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Materials analysis

Good vibrations

A newly constructed electron-energy monochromator for an atomic-resolution transmission electron microscope has resolved spectroscopic signatures of chemical-bond vibrations which are spatially highly localized. See Letter p.000

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It is extremely rare for developments in instrumentation to deliver an order of magnitude improvement in resolution or sensitivity for a particular analytical technique, whilst maintaining existing performance in other areas. As such the paper of Krivanek *et al.*1 on page 000 of this issue, focusing on high-energy-resolution electron energy loss spectroscopy (EELS) in an electron microscope, promises a new territory for experimental investigation of both fundamental physics and the structure of advanced materials at the atomic scale.

The work is a true collaboration between a small manufacturer of electron microscopes and a number of academics, including teams from two US universities who have recently installed this instrumentation. It represents a good example of a research community working together to drive forward a particular technique. The paper describes the practical implementation of a design2,3 for an electron monochromator —a device that produces an electron beam that has a narrow electron-energy distribution. The electron monochromator acts on the high-energy electron beam of a scanning transmission electron microscopethat is corrected for aberrations in the lens that focuses the electron beam into a small probe of atomic dimensions4.

In a scanning transmission electron microscope (STEM),a high-energy electron probe is transmitted through a thin specimen, undergoing energy losses owing to scattering from atoms in the sampled volume. The probe is scanned over the specimen to form images of it as a function of probe position. If an electron spectrometer is added to a STEM, a spectrum of the transmitted electron intensity versus energy loss — which is EELS — is also obtained.Krivanek and colleagues show that, with the inclusion of appropriate energy-stabilization schemes, the monochromator design that they have implemented is able to achieve an electron-energy resolutionfor EELS in a STEMof around 10 millielectronvolts (Fig. 1), whilst maintaining a sufficiently small probe diameter containing enough electron current to maintain a capability for atomic-resolution imaging and analysis.

With anatomic-sized probe, STEM imaging usingelectrons scattered from atomic nuclei through high anglescan already generatedirectly interpretable maps of the projected atomic structure of thin crystalline samples. In most materials, however, these images tend to be dominated by scattering from the heavier elements in the samples, making precise location of light elements difficult. EELS is an established technique in STEM imaging***[ok?]*** for studying electronic excitations in thin samples which are induced by the high-energy electron beam5. Such EELS spectracan already provide maps of the distribution in elemental composition and chemical bonding at atomic resolution in two and more recently three dimensions.

The electron-energy resolution for EELS demonstrated by Krivanek *et al.* now enables the resolution of energy losses associated with lattice vibrations in solids, in particular those related to longitudinal optical phonons6. These are lattice vibrations in the plane of the thin sample which are incoherent (out of phase) motions of the atoms arising when neighbouring atoms in the lattice have different charge or mass.

Up until now, lattice vibrations were something electron microscopists have only had to worry about in terms of the sample damage that they induce, or in matching experimental images to simulations7. However, the main point here is that optical phonons are key signatures of chemical bonds, particularly those involving light elements such as hydrogen, as is well-established by the techniques of infrared and Raman (optical) spectroscopy. The implication is therefore that STEM/EELS may provide a potential route for the direct mapping of chemical bonding, including that associated with light elements at near-atomic resolution.

This achievement would present tremendous benefits in a number of highly topical areas of research into new advanced materials and devices. The improvements in overall energy resolution in EELS will undoubtedly aid the study of the local spatial variation of energy-band gaps in semiconducting structures, and the identification of localized collective oscillation of electrons in ‘plasmonic’ structures for light capture.The ability to detect and map light elements including hydrogen could extend the existing capability of analytical electron microscopy for the study of organic materials including polymers and pharmaceuticals, as well as energy-storage materials, if issues associated with electron-beam-induced damage can be addressed. Directly measuring phonons could potentially help the study of chemical interactions in reactions involving the surfaces of nanoscale heterogeneous catalyst particles and the investigation of the transmission of lattice vibrations across micro- and nanostructural features, such as interfaces and defects in thermal and optical materials. As with the emergence of any new technique, many additional research areas may ultimately prove to be the most fruitful.

Existing theory suggests that electrons having undergone phonon scattering would be scattered through large angles and the resulting phonon signal would be spatiallyhighly delocalized, preventing atomic-resolution analysis. However, Krivanek and colleagues present some initial findings which, together with recent theoretical predictions8, suggest that, under appropriate conditions, the phonon signal may be sufficiently localized to study vibrations at a spatial resolution better than that achieved by scanning probe tip-enhanced vibrational spectroscopies9. The authors observed an exponential delocalization of the phonon signal as an electron probe is moved away from the surface of a sample and into the surrounding vacuum. However, there seems to be a more localized component of the signal that peaks in intensity close to the surface itself, and the researchers discuss a possible experimental geometry for signal collection which would enhance this more localized contribution. Furthermore,if the probe is inside the sample, it appears that the delocalization may be screened at the interface between two materials with different types of electrical properties.***[ok? and are these materials inside the sample? – yes these materials make up the sample]***

The authors also demonstrate a method for remotely exciting such phononsat a surface using the inherent delocalization of the signal; here the beam is located in the vacuum close to the edge of a sample which may potentially mitigate against electron-beam-induced damage of radiation-sensitive samples. These experiments investigating the spatial resolution of thephononsignal represent a clear example of experiment leading theory in terms of the interpretation of the results, and is indicative of the new experimental landscape which this development in instrumentation unfolds. Undoubtedly many more exciting experiments with this new technology will follow in the forthcoming years, aided by the delivery later in 2014 of a third-generation instrument to a shared user facility: the UK National Centre for Aberration Corrected STEM — SuperSTEM10 at Daresbury Laboratories, which is funded by the Engineering and Physical Science Research Council as a mid-range facility. I look forward to the community charting this new frontier of research.

**Figure 1 | Spatially resolved vibrational spectroscopy.** In a scanning transmission electron microscope corrected for aberration effects, a focused beam of high energy electrons is incident on a thin sample, forming a probe of atomic dimensions. The electron beam transmitted through the sample (which in this case comprises different types of atoms and bond lengths)***[ok?]*** contains electrons which have experienced energy losses due to (inelastic) scattering events with atoms in the sample. These electrons can be dispersed in energy using a magnetic prism spectrometer (not shown), enabling a spectrum of scattered electron intensity versus energy loss to be obtained.Krivanek *et al.*1 show that, if the incident electron beam is energy-monochromated, then the energy spread associated with a beam that undergoes zero energy loss can be improved from 250 millielectronvolts (meV) to about 10 meV. This improvement allows the detection of spectroscopic signatures of spatially localized chemical-bond vibrations (phonons).

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