Hollow $MnCO_3$ and $MnSiO_3$ nanospheres

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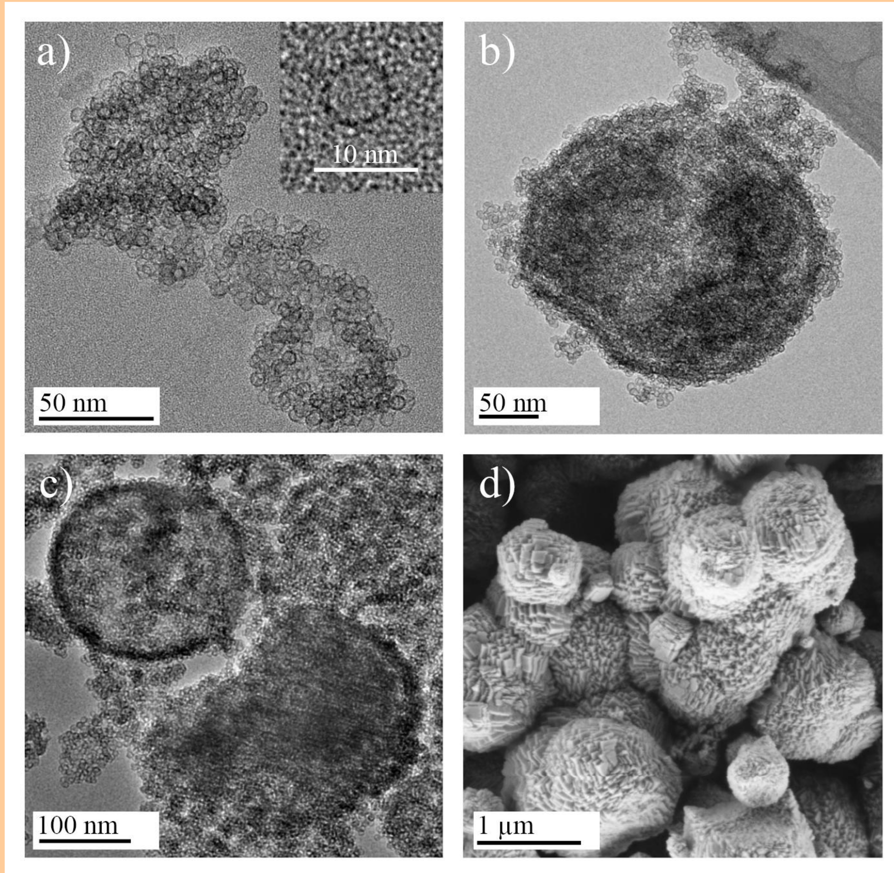
INTRODUCTION AND MOTIVATION

Magnetic nanoparticles can be used in many different applications ranging from medicine, electromagnetic wave detectors to digital information storage. Hollow nanospheres offers additional functionality. For example they show improved electrochemical performance for batteries or can be used for drug delivery. We synthesised $MnCO_3$ and $MnSiO_3$ hollow nanospheres (**HNSs**) with a diameter of few nanometers and thickness of only about two atomic layers. Our $MnCO_3$ HNSs can be considered as a physical realization of a magnetic structure on a nano-dimensional spherical surface geometry.

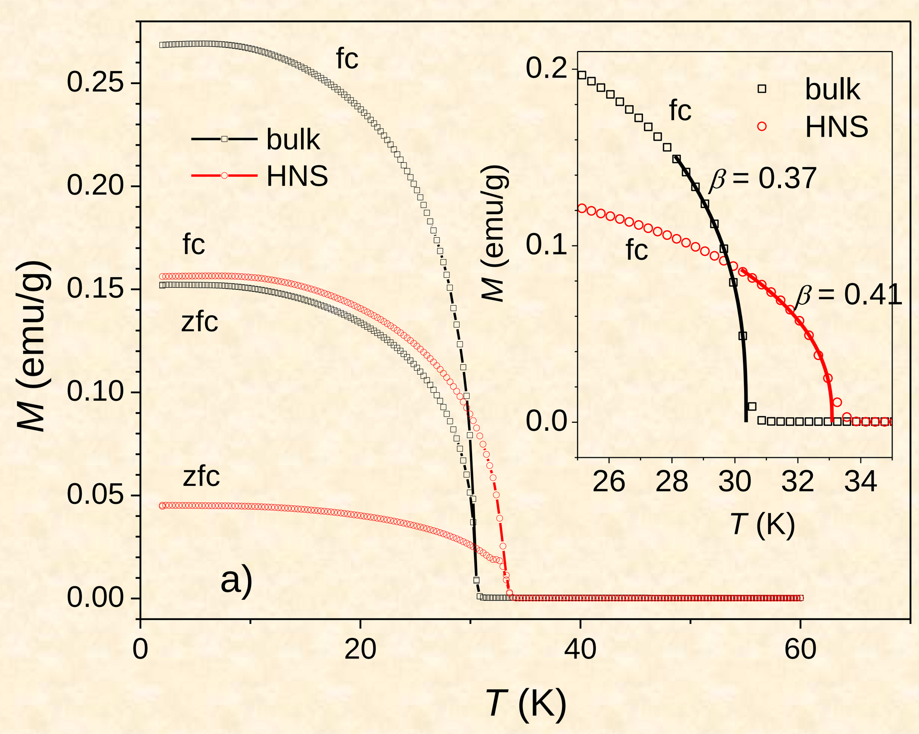
SAMPLE PREPARATION AND STRUCTURE

The $MnCO_3$ HNSs were obtained as an intermediate product in an effort to synthesize manganese silicate $MnSiO_3$ HNSs by a hydrothermal process in an ethanol solvent system that uses CO_2 bubbles, generated by dry ice, as a soft template. $Mn(NO_3)_2{\bullet}4H_2O$ was dissolved in ethanol and dry ice added into the solution.

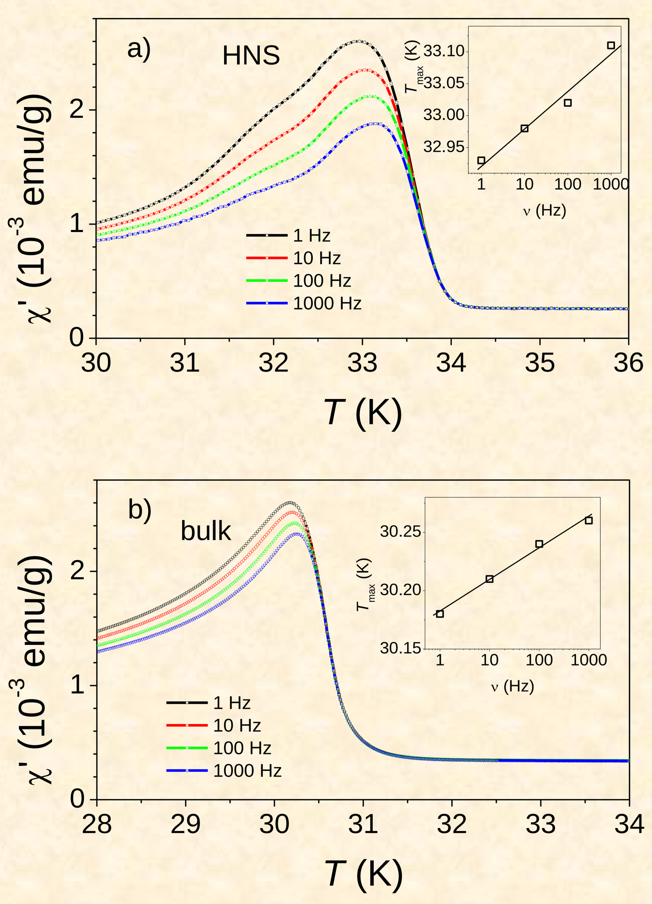


(a) Representative TEM image of the HNSs of 7 nm outer diameter (valid for both the $MnCO_3$ and the $MnSiO_3$). The inset shows HR-TEM image of an individual nanosphere, revealing its hollow morphology with the 0.7 nm wall thickness. (b) A $MnCO_3$ mesosphere (an aggregate of HNSs) in the as-prepared material before the final annealing step. (c) $MnSiO_3$ mesospheres after annealing at 400 ºC. (d) SEM image of the bulk $MnCO_3$ material, showing morphology of intergrown spherical-like grains constituted of small plate-like crystals.

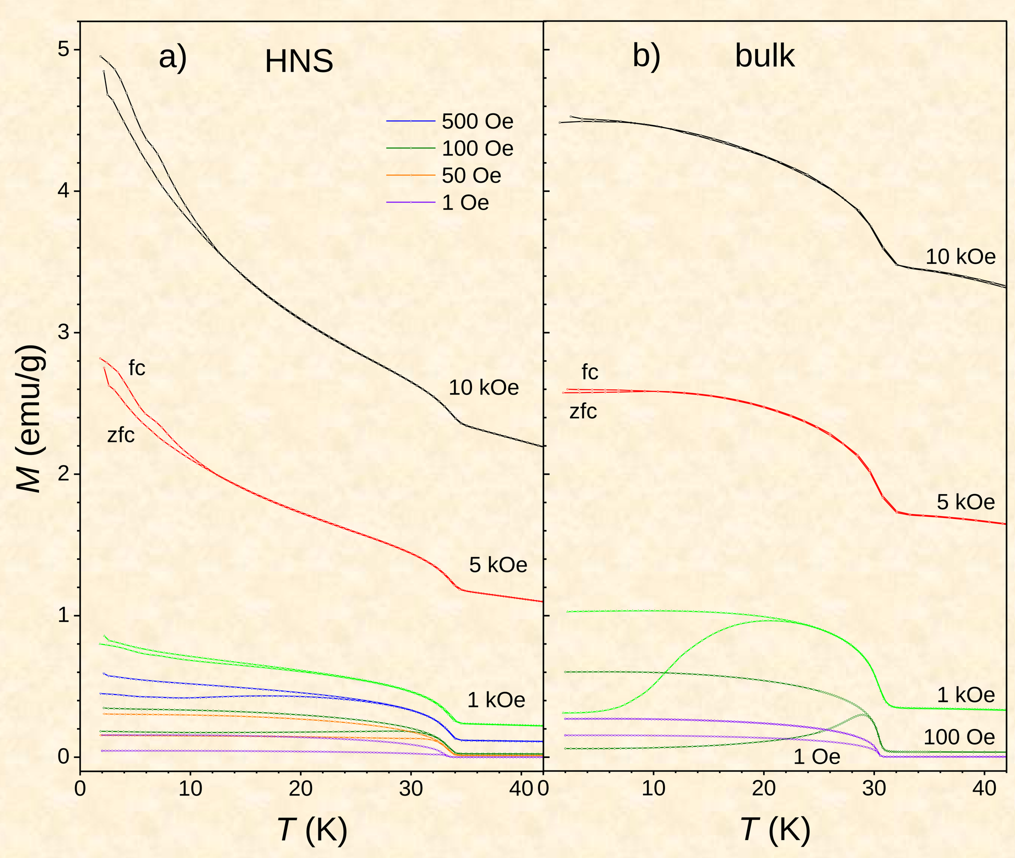
MAGNETIC PROPERTIES of $MnCO_3$ HNSs versus bulk material



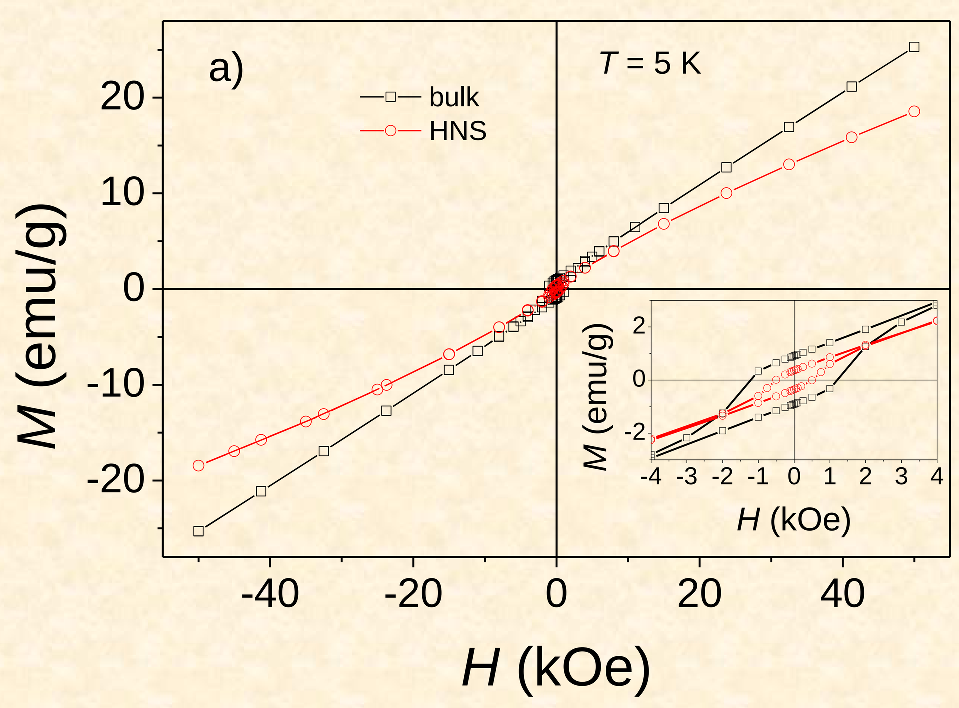
Fits with $M_{fc} = M_0(T_N\text{-}T)^\beta$ yielded T_N = 33.1 K (HNSs) and 30.4 K (bulk).



A relative shift $\Delta T_{max}/(T_{max}\Delta\log\nu)$ = 0.002 (HNSs), 0.001 (bulk) is smaller as in spin glasses.



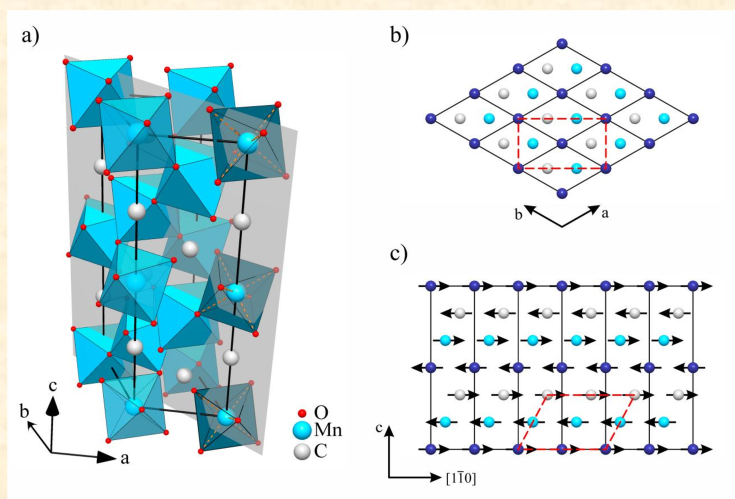
Paramagnetic (HNSs) vs. saturated (bulk) susceptibility below 30 K.



M(*H*) of HNSs deviates from linear dependence for *H* > 10 kOe showing weak paramagnetic behaviour.

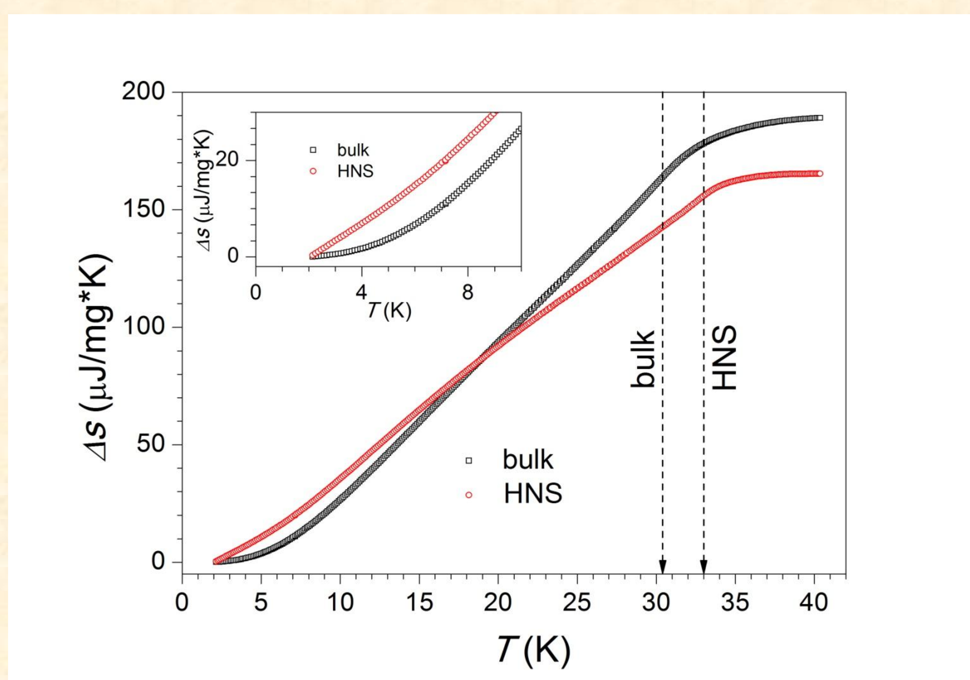
Structure and magnetic structure of bulk $MnCO_3$

Hexagonal unit cell: **Only Mn atoms:**



Dark blue, light blue and white circles represent Mn atoms with *c* coordinates of 0, 1/2; 1/6, 2/3; and 1/3, 5/6, respectively. The monoclinic magnetic unit cell is shown by a dashed box. The spins lie in the basal plane and the AFM spin sublattices appear to be canted by about 0.2º out of the plane of the paper, which causes weak ferromagnetism in the basal plane.

HEAT CAPACITY -> Magnetic entropy



Zero slope vs. final slope: magnetic ordering process has not been completed in HNSs down to 2 K and some low-energy excitations are still thermally excited.

We observed differences in magnetic properties between the HNSs and the bulk $MnCO_3$ due to the weakened interspin interactions and reduced atomic coordination by the neighboring atoms in the HNSs. This makes the canted AFM structure of the HNSs more soft and fragile with respect to external forces like the magnetic field, as compared to the rigid and robust structure of the bulk material.