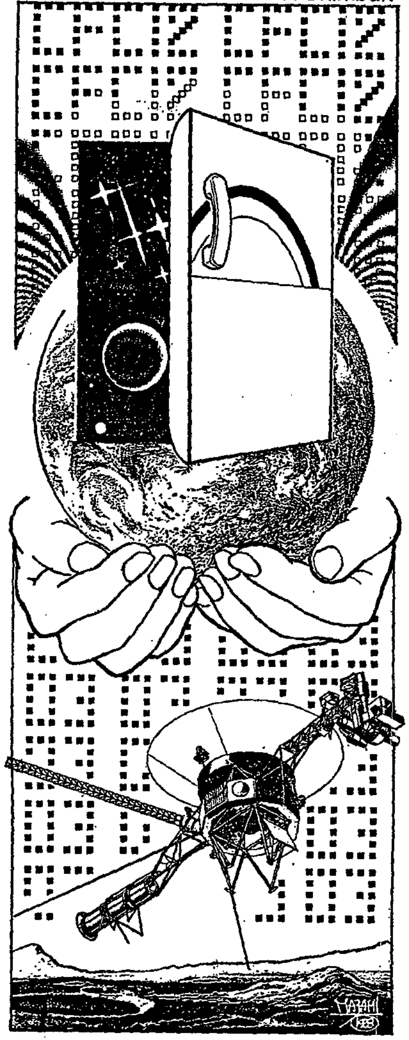
ITS The International Thermoelectric Society

SCT- 93

SHORT COURSE ON THERMOELECTRICS

1993-8-1 The Nihon Keizai Shimbun



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Short Course on Thermoelectrics - 1993 (SCT-93)

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SCT-93 Short Course on Thermoelectrics
Nov. 8, 1993

An Overview of Thermoelectricity
by Prof. David D. Allred
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Philosophy of this talk: History and review

History because it is interesting, fairly easy to grasp and a good way to introduce the subjects.

Review because we come from a variety of disciplines and backgrounds. It is good to come together before we start the more rigorous parts of the course. This can provide the comfort that you will be able to understand what is coming.

An Outline:

I. Introduction
  A. Some Triumphs:
    1. Remote **power** supplies for outer space& terrestrial appli.
    2. **Cooling.** Both commercial and scientific/technological
  B. **History** of TE:
    1. **Discovery** of Thermoelectric effects.
      a. 1821- **Seebeck-** The symbol S, α
      b. 1833- **Peltier**-temp changes- Π
      c. 1838- **Lenz** explains.
    2. **Thermodynamics** is explored.
      a. Lord Kelvin- The interrelation of S, Π
      b. 1885- Rayleigh- **power generation?**
      c. 1911- **The discovery of Figure of Merit, Z.** Altenkirch
      d. A discussion of notation (can vary):

3. Modern period- *Semiconductors.*
   a. "Minerals vs Metals"- The importance of **high S**.
   b. 1930's- **Synthetic semiconductors**
   c. 1947 Telkes- **a 5%** generator.
   d. 1949 Ioffe- **Theory of Semiconductor TE.**
   e. 1953 first **refrigerator**.
   f. 1956 Ioffe's idea of alloying.
4. Applications & Optimism- Early '60's.
   a. **Space** applications of generators.
   b. **Solid State** was magic word.
5. Reassessments.
   a. The stubborn **practical limit** of $ZT=1$ niche markets.
   b. Oil Embargo.
   c. Government- **Star wars** and SP-100.
   d. **Commercial** applications of cooling.
6. Will there be $ZT>>1$? The future.

Fig. 4. SP-100 Class Reactor Powering an Electric Propulsion Spacecraft Past Io

C. **History** of TE:

1. **Discovery** of Thermoelectric effects.

a. 1821- **Seebeck** discovered that a compass needle would be deflected when placed near a closed loop made of two dissimilar metal when one of the junctions was heated. *Was this then a magnetic phenomena? The formulation of the Seebeck series.* A voltage difference can be found which depends on the temperature and the **pair** of materials used. $\Delta V = S \cdot \Delta T$. We will talk as though the properties of single materials, rather than pairs, were available.

S or α has units of μV/K
Metals up to about 10 μV/K
Semiconductors >200μV/K

b. 1833- **Peltier** announced that there are temperature changes at a junction of dissimilar metals when current is caused to flow.

$$Q = \Pi i$$

Here Q is the rate at which heat is absorbed or rejected, i is the electrical current and Π is the Peltier coefficient.

c. 1838- Lenz explains that **heat is either absorbed or released** at a junction depending on the direction of current flow.

2. **Thermodynamics** is explored.

a. Lord Kelvin- relates Seebeck and Peltier coefficients and announces a **third** TE effect: The **Thompson effect-** *Heating or cooling of a single, homogeneous conductor in a temperature gradient.* $\Pi = S \bullet T$

b. 1885- Rayleigh considers using Seebeck effect for the **generation of electricity**.

c. 1911- **The discovery of Z.** Altenkirch creates a satisfactory theory of thermoelectricity for power generation and cooling. *There needs to be high S, low thermal conductivity and high electrical conductivity* .

A discussion of notation (which can vary):

There are three things:

1. **Power factor** = $S^2 \sigma$
2. **Figure of Merit**, $Z = S^2 \sigma / \kappa$ has units of inverse temp: 1/kelvin
3. **Dimensionless** Figure of Merit, ZT

Heat conduction is factor in Figure of Merit, $Z=\alpha^2\sigma/\kappa$

Thermal conductivity is represented as k, K, κ(kappa) or λ(lambda) and has units of watts/kelvins•meters. (There are other important quantities like thermal resistivity, $W=1/\kappa$ and thermal diffusivity.) I will mix symbols.

Typical values of κ are:

100 to 300 W/K•m or 1 to 3 W/cm•K for metals. Electrons are also carrying heat. Wiedemann Franz law. $\kappa/\sigma=L$ Lorentz constant. This was evidence for the free electron theory of metals.

~2 to 8 W/K•m for TE grade semiconductors but,

90 to 1000 W/K•m for pure diamond lattice solid like Ge, Si, diamond. Stiff lattices conduct heat with vibrations like sound called longitudinal phonons $k=k_{carriers}+k_{lattice}$

$Z=\mathbf{S^2\sigma/\kappa}$ = up to $\sim 10^{-3}$ for very good TE at their **maximum.**

WARNING: S,σ,κ are interrelated. If usually σ ↑, S ↓. κ↓, σ⇓

3. Modern period- *Semiconductors.*

a. "Minerals vs Metals"- The importance of **high S.**

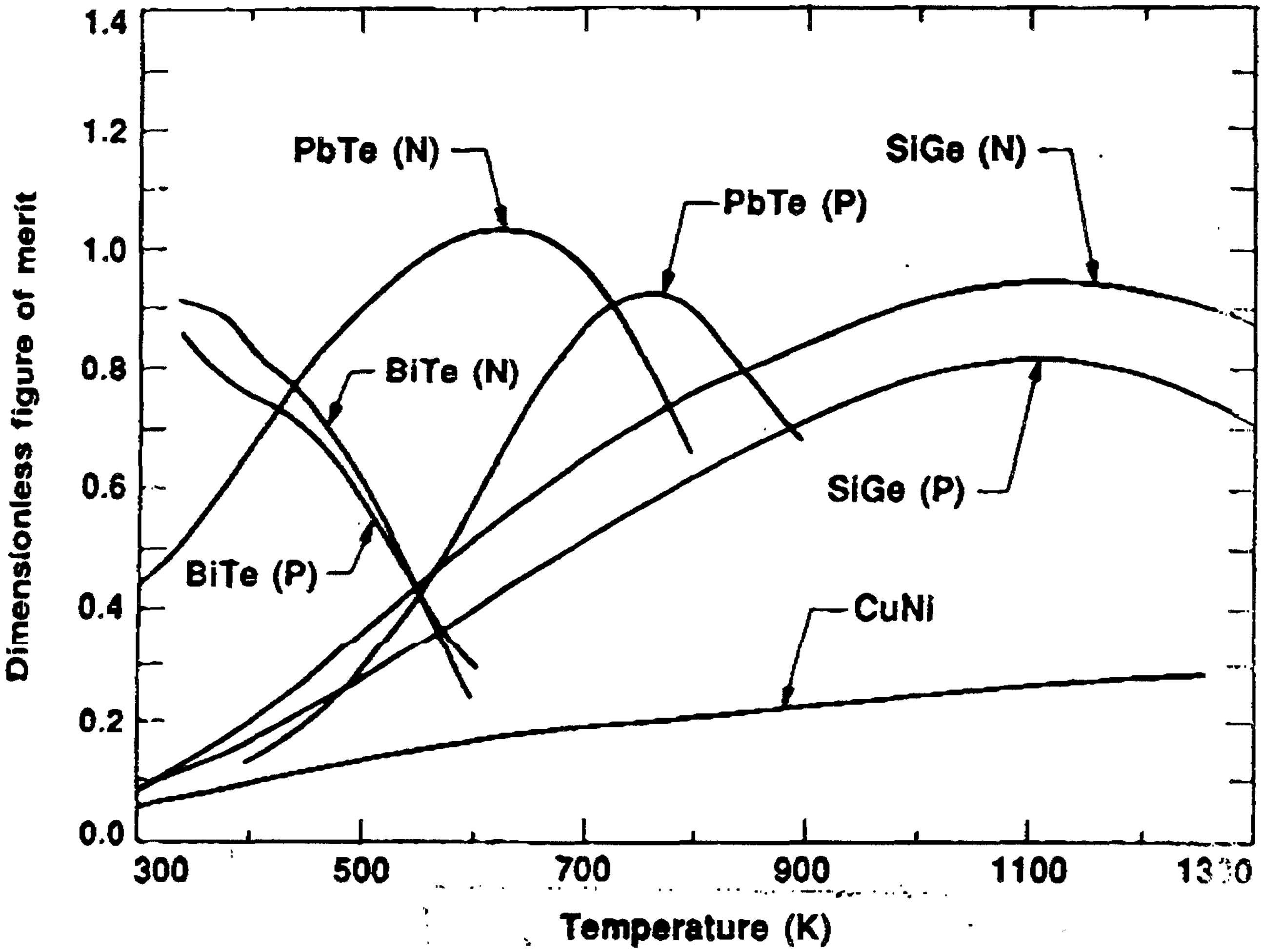
	advantages	disadvantages	uses
metals	malleable, properties relatively constant, stable	low S, low Z W-F limit	thermocouple wire
semiconductor (heavy doped)	high S, moderate Z	brittle, temp. depend properties, unstable	TE devices, composed of small modules.

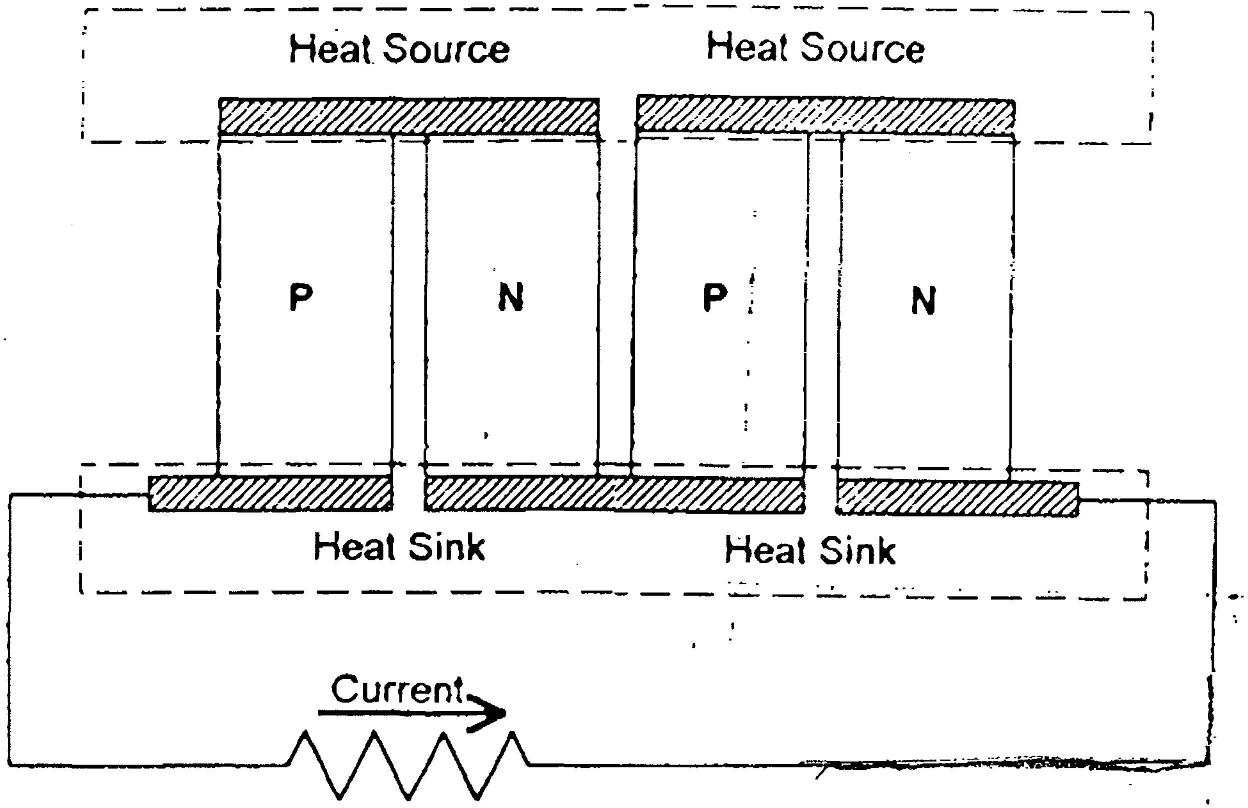
Many of the technological difficulties of TE comes out of the fact that they are semiconductors not flexible metals.

b. 1930's- **Synthetic semiconductors** are studied.

c. 1947 Telkes- **a 5%** generator.

Some facts- Balance of system also must be figured into the system calculations, weight and expense. **Presentations # 5-8**


PbTe (N)
PbTe (P)
SiGe (N)
BiTe (N)
BiTe (P)
SiGe (P)
CuNi
Dimensionless figure of merit
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
300
500
700
900
1100
1300
Temperature (K)



. Schematic of typical thermoelectric power generator. tion is achieved by replacing the resistor with a current d reversing the current flow.

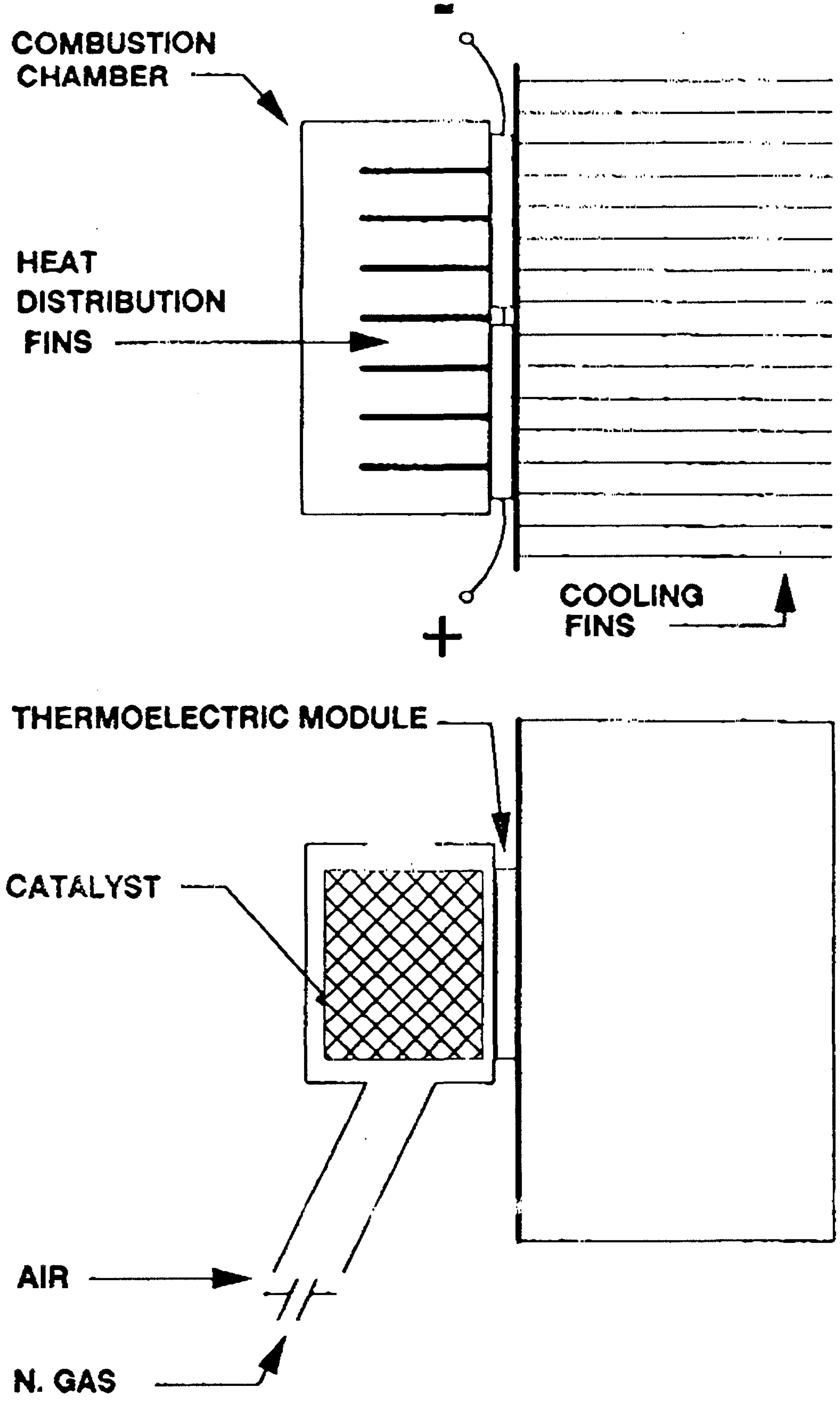


FIG. 1.1 TELEDYNE THRMOELECTRIC POWER ASSEMBLY

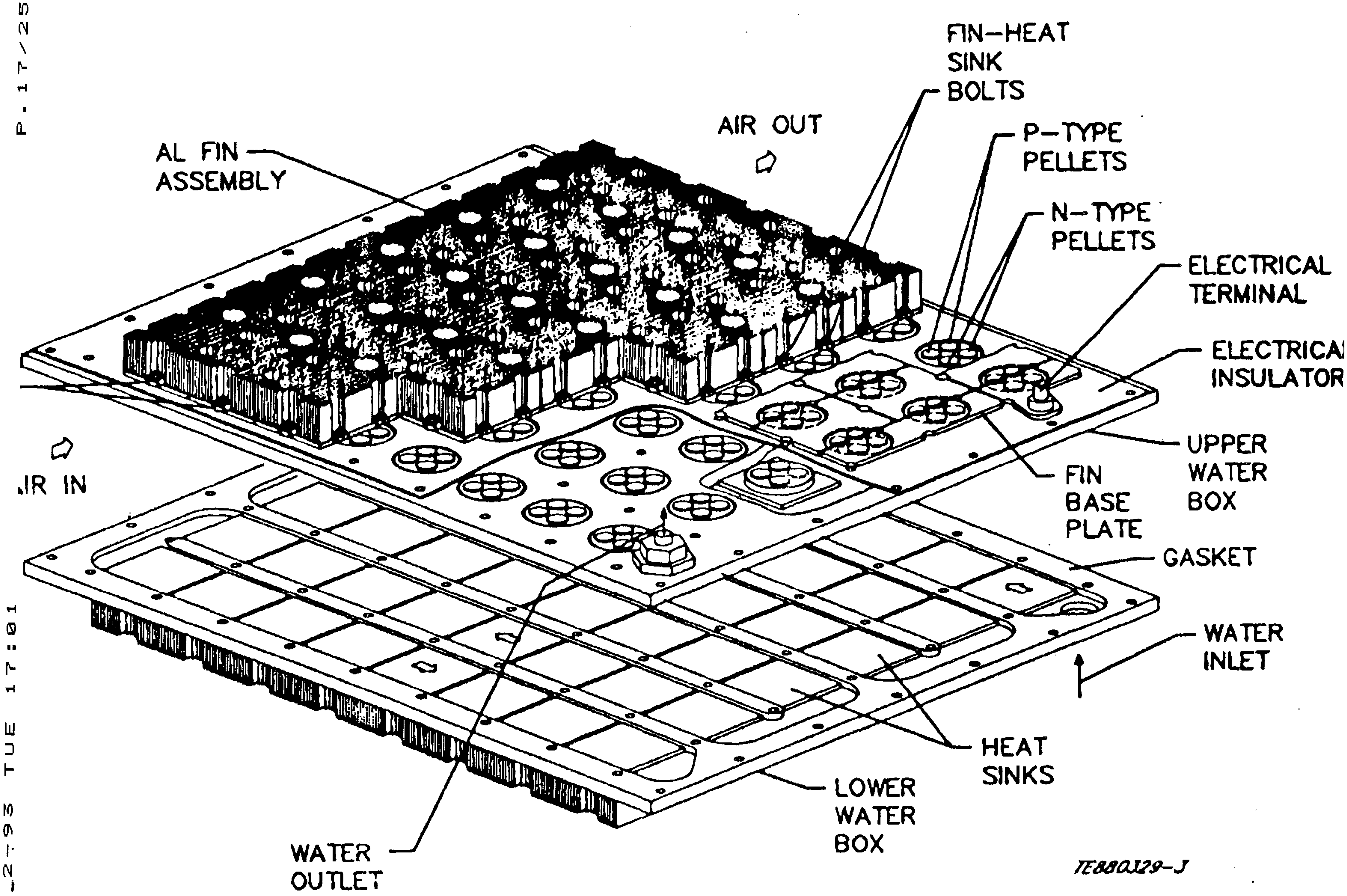


Figure 15. Water Box Module Exploded View

d. 1949 Ioffe- **Theory of Semiconductor TE.**

See 2nd & 4th presentations. These are heavily doped: 0.1 to several % of atoms contribute carriers. Most are low to moderate band gap and involve elements of higher atomic number. Many are soft or brittle, covalent, somewhat unstable or reactive compounds of low or moderate melting points.

e. 1953 first **Refrigerator or Heat Pump.**

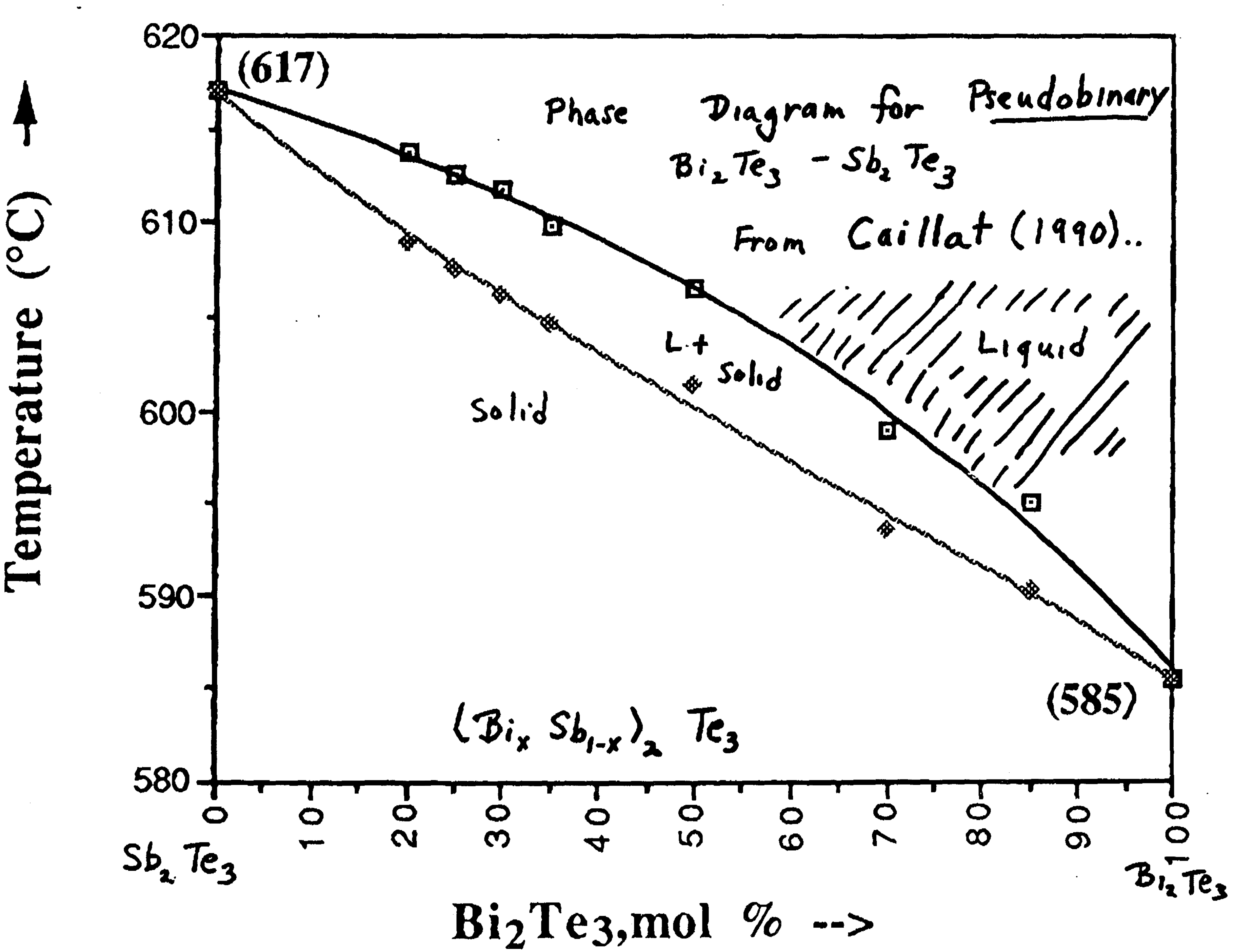
Diagram of cooler

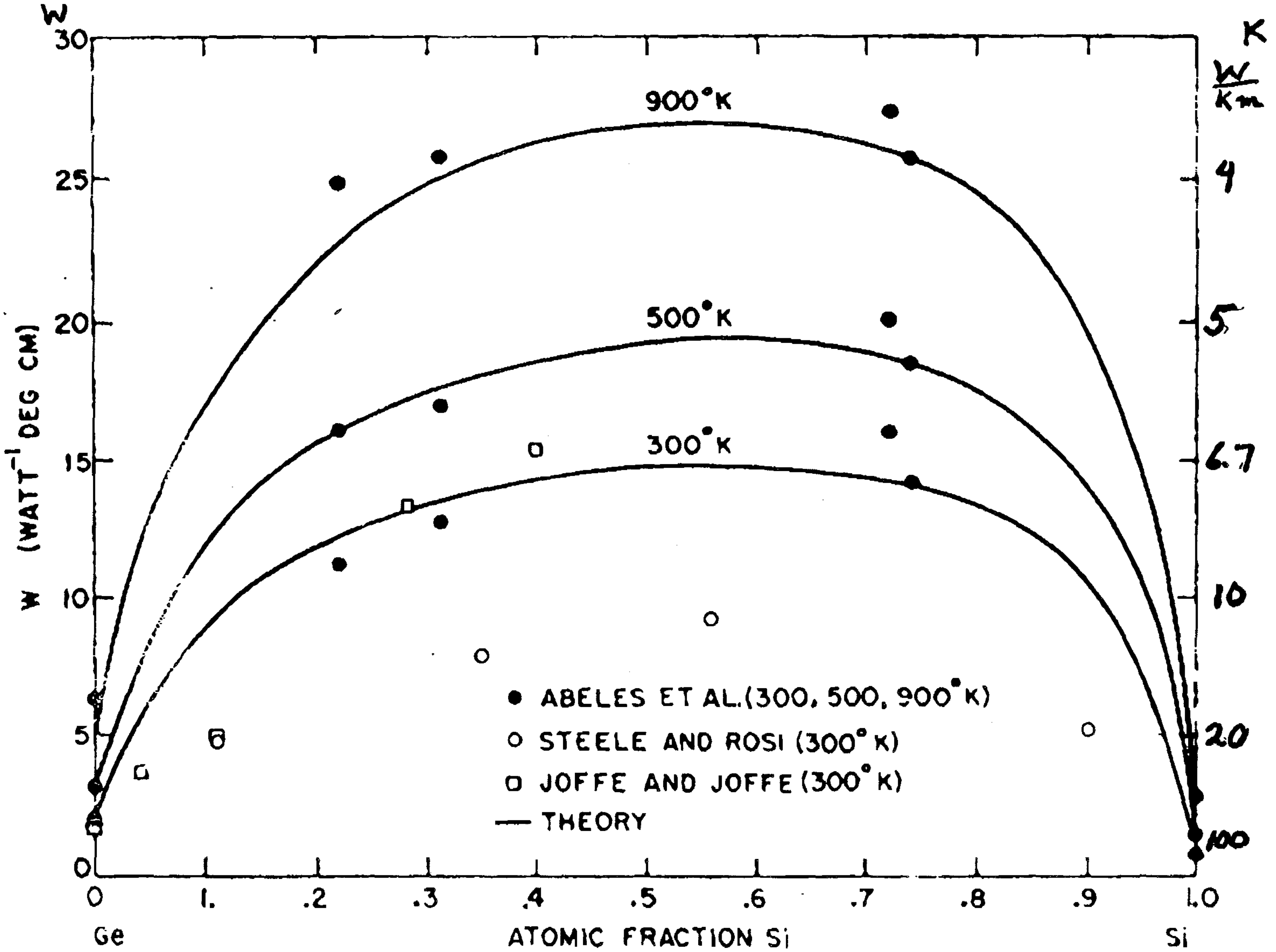
Note: Thermoelectrics are not heat annihilators-- A story
Discussion of COP

f. 1956 **Lowering** κ Ioffe's idea of alloying of **isomorphic** compounds to lower thermal conductivity. What is heat conduction? What are the mechanisms of heat conduction? (see **presentation #2**)

The role of current carriers: Wiedemann Franz law. κelectronic is proportional to σ.
*Microscopic view of solids as a lattice. What is a phonon? Phonon dispersion curve.

Imperfections in crystals
a) carriers
b) phonons
c) variations in atoms-point defects-charge, mass
d) extended defects...Grain boundaries


Phase Diagram for Pseudobinary
Bi₂Te₃ - Sb₂Te₃
From Caillat (1990)..
(617)
(585)
Liquid
L + Solid
Solid
(Bi$_x$ Sb$_{1-x}$)$_2$ Te$_3$
Temperature (°C)
620
610
600
590
580
0
10
20
30
40
50
60
70
80
90
100
Sb₂Te₃
Bi₂Te₃
Bi2Te3,mol % -->



Thermal Resistivity of Si_xGe_{1-x} alloy

Note W= 1/K

4. Applications and Optimism- Early 1960's.
   a. **Space** applications of generators.
   b. **Solid State** was magic word and there were projections of replacing many common, fluid-based thermodynamic cycles for terrestrial power and refrigeration.

5. Reassessments.

a. The stubborn **practical limit** of $ZT=1 \rightarrow \phi=\eta/6$, $\Rightarrow$ niche markets. (see **presentations #3, 4, 5 & 8**)

Max Power output: generators $\phi \approx \eta/[2.0 + 4/ZT]$, where $\eta = (T_h - T_c)/T_h$, which is the carnot efficiency. This is for cold side about equal to hot side temp; if cold it much lower than hot the constant in denominator tends to 1.5.

Max effic. : generators

$$\phi=\gamma\eta=\eta[\surd 1+ZT_{av}-1]/[\surd 1+ZT_{av}+T_c/T_h]$$

Coefficient of Performance (COP) of coolers is best given graphically but often less than 1. ε=cooling/input power.

$$\varepsilon=\gamma'\eta=\eta[\surd 1+ZT_{av}-T_h/T_c]/[\surd 1+ZT_{av}+1]$$

fig 2.5 if possible

6. Will there be ZT>>1? The future.

A ZT of 2 would give generators with $\eta_{\mathrm{max\ pow}} \sim 1/4$ of Carnot and $\eta_{\mathrm{max\ eff,}} = 0.3$ of Carnot. It would provide a cooler with 1/4 of Carnot.

A ZT of 3 would give generators with $\eta_{\mathrm{max\ pow}} = 1/3$ of Carnot and $\eta_{\mathrm{max\ eff,}} = 0.3$ to 0.4 of Carnot. It would provide a cooler with 1/3 of Carnot.

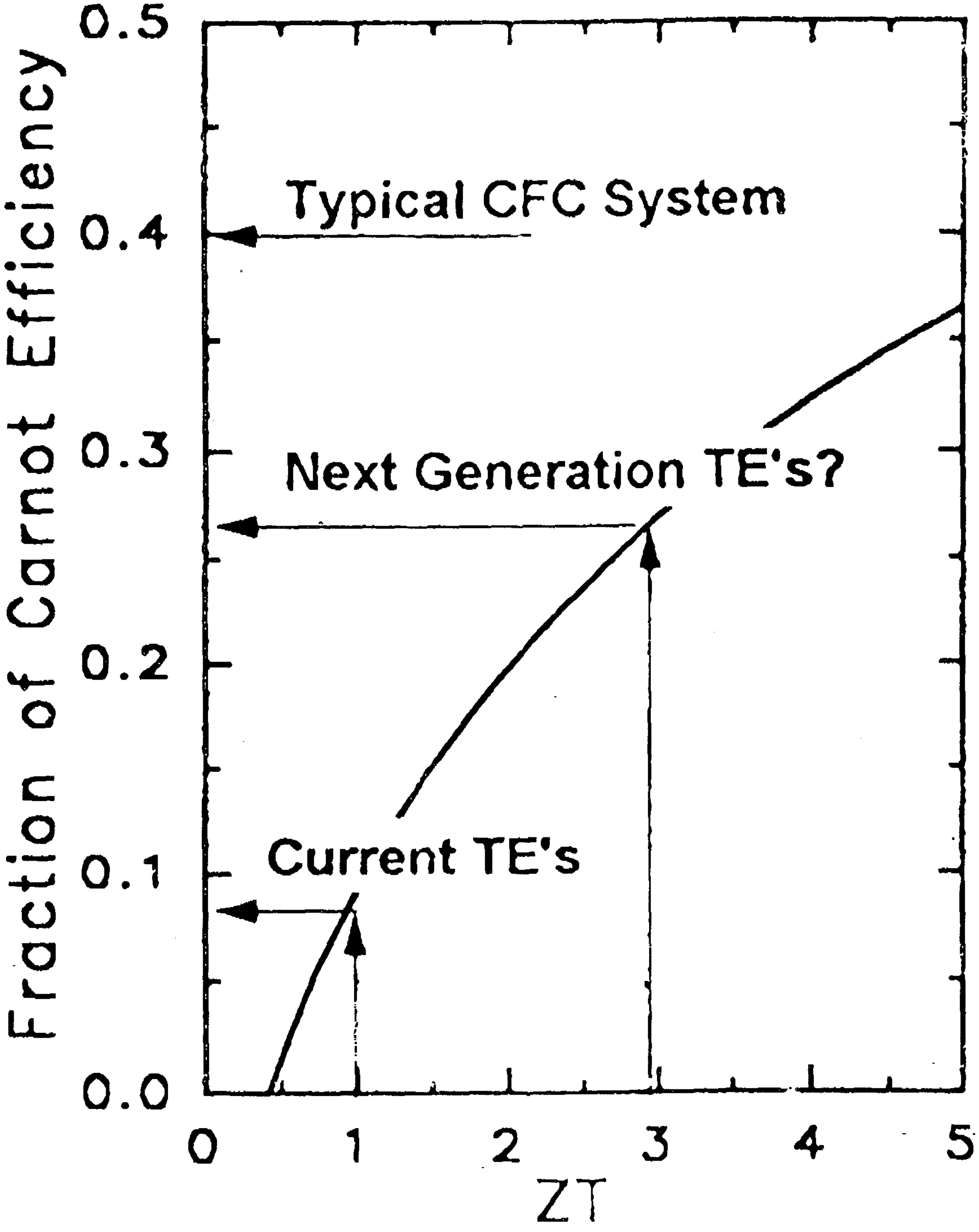


Figure 3. Effect of the Thermoelectric Figure of Merit on the Performance of a Thermoelectric Cooler.