Growth of CuMnAs by MBE

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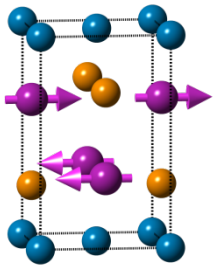

Colleagues

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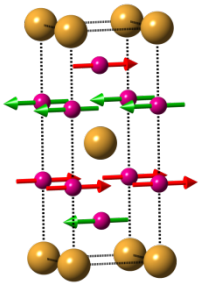
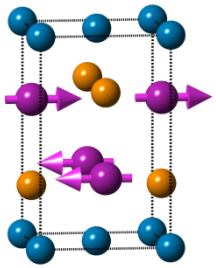
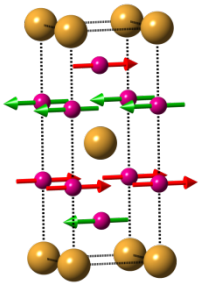




Outline

- Early ideas
- Bulk CuMnAs
- CuMnAs thin films
- Conclusions



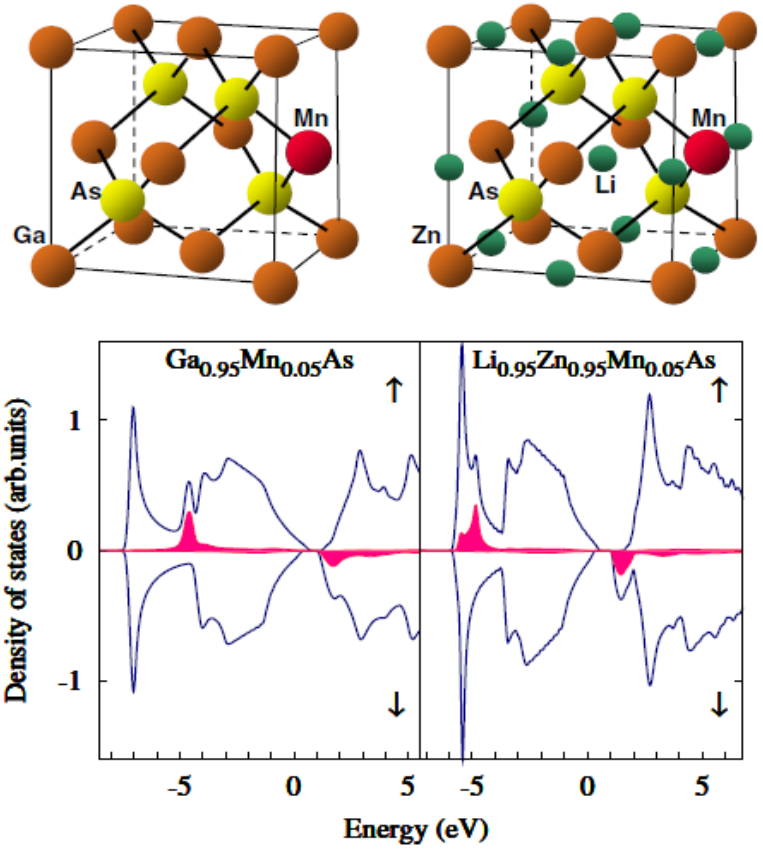
A bit of history

A few years ago we proposed a new ferromagnetic semiconductor Li(Zn,Mn)As. In this case the Mn is not a dopant. In GaMnAs you cannot increase the Mn concentration without increasing the p-doping – ultimately leads to compensating defects

We (Nottingham) were not keen on putting Li in our MBE, but Prague had an old machine. Nottingham provided some components and work started. It became clear that LiMnAs was interesting, an anti-ferromagnet and unstable

We started looking at other possible variants, specifically the group IB elements of which the first and cheapest is Cu

We (Nottingham) were happy with Cu so growth work commenced after some preliminary bulk synthesis



Dilute Moment *n*-Type Ferromagnetic Semiconductor Li(Zn,Mn)As
J. Masek, J. Kudrnovsky, F. Maca, B. L. Gallagher, R. P. Campion, D. H. Gregory, and T. Jungwirth. PRL **98,** 067202 (2007)

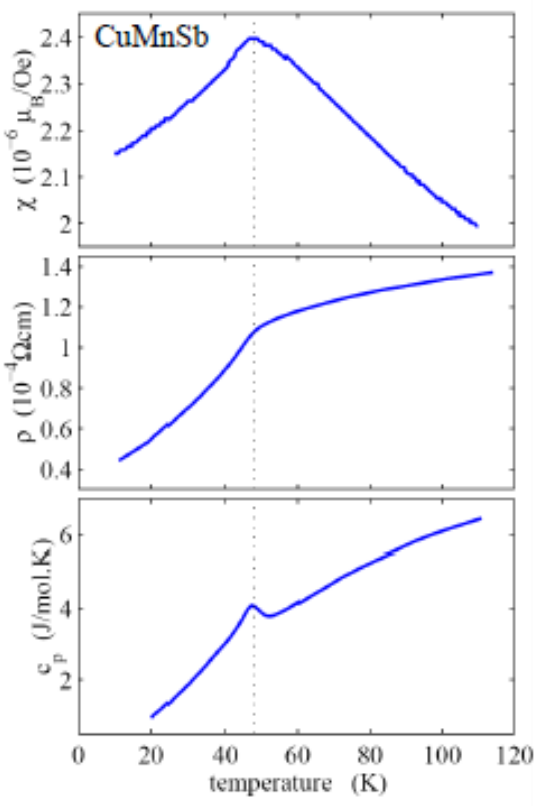
HT synthesized bulk CuMn-V's

The antimonide, arsenide and phosphide were all synthesized in bulk form

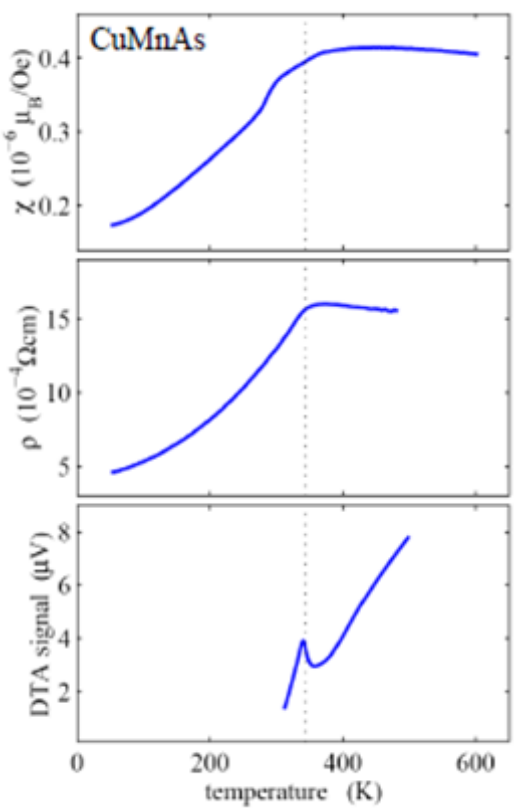
Magnetic data were promising

Band structure modelling suggests that the antimonide is a semi-metal, the arsenide may have a small gap (or not) and the phosphide a true gap

The phosphide was probably the most promising, but we felt this might be harder to start with due the reactivity of phosphorus and the occurrence of competing phases in the bulk



T_N~ 50 K



T_N~ 370 K !

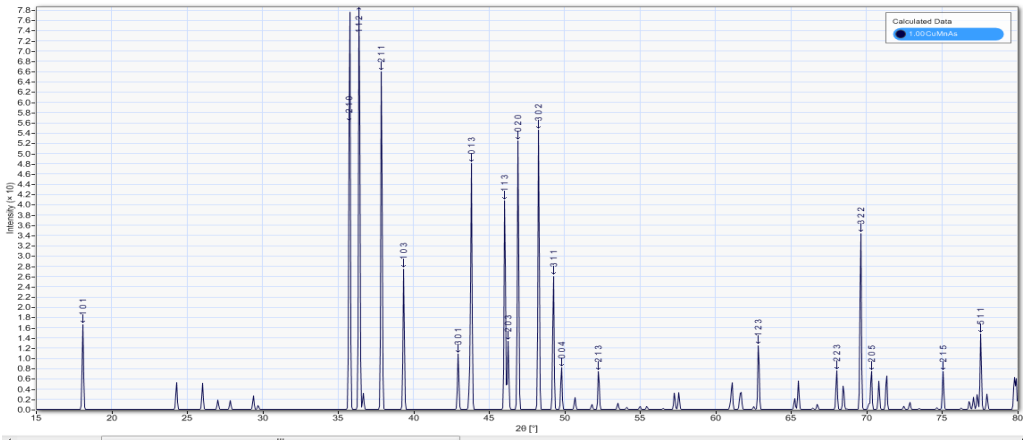
F Maca, X. Marti, T. Jungwirth, et al JMMM 2012

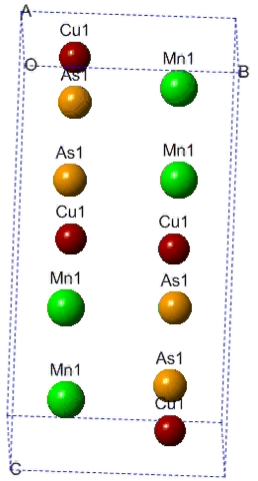
Antiferromagnets didn't sound very interesting in the past, but there is now a wealth of evidence that suggests they may be very useful in spintronic devices

Bulk structure determination

- This is relatively easy in bulk single crystals and powders.
- X-ray powder diffraction provides ‘finger print’ of structure
- Positions of peaks ⟶ lattice parameters and space group
- Intensities ⟶ atomic positions

For bulk CuMnAs:





Yields an orthorhombic structure ($a \neq b \neq c$) – not very promising from the point of view of substrate selection!

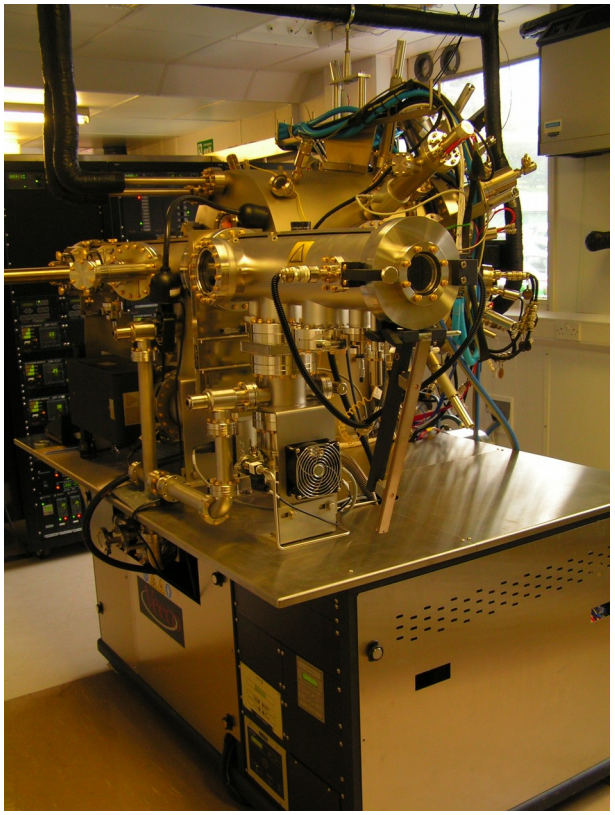
Time to have a go at MBE

Clearly the choice of substrate is challenging, given the orthorhombic structure

We would like a semiconductor with matching lattice dimensions in the plane, but there are no easy candidates.

After quite some time playing with crystal model software and tables of structures we realised it was time to wheel out the **universal substrate**.

What universal substrate you ask?



The one you have most of in the cupboard

In our case this was GaAs so that is what we used
Also allows us to use our Bandit (band edge thermometry)

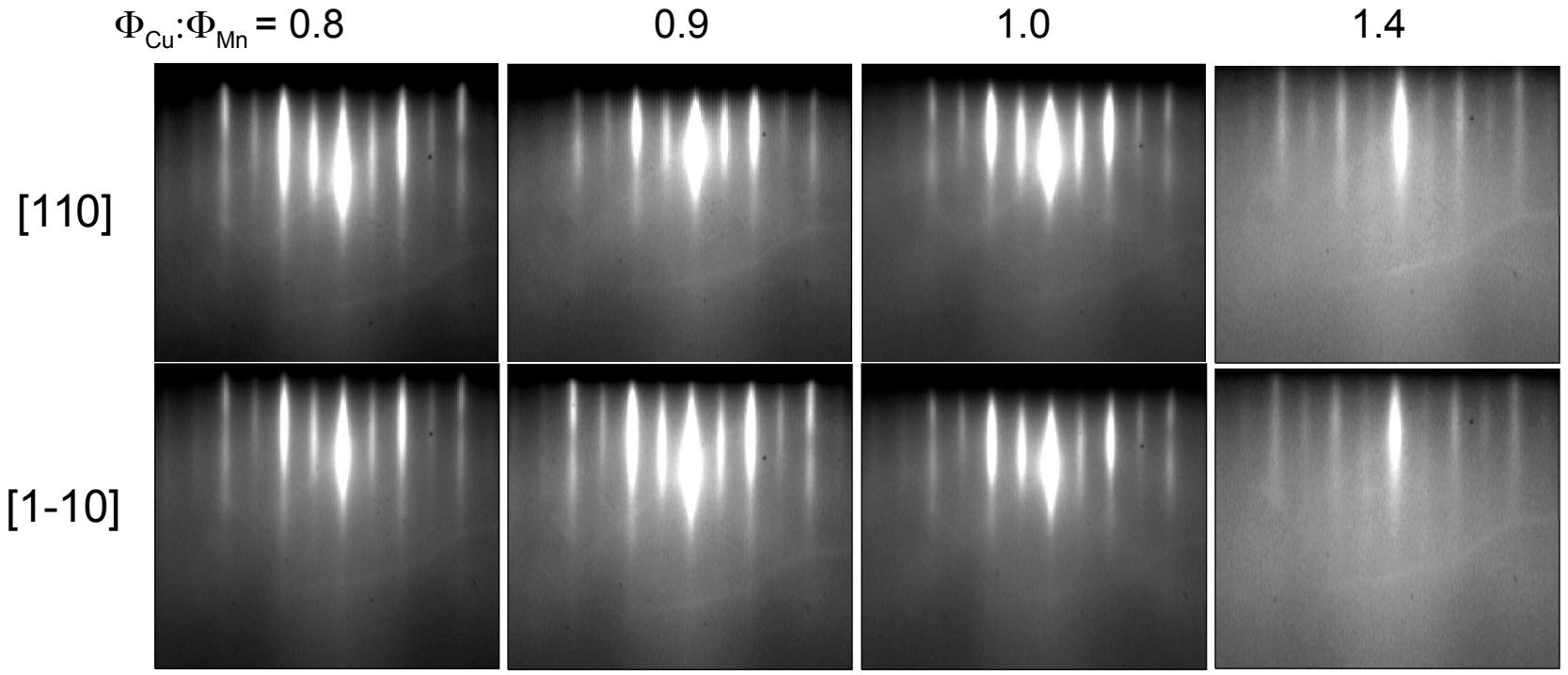
Time to have a go at MBE

So we have:

- Orthorhombic structure
- No suitable substrate
- Substrate temperature – a total guess
- Uncertainty about stoichiometry

Hands up who thinks this will be a complete mess!

Wow! Rheed – Growth at 300°C

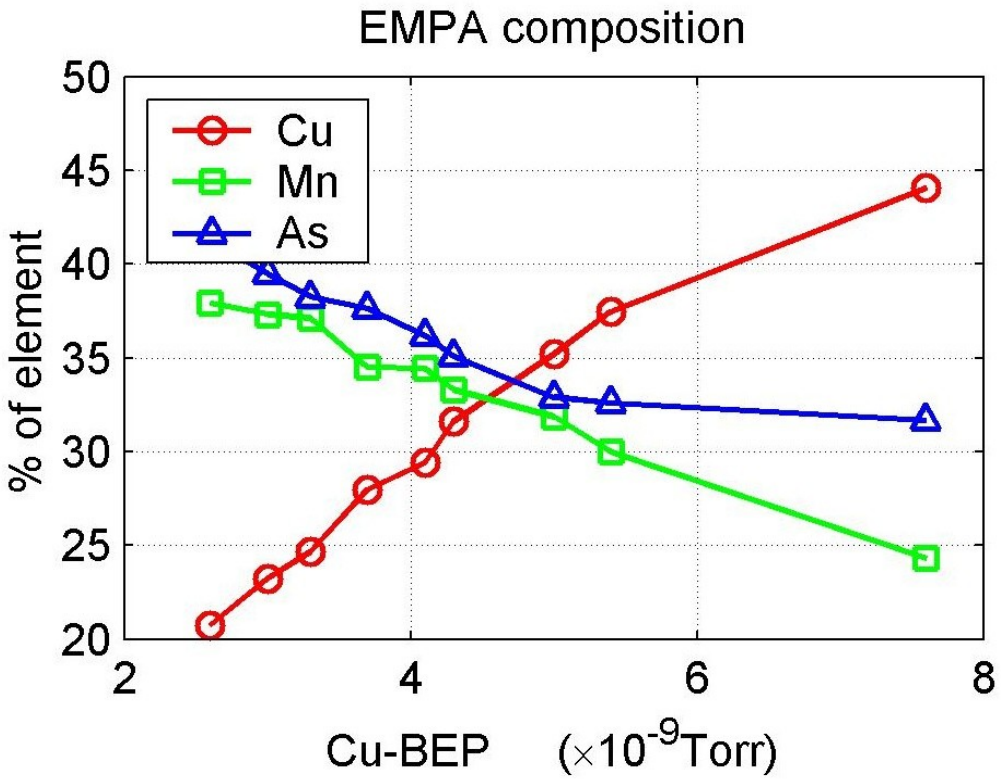


GaAs (100) : 4-fold symmetry – very robust and quite unexpected
GaAs (110) : 2-fold symmetry
MnAs pseudo substrate on GaAs: 2-fold symmetry
Sapphire: 6-fold symmetry

- CuMn : very different surface reconstruction

EPMA analysis

CuMnAs on GaAs(100), varying the Cu flux :



Interestingly the Cu BEP at stoichiometry is considerably lower than the traditional calculation would predict.

Evidence of precipitates (Cu-rich and MnAs) far from stoichiometry

Clearly not orthorhombic – what is it?

- Standard procedure relies on the thin film being a distorted version of the bulk
- Find a few peaks and work out the nature of the distortion, and the rest are easy to find.
- In our case it became increasingly difficult to reconcile the data with a distorted version of the orthorhombic structure of the bulk
- XRD, XAS and RHEED suggest that the structure is cubic in-plane

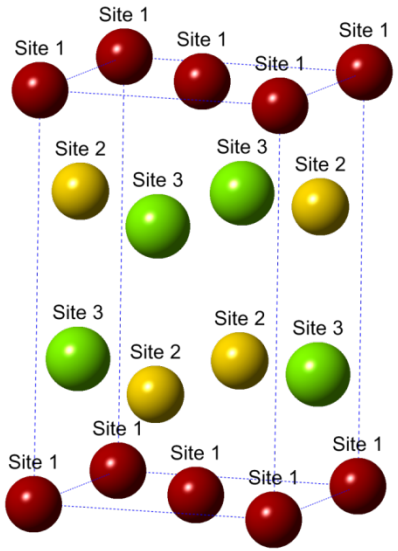
- After searching databases, we found an obscure paper on Mn_2As doped with Cu, Zn and Ni (Ryzhkovskii et al *Известия Академии наук С.С.С.Р. Неорганические материалы* ; v.27,no.12(1991).)
- Whole family of Cu_2Sb structure compounds (Pearson *Zeitschrift für Kristallographie,* 171, 23 - 39 (1985))
- Possible to guess a model based on Cu_2Sb and Mn_2As

Clearly not orthorhombic – what is it?

- Proposed structure is tetragonal p4/nmm (129)
- 3 unique sites (Pearson paper provides good rules for elemental occupation but Mn_2As is an exception, Cu_2As not!)
- Distorted the unit cell to fit with already measured lattice parameters (XRD). a=b= 3.83 Å, c=6.30 Å, c/a=1.64

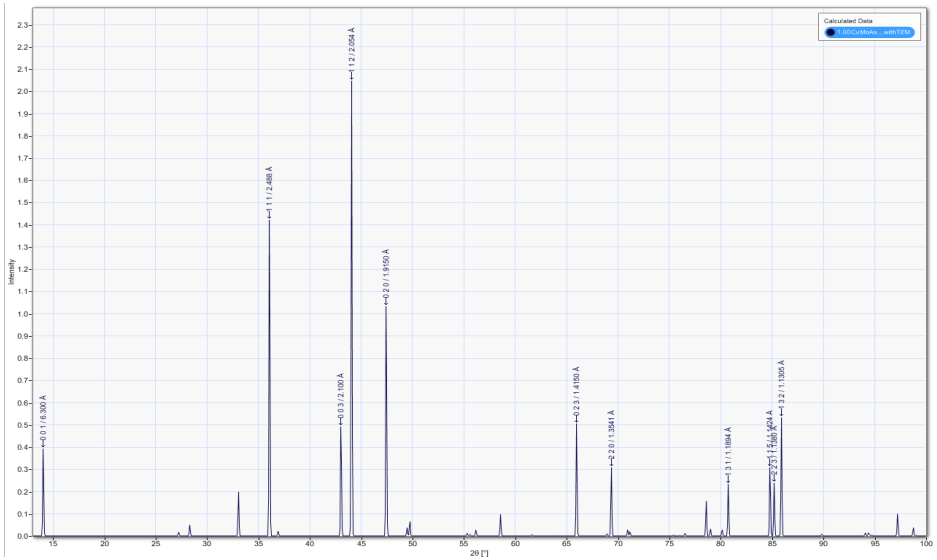
extract from Pearson paper

"In these phases it appears that the larger atom always occupies site 2, although CuMgAs, Fe_2As, Mn_2As and Cr_2As appear to be exceptions to this rule"

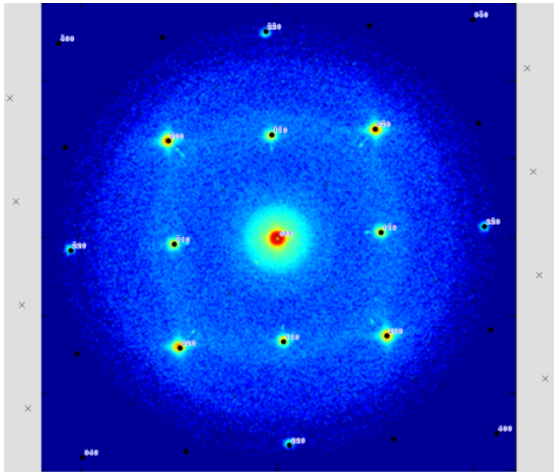


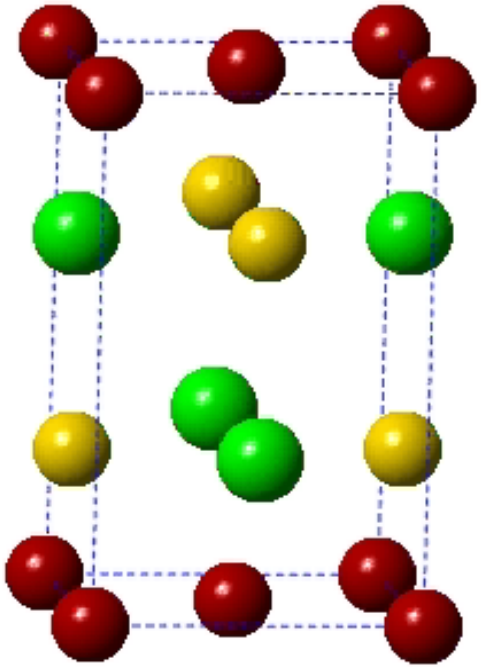
Simulated diffraction pattern fits beautifully with all the of the data!

It's tetragonal (rotated by 45° w.r.t. GaAs)



Simulated powder scan

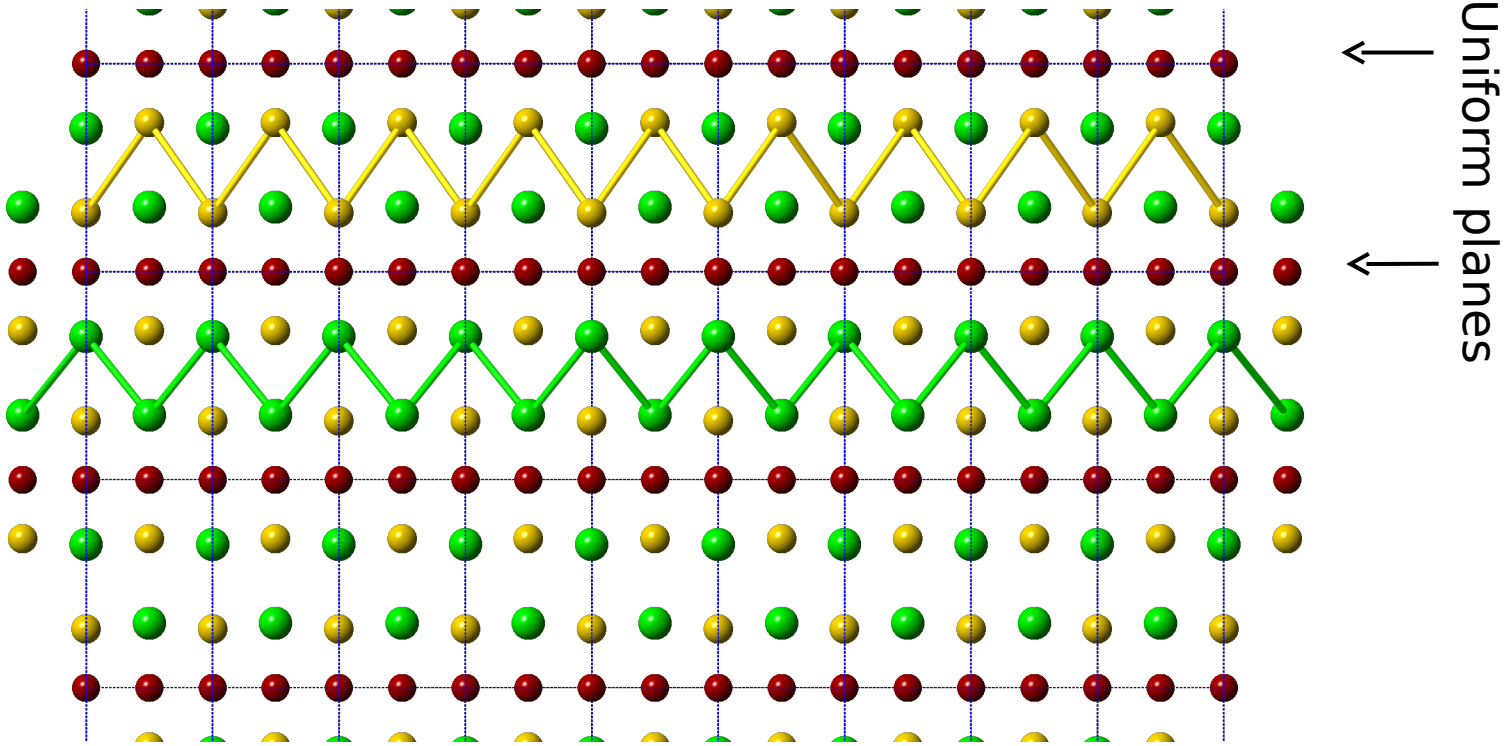


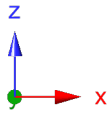


Simulated single crystal overlaid on XRD collected by x-ray area detector

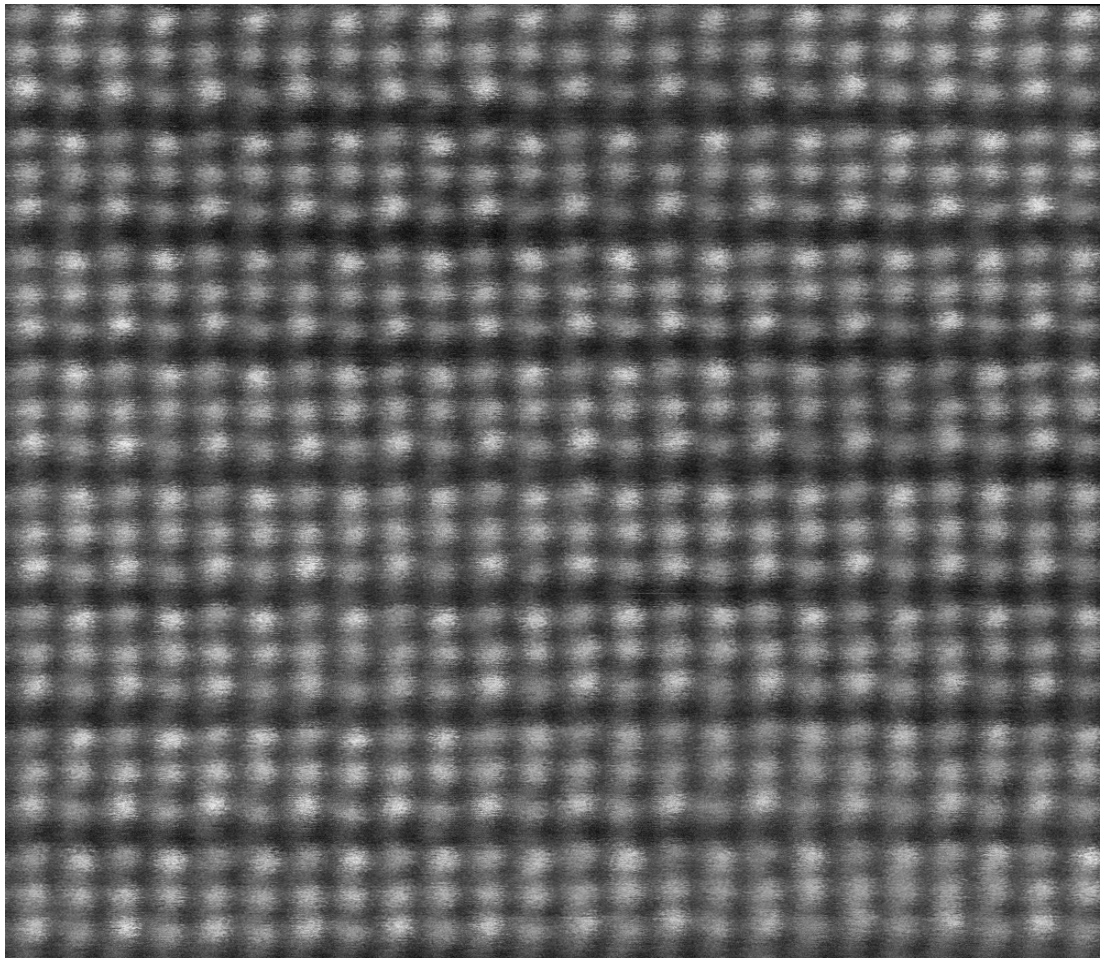
It’s tetragonal – Expected TEM

Viewed along either the [100] or [010] the model displays a distinctive pattern ideal for transverse microscopy, if you have an element resolved technique.





It’s tetragonal – Actual TEM

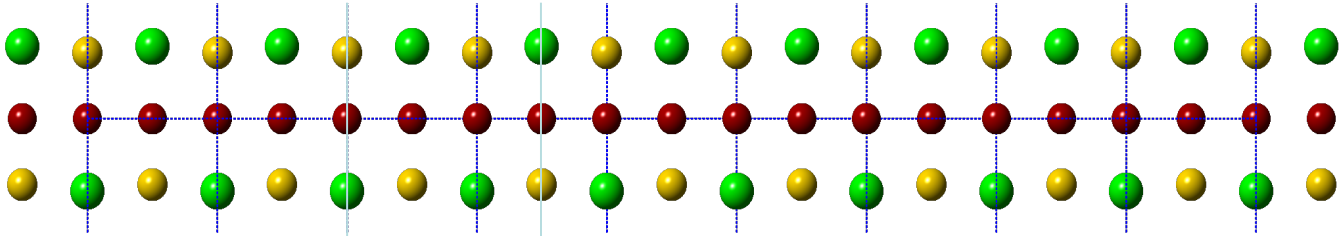


- Clearly displays same in-plane structure as model
- All 3 elements resolved!

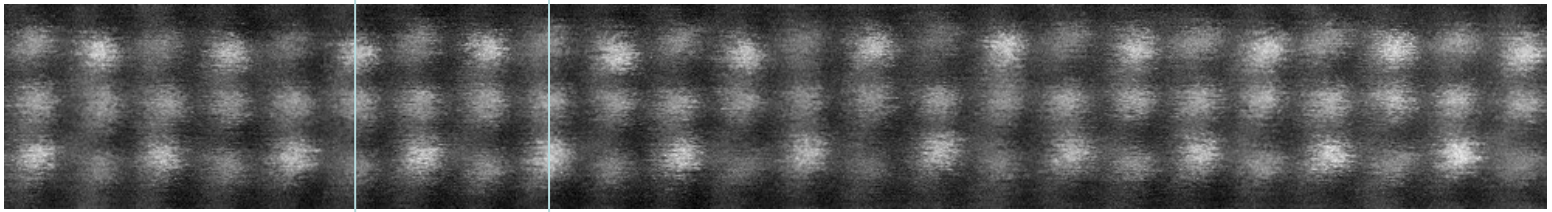
Z-resolved TEM image - Jaume Gasquez ICMAB, measured in Oakridge national laboratory, USA

It's tetragonal – Atomic number evidence

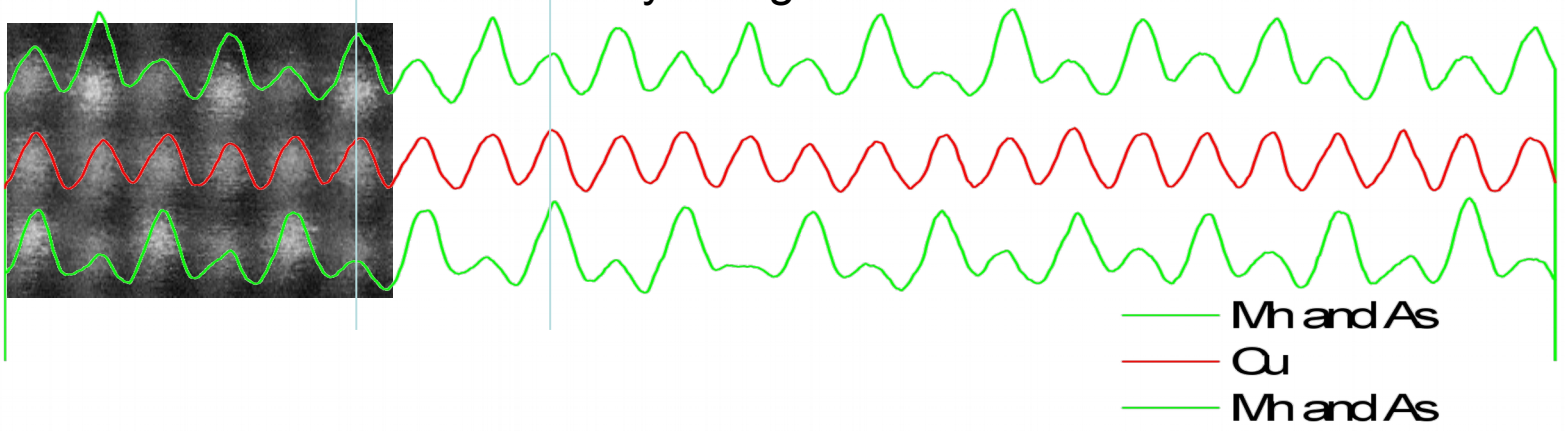
Model viewed along 100



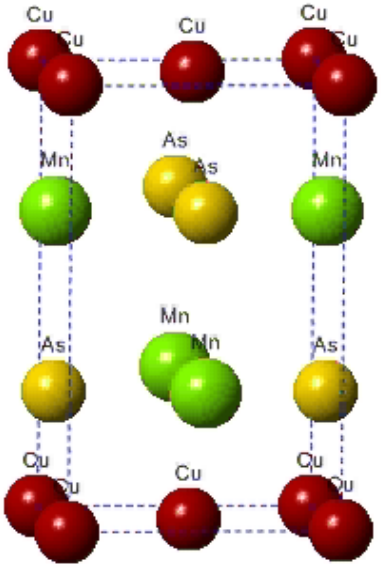
Raw z-resolved TEM image

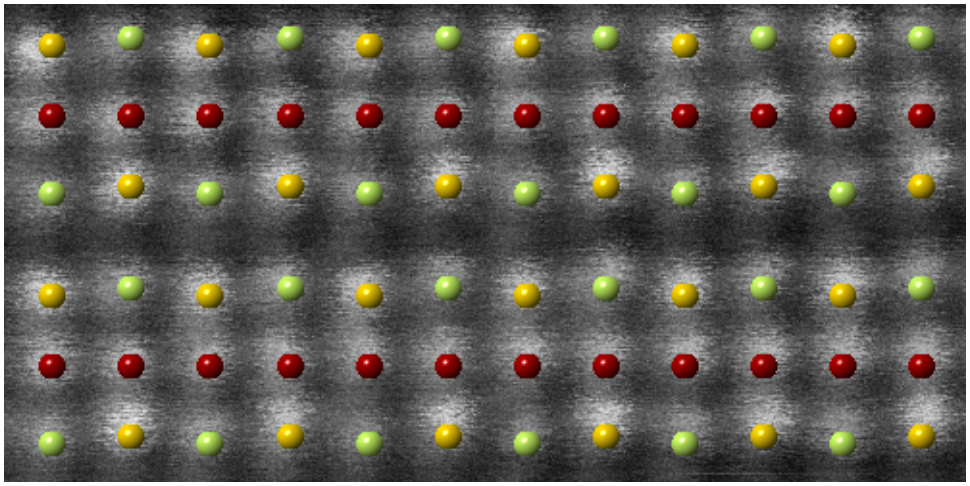


Intensity along rows



The structure





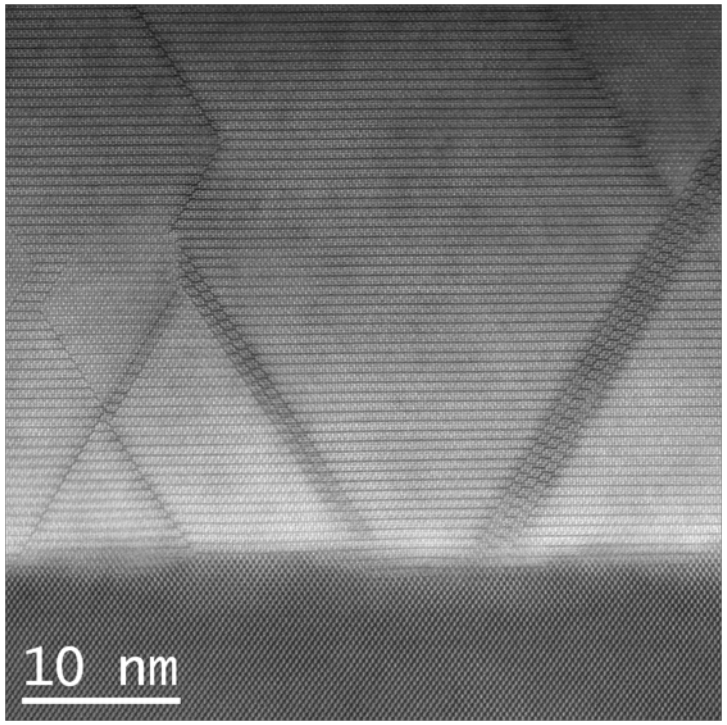
Looks very nice, so is this material defect free?

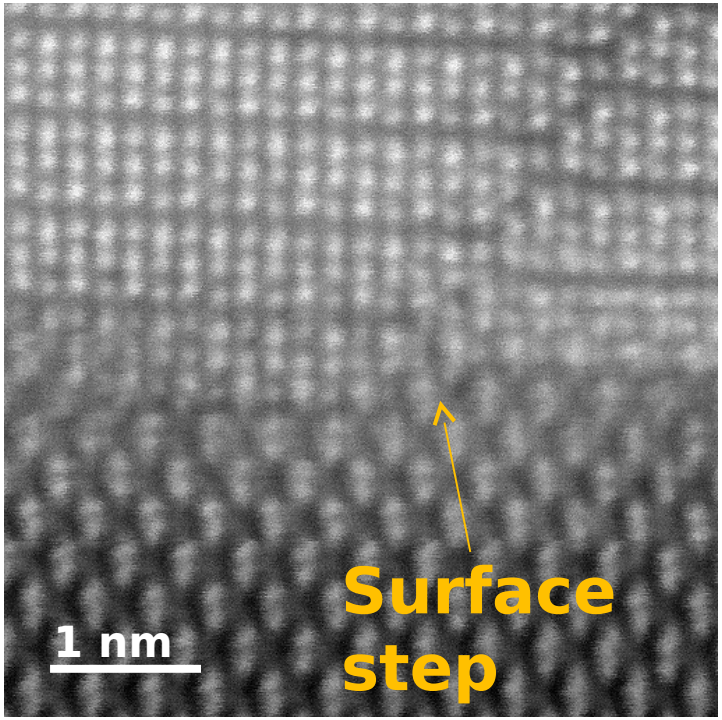
The defect structure

Not defect free!

There are inevitable mis-fit defects due to the mismatch between the unit cell height of CuMnAs and GaAs/GaP

Anti-phase domain boundaries



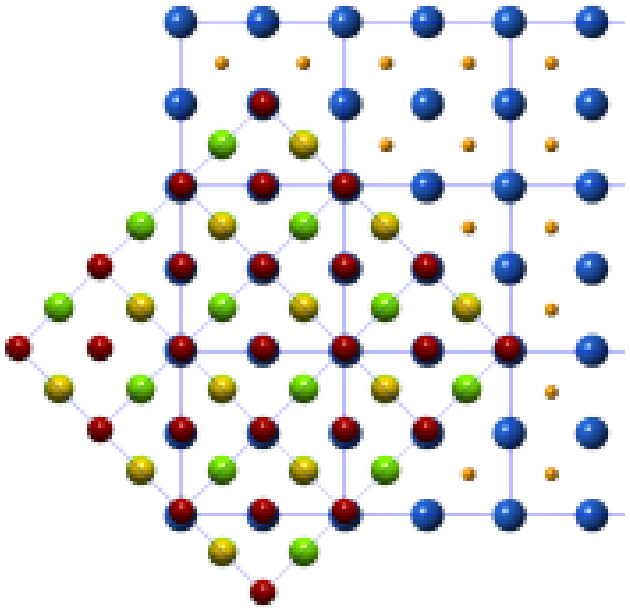


Since these early days we have improved the nucleation stages of growth and reduced the defect density considerably, but have not yet eliminated them.

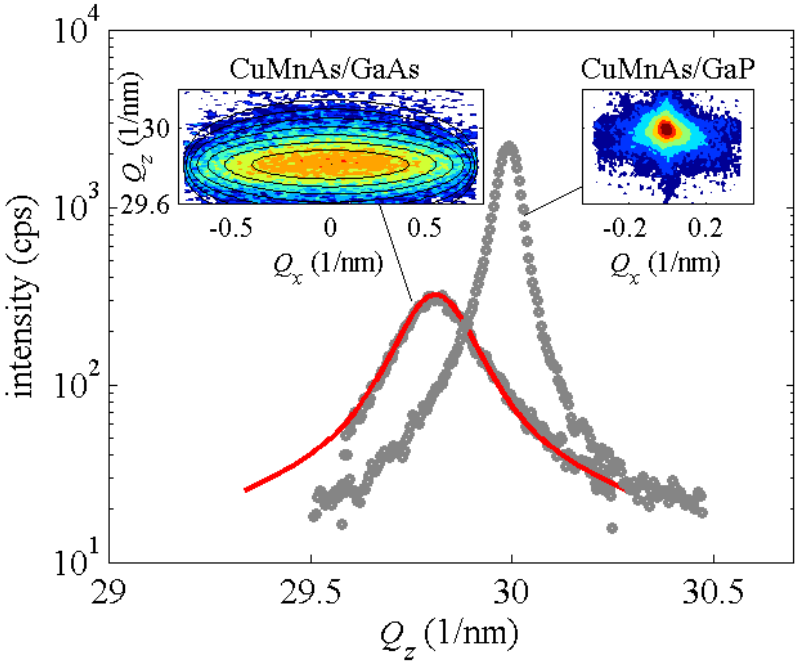
Does this matter?

Tetragonal CuMnAs

- Grown using molecular beam epitaxy on GaAs and GaP substrates
- Tetragonal Cu_2Sb structure
- Single crystal growth
- Relaxed mosaic block structure on GaAs
- Strained and more coherent on GaP



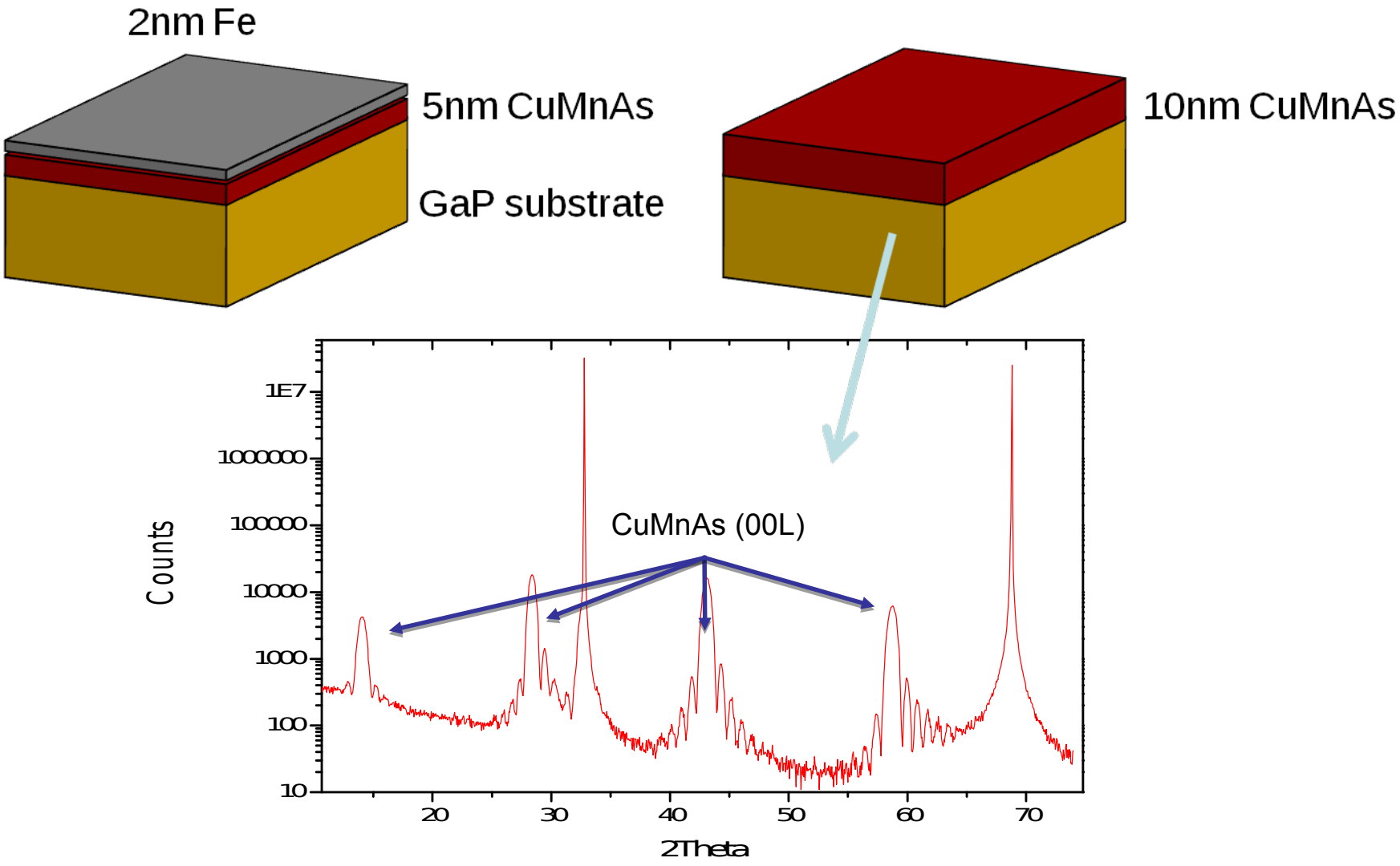
Wadley, Campion *et al* *Nat. Commun.* *(13) DOI: 10.1038/ncomms 3322*



Take away message:

The tetragonal phase is a meta-stable polytype that is driven by the surface reconstruction of the substrate

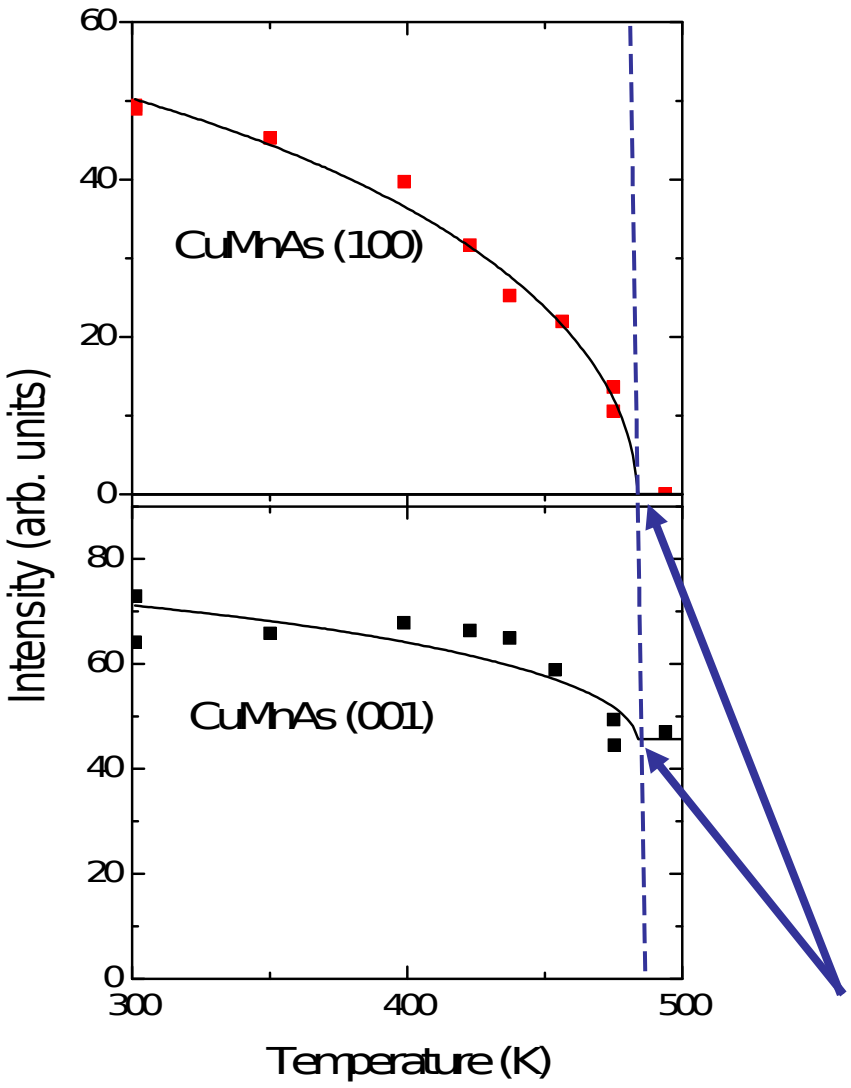
CuMnAs thin films

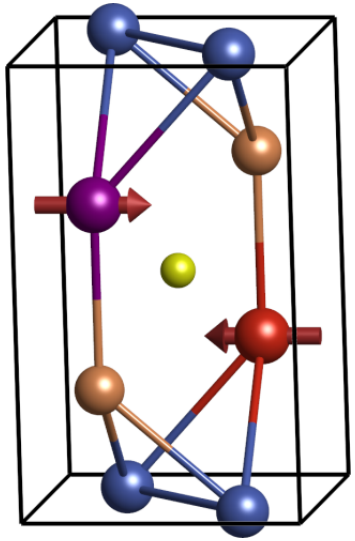


XRD

Neutron diffraction data

Brillouin-like decay of magnetic intensity





- AF ordering with same dimensions as the structural unit cell
- Measured on the WISH instrument at ISIS
- Collinear layered antiferromagnet with spin axis in the *ab* plane
- Mn moment ≈ $3.6\mu_B$
- Antiferromagnetic ordering (Néel) temperature $T_N \approx 485K$

Conclusion

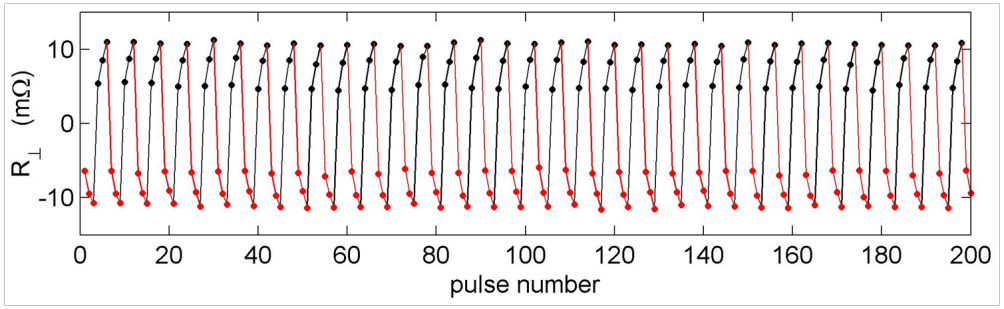
- We have grown CuMnAs over a wide range of Copper fluxes and determined a suitable growth temperature window

- We have shown the material to be a tetragonal co-linear antiferromagnet T_N~485K

- Exchange bias (between CuMnAs and an iron overlayer) and other anti-ferromagnetic signatures (neutron diffraction etc.) have been demonstrated

- Electrical switching and readout have now been demonstrated

- We believe that there must be other materials that would display similar electrical switching. Mn_2Au should work and analytic methods may be used to explore the periodic table. (Marcus Meinert et.al of U. Bielefeld – High throughput ab-initio + DFT method and Jakub Zelezny et. al. of Max Plank Inst.)



P.Wadley, RPC, VN, TJ et. al. Science, Volume 351(6273):587-590. February 5, 2016.