Observing the Interaction Between Magnetic and Chemical Microstructures at the Nanometer Scale Using Electron Holography

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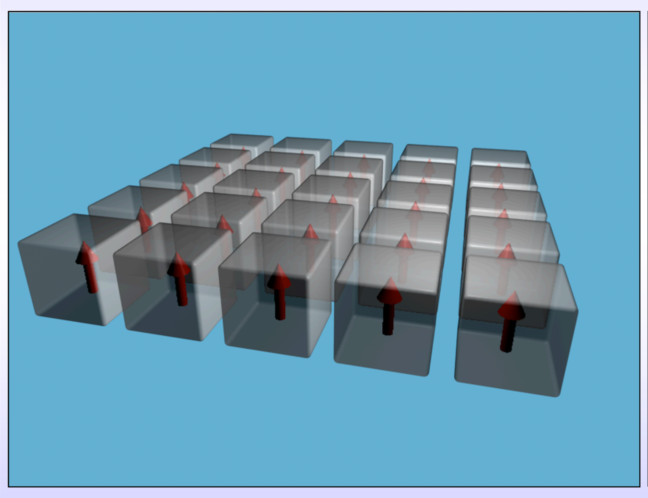
ABSTRACT

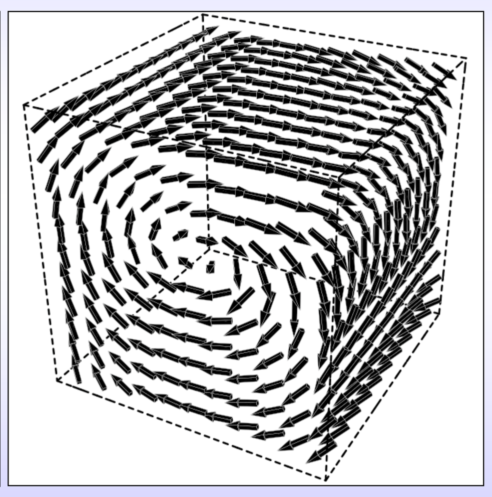
Off-axis electron holography in the transmission electron microscope has been used to image the spatial distribution of magnetic fields in a natural intergrowth of magnetite and ulvospinel with nanometer resolution. The morphology of these intergrowths consists of cuboidal blocks of magnetite with average size 100 nm within a matrix of ulvospinel. Since ulvospinel is paramagnetic at ambient conditions, the initial MD grain is subdivided by the non-magnetic lamellae to yield an approximately cubic array of interacting SD or PSD magnetite particles. The technique allows both single-domain and vortex states within individual blocks to be imaged, and provides detailed information about the magnetostatic interaction fields between neighbouring blocks. Combined with high-resolution chemical maps obtained using electron spectroscopic imaging, we are able to present a comprehensive analysis of the relationship between the magnetic and chemical microstructures of the intergrowth. The observations provide new insight into the question of whether such intergrowths are a potential source of strong and stable remanent magnetization on the Earth and other planets. The high spatial resolution of the technique makes it ideal for the study of nanoscale particles at the boundary between SD and PSD behaviour, and provides the opportunity to study the crystallographic, chemical, and defect microstructures of the sample simultaneously with the holographic measurements. This is the first study to apply electron holography to one of the central problems of rock magnetism, and paves the way for a new era of magnetic microscopy in this field.

Magnetic behaviour of arrays of magnetite cubes

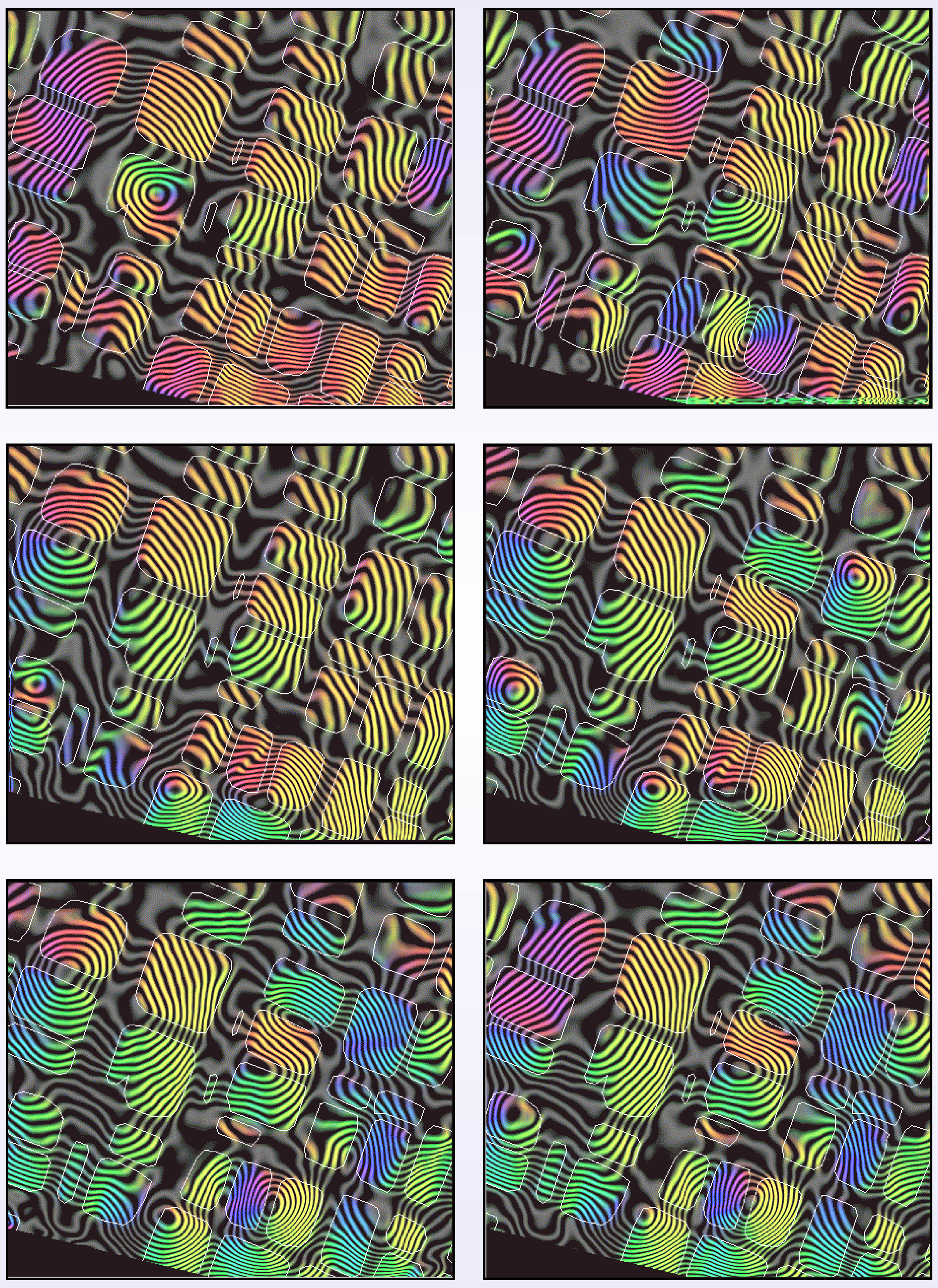
Subdivision of MD grains into an array of SD particles via subsolvus exsolution or high-temperature oxidation has long been considered a possible mechanism of increasing the stability of NRM



Collective behaviour of cubic arrays of magnetite blocks

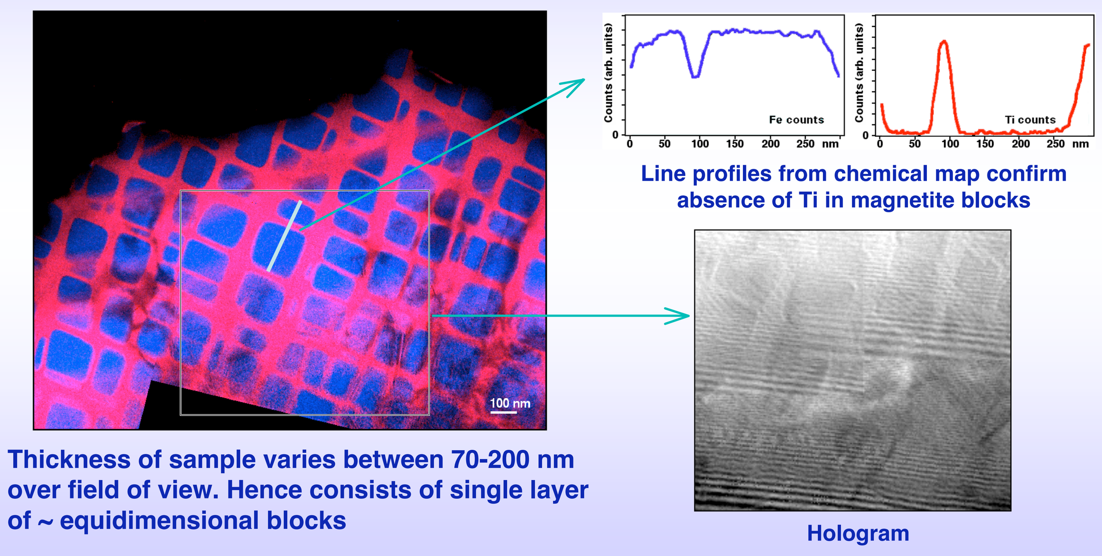


Vortex magnetisation state in 200 nm magnetite cube (Fabian et al. 1996)



Chemical map of block texture

Rock magnetism: Natural intergrowth of ~100 nm magnetite (Fe_3O_4) blocks in non-magnetic ulvöspinel (Fe_2TiO_4) matrix



Line profiles from chemical map confirm absence of Ti in magnetite blocks

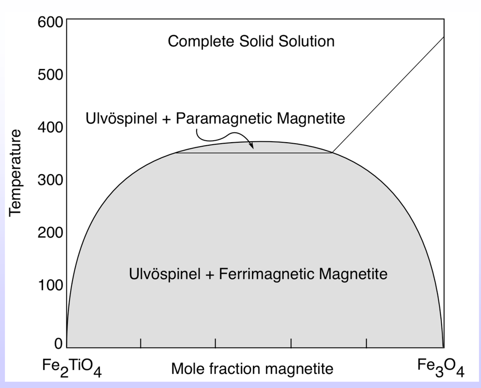
Thickness of sample varies between 70-200 nm over field of view. Hence consists of single layer of ~ equidimensional blocks

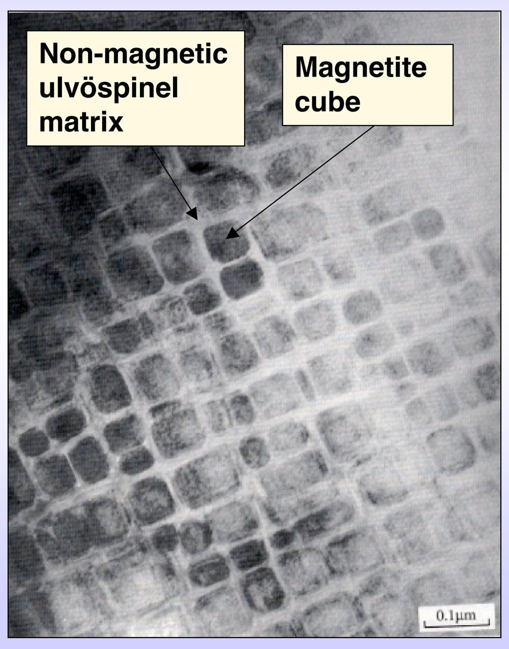
Hologram

Chemical map: Blue = Fe_3O_4 (magnetic)
Red = Fe_2TiO_4 (non-magnetic)

Subsolvus exsolution in the magnetite-ulvöspinel solid solution

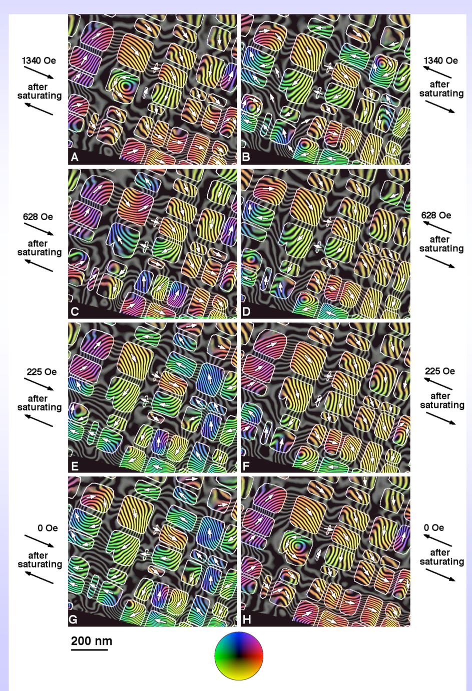
Slowly-cooled samples of intermediate composition exsolve into an intergrowth of magnetite-rich and ulvöspinel-rich phases. Exsolution occurs parallel to the {100} planes of the host phase.

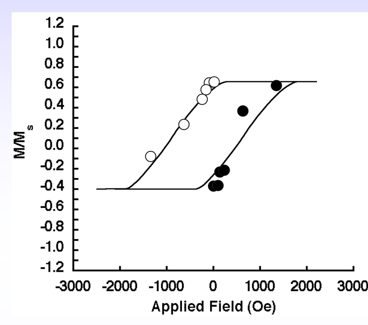




Holography results

Magnetic remanent states





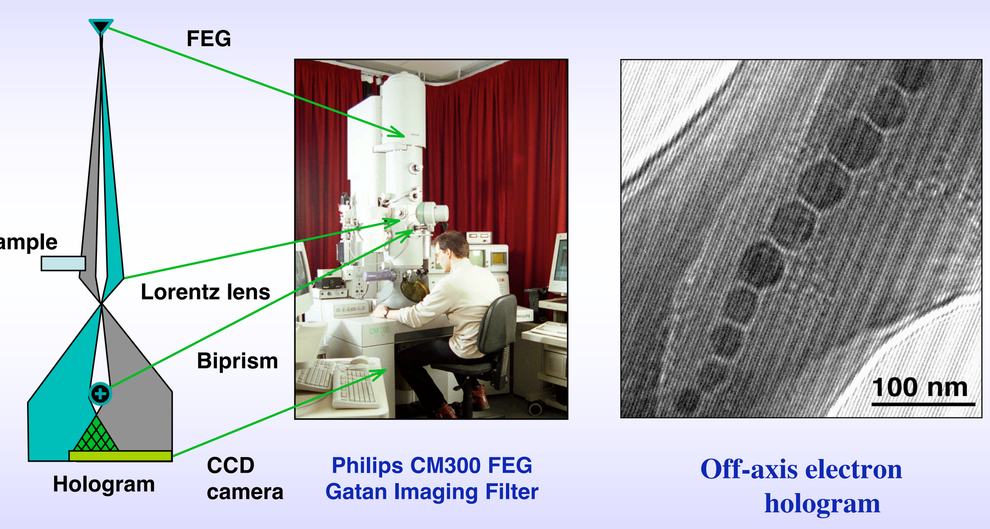
Remanent hysteresis loop measured from holographic phase images

$M_{rs}/M_s > 0.5$

$H_{cr}/H_c \sim 7$

(assuming $H_c \sim 100$ Oe, Williams and Wright 1998)

Experimental details



Philips CM300 FEG Gatan Imaging Filter

Off-axis electron hologram

Theory

If V(x) and B(x) do not vary in the incident electron beam direction, then :

Phase shift:

$$\phi(x) = C_E V(x)t(x) - \left(\frac{e}{\hbar}\right)\int B_\perp(x)t(x)dx$$

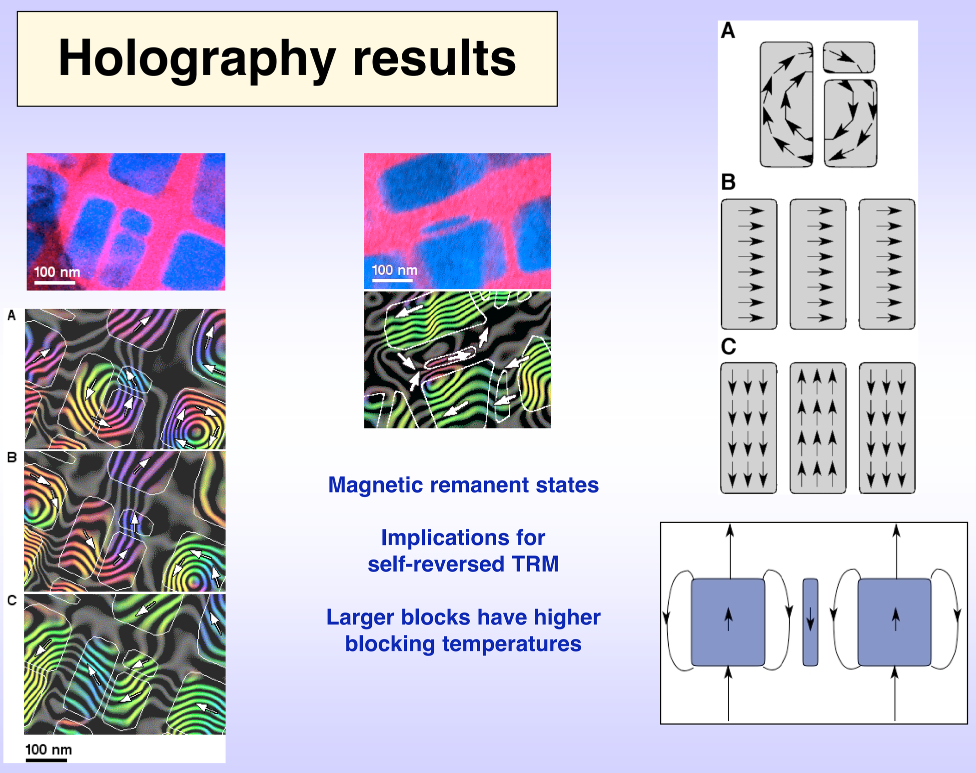
$$C_E = \left(\frac{2\pi}{\lambda}\right)\left(\frac{E+E_0}{E(E+2E_0)}\right)$$

Sensitive to:

magnetic fields
electric fields

composition
density
bonding/ ionicity
electrostatic fields at depletion layers
electrostatic fringing fields outside materials

Holography results



Magnetic remanent states

Implications for self-reversed TRM

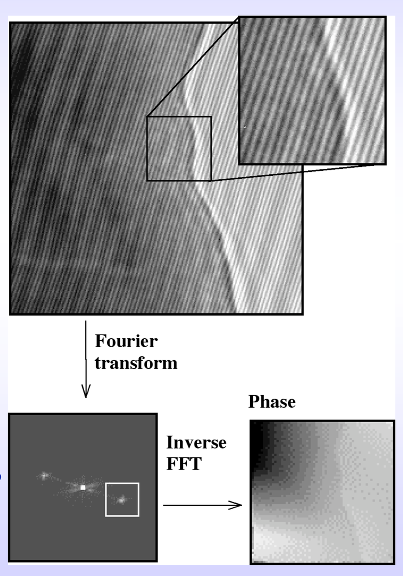
Larger blocks have higher blocking temperatures

Schematic diagrams

Digital processing of electron holograms

provides amplitude and phase of electron wave

Off-axis electron hologram from thin crystal showing interference fringes within sample



Phase image obtained from inverse Fourier transform of one 'sideband' selected from Fourier transform of hologram

Theory

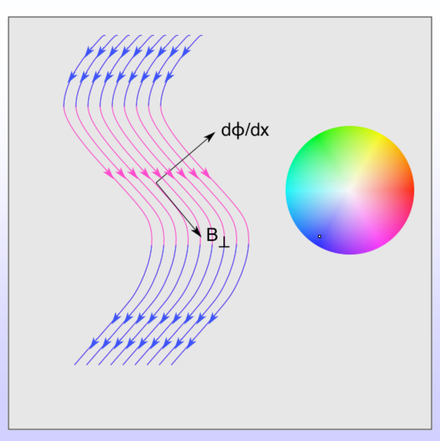
Phase gradient:

$$\frac{d\phi(x)}{dx} = C_E \frac{d}{dx}\{V(x)t(x)\} - \left(\frac{e}{\hbar}\right)B_\perp(x)t(x)$$

In a sample of uniform thickness and composition:

$$\frac{d\phi(x)}{dx} \propto B_\perp(x)$$

- The mean inner potential contribution to the phase must be removed to quantify the magnetization.
- This contribution can be obtained by averaging pairs of holograms that have exactly opposite magnetic configurations.
- Spatial resolution: optimally 2 nm in field-free conditions.



Conclusions

- Majority of blocks in non-uniform SD (flower) or single vortex states. Smallest block containing a vortex state was 115x90x145 nm. Largest block to contain SD state was 165x160x100 nm. Individual blocks were observed to switch between SD and vortex states as a function of applied field.
- SD states are more abundant than vortex states, indicating that SD has lower energy than vortex state in this size range and in the presence of strong interactions.
- Results suggest that switching of SD blocks may occur via an intermediate vortex state.
- Overall anisotropy is low, with SD blocks displaying a large number of easy axes. This appears to be a consequence of competition between the shape anisotropy of individual blocks and the interaction with neighbouring blocks.
- Magnetic "superstates" are formed by several blocks acting collectively. Vortex superstates and 3-domain superstates have been observed. Strong interactions increase effective size of blocks.
- Macroscopic behaviour shows mixture of SD ($M_{rs}/M_s > 0.5$) and M_D ($H_{cr}/H_c \sim 7$ characteristics