Improvement of Thermoelectric Properties through Reduction of Thermal Conductivity by Nanoparticle Addition and Stoichiometric Change to Mg_2Si

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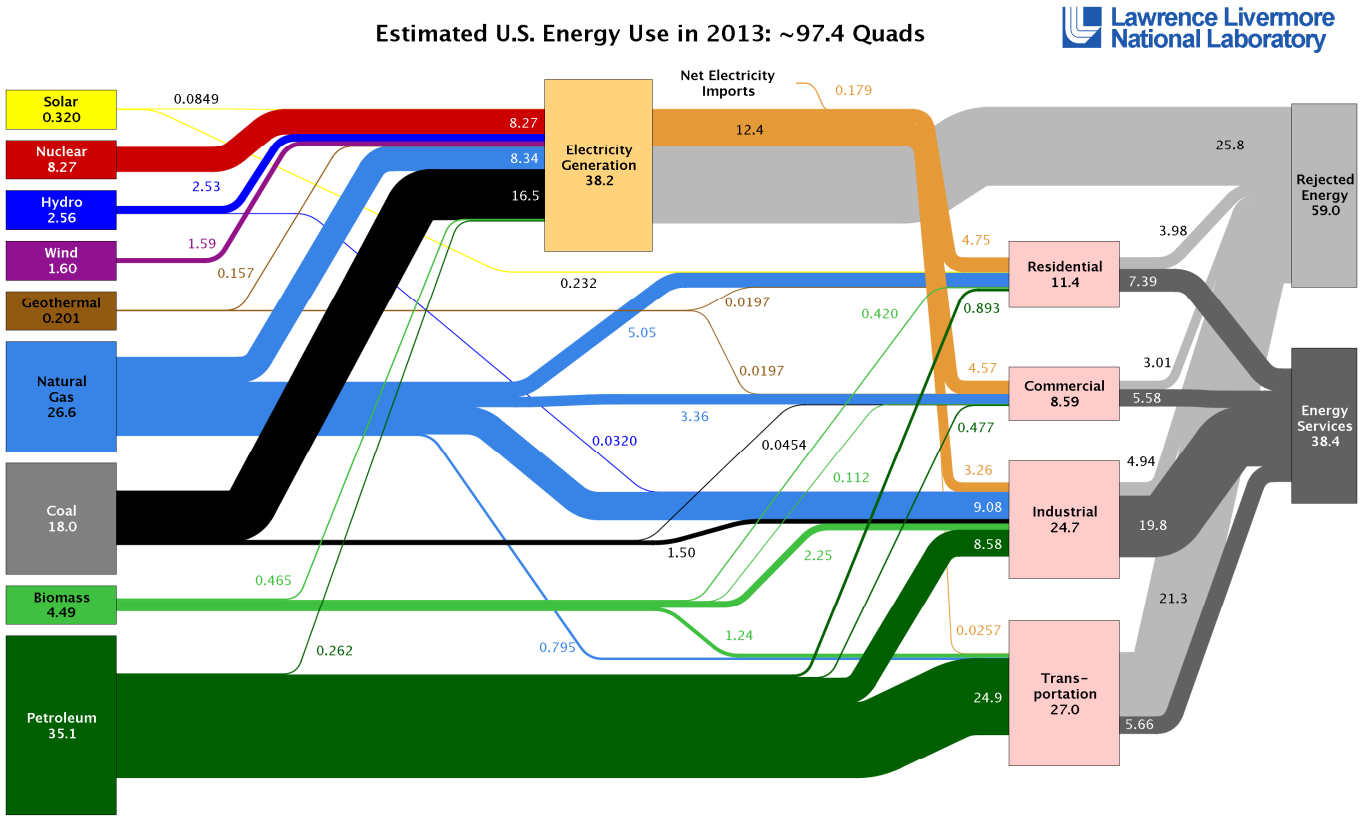
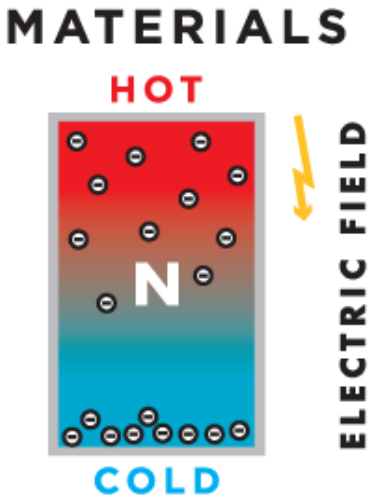
Motivation

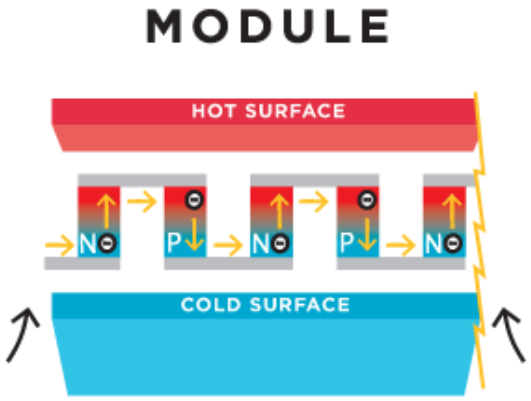


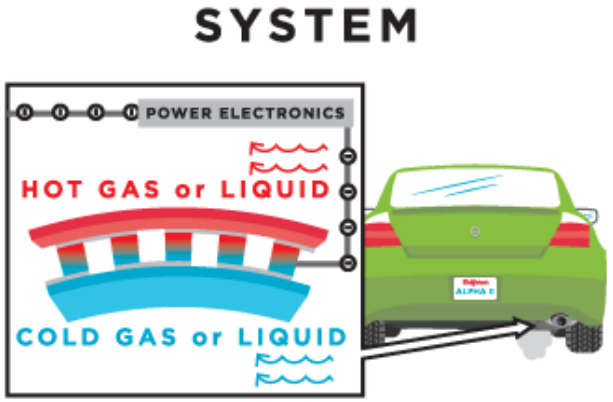
Source: LLNL 2014. Data is based on DOE/EIA-0035(2014-03), March, 2014. If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboratory and the Department of Energy, under whose auspices the work was performed. Distributed electricity represents only retail electricity sales and does not include self-generation. EIA reports consumption of renewable resources (i.e., hydro, wind, geothermal and solar) for electricity in BTU-equivalent values by assuming a typical fossil fuel plant "heat rate." The efficiency of electricity production is calculated as the total retail electricity delivered divided by the primary energy input into electricity generation. End use efficiency is estimated as 65% for the residential and commercial sectors 80% for the industrial sector, and 21% for the transportation sector. Totals may not equal sum of components due to independent rounding. LLNL-MI-410527

https://flowcharts.llnl.gov/archive.html

Motivation





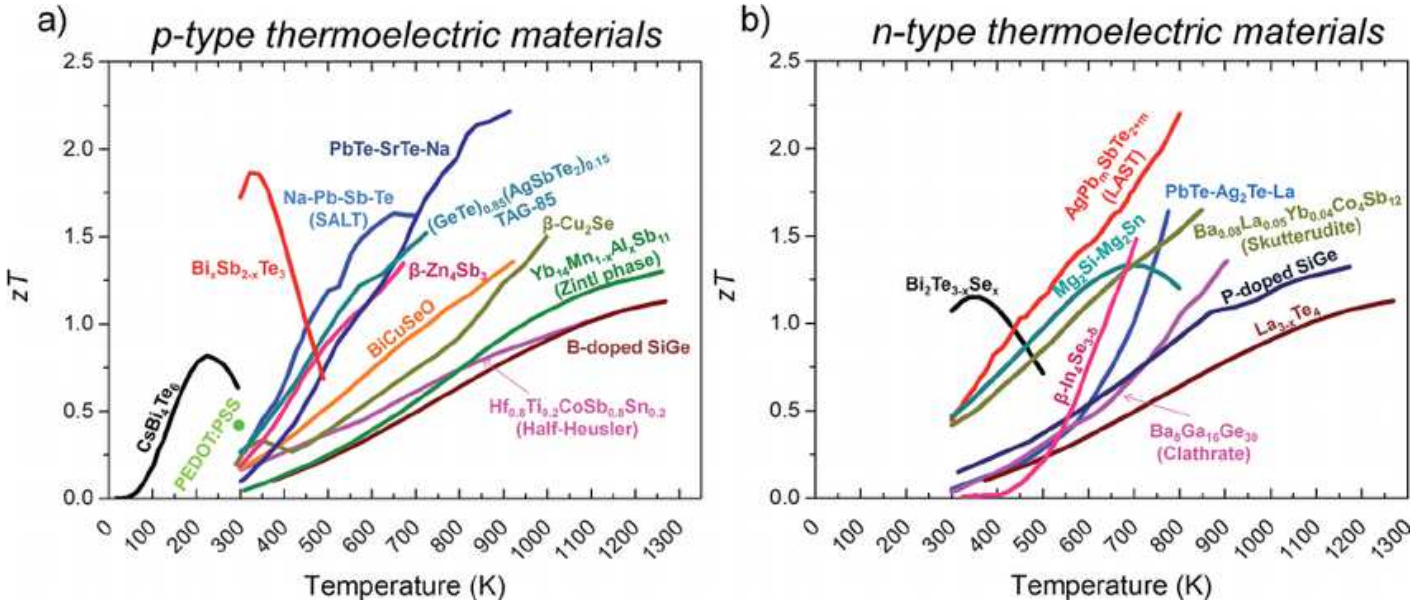


https://www.alphabetenergy.com/how-thermoelectrics-work/

Motivation

Figure of Merit (*ZT*) is a measure of the thermoelectric material's efficiency in converting thermal energy to electrical current.

It is defined by the following equation: $ZT = S^2 \frac{\sigma T}{k}$

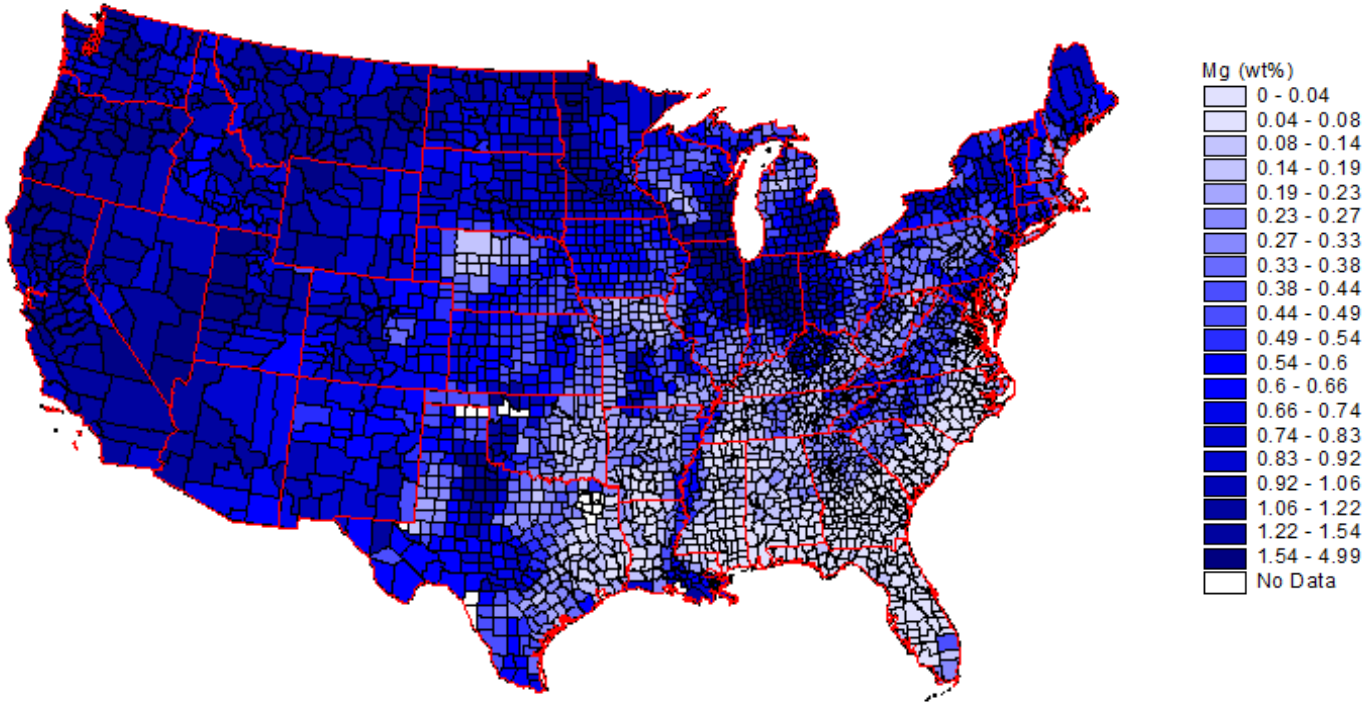


Rull-Bravo, RSC Advances, 2015

Motivation

Why Use Mg_2Si?

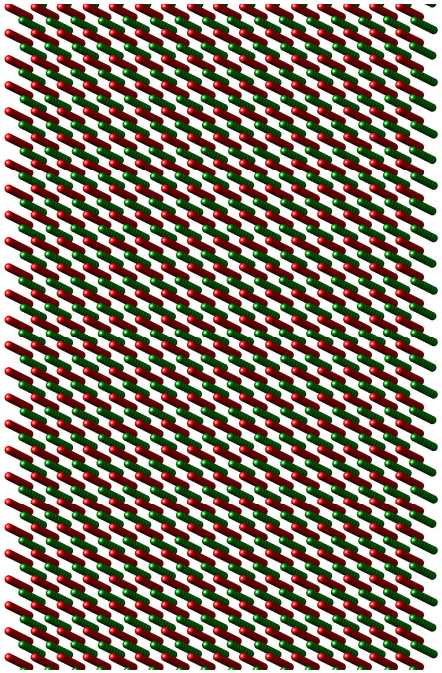
- Mg is earth abundant in Utah and much of the US
- Mg_2Si is a relatively simple compound when compared to the other thermoelectrics
- Mg is inexpensive, resulting in the production of Mg_2Si being less expensive

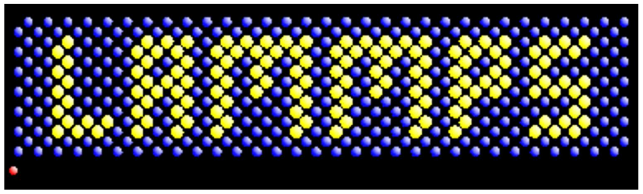


https://mrdata.usgs.gov/geochem/doc/averages/mg/usa.html

Methodology

Molecular Dynamics





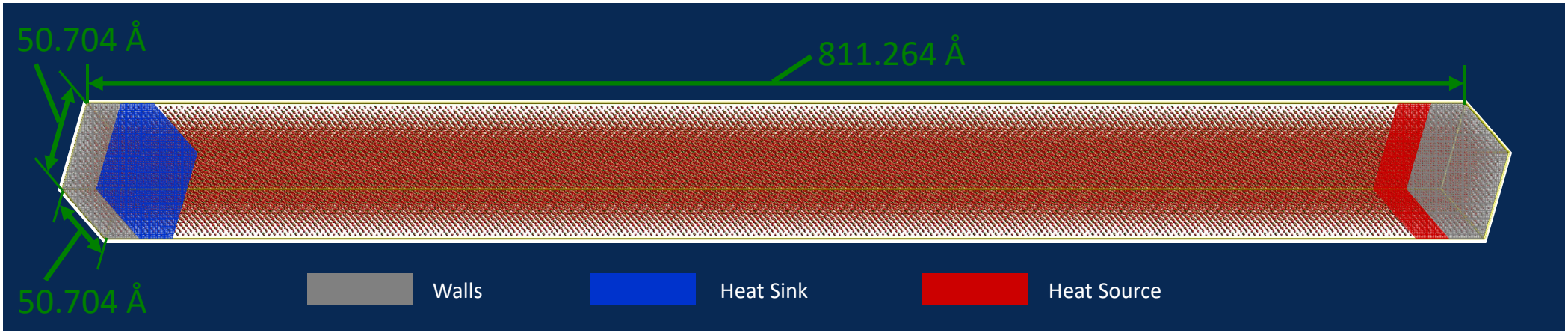
(Large-scale Atomic/Molecular Massively Parallel Simulator)

$$ZT = S^2 \frac{\sigma T}{k} \rightarrow k = k_p + k_e$$

LAMMPS can only calculate k_p, which makes the follow up of experimental research to measure *ZT* critical

http://lammps.sandia.gov/#nogo

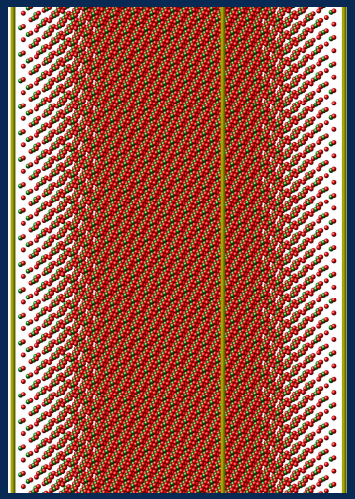
Experimental Setup



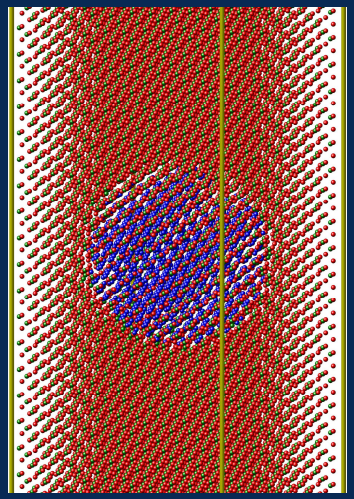
- Periodic Boundaries
- Extended modified embedded atom method (MEAM) potential

Zhang, Hengji, CMS, 2015

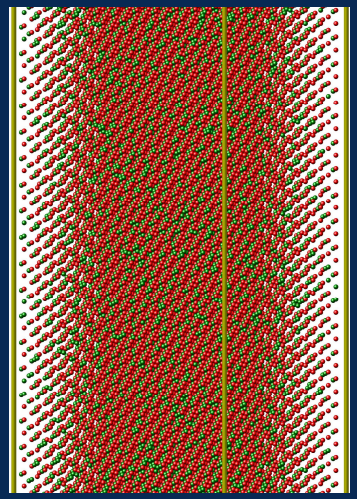
Experimental Setup



Pure Mg_2Si



Pure Mg_2Si with Si NP



Mg_xSi_x with 41.37% Si (matching the Si % of the sample with 8 Si NPs)

Experimental Setup

Nanostructure	300 K ($Wm^{-1}K^{-1}$)	600 K ($Wm^{-1}K^{-1}$)	900 K ($Wm^{-1}K^{-1}$)
Pure Mg_2Si	k_p = ?	k_p = ?	k_p = ?
Mg_2Si with 1 Si NP	k_p = ?	k_p = ?	k_p = ?
Mg_2Si with 2 Si NP	k_p = ?	k_p = ?	k_p = ?
Mg_2Si with 4 Si NP	k_p = ?	k_p = ?	k_p = ?
Mg_2Si with 8 Si NP	k_p = ?	k_p = ?	k_p = ?
Mg_2Si with 16 Si NP	k_p = ?	k_p = ?	k_p = ?
Mg_xSi_x 34.29 % Si (matching stoichiometry of Mg_2Si with 1 Si NP)	k_p = ?	k_p = ?	k_p = ?
Mg_xSi_x 35.32 % Si (matching stoichiometry of Mg_2Si with 2 Si NP)	k_p = ?	k_p = ?	k_p = ?
Mg_xSi_x 37.29 % Si (matching stoichiometry of Mg_2Si with 4 Si NP)	k_p = ?	k_p = ?	k_p = ?
Mg_xSi_x 41.37 % Si (matching stoichiometry of Mg_2Si with 8 Si NP)	k_p = ?	k_p = ?	k_p = ?
Mg_xSi_x 49.55 % Si (matching stoichiometry of Mg_2Si with 16 Si NP)	k_p = ?	k_p = ?	k_p = ?

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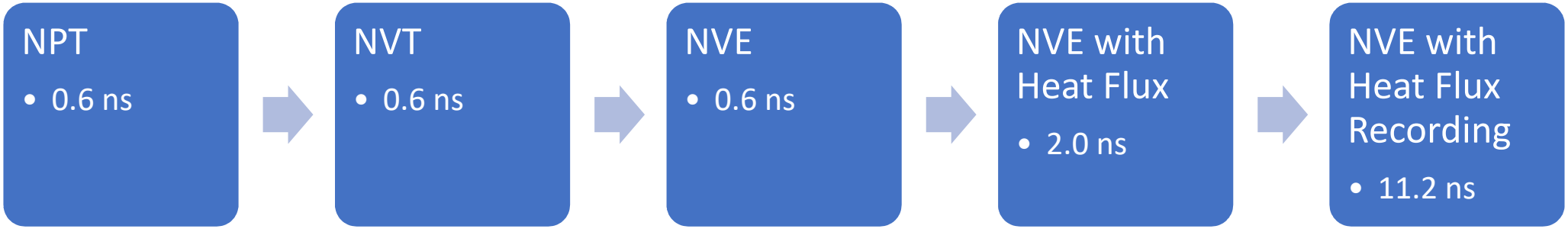
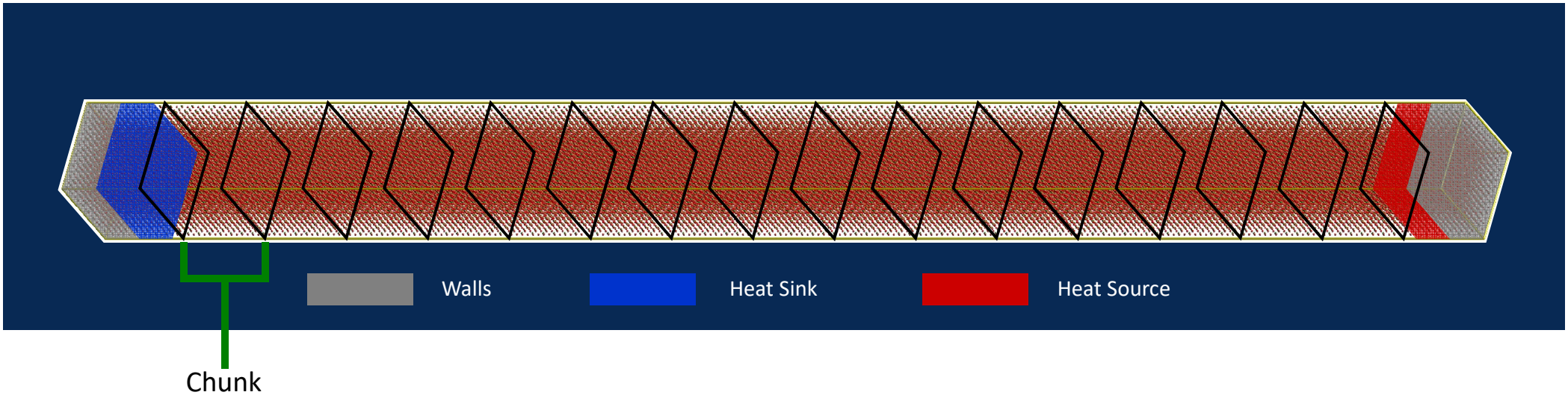
Methodology



- Nonequilibrium Molecular Dynamics (NEMD)
- Applied Heat Flux
- Total simulated time of 15 ns

Methodology



Fourier's Law

$$q = -k\frac{\Delta T}{\Delta x} \quad \Rightarrow \quad k = -q\frac{\Delta x}{\Delta T}$$

Uncertainty Calculations

- Simulations were run at the 3 different equilibration temperatures as previously described, except that no heat flux was applied (we assumed stoichiometry did not significantly affect the uncertainty in temperature)

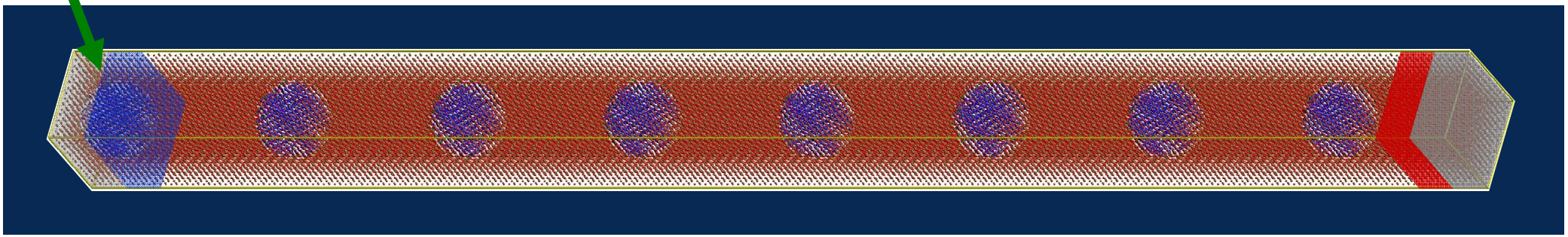
- The temperatures for each chunk were then averaged all together
- The absolute value of the difference between this value and the target equilibration temperature was taken as our uncertainty in temperature

Equilibration Temperature (K)	Uncertainty (K)
300	0.774
600	0.721
900	0.96

- This value was then added to and subtracted from the ΔT in Fourier's Law to obtain the minimum and maximum k_p values, and therefore their associated k_p uncertainties

Effect of NP Placement on k_p

Si NP in the wall and heat sink



- Some simulations had Si NPs in the walls and heat source/sink
- To ensure that this wasn't a problem, 2 simulations were run with 8 Si NPs each; one had an Si NP in the heat sink/wall area, the other did not.
- Their k_p values were 2.876 ($Wm^{-1}K^{-1}$) and 3.063 ($Wm^{-1}K^{-1}$), respectively, resulting in a percent change in k_p of 6.499%, which we considered negligible.

Results – Pure Mg_2Si

Work	k_p of Pure Mg_2Si at 300 K ($Wm^{-1}K^{-1}$)
LaBotz	7.8
This Work	8.454 ± 1.094

We determined that our calculated value for k_p above was sufficiently close that of Labotz, such that we could begin simulation of off-stoichiometry samples of Mg_2Si and calculation of their respective values for k_p.

LaBotz, JES, 1963

Results – Mg_2Si with Si NPs

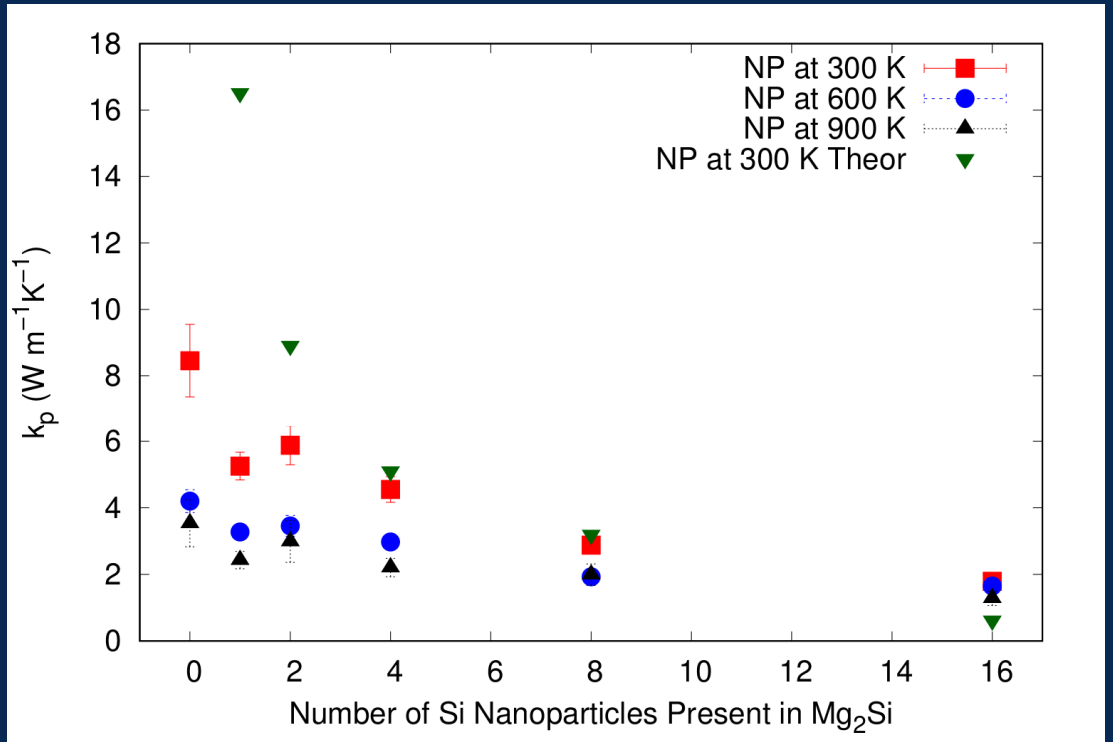


FIGURE 3: Lattice thermal conductivity (k_p) vs. number of Si NPs present in Mg_2Si samples at 300, 600, and 900 K. Included is an estimation of k_p for the 300 K equilibration temperature case, using Eqn 4 [8], denoted by NP at 300 K Theor.

Results – Mg_2Si with Si NPs

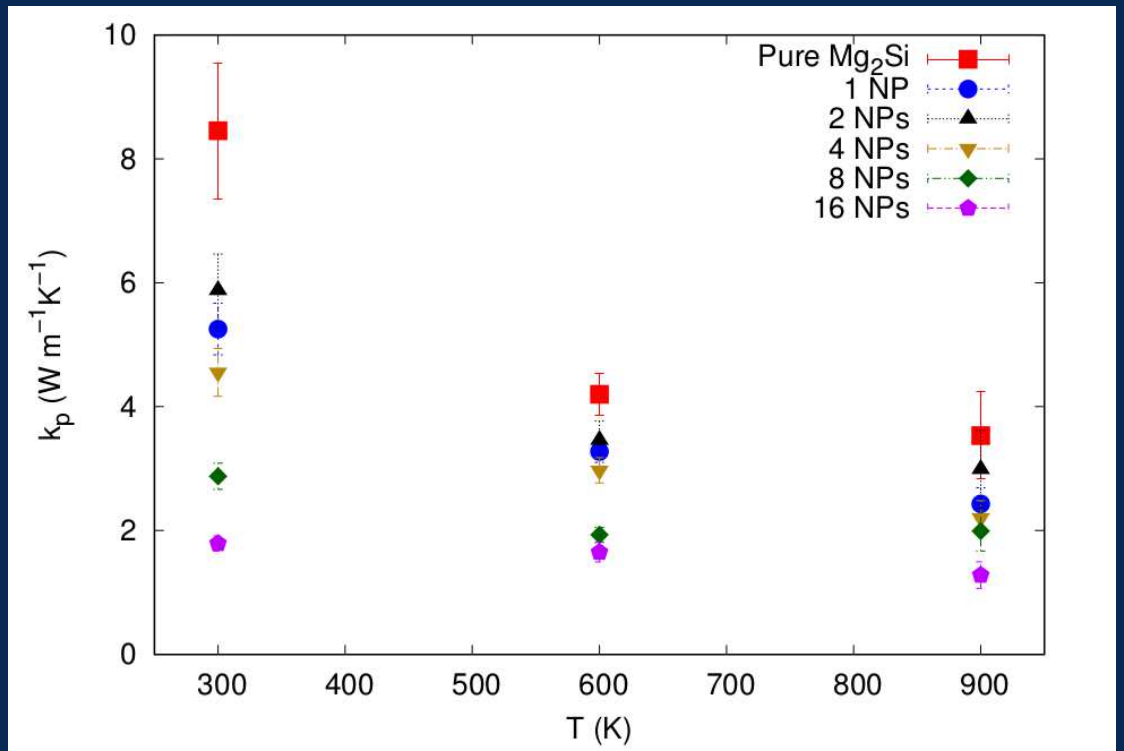
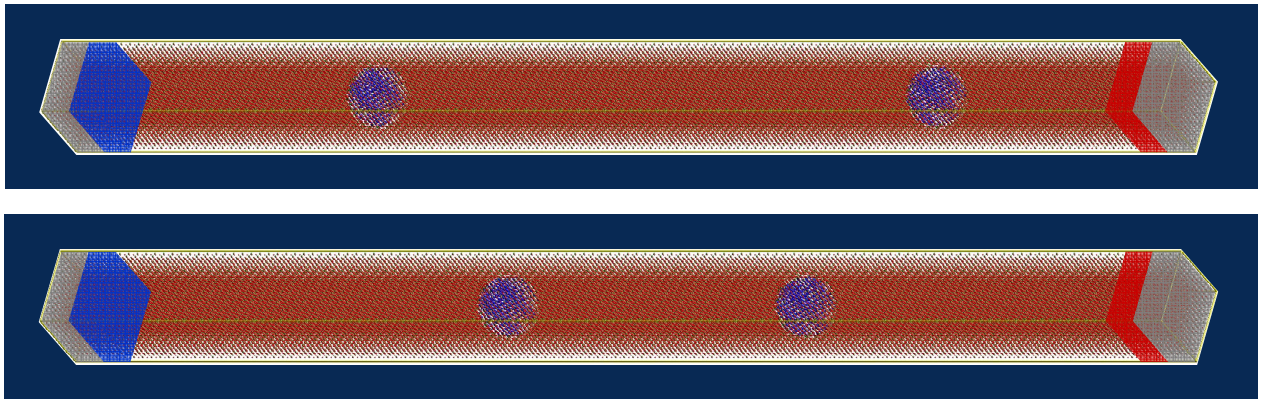


FIGURE 5: Lattice thermal conductivity (k_p) vs. temperature (T) for pure Mg_2Si (0 NPs) and Mg_2Si samples with 1, 2, 4, 8, and 16 Si NPs.

One Si NP Case

- Unexpectedly, the 1 NP cases resulted in lower in k_p values than their respective 2 NP cases
- We thought this might have to do with the NP spacing



- NP Spacing: 405.632 Å
- k_p: 5.877 $Wm^{-1}K^{-1}$

- NP Spacing: 215.492 Å
- k_p: 4.403 $Wm^{-1}K^{-1}$

- It appears that the closer the Si NP concentration is to the center of the sample, the lower the k_p, despite no change in stoichiometry

Results – Mg_2Si with Si Substitutionals

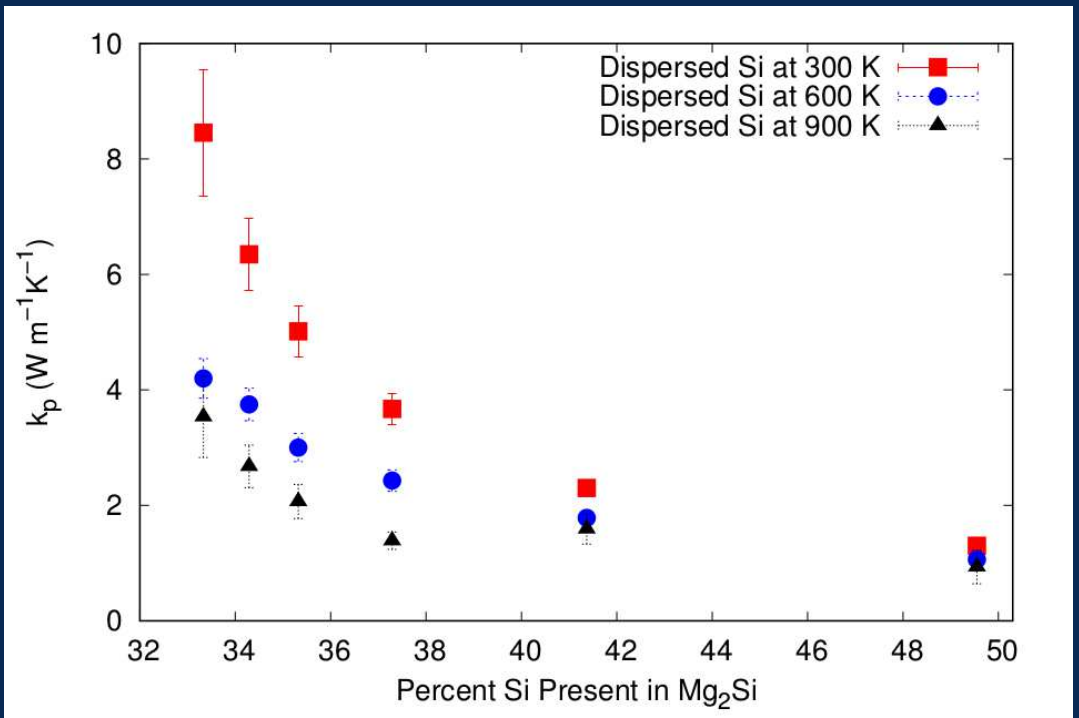


FIGURE 4: Lattice thermal conductivity (k_p) vs. percent Si present in Mg_2Si samples at 300, 600, and 900 K. The percent Si values correspond to the stoichiometry of the sample of pure Mg_2Si (33.33% Si), and respective samples of Mg_2Si having 1, 2, 4, 8, and 16 Si NPs.

Results – Mg_2Si with Si Substitutionals

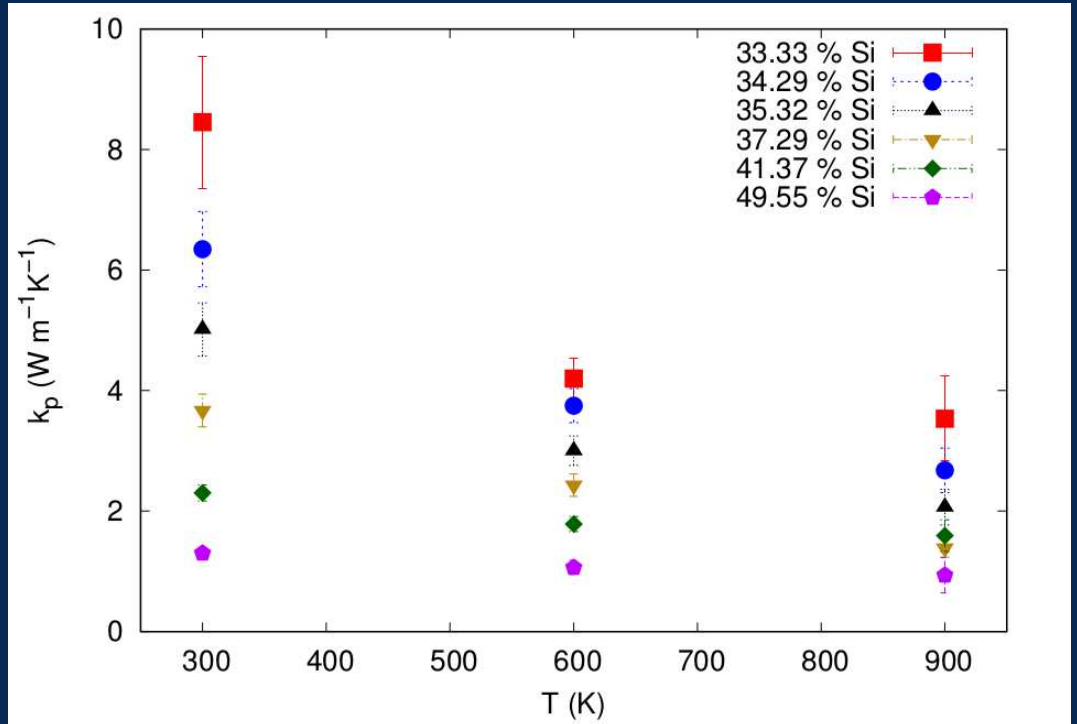


FIGURE 6: Lattice thermal conductivity (k_p) vs. temperature (T) for Mg_2Si samples with dispersed Si atoms, respectively matching the stoichiometry of the Mg_2Si samples with 0, 1, 2, 4, 8, and 16 Si NPs.

Results – Table Summaries

Nanostructure	300 K ($Wm^{-1}K^{-1}$)	600 K ($Wm^{-1}K^{-1}$)	900 K ($Wm^{-1}K^{-1}$)
Pure Mg_2Si	8.454 ±1.094	4.199 ±0.342	3.533 ±0.705
Mg_2Si with 1 Si NP	5.252 ±0.416	3.275 ±0.176	2.428 ±0.261
Mg_2Si with 2 Si NP	5.877 ±0.586	3.456 ±0.312	2.987 ±0.626
Mg_2Si with 4 Si NP	4.553 ±0.387	2.972 ±0.205	2.204 ±0.277
Mg_2Si with 8 Si NP	2.876 ±0.211	1.930 ±0.119	1.992 ±0.323
Mg_2Si with 16 Si NP	1.791 ±0.124	1.649 ±0.157	1.280 ±0.214
Mg_xSi_x 34.29 % Si (matching stoichiometry of Mg_2Si with 1 Si NP)	6.346 ±0.624	3.749 ±0.283	2.676 ±0.369
Mg_xSi_x 35.32 % Si (matching stoichiometry of Mg_2Si with 1 Si NP)	5.015 ±0.441	3.001 ±0.244	2.065 ±0.296
Mg_xSi_x 37.29 % Si (matching stoichiometry of Mg_2Si with 1 Si NP)	3.669 ±0.272	2.430 ±0.186	1.387 ±0.151
Mg_xSi_x 41.37 % Si (matching stoichiometry of Mg_2Si with 1 Si NP)	2.300 ±0.133	1.784 ±0.126	1.591 ±0.264
Mg_xSi_x 49.55 % Si (matching stoichiometry of Mg_2Si with 1 Si NP)	1.300 ±0.053	1.064 ±0.117	0.9347 ±0.292

Conclusions

- Increasing the atomic percent Si, either through substitutional atoms or Si NPs, decreases k_p
- Samples with substitutional Si atoms resulted in greater decreases in k_p when compared to the k_p of the samples with Si NPs
- Boundary resistance, rather than reduction in mean free path, seems have the greater influence in reducing k_p in the samples with Si NPs for the 1 and 2 NP cases

Future Work

- Experimental research will need to verify that these nanostructures actually result in an increased *ZT* for Mg_xSi_x as LAMMPS cannot account for changes in k_e
- Further work should be done to understand why substitutional Si atoms lower k_p more than the stoichiometric equivalent of Si NPs in Mg_2Si
- Further should be done to understand more fully how concentrations of stoichiometric changes at certain locations, such as Si NPs at the halfway point between a heat source and sink, can change k_p

References

1. LaBotz, R. J., and Mason, D. R., 1963. “The thermal conductivities of mg2si and mg2ge”. Journal of The Electrochemical Society, 110.2, pp. 121–126.
2. Plimpton, S. LAMMPS - large-scale atomic/molecular massively parallel simulator. http://lammps.sandia.gov/.
3. Rull-Bravo, Marta, et al. "Skutterudites as thermoelectric materials: revisited." *Rsc Advances* 5.52 (2015): 41653-41667.
4. Zhang, Hengji, e. a., 2015. “The effect of point defects and nanoparticles on thermal conductivity of magnesium silicide”. Computational Materials Science, 104, pp. 172–176.

Acknowledgements

1. The Utah Energy Research Triangle Program from the Governor's Office of Energy Development provided the funding for this project.

Questions?