Ferromagnetism in bulk Cr-doped TiO_2?

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Introduction

- Room temperature ferromagnetism (FM) was predicted in dilute magnetic semiconductors (DMS) by Dietl in 2000 [1]: a hunt for room temperature DMS materials followed, motivated by applications in spintronic devices.
- FM has been observed in TM doped TiO_2 in thin film form [2]; however, **studies of the bulk have proven inconclusive** [3].
- It is not clear if the TM inclusions in bulk act as lattice impurities or whether a collective interaction of these dopants leads to FM.
- Oxygen content plays a critical role in the whether FM is observed [4,5], careful attention to the growth of the crystals is a must.

This work looks at whether chromium, a bulk antiferromagnet, when added to rutile TiO_2, makes a DMS.

Crystal Growth

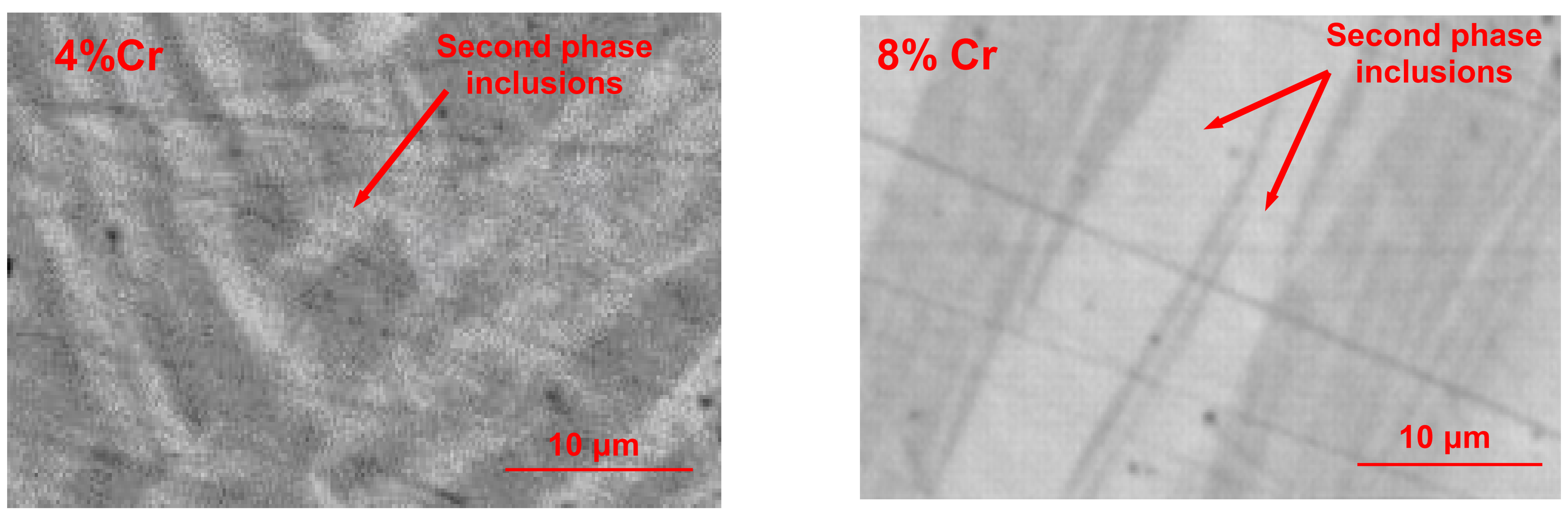
- Single crystals grown using a floating zone (FZ) image furnace.

Advantages of FZ method:

⇒ Large single crystals in near equilibrium growth avoid lattice mismatch (cf. thin film growth) and any resulting magnetic behaviour.

⇒ Crucible contamination avoided: critical for small sample volumes.

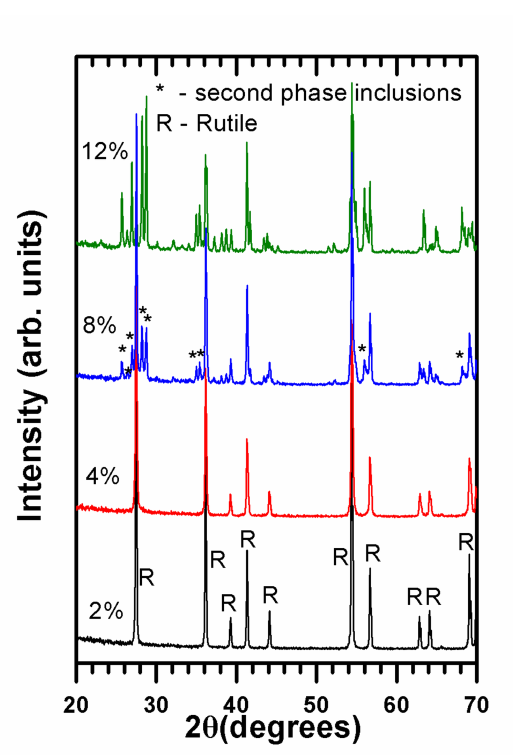
- SEM: - for Cr $<$ 4%, Cr incorporated into rutile structure; band structure matching & good for spintronics!
  - evidence for second phase in samples Cr $>$ 4%.



Above: SEM micrographs showing Cr incorporated in rutile (dark) and second phase (light)

X-ray Diffraction

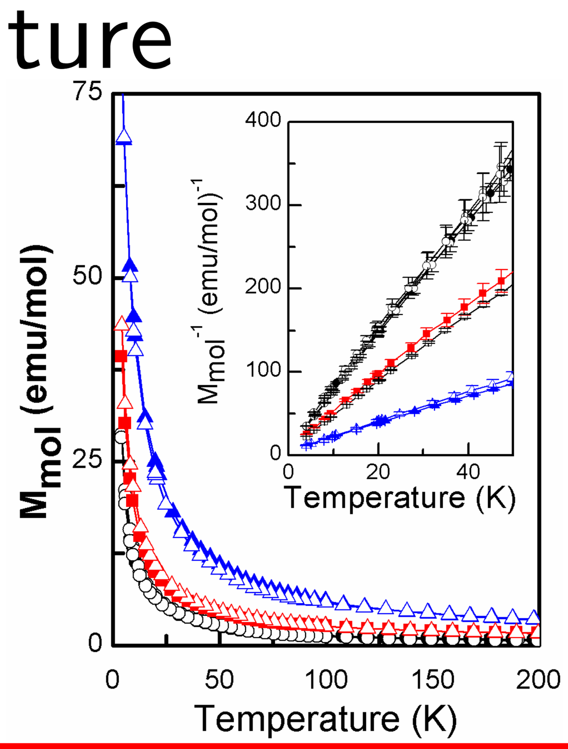
- XRD also shows rutile structure decreasing with increasing Cr doping
- Lattice parameter unchanged with Cr concentration.
- Large mismatch in lattice parameter in 12% sample causes microcracks



Left: Powder XRD from FZ grown crystals.

Magnetisation vs Temperature

- Asymptotic rise in M at T=0K (from fit).
- AC susceptibility measurements carried out
- No evidence for FM ordering/phase transition was found.

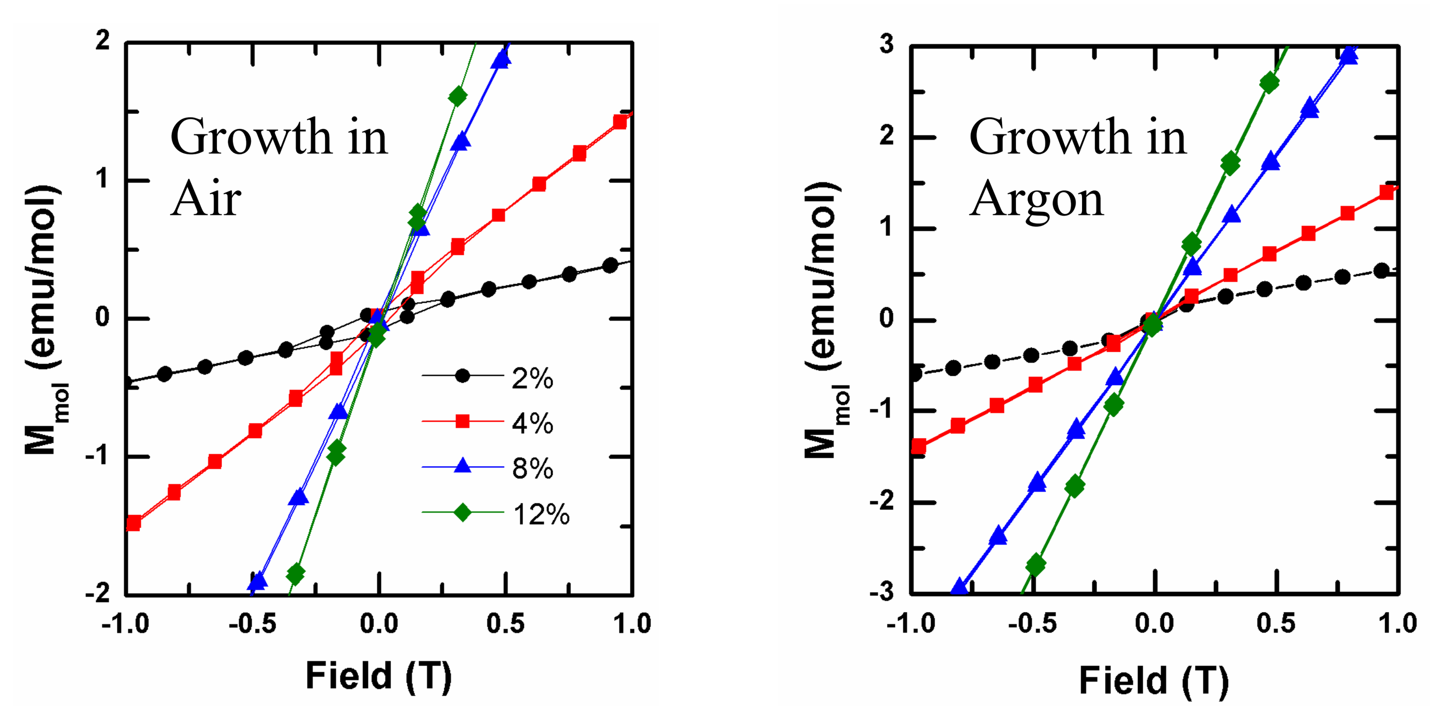


Right: magnetisation dependence on temperature in 0.1T applied field along c-axis

Magnetisation field dependence

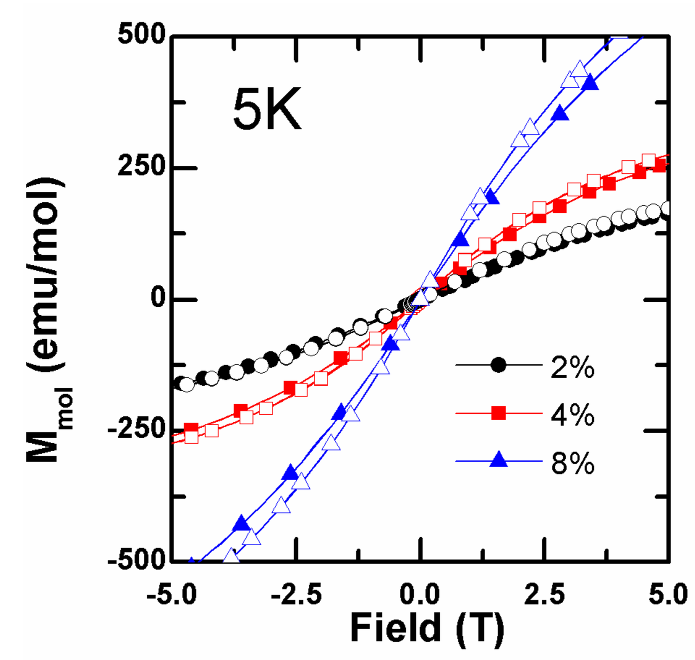
Sintered Powder Samples

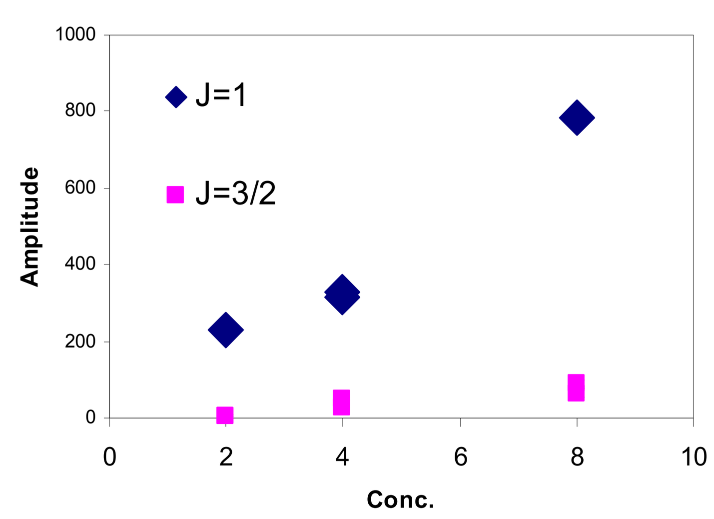
- Weak FM seen in sintered powder samples for Cr ≤ 4%.
- Synthesis atmosphere has some effect.
- Origin for FM unknown: possibly second phase formation under XRD/SEM detection limit?



FZ Grown Crystals

- PM behaviour seen in samples from RT down to 5K.
- Magnetic anisotropy between axes, possibly due to L.S coupling between Cr ions & the tetragonal lattice.





Fitting using Brillouin functions with:

J=1 - Cr^{4+} ions substitution for Ti

J=3/2 - Cr^{3+} in Cr_2O_3 clusters

- Saturation magnetization linear with Cr concentration and gives 1.9±0.2 μ_B per Cr atom (as expected for oxidation state).

Conclusions

- **No evidence was found for FM in bulk samples containing 2-8% Cr [6].**
- This contrasts other observations of weak FM in bulk Cr doped TiO_2 [3].
- If FM does occur in Cr:TiO_2, this is non-equilibrium effect particular to thin films.

References:

[1] T. Dietl et al : Science **287** 1019-22 (2000)

[2] Z Wang et al: J. App. Phys. **95** 11 7381-83 (2004)

[3] L. Sangaletti et al: J. Phys. Condens. Matter **18** 7643-50 (2006)

[4] S. D. Yoon et al: J. Phys. Condens. Matter **18** L355-61 (2006)

[5] S. M. Koohpayeh et al: J. Magn. & Magn. Mater **320** 887-94 (2008)

[6] S. M. Koohpayeh et al: J. Appl Phys **108** 073919 (2010)