3D imaging of crystal defects

A clever combination of existing techniques has produced three-dimensional atomic images of individual platinum nanoparticles, disclosing the atomic structure of crystal defects within them.

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Crystals without defects are the 'Stepford wives' of materials science: all too perfectly, almost robotically, ordered, and relatively uninteresting. However, when one adds defects to these perfectly ordered solid-state arrangements of atoms or molecules, the materials acquire useful attributes, including the altered conducting or optical properties of semiconductor devices. But although well-tested theories exist to account for these defects at the atomic level, imaging them, and in particular doing so non-destructively, has proven a challenge. In a paper published on Nature's website today, Chen et al.1 have made remarkable strides in producing three-dimensional (3D) images at atomic resolution of a number of structural defects inside a solid crystalline platinum nanoparticle.

Crystallography has a distinguished history of using macro-observational data — for example, measuring the interfacial angles in naturally occurring crystals such as rock salt or pyrite — to infer the existence at the atomic scale of 3D ordering in these solids. In the late eighteenth and early nineteenth centuries, French mineralogist René-Juste Haüy postulated that these naturally occurring crystals were composed of well-ordered assemblages of polyhedra, each of which was composed of elemental atoms2. Almost exactly 101 years ago, this was confirmed in the famous experiment3 of Friedrich, Knipping and von Laue, in which a beam of Wilhelm Röntgen's newly discovered X-rays was directed at samples of crystalline copper sulphate and zinc sulphide. The X-rays did not just pass through these crystals, but rather diffracted through them, producing ordered arrays of spots on a recording film. The location of these spots on the film corresponded to diffraction of the X-rays by individual, ordered atomic planes4, and confirmed the existence of atomic ordering in crystals.

Research in the intervening century has often tended to focus on the imperfections — the breakdown of local order — in these atomic arrays. Such imperfections can take the form of missing atoms (vacancies), atoms sitting in small gaps in these ordered arrays (interstitials) and many extended defects, of which the most common are dislocations (essentially, micro-cracks following specific allowed paths within the crystals) and interfaces including low-angle grain boundaries and twins5. Researchers have imaged these dislocations using optical or electron microscopy, or X-ray-diffraction imaging techniques. Although they can image the extent of dislocations6, such techniques are incapable of imaging or producing meaningful measurements of the atomic structure of these defects.

The work by Chen et al. builds on a technique known as electron tomography. In this, a two-dimensional (2D) slice image of the sample under test is acquired using a fixed angle between the sample and the electron beam that passes through and undergoes diffraction. Thereafter, the sample is tilted at different angles with respect to this 'zero position' and a series of these 2D projections is recorded. The 2D images are then combined to produce a 3D image of the object. Until now, the ultimate spatial resolution of the 3D image has been limited by the steps in the sequential tilting of the sample, although this has been improved on by the development of what is known as equally sloped tomography (EST). In this approach, the tilt series of images is acquired by altering the tilt angle using an algorithm that ensures that the alteration occurs with equal slope increments6,7.

Another problem commonly encountered is that the acquired images are noisy (they possess a low signal-to-noise ratio), which greatly impedes the 3D rendering and impairs the spatial resolution. This signal-to-noise problem can be lessened by using mathematical operations known as Fourier transforms. These are used to relate the 3D $x$–$y$–$z$ positional coordinates of the recorded image pixels to the 3D occurrence of their spatial-frequency components. Smooth variations in the pixel intensities across the image are termed low-frequency variations, whereas sharper, more regularly occurring ones are termed high-frequency variations. The Fourier-transform methods can extract this frequency information and filter those components that have a deleterious impact on the signal-to-noise ratio.

To overcome the signal-to-noise problem in their work, Chen et al. have subjected the EST images to Fourier transformation and used a 3D Fourier filtering method that identifies the Bragg peaks recorded on the EST images (Bragg peaks are electron-diffraction peaks that are the equivalent of the most commonly occurring spatial frequencies). This method also cleans up the data around the peaks and applies an inverse Fourier transform that converts the data back into the $x$–$y$–$z$ space to produce spatially sharper 3D reconstructions.

The major contribution of Chen and colleagues’ work is that it combines techniques that are already available, namely EST and 3D Fourier filtering, to produce images of most of the platinum nanoparticle, which has a volume of approximately 850 cubic nanometres. The authors have proved the existence of atomic-size steps at the boundaries between regions known as twins inside the nanoparticle (these twins comprise regions in which the atomic ordering within each twin is perfect but the twins themselves differ from each other in their local atomic arrangements). In addition, they have produced what I believe are the first images of the 3D atomic structure right at the core of two types of well-known dislocation — edge and screw dislocations — in the nanoparticle. Many of us remember materials-science lectures and textbooks in which we saw classical 3D block images of an edge or a screw dislocation (Fig. 1), but it is remarkable to see this realized for individual atoms (see Figs 3 and 4 of the paper).

Figure 1 | Edge dislocation in a cubic crystal. This type of crystal defect is caused by the insertion of an extra atomic plane. Chen et al.1 imaged edge dislocations at atomic resolution in a platinum nanoparticle that has a decahedral, rather than a cubic, atomic lattice.

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Looking to the future, of particular interest for this 3D Fourier electron-tomography technique would be the development of a capability to map the exact location of every atom in a crystal. This is achievable to some extent in macromolecular or protein crystallography, although in these situations researchers have a priori knowledge of the molecular peptide sequence and stereochemistry, which helps greatly in refining the atomic positional modelling. The extension of 3D Fourier electron tomography to structures larger than nanoparticles should also be possible in principle, because the technique seems to be mainly constrained by electron scattering, and so imaging should depend chiefly on the electron-beam energy and the composition of the material under test.

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