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Mossbauer studies of dilute magnetic semiconductors

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Summary

The recent discovery of (dilute) magnetic semiconductors with wide band gaps, e.g. GaN, ZnO and other oxides, having Curie temperatures, T_C, well above room temperature, has prompted extraordinary experimental and theoretical efforts to understand, control and exploit this unexpected finding not least in view of the obvious potential of such materials for the fabrication of "spin-(elec)tronic" or magneto-optic devices. Ferromagnetism (FM) was achieved mostly by doping with dilute 3d transition metal impurities, notably Mn, Fe, and Co (in % concentrations), during growth or by subsequent ion implantation. However, it is fair to state that experimentally the conditions for the occurrence of ferro-, antiferro- or paramagnetism with these impurities are not yet controlled as generally at least two conflicting forms of magnetism or none have been reported for each system - albeit often produced by different techniques. Theory is challenged as "conventional" models seem to fail and no generally accepted understanding of this novel type of magnetism has been achieved yet.

Only a few analytical techniques, which can give atomic scale information on electronic configurations and magnetic properties have been applied; among them Mössbauer spectroscopy utilizing the ^{57}Fe Mössbauer isotope. Here we propose to implant radioactive $^{57}Mn^{+}$ ions, which decay to the ^{57}Fe Mössbauer state. This approach has several pronounced benefits:

- Truly dilute semiconductors are easily produced as only ~$3\cdot10^{11}$ implanted probe atoms are needed to obtain a good spectrum (local concentration ~10^{17} cm^{-3}).
- Impurity concentrations and depth profiles are controllable.
- Lattice defects are produced simultaneously and their interaction with the implanted probe atoms, possibly decisive for the occurrence of FM, can be studied, e.g. by varying the implantation temperature.
- The half-life and decay properties of ^{57}Mn are favourable for such studies.
- ^{57}Fe Mössbauer spectroscopy has sufficient sensitivity and resolution to obtain atomic scale information over a large temperature range of ~ 10 – 1000 K for studies of high T_C magnetism.

First results from a test beam time have validated these characteristics of the approach and reveal the importance of lattice defects for the occurrence of high T_C magnetism in ZnO. More detailed experiments employing differently pre-doped material, external magnetic fields, lower temperatures and angular dependent measurements are planned to gain further insight into the origin of the

magnetic ordering. Related systems, in particular other oxides, e.g. HfO_2, SnO_2, are to be tested as well, as this can give insight into properties not easily observable in ZnO.

Commercial material is available to some extent, e.g. for ZnO, however, most materials with specific doping are to be produced and characterised by complementary, conventional techniques, which are available in the home laboratories.

Beam time request: 20 shifts of $^{57}Mn^{+}$ ions over a period of 2-3 years.

Introduction

The quest for producing dilute magnetic semiconductors (DMS) with high T_C for practical room temperature (RT) device applications started with III-V materials, where by doping with 3d impurities, e.g. p-type $Ga_{1-x}Mn_xAs$, Curie temperatures up to $T_C \approx 170$ K have been reached [1]. Long-range ferromagnetic exchange interaction has been explained as hole-mediated in spin-polarized bands with Mn acting as both acceptor and magnetic impurity [2]. A theoretical prediction that ferromagnetism with $T_C >$ RT could be achieved in GaN or ZnO doped with 5% of Mn [2] or other 3d elements [3] initiated extensive experimental activity; today $T_C \geq$ RT has been claimed for GaN and AlN as well as for about five different oxides, all doped with several % of various 3d impurities on cation sites [4]. Characteristically, 3d ions with about half-filled shells, Mn^{2+}, Fe^{3+} or Co^{2+}, i.e. with potentially large magnetic moments, resulted in the highest T_C values. However, e.g. for ZnO, para- or ferromagnetism has been found for nominally equivalent 3d doping by different groups [5-10]. In some cases the disputed origin of ferromagnetism could be attributed to (precipitated) second (magnetic) phases in the material [11-13]. The generally applied macroscopic magnetisation measurements on thin layers are vulnerable to misinterpretations in the presence of small magnetic precipitates in the film or substrate material. As most oxides are insulators or show n-type conductivity (most likely due to O vacancy donors), alternative models are emerging, e.g. bound polaron-mediated ferromagnetic coupling of 3d magnetic moments within polaron orbits and by polaron orbit percolation [4]. Magnetic moments on defects and two-electron coupling with adjacent anion vacancies [4] or cation vacancies [14] have also been proposed and might contribute to the magnetism. This proposition appeared corroborated by recent claims of ferromagnetism in materials without magnetic 3d elements, i.e. Cu doped ZnO [15] and undoped HfO_2 [16]. In the latter case, originally the magnetism has been attributed to O vacancies [16], whereas this was ruled out theoretically but Hf vacancies were found to have ferromagnetic ground states [17]. Experimentally, however, strong evidence appeared that pure HfO_2 is non-magnetic and 3d surface contaminations result in very similar magnetic characteristics [18] as those reported in ref. 16 and also observed for 3d-doped ZnO by the same group [7]. For ZnO, Zn vacancies as well as Zn interstitials, acting as hole and electron dopants, respectively, have been proposed theoretically to promote ferromagnetism in Mn- and Co-doped material [19]. For Mn and Fe doping of ZnO small magnetic moments ≤ 0.5 μ_B/ion have been deduced experimentally, whereas values exceeding 1 μ_B/ion have been found for Co [7]. The only known Mossbauer experiment for ^{57}Fe in ZnO did possibly show ferromagnetism at temperatures ≤ 20 K and paramagnetism above that temperature [20].

The approach proposed here to study the magnetism of Fe ions (e.g. in ZnO) directly by Mössbauer spectroscopy appears rewarding as it is not affected by the mentioned pitfalls and/or ambiguities of macroscopic techniques and it has an unprecedented large temperature range. In addition the Fe valence electron configurations, lattice sites and symmetries and lattice vibrational properties can be determined. Most importantly, it emerges from the test experiments that the role of defects is of

utmost importance for the occurrence of magnetism; these are abundantly provided and controllable to some extent in the ion implantation process. Ion implantation of Mn/Fe impurities is known to result in a predominant incorporation on substitutional Zn sites [21], stable to > 1000 K. Last, but not least, the recoil imparted on the ^{57}Fe daughter atom in the nuclear decay creates also interstitial Fe probe atoms (and a Zn vacancy by relocation from substitutional sites).

Preliminary results:

To elucidate these merits of the proposed approach, preliminary results from implantations of $^{57}Mn^{+}$ ions into ZnO will be briefly discussed.

Fig. 1 shows ^{57}Fe Mössbauer spectra from single ion implantations of 60 keV $^{57}Mn^{+}$ ions (fluence < 10^{12}/cm^2) into a hydrothermally-grown, bulk ZnO crystal at the temperatures indicated.

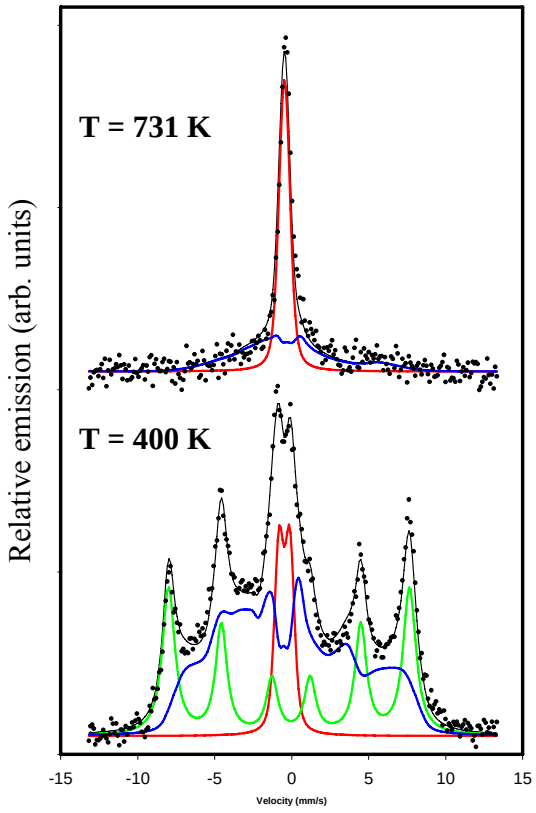

Fig. 1: ^{57}Fe Mössbauer spectra obtained after implantation of ^{57}Mn into a bulk ZnO crystal held at the temperatures indicated. The solid lines show the individual fitting components and their sum.

Apart from a minor quadrupole-split doublet in the centre of the spectrum at 400 K (red), two dominant magnetic components are present, a relatively well-resolved, magnetically-split sextet (green) and a broad distribution of sextets (blue); the magnetic components represent > 80% of the spectral area. Deduced magnetic hyperfine fields of, respectively, B_{hf} = 48 T (sextet) and about 31 T (distribution) give evidence of Fe magnetic moments > 1 μ_B and, in conjunction with the isomer shift, of a Fe^{3+} high-spin configuration for the sextet and most of the distribution. The latter component is still visible in the spectrum at 731 K, whereas the sextet is converted into the (almost) single line (red). A detailed discussion of the incomplete data is not intended here, however, it is evident that the majority of the Fe atoms probe a magnetically-ordered local surrounding up to ≈ 600 K and that the Fe magnetic moments are close to their maximal values. From the temperature dependence of the magnetic hyperfine splitting for the sextet an even higher T_C value is indicated;

thus by ion implantation a dilute magnetic semiconductor with $T_C >> RT$ can be produced. It is the major objective of this proposal to clarify the nature of the magnetism. Since the magnetic signals in the spectra were visible already after implantation of only 10^{10} probe atoms, a carrier-mediated ferro- or antiferromagnetic coupling appears unlikely as well as a bound polaron coupling. The evolution of the magnetic components as a function of temperature on the time scale of the ^{57}Mn lifetime ($T_{1/2}$ = 1.5 min) points rather to the formation (and dissolution at high temperatures) of very small, isolated magnetic clusters involving the substitutional Mn/Fe atoms on Zn sites and at least one vacancy for the sextet, whereas the fraction showing a B_{hf} distribution is attributed to (interstitial) ^{57}Fe atoms replaced from Zn sites by an average recoil energy of 40 eV in the ^{57}Mn nuclear decay. The doublet with a temperature dependent quadrupole splitting is attributed to paramagnetic ^{57}Fe on Zn sites in locally unperturbed surrounding; this line increases finally at high temperatures.

Planned experiments:
Based on our experience with the application of the ^{57}Mn beam at ISOLDE, the test experiments performed during 2005, the following task list is proposed in order to gain in-depth knowledge of the systems involved:

- Low temperature measurements to see in more detail the effects of interstitial defects, which become mobile in the temperature range 77 – 300 K [22] as well as a possible mobility of Zn vacancies V_{Zn}. This should allow for better determination of the nature of the defects involved (~ 4 shifts).
- Measurements in external magnetic fields to determine easy magnetisation axes and the sign of the magnetic hyperfine fields. In our current setup, we can reach external magnetic fields ~0.7 T utilizing permanent magnets (~3 shifts).
- Angular dependent measurements to determine V_{zz} axes and/or the angle between V_{zz} and B_{hf} (~3 shifts).
- Measurements on differently doped ZnO, pre-implanted/incorporated with 3d impurities and n- and p-type doping. (~4 shifts).
- Measurements on other oxides and/or related systems (HfO_2, Lu_2O_3, SnO_2, TiO_2, GaN, AlN and InN) (~3 shifts):
- Time-delayed measurements: These are performed at a constant, critical temperature and spectra are measured in different time intervals after the implantation to give the annealing behaviour on a minute timescale. (~3 shifts)

Beam time: in lumps of 6-10 shifts, during 2-3 years 20 shifts in total.
The UC_2 target and the laser ion source are requested.

Complementary activities.
In parallel to the experiments planned at ISOLDE, a similar program involving stable ^{57}Fe atoms will be pursued in the home laboratories, however, much larger concentrations are needed for measurable effects.

For 2006 ^{57}Fe recoil implantation experiments are also planned at HMI in Berlin. These experiments are complementary (^{57}Fe implantation and measurements during 100 ns) to those planned at ISOLDE.

Within the planned activity, we also foresee a collaboration with the PAC and PL groups at ISOLDE.

Resources at home institutions.
In the following a short resume of synthetic and analytical techniques relevant for the proposed activity available in home institutions is provided.

CNR-INFM MDM National Laboratory (M. Fanciulli, R. Mantovan):
Conversion electron Mössbauer spectroscopy (MS) at RT and at 120 K
ESR and EDMR (X and Q band, 300 mK – 600 K, up to 12 T)
Growth by Atomic Layer Deposition (ALD) of oxides (G. Scarel)
First principle calculations of magnetic properties of Fe doped ZnO (A. Debernardi)

University of Aarhus:
Conversion electron Mössbauer spectroscopy (MS) at RT and transmission MS at 14-300 K on samples with stable isotopes. (H. P. Gunnlaugsson)
Theoretical calculation of Mössbauer parameters of model defects (A. Svane)

University of Iceland:
MBE growth of GaN, AlN and InN samples, with or without Mn doping, C-V and Hall effect and PL characterisation, (S. Olafsson and Prof. H. P. Gislason).
Transmission MS from 300-1000 K, (Prof Ö. Helgason).

University of KwaZulu-Natal, Durban, and iThemba LABS, South Africa (K. Bharuth-Ram):
Transmission MS at 80 – 1000 K; CEMS at RT
Vibrating sample magnetometer

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