Do embedded nanodots make better thermoelectrics?

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Effects of nanoscale precipitates on lattice thermal conductivity are not clear

- Alkali halides studied in 1960s. No effect at T>100 K but concentration is small $F<10^{-3}$
- PbTe/PbSe nanodot superlattices (NDSL)
  - indirect measurement at room temperature using one-leg ΔT: Λ_{lat} = 0.33 W/m-K.
  - ICT 2005: Λ_{lat} = 0.45 W/m-K
- InGaAs:ErAs studied extensively. Beats the alloy limit.
- LAST: low lattice conductivity but systematics are mostly lacking (i.e., controlled variations in nanodot size or spacing)

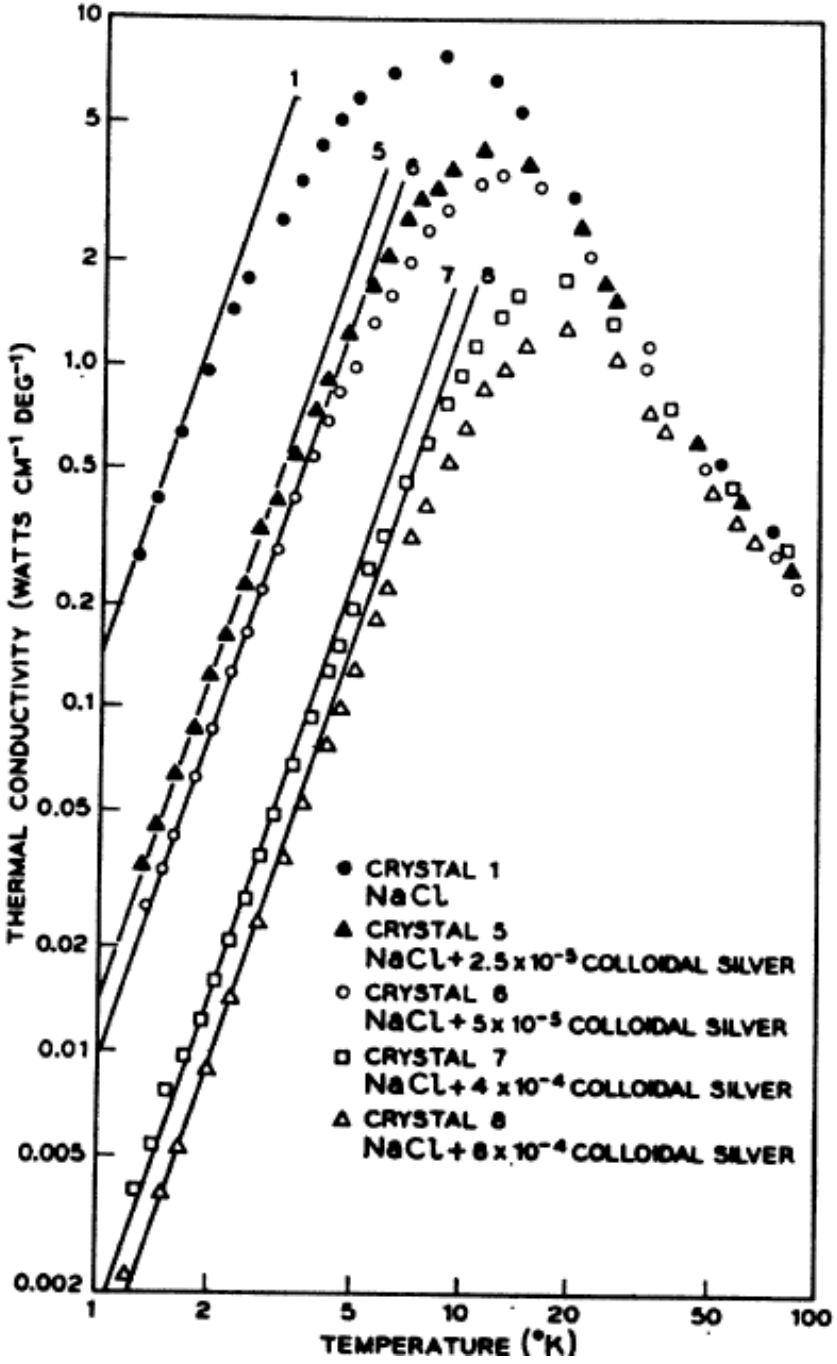
…and $AgSbTe_2$ is a strange material…

Need to scatter low frequency phonons that have long mean-free paths

- Anharmonicity $\tau^{-1} \propto \omega^2 T$
- Rayleigh scattering $\tau^{-1} \propto \omega^4$
- Boundary scattering $\tau^{-1} \propto 1/d$

Colloidal Ag in NaCl limits phonon mean-free-path

- Reduction of NaCl:AgCl mixed crystal in K vapor at 600 °C.
- Ag particle radii:
  - r<20 nm by optical spectroscopy
  - r~10 nm by phonons
- Mean-free-path is ℓ =40 μm at the highest concentration
- Data gives $\ell \sim r/F$, where F is the volume fraction



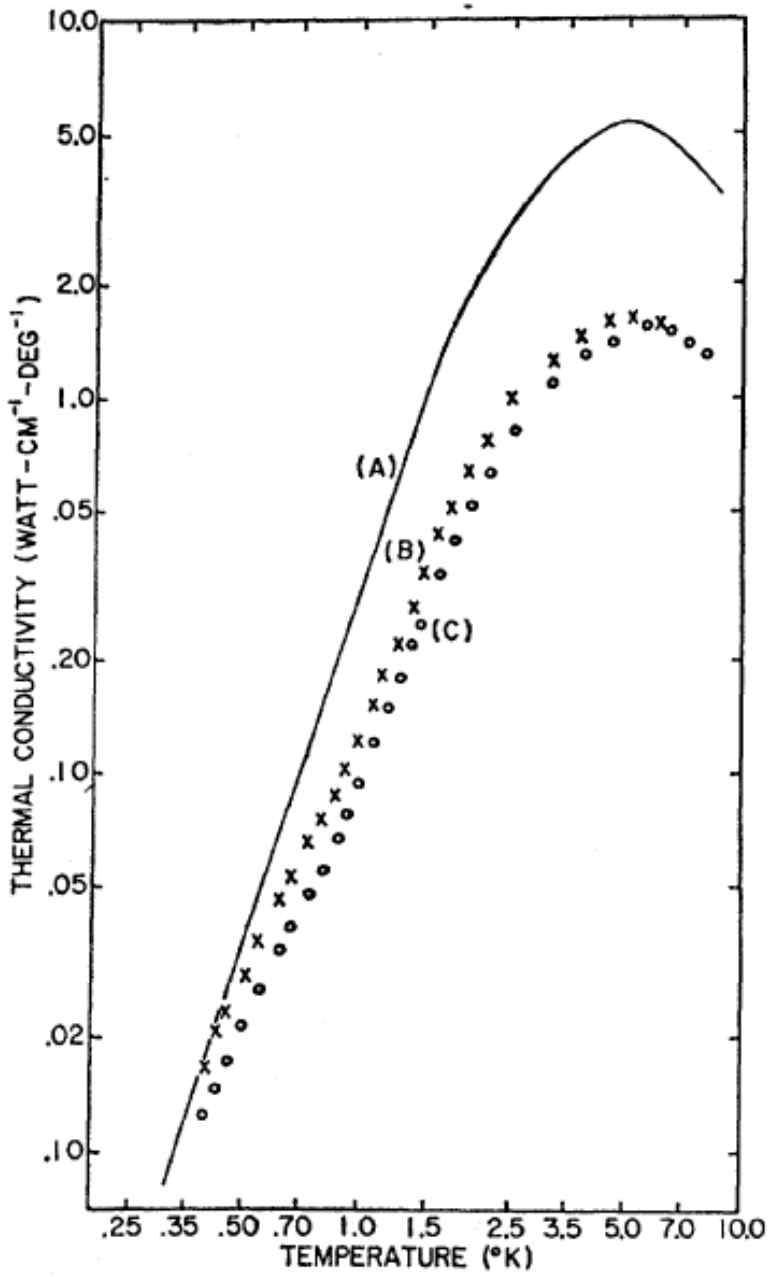
Worlock, PR 147, 636 (1966)

Best-case scenario is geometrical scattering of all phonons

- Cross section is projected area $\sigma = 4\pi r^2$
- Volume fraction $F = \frac{4\pi}{3} r^3 N$ where N is the number density
- Mean free path $l = \frac{1}{N\sigma} = \frac{r}{3F}$
- Expect transition to Rayleigh scattering for $kr << 1$ (k phonon wavevector)

Transition observed directly at low T

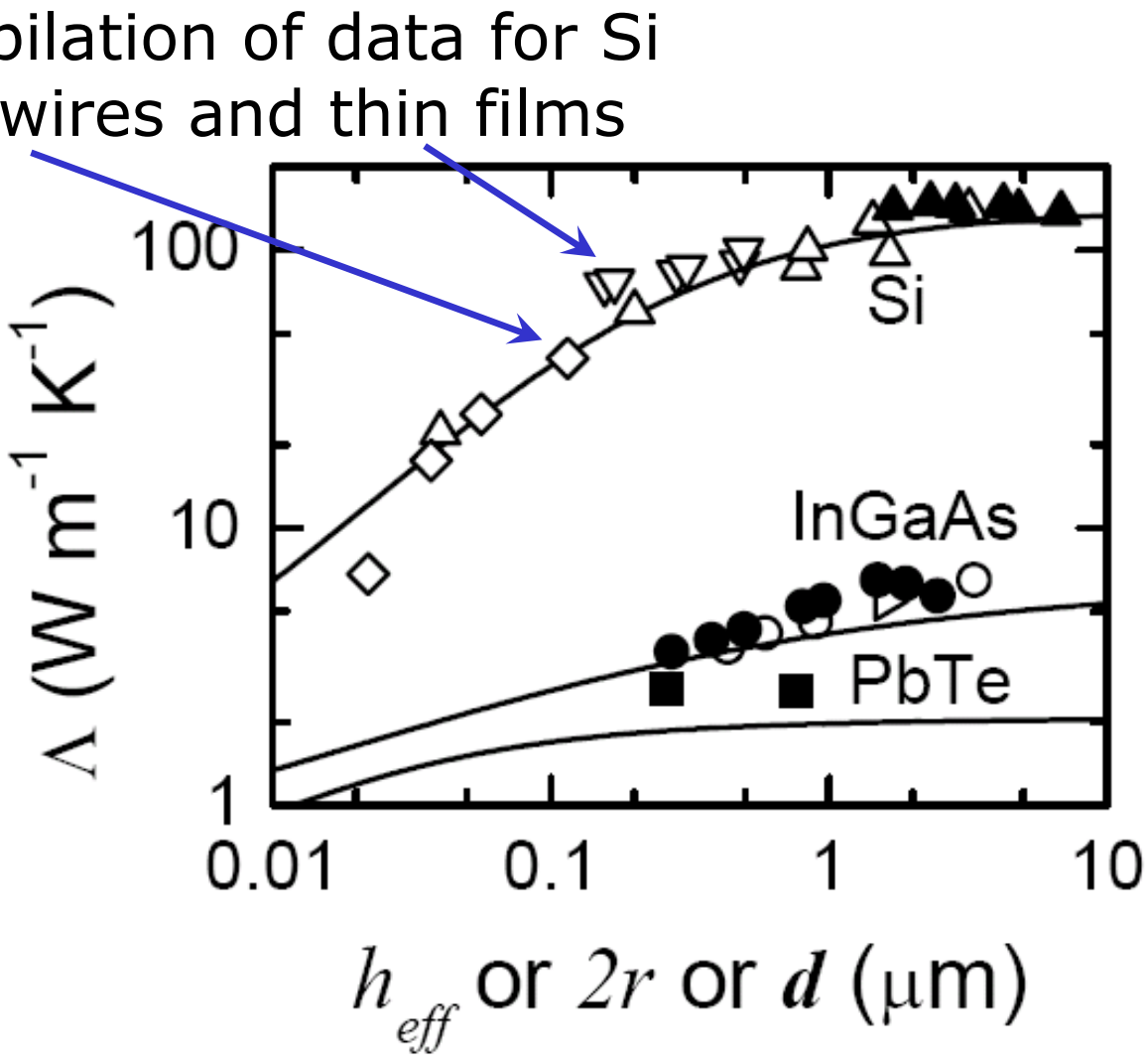
- (A) KBr doped with (B) Sr^{++} and (C) Br^{++} at the level of 10^{-4}.
- 10 nm precipitates



Schwartz and Walker, PR 155, 969 (1967)

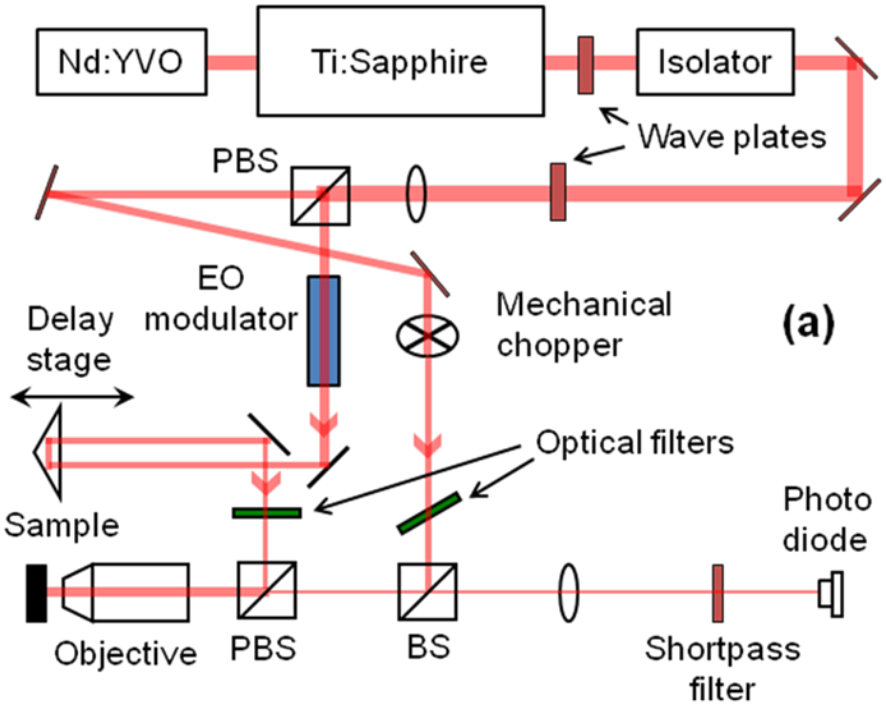
Strong boundary scattering reduces the thermal conductivity

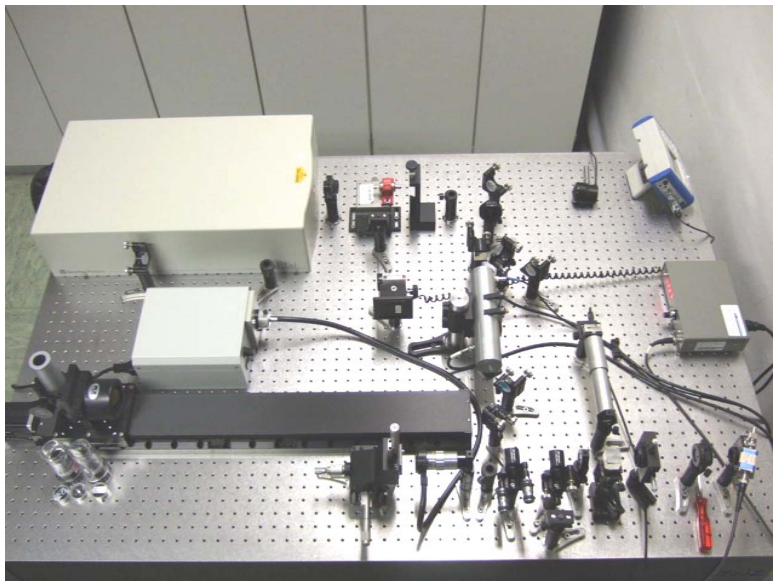
- Debye-Callaway-Morelli model
- Length-scale that reduces Λ by x2
  - Si: 300 nm
  - InGaAs: 200 nm
  - PbTe (predicted) 15 nm



Time domain thermoreflectance since 2003

- Improved optical design
- Normalization by out-of-phase signal eliminates artifacts, increases dynamic range and improves sensitivity
- Exact analytical model for Gaussian beams and arbitrary layered geometries
- One-laser/two-color approach tolerates diffuse scattering

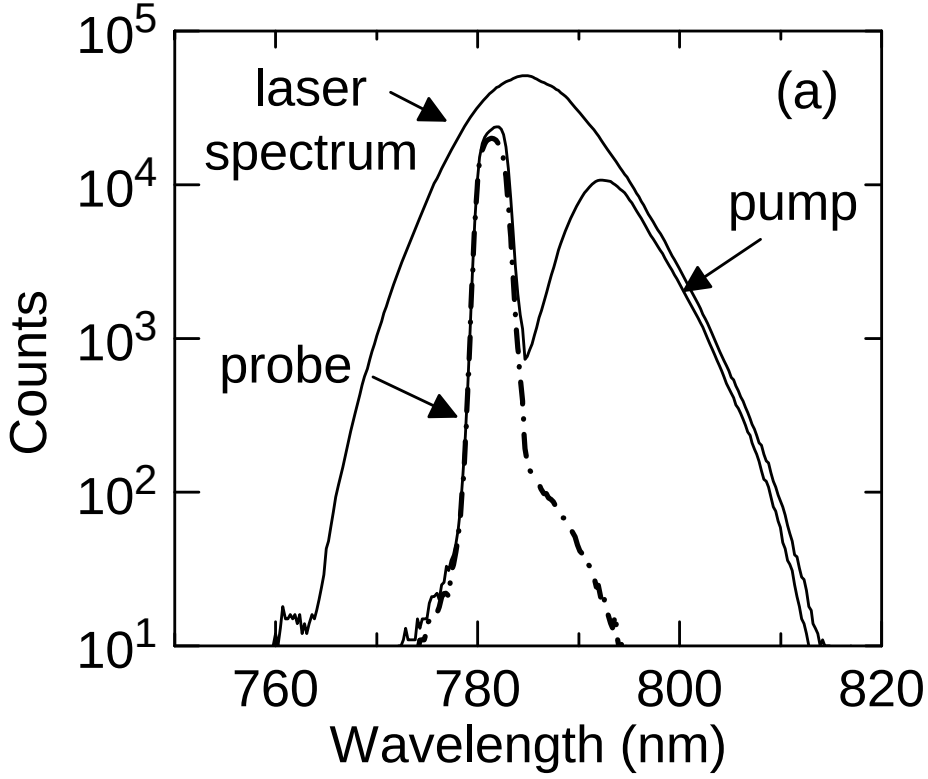




Clone built at Fraunhofer Institute for Physical Measurement, Jan. 7-8 2008

One of many possible configurations for the "two-tint" method

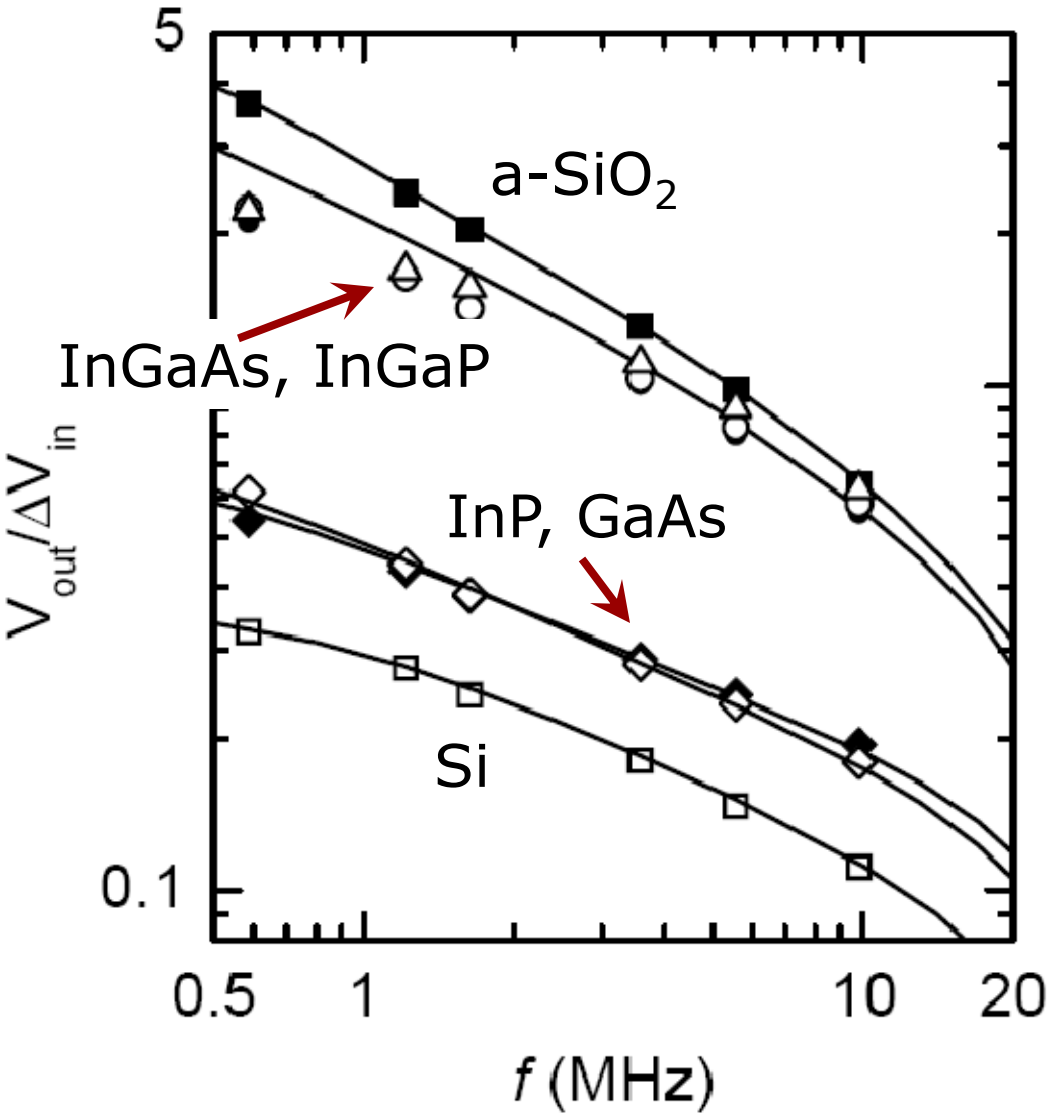
- 790 nm low-pass filter on pump
- 785 nm band-pass filter on probe, tilted to shift to 782 nm
- 780 short pass filter at photodiode detector



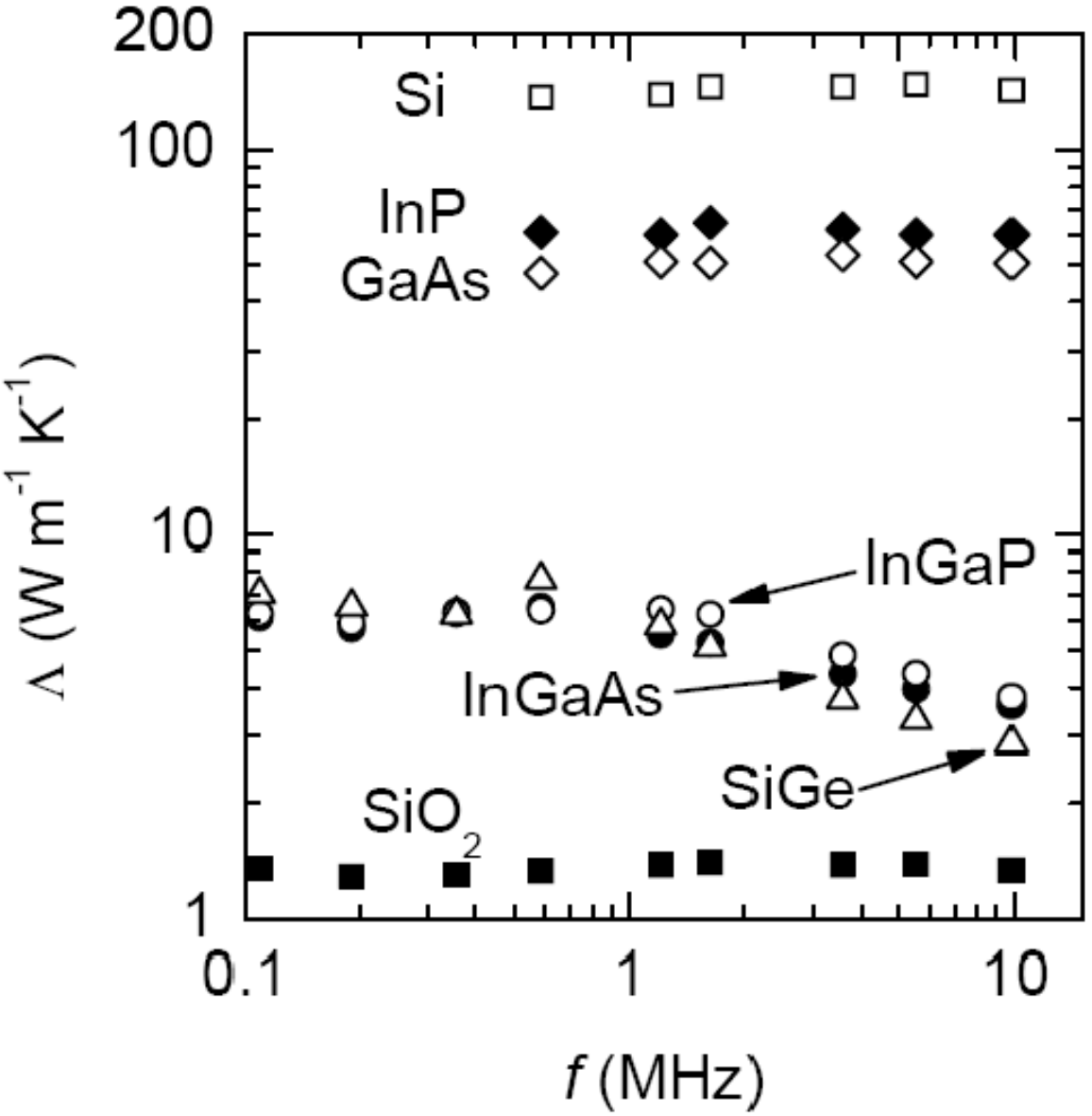
Kang et al., Rev. Sci. Instrum. **79,** 114901 (2008)

Thermoreflectance raw data at t=100 ps

- fix delay time and vary modulation frequency *f.*
- semiconductor alloys show deviation from fit using a single value of the thermal conductivity
- Change in V_{in} doesn't depend on *f.* V_{out} mostly depends on $(f\Lambda C)^{-1/2}$



Same data but allow Λ to vary with frequency *f*



How can thermal conductivity be frequency dependent at only a few MHz?

- $2\pi f\tau << 1$ for phonons that carry significant heat. For dominant phonons, τ ~100 ps, and $2\pi f\tau \sim 10^{-3}$.
- But the thermal penetration depth d is not small compared to the dominant mean-free-path ℓ_{dom}.

$$d = \sqrt{\Lambda / \pi C f}$$

- Ansatz: phonons with $\ell(\omega) > d$ do not contribute to the heat transport in this experiment.
- True only if the "single-relaxation-time approximate" fails strongly. For single relaxation time τ, $\ell << d$ because $f\tau << 1$.

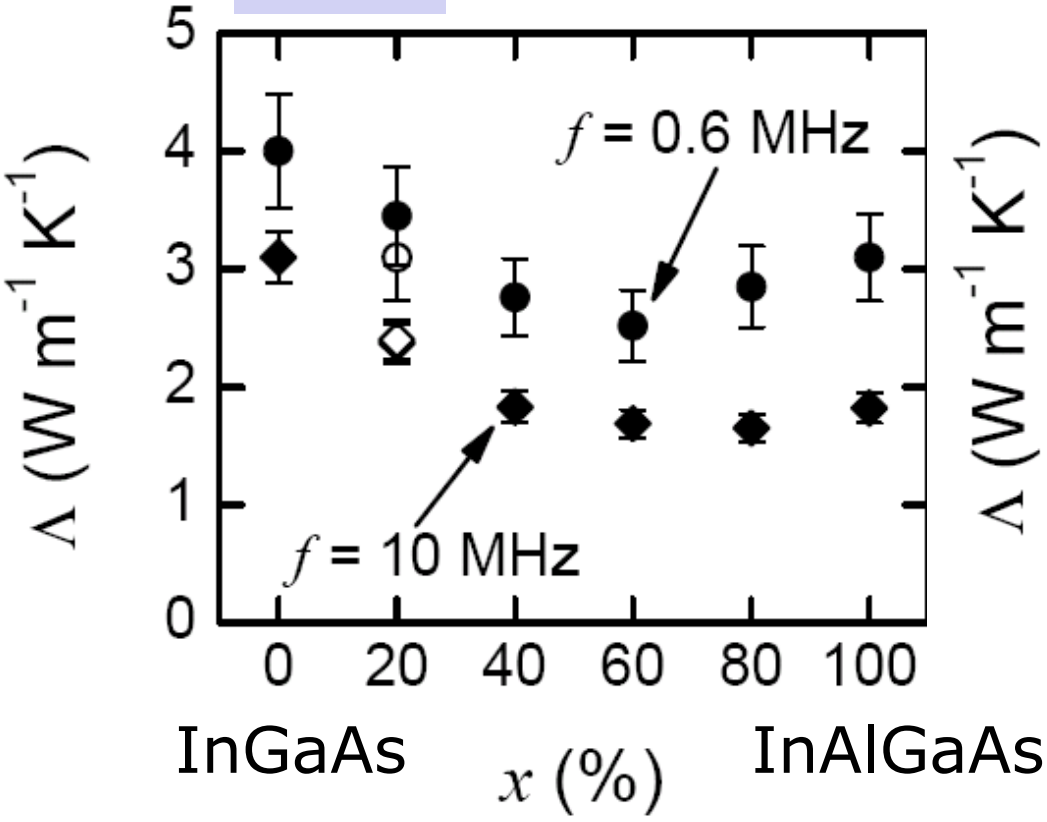
0.3% ErAs nanodots decreases thermal conductivity of InGaAs but not InAlGaAs

Open symbols: no ErAs

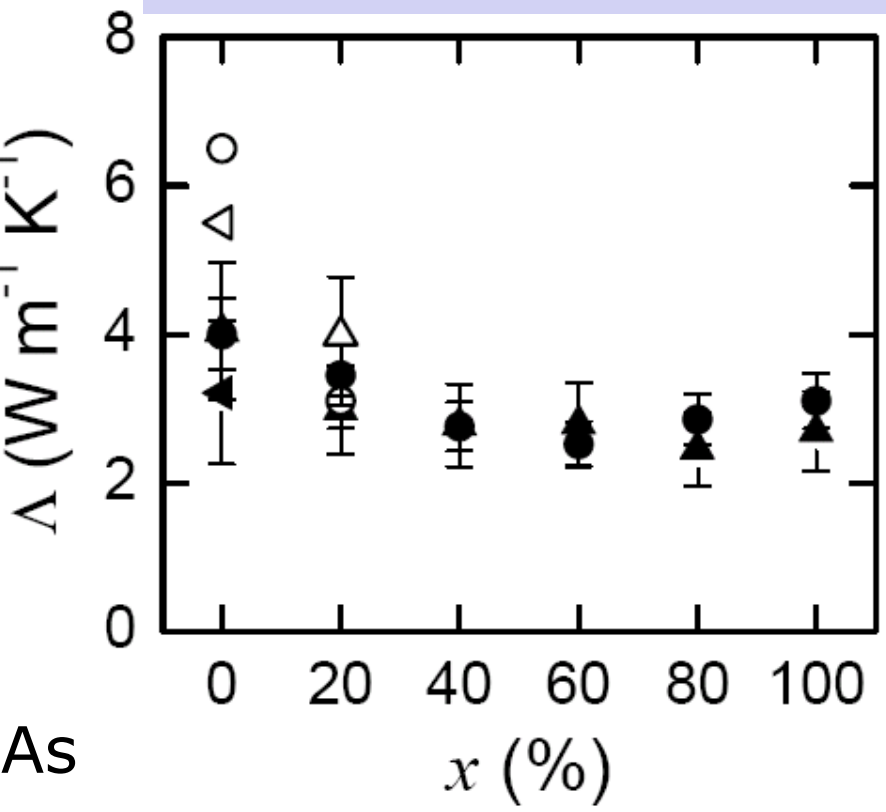
Circles: TDTR

Triangles: 3ω

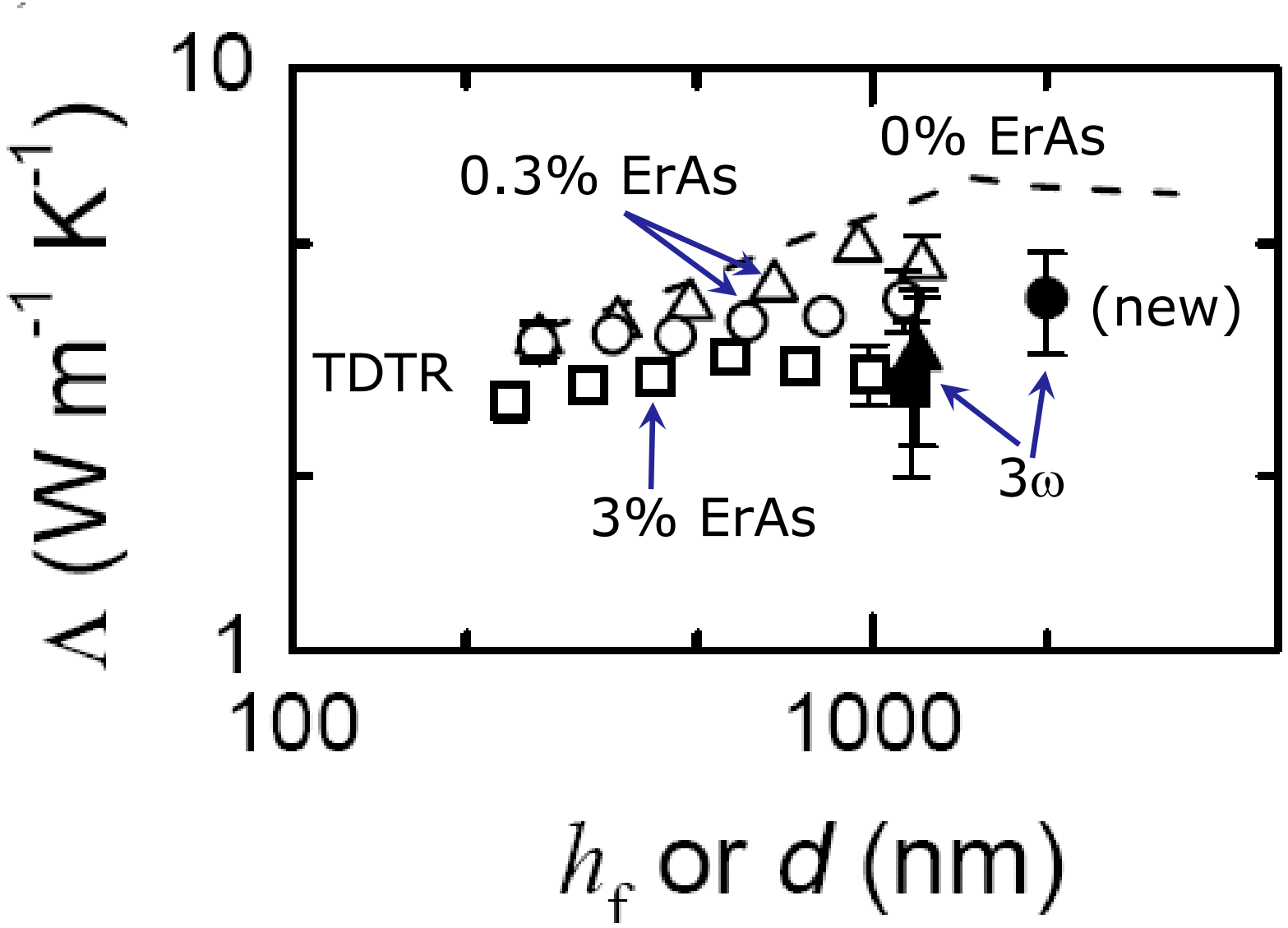
TDTR



0.6 MHz TDTR and 3ω



ErAs in InGaAs lowers thermal conductivity and reduces frequency dependence



InGaAs:ErAs conclusions

- Lots of uncertainties…
- … but frequency dependence of thermal conductivity of ErAs in InGaAs is consistent with boundary scattering length of 400 nm in 0.3% samples and 100 nm in 3% samples.
- Within the error bars of $l = \frac{1}{N\sigma} = \frac{r}{3F}$??

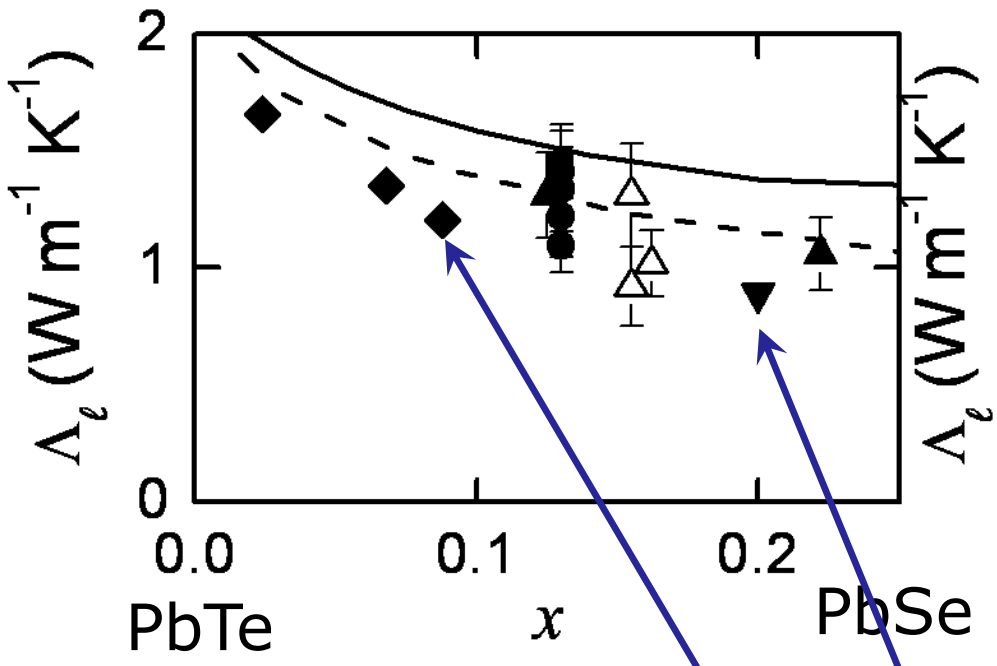
See Kim and Majumdar, JAP **99**, 084306 (2006) for a more sophisticated analysis of scattering rates

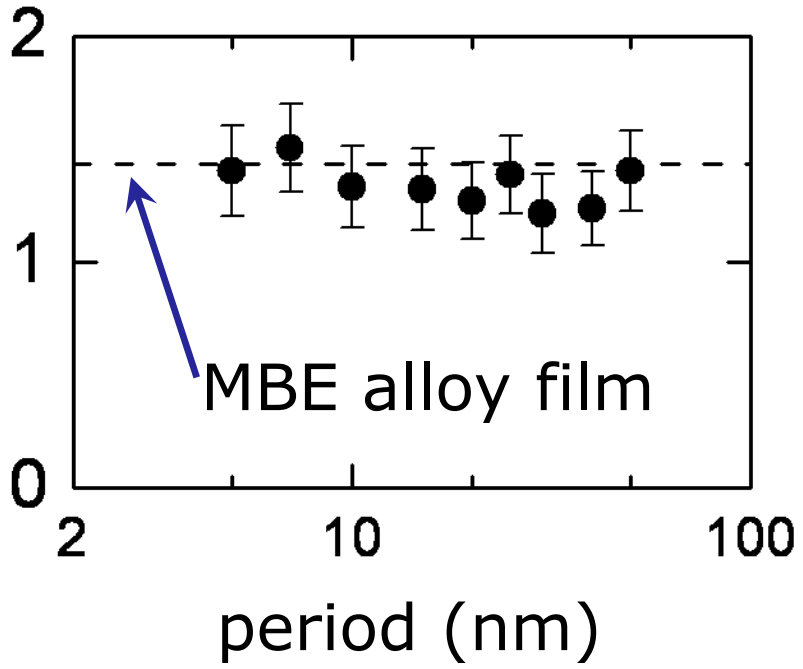
ZT=1.6 reported for PbTe/PbSe nanodot superlattices

- Power factor is not enhanced so lattice thermal conductivity is assumed to be very small
- Limited data for thermal conductivity
- Use TDTR to measure the total thermal conductivity in the top ~0.5-μm of a large number of ~5-μm-thick NDSL samples grown at MIT/Lincoln-Lab
- In-plane electrical measurements (conductivity, Hall) give estimate of electrical thermal conductivity, $\Lambda_{lat} = \Lambda_{total} - \Lambda_{elec}$
- Assume that anisotropy is "not too strong"

Lattice thermal conductivities of PbTe/PbSe NDSLs do not fall below 1 W/m-K

- Organize by average composition and by period
- Filled symbols n-type; open symbols p-type



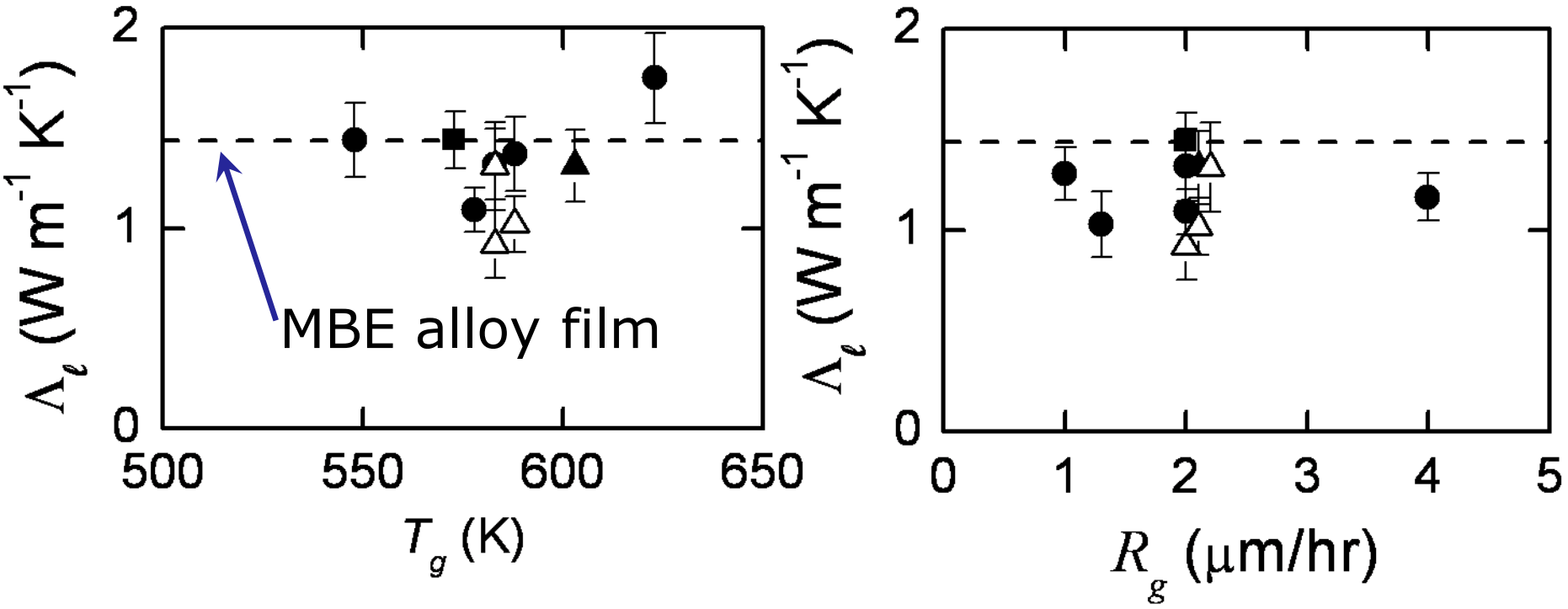


in-plane superlattice (IPM)

alloy superlattice (3ω)

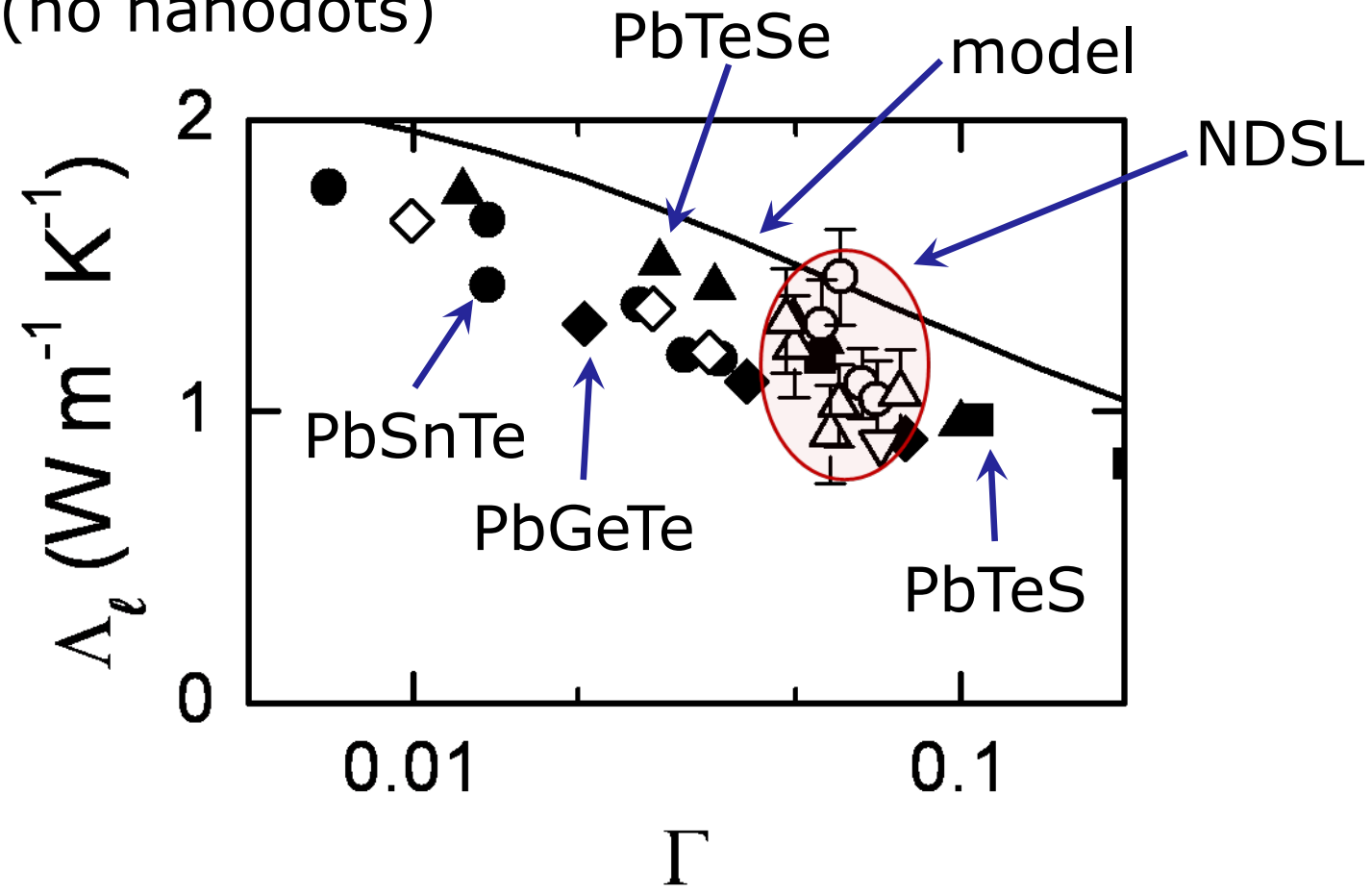
Lattice thermal conductivities of PbTe/PbSe NDSLs do not fall below 1 W/m-K

- Organize by growth temperature and growth rate



NDSL and superlattice PbTe do not significantly beat the alloy limit

- nanostructured (open symbols); random alloys (filled symbols);
- Rayleigh scattering strength Γ calculated for random alloy (no nanodots)



Summary and Conclusions

- ErAs nanodots lower the thermal conductivity of InGaAs and reduce the TDTR frequency dependence. Nanodots in InGaAs are effective in scattering phonons with mean-free-paths in the range of hundreds of nm. (InGaAlAs digital alloy superlattices are another story…)
- PbSe nanodots are not as effective in lowering the thermal conductivity of PbTe; essentially the same thermal conductivity is observed in alloys with the same average composition. This can be understood based on the small acoustic mismatch between PbTe and PbSe and the strong anharmonicity of PbTe.