. The 3D objects denotes the structures formed from smaller building blocks or crystallite such as the nanocrystalline materials. The structural, electronic and magnetic properties of nano-objects are often peculiar, being qualitatively different from those of their constituent parts and from those of macroscopic pieces of matter. Further, these novel properties changes significantly as function of size. This opens the possibility of tuning their properties by controlling precisely their formation process.

Among various nano-particles, the nanoclusters occupy a central place due to their intermediate position between single atoms and molecules and bulk matter. A cluster is defined as a group of same or similar elements gathered together. The clusters are different from nanoparticles w.r.t to the fact that the size and composition of clusters can be controlled one atom at a time while in general the number of atoms in a nanoparticle cannot be determined with the same precision. Therefore, clusters are the ultimate nanoparticles where the size and composition are known with atomic precision and the evolution of their properties can be studied one atom at a time. From basic science point of view, nanoclusters are species which display properties very different from their molecular and bulk counterparts.

The properties including interatomic distance, electronic, magnetic, and optical property, varies as a function of cluster size. In clusters consisting of a few atoms, the properties change non-monotonically, often varying widely with the addition of a single atom. The change in the physical and chemical properties of small particles as a function of their size may be attributed due to the increased fraction of the ‘surface’ atoms and confinement effects. The structural and electronic properties of the clusters are strongly influenced by the nature of bonding i.e. different kinds of forces: strong attraction between oppositely charged ions, van der Waals attraction, covalent chemical bonds or a metallic bond.

Recent advances in the experimental work to synthesize and characterize nanoclusters consisting of up to a few hundred atoms has given birth to a new field that forms a bridge not only between atoms, molecules, nanoparticles, and bulk matter but also between the disciplines of physics, chemistry, materials science, biology, medicine, and environmental science. The nanometer size and tunable composition allow clusters to have unusual combinations of physical and chemical properties. Metallic elements can become insulating, semiconductor elements can
become metallic, nonmagnetic materials can become magnetic, opaque materials can become transparent, and inert materials can become reactive. The clusters can be designed and synthesized by varying their size and composition such that they mimic the electronic properties of atoms [4]. These clusters, originally termed unified atoms [5], are now commonly referred to as superatoms [6]; they can form the basis of a new three-dimensional periodic table with superatoms constituting the third dimension [6, 7]. A new class of cluster assembled materials where clusters instead of atoms form the building blocks can usher an exciting era in materials science with unlimited possibilities for new materials.

1.1 Motivation

The charge and spin of electrons in the solid state electronics lay the foundation of the information technology we use today. Integrated circuits and high-frequency devices made of semiconductors have had great success using the charge of electrons in semiconductors. Mass storage of information is carried out by magnetic recording using spin of electrons in ferromagnetic materials. The researchers in the last decade have been exploring the possibility of using both the charge and spin of electrons for further enhancing the performance of the devices. This has lead to emergence of spintronics as emerging area of futuristic research.

In spintronics, it is essential to develop semiconductors with ferromagnetically polarized carriers at room temperature such that spin as well as charge of the carriers can be coupled with an external magnetic field. These materials are predicted to integrate the semiconducting, magnetic and optical functionalities in a single material. Thus reducing the cost, enhance the speed and reduce the size of device operating at very low power.

Theoretical studies had predicted the possibility of realizing dilute magnetic semiconductors (DMS), which combines ferromagnetic and semiconducting properties at room temperature [10]. This has lead to series of experiments predicting magnetic semiconductors in various host semiconducting materials (Si, Ge, GaAs, ZnO, GaN etc) by doping with series of 3d transition metals [11, 12]. The room temperature FM has also been reported in II-VI compound semiconductors when doped with nonmagnetic impurities such as C, N and B. However, the real origin of ferromagnetism could not be explained due to conflicting and controversial experi-
mental results. The central questions about the origin of FM in semiconductors are still debated such as intrinsic or extrinsic origin of FM, effect of donor and acceptor impurity bands on magnetic interactions and effect of native point defects. Therefore, the contradicting experimental results on DMS have highlighted the challenge to identify atomic structure and electronic configuration responsible for the magnetism in such system and offers numerous possibilities for their proper use in the field of spintronics.

Recently, magnetism was reported in host material of DMS when the size of crystallites is in nanometers [13]. Consequently, the dimension of host material along with magnetic impurities would be exploited for enhancing FM at room temperature. Therefore, to explain the origin of the FM in semiconducting materials, it is essential to understand their magnetic behavior at molecular and nanocluster level. There is a possibility that the investigation of magnetic nanoclusters might lead to the emergence of other interesting novel properties at nanoscale.

The evolution of the magnetic behavior due to magnetic impurity doping in small clusters needs to be understood before tuning their stability and spin multiplicity. Recent experiments on magnetism in carbon based materials have renewed interest in carbon systems as possible new magnetic materials due to their technological advantages over conventional magnetic materials. The stability and availability of carbon nanostructures especially fullerenes makes them interesting candidate for DMS. The magnetism can be induced in fullerenes by encapsulating magnetic impurities (3d transition metals). The origin of room temperature FM in wide band gap ZnO due to non-magnetic impurities and effect of non-magnetic impurities as co-dopants are of immense importance and have been addressed in the thesis work.

1.2 Semiconducting Clusters

Semiconductor nanoclusters are crystallites of semiconductor material with diameters between 10 Å and 100 Å. Their optical and electronic properties differ markedly from the bulk and are strongly size-dependent. The electronic properties of nanoclusters are explained qualitatively by assuming that the electrons and holes are confined within the nanocluster. This confinement property is called the "quantum size effect". The quantum size behavior in semiconductor clusters has been verified using scanning tunneling spectroscopy and scanning capacitance microscopy on
Single clusters [10]. The field is robust and expanding and we expect many novel phenomena to emerge.

Semiconductor nanoclusters are of practical interest because of their fascinating electronic, magnetic and physical properties at nanoscale. Polarizabilities, permanent dipole moments, and absorption spectra of semiconductor clusters over the size range from 10^3 to 10 atoms, a gradual transition occurs from localized solid-state-like bonds to molecule-like bonds. Interestingly, quantum size effects are found even in relatively small particles with about 10^2 atoms. These effects can be observed in the form of unusually small static polarizabilities or in the absorption bands of smaller clusters. These effects disappear over the size range 10^2-10 atoms [5].

In comparison with pure semiconductor clusters, the compound semiconductors and doped semiconductor clusters exhibit different properties. For example, gallium arsenide (GaAs) has six times higher electron mobility than silicon, which allows faster operation; wider band gap, which allows operation of power devices at higher temperatures, its direct energy band gap gives it a more favorable optoelectronic properties than the indirect band gap of silicon.

In the last decade, semiconductor cluster branch has expanded enormously and clusters are classified according to their place in the periodic table as: Group IV semiconductors, III-V semiconductors, II-VI semiconductors, IV-VI semiconductors, V-VI semiconductors. II-VI semiconductors and Oxides etc.

Electronic structure of semiconducting nanoclusters

In atoms, the electron energy levels are quantized and discrete and the energy gap between the highest occupied and lowest unoccupied orbital (HOMO-LUMO) determines to a large degree their stability, reactivity, and electronic properties. As atoms aggregate to form clusters or molecules, these energy levels overlap, the gap between the highest occupied and lowest unoccupied energy levels change, as shown in Figure 1.2 and electrons are primarily distributed along the bonds formed by the atoms.

In bulk, the overlap between the discrete energy levels becomes high and energy bands give way to energy bands. When the energy bands exhibit a gap at the Fermi energy, the crystals are either semiconducting or insulating and the bonding can range from weak Vander Waals to strong covalent, or ionic.

In small nanoclusters, the energy gap exists between the highest occupied and lowest unoccupied orbital (HOMO-LUMO gap) irrespective of whether the clusters
Figure 1.2: Variation in band-gap with respect to size of cluster. [14].

Figure 1.3: Increase in band-gap with decrease in size of nanocluster.
are composed of metallic or nonmetallic elements. The band-gap of Si nanoclusters shows a variation as a function of cluster size when approaches 3 nm as shown in Figure 1.2. The band-gap increases with decreases in size from 3 nm. The band-gap for bulk Si is 1.1 eV but it increases as the size of nanocluster becomes less than 3 nm [14]. However in small nanoclusters there is increase in band-gap due to quantum confinement as shown in Figure 1.3.

**Magnetism in semiconducting nanoclusters**

The scientific quest in nanomagnetism can be framed quite concisely as to (i) create (ii) explore, and (iii) understand new nanomagnetic materials and phenomena. Presently, unique magnetic properties of nanostructures are under intensive research [10, 15, 16]. The magnetization (per atom) and the magnetic anisotropy of nanoparticles is greater than those of a bulk specimen, while differences in the Curie ($T_C$) or Néel ($T_N$) temperatures, i.e. between nanoparticles and the corresponding microscopic phases reach hundreds of degrees. In addition, magnetic nanomaterials are found to possess giant magnetoresistance, abnormally high magneto-caloric effect, and so on. Room temperature ferromagnetism is observed in various DMS as shown in Figure 1.4 (a and b). Figure 1.4(a) shows curie temperature w.r.t. band-gap of various host semiconductors. The curie temperature of ZnO cluster is close to room temperature and band-gap is also high. Figure 1.4(b) shows that GaN (group III-V), ZnO (group II-VI) and C (group IV) are the strongest candidates as semiconducting host for realizing room temperature FM. ZnO satisfies both the elementary conditions for ideal host material for DMS. Curie temperature of doped semiconductor clusters of group III-V, II-VI and group IV DMS are tabulated in Table 1.1, along with percentage of doping.

The magnetic properties of nanoparticles are determined by the chemical composition, type and degree of defectiveness of the crystal lattice, the particle size and shape, the morphology (for structurally inhomogeneous particles), the interaction of the particle with the surrounding matrix and the neighboring particles. However, these factors are difficult to control during the synthesis of nanoparticles nearly equal in size and chemical composition; therefore, the properties of nano-materials of the same type can be markedly different. This has resulted in the development of efficient methods for preparation and stabilization of nano-sized magnetic particles as well as with the progress in the physical methods for the investigation of such particles. At present spin can be injected in the semiconducting material of various dimension (thin film and nano-objects) for inducing magnetic functionality.
Figure 1.4: (a) Curie temperature variation w.r.t. band-gap of different semiconductors [17]. (b) Curie temperature $T_c$ variation for different Mn doped p-type semiconductors [10].
At present, main challenges in Nanomagnetism are quest for Ultrastrong Permanent Magnets, ultra high density media, spin transistor, spin-polarized materials, room temperature magnetic semiconductors, magnetic logic, spin based qubits and nano-biomagnetic sensors.

<table>
<thead>
<tr>
<th>Type</th>
<th>Cluster</th>
<th>x-percentage</th>
<th>Curie-temp(T_c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>III−V</td>
<td>(In_{1-x}Mn_x)As</td>
<td>6.3</td>
<td>60K</td>
</tr>
<tr>
<td>III−V</td>
<td>(Ga_{1-x}Mn_x)As</td>
<td>5.3</td>
<td>110K</td>
</tr>
<tr>
<td>III−V</td>
<td>(Ga_{1-x}Mn_x)As:Be</td>
<td>6.6</td>
<td>150K</td>
</tr>
<tr>
<td>II−VI</td>
<td>(Cd_{1-x}Mn_x)Te</td>
<td>5.6</td>
<td>2-3K</td>
</tr>
<tr>
<td>II−VI</td>
<td>p-(Zn_{1-x}Mn_x)Se:N</td>
<td>1.9</td>
<td>1.5K</td>
</tr>
<tr>
<td>II−VI</td>
<td>(Zn_{1-x}Cr_x)Te</td>
<td>20</td>
<td>300K</td>
</tr>
<tr>
<td>IV</td>
<td>(Ga_{1-x}Mn_x)</td>
<td>3.5</td>
<td>116K</td>
</tr>
</tbody>
</table>

1.3 Theoretical methods for investigation of nanoclusters

1.3.1 Quantum Mechanical methods

The electrons and nuclei are the fundamental constituents which determine the nature of the matter around us atom, molecule, condensed matter and nanostructures. The electrons apart from participating in bond formation in solids, and molecules also determine electrical, optical and magnetic properties of materials. The exact theory of electrons in matter is one of biggest challenges of theoretical physics.

In last few decades, there have been significant developments in developing theoretical approaches and computational methods which can treat interacting system of many electrons and nuclei found in condensed matter; molecules and clusters.

The theoretical methods for obtaining ground state structure and predicting various physical, electronic and magnetic properties of materials can be divided into two classes: the quantum mechanical and classical (empirical or semi-empirical potential) methods. They differ from each other as in the later approach the potential
energy is described by an analytical function of atom coordinates usually fitted to experimental data whereas in the former the energy is calculated by solving the Schrödinger equation for electrons in the field of atom cores (in the vast majority of methods). The empirical methods rely solely on the experimental data rather than theoretical information whereas the quantum mechanical methods (often called ab initio, or first-principle) do not use any empirically or experimentally derived quantities.

Many computational methods are developed nowadays which are based on quantum mechanical approximation up to different levels such as effective potential, Hartee-Fock, Tight-Binding and Density Functional Theory. Among different quantum-mechanical approaches in computational physics, density functional theory (DFT) has witnessed the most rapid development. DFT is used to investigate electronic structure in the ground state of many body system such as atoms, molecules, clusters and condensed phases. It provides better answers than other formulations for large systems such as clusters and solids.

1.3.2 Computational methods for ab initio calculations

Within the last two decades, the first-principle simulations of condensed matter systems has expanded spectacularly, from physics and chemistry into life, earth, nanoscale and materials sciences. This success has been based on both the steady growth of computing power and the development of methods based on density-functional theory (DFT). There are a large number of DFT based codes which are known today. These include TBLMTO, WEIN2k, CRYSTAL, FPLO, VASP, ABINIT, PWSCF, SIESTA and many others. There are differences in the practical realization of above codes as account of choice of basis sets, nature of pseudopotential, description of exchange-correlation effect of electrons and optimization procedures. The first important distinction comes along the line of all-electron and pseudopotential methods. TBLMTO, WIEN2k, CRYSTAL, FPLO are all-electron methods, which take into account, and re-adjust in every iteration, the wave functions of all electrons in each atom, from 1s upwards. On the contrary, SIESTA, ABINIT, PWSCF, and VASP are pseudopotential methods. In such methods, only valence electrons (down to some depth, probably including so-called semi-core states) are explicitly included in the equations, whereas deep core states is excluded from the treatment. This is accurate for describing chemical bonding, equilibrium geom-
etry, phonons etc. However, the properties immediately related to core electrons, like e.g. hyperfine field at atom cores, isomer shift, electric field gradient are not well explained.

Another important distinction concerns the choice of basis functions which are used to expand the solutions of the Kohn-Sham equation. There are three different methods in this regard: (i) those which use atom centered bases, usually relatively compact ones (of the order of $\sim 10^5$ functions per atom), and (ii) atom-independent ones such as plane waves, and the number of plane waves in a calculation may easily go into thousands, but they allow simple evaluation of matrix elements, and easy parallelization. (iii) hybrid methods, which combine numerical accuracy in intra atomic regions with reasonable flexibility in the interatomic region. The above methods are applicable in range of DFT based codes mentioned above. TBLMTO, CRYSTAL, FPLO and SIESTA use atom-centered bases, commonly called (tight-binding) group of methods; ABINIT, PWSCF, VASP use plane waves, and the basis in WIEN2k is a hybrid one. For this thesis work we have used VASP and SIESTA codes for performing spin-polarized DFT calculations.

1.4 Synthesis of semiconductor nanoclusters

The nanoclusters are synthesized by breaking up a bulk material into atoms or ions and then allowing them to condense into nanoparticles. In the laboratory, equipments are designed to synthesize nanoclusters by breaking down more of the raw material to the atomic level under controlled conditions to condense atoms together and form nanoparticles. Nanoclusters are produced from mass-selective cluster beams and are studied in the gas phase or within an inert matrix, or adsorbed onto a surface.

In recent times technologies such as mass spectrometry; ion mobility spectrometry; photo and collision induced dissociation; photo-ionization, photoelectron, and infrared spectroscopies; electron paramagnetic resonance; Stern-Gerlach molecular beam deflection; and optical spectroscopy have been advanced to measure the energy, ionization potential, electron affinity, magnetic moment, and optical absorption of nanoclusters.

The most commonly used methods for synthesizing the semiconductor clusters are discussed below briefly.
1.4.1 Pulsed laser ablation method

The ideal experimental technique for synthesizing nanoclusters and the cluster film is by PLA. The method can be separated into four independent steps: cluster nucleation, growth, cluster cooling and deposition.

- The nucleation is determined by the thermodynamic parameters of the material and by the initial conditions, like temperature and density of the vapor ejected after PLA. The nucleation process is characterized by the condensation temperature which can be found from general thermodynamic considerations.

- The cluster growth will occur only during the collisional expansion between the ablated particles; thus, the main process determining the growth will be the plume expansion dynamics. The expansion dynamics can be strongly influenced by ambient gas effects such as the plume confinement due to collisions between the ablated particles and gas molecules.

- Clusters are generally generated with a large amount of internal energy in liquid-like or solid-like states. The main paths of cluster stabilization are radiative, evaporative and collisional cooling. The first two mechanisms are evidently dominant in plume expansion under vacuum and the last one is present during the diffusive expansion of the plume into the ambient gas. The efficiency of collisional cooling will strongly depend on the temperature and density of the ambient gas determined by the hydrodynamics of the plume expansion.

- The critical parameter of deposition of free clusters on a substrate is the kinetic energy $E$ per atom $(E,N)$ in a free cluster of $N$ atoms. Roughly, if $E,N$ is less than the binding energy, one could expect the deposition of free clusters without fragmentation and structural rearrangement on the substrate. In the opposite case, the energy of the impact may be high enough to melt or to evaporate the clusters. Thus, strong deceleration of clusters is a necessary condition for cluster deposition [18].
1.4.2 Laser vaporization Supersonic method

This method is originally developed by Smalley and co-workers. The cluster vapor is produced by laser vaporization of the appropriate target material, situated near the exit of a pulsed high pressure nozzle. A laser pulse is focused on the face of a target wafer. The target is rastered across the laser spot so that the laser beam vaporizes a uniform pattern on the wafer without creating a hole. The target vapor is quenched with a high pressure pulse of helium gas (typically 2 atoms) which expands into the vacuum chamber from the supersonic nozzle. The nozzle is fired a short time before the laser so that the vaporization process occurs in several atmospheres of helium. Collisions of the cluster vapor with the supersonic helium flow cool the vapor below its condensation temperature and clusters grow. Different conical nozzle attachments can be fitted to the exit of the vaporization region to allow various degrees of clustering and cooling. Certain configurations can actually reheat already cooled clusters in a strong shock wave present at the cone exit. This provides a coarse control of the cluster temperature and size distribution [19].

1.5 Literature survey on Doped Semiconductor Clusters

Over the last several years, understanding the origin and effect of reconstructions that occur in small semiconductor clusters as compared to bulk material is a problem of both fundamental and technological interest. If current miniaturization trends continue, minimum device features will soon approach the size of atomic clusters. The clusters of group-14 elements have attracted attention because they are important for fine processing of semiconductors and synthesizing novel materials. However both Si and Ge are chemically reactive. Previous investigations indicate that the pure silicon is unfavorable for forming large-sized clusters and bulk solids; however, the encapsulation of transition metal in the large sized silicon cluster contributes to enhancing stability of pure silicon clusters and simultaneously exhibiting many magic behaviors, e.g., sized selectivities, different frontier orbital properties, and polarizabilities [13,20–31].

Among the group IV clusters, the $Si_n$ clusters doped with TM dopants (Cr, Mo, W, Mn, Cu, Zn) [34,41,42,44–46] have been studied extensively theoretically and experimentally to explore the possibility of incorporating magnetism in semiconducting
clusters. When TMs are encapsulated into large sized silicon cages some interesting phenomena appears such as tenability of HOMO(Highest occupied molecular orbital)-LUMO(Lowest unoccupied molecular orbital) gap. The TM dopants have shown to enhance the symmetry (related geometric stability) of the host cluster or enhance the HOMO-LUMO gap into the visible range. The magnetic moment of few TM dopants is completely quenched in Si [30,35]. Therefore, search for group-IV based DMSs has extended to higher mass congeners such as Ge and Sn [36-38].

**Germanium Clusters:** As compared to Si$_n$ clusters, only a few theoretical contributions have been made by different groups on the endohedral doping of TM elements in pure as well as hydrogenated Ge cages [39,10,10]. Theoretical studies on TM-doped caged Ge$_n$TM (n = 11-16) [39] clusters indicate that the growth behavior of these clusters are different from metal encapsulated silicon clusters. The mass spectra of Si$_n$ and Ge$_n$ appear nearly the same, with magic numbers for cations at n = 4, 6, and 10 [41,42]. However, Shvartsburg et al. showed, on the basis of binding energy and fragmentation energy that Ge$_{10}$ is relatively more stable. The medium-sized Ge$_n$ clusters are stacks of tri-capped trigonal prism subunits. But the structures of Ge$_n$ and Si$_n$ for n = 13 and n = 15, 16 differ in details [43]. The highest-occupied molecular orbital to lowest unoccupied molecular orbital (HOMO-LUMO) gaps in such clusters are much higher than their Si counterparts.

The ferromagnetism have been reported in group-IV semiconductor Mn$_x$Ge$_{1-x}$ [44], Cr$_x$Ge$_{1-x}$ [45] and Cr, Fe doped bulk Ge single crystals [46]. The Cr doped Ge single bulk crystal using vertical gradient solidification method has shown ferromagnetic ordering at 126 K [11] where as Cr doped Ge film using molecular beam epitaxy(MBE) has shown weak paramagnetic behavior between 1.8 K-300 K [11]. Recent work on germanium clusters have shown doping of Ge$_n$ clusters with halogens [22,30,48-51], Zn [52], Cu [53], Fe [54,55], W [56], Mn [57] and Co [15]. Ge$_n$ clusters have shown high magnetic moment in small Ge$_n$Cr clusters for n = 1-5 [58]. However, despite various attempts based on different theoretical calculations, the origin of observed magnetism in TM doped Ge clusters is still a debate. The isolated investigations reported in literature fails to explain comprehensively the magnetic behavior due to TM doping. Therefore it is necessary to study the structural and magnetic properties of TM doped Ge clusters.

**Carbon nanostructures:** Since the discovery of the C$_{60}$ fullerene in 1985 [59]. The study of carbon clusters has revealed a surprisingly rich variety of physical and chemical properties. Fullerene clusters are synthesized in macroscopic quantify-
ties with suitable conditions and can be used for development of new and useful materials.

Fullerene based materials have high degrees of freedom for their atomic and electronic structure in various dimensions. Single molecule quantum dots, linear chain in nanotubes, planar nano and crystalline solids [60]. Functionalising or chemical modification of fullerene is a promising approach to realize the tuning of the electronic and magnetic properties of pure fullerene [61].

Besides exohedral and substitutional doping of the fullerene, endohedral doping represents an interesting possibility of functionalising the fullerene molecule. As for material research of endo fullerene much progress has been made over the last decade. First synthesis, isolation and characterization of endohedral TM was reported for Cu at C60 [62].

The quest for carbon based ferromagnetism has occupied theoreticians for many years and its origin has been proposed due to the dislocations, vacancies and impurity atoms [63]. Till date the focus has been to understand the magnetic properties of metallofullerenes larger than C60 [64-66] due to their stability and larger volume available for encapsulation.

López et al. [61] have studied magnetic properties of carbon clusters, clusters inside fullerenes and graphitic nanoribbons. Surprisingly, small endohedral metallofullerenes remains unexplored and their magnetic properties have not been investigated inspite of the successful production of many small fullerenes [67-70]. The smaller fullerenes violate the isolated pentagon rule and the fused pentagon structures in this class of fullerenes have strong effect on their stability and electronic properties. The recent work on successful synthesis of some endohedral derivations of smaller fullerenes have acquired special significance. U@C28 films were produced successfully in cationic form by laser vaporization of the mixture of UO2/graphite [71]. Besides U@C28, the signals of U@C36, U@C44 and U@C58 were also observed in the mass spectrum but with lower intensities. Thus the internal uranium atom has apparently stabilized the fullerene cage and made U@C28 the end point of laser shrinking. The presence of Zr, Hf, Ti and Sc inside C28 cage has been confirmed in the mass spectrum obtained from laser vaporization of graphite/metal-oxide composite discs [71]. Following these experiments, many theoretical groups have performed a systematic investigation of series of M@C28 (M = Mg, Al, Ca, Sc, Ti, Ge, Zr and Sn) [72] and found that only Sc@C28 and Zn@C28 are thermodynamically stable in consequence of their large binding energies. Sun et al. [73] studied the encapsulation

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of thirteen atoms from group IA to group VA (i.e. H, Li, Na, K, Be, Mg, Ca, Al, C, Si, N, P) and nine cations from group IA to group IIIA (i.e. \(H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Bi^+, \) and \(Al^{3+}\)) inside \(C_{32}\) cage. Recently, Chen et al. [74] investigated the stabilities and molecular structures of noble gas atoms (i.e. He, Ne, Ar, and Kr) inside \(C_{32}\) cage. Subsequently, inspired by the finding of \(U\alpha C_{36}\), Kang [75] gave a detailed calculation of the possible encapsulation of alkali metals (i.e. Li, Na, K) inside \(C_{36}\). However, so far the trapping of TM inside small fullerene cage structures has not been investigated experimentally and theoretically.

**ZnO clusters:** In the past decade, there has been advances in the development of wide band gap semiconductors in devices ranging from blue lasers to solar cells. Zinc oxide ZnO is an "wide band-gap" semiconductor that has attracted lot of interest as an electronic material for numerous applications [76]. ZnO may become a key material for spintronics applications due to its high electron mobility and wide band gap of 3.4 eV at room temperature, [77] with potential applications in optoelectronics, transparent electronics and spintronics [78–80]. In nonvolatile memory systems, ferromagnetism is used to store data for extended periods of time [81]. Semiconductors such as ZnO offer the possibility of devices that combine optical and magnetic effects, such as spin light-emitting diodes (LEDs) [82] spin-polarized solar cells, [83] and magnetooptical switches [84]. The development of room-temperature ferromagnetic materials are essential for the widespread realization of these technologies. ZnO is a field of great interest because

- No systematic study of size and dopant-concentration dependence on magnetic and optical properties of nanoclusters has been undertaken experimentally.
- The fundamental magnetic and optical properties of TM-doped ZnO nanoclusters remain essentially conflicting.
- Most recent reports have focused on the synthesis, structural properties, UV-visible optical, and magnetic properties of ZnO-based on thin films.

Baolin et al. had predicted perfect cage structures in \((ZnO)_{12}\), \((ZnO)_{15}\), \((ZnO)_{16}\), and \((ZnO)_{18}\) with relatively higher binding energies and larger HOMO-LUMO gaps. These magic number clusters are similar to \((BN)_n\) clusters of the same size [85]. The HOMO-LUMO gap in \((ZnO)_n\) for \(n = 1\) and \(2\) is significantly smaller than other clusters which is contrary to the general behavior in elemental semiconductors. Theoretical work predicted ferromagnetism above room temperature for Mn-doped ZnO,
given a sufficiently high hole concentration [86]. The room temperature ferromagnetism has been reported in dilute magnetic semiconductors when functionalized with transition metals (TM) [87]. However, the TM doping is a traditional way to obtain room temperature FM in ZnO system and inconsistent experimental results possess a difficult situation for explaining the real mechanism of the FM. There is a strong possibility of formation of secondary phase of TM oxides or TM dopant cluster [88]. Consequently, focus has been shifted to non-TM element doped ZnO to provide evidence of intrinsic DMS [89]. To maximize the Hund’s exchange at the impurity sites, doping by elements with strong electronegativity Carbon (C) or nitrogen (N) appears most promising and have been synthesized successfully. Pan et al. [90] have provided first evidence of FM in C doped ZnO system. However, the wide fluctuation reported in FM of C doped ZnO in subsequent experiments have suggested strong dependence of magnetism on preparation method of the sample [91–93]. Native point defects have been studied and found that oxygen vacancies are deep donors and zinc interstitials are shallow donors [94]. Two magnetic regimes are found in Mn and Co doped ZnO clusters [95]. Intrinsic room-temperature ferromagnetism has been observed in B doped ZnO [96]. Origin of green band emission is found in high temperature annealed N-doped ZnO [97]. A few studies has been reported on the co-doped ZnO clusters. C and N co-doped ZnO clusters have been fabricated using metal-organic chemical vapor deposition [98]. However theoretical studies on co-doped ZnO clusters are in scarce.

1.6 Importance and future scope

This thesis work focuses on the investigation of structural, electronic and magnetic properties of doped semiconductor clusters using first principle calculations. Since the properties of clusters can be altered and tuned by the introduction of various intrinsic and extrinsic defects. We have studied doped semiconductor clusters of Ge_n, C_n, (ZnO)_n with magnetic and non-magnetic impurities. We have obtained the ground state structures and investigated their structural and magnetic properties.

The point defects in semiconductor clusters effect the magnetic properties significantly. The defects can tune doping, compensation, minority carrier life time, catalytic activity and luminescence efficiency. In the recent past there has been an intense focus on ZnO-based ferromagnetic semiconductors with co-existence of ferro-
magnetic and spin transport properties, which are desirable for practical spintronic applications. Room temperature FM is observed in 3d transition metal doped ZnO clusters. However the detected FM is rather weak.

DMS prepared by substituting magnetic ions such as Cr, Mn, Co, Fe and Ni into nonmagnetic semiconductors, have recently attracted great interest due to their potential to create new classes of spin-dependent electronic devices. TM doped group IVA clusters are studied extensively in view of the possible tuning effect of the dopant atoms on the opto-electronic, magnetic or stability properties of the host (Si and Ge) clusters. The metal encapsulated clusters can be very symmetric with band gaps in the visible region which can be used in photonics that could be combined with electronics to lead new optoelectronic devices. Pure Si and Ge are chemically reactive and need to be stabilized for potential applications. TM encapsulation in large Si cages makes them very stable. As compared to Si, TM doped caged \( (n = 14-16) \) Ge clusters have much large highest occupied molecular orbital to lowest unoccupied molecular orbital (HOMO-LUMO) gap. However only a few theoretical and experimental investigations focussed on TM doped Ge clusters. We investigated the electronic and magnetic properties of TM (TM = Mn, Co, Ni and Cr) doped Ge \( (n=1-13) \) clusters. The clusters become more stable as the size of cluster increases. The non-magnetic Ge semiconductor shows appreciable magnetic moment even on the doping of single TM atom.

Since the discovery of fullerene, a new field of research dedicated to the carbon nanostructures has evolved. Fullerenes form a rigid structure with pyramidalized \( sp^2\)-C atoms and has an inert inner concave surface due to which they can be used as ideal containers for reactive and hardly accessible species such as radicals. The properties of these clusters can be tuned by fictionalizing the surface with different dopants. Endohedral metallo-fullerenes hold great promise for applications in optoelectronic and magnetic devices since varying the encapsulated metal cluster can alter the optical, magnetic and electronic properties, without changing the structural features of the outer carbon shell. The entrapped atoms alter fullerene properties with possible applications in electronic devices [99], organic solar cells [100], spin-based quantum computing [101, 102], medicine [103], specifically contrast agents for magnetic resonance imaging (MRI) as well as for radiopharmaceutical candidates [104]. As compared to \( C_{60} \) small carbon clusters are focussed rarely. These clusters are expected to have different properties as the curvature of C cage in small clusters is different as compared to \( C_{60} \). So the study of small C cluster is important.
and need to be explored. We investigated a systematic study of the electronic and magnetic properties of $T M@C_n$, $n = 20, 28, 32, 36$ where $T M = T i, V, C r, M n, F e, C o, N i$ and $C u$ using spin polarized density functional theory. Our results show that magnetic properties of $T M@C_n$ apart from dependence on 3d configuration and charge transfer from $T M$ atom to carbon cage also depend on the specific geometric structure of the cage as well as location of the $T M$ atom. The results highlight the possibility of designing magnetic devices if high spin configurations of 3d $T M$s can be preserved as the ground state or different spin manipulation.

Recently, unexpected room-temperature ferromagnetism is found in ZnO semiconductors in the absence of magnetic ion dopants, which is referred as $d^0$ magnetism since the magnetism is not induced by the partially filled d orbitals [105]. These types of ferromagnetic materials challenge our understanding of the origin of the $d^0$ ferromagnetism. Theoretical calculations indicated that cation vacancies may be responsible for the ferromagnetism in undoped oxides and nitrides. The origin of ferromagnetism observed in C or N-doped oxides has also been studied. Electronic structure calculations showed that the N and C dopants lead to spin magnetic moment, and the p-d exchange like p-p coupling interaction was suggested to be responsible for the ferromagnetism. Therefore, doping of non-TM element is significant because it demonstrates alternative way to produce DMS. In $d^0$ ferromagnetism clusters or secondary phases formed by the dopant do not contribute to the source of magnetism. However, the mechanism of $d^0$ ferromagnetism is not well understood. A complete understanding of the physics of $d^0$ ferromagnetism is essential for identifying robust DMS for practical applications. ZnO offer the possibility of devices that combine optical and magnetic effects, such as spin light-emitting diodes, spin-polarized solar cells and magneto-optical switches. The development of room-temperature ferromagnetic materials will be essential for the widespread realization of these technologies. Theoretical work predicted ferromagnetism above room temperature for Mn-doped ZnO, given a sufficiently high hole concentration. Spurred by that prediction, research into ZnO crystals for spintronic applications is an active area of experimental research.

Carbon impurity is usually unintentionally introduced in N-doped ZnO by metal-organic chemical vapor deposition which may form graphite clusters along grain boundaries resulting in n-type domains and possibly be a big obstacle for the realization of p-type conductivity. So the effect of co-doping is also necessary to understand the problem of unintentional doping of C in N doped ZnO clusters.
We studied the structural and magnetic properties of \((ZnO)_{n-m}X_m\) clusters where \(X\) Carbon(C), Nitrogen(N) and Boron(B) and \(n, m = 1-16\). We investigated ferromagnetism in ZnO clusters due to vacancy defects and (C and N) impurities. The enhanced magnetic properties of these clusters make them most promising candidate for spintronics devices. N-C, B-N and B-C co-doping in \((ZnO)_n\) clusters is also studied can be used to tune the magnetic, luminescence and catalytic properties of ZnO clusters.

1.7 Outline of Thesis

As discussed in the preceding sections, semiconductor clusters show very interesting electronic and magnetic properties when doped with any foreign element irrespective of its position. Keeping in view the above mentioned applications of doped semiconductor clusters based materials; we have carried out ab-initio calculations based on density functional theory on doped semiconductor structures. We have studied the interesting aspects of C, N and B doped \((ZnO)_n\) \((n = 1-16)\) clusters, TM doped Ge\(_n\) clusters and effect of confinement on metal clusters in fullerene. In this Chapter, we have described different types of doping schemes and their brief literature review as well. The subsequent chapters of the thesis are organized below:

In Chapter-2 a brief description of the methodology applied for all our calculations mentioned above have been discussed. We employed first principle methods based on density functional theory to calculate the structural, electronic and magnetic properties of the clusters considered. Density functional theory is described in detail along with the brief detail of the computational codes used.

Chapter-3 explains the modification in structural, electronic and magnetic properties of Ge\(_n\) clusters with the substitution of Cr. We optimized pure Ge clusters and then doped them with Cr, we continued our discussion for the modification in structural, electronic and magnetic properties of Ge\(_n\) clusters with the substitution of Mn, Co and Ni. We optimized pure Ge clusters and then doped them with Mn, Co and Ni.

Chapter-4 is devoted to endohedrally doped smaller fullerenes. Further the effect of confinement on the clusters is seen by encapsulating them inside varying diameter carbon clusters. Structural and magnetic properties of \(TM@C_n\), \(n = 20, 28, 32, 36, 40, 44\) and \(50\) where \(TM = Ti, V, Cr, Mn, Fe, Co, Ni\) and \(Cu\) have been
explained in this chapter.

**Chapter-5** addresses the investigation of the role of p-element doping in ZnO clusters. The effect of C dopant and vacancy defects on magnetism in \((\text{ZnO})_n\) \((n = 1-16)\) clusters is studied. We have extended our investigations to explain the role of the N dopants in \(\text{Zn}_n\text{O}_{n-m}\text{N}_m\) for \(n = 1-16\). We have carried out a systematic search for the optimized ground-state structures of C and N doped \((\text{ZnO})_n\) clusters. Such kind of systematic study in \((\text{ZnO})_n\) clusters have not been done till date though some studies on thin films are available.

In **Chapter-6** the effect of co-doping in ZnO clusters on magnetism and stability has been investigated. The effect of co-doping has been investigated for C:N, B:N and B:C on structural electronic and magnetic properties of \((\text{ZnO})_n\) clusters.

**Chapter-7** summarizes the results and conclusions of the work reported in this thesis.
Bibliography


