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PHYSICAL PROPERTIES OF NANOMATERIALS

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Summary:

Nanotechnology deals with the creation of materials, devices and systems through manipulation of matter at the nanometer length scale. The created object itself does not have to be a nanoscale size object, it might be a micro or macro size object. Significant changes have been observed in physical, chemical, mechanical, electrical, optical, magnetic, and other properties when going down from bulk to nanoscale materials.

Key words: nanotechnology, nanomaterials, nanoparticles, properties of nanomaterials.

Introduction

Although the interest in nanotechnology has reached its peak only recently, the concept of nanotechnology itself has been known for more than 50 years. In the article titled "There's Plenty of Room at the Bottom"(1959), physicist Richard Feynman concluded that according to the existing physics laws, there is no reason why materials could not be "created/manufactured" by manipulating single atoms. Besides Richard Feynman, we need to mention Professor Nori Taniguchi, who first introduced the word "nanotechnology" (1974), as well as the recipients of the Nobel Prize Harold W. Kroto, Richard E. Smalley, and Robert E. Curl, who discovered the fullerene = a .ball-like form of carbon that showed a lot of potential as a building material in manufacturing miniature size objects. An unexpectedly discovered form of carbon, named Buckyballs or Fullerenes after eccentric architect Buckminster Fuller, was declared the molecule of the year by the "Science" magazine in 1991. (Hawkins et al, 1991, pp.312-313)

Progress in the field of nanotechnology was prompted by the development of advanced electron-scanning tunneling microscopes used for observing nano objects. The variety of nanomaterials is vast, just as is the range of their properties and possible applications. We can say that, with nanotechnology, the boundaries between different scientific disciplines are disappearing. Therefore, we can label it as converging technology and we need an interdisciplinary approach to it. Because of its far-reaching and various fields of applications, it is believed that nanotechnology has an enormous potential.

Nanomaterials and Nanoparticles

Nanometer, nanoparticle, ultramicrosize, nanophase materials are all different terms used for materials with their grain size of the order of a few nanometers (El-Shall & Edelstein, 1996, pp.29-70).

The prefix “nano” comes from a Greek word that means something extremely small. For example, one nanometer equals to 3-5 atoms lined up in a straight line, the diameter of a human hair is about five times that of a nanoparticle, a red blood cell has a diameter ~7000 nm, while a virus has a diameter of 100 nm. Quantum physics/chemistry study atoms and molecules, as well as objects smaller than 1 nm. Physics of condensed matter explores/studies bonded atoms and molecules, i.e. objects ranging from 100 nm to infinity. Empty space is between 1-100 nm i.e. from 10 to 10⁶ atoms per particle. Nanoparticle materials in modern physics of condensed matter are considered to be materials that consist of grains smaller than 100 nm. In the above mentioned region, neither the laws of quantum mechanics nor the laws of classical (Newtonian) physics apply. Because of the limited dimensions, there are changes in the crystalline and zone structure, the number of defects, and the size of the active area. The significance of these changes depends on the particle size. It turns out that all the changes in the characteristics have become very interesting for different applications (nanomania). Their chemical and physical characteristics are important; however, their synthesis is the most important one at this time. Some of the very complex questions/requirements in front of the synthesis are: very narrow particles size distribution without agglomeration, control of defects, specific shape and composition, etc. The classification could be based on: dimensions, phase compositions or synthesis methods (Nass et al, 2004, pp.5-10).

Based on the dimensions:

If 3D is smaller than 100 nm, there are nanoparticles, quantum dots, hollow spheres, etc.

If 2D is smaller than 100 nm, there are nanotubes, nano-fibers, nano-wires, nano-platelets, etc.

If 1D is smaller than 100 nm, there are films, coatings, multilayers, etc.

Based on the phase compositions:

One-phased solid objects are: crystallites, amorphous particles and layers, etc.

Multi-phased solid bodies (objects) are: nanocomposites, coated particles, etc.

Multi-phased systems are: colloids, aerogels, ferrofluids, etc.

Based on synthesis methods:

Reactions from a gas phase are: physical and chemical methods of deposition from a vapor phase, condensation in the atmosphere of inert gases, chemical vapor deposition, etc.

Reactions from a liquid phase are: sol-gel, method of sedimentation, hydrothermal method, etc.

Mechanical methods can be the grinding method, the method of plastic deformation, etc.

From a scientific point of view and for practical application purposes, it is of great importance that the physical characteristics of nanomaterials differ significantly from polycrystalline (bulk) materials of the same chemical composition (Table 1). In some cases, for particular physical parameters, these differences could be a few orders of magnitude. A very important characteristic of nanomaterials is that the values of physical parameters are very sensitive to the size and morphology of nanoparticles (Tadić et al, 2009, pp.839-843), (Tadić et al, 2011, pp.7639-7644), (Tadić et al, 2012, pp.28-33). Some of the examples representing significant difference in the values of some physical parameters are: the melting point, change in the unit-cell parameters, change in the magnetic and optical characteristics, conductivity of the material, etc. The surface to volume ratio is an important parameter that has an impact on new characteristics in comparison to those of bulk materials. The number of atoms on the surface (with regard to the total number of atoms) increases as the particle size gets smaller. As particles get smaller, the surface to volume ratio increases and the influence of the shell on the magnetic properties becomes more significant. For example, 3 nm size iron particles have 50% while 30 nm size iron particles have only 5% atoms on their surface that have a significant impact on their physical characteristics (Sorensen, 2001, pp.37-69).

Table 1 – Some of the common properties of nanomaterials that are significantly different from the properties of the bulk materials with the same chemical composition (Nass et al, 2004, pp.5-10).

Таблица 1 – Некоторые из общих свойств наноматериалов, которые значительно отличаются от свойств сыпучих материалов с одинаковым химическим составом (Nass et al, 2004, pp.5-10).

Табела 1 – Неке од карактеристичних особина наноматеријала које се значајно разликују од особина булк материјала истог хемијског састава

Properties	Examples
Catalytic	Increase in surface activity of particles
Electrical	Increase in electrical conductivity of ceramic materials and magnetic nanocomposites Increase in electrical resistance in metals
Magnetic	Change of the point of magnetic phase transition Increase of coercivity Appearance of super-magnetism
Mechanical	Improvement in firmness and hardness of metals and alloys Appearance of super-elasticity
Optical	Shift in optical absorption and change in fluorescent properties Increase in quantum efficiency of semiconducting crystals

Increase of the surface to volume ratio of particles causes lower melting temperatures, lower magnetization, changes in catalytic activity, etc. A large number of atoms on the surface significantly increase "surface activity" that is very favorable for chemical reactions. However, due to increased activity, nanoparticles have tendency to form aggregates and agglomerates that could cause loss of preferred characteristics. Therefore, it is necessary to stabilize particles with some additional treatment. For example, it is possible to put particles in an adequate matrix or to coat them with a different material even though their characteristics change with this kind of surface modification. The coordination number of atoms on the surface is lower than the one for the atoms inside the particle, which would cause an increase in the surface energy. Therefore, the diffusion of atoms can take place at lower temperatures. For instance, the melting point of gold is 1063 °C, while nanoparticles of gold with particle diameters under 5 nm have the melting

point of $\approx 300\text{ }^{\circ}\text{C}$ (Buffat & Borel, 1976, pp.2287-2298). Decreasing the particle size has a significant influence on firmness and hardness of materials (Weertman, Averback, 1996, pp.331-353).

Measurements of firmness of copper for crystallite of different sizes have shown that firmness increases as the crystallite size decreases. Firmness of the copper samples with 50 nm size crystallites is 2 times higher, while in the copper samples with 10 nm size crystallites it is 6 times higher than for the bulk. The elasticity limit of copper increases 2 times when crystallites decrease in size from 100 μm to 10 μm (Adams et al, 1989, pp.9479-9484).

One of the characteristics specific for nanomaterials is superplasticity. As opposed to bulk materials, nanomaterials have the ability to withstand the tension beyond the point of fracture. Superplasticity is explained by diffusion of atoms, i.e. moving of dislocations and sliding of the boundaries between particles.

Magnetic properties of nanoparticles

The magnetic properties of nanoparticles can be controlled with a more precise control of size and shape of nanoparticles. Namely, below a certain size, nanoparticles become mono-domain particles because that is energetically preferable and they show super-magnetic behavior that takes place above certain temperatures, so-called blocking temperatures (TB) (Chikazumi, 1999, pp.453-457).

Above blocking temperatures, magnetic moments of particles fluctuate in all directions with the help of thermal activation, similarly to paramagnetic materials, while below this temperature, magnetic moments of particles are locked in the direction of the axis of easy magnetization (Kulal et al, 2011, pp.2567-2571).

The difference from common paramagnetism is that all magnetic moments within a particle rotate coherently creating a super moment that could be of the order of a few thousand Bohr magnetos. The external field tends to align this super magnetic moment in its direction; however, thermal energy disrupts that alignment in the same way as it happens with paramagnetic materials, and that is the reason why this phenomenon was named super-magnetism.

Since the surface effect plays a significant role in investigating the magnetic properties of nanoparticle materials, the "core-shell" model has been used for their description. According to that model, a particle consists of a magnetically aligned nucleus and a non-aligned shell (Fig.1). When temperature decreases, the shell gets aligned.

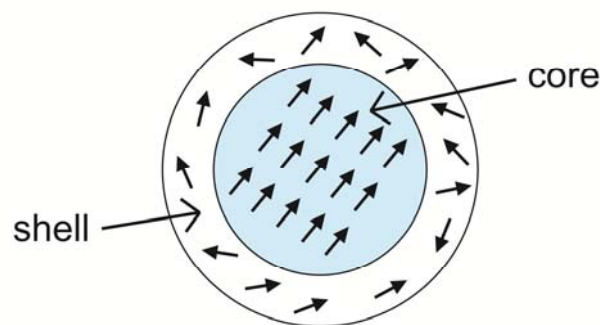


Figure1 – Schematic of the core-shell structure, i.e., the spin alignment of a spherical nanoparticle

Рис.1 – Схема структуры ядра оболочки, т. е. выравнивание спинов сферической наночастицы

Слика 1 – Шематски приказ core-shell структуре, тј. спинско уређење једне сферне наночестице

The particle nucleus keeps the same physical properties of the bulk material, while the shell is responsible for the appearance of new properties. Namely, in the outer shell, magnetic interactions are modified due to the surface effects such as: defects, vacancies, tension, and broken chemical bonds. In addition, these effects are responsible for a decrease in the temperature of a phase change, magnetic saturation and an increase of coercivity in comparison to bulk materials.

The magnetic alignment of a nanoparticle shell is achieved by lowering its temperature (Fig.2).

For super-magnetic systems, the following specific characteristics are noticed: magnetic properties depend on the previous treatment of ZFC (zero - field cooled) and FC (field - cooled) measurements, the existence of a hysteresis loop below the block-temperature (TB) and its appearance above the TB, the appearance of a maximum during ZFC measurements (blocking temperature), and the existence of overlapping magnetization curves at various temperatures above the blocking temperature when magnetization M is shown as a function of H/T (H - magnetic field strength, T - temperature) (Sorensen, 2001, pp.37-69), (Tadić & Čitaković, 2014, pp.47-64), (Tadić & Čitaković, 2011, pp.91-105).

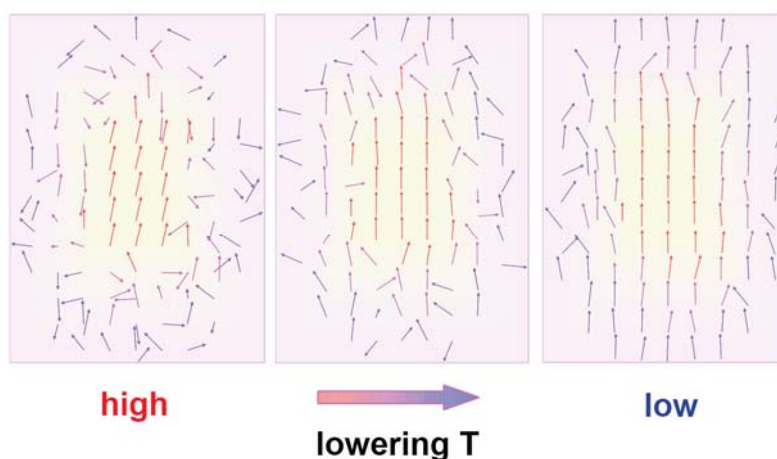


Figure 2 – Schematic of the magnetic alignment of a shell by lowering its temperature

Рис. 2 – Схема магнитного выравнивания оболочки при снижении ее температуры

Слика 2 – Шематски приказ магнетног уређивања shell-а снижавањем температуре

In Figure 3, the strength of a coercive field is shown as a function of particle size (Pelecky et al, 1996, pp.1770-1783). Above a certain critical particle size characteristic of the material D_S (Table 2), a material is composed of many domains (multi-domain structure), while below the critical particle size, a material D_S becomes mono-domain.

The figure shows that the coercivity increases as the particle size decreases up to a critical size for a mono-domain particle of a given D_S material, beyond which it starts decreasing and, after a certain D_{SP} value, the material becomes super-magnetic, i.e. the coercive field strength goes down to zero. In Figure 3, it could be noticed that, for very high values of the particle diameter $D \gg D_S$, the value of the coercive field strength approaches a constant value, which is a characteristic of the material in its bulk form.

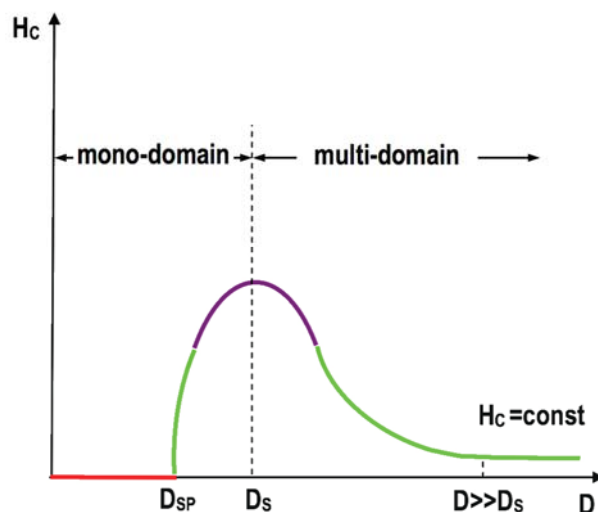


Figure 3 – Coercive field strength as a function of a nanoparticle diameter at a constant temperature. DSP - diameter below which a material shows super-paramagnetic behavior; DS - critical diameter

Рис. 3 – Схема зависимости силы коэрцитивного поля от диаметра наночастиц, при постоянной температуре. DSP - диаметр, ниже которого материал демонстрирует суперпарамагнитное поведение; DS - критический диаметр
Слика 3 – Шематски приказ зависности јачине коерцитивног поља од пречника наночестица при константној температури. DSP – пречник испод којег материјал показује суперпарамагнетно понашање, DS – критични пречник

The critical diameter size for spherical nanoparticles depends on the material type (Table 2 shows the critical diameter values for some materials) (Sorensen, 2001, pp.37-69).

Below the critical diameter-DS, the coercive field strength decreases, according to the following functional relationship:

$$H_c = g - \frac{h}{D^{\frac{3}{2}}}$$

where g and h are constants (Kumar et al, 1994, pp.354-358).

Table 2 – Diameters of the spherical particles of some substances below which they are mono-domain

Таблица 2 – Диаметры сферических частиц некоторых веществ снизу, которые являются монокристаллическими

Табела 2 – Величине пречника сферних честица неких супстанци испод којих су оне монокристаллическе

Substance	D _s (nm)
Fe	14
α-Fe ₂ O ₃	41
Ni	55
Co	70
Fe ₃ O ₄	128
γ-Fe ₂ O ₃	166

Except the particle size and microstructure, the shape i.e. the elongation of the particle (ratio of the longest dimension and the shortest dimension) also affects the coercive field strength.

(Baibich et al, 1986, pp.2472-2475), (Buffat et al, 1976, pp.2287-2298), (Chikazumi, 1999, pp.453-457), (Tadić et al, 2011, pp.7639-7644), (Kulal et al, 2011, pp.2567-2571), (Pelecky et al, 1996, pp.1770-1783), (Kumar et al, 1994, pp.354-358), (Zboril et al, 2002, pp.969-982), (Wang, 2000, pp.1-11), (Krill & Birringer, 1998, pp.621-640), (Audebrand et al, 1996, pp.83-87), (Huang et al, 2001, pp.1497-1505), (Gupta et al, 2011, pp.1095-1098).

For example, in the case of the Fe nanoparticle, the increased elongation of ~5 times (from 1 to 5) increases the coercive field strength for ~10 times (Krill et al, 1998, pp.621-640). In general, the coercive field strength increases as elongation increases, i.e. with the increase of the anisotropic shape (Krill & Birringer, 1998, pp.621-640).

The field of magnetic nanoparticle materials still has not been studied enough. One of the reasons is that synthesized nanoparticles have different shapes and sizes so their effects on magnetic properties could not be clearly observed. The basic aim in the process of the

synthesis of nanoparticles is the creation of a desired shape and a size of particles (narrow particles size distribution). Some of the methods used for the synthesis of magnetic nanoparticle materials are: sol-gel, mechanical-chemical, glycerin-nitrate, micro-emulsion, and spray pyrolysis.

Conclusion

Nanotechnology is a growing field of research. During the last decade, interest for nanoparticle materials has been connected to their new and specific physical characteristics and possibilities for their application in all aspects of the human life. It has been noticed that there is a change in the physical characteristics (magnetic, mechanical, and optical properties, as well as in melting temperature, material conductivity, etc.) of nano-particle materials in comparison to bulk materials. In some cases, for some physical parameters, differences are up to a few orders of magnitude and can vary significantly. Nanoparticle materials are objects of intense research, because they represent a significant potential for the development of new materials that can be used/applied in various areas of science and technology. It is expected that nanoparticle materials will soon have a leading role in technology, medicine, etc. and that the production of nanoparticle based materials will be increasing in the near future.

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ФИЗИЧКИЕ СВОЙСТВА НАНОМАТЕРИАЛОВ

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ОБЛАСТ: физика материјала (физика кондензованог стања)

ВИД СТАЊИ: професионална статија

ЈАЗИК СТАЊИ: енглески

Резюме:

Нанотехнологија занима се стварањем материјала, уређаја и система путем контролисаног манипулирања материјом на атомном нивоу у мањем нивоу. При овом не обавезно да створени објект била нано-размерним, он може бити микро или макро величине. Суштинске промене примећују се у физичким, хемичким, механичким, електричким, оптичким, магнетним и другим својствима при прелазу од масовних материјала до нано-размерних материјала.

Кључне речи: нанотехнологија, наноматеријали, наночестице, својства наноматеријала.

ФИЗИЧКЕ ОСОБИНЕ НАНОМАТЕРИЈАЛА

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ОБЛАСТ: физика материјала (физика кондензованог материјала)

ВРСТА ЧЛАНКА: стручни чланак

ЈЕЗИК ЧЛАНКА: енглески

Сажетак:

Нанотехнологија бави се стварањем материјала, уређаја и система директном манипулацијом супстанце на нанометарском (атомском) нивоу. Сам креирани објект не мора да буде нановеличине, већ микро или макровеличине. Постоје значајне промене физичких, хемијских, механичких, електричних, оптичких, магнетних и других карактеристика при прелазу од материјала до наноматеријала.

Кључне речи: нанотехнологија, наноматеријали, наночестице, особине наноматеријала.

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