RESNICK INSTITUTE
science + energy + sustainability

RESEARCH HIGHLIGHTS

From the Resnick Sustainability Institute Graduate Research Fellows at the California Institute of Technology

Phase Transition Enhanced Thermoelectrics

David Brown

Phase Transition Enhanced Thermoelectrics

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Global Significance

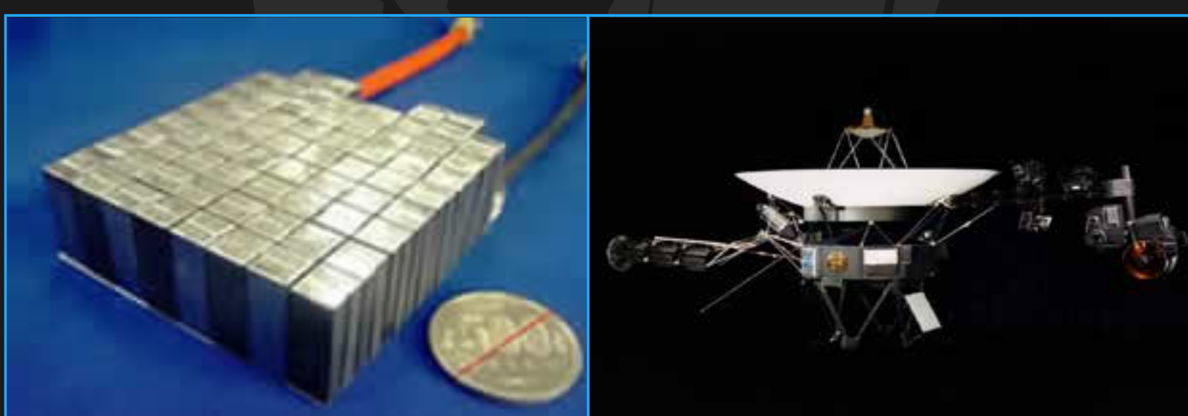
The United States produces 28 Terrawatt-hours of energy every year, of which 58%, or 16 Terrawatt-hours, is lost. Much of this lost is in the form of waste-heat in the automotive sector. Technology that can capture part of that waste heat and convert it into electricity could significantly mitigate this problem, without interfering with the normal operation of a car's engine.

Thermoelectrics are a physically compact and robust means of converting heat into electricity. They have been successfully demonstrated as devices in both proof-of-concept and niche applications such as the Mars Curiosity Rover. However, they are currently not efficient enough for grid-scale integration.

This project assesses a new class of thermoelectric materials, mixed ion-electron conductors. It examines a new method for thermoelectric enhancement that utilizes the relationship between structural phase transition and electron transport.

Potential Impact

- In order to charge the battery of a car, extra fuel is used to run an alternator. Thermoelectrics could displace the car alternator by transforming waste heat into electricity to charge the battery. This would reduce fuel consumption by 5-10%.
- If successful, this project would give the same energy and carbon impact as removing 2.5 million cars from the road.



A typical thermoelectric device and a common application.

Phase Transition Enhanced Thermoelectrics

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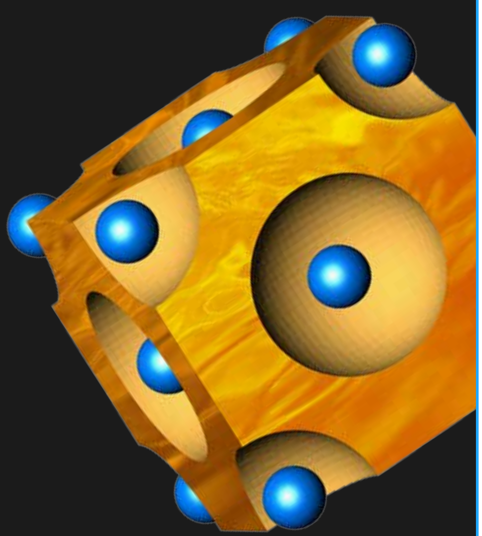
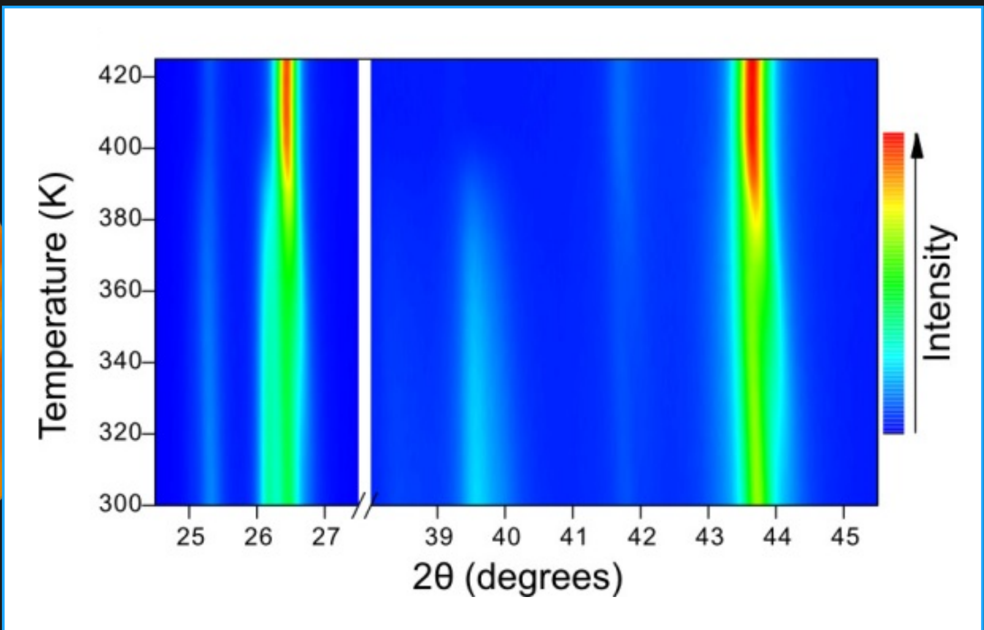
Project Summary

We have developed a new thermoelectric material, Cu_2Se, that shows enhanced efficiency near its structural phase transition temperature. At this temperature, the Cu+ ions in Cu_2Se disorder and the ion conductivity increases. The entropy changes rapidly and repeatably during this transformation, which we believe affects the electrical transport—boosting efficiency and enhancing the thermoelectric effect. Via material engineering, including electrochemical investigations, this project aims to understand and engineer this enhanced thermoelectric effect.

This project crosses the disciplines of electrochemistry, thermoelectricity, solid state chemistry, and condensed matter physics.

In this diagram, the blue spheres represent selenium atoms forming a crystal lattice. The orange regions in between the atoms represent the copper atoms that flow through the crystal structure like a liquid. This liquid-like behavior is what gives the selenium-copper material its unique thermoelectric properties.





Continuous transformation of the XRD spectrum of Cu_2Se on slow heating (1K/min). The continuous disappearance and transformations of peaks are indicative of a 2nd order transformation of the structure. The same is observed under slow cooling (not shown), indicating the gradual transformation is not due to kinetic limitations.

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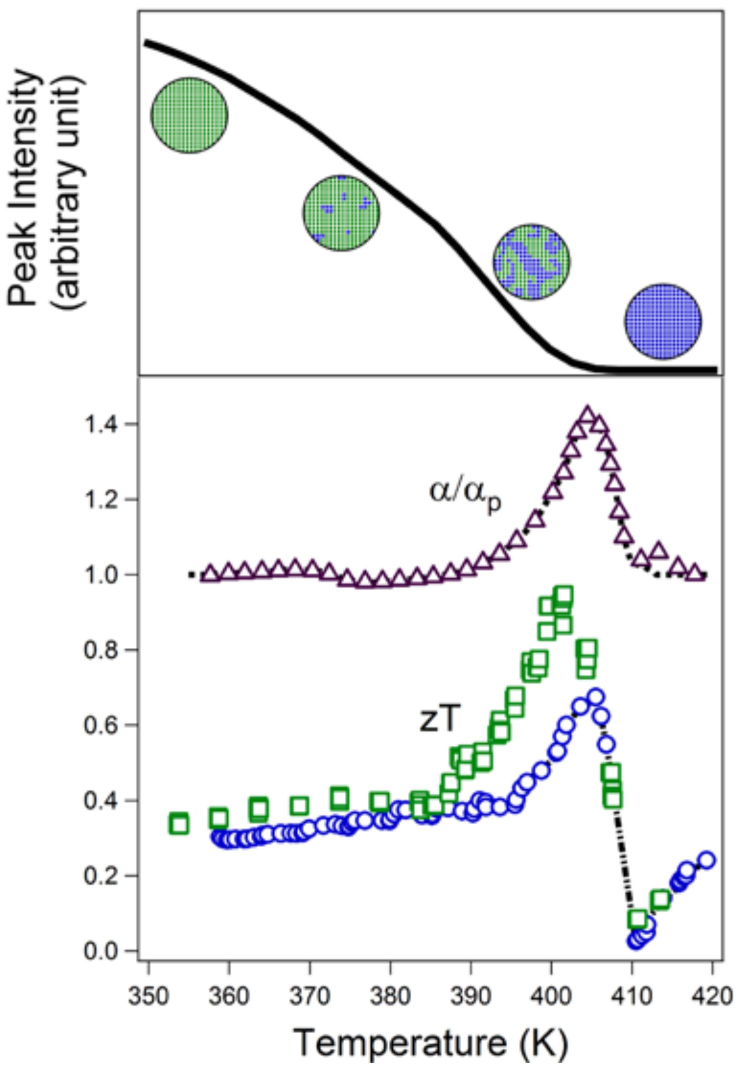
The Science

The thermoelectric effect is characterized by a dimensionless figure-of-merit, zT, which is proportional to the square of the entropy transported by each electron charge (the thermopower), while inversely proportional to the thermal conductivity. The thermal conductivity includes a contribution from lattice vibrations which are loss terms. Upon approaching the second order phase transition of Cu_2Se, the thermopower increases dramatically, resulting in an increase in zT thermoelectric conversion efficiency. We believe this to be the result of a coupling between the structural transition entropy and the transport of electrons, the mechanism of which we believe to be the coupling of transport of Cu+ ions and electrons.



Dramatic increase in thermoelectric efficiency near the phase transition in Cu_2Se (blue circles) and $Cu_{1.97}Ag_{.03}Se$ (green squares). In a continuous phase transition, peaks that break the symmetry of the higher temperature phase (top) decrease smoothly to zero at the critical temperature T_c

The integrated intensity corrected for the background intensity of the Cu_2Se XRD peak located at 26 degrees is plotted here. In this transition region fluctuations lead to correlations at a critical length scale, which changes with temperature, and also to an increase in entropy. Ordering is represented by green squares and disordering by blue rectangles. The thermoelectric figure of merit, zT (bottom), doubles in the critical region below the phase transition at 410K. The doubling in zT above 390K in Cu_2Se is primarily due to the increase in measured thermopower (α) compared to that expected from a rigid band model (α⩔ρ) and the measured Hall carrier concentration.

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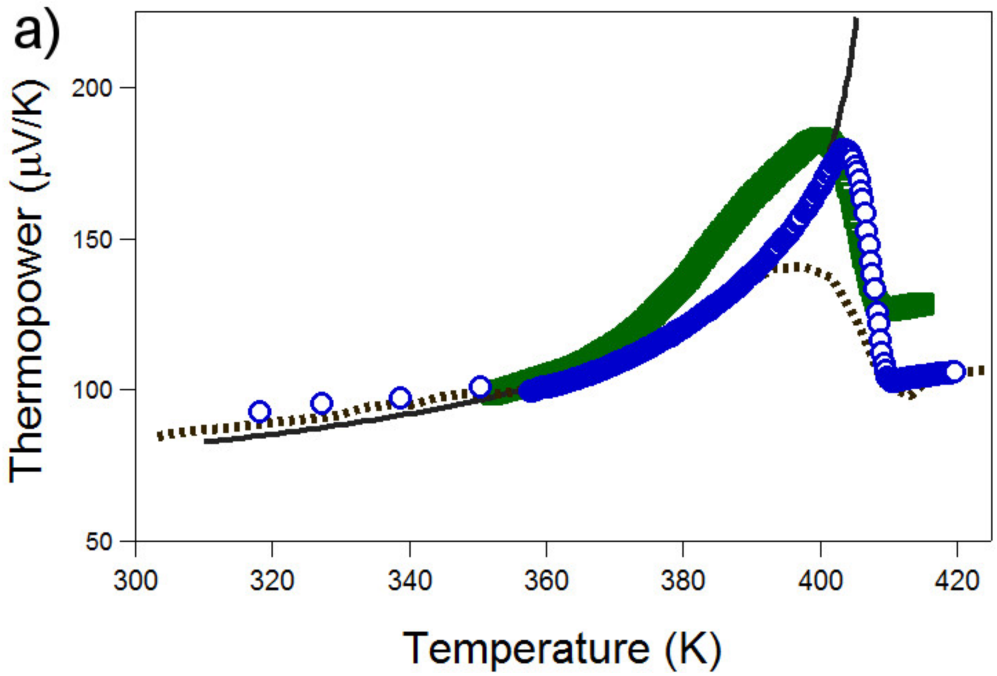

Thermopower (α) peak in Cu_2Se (blue circles) and $Cu_{1.97}Ag_{.03}Se$ (green squares). The increase in thermopower, shown with a critical exponent fit, is clearly associated with the continuous phase transition. Between 390K and 410K, there is a significant increase in the measured thermopower above that predicted by the change in Hall carrier concentration (dotted line). In this region, the entropy of the phase transition also increases the thermopower.

Key Results & Future Steps

We have demonstrated an anomalous 100% increase in the zT of Cu_2Se at 406K and have shown that it cannot be simply explained through its band structure. We have shown an even larger increase in the $Ag_{.03}Cu_{1.97}Se$ and a highly competitive peak zT of 1.0 at 401K. Our work has shown the 2nd order nature of the phase transition in Cu_2Se.

We intend to further our study of Ag-doped Cu_2Se in the hopes of obtaining a record zT at 400K of 1.5. We are building a combination thermoelectricity/electrochemistry apparatus that will allow us to directly measure the coupling between Cu+ transport and electron transport, thereby providing experimental proof of our proposed mechanism. It will also perform Coloumb titration, thereby allowing rapid measurement of a wide range of compositions.

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