Eur. Phys. J. B **59**, 457–461 (2007)
DOI: 10.1140/epjb/e2007-00063-1

THE EUROPEAN PHYSICAL JOURNAL B

Ferromagnetic behaviour in semiconductors: a new magnetism in search of spintronic materials

A. Quesada[1,2], M.A. García[1,2], J. de la Venta[1,2], E. Fernández Pinel[1,2], J.M. Merino[1,3], and A. Hernando[1,2,a]

[1] Instituto de Magnetismo Aplicado (UCM-CSIC-ADIF), P.O. Box 155, 28230 Las Rozas, Madrid, Spain
[2] Depto. de Física de Materiales, Universidad Complutense, 28040 Madrid, Spain
[3] Depto. de Quim. Inorgan., Fac. Quím., Universidad Complutense, 28040 Madrid, Spain

Received 30 September 2006 / Received in final form 31 January 2007
Published online 2 March 2007 –

Abstract. The future of the spintronic technology requires the development of magnetic semiconductor materials. Most research groups have focused on diluted magnetic semiconductors because of the promising theoretical predictions and initial results. In this work, the current experimental situation of ZnO based diluted magnetic semiconductors is presented. Recent results on unexpected ferromagnetic-like behaviour in different nanostructures are also revised, focusing on the magnetic properties of Au and ZnO nanoparticles capped with organic molecules. These experimental observations of magnetism in nanostructures without the typical magnetic atoms are discussed. The doubts around the intrinsic origin of ferromagnetism in diluted magnetic semiconductors along with the surprising magnetic properties in absence of the typical magnetic atoms of certain nanostructures should make us consider new approaches in the quest for room temperature magnetic semiconductors.

PACS. 85.75.-d Magnetoelectronics; spintronics: devices exploiting spin polarized transport or integrated magnetic fields – 75.50.Pp Magnetic semiconductors – 75.70.-i Magnetic properties of thin films, surfaces, and interfaces – 75.75.+a Magnetic properties of nanostructures

1 Introduction

Spintronics is an emergent technology that exploits the spin of the electrons as well as their charge. The primary requirement to obtain a spintronic device is to be able to generate spin-polarized currents, and the simplest method of generating them is to inject the current through a ferromagnetic material. Spintronic devices are already operating, being the spin valve the most successful, but future applications of this technology require the development of magnetic semiconductors with Curie temperature above room temperature (RT). These materials are predicted to intrinsically generate spin-polarized currents.

The fact that the potential applications of magnetic semiconductors are unimaginable has motivated the work of a great deal of research groups around the world. The main efforts have been concentrated on finding a Diluted Magnetic Semiconductor (DMS) [1,2], consisting on a semiconductor matrix containing a small amount of magnetic impurities. The main challenge for this kind of materials is to obtain Curie temperatures above RT. As the ferromagnetism (FM) is mediated by carriers (a weak interaction) the Curie temperatures are expected to be low. Despite the promising initial experimental results using ZnO as the host semiconductor [3–5], controversy has marked the discussion around the origin of FM in these materials [6–8]. Several authors have claimed that the RT ferromagnetism reported in these materials can be due to defects in the semiconductor matrix [9–13], pointing on the alteration of the electronic structure of the semiconductor as responsible for FM.

The surprising FM recently found in Au nanoparticles (NPs), thin films capped with thiols and Pd NPs [14–16] has also been ascribed to the electronic structure alteration produced by the thiol chains bonded to the NPs in the case of Au and by the twin boundaries appearing at the Pd NPs [16,17]. Different amazing experiments on the magnetic properties of other nanostructures have been recently published [12,18–23] that challenge our classical understanding of magnetism based upon the unfilled character of $3d$ and $4f$ electron energy levels.

RT hysteresis has been found in thiol capped ZnO NPs [24], pointing out the possibility to observe magnetism at the nanoscale in semiconductors without typical magnetic atoms. The number of experiments showing RT ferromagnetism in materials that do not contain magnetic atoms is increasing. Although a thorough understanding

[a] e-mail: antonio.hernando@adif.es

of the mechanisms that account for this new magnetism is yet to be reached, the up to date progresses may be showing us a new approach in the quest for magnetic semiconductors.

2 Diluted magnetic semiconductors

2.1 Background

The search for magnetic semiconductors has gathered the attention of researches for many years [25]. They are rare in nature, and when they do occur, they possess low Curie temperatures, and their potential technological applications depend on their capacity to keep the ferromagnetic order up to RT. Since the work of Ohno was published [1] a great number of research groups have focused on the new approach proposed. It consists of substituting some atoms from a semiconductor matrix by atoms that possess a magnetic moment. These magnetic impurities polarize the conduction electrons leading to the appearance of FM in the system via a RKKY interaction.

There is a long history of magnetic substitution in semiconductors [26,27], but the magnetic order temperatures observed were very low. The proposal by Ohno led to the highest Curie temperature ever reported in an intrinsic DMS: 150 K in Mn-substituted GaAs [28].

This carrier mediated ferromagnetism is expected to be weak, but the theoretical work by Dietl et al. [2] predicted that Mn-doped GaN and ZnO could present Curie temperatures above 300 K, provided an appropriate number of holes for the coupling.

A review on this topic has been published by Seshadri [29].

2.2 Mn doped ZnO

Sharma et al. [3] published the first experimental observation of RT FM in thin films and bulk samples of $Zn_{1-x}Mn_xO$ with x near 0.02, but short after numerous publications refuted these observations. Some authors claimed that a single $Zn_{1-x}Mn_xO$ phase, non ferromagnetic, only stabilizes at 900 ^oC [30], while Kundaliya et al. [6] suggested that a secondary metastable $Zn_xMn_{2-x}O_y$ phase was the responsible for FM in the Mn doped ZnO system. Lawes et al. [7] found no ferromagnetic order down to 2 K in bulk Mn-substituted ZnO made by the oxalate decomposition method with a controlled substitution of Mn into Zn sites.

In this frame, the work published by García et al. [8] focused on bulk Mn-Zn-O samples prepared by a low temperature standard solid state reaction method using MnO_2 and ZnO as starting powders [3,31]. The samples presented a ferromagnetic behaviour that was ascribed to a double-exchange mechanism taking place between Mn^{3+} and Mn^{4+} ions. Zn diffuses into MnO_2 at low temperatures, modifying the kinetics of the MnO_2 to Mn_2O_3 reduction process and favouring the coexistence of the two Mn oxidation states that account for double-exchange at the interface of the ZnO and MnO_2 grains. Figure 1 shows a scheme of the interface.

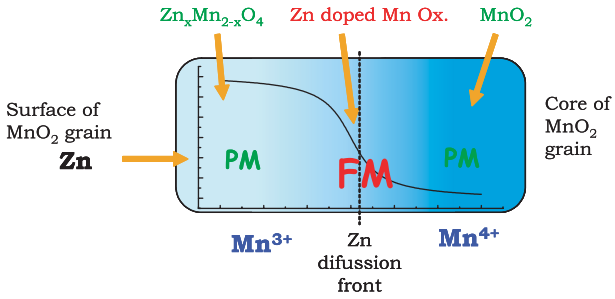

Fig. 1. Scheme of the different phases and the Mn oxidation states at the MnO_2 grains after annealing at 500 ^oC. Extracted from reference [8].

The number of publications claiming that the origin of FM in this system is extrinsic, as opposed to carrier mediated, is increasing.

2.3 Co doped ZnO

The origin of the magnetic properties of the Co-Zn-O system has often been called into question as well. In spite of the promising first experimental reports [4,5], the situation in this system is more complicated as segregation of metallic Co clusters can lead to RT FM [32–34]. Some authors claim that the FM observed is mediated by carriers in a spin-split impurity band derived from extended donor orbitals [35]. Risbud et al. [36] used the oxalate decomposition method to prepare homogenous $Zn_{1-x}Co_xO$ and no trace of magnetic order was found down to 2 K. They suggested Curie-Weiss paramagnets with the local interaction being antiferromagnetic. These results were confirmed and extended by Lawes et al. [7].

Quesada et al. [37] prepared Co-Zn-O bulk samples by the ceramic method and found FM at RT. The magnetic properties were ascribed, as in the case of Mn-Zn-O, to the partial reaction of the starting powders, the FM arising at the interfaces of the grains because of a mechanism yet to be elucidated, but different than carrier mediation and metallic cobalt.

2.4 Discussion

Although controversy has marked the search for ZnO based DMS, some conclusions can be drawn. Studies on carefully characterized homogenous bulk samples seem to suggest a complete absence of ferromagnetic ordering, and an increasing number of works claim that the origin of FM in these systems is extrinsic. Although the saturation magnetizations measured are often weak, and the results must be examined critically, the presence of impurities in the samples does not always explain the magnetic properties observed. The differences in the experimental results depend critically on the preparation route chosen and the

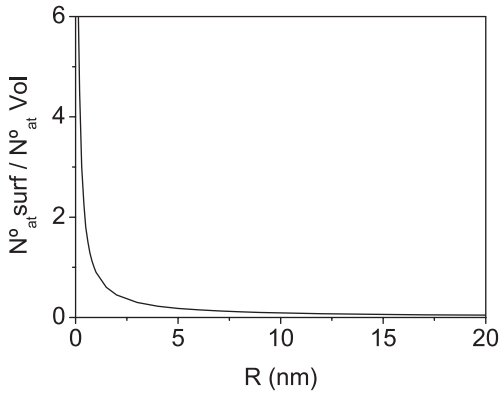

Fig. 2. Ratio of surface atoms respect to the volume atoms as a function of the particles radius R, considering spherical sized NPs with an interatomic distance of 0.3 nm.

reproducibility is low, indicating that the magnetic properties of these materials are far from being thoroughly understood. The role of the defects and the interfaces, i.e. the surfaces, seems to be crucial.

3 Magnetic nanostructures

3.1 Surprising magnetic properties

Magnetism at the nanoscale presents surprising properties, as the size and surface effects modify the physical properties and new physics appear. The fraction of atoms corresponding to the surface of the material respect to the number of bulk atoms becomes comparable at the nanoscale. It is plotted in Figure 2.

An outstanding example of these surface effects is the appearance of huge magnetic anisotropy that blocks the magnetic moments of single Co atoms deposited onto Pt surfaces reported by Gambardella et al. [38]. A set of amazing experimental results of other particular nanostructures has been reported. Ferromagnetic hysteresis at RT has been reported in graphite [18–21], and permanent giant magnetic moments were detected at the surface layers of thin films of oxides and borides [12,22,23]. Pd NPs also showed ferromagnetic-like behaviour at RT [16]. These results challenge our understanding of magnetism, as the classical interpretations in terms of unfilled $3d$ or $4f$ electron energy levels do not explain the features of this new magnetism. In most cases, the broken symmetries (lattice defects, twin boundaries and surfaces) of the materials were invoked as the cause for FM.

3.2 Au nanostructures

Recently, magnetism has been observed in 1.4 nm Au NPs capped with thiols despite the diamagnetic character of bulk Au and thiols separately [14]. The authors state that the inner metallic core of the NPs is diamagnetic, but the surface atoms are chemically bounded to the S atom at the end of the thiol chain. This bond leads to a charge transfer from the Au to the S generating holes at the $5d$ orbital of Au and yielding a magnetic moment. These moments are strongly fixed along the bond direction as Figure 3 shows.

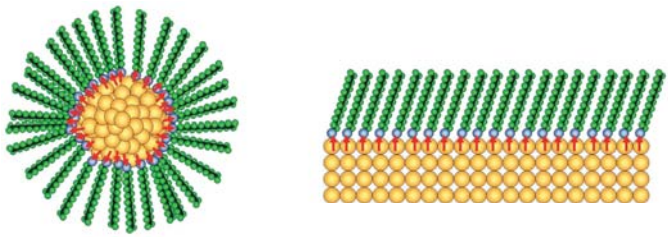

Fig. 3. Schema of the magnetic moments arising at surfaces capped with organic molecules. The magnetic moments are fixed in the bond direction that for NPs are uniformly distributed while for films there is a unique orientation perpendicular to the surface.

The magnetization is temperature independent in the 5–300 K range which is the fingerprint of a huge anisotropy and thus the ferromagnetic-like behavior is observed even at RT. In fact, thiol capped thin films were also studied and hysteresis at RT was again measured [17]. The magnetization curves are clearly different upon applying field parallel or perpendicular to the surface confirming the huge anisotropy. The magnetic moments are giant [15, 17]. Similar features have been observed in the experiments described in the previous section, and in DMS thin films, suggesting a possible common origin of these effects in some cases.

3.3 Discussion

The presence of lattice defects, surface or interface effects (i.e. broken symmetries in the system) and blocking of the magnetic moments because of an electronic structure alteration are the sources of the magnetic properties suggested by the authors. Hernando et al. propose an origin of the magnetic properties of the Au nanostructures that is accurately explained in references [17,39]. The thiol chains form domains at the gold surfaces inducing a contact potential that yields a radial electric field. This potential step traps quasifree electrons in atomic-like orbits. If the domain is large enough, the energy shall reach a minimum value when the orbital momentum is giant. The spin and orbital moments are coupled for each electron and exchange interactions tend to align their spins. The spin-orbit coupling leads to an alignment of the orbital momentum, yielding a permanent magnetic moment at the surface. This orbital magnetism explains the giant values of the Bohr magnetons per surface atom reported [15, 17], the magnetization independence from temperature up to RT and above all, the appearance of permanent magnetism at RT in a material without the typical magnetic atoms.

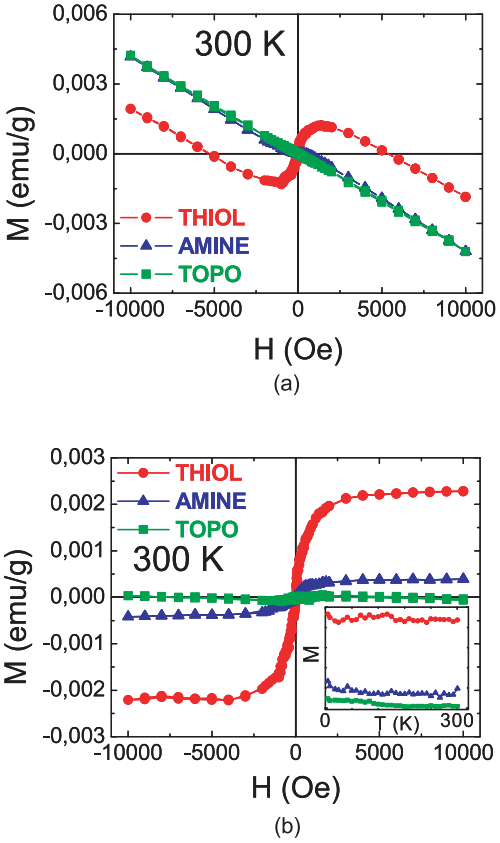

Fig. 4. (a) Hysteresis loops from ZnO NPs capped with different molecules. (b) The loops after subtracting the diamagnetic/paramagnetic background. Inset shows the thermal dependence of the magnetization under an applied field of 500 Oe after subtracting the corresponding constant diamagnetic background.

4 Magnetic ZnO nanoparticles

4.1 Experiments

García and co-workers [24] prepared ZnO nanoparticles with average size around 10 nm and capped with three different types of organic molecules: dodecanethiol, tryoctylphosphine and dodecylamine (named after here thiol, amine and TOPO respectively). The Zinc Acetate (used as reactant) was separately measured and an expected diamagnetic response was observed. For the amine and thiol capped NPs, a ferromagnetic-like contribution was observed over a diamagnetic background at RT. Figure 4 shows the magnetization curves measured.

Identical results were obtained at 5 K. The chemical analysis provided by the precursors suppliers showed that possible traces (lower than 0.5 ppm) can not account for the experimental magnetization values measured. X-ray Absorption Near Edge Spectroscopy (XANES) and photoluminescence (PL) experiments were performed. From both techniques it is inferred that the capping molecule alters the electronic structure of the ZnO NPs, modifying the energy levels. A perfect correlation is found in the evolution of the magnetic properties with the capping molecule: Thiol NPs present the largest alteration of the electronic structure as evidenced by XANES and PL results, and the largest magnetic moments. On the other side, the TOPO sample has an electronic configuration very similar to bulk ZnO and possesses a diamagnetic behaviour. The amine NPs present an intermediate result.

4.2 Discussion

This result points out the possibility to observe magnetism in semiconductors without magnetic atoms, and the mechanism yielding these magnetic properties may be explained in the frame of Hernando's theory [17,39]. In fact, the orbital magnetism arising from electronic configuration alteration may be at the origin of the magnetic properties of some of the controversial results about DMS. The presence of 3*d* magnetic impurities in these materials can be seen as a second contribution to the magnetism observed. Actually, the presence of magnetic impurities in a host semiconductor is also an alteration of the energy levels of the matrix. Recent experiments have shown that when both contributions are present, they are coupled [9, 10].

Small differences in the electronic configuration may lead to large variations in the magnetic properties, indicating that the sample preparation method is a critical factor and explaining the low reproducibility. Obviously, not any alteration leads to RT FM, but what has been demonstrated by García et al. [24] is the possibility to observe RT hysteresis in semiconductors at the nanoscale without the contribution of 3*d* magnetic atoms.

5 Conclusions

A new magnetism is emerging at the nanoscale that needs further research in order to achieve a deep understanding of the underlying mechanisms. The search for magnetic semiconductors has been focused on DMS in the past few years, but the amazing recent magnetic experiments on nanostructures without typical magnetic moments are showing us new approaches that open a new world of possibilities. The challenge now is to know which configurations, structures and conditions lead to magnetism in semiconductors, the materials for next generation spintronic devices.

References

1. H. Ohno, Science **281**, 951 (1998)
2. T. Dietl, H. Ohno, F. Matsukura, J. Cibert, D. Ferrand, Science **287**, 1019 (2000)
3. P. Sharma et al., Nature Mater. **2**, 673 (2003)
4. H.J. Lee, S.Y. Jeong, C.R. Cho, C.H. Park, Appl. Phys. Lett. **81**, 4020 (2002)
5. W. Prellier, A. Fouchet, B. Mercey, C. Simon, B. Raveau, Appl. Phys. Lett. **82**, 3490
6. D.C. Kundaliya et al., Nature Mater. **3**, 709 (2004)

7. G. Lawes, A.S. Risbud, A.P. Ramírez, R. Seshadri, Phys. Rev. B **71**, 045201 (2005)
8. M.A. García et al., Phys. Rev. Lett. **94**, 217206 (2005)
9. K.R. Kittilstved, D.R. Gamelin, J. Am. Chem. Soc. **127**, 5292 (2005)
10. K.R. Kittilstved, N.S. Norberg, D.R. Gamelin, Phys. Rev. Lett. **94**, 147209 (2005)
11. J.M.D. Coey, M. Venkatesan, C.B. Fitzgerald, Nature Mat. **4**, 173 (2006)
12. M. Venkatesan, C.B. Fitzgerald, J.M.D. Coey Nature **430**, 630 (2004)
13. K.R. Kittilstved, W.L. Liu, D.R. Gamelin, Nature Mat. **5**, 291 (2006)
14. P. Crespo et al., Phys. Rev. Lett. **93**, 087204 (2004)
15. I. Carmeli, G. Leitus, R. Naaman, S. Reich, Z. Vager. J. Chem. Phys. **18**, 10372 (2003)
16. B. Sampedro et al., Phys. Rev. Lett. **91**, 237203 (2003)
17. A. Hernando et al., Phys. Rev. B **74**, 052403 (2006)
18. S. Talapatra et al., Phys. Rev. Lett. **95**, 097201 (2005)
19. A.V. Rode et al., Phys. Rev. B **70**, 054407 (2004)
20. J.M.D. Coey, M. Venkatesan, C.B. Fitzgerald, A.P. Douvalis, I.S. Sanders, Nature (London) **420**, 156 (2002)
21. T.L. Makarova, Semiconductors **38**, 615 (2004)
22. K. Kusakabe, M. Maruyama, Phys. Rev. B **67**, 092406 (2003); P.O. Lehtinen, A.S. Foster, Y. Ma, A.V. Krasheninnikov, R.M. Nieminen, Phys. Rev. Lett. **93**, 187202 (2004)
23. L.S. Dorneles, M. Venkatesan, M. Moliner, G. Lunney, J.M.D. Coey, Appl. Phys. Lett. **85**, 6377 (2004)
24. M.A. García et al. (to be published)
25. P.K. Baltzer, H.W. Lehmann, M. Robbins, Phys. Rev. B **15**, 493 (1965)
26. R.W. Cochrane, M. Plischke, J.O. Ström-Olsen, Phys. Rev. B **9**, 3013 (1974)
27. T. Story, R.R. Galazka, R.B. Frankel, P.A Wolff, Phys. Rev. Lett. **56**, 777 (1986)
28. D. Chiba, K. Takamura, F. Matsukura, H. Ohno, Appl. Phys. Lett. **82**, 3020 (2003)
29. R. Seshadri, Curr. Opin. Solid State Mater. Sci. **9**, 1 (2005)
30. S. Kolesnik, B. Dabrowski, J. Appl. Phys. **96**, 5379 (2004)
31. J.L. Costa-Krämer, F. Briones, J.F. Fernandez, A.C. Caballero, M. Villegas, M. Diaz, M.A. García, A. Hernando, Nanotechnology **16**, 214 (2005)
32. S.R. Shinde, S.B. Ogale, J.S. Higgins, H. Zheng, A.J. Millis, V.N. Kulkarni, R. Ramesh, R.L. Greene, T. Venkatesan, Phys. Rev. Lett. **92**, 166601 (2004)
33. J.H. Park, G. Kim, H.M. Jang, S. Ryu, Y.M. Kim, Appl. Phys. Lett. **84**, 1338 (2004)
34. E.C. Lee, K.J. Chang, Phys. Rev. B **69**, 085205 (2004)
35. C.B. Fitzgerald, M. Venkatesan, J.G. Lunney, L.S. Dorneles, J.M.D. Coey, Appl. Surf. Sci. **247**, 493 (2005)
36. A.S. Risbud, N.A. Spaldin, Z.Q. Chen, S. Stemmer, R. Seshadri, Phys. Rev. B **68**, 205202 (2003)
37. A. Quesada et al., J. Appl. Phys. **100**, 113909 (2006)
38. P. Gambardella, S. Rusponi, M. Veronese, S.S. Dhesi, C. Grazioli, A. Dallmeyer, I. Cabria, R. Zeller, P.H. Dederichs, K. Kern, C. Carbone, H. Brune, Science **300**, 1130 (2003)
39. A. Hernando, P. Crespo, M.A. García, Phys. Rev. Lett. **96**, 057206 (2006)