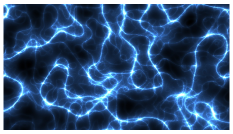
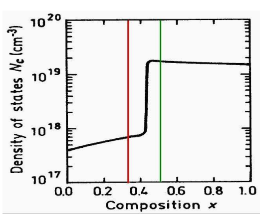
LEDs to ATECs

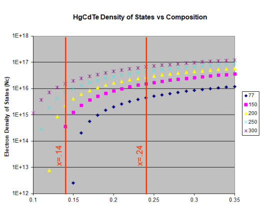


Intro ThermaWatts is about energy. Our reason for being is to make energy clean, fuel-less, scalable, lightweight, compact, low-cost, reliable, durable, safe, and portable.

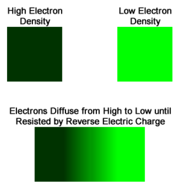
Hi. I'm Peter Orem. I've been poking at the Second Law of Thermodynamics, chasing the possibility that semiconductor behavior enables direct conversion of ambient heat to electricity. Prototypes of our semiconductor-based Ambient Thermal Electric Converters (ATECs) appear to achieve such harvesting. We are going to take you through the experimental results that brought us to this conclusion.

LEDs

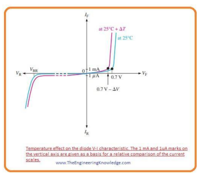




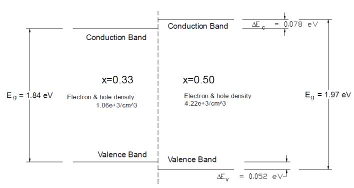
Densities of state Semiconductor materials have differing densities-of-state, which affects the concentration of electrons. Densities of states differ with composition. In aluminum gallium arsenide (or AlGaAs), there are one-and-one-half orders of magnitude difference as the aluminum concentration moves from 33% to 50%. In mercury cadmium telluride (or Mercat), there are about two orders of magnitude of difference available in densities-of-state. This reflects, among other things, changes in the relationship between energy and momentum. [pause] This is a pivotal point! [pause]

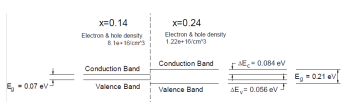


Accepted Accepted physics says that there is nothing in semiconductors to exploit for energy harvesting. For example, physics says that when two semiconductor materials with differing densities of state are joined together (at a “heterojunction”), there is no net flow of electrons and holes. That is to say, the carrier concentration in one material is not affected by other, adjacent materials.



Logical A logical conclusion is that diodes have no net carrier flow at zero bias. A typical textbook graph of diode current versus bias shows a zero current at zero bias. This is a neat and tidy model, and - according to measurements by us and others - ever so slightly wrong

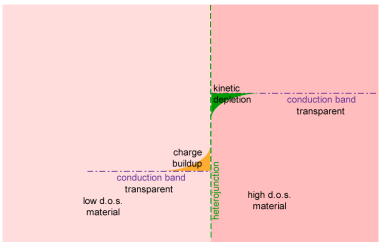




Densities At the same time, accepted physics agrees that there are significant differences in electrical forces among semiconductor materials of differing composition. For example, here are the band gap diagrams for two materials that we have been working with: aluminum gallium arsenide - algas - and mercury cadmium telluride - mercat - with differing compositions. These drawings are to scale, showing the energy levels of the valence and conduction bands, as well as various offsets. We hope that your takeaway from this is that differing densities-of-state are common and well understood in semiconductor technology.

$$J_{n,p} = -q[v_{n2,p2}T_{n2,p2}(n,p)_2 - \left(\frac{m_{n2,p2}}{m_{n1,p1}}\right) v_{n1,p1}T_{n1,p1}(n,p)_1 e^{\left(\frac{-\Delta W_c}{k_B T_{n1,p1}}\right)}]$$

Schroeder This is the ‘book’ form of transport at the junction, as set forth by Schroeder. The term at the center is the direct result of explicitly assuming there is no net current. In other words, detailed balance proves there is no violation of detailed balance, and circular logic is circular.



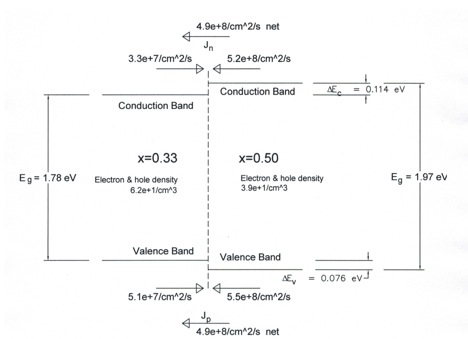
Heterojunction Here is another view of the heterojunction of high density-of-state material on the right and low on the left. It shows the electrons with a negative charge buildup on the left and kinetic depletion region on the right of the heterojunction as shown for the joining materials. These together are often described as a static depletion region. Not much going on. We will come back to this basic picture later with embellishments..

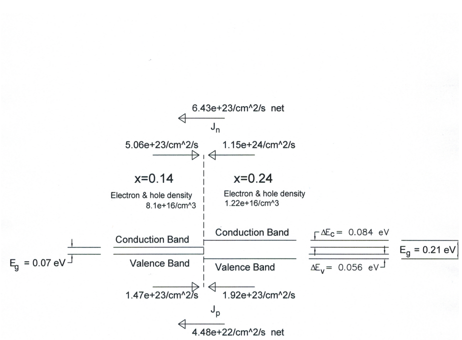
$$J_{n,p} = -q[(1+\sigma_{n,p})v_{n2,p2}T_{n2,p2}(n,p)_2 - (1+\sigma_{n,p})\, v_{n1,p1}T_{n1,p1}(n,p)_1]\; e^{\left(\frac{-\Delta W_C}{k_B T_{n1,p1}}\right)}$$

Yang A paper by Yang, et al., in 1995 developed an alternative model to Schroeder’s for initial carrier flows across a heterojunction. It showed a net flow. We validated the model experimentally using AlGaAs.

	Al fractions			Cd Fractions			Units	Notes and references
	0.33	**0.5**		**0.14**	**0.24**		-	-
ni	1.06E+03	4.22E+02		8.2e+16	1.22e+16		/cm^3	AlGaAs Carrier density at 310 K, per ATLAS HgCdTe carrier density at 300 K, per ATLAS
E_g	1.84	1.97	0.13	0.07	0.21	0.14	eV	Bandgap, Per ATLAS
ΔE_c	-	0.6	0.078	-	0.6	0.084	eV	60/40 rule division between valence and conduction band within a family (an approximation)
ΔE_v	-	0.4	0.052	-	0.4	0.056	eV	
k_BT	-	-	0.025852	-	-	0.025852	eV	k_B from ATLAS
$\Delta E_c/k_BT$	-	-	3.02	-	-	3.25	-	Conduction band mismatch, in k_BT units
$\Delta E_v/k_BT$	-	-	2.01	-	-	2.17	-	Valence band mismatch, in k_BT units
$\exp(\Delta E_c/k_BT)$	-	-	4.89E-02	-	-	0.0388	-	Exponential of Conduction band mismatch
$\exp(\Delta E_v/k_BT)$	-	-	1.34E-01	-	-	0.114	-	Exponential of Valence band mismatch
An**	11.3	93.7		0.647	1.85			
Ap**	83.5	86.8		66.1	66.1			
Nc	7.28E+17	1.73E+19		9.91E+15	4.78E+16			
Nv	1.45E+19	1.54E+19		1.02E+19	1.02E+19			
vn	3.67E+07	2.17E+07	-	3.67E+07	2.17E+07	-	cm/s	Yang Equations (5) and (9)
vp	3.64E+06	3.64E+06	-	3.64E+06	3.64E+06	-	cm/s	Yang Equations (12) and (13)
Densities	-	-	-	-	-	-	-	
n	1.06E+03	4.22E+02	-	8.2e+16	1.22e+16	-	/cm^3	Electrons per cubic centimeter -
p	1.06E+03	4.22E+02	-	8.2e+16	1.22e+16	-	/cm^3	Holes per cubic centimeter
Currents	-	-	**Net**	-	-	**Net**	-	-
J_n	-4.52E+08	1.28E+09	8.32E+08	-5.06E+23	1.15E+24	6.43E+23	/cm^2/s	Net of 0.33 => 0.50 minus 0.50 = 0.33/electrons
J_p	-4.59E+08	1.34E+09	8.77E+08	-1.47E+23	1.92E+23	4.48E+22	/cm^2/s	Net of 0.33 => 0.50 minus 0.50 =>0.33 / holes

Table This table develops carrier flows using the Yang model for AlGaAs and for mercat using accepted material characteristics. What matters is the net flow of electrons and holes shown at the bottom. For Mercat (on the right), electron flow is more than an order of magnitude higher than counterflowing holes, creating a charge imbalance.





Band Gaps Here are the band gap diagrams you saw before, now shown with the initial electron and hole flows across the heterojunctions for AlGaAs and HgCdTe, as computed in the table. In each, we see that there is a flow of electrons in each direction across the interface (heterojunction). Further, the flows are unbalanced, with a net flow from high to low carrier densities of state. There is a similar flow of holes, also imbalanced. If Yang's model is a better approximation of reality than Schroeder's, then there might be a possible exploit for energy harvesting.

A Reminder: Why Models Matter

- If incorrect
  - Create confusion around experimental results
  - Block exploration of interesting possibilities
- If correct
  - Clarify understanding of real things
  - Provide basis for behavior prediction, new solutions

Models I need to pause here to remind you of why models matter. We apply models which we carry in our heads (and which we have mostly learned from others) to filter how we interpret the world. In science, if our models are wrong, we run into inconsistencies in measurements and block exploration of real possibilities. Contrawise, carrying better models brings clarity and progress.

Roadmap of our Evidence

- Single heterojunction
  - Blinking LED (negative, zero bias)
  - Glowing LED (zero bias)
  - Two temperatures in an LED
- Multiple heterojunctions
- Prototype ATECs
  - AlGaAs
  - HgCdTe

"If the experiments and theory disagree, the theory is wrong," with apologies to

Richard Feynman

Roadmap Over the next few minutes, we are going to take you through several experiments we have run and that provide the basis for our claim of a heat-to-electricity conversion device.

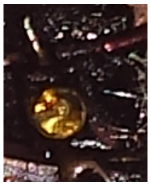
Why LEDs

- Minimal complexity to analyze
- Some of electron activity is visible as light

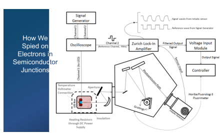
Diodes Diodes can be formed of heterojunctions - where materials with different characteristics, including their "densities of state" are joined together. Semiconductor materials of differing composition have different concentrations of electrons, maintained by characteristic band gap and band structure. Band gap is the energy needed to move electrons between valence and conduction bands in the materials.

Experimental We needed more experimental evidence of an exploitable effect. We started looking at LEDs as a likely place to find evidence because we could measure their light emissions and perhaps make sound deductions of what the carriers might be doing. If there is somehow a continuing net flow of electrons due to imbalance from high to low density as suggested by Yang, then we supposed that unbiased LEDs might "glow in the dark" because of recombinations.

Camera Using a highly sensitive camera, we tested for such glow by photographing an LED alternated at zero and reverse bias. The LED was heated to bring its possible glow into the range of the camera.

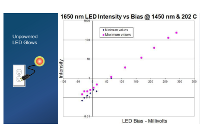



Blinking Here is what we saw: On the left is a LED under normal light. On the right is the same LED as seen by our highly sensitive camera. There, the entire scene is glowing with heat. Blackbody radiation is a constant. The two alternating images in the blinking picture differ only by the connection to the LED - either open or with reverse bias. Under reverse bias, the LED active region is visibly darker. The difference is light emitted by the LED at zero bias. We can precisely measure the difference to see what's happening inside the LED.

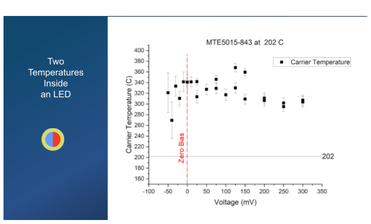


Better Evidence With the help of a recent NSF award, we developed an electronic modulation approach that locks into the thermally-induced optical emissions from the LED. Measuring the electron temperature near zero bias is challenging because of the overwhelming blackbody emission of the surroundings.

We set up this measurement system in an Oregon State University physics lab which measures light output from an LED (blue spot in lower left) while subtracting out blackbody radiation. Then we swept the LED with a bias voltage, crossing zero. From here, we could infer the electron temperature by measuring the emission spectrum.



Two things We found two things. The first, we rather expected, but were still pleased to find. As we swept the voltage past zero, the LED continued to glow (shown on this semilog plot). Distinctly. Zero was clearly outside the range of measured values. Note that our measurement method precluded measuring at exactly zero bias, but we know of no reason for a discontinuity of behavior at the zero-bias point.

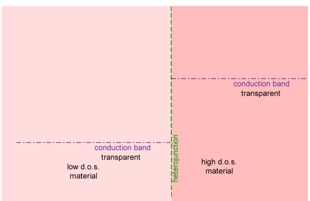


Two temps The second finding was new to us, startling and apparently ground-breaking. The extracted electron temperature plotted suggests the electrons are effectively hotter than the bulk material. The spectrum told us that there were two distinct temperatures within the LED, even at zero bias.

The evidence seems to say electron flow continues at heterojunctions of differing materials. If these four data points are correct, the standard LED model - and underlying Law - is incorrect.

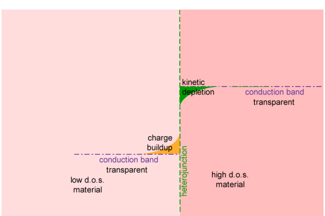
We think our data are correct.

<u>Heterojunctions</u>

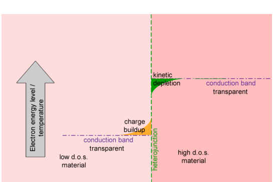


Schroeder heterojunction

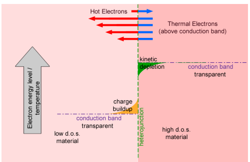
Let's build up an exploit. We'll start with Schroeder's model of a heterojunction. If the doping matches up, the two materials won't form a diode, so nothing interesting will happen. The horizontal axis is position, and the vertical axis is energy.



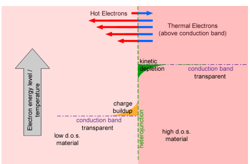
Expanded   Enter kinetics, as from Yang. The electrons on the right are somewhat slower than those on the left, but there are far more of them above the level of the conduction band on the right side. Most of those on the left side are at lower energy levels.

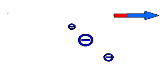


Scale For electrons, 'Temperature' is the local average of electron energy above the conduction band minimum. If all the electrons on the right were suddenly moved to the left, they would be very hot.

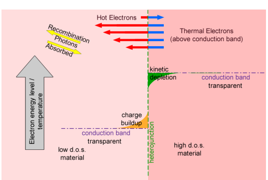


Hot electrons Okay, here is a step that is ~~perhaps obvious on the surface, and is~~ justified by observations of two temperatures. Higher energy electrons diffuse from each material to the other. The high to low density-of-state diffusion statistically dominates that flow. There is a net electron flow from high to low. This is consistent with the Yang model.

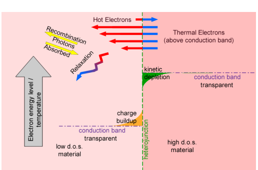




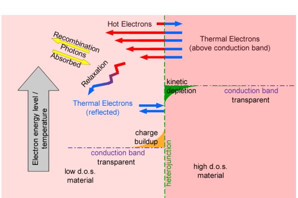
Continuing flow If the flow identified by Yang were to continue, the collection of electrons in the low density-of-state side would build up. Free electron diffusion back to the high density-of-state side would grow to match the high-to-low flow. That would soon give a net flow of zero like the accepted physics model. But with the growing negative charge in the low density-of-state side, other things begin to happen which offset that charge and permit continuing Yang's flow from differing densities-of-state, as follows.



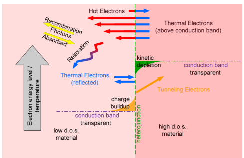
Photons Some of those electrons recombine with holes in the lower density-of-state region and emit photons. We see the evidence of that in the sustained light emissions of the first two LED experiments.



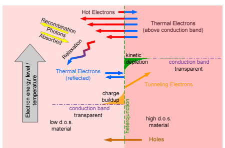
Relax Most of the electrons will cool (relax) as they interact with the electrons on the low side.



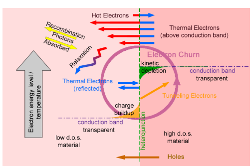
Reflection Electrons that do not have enough energy to cross the junction will generally reflect back.



Tunneling We suppose that most of the excess electrons will tunnel back from low to high density-of-state, drawn by a deficiency of electrons in the high density-of-state region.

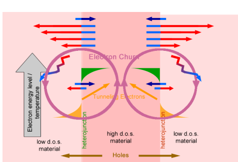


Holes Finally, holes will be drawn from high to low density-of-state by the excess of electrons on the low side.



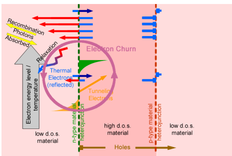
Churning These thermal excitations populate a distribution of hot electrons that dynamically churn at the interface of our low-bandgap heterojunction. This collective electron activity results in an interfacial hot electron temperature that oscillates with the lattice. Then, not unlike a solar cell, these hot electrons can generate a current over the timescales at which the hot electrons thermalize with the bulk lattice.

So the net effect of all this is a churning of electrons as indicated - driven by the statistical effect of higher velocities of some of the newly-generated electrons.

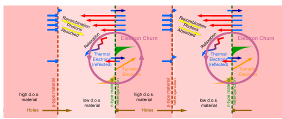


Third layer If we add a third layer with low density-of-state to the right,we are going to create a second churn of electrons, with hot electrons diffusing from high to low density-of-state region. Holes will drift towards the electron-rich layers.

This is not yet an exploit.



Doping This shows the effect of the doping on carrier flows. Electrons continue to move to the left, but not to the right. Holes similarly continue to move to the right, but not to the left. This is now unbalanced.



Five layer If we add yet another high density-of-states and doped layer to each end of this assembly, the cycle is simply repeated. Whatever voltage is developed across an n-doped layer is additive across the cycles.

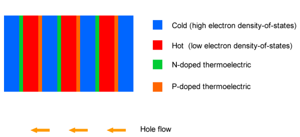
You can see that cycles build voltage and area builds current.

Moving a charge across an established voltage is 'doing work'. This step converts the thermal energy of the electrons into electrical energy. This depletes the internal thermal energy of the device. The condition of insufficient heat allows external heat to flow into the device.

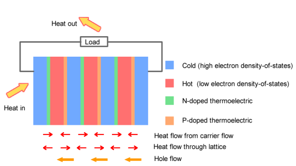
ATECs

[MakeSandwich4.mp4]

Device Our device moves the behaviors just described to a practical energy conversion device. By doping alternating thin layers of HgCdTe or other small-bandgap materials, our technology can harness thermal excitations created by ambient heat.



Our engineering of low-bandgap heterojunctions now suggests that the energy harvested from this dynamic equilibrium may be enough for commercial and defense applications.'

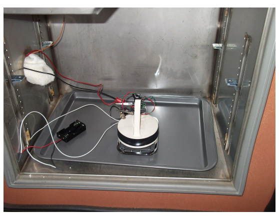


This depicts the flow of heat and electricity within and around the conversion device.

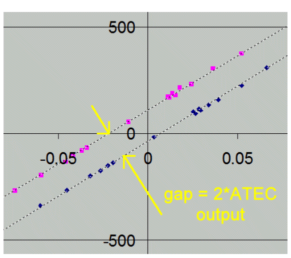
When we put a load across the assembly, electricity flows, which (eventually) is converted to heat. To restore the consumed heat, external heat must be absorbed from the environment into the device.

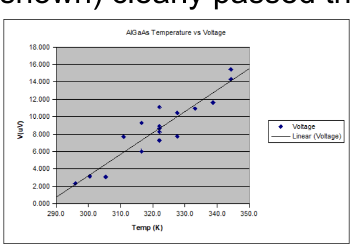
Stanford We had three prototypes fabricated at Stanford University. Each had ten and a half cycles of the four-layer ATEC structure built on a Gallium Arsenide substrate, as described previously.

AlGaAs Tests were run at an elevated temperature (160 F) in a precision oven and with an in-oven 1000-fold amplifier to bring output into a reliably measurable range. The prototype device was mounted in a porcelain stand as shown. The device was swept with a voltage and the difference between sweep and device output was measured.

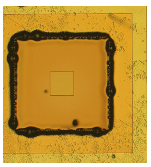


AlGaAs voltage The first image shows the voltage difference with the device in one orientation and then the other. The difference between those is twice the voltage contribution made by the device. A sweep through a resistor with the same setup (not shown) clearly passed through zero-zero on the same scale.



AlGaAs temperature These prototypes also showed voltage that increased with temperature, following the density-of-state characteristics versus temperature..

HgCdTe fabrication Using our NSF grant, we had several HgCdTe prototypes fabricated by EPIR Technologies.



HgCdTe prototype The prototypes were 3.6 millimeter square. The innermost square is the top contact. The outermost square is the bottom contact. The black ring is the edge of an etch to allow us to reach the bottom contact.

[TestPlusPrototypeBW.mp4]
HgCdTe tests We needed probes, a microscope, and a space with stable temperature, shielding from light, EMI, and air currents, plus a 1000-fold amplifier.

HgCdTe Prototype Voltages

#	Voltage	#	Voltage	#	Voltage
1	1.7 mV	2	2.3 mV	3	2.4 mV
4	N/A	5	5.2 mV	6	2.8 mV
7	6 mV	8	N/A	9	7 mV

HgCdTe results Here are test results after amplification. Each prototype had its signature voltage - stable and repeatable. Serial connection of prototypes #7 and #9 added their voltages (to 13 millivolts).

<u>Next Steps</u>

Reaching Practical Performance

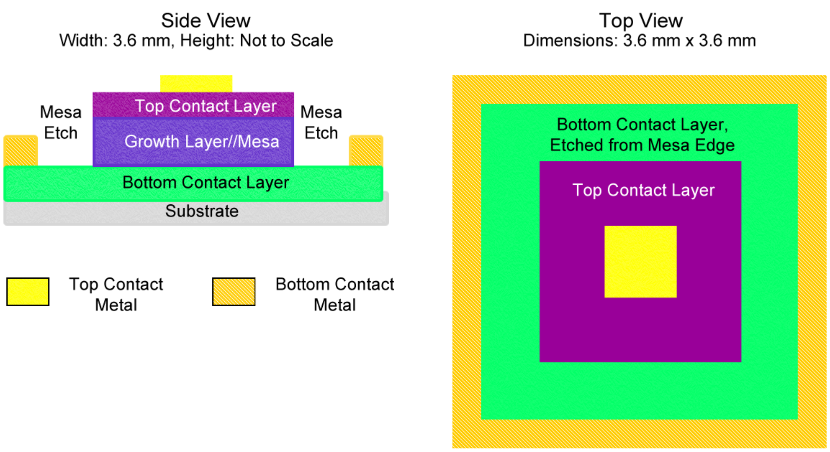
- HgCdTe prototypes eight orders better than AlGaAs
- Models say five more orders possible

- Two orders needed for large, high-value market (IoT, cell power)
- Additional two orders for full energy market

Practical Bringing performance of our ATEC devices to practical levels seems within range.

- In moving from AlGaAs to HgCdTe, our prototypes have improved by eight orders of magnitude
- Models say at least five more orders of magnitude improvement should be possible
- We need two more orders to reach large, high-value market (IoT, cell power)
- We would need an additional two orders to reach the full market for energy

Prototype ATEC Structure as Built by EPIR Technology



Next Steps We have identified the first three steps to take in improving HgCdTe prototypes:

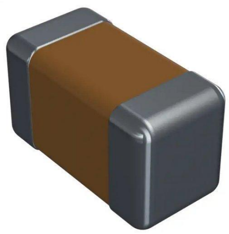
- First, simplify the bottom contact for the device. The contact of the previous design started the contact at the outer ring of the device (in yellow), passed down to the bottom contact layer (in green), and then to the mesa. This is a fairly high-resistance path. The next version will connect through the wafer.
- Second, the edges of the mesa have conductive 'surface states', creating a short circuit between layers. That can be cured by chemical treatment called passivation that turns the edge materials to insulator.
- Third, because of money limits, we deferred fabrication of the p-doped layers. Those will be added in the next rounds of prototypes.

Following that, performance will be optimized by adjusting layer composition and thickness.

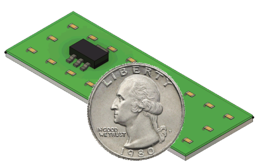
Applications

Applying
ATECs

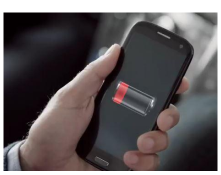
Applying ATEC application will largely be limited by cost and available environmental heat, in turn depending on performance we can achieve.   At the upper end of performance, the range seems limitless.



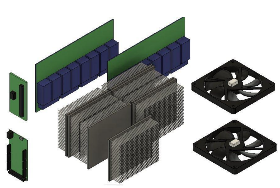
0603 We expect that initial applications of ATECs will use industry standard form factors such as this 0603 device, which is 1.6 millimeters long. The 0603 is cheap (base cost of less than a penny to assemble).   Some applications will use many of these, spread around to assist heat transfer.

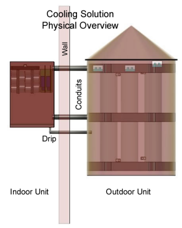


Typical This might be a typical packaging of ATECs for a power supply, perhaps for a cell phone or Internet of Things sensor/transmitter. The yellow spots are 0603 ATECs, the black box is a voltage regulator.

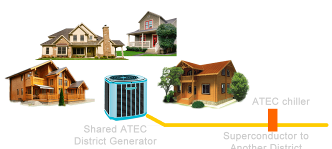


Cell This cell phone has run out of battery power. That won't happen anymore.

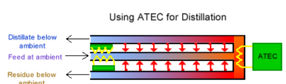




Cooling This image shows preliminary engineering of a 5kw apartment cooling unit. The gray rectangles in the left image are aluminum heat exchangers with ATECs mounted on them. This design dumps generated electricity through convectively-cooled power resistors (for simplicity). Parts for the whole unit were estimated at about $600.



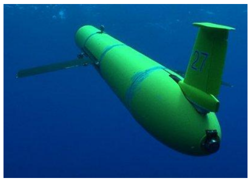
District It will likely make sense to use ATECs to generate electricity at the home level, with some district and interdistrict generation and transmission for backup.



Extraction As ATEC-based generation costs are driven down by mass production, many applications will become cost-effective.

Military There are all sorts of applications for ATEC in military operations and installations energy.

Air drones This drone could be powered for essentially unlimited missions by embedding ATEC units on its surfaces.



Sea drones And similarly, this undersea drone could be powered for very long missions by ATEC units beneath its skin. This drone could be a great improvement over sonobuoys that travel with ocean currents.

Summary

Summary
What makes it go
Why we might care

Summary For summary, we want you to take away two things:

- How our ATEC device works (pretty simple, really), and
- Why we all might care - a lot.

What Makes It Go
Semiconductors features: * Can have large differences in carrier concentration ~~(densities-of-state)~~ * Free electrons diffuse from high to low, causing electron charge and a voltage. Dynamic equilibrium of electron charge * Electrons tunneling from it * Holes diffusing to it Allows continuing flow.

Go So you have seen quite a bit about the theory of operation of our ATEC device. I'm going to give you the short form to carry away:

Operation springs from two well-known features of semiconductors:

* Differences in carrier densities-of-state between differing semiconductor compositions, by as much as two orders of magnitude, and
* Diffusion of free electrons from high to low densities-of-state materials, causing a standing voltage.

A dynamic equilibrium of charge is brought about by:

* Electrons tunneling from the charge, and
* Holes diffusing toward the charge

thus enabling further diffusion of free electrons to maintain the charge and flow.

Why We Might Care
At scale, ATEC devices could: ● Supply the universe of electronics ● Supplant most of the world's fossil fuel use ● Cost much less per installed watt or levelized watt hour than any other known method.

Care At scale, it could supply the universe of electronics, supplant most of the world of fossil fuels, and cost much less per installed watt or levelized watt hour than any other known method.

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