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Energy-Filtered High-Angle Dark Field Mapping of Ultra-Light Elements

T.C. Lovejoy[1], N. Dellby[1], T. Aoki[2], G.J. Corbin[1], P. Hrncirik[1], Z.S. Szilagyi[1] and O.L. Krivanek[1]

[1] Nion Co., 1102 8th St, Kirkland, WA 98033, USA
[2]Center for Solid State Science, Arizona State University, Tempe, AZ 85287, USA

Using the High Energy Resolution Monochromated EELS-STEM (HERMES) system we recently introduced [1] together with Gatan's Enfinium spectrometer with upgraded ultra-high stability power supplies [2], energy resolution as low as 14 meV has been demonstrated in electron energy loss spectra (EELS) acquired in 0.1 s (Fig. 1), and sub-20 meV resolution has become typical for routine acquisitions of several seconds. Because of this performance, new signals, previously obscured by the EELS zero loss peak, are becoming accessible. Here we present preliminary results on energy-filtered high-angle dark field (HADF) imaging that is likely to lead to routine hydrogen mapping. In a related presentation at this meeting, we discuss phonon spectroscopy [3].

When an electron is scattered to a finite angle θ by incoherent Rutherford scattering from an atomic nucleus, a small amount of energy is transferred to the nucleus. Using the "impulse" approximation, in which the nucleus is considered as free, the energy ΔE_R transferred to the nucleus is:

$$\Delta E_R = 4\sin^2(\theta/2)\left(\frac{m_e}{m_a}\right)E_o^* \qquad eq.1$$

where E_o^* is the relativistically scaled incident electron energy, and m_e/m_a is the ratio of the electron mass to the atom mass. m_e/m_a is 1/1836 for hydrogen and up to 200x smaller for other elements. At 100 keV, for carbon or heavier elements and scattering angles less than 100 mrad, ΔE_R <50 meV. Because of this small value, the energy loss of Rutherford-scattered electrons has typically been thought unavailable as an analytical signal in electron microscopy. With the newly available energy resolution of <20 meV, this now calls for a reevaluation.

The expected loss, ΔE_R, from Eq. 1 is shown in Fig. 2 as a function of the scattering angle for 60 keV electrons for hydrogen, helium, and carbon. Two important points are apparent. First, over an angular window between 80 and 100 mrad, the ΔE_R values for the different elements are separated by more than our present energy resolution, meaning that elemental discrimination should be possible at medium to high collection angles. Second, ΔE_R for hydrogen is separated from carbon by ~100 meV in the 50-70 mrad range, implying that hydrogen detection should be possible using EELS collection angles only about 2x larger than is typical for modern STEM-EELS.

Figure 3 shows a "proof of principle" experiment: using ΔE_R to distinguish between Au and C. The sample consisted of ~5nm gold particles supported on carbon film ~20 nm thick. It was illuminated by a 60 keV probe of about 1 nm diameter, ~18meV energy width and 12 mrad convergence semi-angle. The outgoing beam was tilted 120 mrad off axis so that a circular 12 mrad semi-angle EELS aperture defined effective collection angles roughly 100-140 mrad, and hence expected values of ΔE_R for carbon ranging from ~25 to ~50 meV. The scattering signal from the gold areas (ΔE_R=2 meV) was used as a reference for zero energy loss. Due to the difficulty of tuning EELS aberrations at such high scattering angles (and correspondingly low signal levels), the observed energy width was broadened to ~40 meV. Figure 3A

shows a normalized spectrum from gold only (line), with the uniform carbon background subtracted, and the spectrum from carbon areas (filled), with a sizeable contribution from the Au. Fig. 3B shows an image for an energy window ±10 meV wide that was centered on zero energy loss, and Fig. 3C shows an image for a window centered on 85 meV loss. Fig. 3B shows gold particles clearly; Fig. 3C shows only the carbon support film.

We note that ΔE_R is proportional to E_0^{-2} and that the above experiments would therefore have been easier to carry out at 100 or 200 keV. To optimize the collection geometry into the spectrometer, an annular aperture spanning a small range of angles would be ideal, and we intend to use such apertures in the future. The challenge of correcting the EELS aberrations for collection angles spanning up to ±100 mrad and more will then be considerable even for the latest spectrometers. In summary, mapping by energy-filtered high-angle dark field imaging now appears to be possible for ultra-light elements such as H and He, and also for light elements such as C. Hydrogen mapping may prove to be especially useful in view of the element's importance to sustainable energy technologies, and the dearth of analytical signals available for mapping it in the electron microscope.

References:
[1] OL Krivanek et al., Microscopy **62** (2013) 3-21.
[2] OL Krivanek et al., Proceedings 2013 EMAG meeting, in print (2014).
[3] OL Krivanek et al., these proceedings (2014).
[4] We gratefully acknowledge the use of facilities within the LeRoy Eyring Center for Solid State Science at ASU, and grant DE-SC0007694.

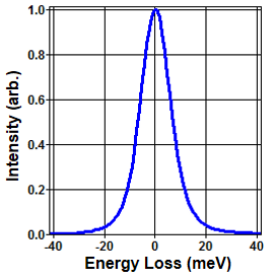

Figure 1. Zero-loss peak acquired in 0.1s at 60 keV showing 14 meV FWHM

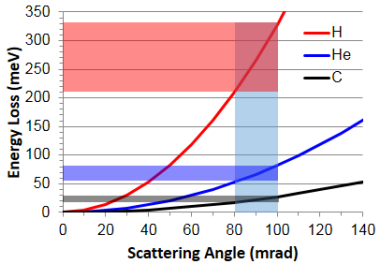

Figure 2. Expected energy losses for 60 keV electron scattering as a function of angle for H, He, and C. Vertical bar indicates 80-100 mrad collection, horizontal bars indicate the corresponding well-separated energies.

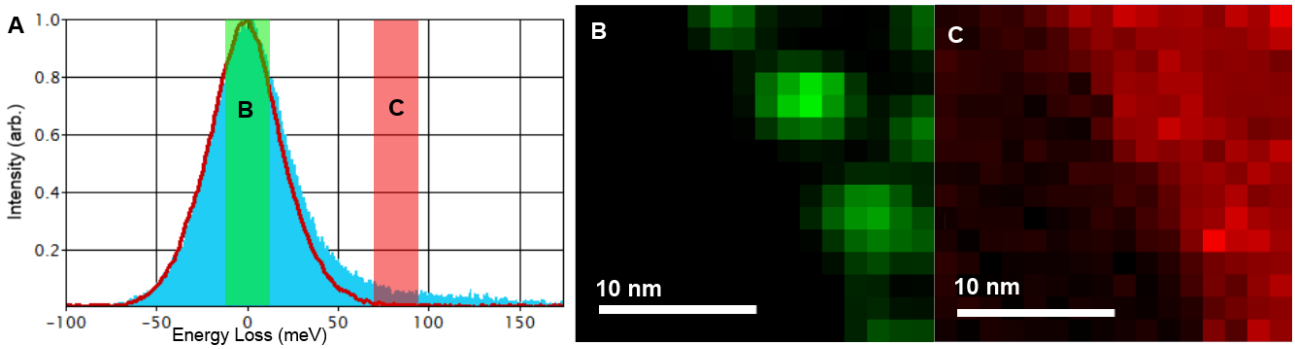

Figure 3. (A) integrated spectrum for mostly carbon regions (filled) and from gold regions with uniform carbon background subtracted (line) (B) 20 meV wide slice centered at ΔE=0 (C) 20 meV slice centered at ΔE=85 meV, all from the same spectrum image.