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Short communication

Vibrational-loss EELS and the avoidance of radiation damage

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ABSTRACT

We discuss vibrational-mode energy-loss spectroscopy using an aloof beam of electrons positioned a small distance b from the edge of a specimen in a probe-forming TEM or STEM equipped with a high-resolution monochromator. Due to the delocalization of inelastic scattering, a strong vibrational-loss signal can be recorded without causing significant damage to a beam-sensitive specimen. Calculations for $b=20$ nm suggest that damage is reduced by typically a factor of 1000 (relative to electrons of the same energy transmitted through the specimen) for the same signal strength and spatial resolution. About 50% of the vibrational-loss signal comes from material lying within a distance b of the edge of the specimen and extending over a length $2.5b$ parallel to the edge. Although energy-filtered imaging appears impossible in aloof mode, an undersampling STEM technique is proposed, taking advantage of scattering delocalization to obtain a vibrational-loss image that leaves most of the imaged area undamaged.

1. Introduction

Improved monochromator designs have made possible electron energy-loss spectroscopy in a transmission electron microscope (TEM-EELS) with an energy resolution down to about 10 meV [1]. This capability allows local measurement of defect states within the band gap of semiconductors and insulators [2] together with more accurate measurement of energy gaps [3]. It also permits vibrational-mode energy-loss spectroscopy (vibEELS), with the prospect of obtaining atomic-bonding information similar to that provided by infrared spectroscopy or reflection-mode high-resolution energy-loss spectroscopy (HREELS) but at higher spatial resolution. Related tip-based spectroscopies also provide high resolution [4] but they typically sample only a thin surface layer, whereas transmission techniques extract information from within the interior of a specimen. In addition, TEM-EELS covers a wide range of energy loss (equivalent to infra-red up to x-ray photon energies) and allows diffraction and other techniques to be used in the same instrument.

Transmission-mode vibEELS data was obtained many years ago by Boersch, Geiger and colleagues, initially from gases [5–7] and then from various types of solid specimen [8–11], using an apparatus that generated a 30-keV beam of electrons with a diameter of the order of 10 μm. Use of a conventional or scanning TEM allows similar data to be obtained from much smaller regions of specimen, within the limitations imposed by radiation damage and by delocalization of inelastic scattering [12]. Although delocalization is often a disadvantage, we discuss in this paper how it can be beneficial in reducing the radiation damage that would otherwise occur in beam-sensitive specimens, consistent with recent experimental findings [1,31,34].

2. Delocalization of inelastic scattering

Using 33-keV electrons and gaseous samples of CO_2, N_2O and C_2H_4, Geiger and Wittmaack [7] measured scattering cross sections for several vibrational peaks, using a very small collection aperture (semiangle $\beta=0.11$ mrad). These cross sections were within a factor of two of those calculated using dipole theory, which predicts a Lorentzian angular distribution of intensity: $dI/d\Omega \propto 1/(\theta^2+\theta_E^2)$, whose halfwidth is the characteristic angle $\theta_E \approx E/(2E_0)$. For $E < 0.5$ eV and an incident-electron energy $E_0 = 60$ keV, θ_E is less than 5 μrad and as a result of this very narrow angular width, the scattering is expected to be relatively delocalized.

To understand why, suppose θ_{50} is the median angle of inelastic scattering, such that half of the scattered electrons acquire a transverse momentum within the range $\Delta p_x = \pm(h/\lambda)\theta_{50}$, where λ is the de Broglie wavelength of the incident electrons and h is the Planck constant. The Heisenberg uncertainty relation ($\Delta p_x\, \Delta x \approx h$) then suggests that the region scattering 50% of the electrons cannot be defined to better than about $L_{50} \approx \Delta x \approx (0.5)\lambda/\theta_{50}$. Alternatively, the Rayleigh criterion can be used to predict a delocalization distance of $L_{50} \approx (0.6)\lambda/\theta_{50}$. For an angular distribution that is Lorentzian up to θ_c and then falls off much more rapidly, the median scattering angle is $\theta_{50} \approx (\theta_E\theta_c)^{1/2}$. The *observed* value of L_{50} is of the order of 100 nm for $E_0=60$ keV and $E \approx 0.15$ eV (a

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typical vibrational-peak energy), implying an effective cutoff angle $\theta_c \approx 0.65$ mrad $\approx 500\ \theta_E$. For comparison, θ_c/θ_E is of the order of 100 for plasmon losses and in the range 10–50 for most inner-shell losses.

Scattering delocalization is characterized more completely in terms of a point-spread function (PSF). For a Lorentzian angular distribution with a cutoff at a high scattering angle, Fourier analysis suggests [13] that this PSF is also approximately Lorentzian, with a sharp central maximum and a long tail whose intensity is proportional to $1/r^2$, where r represents radial distance from the primary-electron path. This tail extends up to the Bohr adiabatic limit $b_{max}=\gamma hv/(2\pi E)$, beyond which the intensity falls exponentially [40]. For small E, the tail contains much of the intensity, leading to a large value of L_{50}, whereas the sharp central peak offers the possibility of high image resolution [14], analogous to the atomic resolution seen in secondary-electron images recorded using a thin specimen and an aberration-corrected STEM [15–17].

There is also a possibility that non-dipole scattering (known as impact scattering in the HREELS community), whose angular distribution is broad, may provide high spatial resolution [18–22]. Indeed, recent calculations [23–26] have predicted atomic resolution from vibrational losses, subject to adequate signal/noise ratio and the absence of radiation damage. However, making use of this signal requires energy-loss spectroscopy at high scattering angles, which is technically difficult (especially at 20 meV resolution) because of spectrometer and lens aberrations. So far, vibrational spectroscopy in the STEM has used collection angles up to 15 mrad and under such conditions dipole scattering appears to predominate.

3. Aloof-beam spectroscopy

If a finely focused STEM probe is positioned at a small distance b (known as the impact parameter) just beyond the edge of the specimen, an energy-loss spectrum can be recorded in the so-called aloof mode [1,27,35,36]. This spectrum is heavily weighted towards energy-loss processes whose delocalization distance is comparable to or larger than the impact parameter. Surface losses tend to predominate over bulk losses and vibrational peaks are particularly favored, due to their large delocalization distance. Elastic scattering should have negligible effect on the aloof spectrum because its angular distribution is broad and the delocalization distance correspondingly small.

One perceived advantage of aloof mode is that radiation damage (radiolysis) to beam-sensitive materials may be reduced [32–35]. This idea was originally based on the possibility that damage to aromatic organic compounds might require K-shell excitation, implying $E > 280$ eV (corresponding to $L_{50} < 0.3$ nm). However vibEELS spectroscopy presents a more compelling case for aloof spectroscopy, since the energy losses involved correspond to $L_{50} \approx 100$ nm, compared to $L_{50} < 5$ nm for the valence-shell excitation ($E > 5$ eV) that causes radiolysis in most beam-sensitive materials. For this reason, energy-loss spectra of hydrides and nucleic acids have been recorded in aloof-beam mode [1,31,34]. However, no quantitative measurements of the benefit of aloof mode are available, so this paper aims to evaluate the situation by means of simple calculations.

Knock-on displacement damage (which predominates in electrically conducting specimens) arises from large-angle elastic collisions and the corresponding delocalization distance has subatomic dimensions. As a result, knock-on damage should be completely absent in aloof mode.

4. Dielectric formulation of energy loss

Yet another description of delocalization is provided by dielectric theory, in which energy-loss intensity is related to the photon-energy dependence of the complex relative permittivity $\varepsilon(E)$. For aloof-beam spectroscopy, the inelastic-scattering probability (per unit energy loss E) is [27]

$$\mathrm{dP/\ dE} = (t/a_0)(\pi T)^{-1} Im\{-2/[\varepsilon(E)+1]\} K_0(4\pi bE/[\gamma vh]) \quad (1)$$

where t is the specimen thickness, $a_0=0.0259$ nm is the Bohr radius, m_0 is the electron rest mass, v is the incident-electron speed, $\gamma = 1/(1-v^2/c^2)^{1/2}$ and $T=m_0v^2/2=(E_0/\gamma^2)(1+\gamma)/2$, equal to 50.9 keV for an incident energy $E_0=60$ keV. The function K_0 (a zero-order Bessel function of second kind) represents the dependence of the inelastic signal on the distance b between the electron probe and the edge of the specimen. In the case of vibrational losses, this K_0-dependence has been found to be consistent with measurements [1].

In Fig. 1, the b-dependence of Eq. (1) is shown on a logarithmic scale, for $E = 0.1$ eV and 0.4 eV (defining the region containing most vibEELS peaks) and for a typical valence-electron loss ($E = 20$ eV). Comparison of these curves illustrates how the vibEELS signal persists at much larger impact parameters than the valence-loss signal, as seen experimentally [1].

Although the K_0 function has an exponential tail, the straight-line behavior in Fig. 1 reveals that dP/dE approximates to a logarithmic function over most of its useful range, and we can argue that this behavior is consistent with the r^{-2} dependence of the inelastic-scattering PSF. Considering a small range 2ϕ of azimuthal angles about an x-axis drawn through the probe and perpendicular to the edge of the specimen (Fig. 2), the energy-loss probability is approximately $dP/dE \propto \int r^{-2}(2\phi\, r)\, dr \propto \log(r_{max}) - \log(b)$.

As seen in Fig. 1, a nearly logarithmic b-dependence is also expected for valence-electron (plasmon) scattering and experimental evidence for this behavior is given in Fig. 3. In this case, the data were acquired with an aloof STEM probe by Zhou et al. [28] and are here replotted with a logarithmic distance scale. This experimental verification supports the assumptions we will use to calculate damage rates and the spatial resolution of aloof-mode spectroscopy.

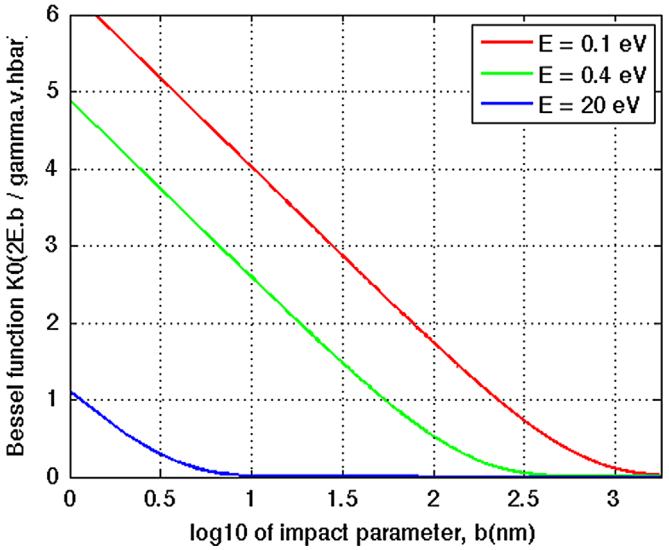

Fig. 1. Bessel function $K_0(4\pi bE/[\gamma vh])$ plotted as a function of $\log_{10}(b)$, showing how the intensity of inelastic scattering at three energy losses (0.1 eV, 0.4 eV and 20 eV) varies with the impact parameter b of an aloof probe of 60 keV electrons. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)