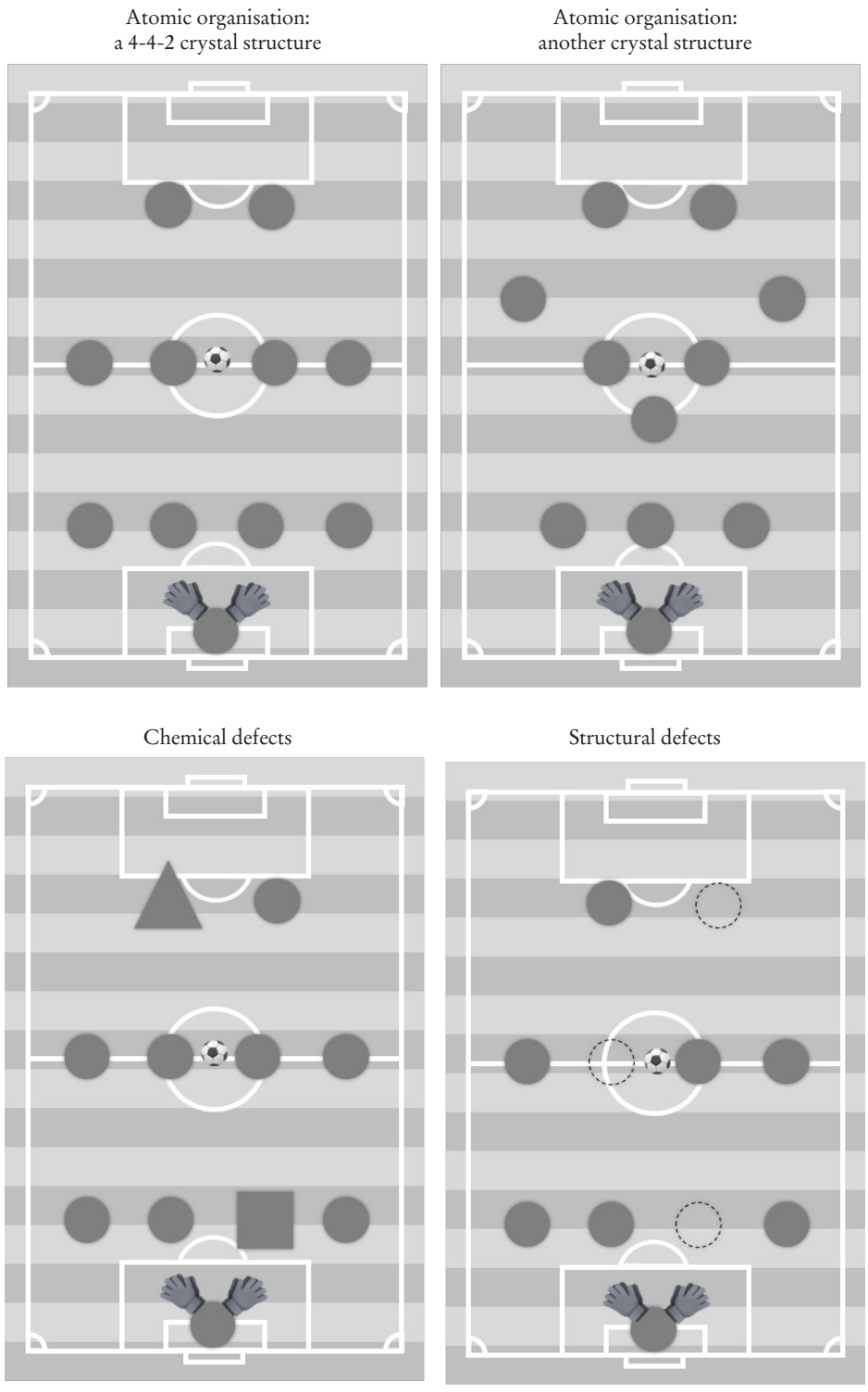
Baptiste Gault. Foto: Vladimir Unkovic

Materials are complex hierarchical arrangements of atomic species. Imperfection, defects in these arrangements change the properties of the material, potentially dramatically. In order to guide the design of the next generations of materials and devices, while avoiding the costly and time-consuming trial-and-error, it has become critical to observe materials at the scale that is relevant to the property-enhancing microstructural features: from the nanometre and below. We are introducing the main two techniques used in our project, transmission-electron microscopy and atom probe tomography, and showcase their application on the example of a hard magnetic material.

Seeing is believing – maybe, but it is also understanding

Why advanced microscopy and microanalysis have become crucial to advancing materials science and technology

By Baptiste Gault & Leopoldo Molina-Luna



(1) Materials depicted in the form of a football field.
Source: own illustration

All materials, including those at the core of technologies for energy generation, conversion or storage, draw their properties from the arrangement of atoms that constitute the material. These atoms normally assemble into crystals in which atoms occupy specific positions – think of the organisation of players on a football field, as suggested by the illustrations in Figure (1). Sometimes, these crystals contain imperfections that can be either chemical or structural. For the former, imagine a player swapping teams on the pitch in the middle of a game and how this would disturb the transmission of the football and suddenly make their original team weaker: this demonstrates how replacing just a few atoms out of a billion changes the electronic conducting properties of silicon sufficiently to make its use in transistors possible, for instance. For the latter, imagine how much harder it is to get the ball across the field for a team with two players having received red cards: these defects in materials are called vacancies and they arise during the fabrication of the material or as a result of damage in service for example. Collectively, structural and chemical imperfections or defects form what is often referred to as the microstructure of a material – even if these defects happen to mostly exist on the near-atomic or nanoscale. It is often the imperfections in the material's structure that underpin its true physical properties. Magnets are a famous example: the coercivity of the strongest permanent magnets, e.g. Sm-Co and NdFeB [1,2], currently only reaches 20–30 % of the theoretical limit [3] – an issue referred to as Brown's paradox [4]. Why? Because of imperfections in the materials' structure.

Controlling the nature and density of defects is therefore necessary to obtain materials with new sets of physical properties. By establishing precise relationships between the processing, the microstructure and the resulting properties, the design of future materials can be made into a targeted process instead of relying on empiricism, i.e. trial and error. For instance, we know that a material's microstructure develops based on the chemistry of the system, i.e. its composition, which leads the mixture of atoms to physically adopt an organisation that satisfies both thermodynamic and kinetic constraints. The chemistry and physics of a material system are not independent from one another, and ultimately combine to provide the material with a given set of properties that make it suitable for one or more applications.

Materials science must be seen as a sum of several parts: it is chemistry and physics and engineering, and is ultimately the science of defects! Defects in the crystalline structure [5,6] include, for example, dislocations and grain boundaries [7], as well as foreign chemical species that occupy interstitial sites in the crystal structure or that substitute atoms on the lattice (Fig. 1) or form secondary phases. Overall, these general considerations imply that assessing the microstructure of a material at all stages of its synthesis and processing, as well as over the course of its operation service. This is crucial to understand a material's set of properties, how they evolve, and potentially predict the lifetime of engineering components made from this material. However, this is not done systematically, in part because of the challenges associated with the required measurements: the characteristic scale of the property-controlling microstructural features requires advanced instrumentation and expertise. Both the structure and composition of a material must be assessed down to the atomic scale.

What do we do?

Our Collaborative Research Centre TR270 has a strong emphasis on the design of materials with controlled, novel sets of physical properties. These must be based on detailed observations of these materials in correlation with property measurements in order to guide their optimisation. To do this, some of the most advanced microscopy techniques are applied to help contribute to all other materials development and fabrication projects. Two advanced techniques are being used primarily: transmission electron microscopy (TEM) and atom probe tomography.

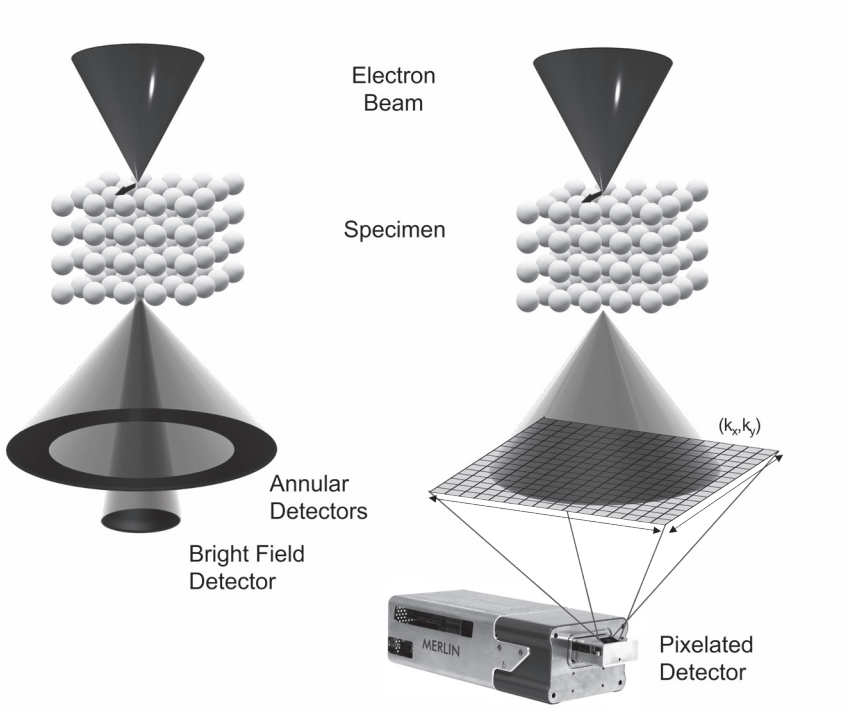
(Scanning) Transmission electron microscopy and related techniques

The impact of electron microscopy on materials research and technology cannot be overestimated. Multiscale and correlative approaches are now more essential than ever for establishing structure-property correlations in materials for energy technology and are fundamental to improving and tailoring the properties of materials. The ability to investigate materials down to the atomic level allows us to study the role of defects. Crystal lattice defects (defects in short) are usually classified according to their dimensions. Zero-dimensional defects or 'point defects' are, for example, vacancies and interstitials. One-dimensional defects include all kinds of dislocations, such as: perfect dislocations, partial dislocations (always in connection with a stacking fault), dislocation loops, grain boundary and phase boundary dislocations. Two-dimensional defects comprise stacking faults (SF), grain boundaries in the crystals of a material or phase, phase boundaries and a few special defects such as boundaries between ordered domains. Three-dimensional defects include precipitates, usually involving impurity atoms, voids (little holes, i.e. agglomerates of vacancies in three-dimensional form) which may or may not be filled with a gas, and special defects, e.g. stacking fault tetrahedra and tight clusters of dislocations.

There has been significant interest in the study of dynamic processes in smart energy materials

and devices, where the properties can be controlled by an external stimulus. For example, the possibility to manipulate the electronic band structure, magnetic spin and catalytic properties of such materials opens up a plethora of new applications. The nature of these dynamic materials requires operando microscopy techniques to characterize their physical properties while simultaneously measuring their functional performance. Recent technological and computational advances in transmission electron microscopy are transforming which dynamic material science processes and phase changes can be explored. In combination with theoretical methods such as first-principles calculations, phase-field models, micromagnetics, finite-element based modelling and simulations, the application of in situ/operando TEM techniques that include heating, biasing, cooling, magnetic fields and mechanical testing to induce and probe phase transitions in functional materials and devices at the nanoscale helps unravel the structure and properties of materials down to the atomic scale. Furthermore, as data collection, analysis and the recording of dynamic information is becoming increasingly demanding, computer-aided image analysis and big data processing, including analytics based on artificial intelligence algorithms, are becoming increasingly important to understand the fundamental physics governing the nano-to-atomic scale phase transitions of functional materials and devices.

Figure (2) shows diagrams illustrating scanning transmission electron microscopy (STEM) modes. By implementing novel detector technology, such as direct electron detectors (DED). The full distribution of electrons collected at each scanning point can now be simultaneously acquired. This means the newest STEM is now four-dimensional scanning transmission electron microscopy (4D STEM). In this method, an electron probe

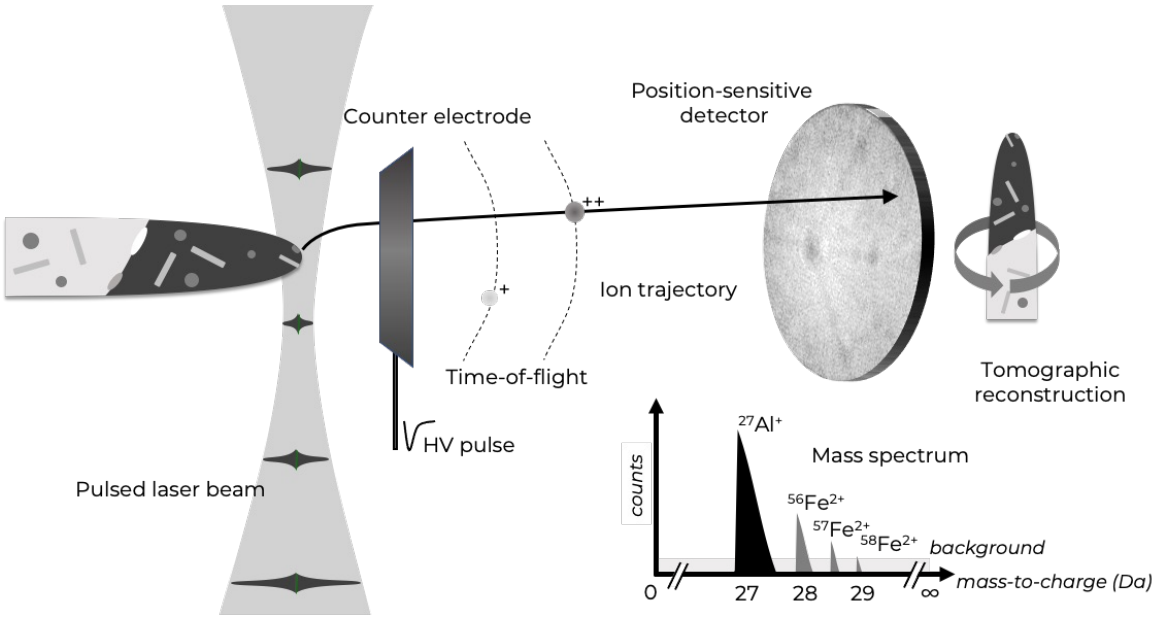


(2) Schematics of scanning transmission electron microscopy
Source: own illustration

rasters over the sample and utilizes a pixelated electron detector to capture a convergent beam electron diffraction (CBED) pattern at each scan location. This technique captures a two-dimensional reciprocal space image associated with each scan point as the beam rasters across a two-dimensional region in real space, hence the name 4D STEM. Its development was enabled by evolution in STEM detectors and improvements in computational power. The technique has applications in visual diffraction imaging, phase orientation and strain mapping, and phase contrast analysis, among others.

Atom probe tomography

Atom probe tomography originated from field-ion microscopy, the first technique to provide direct images of individual atoms in the 1950s. Atom probe tomography is a burgeoning microanalysis technique, which maps the distribution of the elements constituting a material with a precision that is better than 1 nanometre in three-dimensions. Atom probing has, in principle, no lower or upper limits in terms of the mass of the elements that can be analysed. Thus, it can be used to study where hydrogen hides inside materials, which has been a strong focus of the group at the Max-Planck-Institut für Eisenforschung over the past five years. Another field of application is the examination of very heavy elements including, for example, uranium. In this field, there is very interesting literature on using the decay of 238U to 206Pb to date some of the oldest minerals on Earth, some of which even come from Mars [8]. Primarily a compositional mapping tool, atom probe tomography can provide images of chemical segregation to defects, and their precise structure can be obtained by using transmission electron microscopy directly on the same specimen [9]. From approximately two dozen research groups with the required instruments in 2000, the community has grown to over 80 by 2022, including more than a dozen groups in leading semiconductor and steel companies, allowing a larger user base to use this technique to analyse a much broader range of materials systems.



(3) Schematic of an atom probe
Source: own illustration

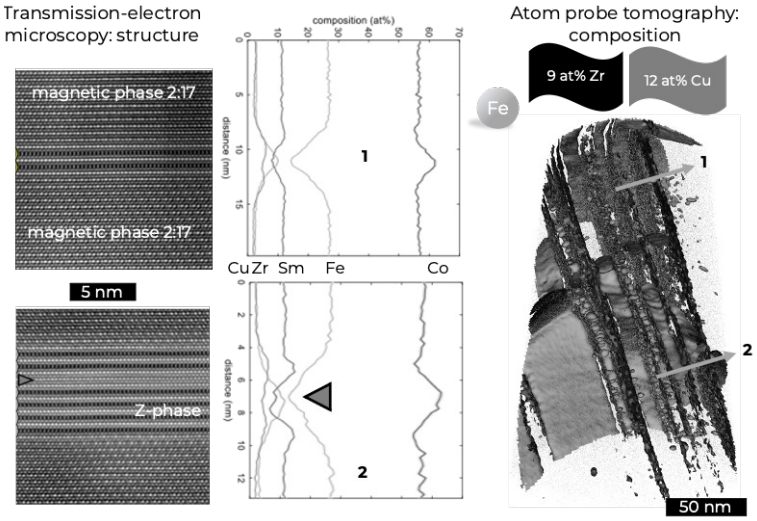
In atom probe tomography, the atoms that constitute the surface of a sharp, needle-shaped specimen are ionized and desorbed by the application of an intense electrostatic field. The ions that are generated are accelerated away from the surface, with the specimen itself acting as ion optic, with no additional lenses, projecting the ions nearly radially onto a position-sensitive, time-resolved particle detector. With specimens having an end radius of the order of less than 100 nm, this projection is well defined and, with a magnification in the range of millions, it nearly allows imaging of interatomic distances, i.e. 10–10 m. In addition, the flight time of an ion from the specimen's apex to the detector is proportional to its mass and its charge: for a given amount of energy a heavy ion is slower and hence its flight is longer than that of a light ion, and the more charge an ion bears, the more energy it acquires and hence the faster it gets. To enable the measurement of this time of flight, high voltage pulses lasting approximately 1 ns or laser pulses lasting approximately 10 ps are used to trigger the departure of the ions.

Ultimately, the information on the time of flight and the impact position are combined to build a point cloud in which each point is a single atom that was identified and repositioned with a precision better than 1 nm. This is summarized in Figure (3).

So why does this matter?

We will use the example of one of the strongest permanent magnets, which is made up of a mixture of complex magnetic phases containing the rare-earth element samarium (Sm) and the common magnetic elements cobalt (Co) and iron (Fe) to illustrate the importance of the previously described developments. The magnetic properties can be improved by making the material into an assembly of individual magnets with a size of a few tens of nanometres. For this magnet to lose its properties, it would not only be necessary to make one magnet inefficient but billions of them. Each of the small magnets is confined by phases with different magnetic properties. One such phase is the so-called Z-phase that contains zirconium (Zr) and forms large plates crossing through the microstructure [10]. This phase's atomic structure as revealed by transmission electron microscopy is shown in Figure (4). However, during the formation of some of these plates, multiple layers can form and result in defects in the stacking of the atomic layers (see arrow). This image does not provide information on elemental distribution. An atom probe analysis of the same material reveals the distribution of species in 3D and these Z-plates are visible as a dark isoconcentration surface. The larger plates that are likely to have defects, have a different concentration of Sm and Co and also a different distribution at the interface with the surrounding phase. These differences can potentially make this defected plate less effective at demagnetisation.

With input from the combination of transmission electron microscopy and atom probing, both atomistic and mesoscale, physics-based simulations can be performed to understand the fundamental properties of the magnet. These results then help us inform the design and processing of the next generation of materials – for example, how can we manipulate the composition of the magnet to avoid these defects?



(4) Combining scanning transmission electron microscopy and atom probe tomography in the analysis of hard magnetic materials.
Source: own illustration

Zusammenfassung

Werkstoffe sind komplexe hierarchische Anordnungen von Atomen. Defekte in diesen Anordnungen verändern die Eigenschaften des Materials – und dies teilweise dramatisch. Um den Entwurf der nächsten Generationen von Werkstoffen und Geräten zu steuern und gleichzeitig das kostspielige und zeitaufwändige „Trial-and-Error"-Verfahren zu vermeiden, ist es von entscheidender Bedeutung, Werkstoffe auf der Skala zu beobachten, die für die eigenschaftsverbessernden mikrostrukturellen Merkmale relevant ist: im Nanometerbereich und darunter. Wir stellen hier die beiden wichtigsten Techniken vor, die in unserem Projekt zum Einsatz kommen: die Transmissionselektronenmikroskopie und die Atomsondentomographie. Ihre Anwendung demonstrieren wir am Beispiel eines hartmagnetischen Materials.

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The authors

After a PhD in physics obtained from the University of Rouen (2006) under the guidance of Prof. François Vurpillot, where **Baptiste Gault** contributed to developing a new generation of pulsed-laser atom probe microscopes, he worked as a the Atom Probe Scientist at the Australian Centre for Microscopy and Microanalysis at the University of Sydney from 2007–2009 and 2010–2012 (on a joint position with ANSTO). In-between, he was a Marie Curie postdoctoral fellow at the Department of Materials, University of Oxford where he worked on the analysis of thermoelectric materials by atom probe. In 2012, he was appointed Assist. Prof. at McMaster University in Canada, but quit after 6 months. From Dec. 2012 – Dec. 2015, he interrupted his research career to work as Senior Publisher with Elsevier Ltd. in Oxford. During that time, he became an academic visitor at the Department of Materials, University of Oxford. On 1st January 2016, he became the Group Leader for Atom Probe Tomography at the Max-Planck-Institut für Eisenforschung in Düsseldorf. Since October 2018, he also holds a part-time appointment at the Department of Materials, Imperial College London. He holds an ERC-CoG grant and received the Leibniz Prize 2020 for his work on the development of the pulsed-laser atom probe tomography.

Leopoldo Molina-Luna obtained a Masters Degree in Physics (2003) at the University of Stuttgart, Germany, and the Max Planck Institute for Solid State Research. For his PhD, he joined the Electron Microscopy and Applied Materials Science Group of Prof. Oliver Eibl at the Institute of Applied Physics of the University of Tübingen, Germany. From 2010–2012, he worked as a Post-Doctoral Research Fellow at the Electron Microscopy for Materials Science (EMAT) Research Group of the University of Antwerp, Belgium. His fellowship was funded by the ERC Advanced Grant Counting Atoms in nanomaterials (COUNTATOMS) of his supervisor, Prof. Guustaf Van Tendeloo. In 2013, he joined the Technical University of Darmstadt (TU Darmstadt), as a Post-Doctoral Researcher. In 2018, he was awarded an ERC Starting Grant (FOXON) and was promoted to Assist. Prof., starting his own research group. In 2020, he obtained an ERC Proof-of-Concept Grant (STARE) and an MIT-Germany Seed Fund. Currently, he is Head of the Advanced Electron Microscopy (AEM) Division at the Institute of Materials Science and Head of the In Situ Microstructural Analytics Lab of the Center for Reliability Analytics (CRA) at TU Darmstadt. In 2023, Prof. Molina-Luna was awarded an ERC Consolidator Grant. He has been an Invited Speaker and Symposium Organizer at numerous Electron Microscopy and Materials Science Conferences and Workshops. His current research interests and efforts are focused on understanding Structure-Property Correlations in Functional Materials and Devices and on the development of MEMS-based in situ/operando TEM.

Leopoldo Molina-Luna. Foto: Alexander Zintler

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