EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

Letter of Intent to the ISOLDE and Neutron Time-of-Flight Committee

Surface mediated magnetism in metal-oxide semiconductors

[25 September 2013]

M. Deicher[1], K. Johnston[1,2], J. Lehnert[1], Th. Wichert[1], H. Wolf[1], H. P. Gunnlaugsson[3]

[1]*Experimentalphysik, Universität des Saarlandes, 66041 Saarbrücken, Germany*
[2]*PH Dept., CERN, 1211 Geneva 23, Switzerland*
[3]*Department of Physics and Astronomy, Aarhus University, Ny Munkegade 120, DK-8000 Aarhus, Denmark*

Spokesperson: M. Deicher (manfred.deicher@tech-phys.uni-sb.de)
Local contact: K. Johnston (karl.johnston@cern.ch)

CERN-INTC-2013-035 / INTC-I-147
25/09/2013

Abstract

Building on experience gained over the past years at ISOLDE where the nature of magnetism in semiconductors has been extensively studied, we propose to investigate the role of the surface in so-called dilute magnetic semiconductors, an area which has not been accessible in recent years at ISOLDE. If the results prove to be promising this is an area which will develop into a full proposal in the coming years.

Requested shifts: 4 shifts, (split into 2 runs over 1-2 years)

The prediction by Dietl *et al* [1] that ordered ferromagnetism could exist at room temperature in wide band-gap semiconductors such as GaN and ZnO set off a fire-storm of research activity in the past 10 years. In the intervening period much disputatious research findings have been published. Both ferromagnetism and paramagnetism have been reported in ZnO for a variety of experimental situations [2]. However, when one excludes the formation of ferromagnetic precipitates from the picture, the overall consensus in recent years is that the magnetic behaviour exhibited by ZnO is paramagnetic rather than ferromagnetic. This is an area which has been explored in some detail – and with considerable success – by existing experiments at ISOLDE[1] using emission channelling and Mössbauer spectroscopy [3,4,5].

However the aforementioned experiments have been limited to probing the bulk properties of the material. This letter of intent aims to study an area which hasn't previously been accessible at ISOLDE: the surface. Experimental work presenting interesting, albeit inconclusive, data on possible ferromagnetic behaviour at the surface level [6] in ZnO nanoparticles motivated Sanchez *et al* [7] to consider the effect of hydrogen adsorption on the Zn-terminated (0001) surface. This work predicted that a metal to insulator may be observed by varying the hydrogen coverage of the surface. Furthermore, the H-covered surface was predicted to exhibit spin-polarisation in the bands, extending into the ZnO subsurface. The predicted strength of the polarisation was $0.5\mu_B$ per hydrogen atom. Experimental confirmation of these predictions has not yet been achieved, although work in a similar spirit – although extending beyond the surface region – has been reported by Khalid *et al* on the apparent observation of *hydrogen-induced* ferromagnetism in ZnO crystals following the implantation of low energy H^+ ions [8].

With the re-activation of the ASPIC setup – reborn as the VITO beamline – we will be in a position to study the situation described by Sanchez *et al.* using soft landing of suitable probe atoms on the ZnO surface.

<u>Proposed experiments and beam request</u>

The charge and spin distributions in a solid can be probed at a very local scale by hyperfine techniques such as perturbed angular correlation (PAC). The soft-landing approach which has been previously used at the ASPIC experiment is a highly controlled method for the incorporation of probe atoms on the surface of a semiconductor or metal, where studies on the monolayer level are feasible. A detailed summary of the capabilities of the ASPIC chamber are summarised by Prandolini [9].

^{111m}Cd is a workhorse PAC probe which is delivered at high intensity at ISOLDE and would be a suitable probe for these tests. Cd is isoelectronic with Zn and is predicted to occupy the Zn site.

The proposed experiments would be as follows:

1. Optimise the soft-landing procedure for studying these systems.
2. Determine, using magnetic hyperfine interactions, the magnetic properties of surface of nominally undoped ZnO. The role of both Zn and O-vacancies would be examined.
3. Investigate the effect of native surface defects with hydrogen-related impurities and their interplay in the production of ferromagnetic ordering in ZnO.
4. Investigate the interplay between surface defects and transition metals in ZnO and the subsequent effect on ferromagnetism in ZnO.

From these studies we aim to get a broader picture of the microscopic nature of the role of the surface – if any – in magnetic semiconductors. As mentioned in the introduction, most recent experimental evidence has shown that ferromagnetic states in dilute magnetic semiconductors are not observed. However, with this letter of intent we aim to study the role of the surface which hasn't been accessible using a technique such as Mössbauer spectroscopy. If we observe states as predicted by Sanchez *et al.* we would foresee this approach being extended to other semiconductor materials in a full proposal.

---

[1] IS453: Emission channelling lattice location experiments with short-lived isotopes. IS501: Emission Mössbauer spectroscopy of advanced materials for opto- and nano- electronics

Isotope	Target	Ion source	Yields [ions/μC]
^{111}Cd	Sn (Molten)	VADIS	~5.0e8

Table 1 Summary of the beam request and target and ion source details for this letter of intent.

References

[1] T. Dietl, H. Ohno, F. Matsukura, J. Cibert and D. Ferrand Science **287** 101 (2000)

[2] Hadis Morkoc and Umit Ozgur "Zinc Oxide: Fundamentals, Materials and device Technology" Wiley-VCH, Weinheim (2009).

[3] H. P. Gunnlaugsson, T. E. Mølholt, R. Mantovan, H. Masenda, D. Naidoo, W. B. Dlamini, R. Sielemann, K. Bharuth-Ram, G. Weyer, K. Johnston, G. Langouche S. Ólafsson, H. P. Gíslason, Y. Kobayashi, Y. Yoshida, M. Fanciulli and the ISOLDE Collaboration, *Appl. Phys. Lett.* **97** 142501 (2010)

[4] H. P. Gunnlaugsson, K. Johnston, T. E. Mølholt, G. Weyer, R. Mantovan, H. Masenda, D. Naidoo, S. Ólafsson, K. Bharuth-Ram, H. P. Gíslason, G. Langouche, M. B. Madsen and the ISOLDE Collaboration, *Appl. Phys. Lett.* **100** 042109 (2012)

[5] L. M. C. Pereira *et al* Journal of Applied Physics **113** 023902 (2013)

[6] M. A. Garcia, J. M. Merino, E. Fernández Pinel, A. Quesada, J. de la Venta, M. L. Ruíz González, G. R. Castro, P. Crespo, J. Llopis, J. M. González-Calbet, and A. Hernando, Nano Lett. **7**, 1489 (2007)

[7] N. Sanchez, S. Gallego, J. Cerdá, and M. C. Muñoz, Phys. Rev. B **81** 115301 (2010)

[8] M. Khalid and P. Esquinazi, Phys. Rev. B **85** 134424 (2012)

[9] M. J. Prandolini Rep. Prog. Phys. **69** 1235–1324 (2006)

Appendix

DESCRIPTION OF THE PROPOSED EXPERIMENT

The experimental setup comprises: *(name the fixed-ISOLDE installations, as well as flexible elements of the experiment)*

Part of the Choose an item.	Availability	Design and manufacturing
VITO (previously ASPIC) beamline… Currently being modified	☒ Existing	☒ To be used without any modification
VITO	☒ Existing	☐ To be used without any modification ☒ To be modified
	☐ New	☐ Standard equipment supplied by a manufacturer ☐ CERN/collaboration responsible for the design and/or manufacturing

HAZARDS GENERATED BY THE EXPERIMENT

(if using fixed installation) Hazards named in the document relevant for the fixed VITO installation.

NOTE: Hydrogen diffusion etc will be done at home labs (i.e. Saarbrucken). ZnO samples will be brought to CERN.

Additional hazards:

Hazards	*VITO*	*[Part 2 of the experiment/equipment]*	*[Part 3 of the experiment/equipment]*
Thermodynamic and fluidic			
Pressure			
Vacuum	10^{-7} 10^{-9} mbar		
Temperature	Room temperature		
Heat transfer			
Thermal properties of materials			
Cryogenic fluid			
Electrical and electromagnetic			
Electricity	220 [V]		
Static electricity			
Magnetic field			
Batteries	☐		
Capacitors	☐		
Ionizing radiation			
Target material	ZnO crystals		
Beam particle type (e, p, ions, etc)	Ions		
Beam intensity	5e8 ions sec^{-1}		
Beam energy	30-60kV (from separator; soft		

	landing on sample surface)		
Cooling liquids			
Gases			
Calibration sources:	☐		
• Open source	☐		
• Sealed source	☐ [ISO standard]		
• Isotope			
• Activity			
Use of activated material:			
• Description	☒		
• Dose rate on contact and in 10 cm distance	(estimated) 100µSv/hr @ 10cm		
• Isotope	^{111m}Cd		
• Activity	<1MBq		
Non-ionizing radiation			
Laser			
UV light			
Microwaves (300MHz-30 GHz)			
Radiofrequency (1-300MHz)			
Chemical			
Toxic			
Harmful			
CMR (carcinogens, mutagens and substances toxic to reproduction)			
Corrosive			
Irritant			
Flammable			
Oxidizing			
Explosiveness			
Asphyxiant			
Dangerous for the environment			
Physical impact or mechanical energy (moving parts)			
Mechanical properties (Sharp, rough, slippery)			
Vibration			
Vehicles and Means of Transport			
Noise			
Frequency			
Intensity			
Physical			
Confined spaces			
High workplaces			
Access to high workplaces			
Obstructions in passageways			
Manual handling			
Poor ergonomics			

2 Hazard identification

3.2 Average electrical power requirements (excluding fixed ISOLDE-installation mentioned above): *(make a rough estimate of the total power consumption of the additional equipment used in the experiment)*

Nothing beyond standard electrical usage in the ISOLDE hall.