Peer Review File

Manuscript Title: Measuring phonon dispersion at an interface

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Referee #1 (Remarks to the Author):

This work (2021-03-03921/Qi) uses modified STEM-EELS measurements to probe lattice vibrations in the vicinity of an interface of diamond and cubic BN. Density functional theory calculations of the phonon lend support to the measurement interpretations. The measurement technique balances energy, momentum, and spatial resolution limitations to obtain a signal of dispersive phonons at an interface, which is challenging. For this reason, I was excited upon reading the title. However, the data and comparisons of phonon features is not so impressive as to warrant publication here. I was hoping for a more conclusive map of the interface dispersion rather than the somewhat convoluted spectra shown here. Perhaps I misjudge the novelty, but I do not recommend publication in Nature. I offer the following comments to improve some aspects of the manuscript:

(1) Some word choice and grammar issues: abstract – 'work has begun' is better 'work began'; 'isolated away from' better 'isolated from'; pgs. 3 and 4 choice of the word 'prove' is not good – nothing is 'proven' in science; pg. 3 define TO and LO; pg. 5 'fundamental researches' better 'fundamental research'; define ZLP on pg. 9; top of pg. 3 'providing new opportunities' – opportunities for what?

(2) Interfacial modes are confined to the interface (by definition), so it is hard for me to understand how their strong 'dispersion' across the interfacial region will help them carry heat/conduct. I can imagine that interface modes interact nontrivially with bulk modes on both sides to play a role in transport. I can also imagine that interface modes can carry heat laterally along the interface – such dispersion was not shown here.

(3) The geometry of the experiment seems to be thin film diamond interfaced with thin film cBN. What are the film thicknesses? Doesn't this limit the EELS measurements? What of surface phonon properties relative to interface properties? Does the geometry of the experiment preclude surface effects? What is the lattice mismatch at the interface?

(4) On page 3 it is mentioned they have ¼ BZ resolution, which BZ? Bulk diamond or superstructure?

(5) Calculations: should report the plane wave energy cutoff used, particularly for these stiff, high frequency materials. What of the lattice mismatch, how was this treated? Were there any negative frequencies in the pDOS for the interface system? There is a surface for the experiments, was a surface considered here? Perhaps unimportant given experiment geometry? Were the temperature-dependent Bose and Debye-Waller factors important here? How was the effective charge calculated?

Referee #2 (Remarks to the Author):

In their manuscript, Ruishi Qi et al. use electron energy loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM) to detect interface-specific phonon modes at a single cBN-diamond junction. A combination of experimental geometries is used to measure the local vibrational response and the phonon dispersion at the interface. Their experimental results are supported by ab into calculations. As advances in experimental design are incremental (see e.g., Refs. 20-22, 25-29 and 31-32), and the vibrational responses of a single atom point defect (Ref. 26) and a single stacking fault (Ref. 27) have previously been reported using STEM-EELS, the novelty of this work lies in the detection of interface-induced contributions to the EEL spectrum at high spatial resolution, in particular the measured phonon dispersions. The presented data and their interpretation are convincing, and the manuscript overall makes a strong case for the presence of interface modes. This certainly is of great interest to communities within the fields of chemistry, physics, and materials science however, it is not clear whether this work has a broader appeal. Thus, the manuscript may be better suited for a more specialized journal. I therefore recommend the manuscript be rejected.

Suggested improvements are given below.

The quality and presentation of data is overall excellent however, the authors may want to consider indicating on images the exact regions from which EEL spectra were acquired.

The authors claim in their initial paragraph to directly measure the local phonon density of states (LDOS). This is inaccurate. What the authors measure is an EEL spectrum, which is comparable, but not identical to the LDOS. This is discussed in Refs. 26 and 27.

Another claim made by the authors is that previous related studies "…achieved fine momentum resolution upon sacrificing the beam size to several tens of nanometers [20, 28, 32]." This is not correct for the case of Ref. 20, where a convergence semi-angle of 3 mrad was used, resulting in an estimated probe size of ~ 1 nm. The authors should in this context also cite Ref. 27 (3 mrad convergence semi-angle, spatial resolution 2.6 nm) and Ref. 22 (1.5 mrad convergence semi-angle, typical spatial resolution 4 nm). In Refs. 20, 22 and 27 convergence and collection angles were reportedly chosen to balance resolution in momentum and real space. The authors strike exactly such a balance when optimizing their experimental geometry for phonon dispersion measurements.

Lastly, it would be appropriate to cite literature when the authors report on their results using an "off-axis" experimental geometry. Off-axis vibrational STEM-EELS was first used to achieve better than 2 nm spatial resolution in Ref. 29 and later adapted for atomic resolution in Ref. 31. The latter approach is highly similar to that used by the authors, shown in Extended Data Fig. 3.

Referee #3 (Remarks to the Author):

The work by Qi aimed to measured the phonon response and phonon dispersion at the interface between two materials, cubic BN & diamond. The measurements were performed using the latest generation of monochromated aberration-corrected electron microscopes.

The quality of the data, their discussion in the main text, the figures and the conclusions are all carefully crafted and beautifully presented. The authors do not use any superlative or try to oversell their results. The experimental data unambiguously shows local (at the nanometer level) changes of the phonon response and phonon dispersion between the two materials. Their theoretical calculations agree with their experimental findings, strengthening the discussion throughout the manuscript.
The experimental data and calculations hold the claims presented in the introductory abstract paragraph and in the title of the manuscript.

The results by Qi et al. is something that has been discussed during the last few years in the electron microscopy community as a possible experimental outcome and an experimental landmark that could be obtained using the latest monochromated electron microscopes.

I just have a small criticism on the way that authors present the schematic of their experimental setup in Figures 1a and 1b (which will be stated in detail below).
I think the manuscript by Qi et al could be accepted for publication in Nature once my minor comment gets addressed properly.

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1. Minor comment (Figures 1a & 1b.)
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I understand that the authors try to schematically present the electron optical configuration of their microscope such that a broader audience understand how the electron microscope was aligned. However, by doing so the authors unfortunately are over simplifying and they are portraying the electron optics incorrectly.
For both figures (1a & 1b) the electron rays between the magnetic lens and the diffraction plane cannot be traveling in perfect parallel trajectory. The sample plane and diffraction plane are conjugate planes, and as such the electron trajectories hitting the diffraction plane have to have a convergence angle. I suggest that the authors arrange their schematic as it corresponds.

Author Rebuttals to Initial Comments:

Response to referees' comments

We would like to thank three referees for their highly constructive comments concerning our manuscript. In response to the comments and suggestions, we have conducted further experiments and calculations, and thus enhanced our understanding and improved the manuscript. We believe that all the concerns raised by the referees are addressed appropriately in the revised manuscript.

Major changes made in the revision:

According to the referees' and editor's suggestions and comments, we have revised and improved the manuscript. Major changes made in the revision are briefly described below. They are also highlighted with blue font color in the revised manuscript.

1. Following referee #1's comments and editor's suggestions, we have performed further simulations to link the measured interfacial phonon directly to the properties of thermal transport, which should also mitigate the referee #2's concern on the "broad appeal" of our work. Thermal transport across interfaces has drawn great interest because as the scale of nanodevices continue to shrink it is becoming increasingly important in many applications such as computing circuits, light-emitting diodes, quantum cascade lasers, and thermoelectrics. Interface thermal conductance (ITC) has been a major subject in the field of nanoscale thermal transport, and is usually understood in the framework of the phonon gas model or the atomistic Green's function approach. Both of them assume the ITC can be constructed by the transmittance of bulk phonons across the interface without considering new modes at the interface. This assumption, although extensively used for decades, was challenged by recent theories and molecular dynamics (MD) simulations. In fact, interfacial modes substantially contribute to ITC. To further demonstrate this, we carried out interfacial conductance modal analysis (ICMA) using MD simulations. We found that interfacial modes have strong correlation with almost all other modes, indicating they exchange energy efficiently with bulk phonon modes on both sides and hence give a large contribution to ITC. On a per-mode basis, their contribution is the highest among all modes (Extended Data Fig. 8). Such a significant contribution from interfacial modes has been theoretically predicted in other material systems, e.g., for Si/Ge interface up to 15% of ITC arises from interfacial modes which only occupy < 0.1% of the DOS (*Sci Rep* 6, 23139, 2016). Thus, our experimental measurement of interface phonon modes will be surely interesting to communities involving thermal transport. In the revised manuscript, we include the results in an Extended Data Figure (Extended Data Fig. 8), and add a paragraph in the main text (page 5, line 198-221) to discuss the role

interfacial modes play in thermal transport. The simulation details are also included in the "*MD simulations*" part of Methods.

2. According to editor's suggestion, we also added a brief outlook of other implications of the measured interfacial modes and the demonstrated technique. Besides thermal transport, the interfacial modes can also be important in determining electron mobility near the interface, especially when a two-dimensional electron gas (2DEG) appears at the interface. We supplement DFPT calculations of electron-phonon coupling in Extended Data Fig. 9. Our calculation shows the 2DEG at cBN/diamond interface interact strongly with interfacial phonon modes (orders of magnitude stronger than bulk phonon modes). This means interface phonon dispersion measurements are helpful for understanding electron mobility of 2DEGs, which is one of the most crucial parameters, if not the most crucial one, for practical applications. We also briefly discuss the insights our demonstrated technique can provide for experimental studies of topological phononics. In fact, at the current stage it seems be the only feasible method for experimental observation of topological interface states.

3. Referee #2 has a concern on our resolutions. To address that, we systematically evaluated the spatial resolution at various convergence angles using real experimental data. It turns out our spatial resolution is already close to (only ~15% larger than) the ultimate diffraction limit. In fact, it is much better than all previous momentum-resolved EELS experiments, and there is not too much space for improvement without sacrificing the momentum resolution (see our response to referee #2 below for more details). The results are summarized in Extended Data Fig. 1 and Fig. R3 below, and the method used to evaluate the resolution is explained in "*Spatial resolution estimation*" section in Methods.

4. To better visualize the 4D-EELS data, we supplement a video showing how phonon dispersion changes with the beam scanning on the sample.

5. Other changes following referees' suggestions. Please see our response below for detail.

Point-by-point response:

Referee #1:

This work (2021-03-03921/Qi) uses modified STEM-EELS measurements to probe lattice vibrations in the vicinity of an interface of diamond and cubic BN. Density functional theory calculations of the phonon lend support to the measurement interpretations. The measurement technique balances energy, momentum, and spatial resolution limitations to obtain a signal of

dispersive phonons at an interface, which is challenging. For this reason, I was excited upon reading the title. However, the data and comparisons of phonon features is not so impressive as to warrant publication here. I was hoping for a more conclusive map of the interface dispersion rather than the somewhat convoluted spectra shown here. Perhaps I misjudge the novelty, but I do not recommend publication in Nature.

Response: We greatly thank the referee for carefully reading our manuscript and recognizing the importance of interface phonon measurements. We also appreciate the referee's interest in a more conclusive map of phonon dispersion. As for the data quality, we are confident to say our data already represents top-level EELS data that the newest-generation monochromated STEMs can produce (as noted by other referees). We agree that the dispersion diagram measured at the interface seems convoluted by itself, but this is ultimately limited by the uncertainty principle, not by our data quality (e.g., if we do not need spatial resolution, the bulk dispersion diagrams shown in Extended Data Fig. 5 are much nicer than previous EELS results. This is because we used a slot aperture, which improves acquisition efficiency by at least an order of magnitude compared with previous serial acquisition method demonstrated in refs. 19 and 27). The spatial resolution of our 4D-EELS setting, quantitatively measured to be 1.3 ± 0.2 nm, is the best so far to our knowledge. In fact, it is only ~15% larger than the diffraction limit 1.13 nm (please also see our response to referee #2 below). That is to say, there is not much space for improvement without sacrificing momentum resolution. For the interfacial modes be better resolved in real space (less convoluted in spatial dimensions), momentum resolution has to be sacrificed (more convoluted in momentum dimension) and vice versa. Besides, conceptually one cannot define a phonon dispersion at an infinitesimal space point either. A phonon mode with a specific momentum has to involve vibration of atoms all over the space, and the vibration of a specific atom has to involve phonon modes with all momenta. Therefore, what one can define is phonon PDOS as a function of position (given by our 3D-EELS measurements with atomic resolution), and phonon dispersion as a function of momentum (given by our 4D-EELS measurements with nanometer resolution), but *not* a spatial map of dispersion relation with infinite resolution.

To our understanding, four types of phonon modes (extended, partially extended, interfacial, and isolated) near the interface can be pictured as follows. In the interface region, bulk modes from two materials can hybridize to form extended modes if they are degenerate, or just form partially extended modes if no degenerate mode exists on the opposite side. Their contribution to the measured spectra can be simply written as a linear combination of bulk spectra. What is non-trivial is, new features not present in bulk regions can appear at the interface, forming interfacial modes or isolated modes with enhanced or reduced vibration at the interface. These are new modes associated with the change in force constant or atomic mass arrangement. Their feature must die off away from the interface, and can therefore be obtained by subtracting bulk spectra from the interface spectra (Fig. 3c and Extended Data Fig. 2). They do not have dispersion relation in the direction normal to the interface plane due to the broken symmetry (please also see our reply to the second comment below for a clarification for possible misunderstandings); they do have dispersion in in-plane directions, but this dispersion is not a function of the position relative to the interface. In short, they are dispersive along in-plane directions but non-dispersive (localized) along the out-of-plane direction. With that being said, the somewhat convoluted

spectra (Fig. 3c) obtained in our 4D-EELS experiments already provide complete knowledge of phonon dispersion of interfacial modes and isolated modes.

To help readers better understand this picture, we have added the following sentences when introducing the four types of modes: "…*The first two types originate from bulk modes of two materials, which can hybridize to form extended modes if they are degenerate, or form partially extended modes when no degenerate mode exists on the opposite side. The last two types are new features associated with the broken symmetry at the interface, with enhanced or reduced vibration at the interface…*" (page 3, line 103-106). We also add a supplementary video to better visualize the 4D-EELS data.

I offer the following comments to improve some aspects of the manuscript:

(1) Some word choice and grammar issues: abstract – 'work has begun' is better 'work began'; 'isolated away from' better 'isolated from'; pgs. 3 and 4 choice of the word 'prove' is not good – nothing is 'proven' in science; pg. 3 define TO and LO; pg. 5 'fundamental researches' better 'fundamental research'; define ZLP on pg. 9; top of pg. 3 'providing new opportunities' – opportunities for what?

Response: We thank the referee for these very kind suggestions. We have corrected these issues in the revised manuscript. We also checked that all acronyms have be properly defined.

(2) Interfacial modes are confined to the interface (by definition), so it is hard for me to understand how their strong 'dispersion' across the interfacial region will help them carry heat/conduct. I can imagine that interface modes interact nontrivially with bulk modes on both sides to play a role in transport. I can also imagine that interface modes can carry heat laterally along the interface – such dispersion was not shown here.

Response: We appreciate this pertinent comment. Before discussing the heat conduction mechanism, however, we would like to clarify some misunderstandings the referee might possibly have about the experimental geometry and the interface BZ. Due to the breakdown of translational symmetry across the interface, the interface BZ is a two-dimensional cross section of the bulk BZ. That is, the wavevector **q** can be defined only along in-plane directions, but not along the direction normal to the interface plane. This is in accordance with the fact that interfacial modes are localized: they can propagate along in-plane directions, but are confined along the third dimension (and hence there is no wavevector along it). In our case, the (111) interface breaks the translational symmetry along [111], so the interface BZ lies in the plane spanned by $[1\bar{1}0]$ and $[11\bar{2}]$. For the 4D-EELS measurement discussed in our manuscript, the beam was traveling along $[11\bar{2}]$, and the slot aperture was placed along $[1\bar{1}0]$, as shown in Fig 1b. This means the measured dispersion diagram is along one of the in-plane directions (ΓΣKX), which is exactly what the referee is expecting ("carry heat laterally along the interface"). To avoid similar confusion, we explicitely point out that the aperture is along an in-plane direction in the caption of Fig. 1. On the other hand, measuring their dispersion "across" the interface is not possible. The interface connects two semi-infinite leads so the system does not have periodicity along [111], hence wavevector **q** along it cannot be defined. Placing the slot aperture along [111]

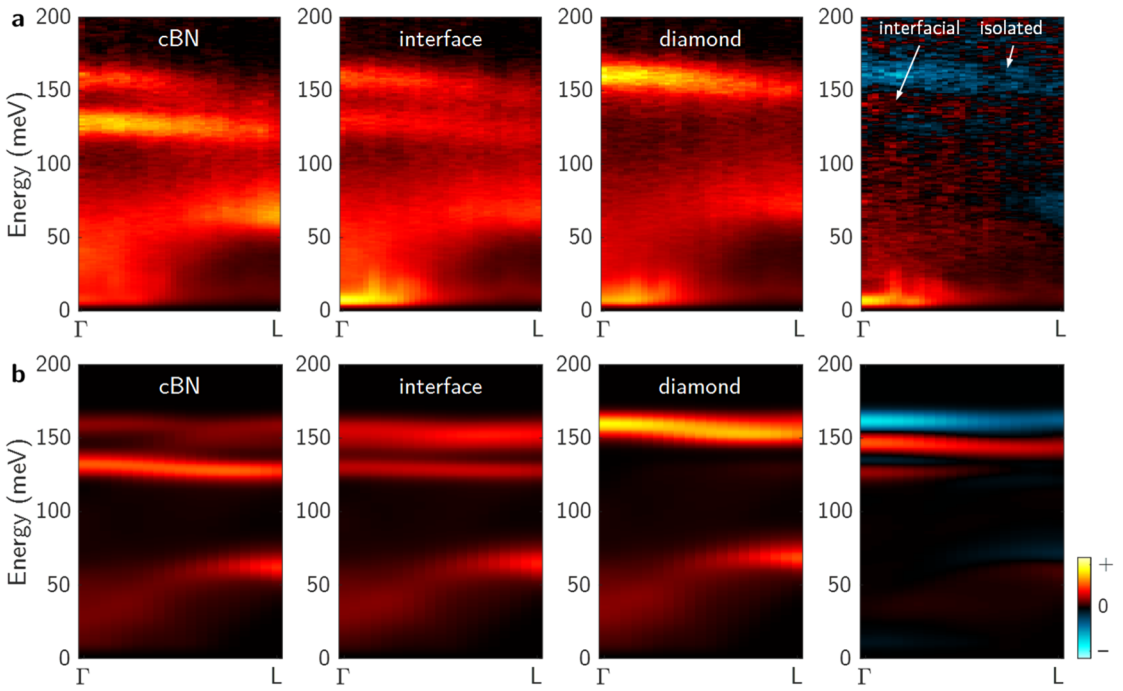

Fig. R1 | Dispersion diagrams measured along [111] direction (ΓL). a, Measured dispersion diagrams. The rightmost panel shows the difference between interface spectra and averaged bulk spectra (similar to Fig. 3c), in which the isolated modes at ~160 meV and interfacial modes at ~140 meV can be observed. **b**, Corresponding calculation results. The horizontal axis is the momentum transfer of the scattered electrons, so the momentum labels "Γ" and "L" cannot be strictly defined for phonons in the interface region, and should be understood as asymptotic limits in the bulk region away from the interface.

will definitely give us some EELS signal as a function of electron momentum transfer, and actually we have carried out this experiment (Fig. R1). By subtracting the averaged bulk spectra from the interface spectra, we extract new features associated with the interface, from which the scattering signal from interfacial modes (positive) and isolated modes (negative) can be observed. They form rather flat lines along this direction. However, it should be noted that the electron momentum transfer can no longer be interpreted as the crystal momentum of phonon modes (electron momentum transfer is always well-defined, but phonon crystal momentum is ill-defined along [111] in the interface region. It is defined only asymptotically in the bulk regions. The presence of the interface breaks the crystal momentum conservation during the scattering). The measured diagrams along [111] near the interface region can therefore only be interpreted as a change of scattering behaviors, not a dispersion relation. For this reason, we decide not to include the diagrams above in the manuscript.

Now we can discuss how interfacial modes affect heat conduction. In general, we totally agree with the overall picture mentioned by the referee. First, for thermal conduction in the in-plane directions, interfacial modes have group velocity along the interface, so they can carry heat laterally as the referee pointed out. Second, in the direction normal to the interface, interfacial modes are localized and do not have group velocity, but they can conduct heat by exchanging energy with bulk modes on both sides. In fact, thermal conduction across the interface is one of

the most important subjects of nanoscale thermal transport studies. Many theoretical approaches, such as the phonon gas model (including diffuse mismatch model and acoustic mismatch model) and the atomistic Green's function method, were developed and extensively used for such studies in the past decades. All of them neglected interfacial modes. However, in fact interfacial modes scatter with bulk modes on both sides frequently and thus serve as an intermediate state for heat transfer across the interface. Our MD simulation confirms interfacial modes have strong correlations with almost all other modes, and their contribution to ITC is very high on a per-mode basis (Extended Data Fig. 8). This is consistent with previous theoretical works, e.g., it was found that for Si/Ge interface up to 15% of ITC arises from interfacial modes which only occupy < 0.1% of the DOS (*Sci Rep* 6, 23139, 2016). Understanding three phonon scattering processes requires knowledge of phonon energy, momentum and eigenvector (i.e., vibration amplitude distribution). Therefore, our 4D-EELS measurements, giving information about interfacial modes' spatial distribution and dispersion relation, can help to understand and control heat conduction at interfaces.

(3) The geometry of the experiment seems to be thin film diamond interfaced with thin film cBN. What are the film thicknesses? Doesn't this limit the EELS measurements? What of surface phonon properties relative to interface properties? Does the geometry of the experiment preclude surface effects? What is the lattice mismatch at the interface?

Response: Our experiments used suspended cBN/diamond films as illustrated in Figure 1a-b. Please note that, in our EELS geometry the electron beam is traveling parallel to the interface plane, not normal to it (Fig. 1a-b). The sample thickness (along the beam trajectory) is 50-60 nm (hundreds of atom layers) as calculated using EELS log-ratio technique. Thus, along this direction the films can be safely considered as bulk materials. Unlike reflection EELS, STEM-EELS uses a much higher acceleration voltage and hence a much larger penetration depth. It is therefore not particularly sensitive to surface layers. Surface states at the top and bottom may give a small contribution to the measured spectra, but their contribution should be negligibly small since surface states only appear within ~2 surface atom layers. The lattice mismatch between cBN and diamond is 1.4% (experimental lattice constants are 3.567 Å for diamond and 3.616 Å for cBN; see, e.g., *Nature* 181, 758–759, 1958 and *Acta Cryst B* 47, 843–848, 1991). The structure of the cBN/diamond interface has been carefully studied by another work (*Nat Comm* 6, 6327, 2015). The small lattice misfit is accommodated by stacking faults, and we focused on the coherent interface region between two neighboring stacking faults, where the atoms are aligned. The film thickness and the lattice mismatch are now included in Methods (page 10, line 276-279).

(4) On page 3 it is mentioned they have 1/4 BZ resolution, which BZ? Bulk diamond or superstructure?

Response: We would like to mention again that, our measured dispersion is along an in-plane direction of the interface (ΓΣKX line). With that being said, the BZ lateral sizes of two bulk materials and that of the superstructure do not differ too much (the BZ lateral size of bulk cBN and bulk diamond differ by only 1.4%, and upon neglection of this mismatch the interface BZ is a two-dimensional slice of the bulk BZ so their lateral sizes are almost the same). For completeness,

now we include a detailed graph showing the momentum resolution in Extended Data Fig. 1c. The momentum resolution of our 7.5 mrad setting is between 1/5 and 1/4 of the ΓX distance. The inset in Extended Data Fig. 1c also illustrates the diffraction spot size relative to the BZ size.

(5) Calculations: should report the plane wave energy cutoff used, particularly for these stiff, high frequency materials. What of the lattice mismatch, how was this treated? Were there any negative frequencies in the pDOS for the interface system? There is a surface for the experiments, was a surface considered here? Perhaps unimportant given experiment geometry? Were the temperature-dependent Bose and Debye-Waller factors important here? How was the effective charge calculated?

Response: We appreciate the professional suggestions and questions regarding the calculations. In our DFPT calculation, the kinetic energy cutoff was 80 Ry (1088 eV) for wavefunctions, and 800 Ry (10885 eV) for charge density and potential. Such a high value should be sufficient even for these stiff materials.

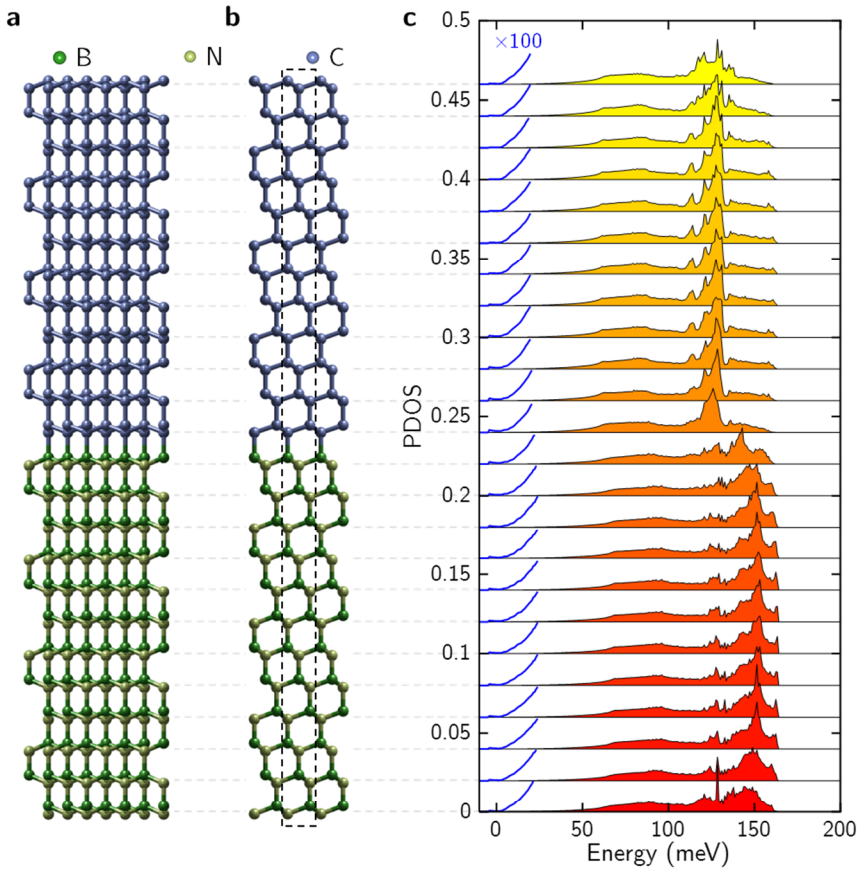

Fig. R2 | Phonon PDOS. a-b, The calculation model viewed along [11$\bar{2}$] (**a**) and [1$\bar{1}$0] (**b**) zone axes. Dashed box shows a unit cell of our calculation model. **c**, Phonon DOS projected onto each atom layer. Each line is successively shifted upward and is aligned with the atomic models in **a**-**b**. Blue line also shows the PDOS but is magnified by a factor of 100. Even after the magnification the DOS at negative frequencies is still hardly visible.

The optimized lattice constants in our calculations are 3.533 Å for bulk diamond and 3.583 Å for bulk cBN, slightly smaller than the experimental values. The lattice mismatch between cBN and diamond is about 1.4%, which is neglected in the interface model. Thus, the superstructure thickness along the (111) direction is large (c = 49.301 Å), but along in-plane directions the cell only contains two atoms in each layer (a = 2.518 Å). This corresponds to the coherent interface region where atoms on two sides are aligned, as shown in Fig. 1c-d. The optimized cell parameter for the superstructure is 0.8% larger than that of bulk diamond and 0.6% smaller than that of bulk cBN. After applying the periodic boundary condition in in-plane directions, the model is shown in Fig. 1e-f and Fig. R2 (they are not merely a schematic but drawn to scale using the optimized atomic coordinates). In fact, it's impractical to consider the in-plane superstructure (the moiré superlattice due to the 1.4% mismatch) in DFT because such a supercell will contain > 10^5 atoms, which is far beyond the calculation capacity.

There are only tiny negative (imaginary) frequencies near the Γ point due to common numerical instabilities. They are small (all above – 4 meV) and extremely rare (only 0.003% of the total DOS) and can hence be ignored. As shown in Fig. R2c, even after a 100× magnification the DOS at negative frequencies is still hardly visible. This can also be seen in Fig. 3e, where at Γ point the acoustic branches start at a small negative frequency but it's very close to zero. There is no negative frequency away from the Γ point, indicating the structure is stable.

As we have mentioned, the sample in our experiment is hundreds of atom layers thick, so surface effects are neglected in our model. Since our experiment was performed at room temperature (293K, or equivalently k_BT = 25 meV), the Bose occupation number is important here because it leads to a higher occupation number for low-energy acoustic modes compared to optical modes. On the other hand, the Debye-Waller factors only play a minor role because they are very small (on the order of (1 × 10^{-3} Å^2) × q^2), so neglecting them could be acceptable. Nevertheless, both factors are considered in our calculations. As mentioned in the Methods section, the effective charge was calculated using (this is equation (9) of *Phys. Rev. B* 99, 094105, 2019, but adapted to our notation)

$$Z_k(\mathbf{q}) = f_k(\mathbf{q})\frac{Z_k^{\mathrm{atom}} - Q_k}{Z_k^{\mathrm{atom}}} + Z_k^{\mathrm{atom}} e$$

where Z_k^{atom} is the atomic number of k^{th} atom, f_k is the atomic form factor, Q_k is the calculated Mulliken charge, and e denotes elementary charge.

We have revised the "*ab initio calculations*" section in Methods to include the additional information above.

Referee #2:

In their manuscript, Ruishi Qi et al. use electron energy loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM) to detect interface-specific phonon modes at a single cBN-diamond junction. A combination of experimental geometries is used to measure the local vibrational response and the phonon dispersion at the interface. Their experimental results are

supported by ab into calculations. As advances in experimental design are incremental (see e.g., Refs. 20-22, 25-29 and 31-32), and the vibrational responses of a single atom point defect (Ref. 26) and a single stacking fault (Ref. 27) have previously been reported using STEM-EELS, the novelty of this work lies in the detection of interface-induced contributions to the EEL spectrum at high spatial resolution, in particular the measured phonon dispersions. The presented data and their interpretation are convincing, and the manuscript overall makes a strong case for the presence of interface modes. This certainly is of great interest to communities within the fields of chemistry, physics, and materials science however, it is not clear whether this work has a broader appeal. Thus, the manuscript may be better suited for a more specialized journal. I therefore recommend the manuscript be rejected.

Response: We thank the referee for pointing out the novelty of our work and recognizing the appeal among the fields of chemistry, physics and materials science. To remove the referee's concern on the uncertain "broad appeal", we have performed MD simulations and DFPT calculations and added more discussions on how the measured interfacial modes affect various properties of the interface. We believe our results along with the demonstrated ability to measure interface phonon dispersion are of interest to communities across multiple fields, as detailed below.

1. Interfacial modes substantially contribute to thermal transport across the interface. Thermal transport across interfaces has drawn great interest because the interface thermal conductance (ITC) is becoming increasingly important as the scale of nanodevices continue to shrink. It has been a major subject in the field of nanoscale thermal transport, and many theories, such as the phonon gas model (including the diffuse mismatch model and the acoustic mismatch model) and the atomistic Green's function approach, were developed and extensively used in the past decades. However, none of them consider the atomic details and vibrational modes at the interface, which is challenged by recent theories and MD simulations. We performed MD simulations to directly show that interfacial modes have strong correlation with almost all other modes, indicating they exchange energy efficiently with bulk phonon modes on both sides and hence facilitates heat conduction. On a per-mode basis, their contribution to ITC is very high (Extended Data Fig. 8). Our calculation is consistent with previous theoretical works, e.g., it was found that for Si/Ge interface up to 15% of ITC arises from interfacial modes which only occupy < 0.1% of the DOS (*Sci Rep* 6, 23139, 2016). Thus, our measurements will be surely interesting to communities involving thermal transport.

2. Interfacial modes interact strongly with electrons near the interface, especially when a 2DEG is present at the interface. 2DEGs show intriguing properties and are practically useful in transistor-like semiconductor structures such as metal-oxide-semiconductor field-effect transistors and high-electron-mobility-transistors. In these devices, high electron mobility is a key property. Electron mobility can be affected by scattering from impurities, boundaries, and phonons. For high quality samples with low density of defects, electron-phonon scattering can become the dominate term. Using DFPT, we calculate the momentum-dependent electron-phonon coupling and the resulting phonon linewidth,

and found the 2DEG interacts almost exclusively with interfacial modes (orders of magnitude stronger than other modes), as shown in Extended Data Fig. 9. Since understanding electron-phonon coupling requires phonon dispersion relation and is often momentum-specific, the measurement of interfacial phonon dispersion can give helpful insights for electron mobility in 2DEGs.

3. The demonstrated interface phonon measurement technique is able to provide direct evidence for the existence of topological phononic states. As the phononic counterpart of topological electronic states, at the interface between two topologically non-equivalent materials topological interface states are predicted to appear. However, it has not been experimentally verified. Once suitable systems are identified, our demonstrated experiment can provide direct evidence. For chiral states especially, they can be observed by a dispersion measurement that can show their chirality.

We think with the additional information, our paper should attract interest among a broad readership, including the communities of electron microscopy, nanoscale thermal transport, electrical engineering, topological phononics, and beyond.

Suggested improvements are given below.

The quality and presentation of data is overall excellent however, the authors may want to consider indicating on images the exact regions from which EEL spectra were acquired.

Response: We appreciate the referee's praise on our data quality and presentation. In our EELS experiments, we acquired HAADF images immediately before and immediately after the EELS acquisition, with various fields of view (FOVs) without moving the sample. This allows us to identify the exact scanning region by comparing with a large FOV image. We add a panel in Extended Data Fig. 3 to show a low-magnification annular dark-field image around the interface region. Colored boxes indicate the regions where the 3D-EELS and 4D-EELS datasets (including those in Extended Data Fig. 3) were acquired.

The authors claim in their initial paragraph to directly measure the local phonon density of states (LDOS). This is inaccurate. What the authors measure is an EEL spectrum, which is comparable, but not identical to the LDOS. This is discussed in Refs. 26 and 27.

Response: Thank the referee for pointing out this. When the EELS collection angle is large enough to cover multiple BZs, the acquired spectrum is close to DOS. In our previous manuscript we called it DOS for conceptual simplicity, as some literatures did (e.g., *Nature* 573, 247–250, 2019). We definitely agree with the referee that quantitatively the acquired spectrum is not identical to DOS. Therefore, in this revision we call it "local vibrational spectrum" for meticulousness. We explicitly mention the difference between DOS and the spectra: "*A large round aperture covers multiple BZs, producing spectra comparable to local phonon density of states (DOS, though quantitatively the spectrum differs slightly from DOS due to momentum-dependent scattering factors and statistical factors[25,32]).*" (page 2, line 73-76).

Another claim made by the authors is that previous related studies "…achieved fine momentum resolution upon sacrificing the beam size to several tens of nanometers [20, 28, 32]." This is not correct for the case of Ref. 20, where a convergence semi-angle of 3 mrad was used, resulting in an estimated probe size of ~ 1 nm. The authors should in this context also cite Ref. 27 (3 mrad convergence semi-angle, spatial resolution 2.6 nm) and Ref. 22 (1.5 mrad convergence semi-angle, typical spatial resolution 4 nm). In Refs. 20, 22 and 27 convergence and collection angles were reportedly chosen to balance resolution in momentum and real space. The authors strike exactly such a balance when optimizing their experimental geometry for phonon dispersion measurements.

Response: Based on the referee's comment, to make it more accurate we have modified the text to "*…either achieved atomic spatial resolution upon losing momentum resolution*[24,25,30] *or achieved fine momentum resolution with a beam size larger than typical phonon localization scales…*" (page 2, line 60-63). However, we would like to respectfully argue that, some of previous papers overestimated the spatial resolution at small convergence angles. There are three major factors that affect the beam size: beam source size, spherical aberrations, and diffraction limit. We would like to refer to the equation in Methods part of *Nature* 589, 65–69, 2021: the beam size $d_r = \sqrt{d_g^2 + d_s^2 + d_d^2}$, where the three terms in the root correspond to the aforementioned three factors. In the Nature paper, the authors neglected the broadening due to aberration (because of the aberration corrector), and calculated that at 60 kV and 3 mrad, a beam size of 2.6 nm can in principle be achieved. However, there is a significant inconsistency between this Nature paper and *Sci Adv* 4, eaar7495, 2018, where the convergence semi-angle is also 3 mrad but the claimed resolution is ~1 nm, as the referee noted. To more accurately evaluate the spatial resolutions, we carried out systematic experimental measurements at both 60 kV and 30 kV by varying the convergence semi-angles, as shown in Fig.R3. It turns out the estimated resolution of 2.6 nm in the Nature paper is reasonable, but the 1 nm resolution claimed in the Sci Adv paper is overestimated. In fact, even if we further neglect the contribution from beam source size (which depends on their beam current) and only consider the diffraction limit, the claimed 1 nm resolution is still impossible:

$$d_d = 1.22\frac{\lambda}{\alpha} = 1.22 \times \frac{4.87\ \mathrm{pm}}{3\ \mathrm{mrad}} = 2.0\ \mathrm{nm}$$

where λ = 4.87 pm is the electron wavelength with 60 keV beam energy, and α = 3 mrad is the convergence semi-angle. The diffraction limit is already twice as large as the claimed resolution of 1 nm. We do not mean to belittle the merit of this seminal paper, but we think the ~1nm resolution is only an order-of-magnitude estimation. Since the Sci Adv paper, the Nature paper and our work all used Nion microscopes, we discussed this with Dr. Tracy Lovejoy (Chief Operating Officer at Nion and a coauthor of the Sci Adv paper), and he said "*The probe will never be smaller than the diffraction limit. My guess is that the Hage et al. paper you are referring to meant to say that the probe size was 'on the nm scale', meaning <10nm.*" With this interpretation, the best resolution in existing momentum-resolved EELS experiments was 2.6 nm reported by the Nature paper. Therefore, we believe our spatial resolution, which is literally below 1.5 nm (quantitatively measured to be 1.3 ± 0.2 nm; please see Methods), is better than all previous works. The excellence of our spatial resolution can also be directly seen in Extended Data Fig. 6,

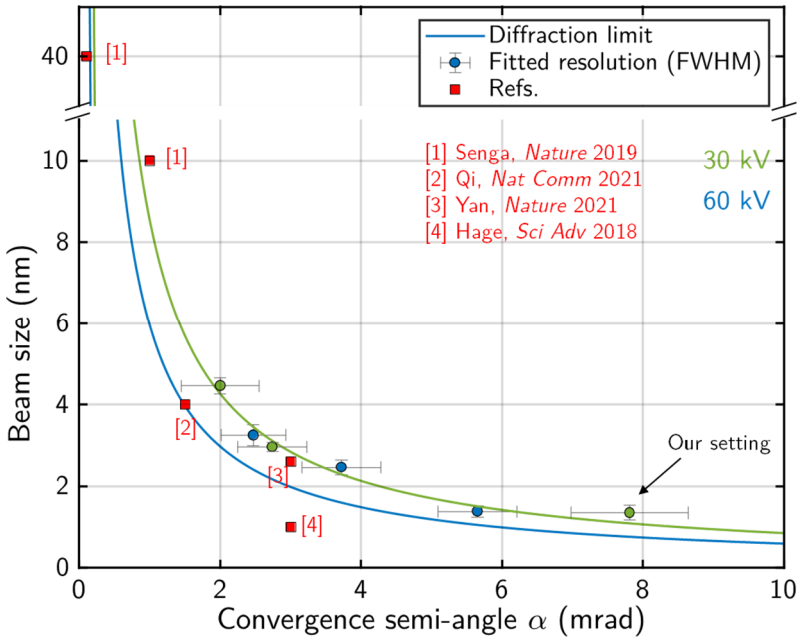

Fig. R3 | Spatial resolution with various convergence semi-angles in comparison with previous literatures. Solid lines are the diffraction limit (theoretical lower bound). Blue and green colors correspond to 60 keV and 30 keV beam energy respectively. Filled circles with error bars, experimentally fitted resolution (see Methods in the revised manuscript for details). Red squares, reported resolution in existing literatures (all using 60 keV beam energy). The resolutions in refs. [1-3] are close to or higher than the diffraction limit, but ref. [4] claims a beam size smaller than the diffraction limit.

where the spectral features changes sharply across the interface, and interfacial modes and isolated modes can be readily observed.

We do appreciate the referee's valuable suggestion to give more details on the balance between spatial and momentum resolutions. Now we add a section (*Spatial resolution estimation*) in Methods and an additional figure (Extended Data Fig. 1) to include the results in the revised manuscript.

Lastly, it would be appropriate to cite literature when the authors report on their results using an "off-axis" experimental geometry. Off-axis vibrational STEM-EELS was first used to achieve better than 2 nm spatial resolution in Ref. 29 and later adapted for atomic resolution in Ref. 31. The latter approach is highly similar to that used by the authors, shown in Extended Data Fig. 3.

Response: Our off-axis geometry is indeed very close to that in these references. We cite them as "*…By collecting scattered electrons at high-order BZs (off-axis geometry[28,30], Extended Data Fig. 4), one of them can be visualized with a higher contrast …*" (page 4, line 150-152).

Referee #3:

The work by Qi aimed to measured the phonon response and phonon dispersion at the interface between two materials, cubic BN & diamond. The measurements were performed using the latest generation of monochromated aberration-corrected electron microscopes.

The quality of the data, their discussion in the main text, the figures and the conclusions are all carefully crafted and beautifully presented. The authors do not use any superlative or try to oversell their results. The experimental data unambiguously shows local (at the nanometer level) changes of the phonon response and phonon dispersion between the two materials. Their theoretical calculations agree with their experimental findings, strengthening the discussion throughout the manuscript.

The experimental data and calculations hold the claims presented in the introductory abstract paragraph and in the title of the manuscript.

The results by Qi et al. is something that has been discussed during the last few years in the electron microscopy community as a possible experimental outcome and an experimental landmark that could be obtained using the latest monochromated electron microscopes.

Response: We would like to thank the referee for positive comments on the importance of our work.

I just have a small criticism on the way that authors present the schematic of their experimental setup in Figures 1a and 1b (which will be stated in detail below).

I think the manuscript by Qi et al could be accepted for publication in Nature once my minor comment gets addressed properly.

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1. Minor comment (Figures 1a & 1b.)
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I understand that the authors try to schematically present the electron optical configuration of their microscope such that a broader audience understand how the electron microscope was aligned. However, by doing so the authors unfortunately are over simplifying and they are portraying the electron optics incorrectly.

For both figures (1a & 1b) the electron rays between the magnetic lens and the diffraction plane cannot be traveling in perfect parallel trajectory. The sample plane and diffraction plane are conjugate planes, and as such the electron trajectories hitting the diffraction plane have to have a convergence angle. I suggest that the authors arrange their schematic as it corresponds.

Response: We greatly appreciate the referee's valuable suggestion. We fully agree that drawing the beam with a converging shape will better represent the real beam trajectory. We have modified this part of the schematics accordingly, showing electron beams converging to the diffraction spots after passing through the magnetic lens.

Reviewer Reports on the First Revision:

Referee #1 (Remarks to the Author):

I am satisfied with this revision of the manuscript accounting for my critiques. I suppose that I need to be more realistic in my expectations for probes of these dynamical features. I recommend publication.

Referee #2 (Remarks to the Author):

The manuscript has improved substantially; I recommend this for publication in Nature.

Referee #3 (Remarks to the Author):

The authors have satisfactorily addressed ALL the comments raised by the three Referees.

The manuscript, which had super data and clearly articulated text on its original version, has really improved.

I think the manuscript has now the quality to be granted publication in Nature.