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PNNL-38640

Electron Energy-Loss Spectroscopy and Differential Phase Contrast Imaging with Active Decision in Multimodal Electron Microscopy

Isotopic detection at the atomic scale

October 2025

Juan Carlos Idrobo
Libor Kovarik

U.S. DEPARTMENT of ENERGY

Prepared for the U.S. Department of Energy
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Abstract

Isotopic engineering provides a powerful route to control phonon behavior in crystalline solids, enabling fundamental studies of lattice dynamics and heat transport at the atomic scale. Here, we directly visualize isotope-dependent phonon propagation in epitaxial Cr_2O_3 using aberration-corrected scanning transmission electron microscopy (STEM) combined with monochromated, high-energy-resolution electron energy-loss spectroscopy (EELS). Guided by ab initio phonon calculations, we demonstrate that optical phonon modes above 70 meV are predominantly oxygen-derived and exhibit measurable redshifts upon substitution of natural ^{16}O by enriched ^{18}O. Spatially resolved vibrational spectrum imaging reveals isotope-enriched tracer layers within Cr_2O_3 thin films, correlating isotope concentration with phonon intensity variations and vibrational energy shifts. At the nanometer and atomic scales, vibrational EELS mapping uncovers coherent phonon propagation across isotopic interfaces, consistent with theoretical phonon density of states and dispersion relations. These results establish vibrational EELS as a quantitative probe for isotope-dependent phonon transport in materials, opening new possibilities for studying energy dissipation and lattice dynamics.

Summary

This project aimed to develop a new methodology within electron microscopy for tracking isotopes at the atomic scale. By doing so, researchers could gain deeper insight into the thermal and diffusion properties of materials—such as heat management in complex oxides or atomic motion during electrochemical processes (for example, lithium migration during charge and discharge).

The central goal was to achieve isotope detection with atomic resolution using advanced electron microscopy techniques. This work was led by Juan Carlos Idrobo (University of Washington and PNNL) and Libor Kovarik, with collaborators including Sandy Taylor, Daniel Schreiber, Tiffany Caspar, Bethany Matthews, and Micah Prange.

The research design involves preparing high-quality TEM samples at PNNL and testing the core hypothesis that heavier isotopes cause a redshift in the phonon density of states of a material. By identifying where this redshift is most pronounced, researchers can determine which phonon modes are most sensitive to isotopic substitution. Ultimately, this understanding enables atomic-scale mapping of isotopic distributions within materials.

Acknowledgments

This research was supported by the Physical and Computational Sciences Mission Seed Investment, under the Laboratory Directed Research and Development (LDRD) Program at Pacific Northwest National Laboratory (PNNL). PNNL is a multi-program national laboratory operated for the U.S. Department of Energy (DOE) by Battelle Memorial Institute under Contract No. DE-AC05-76RL01830.

Acronyms and Abbreviations

ADF	Annular Dark Field
DFT	Density functional theory
EELS	Electron energy-loss spectroscopy
MBE	molecular beam epitaxy
PNNL	Pacific Northwest National Laboratory
STEM	Scanning transmission electron microscopy
UW	University of Washington

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1.0 Introduction

Isotopic engineering has emerged as a new strategy to probe and control atomic-scale processes in complex oxides. By substituting naturally abundant isotopes with their heavier or lighter counterparts, researchers can now track atomic transport pathways, quantify diffusion kinetics, and reveal mechanisms governing defect formation, oxidation, and lattice dynamics without altering the underlying chemistry. In crystalline oxides, isotopic substitution offers a unique handle to study phonon-mediated processes, since variations in atomic mass directly modulate vibrational frequencies while preserving crystal symmetry and bonding.

Recent advances in epitaxial growth techniques, particularly oxygen-plasma-assisted molecular beam epitaxy (MBE), have enabled the synthesis of isotopically enriched thin films with atomic-level precision (Kaspar, 2024). Combined with nanoscale analytical tools such as atom probe tomography and time-of-flight secondary ion mass spectrometry, these model systems have illuminated fundamental processes such as oxygen self-diffusion, surface exchange reactions, and radiation-enhanced transport in Fe- and Cr-based oxides. Understanding isotope behavior in these materials is not only important for energy and catalysis applications but also provides an avenue to manipulate phonon spectra for controlling thermal and vibrational properties.

Despite the advances in epitaxial isotope engineering, direct visualization of isotopic distributions and their influence on phonon propagation at the nanometer and atomic scales remains largely unexplored. Earlier atom probe studies of $^{16}O/^{18}O$ tracer layers in Fe_2O_3 and Cr_2O_3 revealed intermixing during growth, driven by adatom-mediated exchange processes rather than bulk lattice diffusion (Kaspar, 2021; Yano 2021). Molecular dynamics and nudged elastic band calculations suggest that surface adatoms can take subsurface oxygen atoms, enabling the observed isotope interlayer mixing. However, while these studies provided atomistic insight into growth-induced intermixing, the impact of isotopic substitution on lattice vibrations, phonon coherence, and energy transport has not yet been experimentally resolved in real space.

The control of phonon transport through isotopic engineering has emerged as a new tool to tune thermal conductivity and lattice dynamics in crystalline solids. In oxide systems, where vibrational excitations dominate thermal and electronic coupling mechanisms, isotope substitution modifies phonon energies without altering the underlying crystal symmetry or bonding network. Chromium (III) oxide (Cr_2O_3), also known as eskolaite, is a prototypical member of the corundum-structure family of sesquioxides, with a rhombohedral space group R-3c. This arrangement gives rise to alternating cation and anion layers stacked along [0001], establishing a framework with high structural rigidity and pronounced anisotropy in bonding and lattice vibrations. This makes Cr_2O_3 a model platform to study such effects due to its well-defined phonon spectrum and chemical robustness to study its phonon properties at the atomic scale.

Recent advances in monochromated electron energy-loss spectroscopy (EELS) within scanning transmission electron microscopy (STEM) have enabled direct mapping of phonon excitations with energy resolutions better than 15 meV (Krivanek, 2014, Hachtel 2019). This capability bridges the gap between ab initio predictions and experimental observation, allowing for site-specific vibrational spectroscopy of materials with nanometer and even atomic precision.

Here, we combine ab initio first-principles phonon calculations, based on density functional theory (DFT), with isotope tracer synthesis, and vibrational EELS mapping to resolve isotope-dependent phonon behavior in Cr_2O3thin films. By comparing ^{16}O- and ^{18}O-enriched regions, we correlate isotope distribution with vibrational energy shifts and phonon coherence across interfaces.

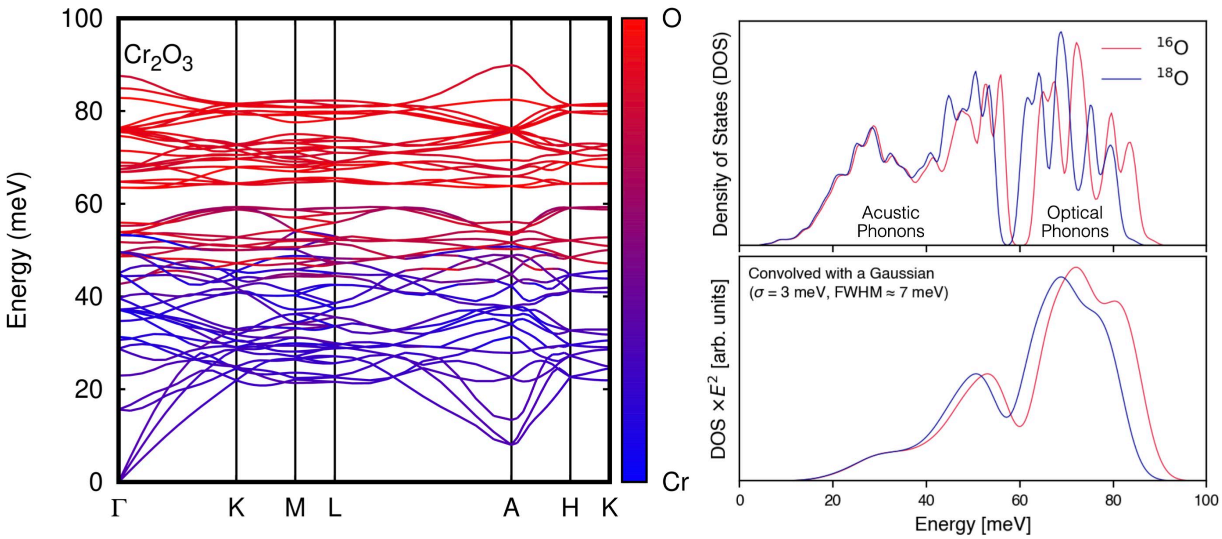

Figure 1. Calculated phonon dispersion and phonon density of states for Cr_2O_3 with oxygen isotope substitution. (Left) Phonon band structure of Cr_2O_3 along high-symmetry directions in the Brillouin zone. The color scale represents the relative atomic contributions, from Cr-dominated modes (blue) to O-dominated phonon modes (red). Optical branches above ~70 meV are primarily oxygen-derived, indicating their sensitivity to isotopic oxygen substitution. (Right) Corresponding phonon density of states (DOS) for ^{16}O (red) and ^{18}O (blue) isotopes. The lower panel shows the DOS after convolution with a Gaussian of σ = 3 meV (FWHM ≈ 7 meV) and weighted by E^2, illustrating the expected redshift of the optical phonon peak upon ^{18}O substitution.

2.0 Results

Figure 1 shows the calculated phonon dispersion and phonon density of states (DOS) for Cr_2O_3. The phonon band structure along high-symmetry directions reveals that optical branches above ~70 meV are primarily oxygen-derived, indicating their sensitivity to isotopic oxygen substitution. The corresponding phonon DOS for natural ^{16}O and ^{18}O isotopes shows a redshift in the high-energy phonon modes, consistent with the expected mass dependence of the phonon frequency.

The experimental setup and energy resolution are summarized in Figure 2. An annular dark-field (ADF) STEM image of the $NiCr/Cr_2O_3/Al_2O_3$ heterostructure reveals the epitaxial layer sequence and the region selected for EELS acquisition. The corresponding diffraction pattern, recorded at the spectrometer entrance, identifies the collection geometry for the vibrational measurements. A representative low-loss EELS spectrum from the Cr_2O_3 layer exhibits a zero-loss peak (ZLP) with a full width at half maximum (FWHM) of 15.2 meV, defining the energy resolution. The inset shows the ZLP-multiplied spectrum (), highlighting vibrational features extending up to 100 meV, consistent with the optical phonon modes predicted in Figure 1.

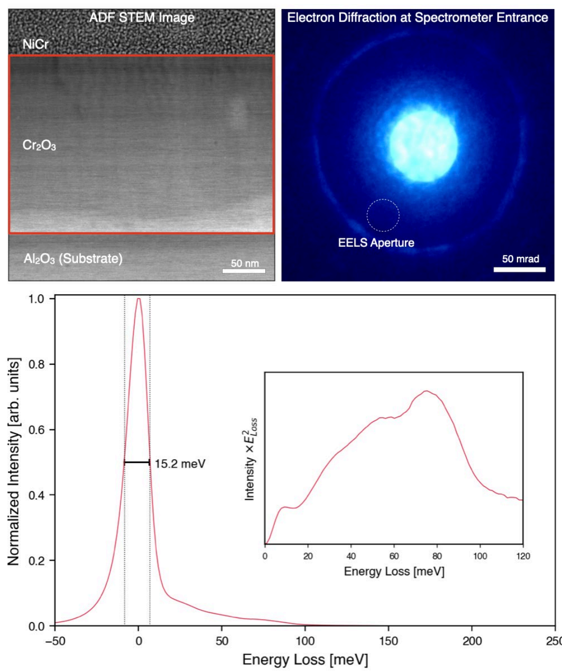

Figure 2. Structural, diffraction, and vibrational characterization of a $NiCr/Cr_2O_3/Al_2O_3$ heterostructure. (Left) Annular dark-field scanning transmission electron microscopy (ADF-STEM) image showing the layered structure of the NiCr/ Cr_2O_3/Al_2O_3 sample. The red box marks the region from which spectroscopic data were acquired. (Right) Electron diffraction pattern collected at the spectrometer entrance, with the position of the EELS collection aperture indicated by a dashed circle. (Bottom) Representative low-loss electron energy-loss spectrum (EELS) from the Cr_2O_3 region, normalized to the zero-loss peak (ZLP). The full width at half maximum (FWHM) of the ZLP is 15.2 meV, defining the experimental energy resolution. The inset shows the same spectrum multiplied by E^2_{Loss}, highlighting vibrational excitations up to ~100 meV.

To directly visualize isotopic modulation of lattice vibrations, Cr_2O_3 films were grown with alternating ^{16}O and ^{18}O layers. Figure 3 presents a vibrational spectrum image integrated over the 78–100 meV range, corresponding to optical phonon modes. The phonon intensity exhibits pronounced spatial variations that coincide with isotope-enriched regions introduced during film growth. Line profiles of optical phonon intensity (red) and ADF signal (blue) show distinct dips at the ^{18}O -rich zones, revealing reduced phonon energy and intensity due to increased atomic mass. The mixed $^{16}O/^{18}O$ region marks the isotopic diffusion boundary, corroborated by previous atom probe tomography (APT) mapping of the oxygen isotope distribution for the same sample. High-resolution vibrational mapping confirms that coherent phonon propagation persists across isotopic interfaces.

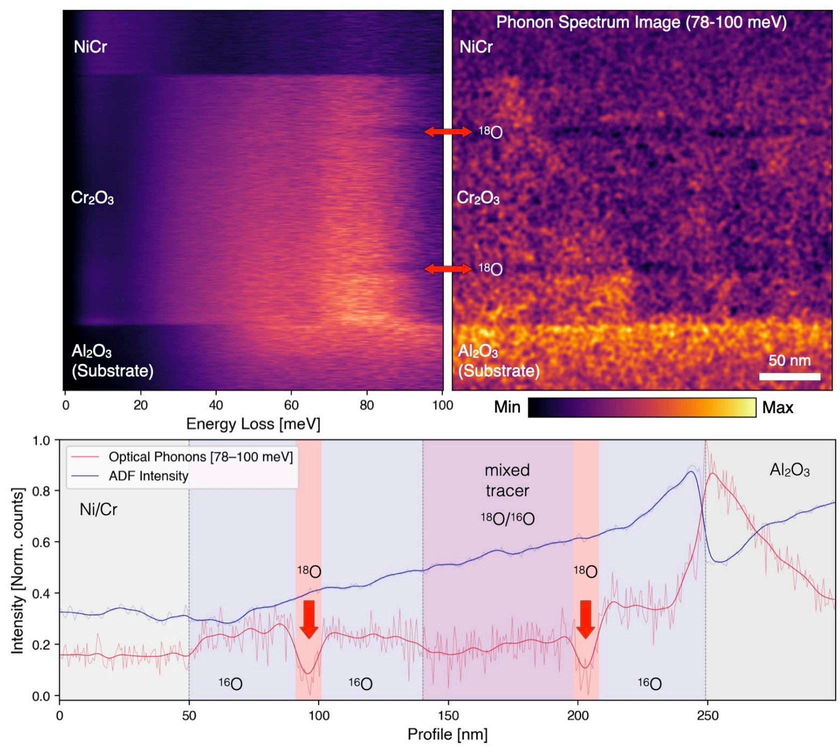

Figure 3. Vibrational spectroscopy of $NiCr/Cr_2O_3/Al_2O_3$ heterostructure. (Top left) Spatially resolved vibrational EELS map showing the energy-loss axis (horizontal) versus probe position (vertical) across the $NiCr/Cr_2O_3/Al_2O_3$ heterostructure. The intensity enhancement between 78–100 meV corresponds to optical phonon excitations in Cr_2O_3. Two ^{18}O-enriched regions (red arrows) are visible as intensity modulations within the Cr_2O_3 layer. (Top right) Phonon spectrum image integrated over the 78–100 meV energy range, revealing spatial variations in phonon signal that coincide with the isotope-enriched layers. (Bottom) Line profiles extracted from the same region, showing the normalized optical phonon intensity (red) and ADF signal (blue) from the image shown in Fig. 2. Dips in phonon intensity correspond to the ^{18}O-rich regions, while the intermediate zone reflects mixed $^{18}O/^{16}O$ diffusion.

Figure 4 shows an ADF-STEM close-up of the Cr_2O_3 lattice, corresponding to the top ^{18}O-enriched region from Figure 3. The isotopically enriched layer, delineated by white dashed lines, exhibits atomically sharp interfaces across a 10 nm-thick lamella. Spatially averaged vibrational EELS spectra from ^{16}O and ^{18}O regions show a measurable redshift of optical phonons in the ^{18}O layer, consistent with the theoretical phonon DOS shift. The inset reveals a continuous vibrational signal across the interface, evidencing partial phonon coherence. Fourier analysis of both the ADF image and vibrational maps identifies periodicities at 0.27 nm and 0.52 nm in both elastic and inelastic channels, indicating that phonon coherence is preserved even across isotopically modulated layers.

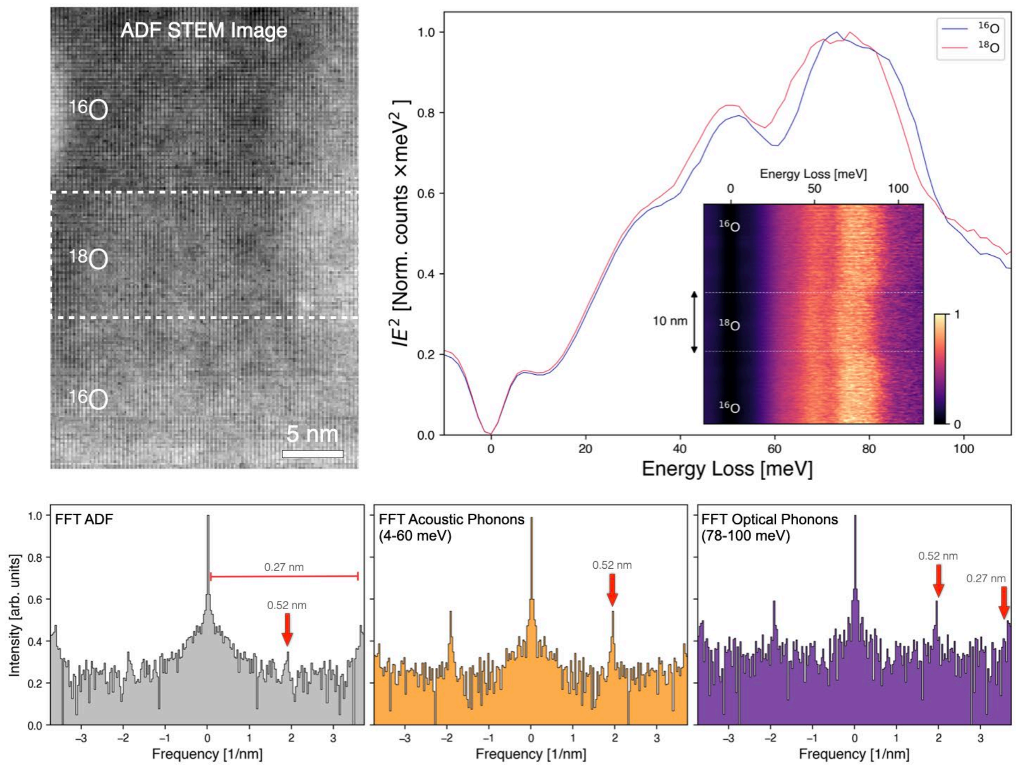

Figure 4. Atomic-scale mapping of isotope-dependent phonon behavior in Cr_2O_3. (Top left) ADF STEM image of the Cr_2O_3 lattice, corresponding to the top ^{18}O-enriched region from Fig. 3 (highlighted by a red arrow). The isotopically enriched layer is delineated by white dashed lines. The isotopic interfaces (dashed lines) are atomically sharp across a 10 nm-thick lamella. (Top right) Spatially averaged vibrational EELS spectra from ^{16}O (blue) and ^{18}O (red) regions, multiplied by E_{Loss}^2 to emphasize phonon modes. The inset shows a spatially resolved EELS map highlighting a measurable redshift in optical phonon energies within the ^{18}O-enriched layer. (Bottom) Fast Fourier transforms (FFTs) of the ADF image (gray), the acoustic phonon map (orange, 4–60 meV), and the optical phonon map (purple, 78–100 meV). Peaks at reciprocal frequencies corresponding to 0.27 nm and 0.52 nm indicate atomic periodicities preserved across both elastic and inelastic channels, revealing coherent phonon propagation through isotopically modulated layers.

3.0 Conclusions

The combined experimental and theoretical results demonstrate that isotope substitution in Cr_2O_3 leads to measurable shifts in optical phonon energies, directly observable by monochromated vibrational EELS. The preservation of lattice periodicities in both the elastic and vibrational FFTs indicates that phonon coherence can persist through atomically abrupt isotope interfaces. The results highlight the capability of vibrational EELS to resolve isotope-dependent phonon behavior at nanometer and atomic scales. This approach provides a general framework for probing phonon-mediated transport, interfacial thermal resistance, and energy dissipation in complex oxides, and can be extended to any materials system where phonons can be resolved with the electron microscope.

4.0 References

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Pacific Northwest National Laboratory

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