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Chemical Nature of Magnetic Properties of Substances

Abstract

Using the example of the mineral magnetite, which is the main component of magnetic volcanic sand, a quantum-chemical analysis of the nature of paramagnetic properties was carried out using the molecular orbital method. Magnetic properties are among the most important characteristics of substances, and magnetic interaction is one of the fundamental forces in the universe. Understanding the chemical nature of magnetic properties allows not only to effectively use materials with magnetic properties, but also to create new materials with the desired characteristics. The magnetic properties of substances depend on their structure and elemental composition, since each charged particle inside the substance has its own magnetic moment-spin.

Keywords: *chemical, nature, magnetic, properties, substances*

Introduction

In technology, substances are divided into paramagnets, diamagnets, ferromagnets, antiferromagnets and ferrimagnets. Ferrimagnets are the most complex in structure – these are crystalline substances whose magnetic structure is represented by several sublattices with signs of spontaneous magnetic ordering, while each individual part has a non-zero resulting magnetic moment (Kurnikov, 2005, p. 120).

Based on this, the purpose of this work was to study the magnetic nature of magnetic sand from Sakhalin Island. The selected average sample weighing 114 grams was sifted through a large sieve to remove large debris, then separated into magnetic and non-magnetic components in the magnetic field of a strong neodymium magnet. It was found that the magnetic part makes up 93,86 %, the main composition of which is represented by a mixed iron oxide – Fe_3O_4. This chemical compound is also interesting because it has a crystalline structure in the lattice nodes of which iron and oxygen alternate, with divalent and trivalent iron – $FeO \cdot Fe_2O_3$. Thus, one stoichiometric unit of the substance contains 24 % Fe (II), 48 % Fe (III) and 28 % O, that is, almost a quarter of the substance is represented by an atom in an intermediate oxidation state, another quarter – in a lower oxidation state and almost half in a state of a higher oxidation state (Kharlamov, 2003, p. 82-85).

The group of magnetic materials primarily includes elements of the iron triad: iron, cobalt and nickel. The chemical properties of these elements are determined by their position in the periodic table. Atoms of Fe, Co and Ni have two 4s-electrons and 6, 7 and 8 electrons in the 3d-sublevel, respectively. For example, in Fe4s2 3d6, filling the 3d-cells with electrons affects the decrease in oxidation states when moving from Fe to Ni. The maximum oxidation state is +6 for iron, +4 for cobalt and +3 for nickel. Most often, iron exhibits oxidation states of +2 and +3, nickel +2, cobalt +3 in simple compounds and +3- in complex compounds (Went, 1952, p. 194).

Obviously, not all electrons of the unfilled 3d-sublevel participate in valence bonds. Formation of complex compounds is typical for Fe, Co and Ni. Pure metals of the iron family are strong and

ductile. The standard electrode potentials for Fe, Co and Ni are -0.441, -0.277 and -0.250 V, respectively. Diluted hydrochloric, sulfuric and nitric acids dissolve these metals, converting them into E2+ ions. When interacting with hydrochloric and sulfuric acids, the metals displace hydrogen, and the reaction with nitric acid proceeds according to the equation (Gutfleisch, 2011, p. 821-842).

4Fe + 10HNO₃ = 4Fe (NO₃)₂ + NH₄NO₃ +3H₂O

More concentrated HNO3 and H2SO4, when heated, oxidize iron to Fe (III) (NO or O2 are released), for example:

Fe + 4HNO₃ = Fe (NO₃)₃ + NO + 2H₂O
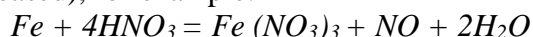
Very concentrated H2SO4 and HNO3 at room and lower temperatures passivate these metals, forming oxide films on their surface. In alkaline solutions, all three metals are quite corrosion-resistant. They do not react with water under normal conditions, but at red-hot temperatures, iron interacts with water vapor:

3Fe + 4H₂O = Fe₃O₄ + 4H₂
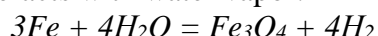
At room temperature in air, nickel oxidizes slowly, cobalt and iron faster. When heated, they burn, forming the oxides Fe2O3, CoO and NiO. Iron also forms the oxides FeO, Fe3O4, FeO3 and FeO4. The last two are very unstable. FeO4 is obtained as a solution in CCl4 by extracting the tetroxide by CCl4 extraction from alkaline aqueous solutions formed during the anodic oxidation of iron:

Fe + 8OH⁻ - 8 ē = FeO₄ + 4H₂O
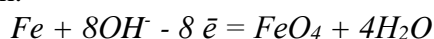
Solutions of FeO4 and CCl4 decompose under normal conditions:

4FeO₄ = 2Fe₂O₃ + 5O₂
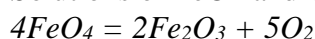
When Fe2O3 is fused into KOH and KNO3, dark red ferrites (VI) are formed:

Fe₂O₃ + 4KOH + 3KNO₃ = 2K₂FeO₄ + KNO₂ + 2H₂O
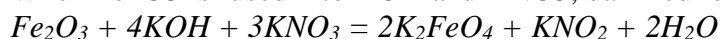
In terms of their oxidizing capacity, they are superior to such an oxidizing agent as KMnO4 (E = 1.9 V > E = 1.51 V).

Cobalt forms oxides CoO, CoO2 and Co3O4. The most stable of them is CoO. Nickel forms oxides NiO and Ni2O3. Of the hydroxides, E(OH)2 and E(OH)3 are of greatest importance. Co(OH)3 and Fe(OH)3 have some signs of amphotericity (5).

The formulas of such oxides as FeO, CoO and NiO are quite arbitrary, since, as a rule, they have a non-stoichiometric composition. For example, a study of the composition of wustite FeO showed that it has vacancies in the iron sublattice, and its composition should be expressed by the formula Fe1 – xO. The composition of wustite under standard conditions is close to Fe0.95O. With an increase in the value of X, the picometry density decreases (Robert, 2012, p. 1191-1334).

To maintain electroneutrality, it is necessary that there are two Fe3+ ions in the lattice for each Fe2+ vacancy. These more highly charged ions can be considered as holes, since at a low activation energy, electrons from neighboring Fe2+ ions can move to them, and the position of the Fe3+ ions is not localized. This positive charge diffuses throughout the crystal, which is characteristic of a hole. The same kind of hole semiconductors are Co1 – xO, Ni1 – xO, etc.

Fe (OH)2 hydroxide is a stronger base than Fe (OH)3, iron (II) salts have a more ionic character than iron (III) salts. The latter are more noticeably hydrolyzed than Fe (II) salts (Smith, 1962, p.25).
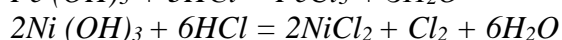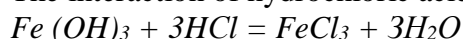
Fe (OH)2 is easily oxidized in the cold by atmospheric oxygen:

4Fe (OH)₂ + 2H₂O + O₂ = 4Fe (OH)₃
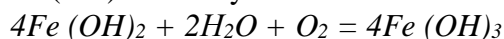
Ni(OH)3 is obtained by the action of strong oxidizing agents on Ni(OH)₂:

2Ni (OH)₂ + Cl₂ + 2NaOH = 2Ni (OH)₃+ 2NaCl.

The interaction of hydrochloric acid with Ni(OH)3 and Fe(OH)3 proceeds as follows:

Fe (OH)₃ + 3HCl = FeCl₃ + 3H₂O

2Ni (OH)₃ + 6HCl = 2NiCl₂ + Cl₂ + 6H₂O

Nickel (II) salts are green; cobalt (II) salts are blue, and their solutions and crystal hydrates are pink; iron (III) salts are brown. Iron, cobalt and nickel absorb hydrogen, but do not form specific compounds with it (Vladimirovich, 2001, p. 23).

Their nitrides are unstable, but when formed on the surface of steel products when saturated with nitrogen in an ammonia atmosphere, they make these products more corrosion-resistant and harder (Abbas, 2015, p. 187-191).

Iron, cobalt and nickel form carbides of the E3C type. Sulfides of the ES type are obtained by the action of ammonium sulfide $(NH_4)_2S$ on salt solutions and by dry means. Iron forms stable cyanides:

$$FeCl_2 + 2KCN = Fe\,(CN)_2 + 2KCl.$$

Fe (CN)3 is obtained in a similar manner. When these cyanides are treated with an excess of KCN, the complex salts potassium hexacyanoferrate (II)K4 [Fe (CN)6] – yellow blood salt and hexacyanoferrate (III)K3 [Fe (CN)6] – red blood salt are obtained. These salts are specific reagents for Fe3+ and Fe2+ ions:

$$4Fe^{3+} + 3\,[Fe\,(CN)_6]^{\,4-} = Fe_4\,[Fe\,(CN)_6]_{\,3}$$
$$3Fe^{2+} + 2\,[Fe\,(CN)_6]^{\,3-} = Fe_3\,[Fe\,(CN)_6]_{\,2}$$
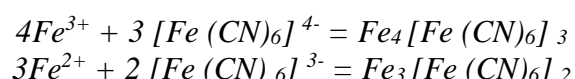
This reaction is very sensitive and is used to detect the Fe3+ ion.

A sensitive reaction to Ni2+ ions is the interaction with dimethylglyoxime (Chugaev's reagent), as a result of which the solution turns bright pink (Kanagesan, 2014, p. 815).

It is known that some substances in a magnetic field become magnetized, i.e. they themselves become sources of a magnetic field. Therefore, the magnetic field in a substance is the result of adding up the fields created by current-carrying conductors (macrocurrents) and a magnetized environment (Meng, 2015, p. 407-411).

The reason for magnetization is that in all substances there are electric currents that close within each atom or molecule (microcurrents or molecular currents). Fig. 3.1 shows a model of molecular currents in a uniformly magnetized magnet and the corresponding surface current.

The existence of microcurrents (molecular currents) in a substance is explained by the fact that each electron rotates around the nucleus at a fairly high speed. Its location and speed at a given moment in time cannot be determined with sufficient accuracy. This means that a rotating electron represents a certain equivalent circular current that has a magnetic moment. To calculate this moment, we assume that the orbit is a circle with radius r, along which the electron moves with a constant speed vo.

The gyromagnetic ratio was determined experimentally in 1915 by Einstein and Haas. In the experiments of Einstein and Haas, an iron rod suspended on a thin elastic thread was placed inside a solenoid (Fig. 3.3). A mirror was attached to the elastic thread, onto which a beam of light was directed. When a direct electric current was passed through the solenoid, a magnetic field was created that magnetized the iron rod. As a result, the rod began to rotate, and the direction of rotation of the rod changed with a change in the current in the solenoid (the magnetic field inside the solenoid). The mirror began to rotate simultaneously with the rod. When the system rotates, the reflected beam shifts along a scale installed to increase sensitivity at a sufficiently large distance. When the mirror is rotated by an angle, the beam deflects by a double angle of 2. The occurrence of rotation during magnetization is called the magnetomechanical effect. The occurrence of the magnetomechanical effect can be explained by the following reasoning. In an unmagnetized rod, the electron orbits have an arbitrary orientation, so their total mechanical angular momentum is 0. When the rod is magnetized, the planes of the molecular currents become parallel, which leads to the occurrence of a total angular momentum.

All substances in nature are magnetic, i.e. they have certain magnetic properties and interact with an external magnetic field in a certain way. The magnetic properties of a substance depend on the magnetic properties of isolated elementary particles, the structure of atoms and molecules, and their groups (12).

The magnetic properties of an atom are mainly determined by the magnetic properties of electrons. The magnetism of other particles is relatively small. Thus, the magnetic moment of an

atomic nucleus is approximately a thousand times smaller than the magnetic moment of the electron shell of an atom. The magnetic moment of an electron arises as a result of the electron's orbital motion (orbital moment) and the presence of spin (spin moment). The magnetic moment of a multi-electron atom is the sum of the magnetic moments of all electrons, including both orbital and spin moments. Each electron makes an independent vector contribution to the total magnetic moment of the atom. According to modern concepts of magnetism, the following main types of magnetic states of matter are distinguished: diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism and ferrimagnetism (uncompensated antiferromagnetism). Substances in which these phenomena are manifested are called, respectively: diamagnets, paramagnets, ferromagnets, antiferromagnets and ferrimagnets. The schematic arrangement of the moments of electrons of atoms of substances with different magnetic properties is illustrated in fig. 1.
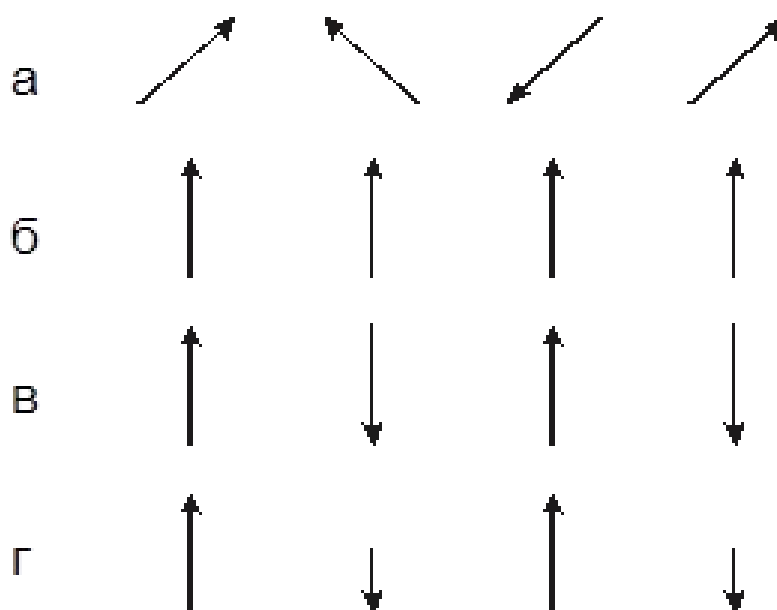
Figure 1. The schematic arrangement of the moments of electrons of atoms of substances

The main magnetic quantities include: magnetization M, A/m, M = k, where k is the magnetic susceptibility, is the magnetic field strength, A/m.

Conclusion

Particularly interesting compounds are the carbonyls of metals of this family. Iron atoms have four free places for electrons in the 3d sublevel and six places in the 4p sublevel. Under a pressure of 107 Pa and at 200 °C, liquid iron pentacarbonyl is quickly formed: Fe + 5CO = Fe (CO)5, in which carbon atoms are electron donors, iron atoms are acceptors of five pairs of electrons. For such an interaction, a rearrangement of electrons in the 3d sublevel is necessary, requiring some activation energy. Nickel atoms can accept only 8 electrons in the same sublevels, so a carbonyl of the composition Ni (CO)4 is formed. At 250 °C, iron carbonyl decomposes, which is used to obtain the purest iron for electrical and radio engineering purposes. Nickel carbonyl decomposes at 200 °C, and cobalt tetracarbonyl is even less stable.

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