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Surface vs. Bulk Phonons in Off-axis EELS

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Acquiring electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM) away from optic axis has been exploited to avoid surface phonons near q=0, which leads to delocalized energy loss signal and poor spatial resolution[1]. This approach has also been used for phonon dispersion measurement[2, 3] when high enough momentum resolution is provided. With a large momentum transfer, contribution from surface modes is expected to vanish, leaving bulk phonons the only signal in an off-axis EEL spectrum. However, the small energy difference between surface and bulk phonons at q=0 makes identifying their contribution a non-trivial task[4].

In this work, we have studied phonons in h-BN and $SrTiO_3$ to re-examine the surface and bulk contributions in phonon spectra by off-axis EELS. The EELS experiments were performed using a monochromated Nion UltraSTEM 200 operating at 60 kV. We have used a convergence half angle of 3 mrad in our experiments. The spatial, energy, and momentum resolutions are about 3 nm, 12 meV, and $\pm 0.4\ \text{Å}^{-1}$, respectively. With this setup, spatial and momentum resolved EEL spectra are taken from h-BN and $SrTiO_3$.

We first use h-BN, a model system, to show that surface phonon contribution still dominates phonon EELS acquired from diffracted beam. Optical phonons near an edge of a h-BN flake are shown in Fig. 1. The energy loss intensities between the transverse optical (TO, 170 meV) and longitudinal optical (LO, 200 meV) phonons are plotted as a function of distance to the h-BN flake edge, x. Variation of phonon intensity with x is clearly observed, which originates from the surface phonon polaritons propagating along the top and bottom surface, as well as those along the flake edge[4, 5]. In Fig. 1(d), the EELS results acquired from a diffracted beam is plotted in the same manner. Similar spectral features are also observed as in Fig. 1(c), suggesting that the bulk LO phonon contribution is still much less compared to the surface modes.

Furthermore, we demonstrate that bulk phonons near q=0 can be obtained from weak reflections. This is shown in Fig. 2, where EEL spectra are acquired from (200), a Bragg reflected beam and from (300), a weak reflection, of $SrTiO_3$. The upper EEL spectrum in Fib. 2(b) have three peaks that lie within the Reststrahlen band of $SrTiO_3$. They are the delocalized surface phonon polaritons. The spectrum taken from (300) show features that align well with the bulk optical phonon energy at q = 0. These results suggest that most diffracted beams carry the same information with direct beam, but surface phonons can be largely avoided at weak or forbidden reflections.

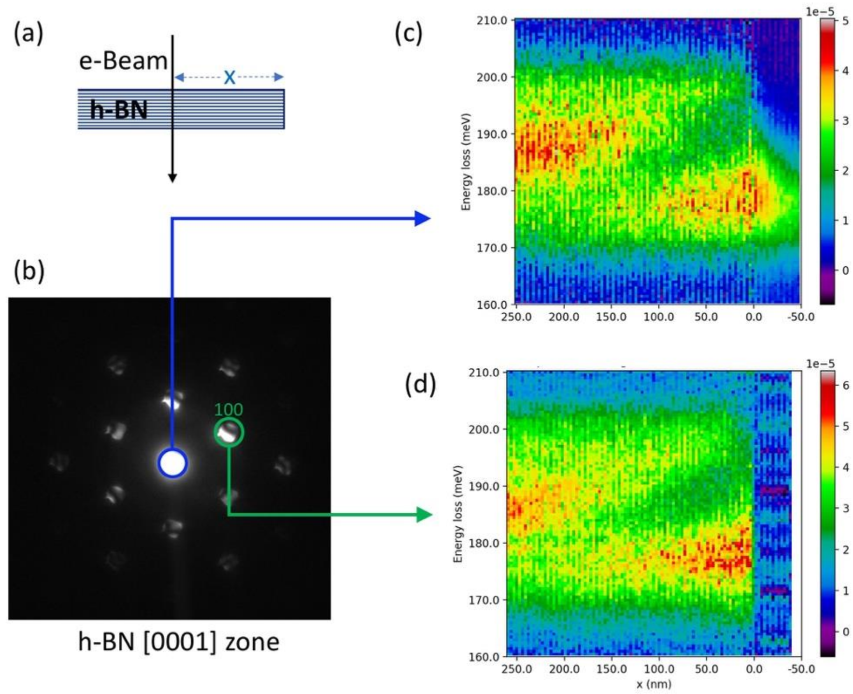

Figure 1. (a) Schematic of the EELS experiment. (b) Convergent beam electron diffraction pattern of h-BN from its [0001] zone. (c) and (d) Normalized EEL intensity from spectra acquired from the direct beam and diffracted beam at (100), shown as a function of distance towards to h-BN flake edge. EELS aperture positions for (000) and (100) are indicated by the blue and green open circle in (b), respectively.

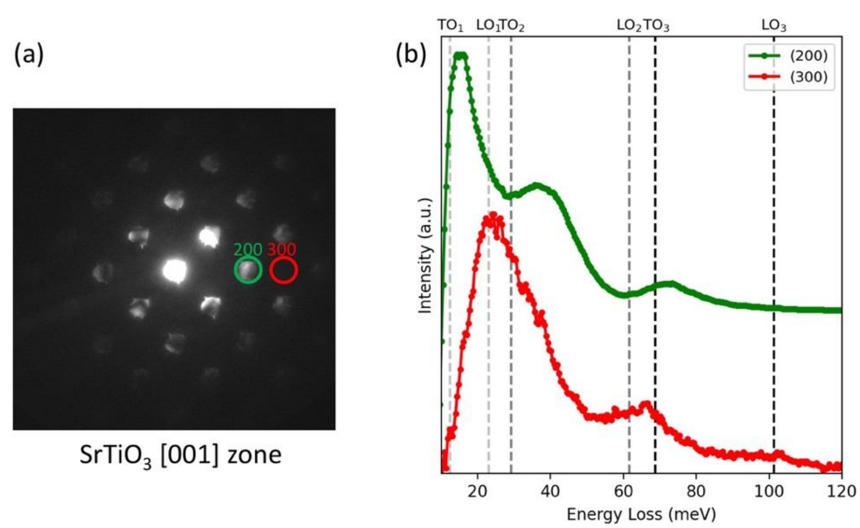

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Figure 2. (a) Convergent beam electron diffraction pattern of $SrTiO_3$ from its [001] zone. (b) EEL spectra of phonons in $SrTiO_3$. EELS aperture positions are indicated by color-matching open circles in (a). Vertical dashed lines indicate TO and LO phonon energies at Γ.

References

1. C. Dwyer, T. Aoki, P. Rez, S. L. Chang, T. C. Lovejoy and O. L. Krivanek, Phys. Rev. Lett. **117** (25), 256101 (2016).

2. S. Hage Fredrik, J. Nicholls Rebecca, R. Yates Jonathan, G. McCulloch Dougal, C. Lovejoy Tracy, N. Dellby, L. Krivanek Ondrej, K. Refson and M. Ramasse Quentin, Science Advances **4** (6), eaar7495 (2018).

3. R. Senga, K. Suenaga, P. Barone, S. Morishita, F. Mauri and T. Pichler, Nature **573** (7773), 247-250 (2019).

4. A. A. Govyadinov, A. Konecna, A. Chuvilin, S. Velez, I. Dolado, A. Y. Nikitin, S. Lopatin, F. Casanova, L. E. Hueso, J. Aizpurua and R. Hillenbrand, Nat. Commun. **8** (1), 95 (2017).

5. N. Li, X. Guo, X. Yang, R. Qi, T. Qiao, Y. Li, R. Shi, Y. Li, K. Liu, Z. Xu, L. Liu, F. J. García de Abajo, Q. Dai, E.-G. Wang and P. Gao, Nature Materials **20** (1), 43-48 (2021).

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