Femtosecond electron imaging of defect-modulated phonon dynamics

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Precise manipulation and control of coherent lattice oscillations via nanostructuring and phonon-wave interference has the potential to significantly impact a broad array of technologies and research areas. Resolving the dynamics of individual phonons in defect-laden materials presents an enormous challenge, however, owing to the interdependent nanoscale and ultrafast spatiotemporal scales. Here we report direct, real-space imaging of the emergence and evolution of acoustic phonons at individual defects in crystalline WSe2 and Ge. Via bright-field imaging with an ultrafast electron microscope, we are able to image the sub-picosecond nucleation and the launch of wavefronts at step edges and resolve dispersion behaviours during propagation and scattering. We discover that the appearance of speed-of-sound (for example, 6 nm ps−1) wavefronts are influenced by spatially varying nanoscale strain fields, taking on the appearance of static bend contours during propagation. These observations provide unprecedented insight into the roles played by individual atomic and nanoscale features on acoustic-phonon dynamics.
P
honons—quantized elastic oscillations—are at the core of innumerable atomic-scale physical processes and mesoscale phenomena, from structural variations associated with lattice fluctuations, phase transitions and bond modulation\(^1\)–\(^3\) to electromagnetic and electronic properties, including electric susceptibility and electron mobility\(^8\)–\(^10\). Consequently, the atomic-scale manipulation and control of phonon modes has been proposed and vigorously pursued for enabling and enhancing myriad technological developments, including electromagnetic confinement in optically driven cavities\(^1\)–\(^3\)\(^,\)\(^12\)\(^–\)\(^18\). Achieving this requires a deep understanding of the profound influence that phonons have on emergent properties in both engineering and advanced materials through the fundamental structure–function relationships at work therein. As such, the formulation of a comprehensive microscopic description of the real-time interaction of propagating modes with individual lattice discontinuities would constitute a significant advance toward ultraprecise directed-energy nucleation and mode guiding in defect-laden materials.

Of particular interest is the development of a detailed understanding of phonon dynamics in nanostructured and disordered semiconducting materials (for example, SiGe alloys and composites)\(^19\)–\(^21\), especially those having tunable band gaps, such as the layered transition metal dichalcogenides (for example, WSe\(_2\), MoS\(_2\), NbSe\(_2\), and so on)\(^5\)–\(^6\)\(^,\)\(^9\)–\(^10\)\(^,\)\(^22\). These compounds have generated an enormous amount of interest owing to dramatic differences in, and tunability of, transport properties (thermal and electronic) along different crystallographic directions and with varying numbers of layers. For example, it was shown with WSe\(_2\) that the cross-plane thermal conductivity could be made several times smaller than the predicted minimum value (indeed, the smallest measured for any fully dense solid) via disordering of the commensurate modulation or re-configuration of the resulting discrete phonon-nucleation events and resolution of propagation velocities and decay times—over fields-of-view on the order of the phonon wavelengths. These observations open the way to detailed study of the effects of individual atomic-scale defects, spatially varying lattice orientations and associated strain fields on ultrafast energy propagation in less-than-pristine materials.

**Results**

**Overview of WSe\(_2\) and Ge specimens.** To locate and characterize specific defects and other nanoscale imperfections of interest, the WSe\(_2\) and Ge specimens were initially surveyed using bright-field imaging and parallel-beam electron diffraction. Static structural and morphological characterization of specific specimen regions of interest, on which subsequent femtosecond electron imaging studies were conducted, are summarized in Fig. 1. As can be seen from the diffraction patterns, the WSe\(_2\) and Ge specimens are oriented such that the electron beam travels approximately down the [001] and [110] zone axes, respectively (Fig. 1c,f)\(^39\). Combined, the bright-field images and corresponding diffraction patterns illustrate the macroscopically crystalline but microscopically disordered nature of the regions. From the images, several features of interest for the present study can be identified, which, conversely, are not readily apparent from the diffraction patterns alone. These include step edges and terraces, wrinkles, folds, vacuum-crystal interfaces and cracks. In addition, bend contours are quite prominent and widespread, as are moiré fringes in the WSe\(_2\) specimen. See the ‘Methods’ section below for descriptions of how the specimens were prepared.

**Imaging acoustic-phonon wavefronts and wavetrains.** With the applied experimental conditions (stroboscopic femtosecond electron microscopy; see ‘Methods’ section), propagating periodic-contrast modulation arising from femtosecond optical excitation was observed in both the specimens (Fig. 2). Owing to the challenge of conveying the behaviour of the observed acoustic-phonon dynamics within a series of static images, the reader is strongly encouraged to view Supplementary Videos 1 through 6, within which the dynamics are striking and more readily apparent. In addition, Supplementary Fig. 1 comprises the same images as shown in Fig. 2, but the display method is different in order to provide additional perspective. From the sequence of femtosecond electron images, phase velocities of 6.5 and 5.5 nm ps\(^{-1}\), commensurate periodicities of 40 and 44 ps, and GHz frequencies (Supplementary Fig. 2) were determined for the travelling contrast modulations in Ge and WSe\(_2\), respectively. This was accomplished by analysing oscillations in the image intensity as a function of both space and time (Fig. 2h;p; see ‘Methods’ section). The close correspondence of the phase velocities to the bulk, in-plane speed of sound indicates the contrast dynamics arise from propagating acoustic phonons—
major energy carriers emerging from electron–phonon coupling and reflecting the onset of coherent thermal transport. Note that GHz lattice-oscillation frequencies have also been observed in crystalline Si with an ultrafast electron microscope via femtosecond convergent-beam diffraction40.

From the image series, it is immediately apparent that the phonon wavefronts do not emerge in a spatially uniform manner. Rather, within the WSe₂ flake, wavetrains are nucleated at a localized region along a distinct step-edge, and the subsequent propagation direction is perpendicular to the interface (see Supplementary Video 1). The wavetrain emerges in 1 ps (see below), is launched and propagates at a velocity of \(5.5 \text{ nm ps}^{-1}\) away from the step edge. In the Ge specimen, the appearance and directionality of the propagating phonon wavefronts are seen to follow existing bend contours present in otherwise pristine crystalline regions (see Supplementary Video 2). Also apparent in the video are relatively weak contrast oscillations in the upper-right portion of the frame. These oscillations occur within a relatively pristine region of the Ge specimen (that is, free of significant defects and crystal bending, as indicated by the relatively weak contrast).

**Emergence of a phonon from a step edge.** To precisely resolve the phonon dynamics at an individual step edge, image series of WSe₂ were acquired with increased magnification and finer temporal sampling (500-fs steps). Within the region of interest highlighted in Fig. 3, the intensity was observed to initially increase at a step edge in the first few-hundred femtoseconds and continue to grow for approximately 10 ps before relaxation via emission of a travelling wave approximately perpendicular to the interface (see Supplementary Videos 3 and 4). The processed difference images (Fig. 3b–f; see ‘Methods’ section) and corresponding time-dependent intensity traces (Fig. 3g) display the emergence mechanism of the in-plane acoustic phonons shown in Fig. 2j–o. Notably, the frequency of dynamic intensity at the step edge is in accord with the interlayer echoing of back-and-forth acoustic phonons and resulting oscillating moiré fringes41–43 (see also Supplementary Fig. 3). It is therefore likely that the differential stress imparted on the interface by dephasing of the longitudinal \(c\) axis waves across regions of differing height gives rise to the formation of the in-plane travelling phonons. Systematic studies to probe this and other aspects associated with the dynamic contrast mechanisms are currently in progress and will be described elsewhere.

**Spatially dependent acoustic phonon properties.** The information contained in the image series can be further illustrated via a space–time surface plot (see ‘Methods’ section). In Fig. 4a, an analysis of contrast dynamics observed in the region between the WSe₂ crystal–vacuum interface and the step edge is summarized (see also Supplementary Video 5). Each streak corresponds to one period of an acoustic phonon, with the slope and width indicative of phase velocity and frequency, respectively. Such an analysis reveals the presence of multiple modes in this region, with a relatively high-frequency oscillation (phase velocity = 5.5 nm ps\(^{-1}\)) generated during the initial moments of excitation,
and slower (0.9 nm ps$^{-1}$), lower-frequency dynamics dominating after a few-hundred picoseconds. Similar spectral features identified with Brillouin light scattering from thin silicon membranes have been attributed to Lamb-wave modes\textsuperscript{44}. Analogously here, the confinement of longitudinal acoustic phonons within the specimen thickness gives rise to in-plane propagating modes. These consist of travelling symmetric ($S_0$) and antisymmetric ($A_0$) interlayer displacements (Fig. 4c). It has been predicted that such dilatational and flexural acoustic modes significantly influence thermal transport in layered materials\textsuperscript{45}.

**Figure 2** | Real-space femtosecond electron imaging of single-phonon wavefronts in Ge and WSe$_2$. (a,i) Bright-field images of the Ge and WSe$_2$ regions shown in Fig. 1 and obtained at $-50$ and $-5$-ps time delays, respectively. For the Ge experiments, the images were acquired with a 25-kHz repetition rate and a 13-s integration time per frame. For WSe$_2$, the images were also acquired with a 25-kHz repetition rate but with an 18-s integration time per frame (see also the captions for Supplementary Videos 1 and 2 for further experimental details). The three coloured lines mark regions from which the mean intensity was quantified and used to generate the time traces in (h) and (p) (described below). The propagation direction is perpendicular to the coloured lines. Scale bars, 500 nm. (b–g) and (j–o) Surface plots generated from an image series (region of interest $= $ white rectangles in a and i) highlighting approximately one period of wavetrain propagation, with a pre-time-zero frame included for reference. Motion of individual wavefronts, which appear as a continuous, deep-red depression, is indicated by the white arrows. The blue and orange arrows map the orientation to the two-dimensional images shown in a and i. (h,p) Image-intensity measurements, obtained at the coloured lines in a and i, as a function of time delay (offset for clarity).
Discussion

For all the studies reported here, the laser-excitation wavelength used was 515 nm (2.41 eV). This photon energy is significantly larger than the band gaps of both WSe2 and Ge (1.6 and 0.66 eV, respectively)\textsuperscript{46,47}. Accordingly, the roles played by charge-carrier excitation and recombination on localized acoustic-phonon nucleation and launch may be non-negligible. Indeed, the question of why acoustic phonons first appear at specific locations in the material is nontrivial to answer considering the sequence of events that occurs following femtosecond excitation—especially in a disordered material—and the mechanisms of contrast formation in the bright-field images (discussed below). Although this topic is the subject of current systematic studies in our lab, it nevertheless is perhaps worthwhile to draw comparisons to multi-photon pump-probe photoemission electron microscopy. In this variant of photoemission electron microscopy, resonant excitation is used to induce surface-plasmon oscillations and image their launch, propagation and evolution with femtosecond resolution\textsuperscript{48,49}. An analogous methodology dubbed photon-induced near-field electron microscopy\textsuperscript{50,51}, which is not reliant on resonant excitation\textsuperscript{52–54}, has recently been used to image wave-particle properties of surface plasmon polaritons and induce Rabi oscillations in swift, unbound electron packets\textsuperscript{55,56}. With the resonant-excitation approach in mind, one can envision femtosecond electron imaging experiments on acoustic-phonon dynamics, where the pump-photon energy is varied with respect to the band gap of the material under study. In this way, one may be able to determine the roles played by the various dynamic and transport phenomena at work.

Beyond the acoustic-phonon excitation and nucleation mechanisms, it will be important to quantify the precise manner in which contrast is formed in the femtosecond electron images. It is well known that deviations of a few milliradians in the local Bragg condition can produce significantly different contrast patterns in bright-field micrographs. Indeed, this sensitivity to local morphology is what enables observation of dynamic contrast from small angular perturbations caused by in-plane propagating waves. It is expected that the nature of the contrast resulting from the acoustic waves is highly dependent on both vicinity to a zone axis and the specific zone axis itself. It is important to note that each of the videos of the WSe2 flake presented in this study are acquired at slightly different orientations (due to the variability of sample insertion from one experiment to the next) and in fact show noticeable differences in static diffraction contrast (compare Supplementary Videos 1 and 5). In each case, however, the waves appear to emanate from the same features, and the frequencies and phase velocities extracted are the same. Nevertheless, the exact dependence of specimen orientation with respect to specific dynamic modulations indeed is an open question (and will be the subject of a forthcoming publication).

In conclusion, we have reported the direct, real-space imaging of acoustic-phonon dynamics in macroscopically ordered but microscopically disordered crystalline WSe2 and Ge. Via femtosecond electron imaging, we have discovered that phonon nucleation and launch occurs at discrete spatial locations along individual step edges, and that the appearance of coherent, propagating wavefronts are extremely sensitive to the shapes of local strain fields (manifested in bend contours) and...
vacuum–crystal interfaces. Further, the analysis of picosecond contrast modulation reveals the phase velocities, frequencies and symmetries of the modes, with the spatial and layer-thickness dependence of the oscillations being resolved. We expect that these observations, and the method used, will open the way to the ultra precise manipulation and control of coherent energy propagation at the atomic scale, with the possibility of exploring the spatiotemporal limits of quantized thermal energy.

Methods

Specimen preparation. The WSe₂ (2-H) flakes were prepared via chemical exfoliation of a single-crystal obtained from Nanoscience Instruments. Isolated flakes were transferred to an atomically flat, cleaved (100) NaCl substrate (Ted Pella) before a polymer support film was deposited by drop-casting 20 μl of a solution of 2 wt% polymethyl methacrylate (PMMA) in anisole. The NaCl substrate was etched for 10 to 15 min in a de-ionized water bath, leaving the flakes supported by the PMMA film. The specimens were then positioned on a 2,000 mesh Cu TEM grid via micromechanical manipulation followed by dissolution of the PMMA support film in an acetone bath overnight.

The Ge specimen was prepared via mechanical polishing at a 2° angle from a bulk (110)-oriented, undoped wafer (MTI Corporation) followed by ion milling to electron transparency. The specimen was then epoxy bonded to a Cu slot grid. The irregularly shaped edges of the Ge specimen result from the polishing process as well as non-uniform material removal during ion milling.

Laser parameters. The Ge and WSe₂ specimens were optically excited in situ with a pump pulse of 270-fs duration full-width at half-maximum and centered at 515 nm (2.41 eV). The pulses were generated with a Yb:KGW (1.03 μm fundamental), diode-pumped solid-state laser and harmonics generation module (Light Conversion; PHAROS and HIRO, respectively). The pulse duration was measured ex situ with an in-house-built autocorrelator. The pump fluences incident on the Ge and WSe₂ were 1.3 and 5.0 mJ cm⁻², respectively. These fluences were calculated on the basis of a laser spot size of 100-μm full-width at half-maximum, as measured ex situ with a beam profiler (Newport LBP-1) using focusing parameters identical to those along the path to the specimen region.

To generate the probing photoelectron packets, the pump line was split, and a portion of the 515-nm pulses was frequency doubled to 257.5 nm and focused into the gun region of the microscope. The experiments highlighted in Figs 2 and 4 of the main text were performed at a repetition rate of 25 kHz, while the
higher-resolution scan in Fig. 3 was performed at 50 kHz. In each case, the repetition rates were such that complete mechanical and thermal relaxation was achieved before each subsequent excitation.

Microscope parameters. All the experiments were performed with a Tecnai Femto ultrafast electron microscope (FEI Company) operated at 200 kV in both thermionic and photocathode electron modes. In both modalities, a truncated, 150-μm flat LaB₆ cathode (Applied Physics Technologies) was used. To capture the greatest number of photoelectrons at the relatively low repetition rates used here, a custom 1.25-mm condenser aperture was used for all of the experiments. For all the bright-field experiments, a 40-μm objective aperture was used. For all the selected-area diffraction experiments, a 200-μm projection aperture was used, which collected electrons passing through a 20-μm² area. This same aperture can be seen in the bright-field-imaging Supplementary Videos 1 and 5. The images were recorded with a Gatan Orius SC200B 2,048 × 2,048 CCD camera and with integration times ranging from 13 to 20 s per frame. On the basis of the total electron counts (approximately (1 × 10⁶) to (5 × 10⁷)) acquired with the beam focused to the size of the CCD chip for a given exposure time and repetition rate, it is estimated that 200 to 1,000 electrons per pulse were used for image formation.

Control experiments. To exclude a host of potential artifacts and undesirable instabilities of the experimental system as the cause of the observed propagating contrast waves, a series of control experiments were performed in duplicate. These were conducted immediately after scans in which the periodic contrast was observed and using the same experimental parameters. (1) A control experiment for specimen drift/tilt was twice performed by acquiring 47 images at a fixed time delay (for example, −100 ps) to replicate the duration of a full-time scan (for example, 200 ps). (2) A control experiment for image fluctuations due to potential photomultiplier electronic instabilities was performed twice by acquiring 50 images over 20 min without specimen excitation. (3) A control experiment for beam instabilities due to movement of the delay stage was performed twice by acquiring 50 images without specimen excitation but still translating the delay stage on the laser table as if a scan (200 ps with 4-ps steps over 20 min) were being performed. (4) A control experiment for the equilibrium thermal effects of pumping the specimen was performed twice by acquiring a series of 50 images over 10 min spanning a delay range of 200 ps but using a thermionic rather than photogenerated electron beam. No propagating contrast waves—indeed, no dynamics of any kind—were observed in the controls.

Data and image processing. In generating panels (b–g) and (i–o) in Fig. 2 of the main text, several steps were taken in converting the photoelectron images to three-dimensional surface plots. First, difference images were created by taking an average of 10 pre-time-zero images (dubbed the reference image) and subtracting it from each frame in the series. This difference image was modified for contrast and brightness to enhance the features of interest. Next, an HSV image was created by placing the original (at some time delay, δ) in the hue channel and the difference image (at t) in the saturation and value channels. Finally, the colour balance was modified to emphasize the dynamic contrast. Each image within a data set was processed identically.

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Author contributions
D.R.C. performed the sample preparation, the experiments, and the analysis on Ge. D.A.P. performed the sample preparation, the experiments and the analysis on WSe2. D.J.F. oversaw the study, provided insight and guidance and aided in the interpretation and presentation of the data. The manuscript was prepared by D.R.C., D.A.P. and D.J.F. D.R.C. and D.A.P. contributed equally to the work.

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