Revealing Nanoscale Energy Flow Using Ultrafast THz to X-ray Beams

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Abstract

We developed novel spectroscopic methods and made use of them to study energy flow and material properties on nanometer length scales and ultrafast time scales. Access to short length scales was provided through the use of light beams with short wavelengths (EUV through hard x-ray spectral ranges) and/or fabricated structural elements with nanometer dimensions. Recent advances in tabletop high harmonic generation of extreme ultraviolet (EUV) pulses were exploited to measure thermal transport and acoustic vibrations using time-resolved diffraction from photoexcited periodic nanostructures, revealing new physics that arises at length scales of tens to hundreds of nm. The tabletop EUV sources as well as the FERMI free electron laser at FERMI-Elettra in Trieste were used to generate as well as measure nanoscale thermoelastic responses without the need for patterned nanostructures, with the short length scale coming from optical interference patterns formed by crossing pairs of beams in transient grating experiments. We also used EUV and optical sources to excite and monitor ultrahigh-frequency acoustic waves (coherent phonons) at ultraflat interfaces and multilayer structures, extending our measurements of the highest-frequency coherent acoustic waves observed to date. Our measurements of acoustic properties allowed direct calculation of thermal conductivities which can be compared with our measurements of thermal transport and with first-principles calculations. Terahertz-frequency acoustic measurements can also be used to reveal complex relaxation dynamics in glass-forming liquids and partially disordered solids. Acoustic measurements were used to investigate the confinement effect in ultrathin liquid layers and to characterize mechanical properties of ultrathin solid layers. The methods we developed have broad fundamental applications and may also enable new practical metrology for use in nanoelectronics, just as earlier methods we developed have found commercial applications in microelectronics metrology.

Recent Progress

Experiments at LCLS: time-resolved phonon spectroscopy with hard x-rays

Coherent phonon excitation in an x-ray split-and-delay experiment

A very exciting recent development at LCLS is the split-and-delay capability for hard x-rays. In December 2017, PI Nelson, in collaboration with D. Reis of SLAC, conducted the first user experiment on this newly developed setup. The sample was irradiated by two 30 fs x-ray pulses at 9.8 keV photon energy, separated by a variable time delay, and the diffuse x-ray scattering was monitored by an area detector. In $SrTiO_3$ and $KTaO_3$ samples we observed an unexpectedly intense modulation of the diffuse scattering intensity (see Fig. 1), comparable to the static thermal diffuse scattering background. Further investigation revealed oscillations of the diffuse scattering intensity at the longitudinal acoustic phonon frequencies up to ~0.5 THz. Our analysis indicates that we are exciting coherent LA phonons at every reciprocal space point up to a wavevector below ~0.06 nm^{-1}. This finding is totally unexpected since there is no apparent mechanism for the generation of a broad spectrum of coherent phonons by spatially uniform irradiation. Our hypothesis is that the x-ray excitation creates a spatially inhomogeneous concentration of photoexcited carriers, resulting in the generation of both acoustic phonons and a "quasistatic" strain pattern reflecting the carrier concentration distribution. We believe that these experiments provide fundamentally important information

on the interaction of hard x-rays with dielectric crystals. Further analysis of the results is currently underway.

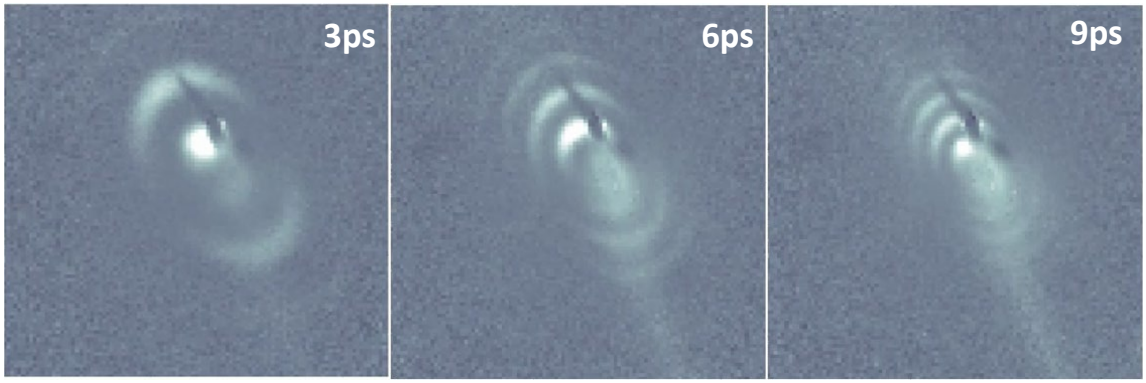

Fig. 1. X-ray pump-probe measurements on $SrTiO_3$ at 9.8 keV: modulation of diffuse x-ray scattering intensity on the detector as a function time delay. The fringes are due to LA phonons excited by the first x-ray pulse.

Phonon spectroscopy of SiGe with time-resolved x-ray scattering by squeezed thermal phonons

In another very recent experiment at LCLS we used the new phonon spectroscopy technique developed by D. Reis and colleagues, based on x-ray diffuse scattering by squeezed thermal phonon populations created by an optical excitation, to study transverse acoustic phonons in a $Si_{0.1}Ge_{0.9}$ alloy across the entire BZ. SiGe in an important thermoelectric material and there has been a lot of recent interest in SiGe in the context of nanoscale thermal transport. The objective of our experiment was to measure thermal phonon lifetimes in SiGe and to probe high-wavevector phonons near the BZ boundary. Some preliminary results are shown in Fig. 2. We were able to measure TA phonons across the entire BZ in the Γ-L direction of the reciprocal lattice; however, in the Γ-X direction the dispersion curve peters out near the BZ boundary. This suggests that we may be reaching the Ioffe-Regel limit, i.e. phonons near the X point no longer exist as plane waves. In the same experimental run, we measured the evolution of the TDS intensity pattern from GaAs and found that the acoustic phonon population remains out of thermal equilibrium within 30 ps following laser excitation. We also observed peculiar oscillations of TDS intensity in the vicinity of Bragg rods. Further analysis of the results of this experiment is currently underway.

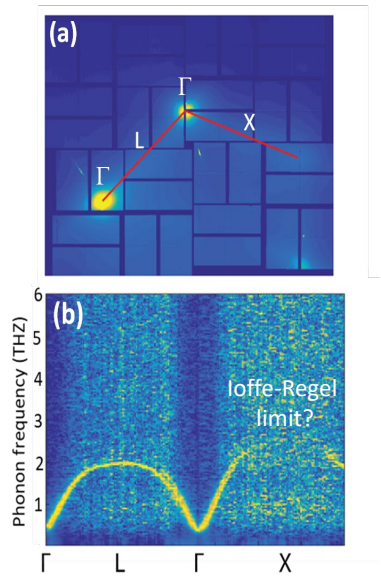

Fig. 2. (a) Diffuse scattering pattern from the $Si_{0.1}Ge_{0.9}$ alloy and (b) TA phonon dispersion along the red lines in (a).

Direct measurement of THz phonon mean free path in GaN

In parallel with phonon lifetime measurements at LCLS, we continued to pursue an alternative approach to measuring phonon lifetime and mean free path (MFP) using a laser pump-probe technique in which semiconductor superlattices are used for optical excitation and detection of THz acoustic phonon wavepackets. Earlier in the current funding period, in a joined study with C-K Sun's group at the National Taiwan University [1], we used two InGaN superlattice structures separated by a 2 μm-thick GaN layer to make the first observation of the propagation of acoustic wavepackets above 1 THz at room temperature. However, we were unable to accurately measure the phonon lifetime because the apparent attenuation was dominated by extrinsic factors such as nonuniformity of the GaN layer thickness within the laser spot. In a new series of experiments, we used temperature dependence of the intrinsic phonon lifetime dominated by

anharmonic phonon-phonon scattering to separate it from extrinsic contributions. The measurements yielded room temperature intrinsic phonon MFPs of 5.4 μm at 1 THz and 3.8 μm at 1.4 THz, in good agreement with ab-initio calculations by our collaborator L. Lindsay of Oak Ridge. This is the first measurement of THz phonon MFPs in a high thermal conductivity material (traditional techniques such as inelastic neutron and x-ray scattering were only measure low thermal conductivity materials in which the phonon MFP is very short, such as PbTe, due to the limited instrumental resolution). This is also the first time that ab-initio calculations of acoustic phonon MFPs was confirmed by experiment. The long-MFP THz phonons we studied are especially important for micro- and nano-scale thermal transport, as they determine the distance scale at which the bulk κ value can no longer be used to describe heat conduction. The paper (T.-H. Chou et al., "Long mean free paths (>5 μm) of THz acoustic phonons in a high thermal conductivity material at room temperature") has been prepared for publication, preprint available.

Controlling nanoscale thermal transport: size- and spacing-dependent cooling of nanostructures

At JILA, in addition to participating in the experiments at the Fermi XFEL, we further explored nanoscale thermal transport because of its relevance both to fundamental materials behavior and also to high efficiency thermoelectric devices and nanoscience. Direct experimental measurements of heat flow in nanoscale systems are challenging, and first principle models of real geometries are not yet computationally feasible. In past work we used ultrafast pulses of short wavelength light to uncover a surprising new regime of nanoscale thermal transport that occurs when the width and separation of heat sources are comparable to the mean free paths of the dominant heat carrying phonons in the substrate. In recent work, to show that we could predict the nanoscale transport properties in this new regime, we systematically compared thermal transport from gratings of metallic nanolines with different periodicities, on both silicon and fused silica substrates. By monitoring the surface profile dynamics with sub-Å sensitivity, we directly measured thermal transport from the nanolines into the substrate [1,2]. This allows us to quantify how the nanoline period significantly impacts thermal transport into the substrate, and thereby confirm the surprising prediction that closely spaced nanoscale heat sources can cool more quickly than when far apart, at early times. These findings are important for benchmarking new theories that go beyond the Fourier model of heat diffusion, and for informed design of nanoengineered systems. Finally, we are working with several theory groups to compare our measurements to the Boltzmann transport equation (BTE), hydrodynamic and super-diffusive views of the BTE, including phononic effects that can modify the thermal transport in nanostructured systems, even at room temperature.

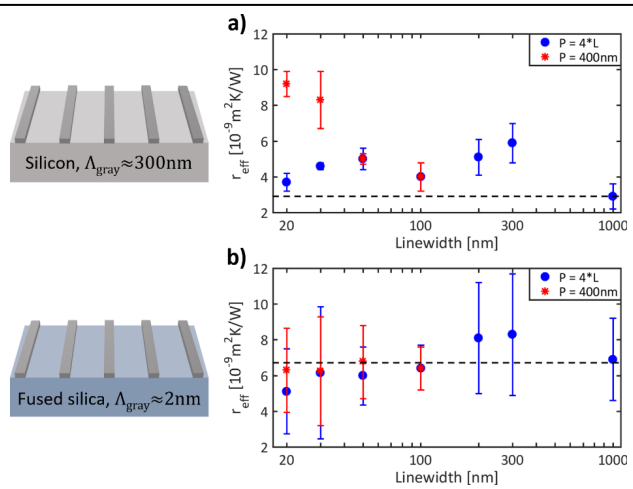

Fig. 3. Best fit effective thermal boundary resistivity for nanolines on silicon and fused silica. (a) For Si, as the linewidth is reduced below 50 nm, the effective resistivity of the constant 25% duty cycle gratings (blue points) decreases, which is a return towards the diffusive prediction. In contrast, the constant 400 nm period gratings' resistivities increase as the linewidth is reduced (red stars). The dotted line shows the 1000 nm grating effective resistivity to highlight the deviations of the smaller linewidth gratings. (b) For fused silica, the resistivities of constant duty cycle (blue points) and 400 nm period (red stars) gratings all agree within error bars. This indicates that there is no non-diffusive transport, as expected.

<u>Future Plans</u>

We continue to focus on the development of short-wavelength transient grating (TG) spectroscopy. While we do not have beamtime at the FERMI FEL this year (our proposal submitted in the fall 2017 was approved, but the beamtime was allocated in July 2019), our collaborators at FERMI (F. Bencivenga, C.

Macchiovecio and colleagues) continued experiments with the all-EUV TG setup started during our beamtime in April 2017 and demonstrated TG measurements with 13.3 nm excitation and probe and a TG period of 28 nm. This opens exciting prospects for probing transport phenomena in materials at ~10 nm spatial scale during our scheduled beamtime in 2019. Furthermore, the recent addition of the 20.8 nm probe wavelength to the EUV TG setup at FERMI will permit probing magnetic circular dichroism at the absorption M-edge of Co and thus enable TG studies of ultrafast magnetic phenomena on the ~10 nm spatial scale. Designing EUV TG experiments to study ultrafast magnetism is currently underway. At the same time, we are working to extend the optical TG setup at MIT extending into the UV range (200 nm wavelengths) to shorten the TG period down to almost 100 nm (further progress will be made using "solid immersion" prism couplers to shorten the wavelength by a factor of the prism refractive index). We are also working with collaborators at SLAC (D. Reis, J. Hastings) and at Paul Scherrer Institute in Switzerland (C. Svetina) to attempt preliminary TG measurements using hard x-rays. A proposal for a demonstration experiment using x-ray excitation and optical probing at SwissFEL has just been submitted. The SLAC and SwissFEL collaborative efforts will open the door to wide-ranging x-ray four-wave mixing measurements.

References

[1] J. Hernandez-Charpak, T. Frazer, J. Knobloch, K. Hoogeboom-Pot, D. Nardi, W. Chao, L. Jiang, M. Tripp, S. King, H. Kapteyn, and M. Murnane, "Reliable characterization of materials and nanostructured systems <<50nm using coherent EUV beams," SPIE Advanced Lithography, 9778, 97780I (2016).

[2] T. Frazer, J. Knobloch, K. Hoogeboom-Pot, D. Nardi, W. Chao, R. Falcone , M. Murnane, H. Kapteyn, J. Hernandez-Charpak, "Engineering nanoscale thermal transport: Size- and spacing-dependent cooling of nanostructures," submitted (2018).

Peer-Reviewed Publications Resulting from this Project (2016-2018)

1. A. A. Maznev, et al., "Propagation of THz acoustic wave packets in GaN at room temperature," Appl. Phys. Lett. 112, 061903 (2018).
2. T. Hecksher, et al., "Toward broadband mechanical spectroscopy," PNAS 114, 8710 (2017).
3. I. Chaban, et al., "Time-domain Brillouin scattering for the determination of laser-induced temperature gradients in liquids," Rev. Sci. Instrum. 88, 074904 (2017).
4. F. Bencivenga et al., "Four-wave-mixing experiments with seeded free electron lasers," Faraday Discuss., 194, 283 (2016).
5. V. V. Temnov, et al., "Towards the nonlinear acousto-magnetoplasmonics," J. Opt. 18, 093002 (2016).
6. A. Vega-Flick, R. A. Duncan, S. P. Wallen, N. Boechler, C. Stelling, M. Retsch, J. J. Alvarado-Gil, K. A. Nelson, and A. A. Maznev, "Vibrational dynamics of a two-dimensional micro-granular crystal," Phys. Rev. B 96, 024303 (2017).
7. A. Vega-Flick, R. A. Duncan, S. P. Wallen, N. Boechler, C. Stelling, M. Retsch, J. J. Alvarado-Gil, K. A. Nelson, and A. A. Maznev, "Contact-based and spheroidal vibrational modes of a hexagonal monolayer of microspheres on a substrate," Wave Motion 76, 122 (2018).
8. P. H. Otsuka, S. Mezil, O. Matsuda, M. Tomoda, A. A. Maznev, T. Gan, N. Fang, N. Boechler, V. E. Gusev and O. B. Wright, "Time-domain imaging of GHz surface waves on an acoustic metamaterial," New J. Phys. 20 013026 (2018). https://iopscience.iop.org/article/10.1088/1367-2630/aa9298/meta
9. A.A. Maznev and A.G. Every, "Bound acoustic modes in the radiation continuum in isotropic material systems without periodic structures," Phys. Rev. B 97, 014108 (2018).
10. A. G. Every and A. A. Maznev, "Fano line shapes of leaky surface acoustic waves extending from supersonic surface wave points," Wave Motion 79, 1-9 (2018).
11. J. Pudell, A. A. Maznev, M. Herzog, M. Kronseder, C. Back, G. Malinowski, A. von Reppert, and M. Bargheer, "Layer specific observation of the slow thermal equilibration in ultrathin metallic nanostructures by femtosecond x-ray diffraction," Nature Commun. 9, 3335 (2018).

Peer-Reviewed Publications Resulting from this Project

1. A. A. Maznev, et al., "Propagation of THz acoustic wave packets in GaN at room temperature," Appl. Phys. Lett. 112, 061903 (2018). https://doi.org/10.1063/1.5008852
2. T. Hecksher, et al., "Toward broadband mechanical spectroscopy," PNAS 114, 8710 (2017). https://doi.org/10.1073/pnas.1707251114
3. I. Chaban, et al., "Time-domain Brillouin scattering for the determination of laser-induced temperature gradients in liquids," Rev. Sci. Instrum. 88, 074904 (2017). https://doi.org/10.1063/1.4993132
4. F. Bencivenga et al., "Four-wave-mixing experiments with seeded free electron lasers," Faraday Discuss., 194, 283 (2016). https://doi.org/10.1039/C6FD00089D
5. V. V. Temnov, et al., "Towards the nonlinear acousto-magnetoplasmonics," J. Opt. 18, 093002 (2016). https://doi.org/10.1088/2040-8978/18/9/093002
6. A. Vega-Flick, R. A. Duncan, S. P. Wallen, N. Boechler, C. Stelling, M. Retsch, J. J. Alvarado-Gil, K. A. Nelson, and A. A. Maznev, "Vibrational dynamics of a two-dimensional micro-granular crystal," Phys. Rev. B 96, 024303 (2017). https://doi.org/10.1103/PhysRevB.96.024303
7. A. Vega-Flick, R. A. Duncan, S. P. Wallen, N. Boechler, C. Stelling, M. Retsch, J. J. Alvarado-Gil, K. A. Nelson, and A. A. Maznev, "Contact-based and spheroidal vibrational modes of a hexagonal monolayer of microspheres on a substrate," Wave Motion 76, 122 (2018). https://doi.org/10.1016/j.wavemoti.2017.10.010
8. P. H. Otsuka, S. Mezil, O. Matsuda, M. Tomoda, A. A. Maznev, T. Gan, N. Fang, N. Boechler, V. E. Gusev and O. B. Wright, "Time-domain imaging of GHz surface waves on an acoustic metamaterial," New J. Phys. 20 013026 (2018). https://doi.org/10.1088/1367-2630/aa9298
9. A.A. Maznev and A.G. Every, "Bound acoustic modes in the radiation continuum in isotropic material systems without periodic structures," Phys. Rev. B 97, 014108 (2018). https://doi.org/10.1103/PhysRevB.97.014108
10. A. G. Every and A. A. Maznev, "Fano line shapes of leaky surface acoustic waves extending from supersonic surface wave points," Wave Motion 79, 1-9 (2018). https://doi.org/10.1016/j.wavemoti.2018.02.005
11. J. Pudell, A. A. Maznev, M. Herzog, M. Kronseder, C. Back, G. Malinowski, A. von Reppert, and M. Bargheer, "Layer specific observation of the slow thermal equilibration in ultrathin metallic nanostructures by femtosecond x-ray diffraction," Nature Commun. 9, 3335 (2018). https://doi.org/10.1038/s41467-018-05693-5
12. "Generation of coherent phonons by coherent extreme ultraviolet radiation in a transient grating experiment," A. A. Maznev, F. Bencivenga, A. Cannizzo, F. Capotondi, R. Cucini, R. A. Duncan, T. Feurer, T. D. Frazer, L. Foglia, H.-M. Frey, H. Kapteyn, J. Knobloch, G. Knopp, C. Masciovecchio, R. Mincigrucci, G. Monaco, M. Murnane, I. Nikolov, E. Pedersoli, A. Simoncig, A. Vega-Flick, and K. A. Nelson, *Appl. Phys. Lett.* **113**, 221905 (2018). https://doi.org/10.1063/1.5048023
13. "Nonlinear XUV-optical transient grating spectroscopy at the Si $L_{2,3}$-edge," R. Bohinc, G. Pamfilidis, J. Rehault, P. Radi, C. Milne, J. Szlachetko, F. Bencivenga, F. Capotondi, R. Cucini, L. Foglia, C. Masciovecchio, R. Mincigrucci, E. Pedersoli, A. Simoncig, N. Mahne, A. Cannizzo, H. M. Frey, Z. Ollmann, T. Feurer, A. A. Maznev, K. Nelson, and G. Knopp, *Appl. Phys. Lett*. **114**, 181101 (2019). https://doi.org/10.1063/1.5048023

1. D. Nardi, M. Travagliati, M. Murnane, H. Kapteyn, G. Ferrini, C. Giannetti, F. Banfi, "Impulsively Excited Surface Phononic Crystals: a Route towards Novel Sensing Schemes", IEEE Sensors Journal **15**, 5142 (2015). https://doi.org/10.1109/ICSENS.2014.6985145
2. K.M. Hoogeboom-Pot, J.N. Hernandez-Charpak, T. Frazer, E.H. Anderson, W. Chao, R. Falcone, X. Gu, R. Yang, M.M. Murnane, H.C. Kapteyn, D. Nardi, "A new regime of nanoscale thermal transport: collective diffusion increases dissipation efficiency", PNAS 112, 4846–4851 (2015). https://doi.org/10.1073/pnas.1503449112
3. K. Hoogeboom-Pot, J. Hernandez-Charpak, T. Frazer, X. Gu, E. Turgut, E. Anderson, W. Chao, J. Shaw, R. Yang, M. Murnane, H. Kapteyn, M. Nardi, "Mechanical and thermal properties of nanomaterials at sub-50nm dimensions characterized using coherent EUV beams", *SPIE Advanced Lithography* **9424**, 942417-1 (2015). https://doi.org/10.1117/12.2085615
4. J. Hernandez-Charpak, T. Frazer, J. Knobloch, K. Hoogeboom-Pot, D. Nardi, W. Chao, L. Jiang, M. Tripp, S. King, H. Kapteyn, and M. Murnane, "Reliable characterization of materials and nanostructured systems <<50nm using coherent EUV beams", in *SPIE Advanced Lithography*, pp. 97780I (2016). https://doi.org/10.1117/12.2219434