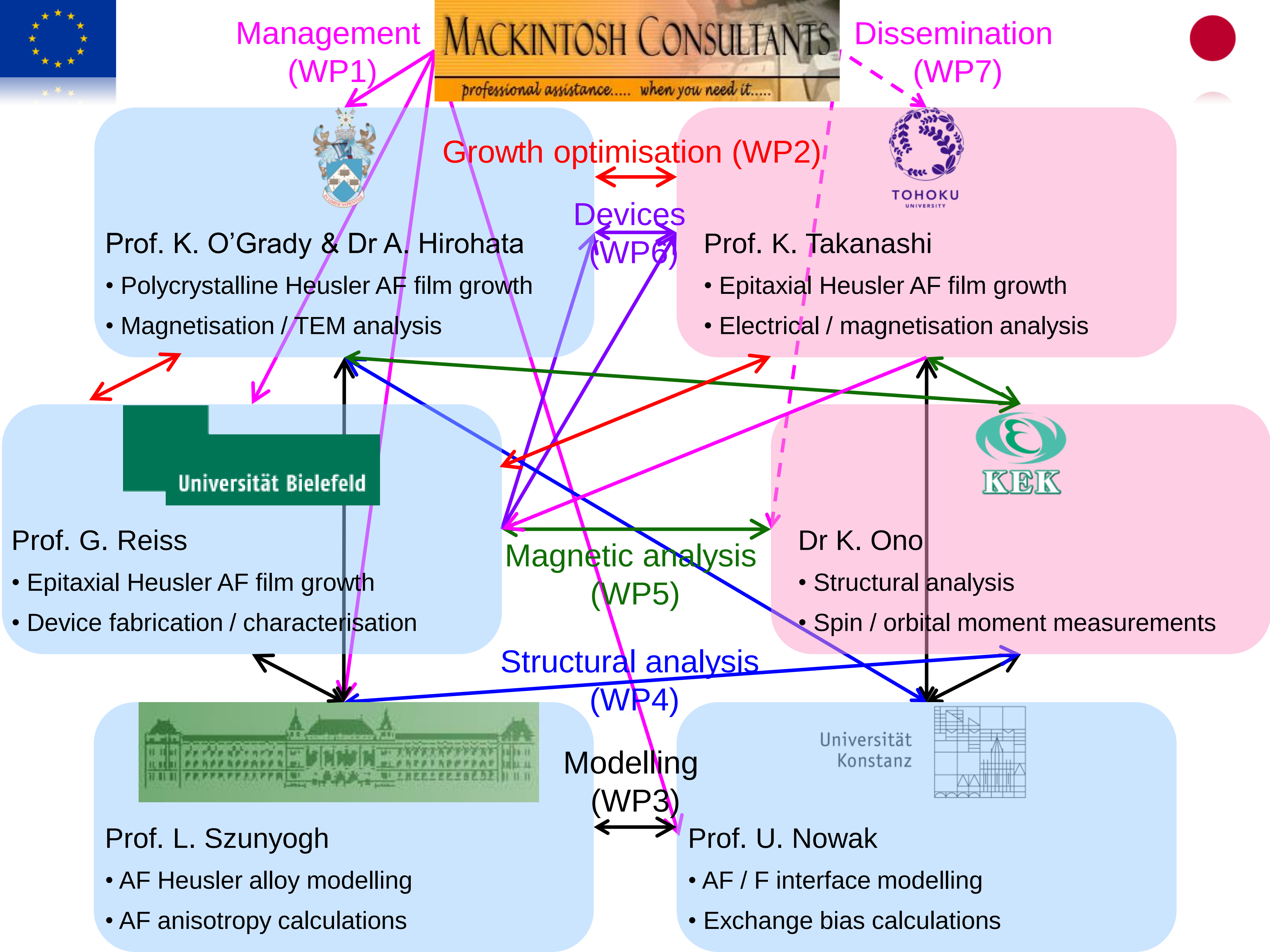
Heusler Alloy Replacement for Iridium

Introductions and Project Overview

HARFIR

Atsufumi Hirohata

THE UNIVERSITY *of York*



Management (WP1)

MACKINTOSH CONSULTANTS

professional assistance….. when you need it…..

Dissemination (WP7)

TOHOKU UNIVERSITY

Prof. K. O'Grady & Dr A. Hirohata

- Polycrystalline Heusler AF film growth
- Magnetisation / TEM analysis

Growth optimisation (WP2)

Devices (WP6)

Prof. K. Takanashi

- Epitaxial Heusler AF film growth
- Electrical / magnetisation analysis

Universität Bielefeld

Prof. G. Reiss

- Epitaxial Heusler AF film growth
- Device fabrication / characterisation

Magnetic analysis (WP5)

KEK

Dr K. Ono

- Structural analysis
- Spin / orbital moment measurements

Structural analysis (WP4)

Modelling (WP3)

Universität Konstanz

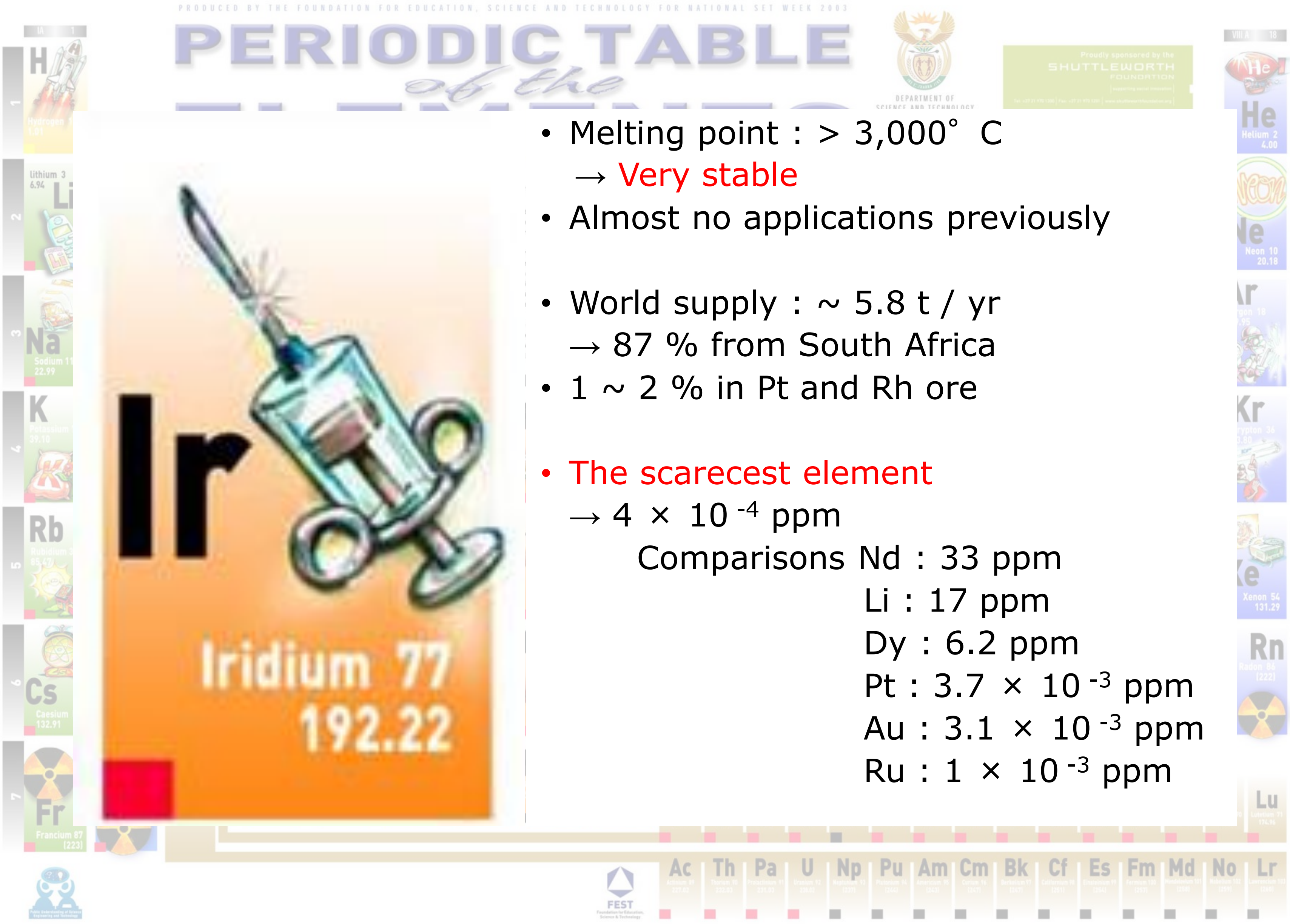
Prof. L. Szunyogh

- AF Heusler alloy modelling
- AF anisotropy calculations

Prof. U. Nowak

- AF / F interface modelling
- Exchange bias calculations

The Scarcest Material



- Melting point : > 3,000° C
  → Very stable
- Almost no applications previously

- World supply : ~ 5.8 t / yr
  → 87 % from South Africa
- 1 ~ 2 % in Pt and Rh ore

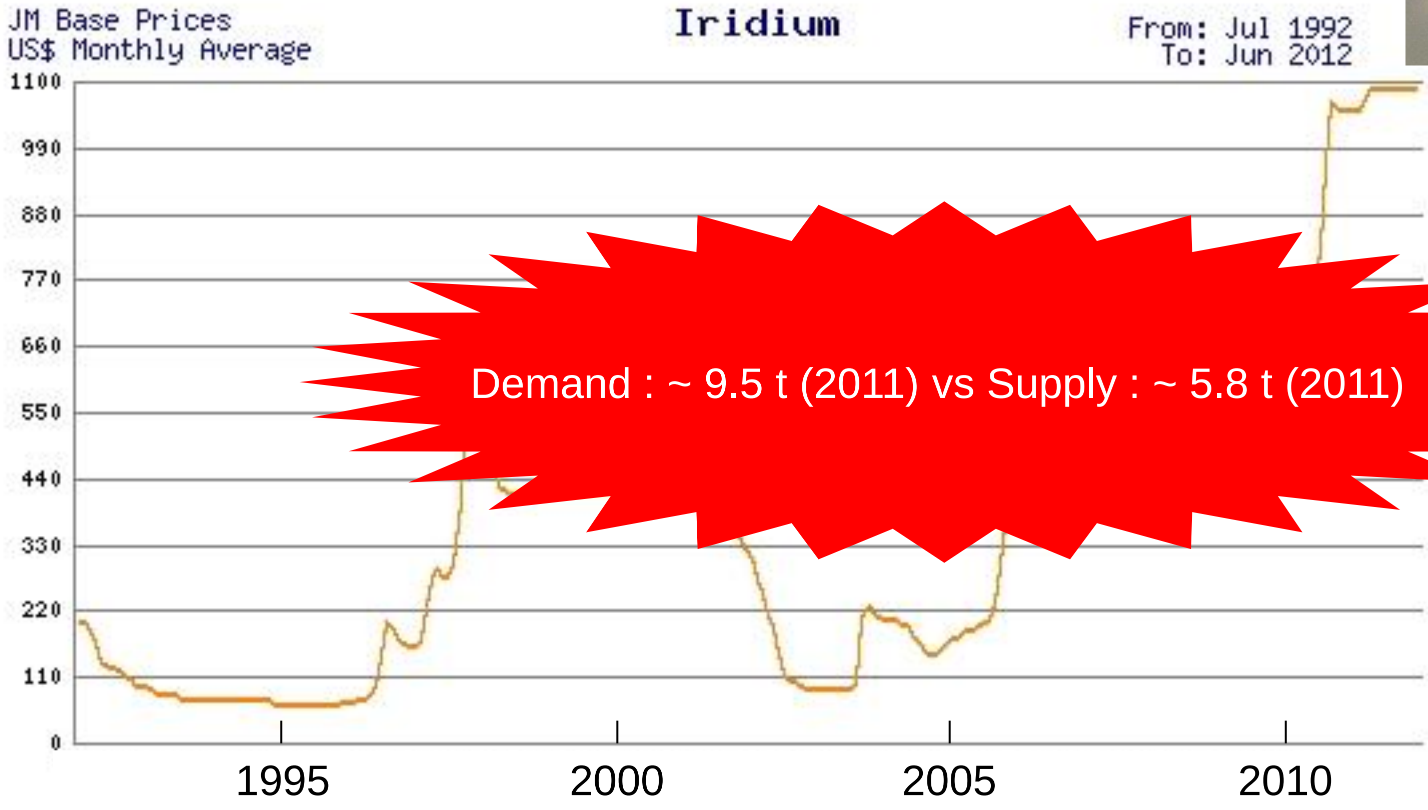
- The scarecest element
  → 4 × 10 $^{-4}$ ppm
  Comparisons Nd : 33 ppm
  Li : 17 ppm
  Dy : 6.2 ppm
  Pt : 3.7 × 10 $^{-3}$ ppm
  Au : 3.1 × 10 $^{-3}$ ppm
  Ru : 1 × 10 $^{-3}$ ppm

* http://www.atheistfrontier.com/people/dmitri-mendeleyev/periodic-table-of-the-elements-for-kids.jpg

Sudden Rise in Iridium Price

Ir price increased over 10 times in the last 8 years : *

~ USD 100 / oz (2003) ❼~ USD 1,100 / oz (2012)



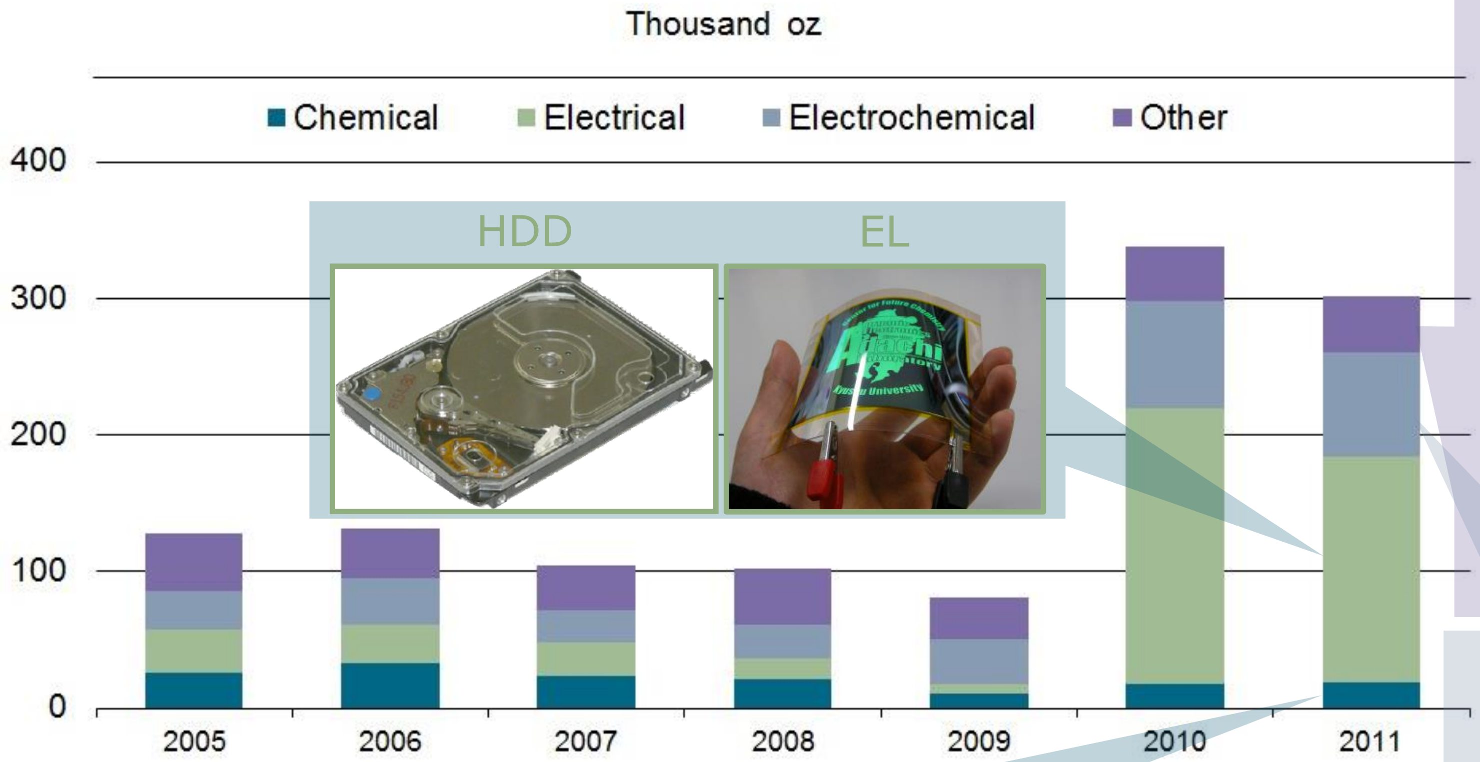
Demand : ~ 9.5 t (2011) vs Supply : ~ 5.8 t (2011)

---

* http://www.matthey.com

Usages of Iridium

Sudden increase in electrical applications : *



Rings

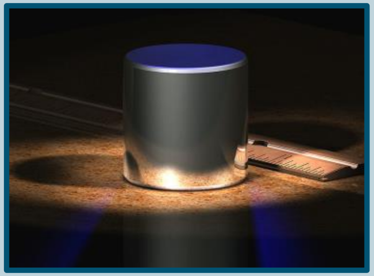
Dip pens

Crucibles

Spark plugs

Radiography

Prototype Kilogram

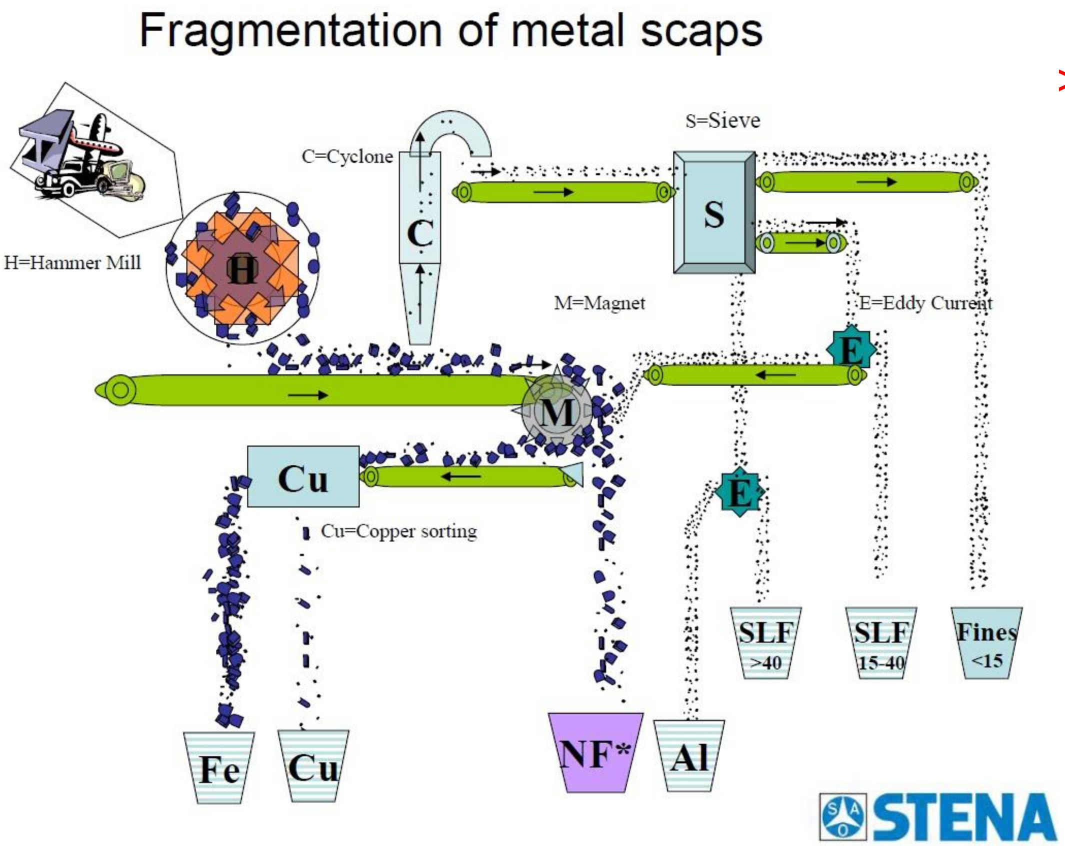


Prototype Metre

* http://www.matthey.com

Solution 1 : Electrochemical Field

Recovery from crucibles : *



> 90 % recovery rate

Aqua regia (HNO_3 + 3 HCl)

↓

PbO solvent + HNO_3

↓

$NaHSO_4$

↓

Na_2O_2

↓

Purification as $(NH_4)_3[IrCl_6]$

↓

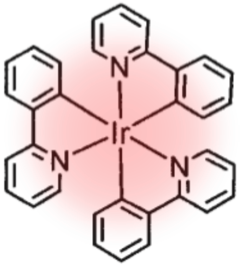
Reduction by H_2 gas

---

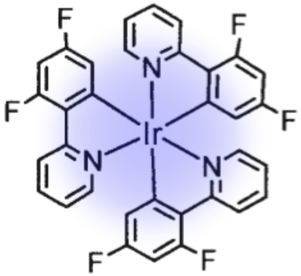
* Sumitomo Mining, *Japanese Patent* (2010-132144).

Electrical Field : Organic EL

Organic electroluminescence (EL) using Ir-complex : *

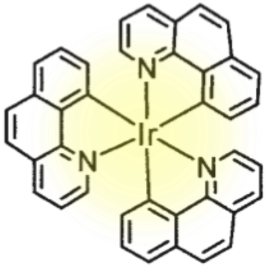


Ir(ppy)$_3$



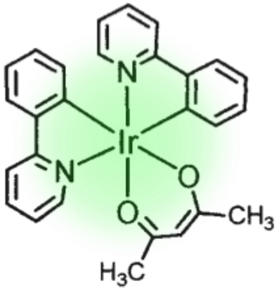
Ir(Fppy)$_3$

Ir(piq)$_3$

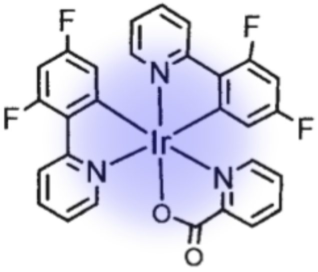


Ir(bzq)$_3$

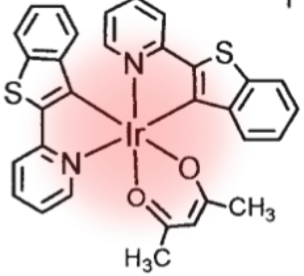
Tridentate Ir-complex *



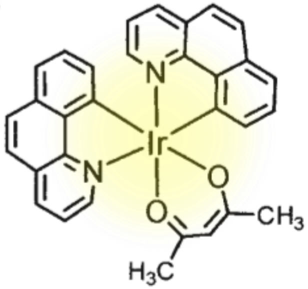
(ppy)$_2$Ir(acac)



FIrpic



(btp)$_2$Ir(acac)



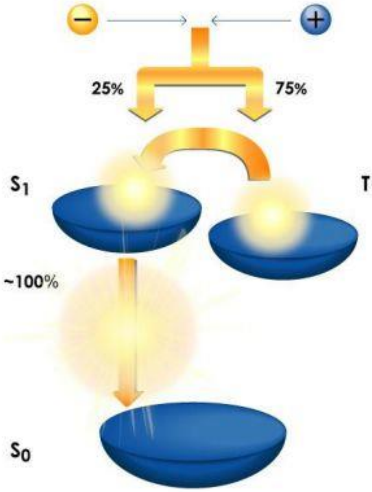
(bzq)$_2$Ir(acac)

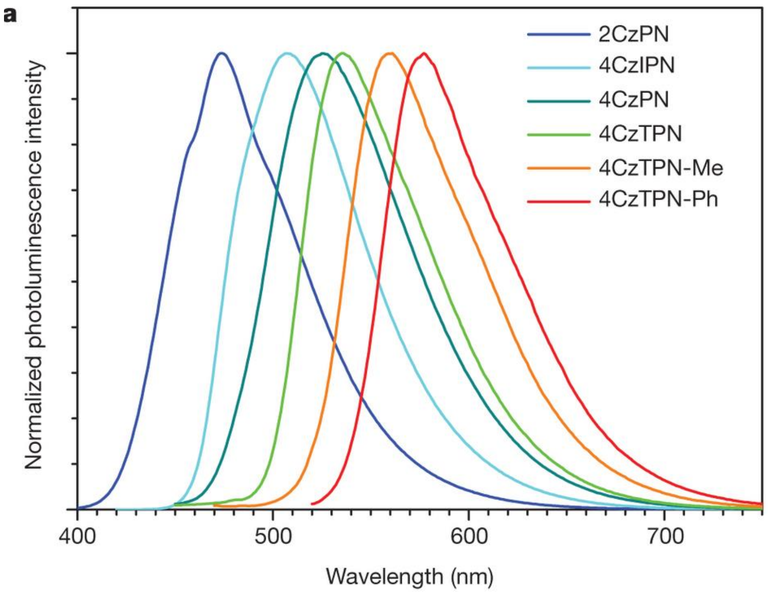
Bidentate Ir-complex **

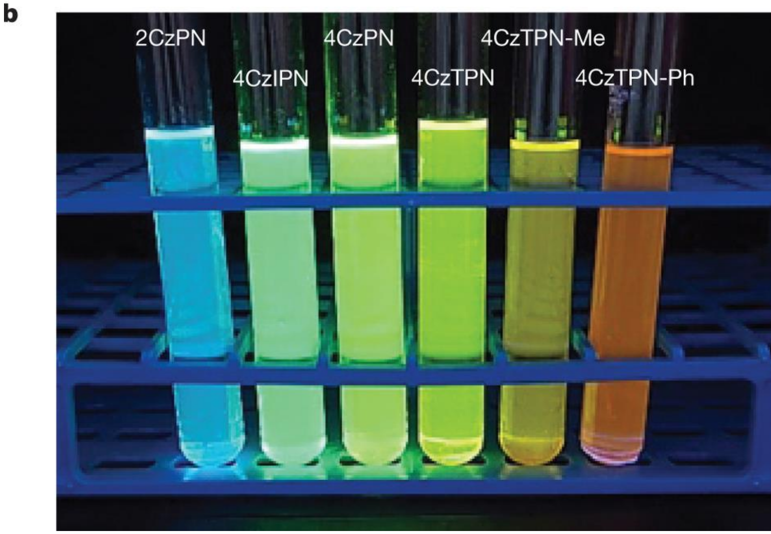
* M. A. Baldo *et* al., *Appl. Phys.* Lett. **75**, 4 (1999);
** H. Konno, *Tech. Chem. Times*, **199**, 13 (2006).

Solution 2 : Electrical Field

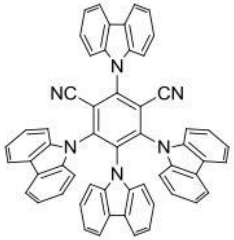
Carbazolyl dicyanobenzene (CDCB) : *



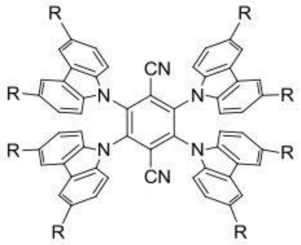




4CzPN: R = carbazolyl
2CzPN: R = H



4CzIPN



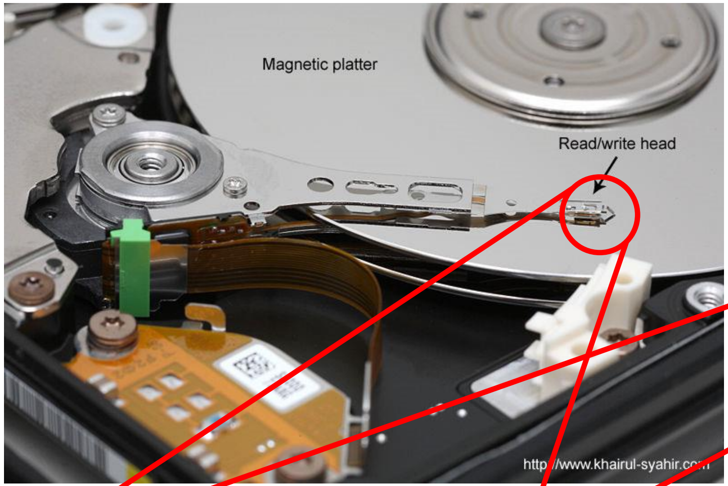
4CzTPN: R = H
4CzTPN-Me: R = Me
4CzTPN-Ph: R = Ph

→ 100 % EL efficiency

* H. Uoyama *et al.*, *Nature*, **492**, 234 (2012).

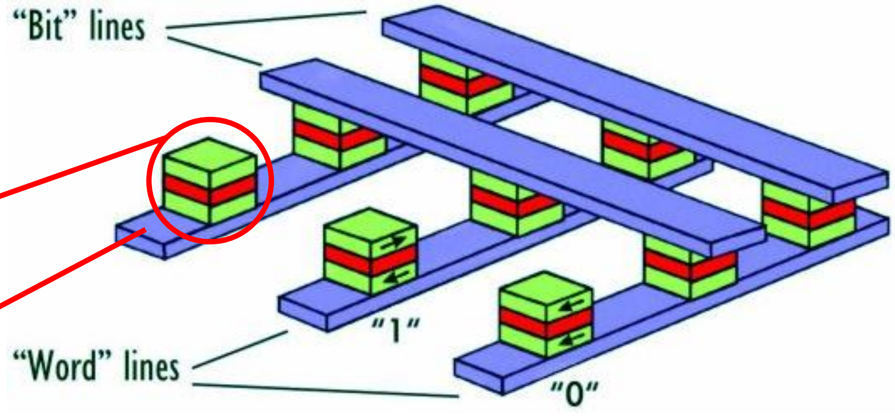
Spintronic Devices and Iridium Alloy

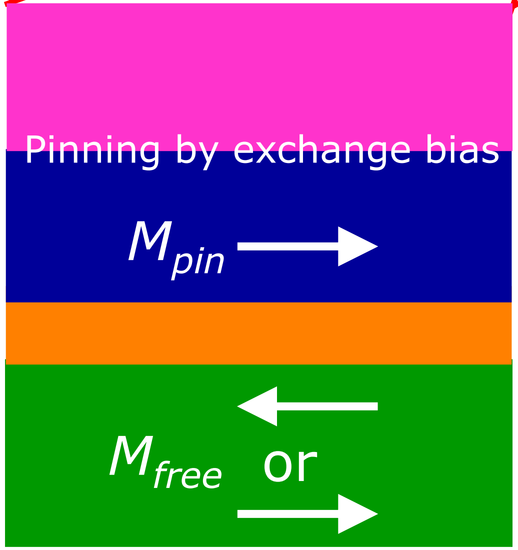
HDD read head :



http://www.khairul-syahir.com

Magnetic random access memory (MRAM) :





Spin-valve structure

Antiferromagnet → IrMn

Pinned ferromagnet

Non-magnet

Free ferromagnet

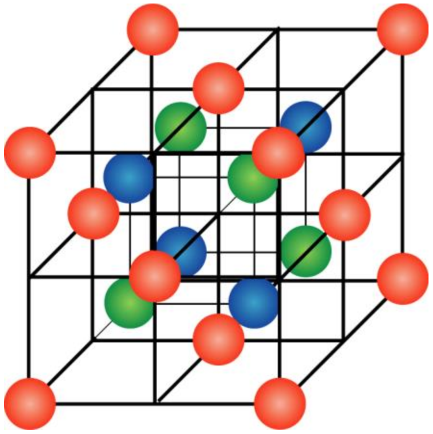
Current

IrMn

- Large exchange bias (> 3.5 kOe)
- Low set temperature (~ 250° C)
- Thin-film form (~ 6 nm)

Replacement with a Heusler alloy

Heusler Alloys

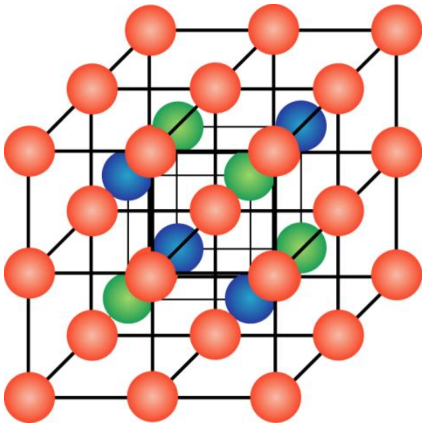


half-Heusler

XYZ

(NiMnSb etc.)

$C1_b$ structure



full-Heusler

X_2YZ

(Co_2MnSi, Co_2FeSi, etc.)

$L2_1$ structure

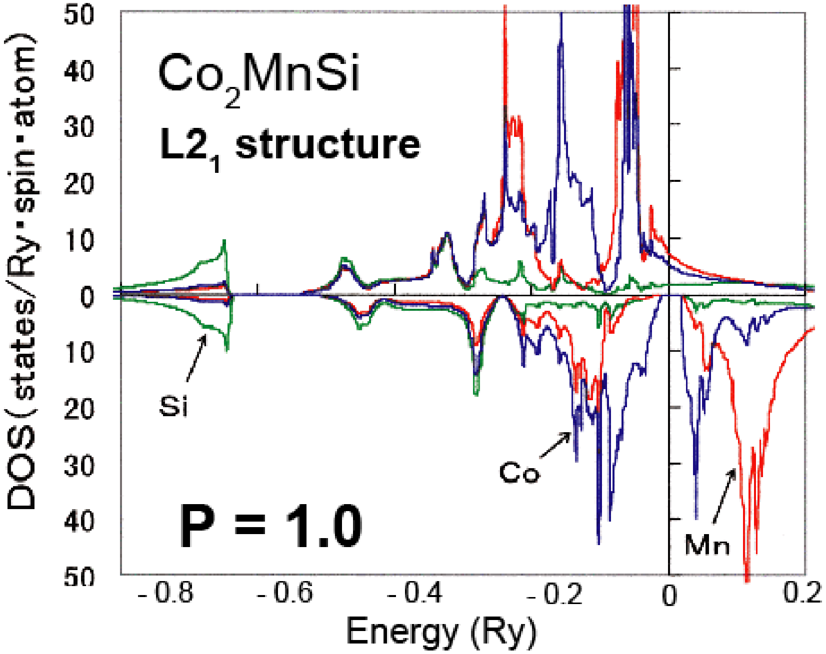
Important spintronic materials

Half-metallic ferromagnet

Spin polarisation = 100 %

→ Large GMR / TMR

Consist of common elements.



Antiferromagnetic Heusler Alloys

Antiferromagnetic Heusler alloys	Lattice constants *a* [nm]	Néel temperatures T_N [K]	References
$Fe_{2.5}V_{0.5}Al$	0.576		[1] (calc.)
Ni_2MnAl	0.5812	353 (*B2*)	[2] (calc.)
Ni_2MnAl		313 (*B2*)	[3] (bulk)
Cr_2MnSb	0.62	342	[4] (calc.)

Ferromagnetic Hesuler alloys	Lattice constants *a* [nm]	Curie temperature T_C [K]	References
Co_2MnSi	0.565	985	[5] (bulk)
Co_2FeSi	0.564	1100	[5] (bulk)
Co_2MnGe	0.574	905	[5] (bulk)

Antiferromagnetic Heusler alloys : almost perfect lattice matching with ferromagnetic Heusler alloys.

[1] D. J. Singh and I. Mazin, *Phys. Rev. B* **57**, 14352 (1998);
[2] I. Galanakis and E. Şaşıoğlu, *Appl. Phys. Lett.* **98**, 102514 (2011);
[3] M. Acet *et al.*, *J. Appl. Phys.* **92**, 3867 (2002);
[4] I. Galanakis *et al.*, *Phys. Rev. B* **75**, 172404 (2007);
[5] P. J. Webster *et al.*, Landort-Bornstein, New Series, Group III 75-185 (1988);

Project Objectives

Aim

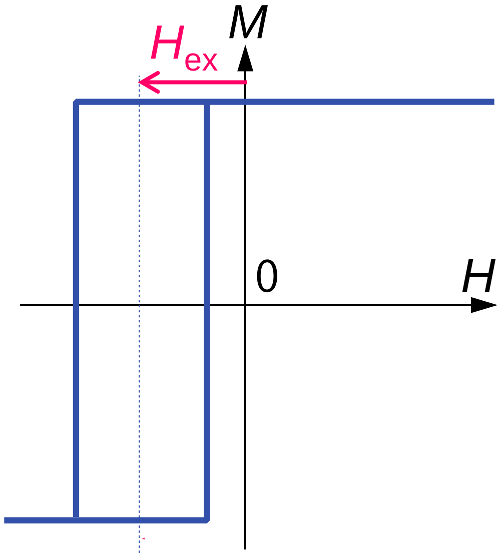
IrMn alloy used in GMR / TMR junctions
→ Antiferromagnetic Heusler alloys with common elements

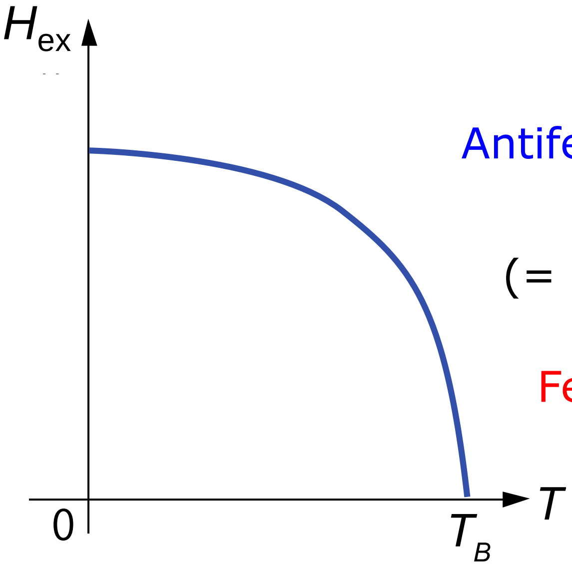
Objectives

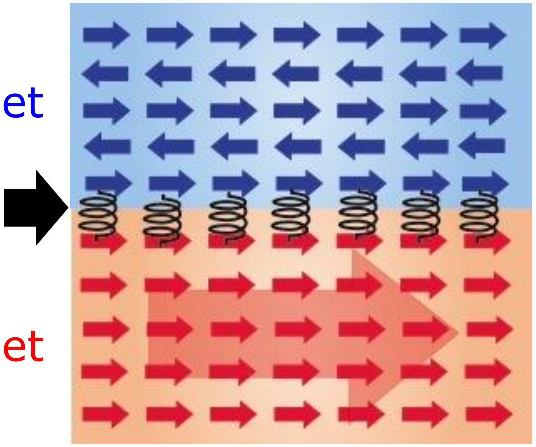
Exchange bias : $H_{ex} > 1$ kOe ($J_K > 1$ erg/cm^2)

Blocking temperature : $T_B > 300$ K

Distribution of the blocking temperature : $\sigma_{TB} < 0.3$







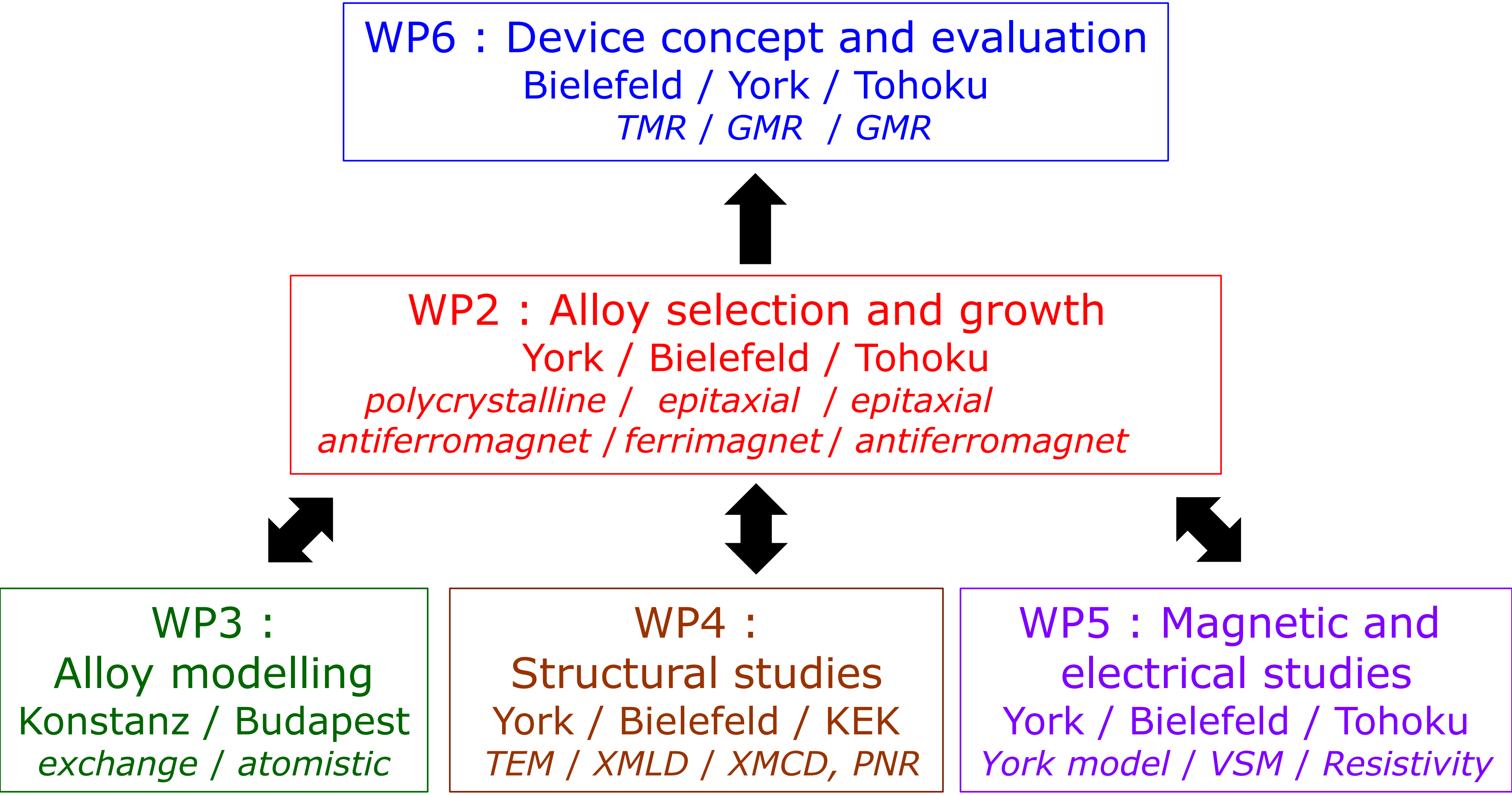
Antiferromagnet

J_K
$(= M_S d_F H_{ex})$

Ferromagnet

Magnetisation M

Work Packages and Partners



WP6 : Device concept and evaluation
Bielefeld / York / Tohoku
TMR / GMR / GMR

WP2 : Alloy selection and growth
York / Bielefeld / Tohoku
polycrystalline / epitaxial / epitaxial
antiferromagnet / ferrimagnet / antiferromagnet

WP3 :
Alloy modelling
Konstanz / Budapest
exchange / atomistic

WP4 :
Structural studies
York / Bielefeld / KEK
TEM / XMLD / XMCD, PNR

WP5 : Magnetic and electrical studies
York / Bielefeld / Tohoku
York model / VSM / Resistivity

WP1 : Financial and administrative management
WP7 : Dissemination and exploitation

Foreground

Applications

By replacing IrMn with antiferromagnetic Heusler alloys,

→ Price decreases by 1/1,000

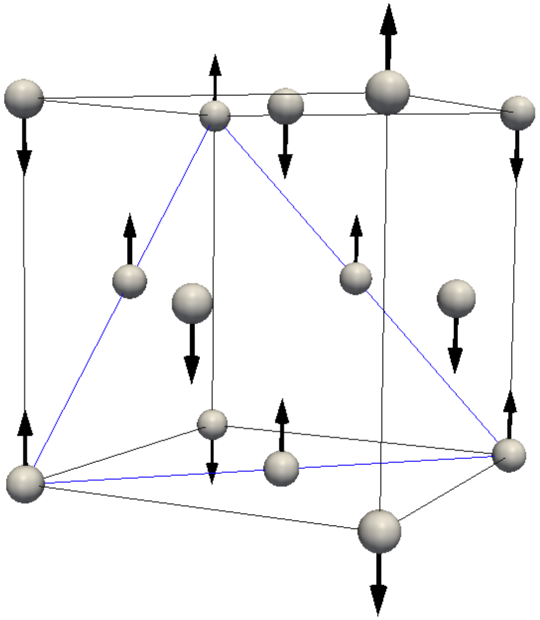
- Implementation into the existing technology

HDD read heads:	> 600M units
MRAM cells:	> 3.5M units

Basic science

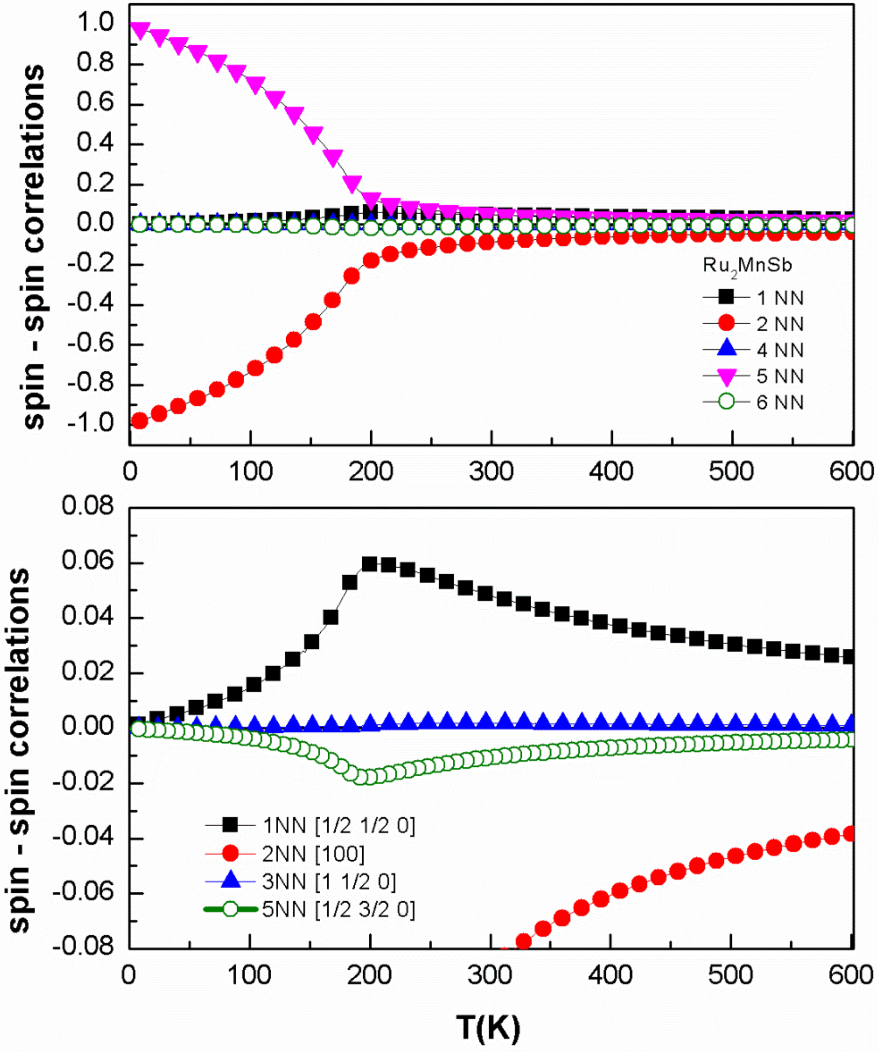
- Evaluation of interfacial exchange coupling mechanism
- Estimation of antiferromagnetic domain size

Modelling Example – Ru_2MnSb



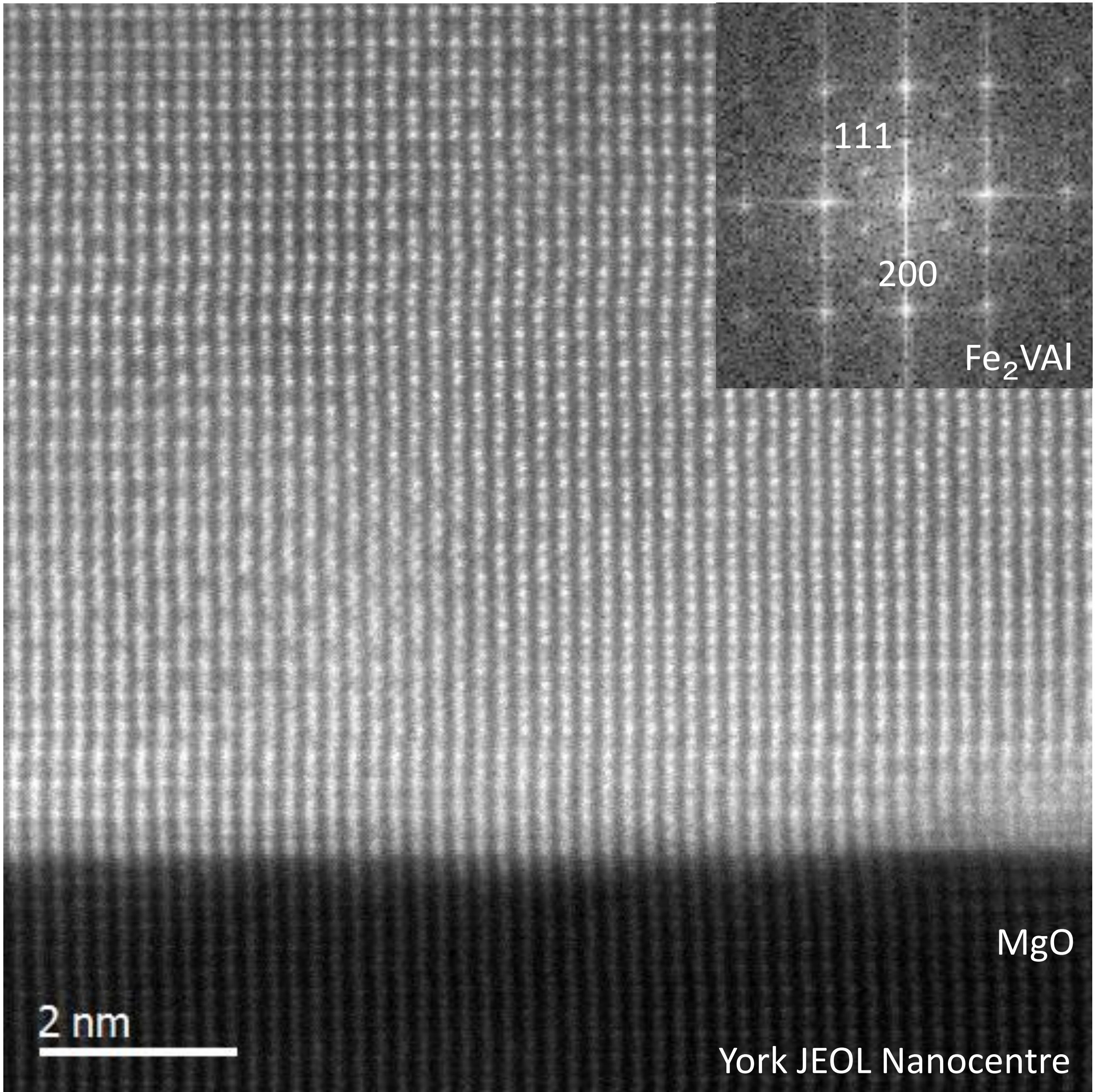
Four interpenetrating cubic AFM lattices (checkboard order) –

The inter-lattices orientations are completely frustrated



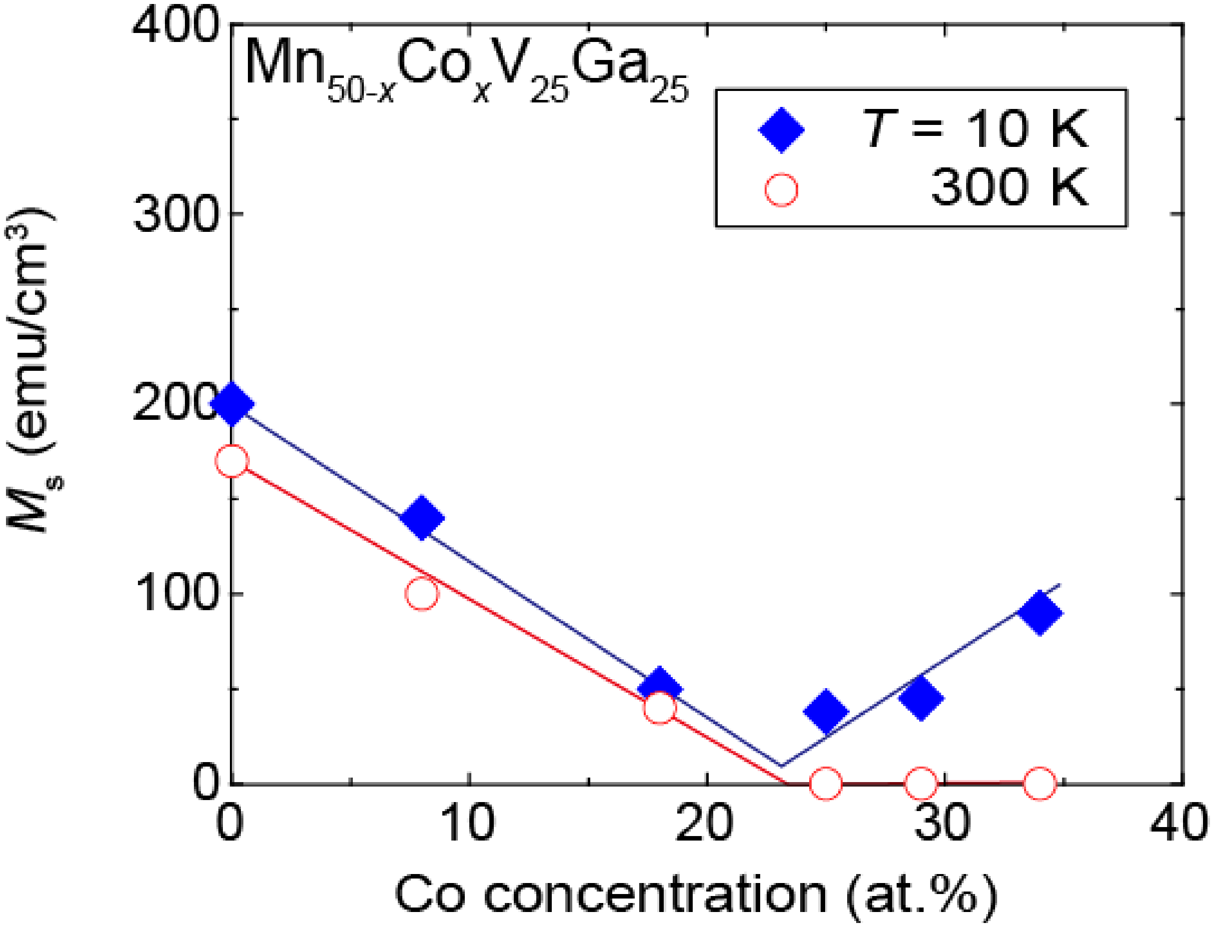
Ru_2MnSb – spin-spin correlation functions

Atomic Structure of Fe_2VAl



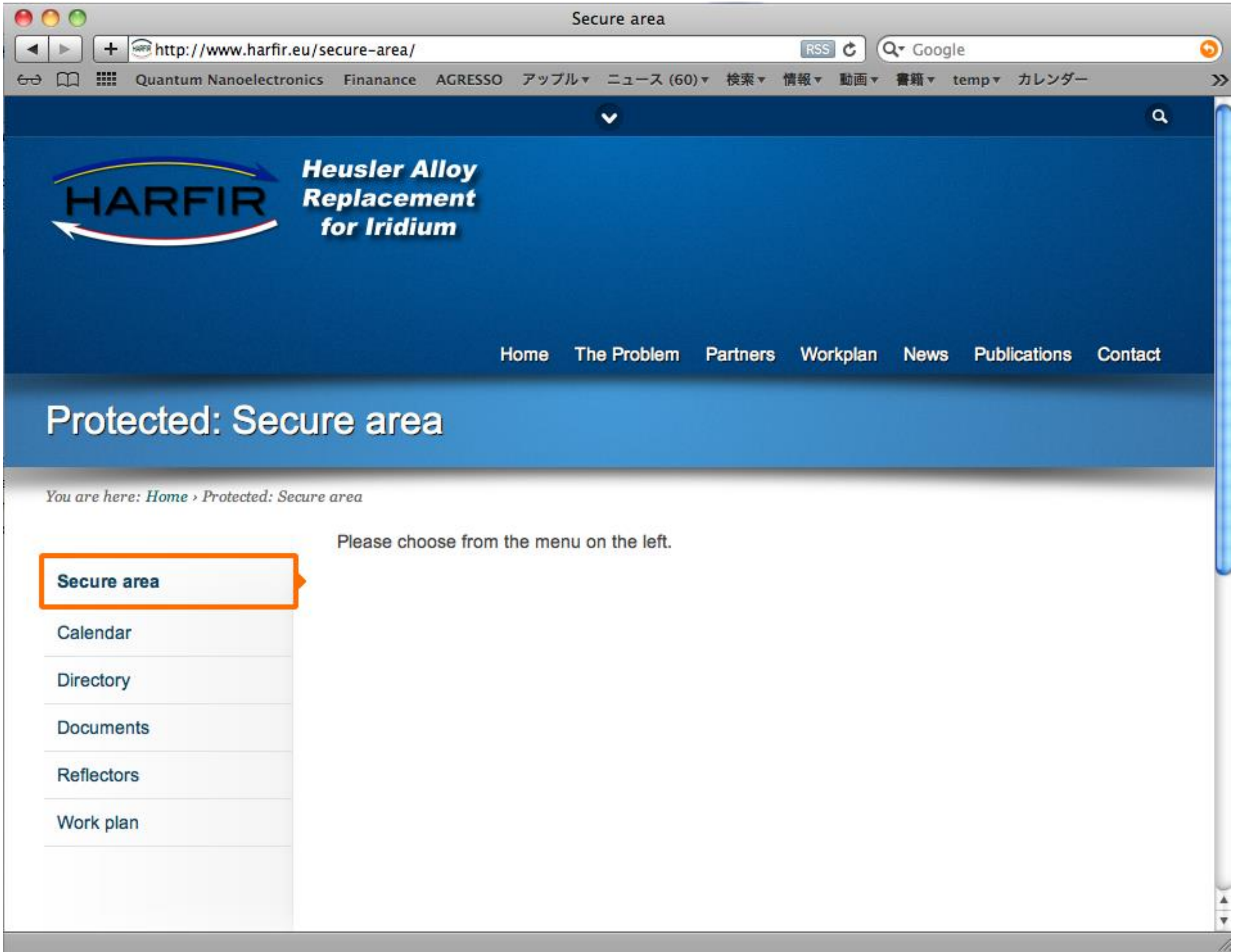
York JEOL Nanocentre

Atomic Substitution



Common Webpages

Both the EU and Japanese teams will upload their progress reports etc. :

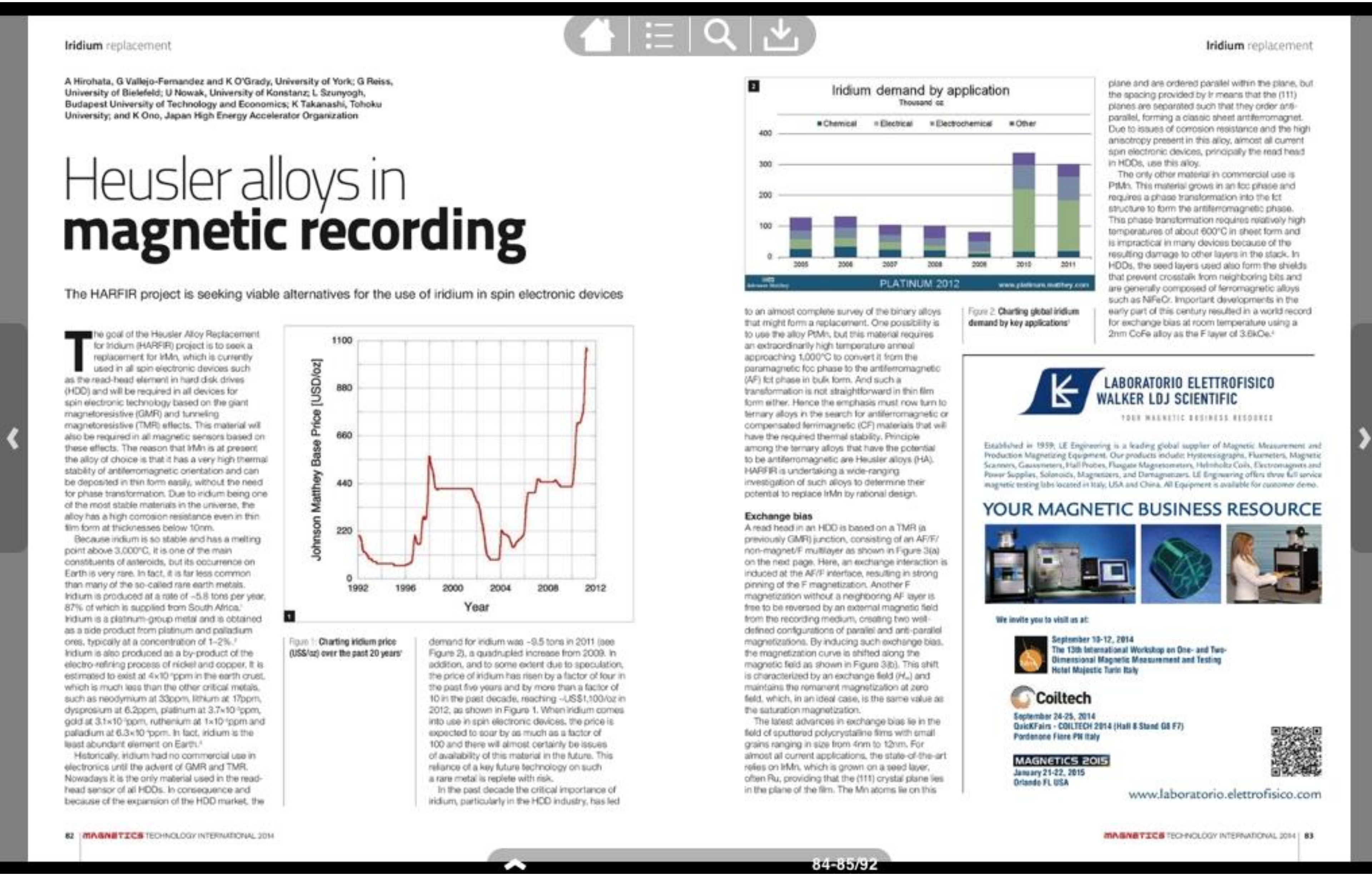


Protected: Secure area

You are here: Home › Protected: Secure area

Please choose from the menu on the left.

Article on HARFIR



A Hirohata, G Vallejo-Fernandez and K O'Grady, University of York; G Reiss, University of Bielefeld; U Nowak, University of Konstanz; L Szunyogh, Budapest University of Technology and Economics; K Takanashi, Tohoku University; and K Ono, Japan High Energy Accelerator Organization

Heusler alloys in magnetic recording

The HARFIR project is seeking viable alternatives for the use of iridium in spin electronic devices

The goal of the Heusler Alloy Replacement for Iridium (HARFIR) project is to seek a replacement for IrMn, which is currently used in all spin electronic devices such as the read-head element in hard disk drives (HDD) and will be required in all devices for spin electronic technology based on the giant magnetoresistive (GMR) and tunneling magnetoresistive (TMR) effects. This material will also be required in all magnetic sensors based on these effects. The reason that IrMn is at present the alloy of choice is that it has a very high thermal stability of antiferromagnetic orientation and can be deposited in thin form easily, without the need for phase transformation. Due to iridium being one of the most stable materials in the universe, the alloy has a high corrosion resistance even in thin film form at thicknesses below 10nm.

Because iridium is so stable and has a melting point above 3,000°C, it is one of the main constituents of asteroids, but its occurrence on Earth is very rare. In fact, it is far less common than many of the so-called rare earth metals. Iridium is produced at a rate of ~5.8 tons per year, 87% of which is supplied from South Africa.[1] Iridium is a platinum-group metal and is obtained as a side product from platinum and palladium ores, typically at a concentration of 1-2%.[1] Iridium is also produced as a by-product of the electro-refining process of nickel and copper. It is estimated to exist at 4×10^{-4}ppm in the earth crust, which is much less than the other critical metals, such as neodymium at 33ppm, lithium at 17ppm, dysprosium at 6.2ppm, platinum at 3.7×10^{-3}ppm, gold at 3.1×10^{-3}ppm, ruthenium at 1×10^{-3}ppm and palladium at 6.3×10^{-3}ppm. In fact, iridium is the least abundant element on Earth.[1]

Historically, iridium had no commercial use in electronics until the advent of GMR and TMR. Nowadays it is the only material used in the read-head sensor of all HDDs. In consequence and because of the expansion of the HDD market, the demand for iridium was ~9.5 tons in 2011 (see Figure 2), a quadrupled increase from 2009. In addition, and to some extent due to speculation, the price of iridium has risen by a factor of four in the past five years and by more than a factor of 10 in the past decade, reaching ~US$1,100/oz in 2012, as shown in Figure 1. When iridium comes into use in spin electronic devices, the price is expected to soar by as much as a factor of 100 and there will almost certainly be issues of availability of this material in the future. This reliance of a key future technology on such a rare metal is replete with risk.

Figure 1: **Charting iridium price (US$/oz) over the past 20 years**[1]

In the past decade the critical importance of iridium, particularly in the HDD industry, has led to an almost complete survey of the binary alloys that might form a replacement. One possibility is to use the alloy PtMn, but this material requires an extraordinarily high temperature anneal approaching 1,000°C to convert it from the paramagnetic fcc phase to the antiferromagnetic (AF) fct phase in bulk form. And such a transformation is not straightforward in thin film form either. Hence the emphasis must now turn to ternary alloys in the search for antiferromagnetic or compensated ferrimagnetic (CF) materials that will have the required thermal stability. Principle among the ternary alloys that have the potential to be antiferromagnetic are Heusler alloys (HA). HARFIR is undertaking a wide-ranging investigation of such alloys to determine their potential to replace IrMn by rational design.

Figure 2: **Charting global iridium demand by key applications**[1]

Exchange bias

A read head in an HDD is based on a TMR (a previously GMR) junction, consisting of an AF/F/non-magnet/F multilayer as shown in Figure 3(a) on the next page. Here, an exchange interaction is induced at the AF/F interface, resulting in strong pinning of the F magnetization. Another F magnetization without a neighboring AF layer is free to be reversed by an external magnetic field from the recording medium, creating two well-defined configurations of parallel and anti-parallel magnetizations. By inducing such exchange bias, the magnetization curve is shifted along the magnetic field as shown in Figure 3(b). This shift is characterized by an exchange field (H_{ex}) and maintains the remanent magnetization at zero field, which, in an ideal case, is the same value as the saturation magnetization.

The latest advances in exchange bias lie in the field of sputtered polycrystalline films with small grains ranging in size from 4nm to 12nm. For almost all current applications, the state-of-the-art relies on IrMn, which is grown on a seed layer, often Ru, providing that the (111) crystal plane lies in the plane of the film. The Mn atoms lie on this plane and are ordered parallel within the plane, but the spacing provided by Ir means that the (111) planes are separated such that they order anti-parallel, forming a classic sheet antiferromagnet. Due to issues of corrosion resistance and the high anisotropy present in this alloy, almost all current spin electronic devices, principally the read head in HDDs, use this alloy.

The only other material in commercial use is PtMn. This material grows in an fcc phase and requires a phase transformation into the fct structure to form the antiferromagnetic phase. This phase transformation requires relatively high temperatures of about 600°C in sheet form and is impractical in many devices because of the resulting damage to other layers in the stack. In HDDs, the seed layers used also form the shields that prevent crosstalk from neighboring bits and are generally composed of ferromagnetic alloys such as NiFeCr. Important developments in the early part of this century resulted in a world record for exchange bias at room temperature using a 2nm CoFe alloy as the F layer of 3.6kOe.[4]

HARFIR and CRM_InnoNet

- Emphasis on the scarcity of Ir as an Pt-family element
- Provision of a new opportunity for electrical applications
- Creation of a new community
- Involvement and dissemination beyond the EU

Thank you !