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Atomic resolution mapping of phonon excitations in STEM-EELS experiments

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ABSTRACT

Atomically resolved electron energy-loss spectroscopy experiments are commonplace in modern aberration-corrected transmission electron microscopes. Energy resolution has also been increasing steadily with the continuous improvement of electron monochromators. Electronic excitations however are known to be delocalized due to the long range interaction of the charged accelerated electrons with the electrons in a sample. This has made several scientists question the value of combined high spatial and energy resolution for mapping interband transitions and possibly phonon excitation in crystals. In this paper we demonstrate experimentally that atomic resolution information is indeed available at very low energy losses around 100 meV expressed as a modulation of the broadening of the zero loss peak. Careful data analysis allows us to get a glimpse of what are likely phonon excitations with both an energy loss and gain part. These experiments confirm recent theoretical predictions on the strong localization of phonon excitations as opposed to electronic excitations and show that a combination of atomic resolution and recent developments in increased energy resolution will offer great benefit for mapping phonon modes in real space.

1. Introduction

Recent developments in aberration-corrected transmission electron microscopy as well as improvements in spectrometers and monochromators [1] provide us with instruments that are capable of obtaining atomic resolution combined with electron energy loss spectroscopy (EELS) at energy resolutions of the order of 100 meV [2–4], and recently even approaching 10 meV [5]. Typical experiments focus on surface plasmons with modes as low as 0.17 eV being experimentally accessible [6]. It is also possible to probe changes in the band-gap of semiconductors at the atomic scale in semiconductor devices [7,8]. Improving the energy resolution further seems attractive in order to study phonon lattice vibrations which typically occur between a few meV and 1 eV at large scattering angles (10–1000 mrad). So far, this signal has not been (yet) resolved in standard transmission electron microscopy. Phonon spectra are however routinely studied with electron energy loss spectra on dedicated surface sensitive HREELS instruments [9]. Combining this capability with atomic resolution seems attractive as it would allow to locally observe phonon modes which is especially attractive at interfaces and defects. The common thinking in the EELS community so far has been that low loss EELS and spatial resolution contradict each other due to the effect of delocalization. Delocalization allows an electronic excitation to be excited even though the fast electron is some distance away from the scattering center due to long range coulomb interaction between the fast electron and the electrons making up the scatterer. This delocalization is described and verified in great detail and was found to scale approximately inversely proportional to the energy loss [10–12]. From this point of view, spatial resolution would suffer dramatically when going from an energy loss of hundreds of eV's (core loss EELS, typical delocalization smaller than the interatomic distance) to losses below 1 eV. Typically this delocalization argument holds in free space at edges of the sample, but its validity is strongly reduced inside materials where screening can strongly reduce its effect. It is important to keep in mind that this type of delocalization is derived for electronic transition where the fast electron excites the sample electrons to higher lying states. For phonon excitations, which are of major interest in the region below 1 eV, the situation is quite different. Here, the fast electron couples to a lattice vibration mode via Coulomb interaction, but now the delocalization is strongly reduced due to the extreme difference in mass between the fast electron and the lattice atoms. This results in high angle scattering (10–100 mrad) and strong localization of the scattering.

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Generalized phonon density of states in cubic $SrTiO_3$ were computed, the phonon spectral range extends from 0 to 120 meV, where the spectral signatures at the end of this energy range are due to the Sr–O and Ti–O bond vibrations [13]. In addition, surface optical phonons on $SrTiO_3$ were detected below 0.1 eV (57 and 92 meV) by high-resolution EELS (HREELS), and multiphonon excitations are also observed around 0.2–0.3 eV [9]. Measurements were performed by conventional techniques like infrared spectroscopy, ultraviolet Raman spectroscopy and HREELS, which are bulk and surface measurements [9,14,15]. However, the spatial resolution is a limiting factor of these techniques, with an expected resolution of a few nanometers at best [11]. More recently, localization of vibrational excitations by a high-energy electron beam has been shown to be theoretically possible by Dwyer [16]. The vibrational EELS images of H_2 and CO molecules were computed with atomic-scale spatial resolution, by using the "so-called" Moller potential for excitation of the vibrational modes.

On the other hand, preservation of elastic contrast in low-loss EELS mapping has been reported by Lazar et al. [17], where the filtered image of the zero loss peak (ZLP) intensity shows the complementary nature of the high angle annular dark field (HAADF) intensity and the elastic contrast. Furthermore, atomically resolved signatures were observed at 3 eV at high collection angle (124 mrad) and addressed as being possibly related to phonon assisted losses. In this paper, we will demonstrate that indeed subtle changes in the low loss region of an EELS spectrum recorded on a canonical sample of $SrTiO_3$ occur when scanning a focussed electron probe of atomic size on the different atomic columns. We center our attention on changes in the low-energy loss region, most remarkably below 0.5 eV. We argue the possibility of mapping "optical multiphonon states" on $SrTiO_3$ within the energy range between 0.14 and 0.5 eV in agreement with the literature [9,13]. This work should encourage the further development of very high resolution spectrometers and monochromators and shows that the combination with atomic resolution is very relevant for the study of phonon behavior near imperfections and interfaces.

2. Experimental

A monocrystalline substrate of $SrTiO_3$ with ~18–20 nm thickness was investigated using a TEM lamella prepared perpendicular to the [100] zone axis orientation by focused ion beam milling. HAADF imaging, scanning transmission electron microscopy (STEM) and EELS experiments were performed using the QuAntEM microscope at the University of Antwerp. This is an FEI Titan^3 microscope, equipped with an aberration corrector for both image and probe forming lenses, and a monochromator to optimize the energy resolution for EELS measurements up to 120 meV, as determined from the full width at half maximum (FWHM) of the ZLP. As we will be looking at very subtle changes near the zero loss peak, we performed experiments at different collection angles to study the effect of possible unwanted spectrometer aberrations. Cerenkov radiation effects were limited by working with thin samples at an acceleration voltage of 120 keV where spatial resolution performance is approximately ~1.3(4) Å (probe size) at a convergence semi-angle of 21 mrad. [18,19]. Experiments performed at 300 kV under similar conditions show strong agreement with these observations (see supplementary information). The collection semi-angle β of the spectrometer was set to ~38, 43, 129 and 225 mrad, respectively. ZLP extraction at the tail of the ZLP is notoriously difficult and error prone. To overcome this, we abandoned direct background subtraction or the use of pre-recorded ZLP spectra in favor of two alternative methods:

- Each spectrum in a spectrum image is first energy drift corrected, scaled to its maximum and then *divided* by the average spectrum obtained by summing all spectra, also scaled to the maximum. This method is extremely sensitive to changes in the spectral shape of the ZLP but leads to spectra that are somewhat hard to interpret as they show the fractional deviation from the average spectrum. Also noise amplification starts to become important for energies where the average spectrum is low.
- Each spectrum is energy drift corrected, scaled to its maximum and then a scaled version of the average spectrum is *subtracted*. Which the scaling chosen such that the difference is zero on the maximum of the ZLP. This leads to more directly interpretable spectra showing the increase or decrease of certain features near the ZLP depending on the spatial position of the probe.

3. Results and discussion

Using STEM EELS, 2D spectrum images were acquired at different acceleration voltage and collection angles. A resulting HAADF image for experiments performed at 120 keV and β=129 mrad, and its corresponding *divided* and *subtracted* 2D maps treated as described previously are shown in Fig. 1(a–c). The following panels (d–f) present normalized spectra taken from the three different positions indicated on Fig. 1b, corresponding to Sr (green), TiO (red) and O (blue) atomic columns, respectively. One clearly recognizes a subtle broadening and shrinking of the width of the ZLP when comparing the three different spectra shown on a logarithmic scale of the electron intensity (Fig. 1d). Fig. 1(e,f) shows the *divided* and *subtracted* spectra profiles in the range of energy −1 to 1 eV. Some deviation from the averaged spectrum extending to 0.5 eV on each side of the ZLP can be noticed.

In order to better filter out the changes in the spectral shape of the ZLP and improve the signal to noise ratio of the experiment, unit cell averaging was applied, averaging over a total of 16 unit cells. The resulting average unit cell HAADF image is shown in Fig. 2a, together with the spectral shape of the ZLP for a region belonging to a Sr (green), TiO (red) and O (blue) column, extracted in a similar manner as for Fig. 1. From these profiles we observe that the ZLP shows symmetric signatures in both sides of the elastic peak, *gain* and *loss* energy regions. A strong positive deviation from the average spectrum on Sr columns up to almost 800 meV is observed on each side of the ZLP, whereas a less intense positive deviation is observed on TiO columns extending only 300 meV on both sides. On pure oxygen columns a negative deviation similar to the ones observed on the Sr columns can be noticed for both data processing. This averaging improves the signal to noise ratio (SNR) in order to better observe the subtle changes when moving the electron probe over the different positions within a unit cell. The results are summarized in Fig. 2.

The same integration was applied on spectral datasets recorded at different collection semi-angles and the results are presented in Fig. 3. The experiments show fundamentally the same effects demonstrating a reproducible but subtle change in the shape of ZLP with atomic resolution. The broadening of the ZLP is observed to be highest on a Sr column, intermediate on a Ti–O column and lowest on an oxygen column on Fig. 3(left panels). We argue that changes in the energy-gain region in the middle and right panels of Fig. 3, can be attributed to thermally excited phonons as recently discussed by [20,21] and the signatures between 0.14 and 0.5 eV might be strongly related to phonon mediated energy losses, confirming the possibility to observe multiple phonon states in this energy range as reported by Baden et al. [9]. Note that for a small collection semi-angle β=36 mrad, the intensity of the Sr and TiO signatures presents similar magnitude in qualitative

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