Iron nitride $Fe_{16}N_2$: intrinsic properties, synthesis, stability and bulk magnets

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Introduction

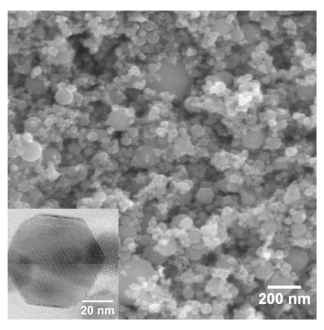
The fascinating phase diagram of iron-nitrogen provides a variety of interesting materials with their magnetic properties tunable in a broad range depending on the nitrogen content. Magnetism correlates with the iron amount, starting from nonmagnetic FeN to ferromagnetic γ′-Fe_4N [1] with high magnetization and even further to α′-Fe_8N [2]. Perhaps the most attention is attracted by the ordered tetragonal superstructure α′′-$Fe_{16}N_2$ due to its unique combination of high saturation magnetization with enhanced magnetocrystalline anisotropy [3]. Unfortunately, the α′′-$Fe_{16}N_2$ phase is metastable and therefore hard to produce in phase-pure form. Moreover, decomposition already below 200 °C [4] hinders large scale production of bulk fully dense magnets using conventional routes. Nevertheless, it has been studied for multiple potential applications, such as rare-earth-free permanent magnets, two-phase nanocomposite magnets [5] as well as biomedical applications [6]. In this contribution we provide a comprehensive overview and assessment of the potential magnet performance based on our own experimental results as well as study of the available scientific literature and patents. We report synthesis of α′′-$Fe_{16}N_2$ nanoparticles followed by production of bulk samples by low-temperature consolidation. The possibility of enhancing the anisotropy field using shape anisotropy is explored in nanowires. Magnetic properties and stability are discussed in the context of possible application in permanent magnets.

Synthesis of α′′-$Fe_{16}N_2$ nanoparticles

- Iron oxide Fe_2O_3 nanoparticles are used as a starting material
- Reduction to pure α-Fe by H_2
- Reduction conditions optimized

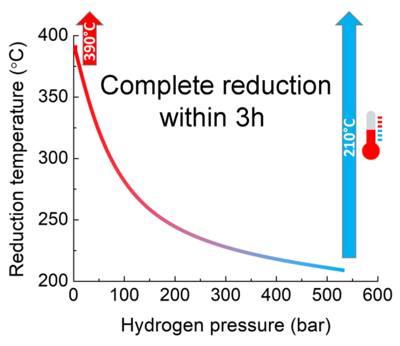
γ-Fe_2O_3 → (H_2) → α-Fe

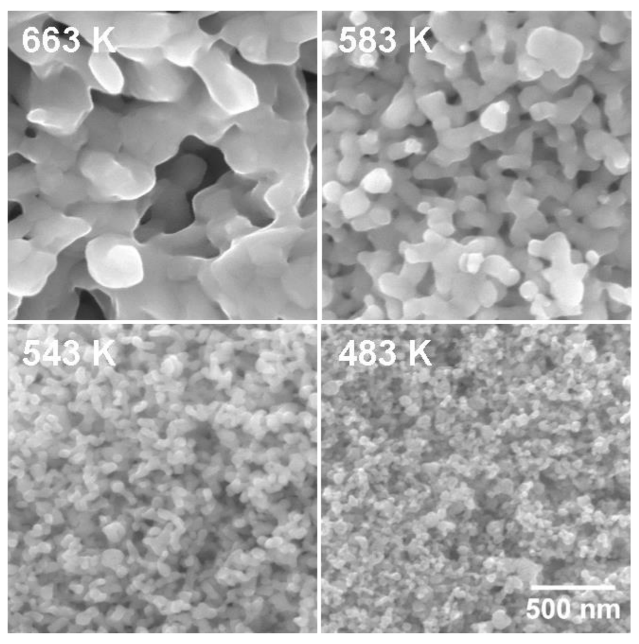
$Fe_2O_3 + 3H_2 \xrightarrow{Heat} 2Fe + 3H_2O$



High-pressure hydrogen reduction enables lower temperatures and particle growth can be successfully avoided [7]

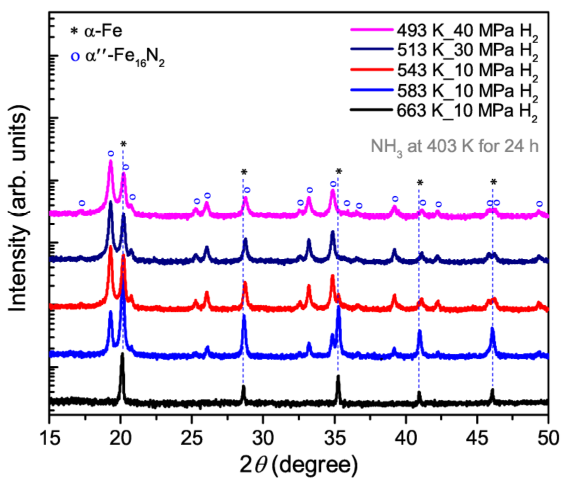
- 663 K (ambient pressure): neck formation, significant coalescence into micrometer-range structures
- 483 K: fine nanoparticles ≈50 nm

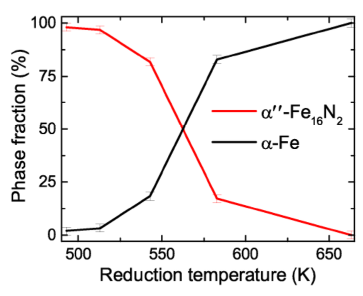


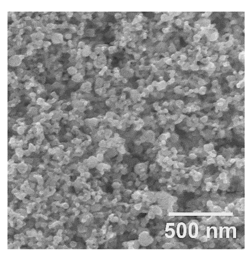


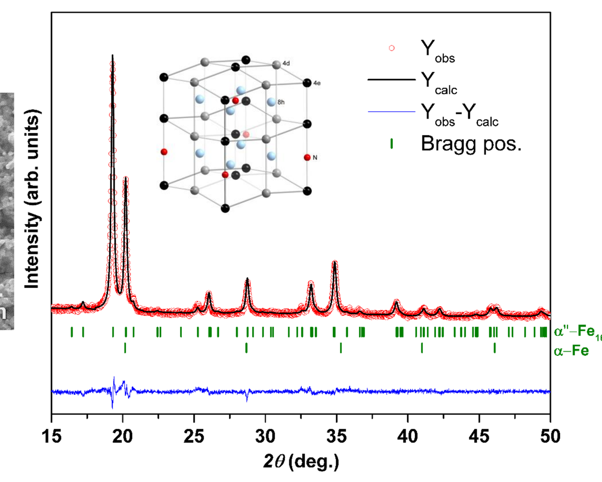
Nitrogenation in NH_3 atmosphere

α-Fe → (NH_3) → α′′-$Fe_{16}N_2$









- **Phase-pure α′′-$Fe_{16}N_2$** nanoparticles synthesized from the fine α-Fe precursors
- No observable particle growth during the synthesis, crystallite size ≈50 nm

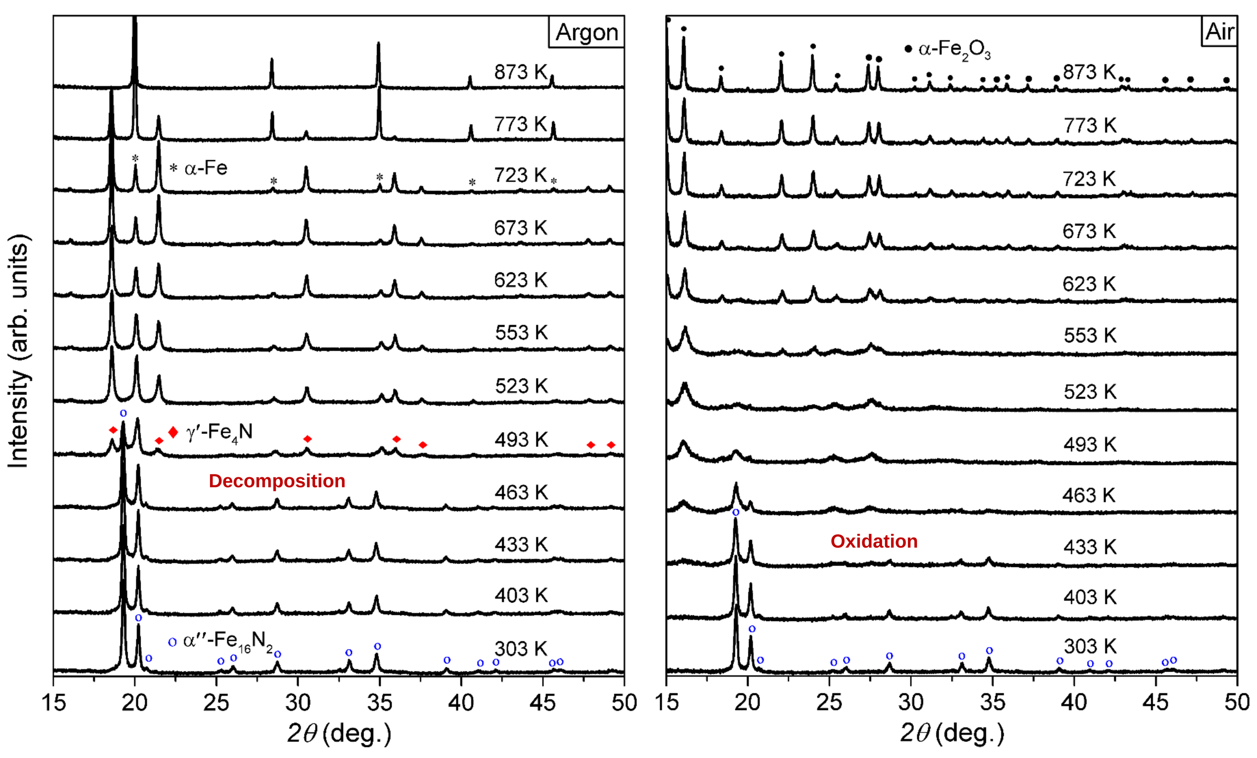
α′′-$Fe_{16}N_2$ thermal stability

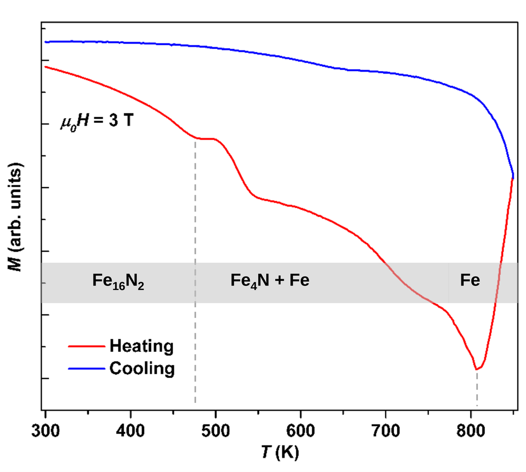
In inert atmosphere (Ar):

α′′-$Fe_{16}N_2$ is stable up to ≈ 463 K. **Decomposition** in α-Fe + γ′-Fe_4N → α-Fe + N_2

In air:

complete **oxidation** begins already at ≈ 433 K.





Temperature-dependent magnetic measurements confirm the XRD results. Decomposition of α′′-$Fe_{16}N_2$ phase starts at ≈460 K transforming first into γ′-Fe_4N and finally into α-Fe.

α′′-$Fe_{16}N_2$ → α-Fe + γ′-Fe_4N → α-Fe + N_2

References

[1] I. Dirba et al., J. Magn. Magn. Mater. 379 (2015) 151–155.
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[5] I. Dirba et al., J. Magn. Magn. Mater. 518 (2021).
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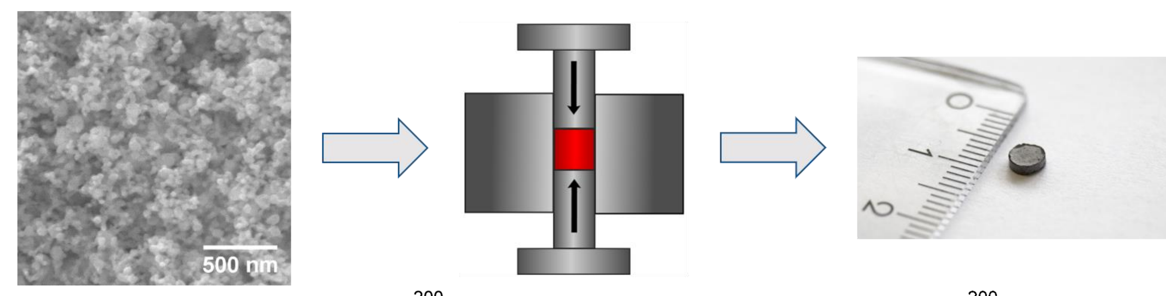
[7] I. Dirba et al., Nanoscale Adv. 2 (2020) 4777–4784.

$Fe_{16}N_2$: Hype, Hope, or Heavy Hitter?

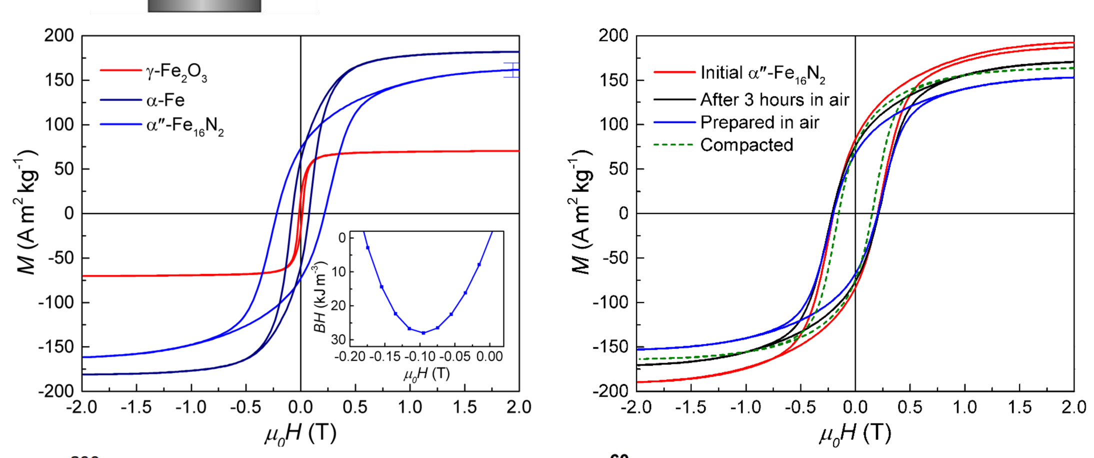
Towards bulk α′′-$Fe_{16}N_2$ magnets

Lab-scale production of bulk α′′-$Fe_{16}N_2$ magnets

α′′-$Fe_{16}N_2$ nanoparticles filled in a steel die	Pressing below decomposition T	Lab-scale samples for characterization

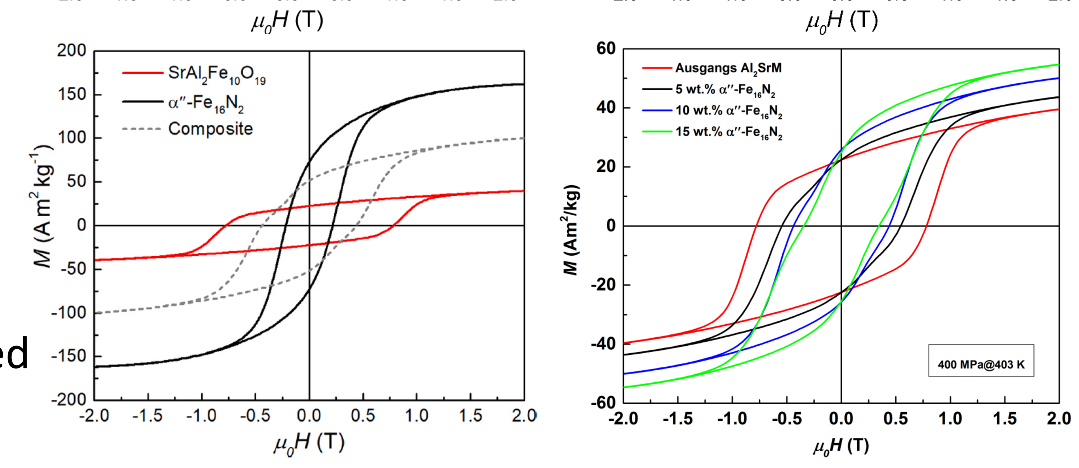


- Saturation M_s = 215 A m² kg⁻¹
- Remanence M_r = 73 A m² kg⁻¹
- Coercivity $\mu_0 H_c \approx 0.25$ T
- Curie Temperature T_c = 634 K
- $(BH)_{max}$ = 28 kJ m⁻³

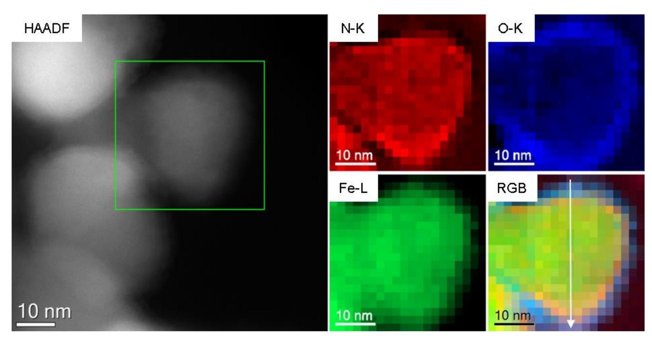


Nanocomposite magnets from Sr hexaferrite as the 'hard' and iron nitride as the 'soft' phase.

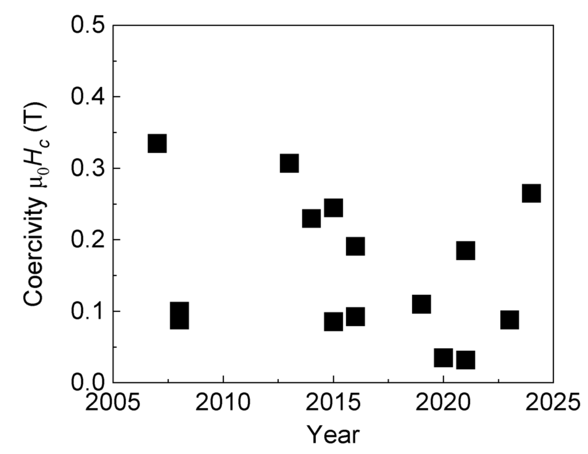
- Coercivity decreases from 0.78 T in the initial ferrite to 0.38 T in the case of 15 wt.% $Fe_{16}N_2$ addition. This is te highest coercivity reported in $Fe_{16}N_2$ samples.



Reason for lower magnetization and lack of coupling is surface oxidation of the $Fe_{16}N_2$ nanoparticles.



Coercivitiesreported in scientific literature for $Fe_{16}N_2$ within the last two decades reach about 0.34 T.



Advantages of $Fe_{16}N_2$ magnets

- Cheap and abundant raw materials
- Better temperature stability of magnetic properties than $Nd_2Fe_{14}B$ due to the higher Curie temperature
- High magnetization

Challenges to be addressed

- Enhancing coercivity to avoid self-demagnetization
- High production costs and complexity in nanoparticles
- Particle alignment for production of anisotropic samples
- Poor stability makes production of bulk magnets difficult

Theoretical potential and future directions

Assessing the theoretically possible performance

Saturation magnetization $M_s \approx 2.3\ T$ Anisotropy constant $K_u \approx 1.0 \frac{MJ}{m^3}$

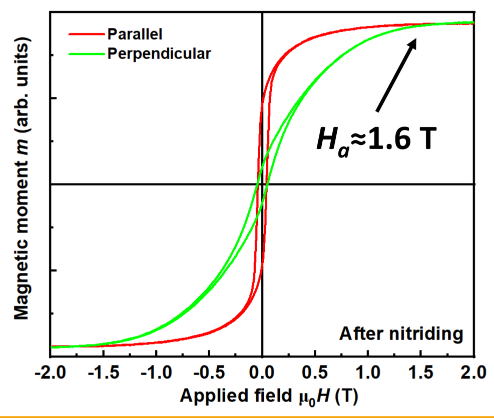
Hardness parameter: $k = \sqrt{\frac{K_1}{\mu_0 M_s^2}} \approx 0.5 < 1$ → **'semi-hard' material**

Anisotropy field: $\mu_0 H_a = \frac{2K_u}{\mu_0 M_s} = \frac{2 \cdot 10^6}{2.3} \approx 1.1\ T$ **Coercivity sufficient for niche applications?**

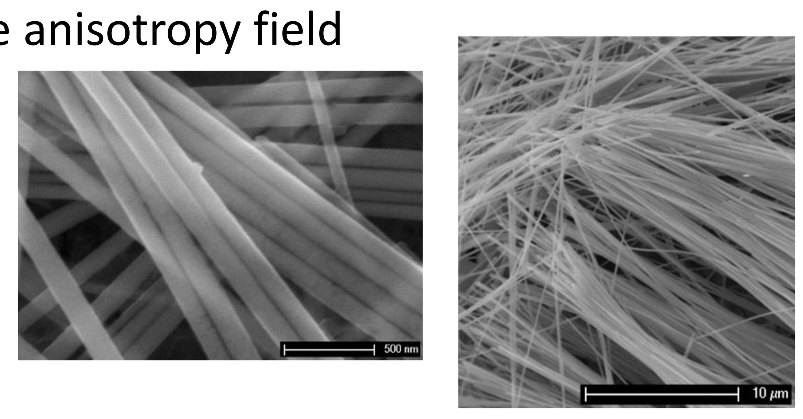
Empirically (Brown's paradox): $H_c \leq 25\ \%$ of $H_a \Rightarrow H_c \leq 0.27\ T$ $\boldsymbol{H_c \ll M_s}$

Potential for coercivity improvements: (i) alloying and (ii) shape anisotropy

- **Alloying** to enhance the magnetocrystalline anisotropy field
- **Shape anisotropy** using nanowires



Fe nanowires as a precursor for synthesis $Fe_{16}N_2$ to benefit from shape anisotropy



Fe nanowires → Field alignment → H_2 treatment → NH_3 treatment

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