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Editorial

Magnetic Materials, Thin Films and Nanostructures

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Abstract: In this first volume, we cover relevant aspects of chemical and physical processes of the production and characterization of magnetic materials in bulk, thin films, nanostructures, and/or nanocomposites, as well as modeling aspects involving such structures. Accordingly, this volume presents eleven original research and review works on the challenges and trends covering fundamental and experimental work, with a special focus on the design, synthesis, and characterization of various types of magnetic materials, and the study of their structure–property relationships. State-of-the-art results on the development of new experimental concepts, leading to the transfer, chemical transformation, and high-resolution patterning of advanced thin films and nanomaterials, and to the design and fabrication of devices, are also presented and discussed.

Keywords: magnetism; nanomaterials; nanostructures; nanoparticles; thin films; electromagnetic shielding; magnetotransport; single-molecule-magnets; magnetic shape memory polymers; magnetic soft materials

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Ever since antiquity, there have been legends circulating about the phenomenon that we generally call today "magnetism". The best known is of a young shepherd from the island of Crete, named Magnes [1]. At one point in his life, while tending the sheep on Mount Ida, he noticed that the metal part of the sole and the nails of his boots were attracted to the ground on which he was treading. To find out what was going on, he began to dig, revealing a strange earth-black stone: a piece of *lodestone*, or "*magnetite*". Magnetite is a natural ferrite exhibiting magnetic properties. Today, we know that is a stoichiometric mixed oxide consisting of FeO and Fe_2O_3, with the chemical formula Fe_3O_4, and its structure is of the "spinel" type. It is a "*ferrimagnetic*" material, and its Curie temperature is 858 K. Just to exemplify for the reader the importance of this mineral, the strongest natural magnet: it is critical in the understanding and evolution of terrestrial paleomagnetism, in the formation and evolution of rocks, and other areas [2].

Of course, observations of such phenomena have been made long before the appearance of the first forms of writing [3], so we cannot rely on such legends. This story might be apocryphal, but in this case, there are many similarities with historic reality, the most important being that the empirical discovery of magnetism and its mention was made by the Greeks, Indians, and Chinese through observing the properties of the rocks that contained the magnetite mineral [4]. Pliny the Elder (23–79 CE) himself wrote about a hill, somewhere on the banks of the Indus River, which was apparently made entirely of something mysterious that attracted iron. The inexplicable nature of magnetic attraction has been exploited over time by storytellers, meaning it has become difficult to separate truth from fiction. It was believed for a long time that there were islands that were completely made up of magnetite and that, by virtue of the "special" properties of this mineral that is part of some rocks, could attract ships to the shore (they contained nails and iron beams in their structure). One of the explanations for the disappearances of the ships was that they had been destroyed on impact with such magnetic islands—a kind of ancient

Greek equivalent of today's "*Bermuda Triangle*". About Archimedes (287–212 BCE), one of the legends says that he also used stones containing magnetite, very strong, to attract and remove nails from enemy ships during wars, and to sink them (very likely that this is just a simple legend). Over time, the term magnetism remained when one explained the phenomenon of attraction between magnetite and objects containing iron. Today, by the concept of "*magnetism*", we understand the nature of this type of interaction and we can explain the phenomenon of attraction and repulsion. Moreover, today, we know of life forms that are guided by terrestrial magnetism: magnetic bacteria, for example, such as those from the Geobacter family (the first discovered was called "*Geobacter Metalloreducens*"), or even certain birds and insects [5].

Since the very first evidence of "scientific" investigations of magnetic phenomena, dating from ancient Greece, when Aristotle (384–322 BCE) recalls the fascinating teachings of Thales of Miletus (625–545 BCE) on magnetic phenomena and his intuitive way (for that time) to explain the cause of their appearance [6], to Peter Peregrinus de Maricourt's "*Epistola de magnete*" (1269 CE)—the first extensive treatise describing the properties of magnets [7], to William Gilbert's published work "*De Magnete, Magneticisqve Corporibvs et de Magno Magnete Tellure*" (1600 CE)—on magnetism, magnetic bodies, and on the great magnet Earth, using his model "terela" [8], to Hans Christian Ørsted, André-Marie Ampère, Carl Friedrich Gauss, Wilhelm Eduard Weber, and Michael Faraday, to James Clerk Maxwell's equations on the "*Theory of electromagnetism*" [9] and to Albert Einstein's paper "*On the Electrodynamics of Moving Bodies*" [10], electromagnetism continued to develop in the 20th century, being incorporated into the much more fundamental theories of the time, e.g., calibration theory, quantum electrodynamics, electroweak theory, and the Standard Model. Our understanding of Earth's magnetism, and magnetism in general, has come a long way in the last 423 years since "*De Magnete*" was first printed. Today, we live in the future: we ride on MAGLEV trains at more than 500 km/h, do magic with the Meissner effect [11] by using strong NdFeB magnets and (close to) room temperature superconductors [12], and we observe the strongest magnets known, pulsars, while taking glimpses at the Universe. All we have left is " … *to boldly go where no one has gone before*"!

Chemistry and magnetism go hand in hand, and magnetochemistry is concerned with the magnetic properties of chemical compounds. Magnetic properties arise from the spin and orbital angular momentum of the electrons contained in a compound. Compounds are diamagnetic when they contain no unpaired electrons [13]. The fundamentals of materials science and magnetism, both experimental and theoretical, encouraged us to edit this first volume as a Special Issue of MDPI's journal *Magnetochemistry*, emphasizing the relevant aspects of chemical and physical processes of the production and characterization of magnetic materials in bulk, thin films, nanostructures and/or nanocomposites, as well as modeling aspects involving such structures. Eleven original research and review works on the challenges and trends are included herein, while covering fundamental and experimental work, with special focus on the design, synthesis, and characterization of various types of magnetic materials, and the study of their structure–property relationships.

An important starting discussion is presented by Robert A. Lawrence et al. in their work entitled "*Magnetic Transition State Searching: Beyond the Static Ion Approximation*" [14]. The effect of structural relaxations on the magnetocrystalline anisotropy energy (MAE) is investigated by using density functional theory (DFT). The theory of the impact of magnetostructural coupling on the MAE is discussed, including the effects on attempt frequency. Two materials are chosen—FePt and PtMn. The MAE for ferromagnetic FePt (3.45 meV/formula unit) and antiferromagnetic PtMn (0.41 meV/formula unit) are calculated within the local density approximation (LDA). The effects of the structural relaxation are calculated and found to give a <0.5% reduction to the MAE for the ferromagnet and $\sim$20% for the antiferromagnet. This divergence is attributed to the difference in coupling between the magnon responsible for the transition and either an acoustic or optical phonon (for FePt and PtMn, respectively), revealing the importance of considering magnetostructural effects when evaluating the MAE of systems in which the magnetic structure cannot be adequately expressed in the same primitive unit cell as the geometric structure, such as an antiferromagnet.

Nanocomposite FePt-based magnets have been under scrutiny as a new class of permanent magnets due to their high corrosion resistance and their high working temperature. An FePt-based nanocomposite is presented and discussed by Alina D. Crisan et al., in their work entitled "*Role of Disordered Precursor in $L1_0$ Phase Formation in FePt-Based Nanocomposite Magnet*" [15]. In order to prove the usefulness of having a structurally disordered precursor to the formation of the FePt $L1_0$ phase and to facilitate the co-existence of exchange-coupled hard and soft magnetic phases with optimized magnetic properties in various conditions of annealing, an Fe-Pt-Zr-B melt-spun alloy has been synthesized and detailed structural and magnetic investigations have been undertaken to probe its phase evolution during annealing. The dynamics of the formation of the hard magnetic $L1_0$ phase during the gradual disorder–order phase transformation has been monitored by using a complex combination of X-ray diffraction methods and ^{57}Fe Mössbauer spectroscopy methods over a wide range of annealing temperatures. It is shown that the formation of the hard magnetic phase, emerging from the chemically disordered precursor, is gradual and occurs via complex mechanisms, involving the presence of a disordered Fe-Zr-B-rich intergranular region which contributes to an increase in the abundance of the $L1_0$ phase for higher annealing temperatures. Magnetic measurements confirm the good performances of these alloys in terms of coercivity and remanence, contributing to the development of these alloys as the next generation of "rare-earth-free" permanent magnets.

In their work entitled "*Electric Field Control of Magnetic Properties by Means of Li+ Migration in FeRh Thin Film*" [16], Gengfei Li et al. investigated the control of the magnetic properties of FeRh films by means of Li^+ migration in FeRh/MgO heterostructures, and found that the migration of Li^+ could reduce the phase transition temperature by 2 K with an applied voltage of 1 V. Meanwhile, the voltage-dependent saturated magnetization exhibited a repetitive switching behavior from high to low magnetization values while the voltage was switched from 4 to −4 V, indicating that the migration of Li^+ in the FeRh film can be reversible, providing a means to control the magnetic properties of FeRh films.

Mohammad Yaghoub Abdollahzadeh Jamalabadi offers a glimpse into their "*Feasibility Study of Cooling a Bulk Acoustic Wave Resonator by Nanoparticle Enhanced Phase Change Material*" [17]. The coupling of a cooling problem with the electromagnetic resonance of a bulk acoustic wave (BAW) material is investigated. The BAW is a device usually composed of a piezoelectric material (i.e., zinc oxide or aluminium nitride) between two electrodes, while the use of nanoparticles facilitates heat removal and decreases the delay time and thermal inertia of the cooling system.

The magnetic, optical, and phonon properties of ion-doped $CuAlO_2$ (CAO) nanoparticles on the Cu or Al site are theoretically investigated by Iliana Naumova Apostolova et al. in their work, entitled "*Size and Ion-Doping Effects on Magnetic, Optical, and Phonon Properties of $CuAlO_2$ Nanoparticles*" [18], and discuss diluted magnetic semiconductors (DMS) that play an important role in interdisciplinary materials science and future spintronics. Ferromagnetic DMS has been studied from first principles within mean-field approximation, revealing that the origin of ferromagnetism in DMS is not yet clear, even if various methods have been proposed. Here, the size and ion-doping effects on the magnetic, optical, and phonon properties of transition metal (TM = Fe, Co, Mn, and Ni) ion-doped CAO nanoparticles on the Cu and Al site are discussed by using a microscopic model and Green's function theory; the results are in good agreement with existing experimental data.

SiO_2(Co) granular films exhibit unusual magnetic and magnetotransport properties which are strongly dependent on the composition of the film and the material of a substrate. For example, the injection magnetoresistance (IMR) coefficient reaches a giant (GIMR) value of 10^5% at room temperature in SiO_2(Co) films on an n-GaAs substrate. However, the IMR effect is negligible in the case of a similar granular film deposited on the n-Si substrate. Natalia A. Grigoryeva et al. discuss the structural and magnetic properties of granular-film SiO_2(Co) on a Si substrate are studied with the aim to understand the cause of the difference in IMR coefficients for SiO_2(Co) thin films deposited on n-GaAs and on n-Si substrates in their work entitled "*Mesostructure and Magnetic Properties of SiO_2-Co Granular Film on Silicon Substrate*" [19]. Investigations are carried out using complementary methods of polarized neutron reflectometry, grazing incidence small-angle X-ray scattering, X-ray reflectometry, scanning electron microscopy, and SQUID magnetometry. It is shown that the interface layer between the granular film and the Si substrate exhibits metallic rather than magnetic properties and eliminates the GIMR effect.

Yuliana de Jesús Acosta-Silva et al. present their "*Study of the Effects of Er Doping on the Physical Properties of CdSe Thin Films*" [20], revealing that the Er incorporation in CdSe nanocrystals provokes drastic changes in the $Cd_{1-x}Er_xSe$ lattice structure, depending on the level of Er doping. Er^{3+} in Cd^{2+} sites induces a crystalline quality of CdSe; thus, Er^{3+} reduces the structural disorder but increases the chemical one. When the lattice expands, the 1LO phonon softens and, as expected, hardens if the lattice contracts.

Antoine Hoëz et al. present a "New Manufacturing Process for Granular Texture Management in Polycrystalline BaM Hexaferrites through the Goethite Crystallite Laths Aspect Ratio, and a Specialized Law of Approach to the Magnetic Saturation for Partly Polarized Uniaxial Materials" [21]. Their aim is focused on the manufacture and the magnetic properties of polycrystalline M-type hexaferrite $BaFe_{12}O_{19}$ (barium ferrite, or BaM) materials of different magnetic texturing grades, going from a random distribution of the BaM crystallites to their almost complete stacking. The Rietveld refinements of powder diffractograms clearly revealed a particle-stacking enhancement, which is dependent not only on the hematite:goethite ratio but also on the optimal aspect ratio of goethite crystallites. This optimization resulted in a significant improvement of the remanent magnetization value, increasing it to 0.82 compared with the most recent literature. Based on this study, BaM materials are further manufactured with a controlled magnetic texture and, therefore, are partly self-polarized.

Andrea Amaro et al. discuss the "Shielding Effectiveness Measurement Method for Planar Nanomaterial Samples Based on Carbon Nanotubes (CNT) Materials up to 18 GHz" [22]. The proposed measurement methodology demonstrates significant advantages, including the simplicity of the sample machining, which means that very specific geometries or tiny dimensions are not required. Some of the samples analyzed have demonstrated to provide a significant attenuation in the 700 MHz–18 GHz frequency range. For those composites based on a polymer matrix with different concentrations of CNT, a value of −81.30 dB has been obtained for the frequency of 7.125 GHz for the 15 w%CNT composite, which is very significant considering the nature of the materials. They highlighted that these types of characterizations are very relevant from a technological and industrial point of view, specifically for those sectors related to 5G technology, since the use of EMI shielding based on plastic materials has numerous advantages, i.e., manufacturing cost-efficiency.

Next, single-molecule magnets (SMMs)—which are low dimensional molecules consisting of coupled paramagnetic metal ions, possessing unique magnetic properties (magnetic hysteresis, slow magnetic relaxations, quantum tunneling effects) available at the molecular level—are presented and discussed by Oleksandr Pastukh et al. in their work entitled "*AC Susceptibility Studies of Magnetic Relaxation in Mn_{12}-Stearate SMMs on the Spherical Silica Surface*" [23].

Finally, in their "*Review of Magnetic Shape Memory Polymers and Magnetic Soft Materials*", Sanne J. M. van Vilsteren et al. emphasize the development of magnetic soft materials (MSMs) and magnetic shape memory polymers (MSMPs), with a specific focus on the role of the magnetic particles which affect the shape memory recovery and programming behavior of these materials [24]. In addition, the synthesis and application of these materials are addressed, since they may exceed conventional shape memory materials such as shape memory alloys or shape memory polymers. The parameters that have been studied are their material composition, shape recovery, and shape recovery simulation, with a specific emphasis on manufacturing methods and applications. The magnetic shape memory effect activation makes it able to activate shape change remotely and with (almost) no surface heat. This makes shape memory materials useful for more applications than heat-activated shape memory polymers activated by conduction or convection. MSMPs often have only one remembered shape and no reversible shape change activated by the magnetic field. It can also take some time to activate the shape change. However, these drawbacks can be avoided by MSMs which offer fast and reversible shape changes. In addition, the effect of the magnetic properties of the magnetic components (Curie temperature, coercivity, remanence) on the shape memory function of these materials is as yet largely unknown and needs to be the subject of future research. Although several successful applications have already been reported (predominantly in the biomedical field), it can be concluded that magnetic shape memory alloys (both MSMs and MSMPs) are merely at the beginning of their development and still need to find their way to large-scale market applications.

To conclude, magnetic materials have the potential for use in information storage and processing, spintronics, drug delivery, cooling technology, etc. [25,26]. Various magnetic transitions are induced by temperature variation, crystal volume change, substitution of other elements, and applications of high magnetic fields and high pressure [27]. Thus, this first volume presents various materials and techniques which are highly relevant to modern electrical engineering and industry. Applications of the magnetization reversal phenomenon in magnetoelectronic and magnetocaloric devices, such as magnetic memory and magnetic cooling/heating-based constant-temperature baths, will be presented and discussed in a second volume.

As a final word of this Editorial for the first volume of "*Magnetic Materials, Thin Films and Nanostructures*", we would like to present the reader with a simple, yet profound thought from one of the greatest minds of the last century: "*The whole of science is nothing more than a refinement of everyday thinking* . . . " (Albert Einstein).

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References

1. Frith, H.; Stepney Rawson, W. *Coil and Current; or the Triumphs of Electricity*; Ward, Lock and Co.: London, UK, 1986; p. 4. Available online: https://books.google.fr/books/about/Coil_and_Current_Or_the_Triumphs_of_Elec.html (accessed on 5 May 2023).
2. Selley, R.C.; Cocks, L.R.M.; Plimer, I.R. (Eds.) *Encyclopedia of Geology*; Academic Press: Cambridge, MA, USA, 2005. Available online: https://www.sciencedirect.com/referencework/9780123693969/encyclopedia-of-geology (accessed on 5 May 2023).
3. Bacon, B.; Khatiri, A.; Palmer, J.; Freeth, T.; Pettitt, P.; Kentridgee, R. An Upper Palaeolithic Proto-writing System and Phenological Calendar. *Camb. Archaeol. J.* **2023**, 1–19. [CrossRef]
4. Shu-Hua, L. Origine de la Boussole II. Aimant et Boussole. *Isis* **1954**, *45*, 175–196. (In French) [CrossRef]
5. Qin, S.; Yin, H.; Yang, C.; Dou, Y.; Liu, Z.; Zhang, P.; Yu, H.; Huang, Y.; Feng, J.; Hao, J.; et al. A magnetic protein biocompass. *Nat. Mater.* **2016**, *15*, 217–226. [CrossRef]
6. Fowler, M. Historical Beginnings of Theories of Electricity and Magnetism. 1997. Available online: http://galileoandeinstein.physics.virginia.edu/more_stuff/E&M_Hist.html (accessed on 5 May 2023).
7. Minecan, A.M.C. Analysis and bilingual translation of epistle of Peter Peregrinus of Maricourt to Sygerus of Foncaucourt: Concerning the magnet (De magnete). *Disput. Philos. Res. Bull.* **2017**, *6*, 277–307. (In Latin) [CrossRef]
8. William Gilbert's Work on "De Magnete, Magneticisqve Corporibvs et de Magno Magnete Tellure" (1600). Bilingual Translation. Available online: https://gallica.bnf.fr/ark:/12148/bpt6k33585/f2.item.r=de+magnete.langFR# (accessed on 5 May 2023). (In Latin).
9. Maxwell, J.C. A Dynamical Theory of the Electromagnetic Field. *Philos. Trans. R. Soc. Lond.* **1865**, *155*, 459–512. [CrossRef]
10. Einstein, A. Zur Elektrodynamik bewegter Körper. *Ann. Der Phys.* **1905**, *4*, 891–921. (In German) [CrossRef]
11. Meissner, W.; Ochsenfeld, R. Ein neuer Effekt bei Eintritt der Supraleitfähigkeit. *Naturwissenschaften* **1933**, *21*, 787–788. (In German) [CrossRef]
12. Saunders, P.J.; Ford, G.A. *The Rise of the Superconductors*; CRC Press: Boca Raton, FL, USA, 2005. Available online: https://www.routledge.com/The-Rise-of-the-Superconductors/Ford-Saunders/p/book/9780748407729 (accessed on 5 May 2023).
13. Orchard, A.F. *Magnetochemistry*; Oxford Chemistry Primers; Oxford University Press: Oxford, UK, 2003. Available online: https://global.oup.com/academic/product/magnetochemistry-9780198792789 (accessed on 5 May 2023).
14. Lawrence, R.A.; Donaldson, S.J.; Probert, M.I.J. Magnetic Transition State Searching: Beyond the Static Ion Approximation. *Magnetochemistry* **2023**, *9*, 42. [CrossRef]

15. Crisan, A.D.; Dan, I.; Crisan, O. Role of Disordered Precursor in L10 Phase Formation in FePt-Based Nanocomposite Magnet. *Magnetochemistry* **2021**, *7*, 149. [CrossRef]
16. Li, G.; Xie, Y.; Wang, B.; Yang, H.; Li, R.-W. Electric Field Control of Magnetic Properties by Means of Li+ Migration in FeRh Thin Film. *Magnetochemistry* **2021**, *7*, 45. [CrossRef]
17. Abdollahzadeh Jamalabadi, M.Y. Feasibility Study of Cooling a Bulk Acoustic Wave Resonator by Nanoparticle Enhanced Phase Change Material. *Magnetochemistry* **2021**, *7*, 144. [CrossRef]
18. Apostolova, I.N.; Apostolov, A.T.; Wesselinowa, J.M. Size and Ion-Doping Effects on Magnetic, Optical, and Phonon Properties of CuAlO2 Nanoparticles. *Magnetochemistry* **2022**, *8*, 169. [CrossRef]
19. Grigoryeva, N.A.; Ukleev, V.; Vorobiev, A.A.; Stognij, A.I.; Novitskii, N.N.; Lutsev, L.V.; Grigoriev, S.V. Mesostructure and Magnetic Properties of SiO_2-Co Granular Film on Silicon Substrate. *Magnetochemistry* **2022**, *8*, 167. [CrossRef]
20. Acosta-Silva, Y.d.J.; Godínez, L.A.; Toledano-Ayala, M.; Lozada-Morales, R.; Zelaya-Angel, O.; Méndez-López, A. Study of the Effects of Er Doping on the Physical Properties of CdSe Thin Films. *Magnetochemistry* **2023**, *9*, 107. [CrossRef]
21. Hoëz, A.; Mattei, J.-L.; Chevalier, A. New Manufacturing Process for Granular Texture Management in Polycrystalline BaM Hexaferrites through the Goethite Crystallite Laths Aspect Ratio, and a Specialized Law of Approach to the Magnetic Saturation for Partly Polarized Uniaxial Materials. *Magnetochemistry* **2023**, *9*, 30. [CrossRef]
22. Amaro, A.; Suarez, A.; Torres, J.; Martinez, P.A.; Herraiz, R.; Alcarria, A.; Benedito, A.; Ruiz, R.; Galvez, P.; Penades, A. Shielding Effectiveness Measurement Method for Planar Nanomaterial Samples Based on CNT Materials up to 18 GHz. *Magnetochemistry* **2023**, *9*, 114. [CrossRef]
23. Pastukh, O.; Konieczny, P.; Laskowska, M.; Laskowski, Ł. AC Susceptibility Studies of Magnetic Relaxation in Mn12-Stearate SMMs on the Spherical Silica Surface. *Magnetochemistry* **2021**, *7*, 122. [CrossRef]
24. Van Vilsteren, S.J.M.; Yarmand, H.; Ghodrat, S. Review of Magnetic Shape Memory Polymers and Magnetic Soft Materials. *Magnetochemistry* **2021**, *7*, 123. [CrossRef]
25. Abdelbasir, S.A.; Shalan, A.E. Intriguing Properties and Applications of Functional Magnetic Materials. In *Functional Materials*; Sahu, D., Ed.; IntechOpen: London, UK, 2019. [CrossRef]
26. Krishnan, K.M. *Fundamentals and Applications of Magnetic Materials*; Oxford Academic Press: Oxford, UK, 2016. [CrossRef]
27. Paes, V.Z.C.; Varalda, J.; Mosca, D.H. Strain-induced magnetization changes and magneto-volume effects in ferromagnets with cubic symmetry. *J. Magn. Magn. Mater.* **2019**, *475*, 539. [CrossRef]