Progress in New Thermoelectric Materials

Fall 2004 MRS Meeting, Boston MA
Symposium S 4.5

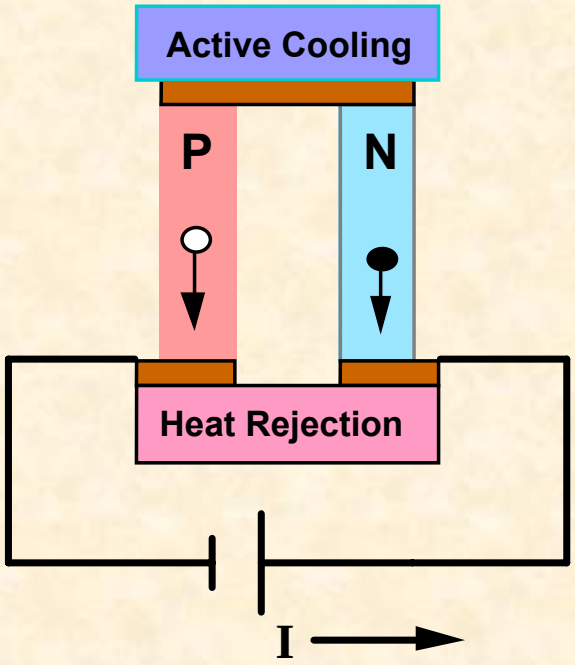
Brian Sales
Correlated Electron Materials Group
Oak Ridge National Laboratory
Oak Ridge, TN

Basic Facts About Thermoelectric Devices

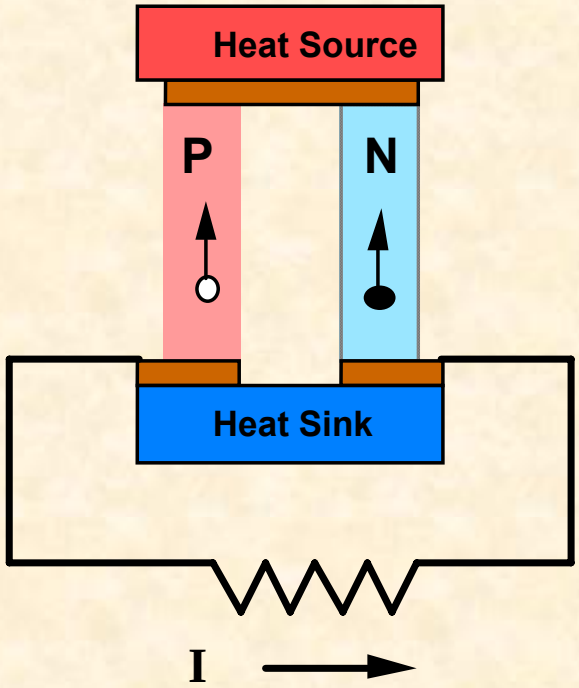
- All solid-state devices (no moving parts except electrons)
- Can be used for refrigeration or power generation
- Refrigeration with no chemical refrigerant (such as Freon)
- Major advantage: reliable and quiet
- Major disadvantage: poor efficiency
- Efficiency determined by figure of merit ZT, depends only on material properties
- $ZT = S^2T\sigma/\kappa$, where S = Seebeck coefficient, σ is electrical conductivity, and κ is the thermal conductivity

Thermoelectric Couples for Refrigeration or Power Generation.

$$ZT = T\,S^2\,\sigma/\kappa$$



Refrigeration



Power Generation

For Power generation:

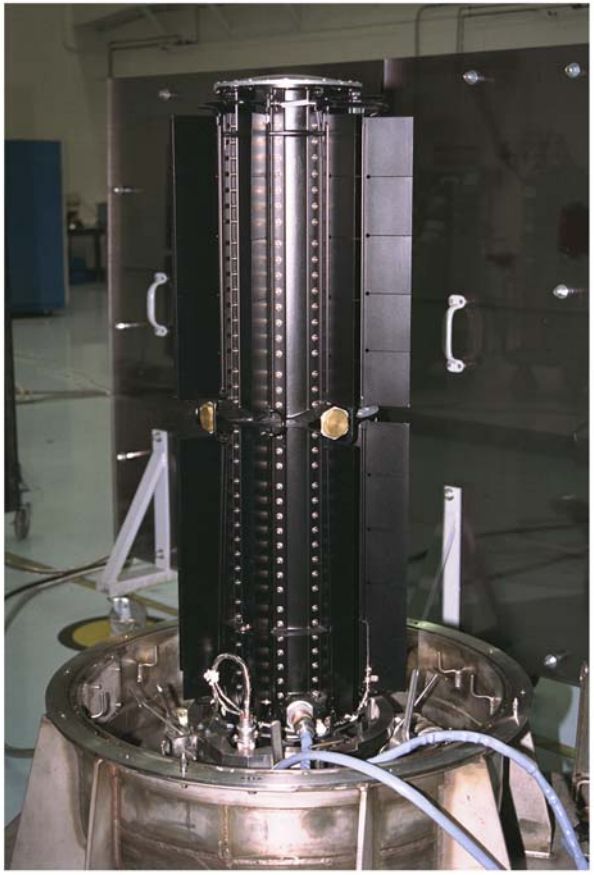
$$Efficiency = \frac{(T_h - T_c)(\gamma - 1)}{(T_c + \gamma T_h)}$$

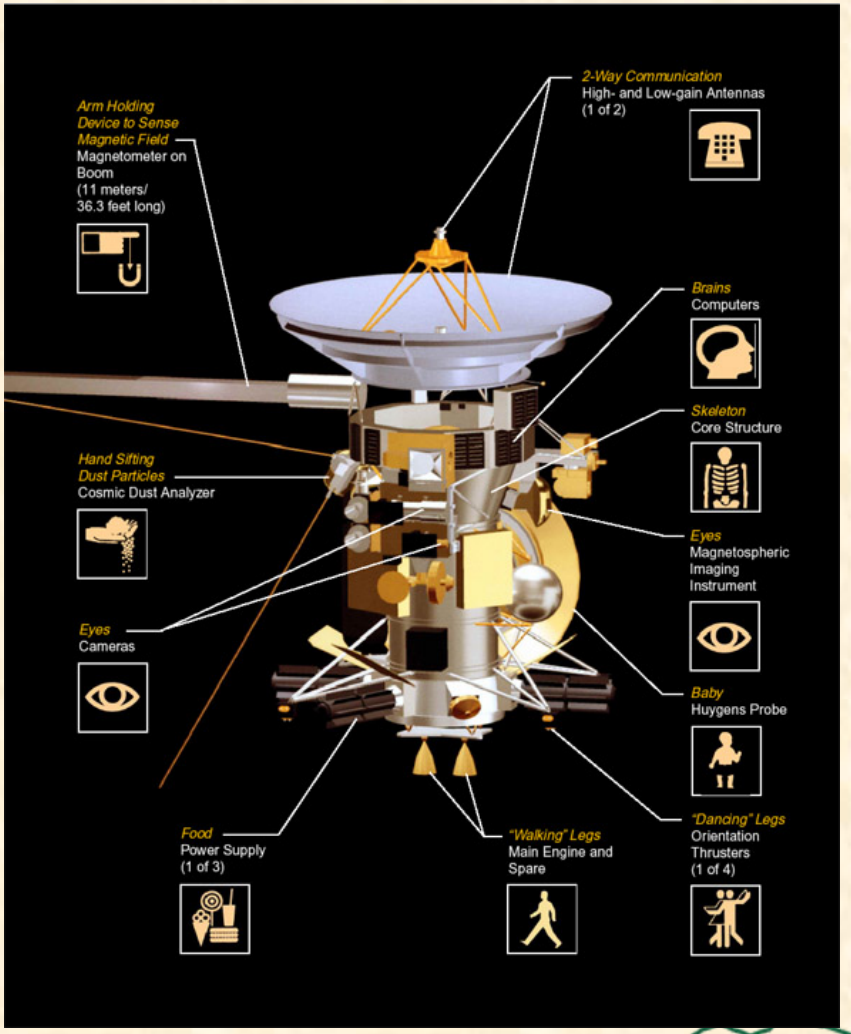
For Refrigeration:

$$COP = \frac{(\gamma T_c - T_h)}{(T_h - T_c)(1 + \gamma)}$$

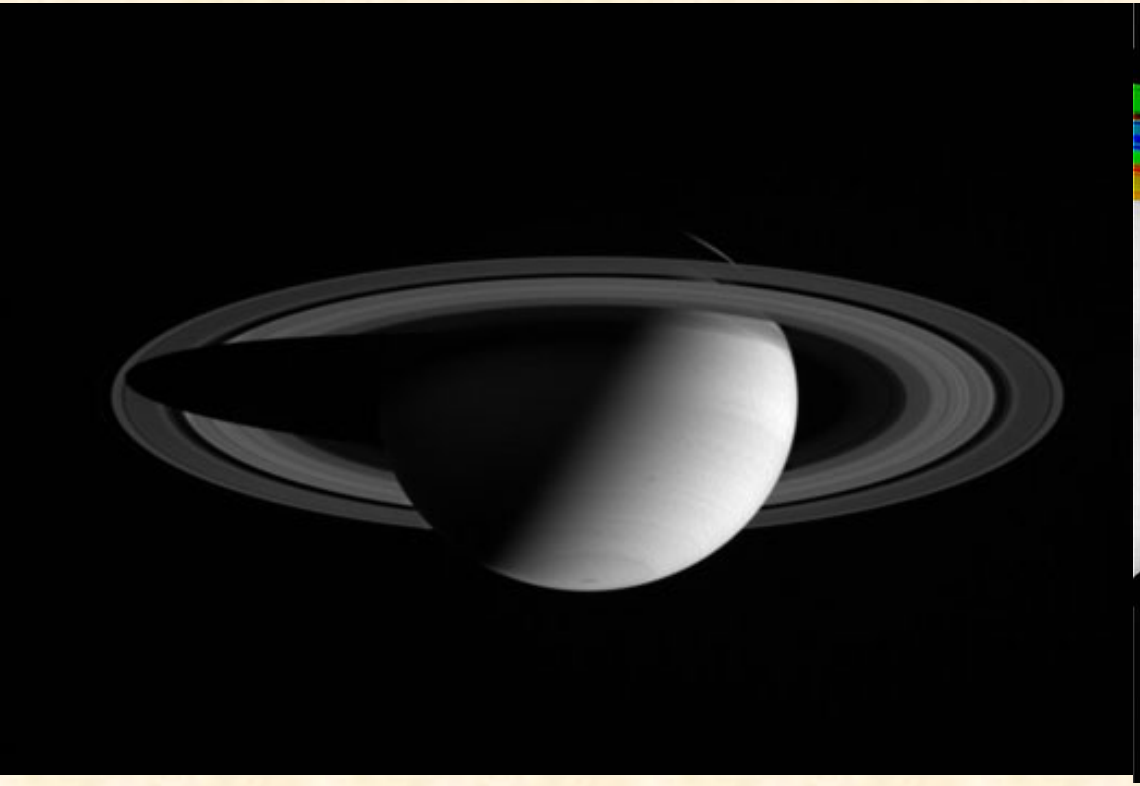
where $\gamma = \sqrt{(1 + ZT)}$

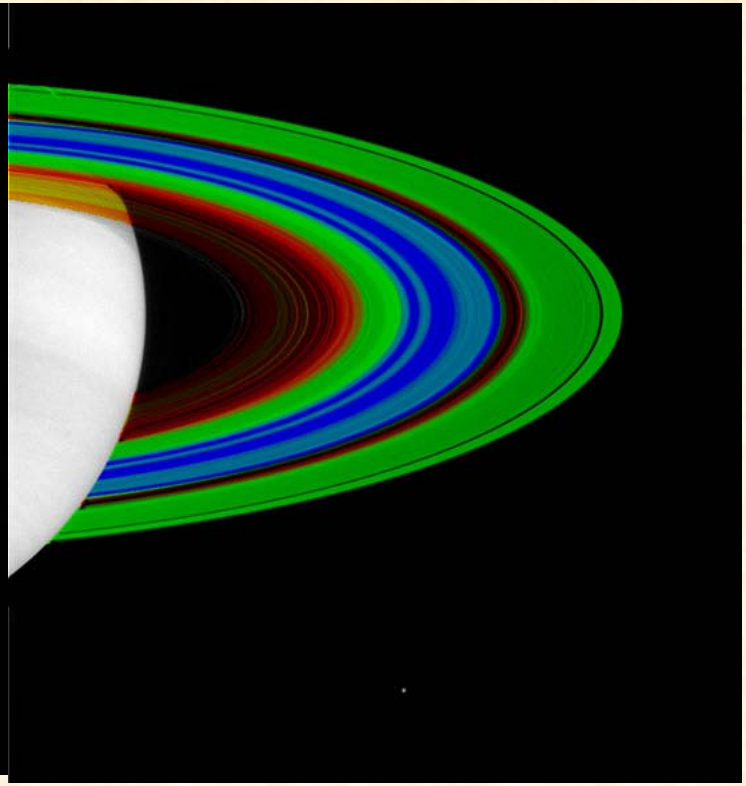
Thermoelectric Modules are Used to Power NASA's Cassini Probe to Saturn and Jupiter





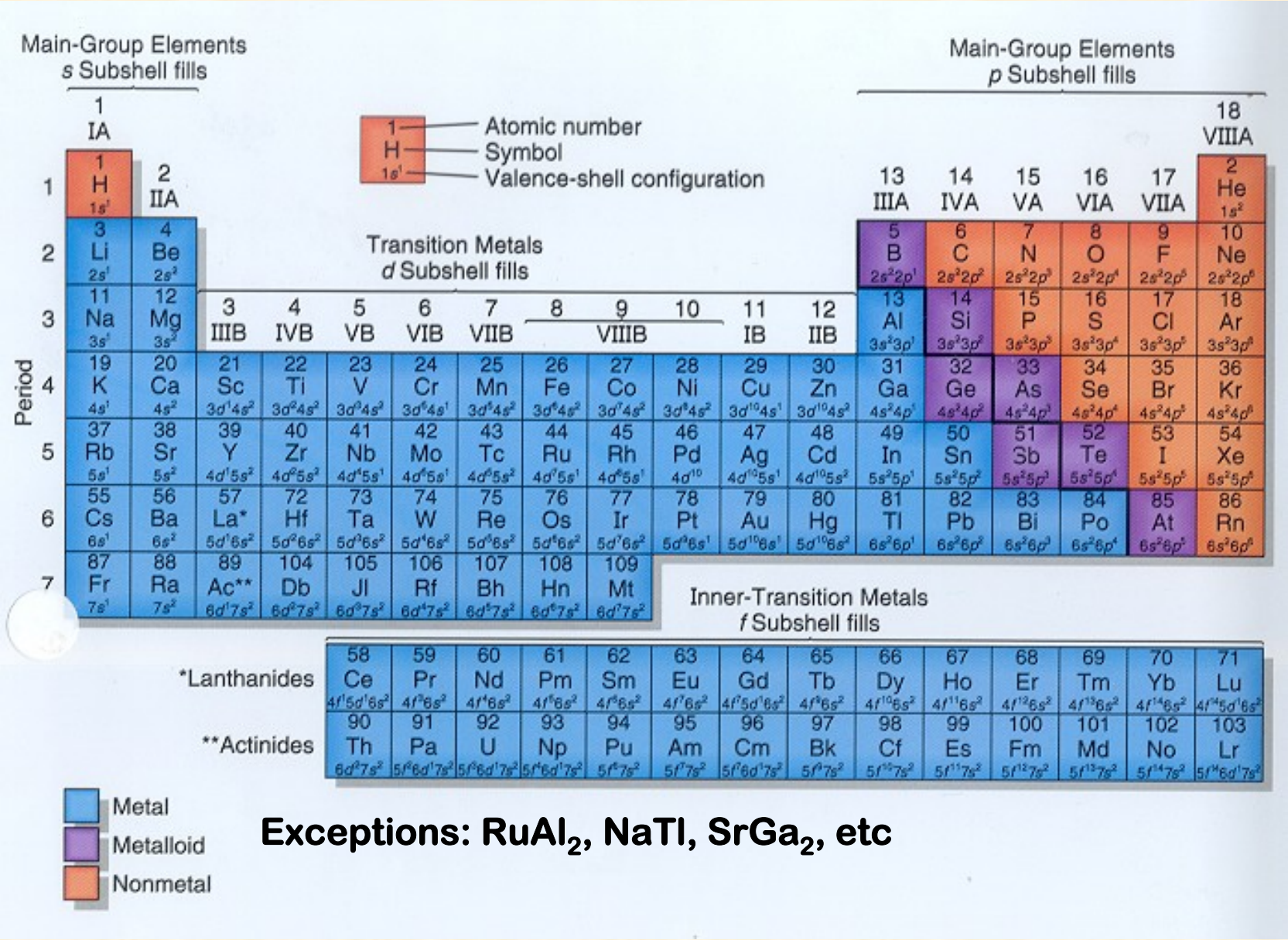
Some of amazing images from Cassini !
(Lifted from NASA web page)





Thermoelectric Refrigerator (Igloo, Wallmart)

Holds 72 12-ounce cans-(44F below ambient)



Exceptions: $RuAl_2$, NaTl, $SrGa_2$, etc

Limitations of "True Intermetallic Compounds" (≈good metals) as Thermoelectric Elements:

$$ZT = T S^2 / \kappa\rho$$

$$\kappa = \kappa_{el} + \kappa_{Lattice}$$

Best Case, Suppose $\kappa_{Lattice} = 0$

Then $ZT = T S^2 / \kappa_{el} \rho$

But for a good metal the Wiedemann-Franz law holds

and

$$L_0 = \kappa_{el} \rho / T = 2.4 \times 10^{-8}\ V^2/K^2$$

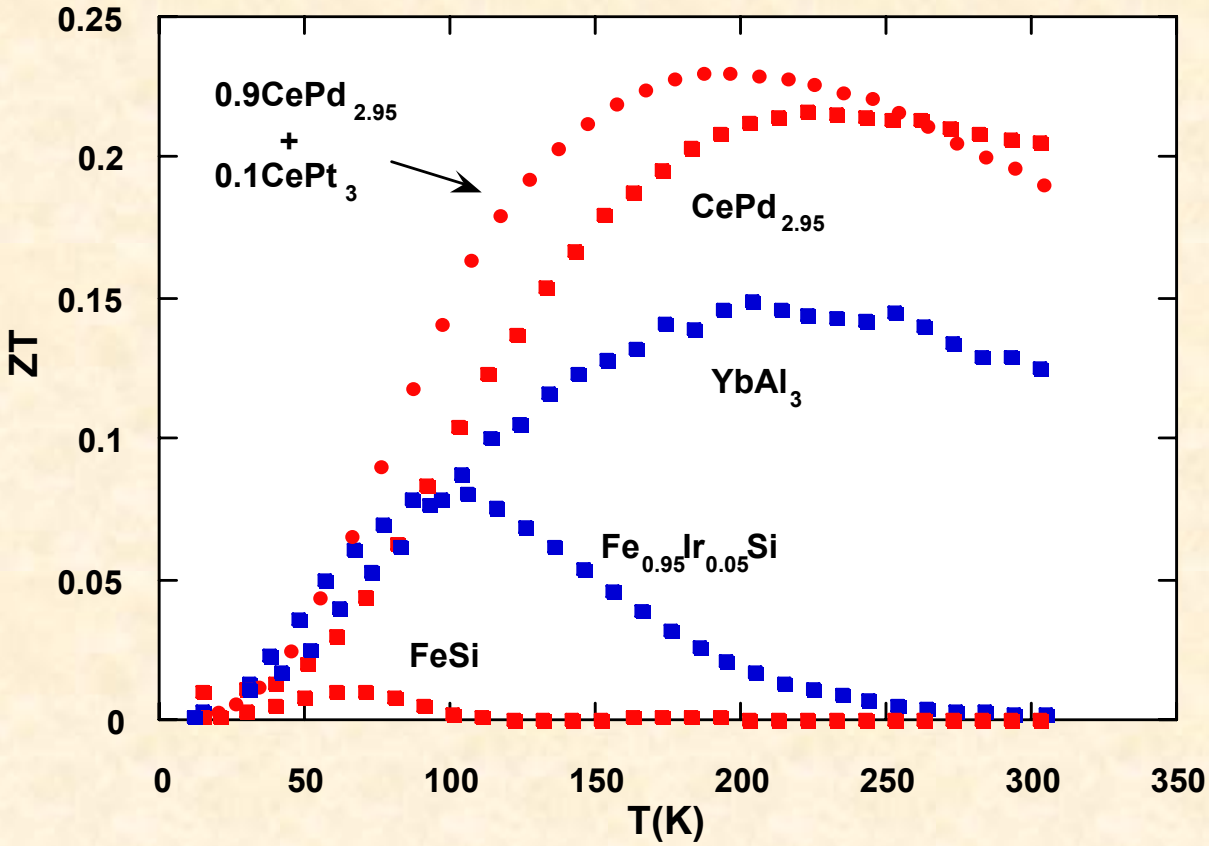
or $ZT = S^2 / L_0$

which means that for ZT=1,

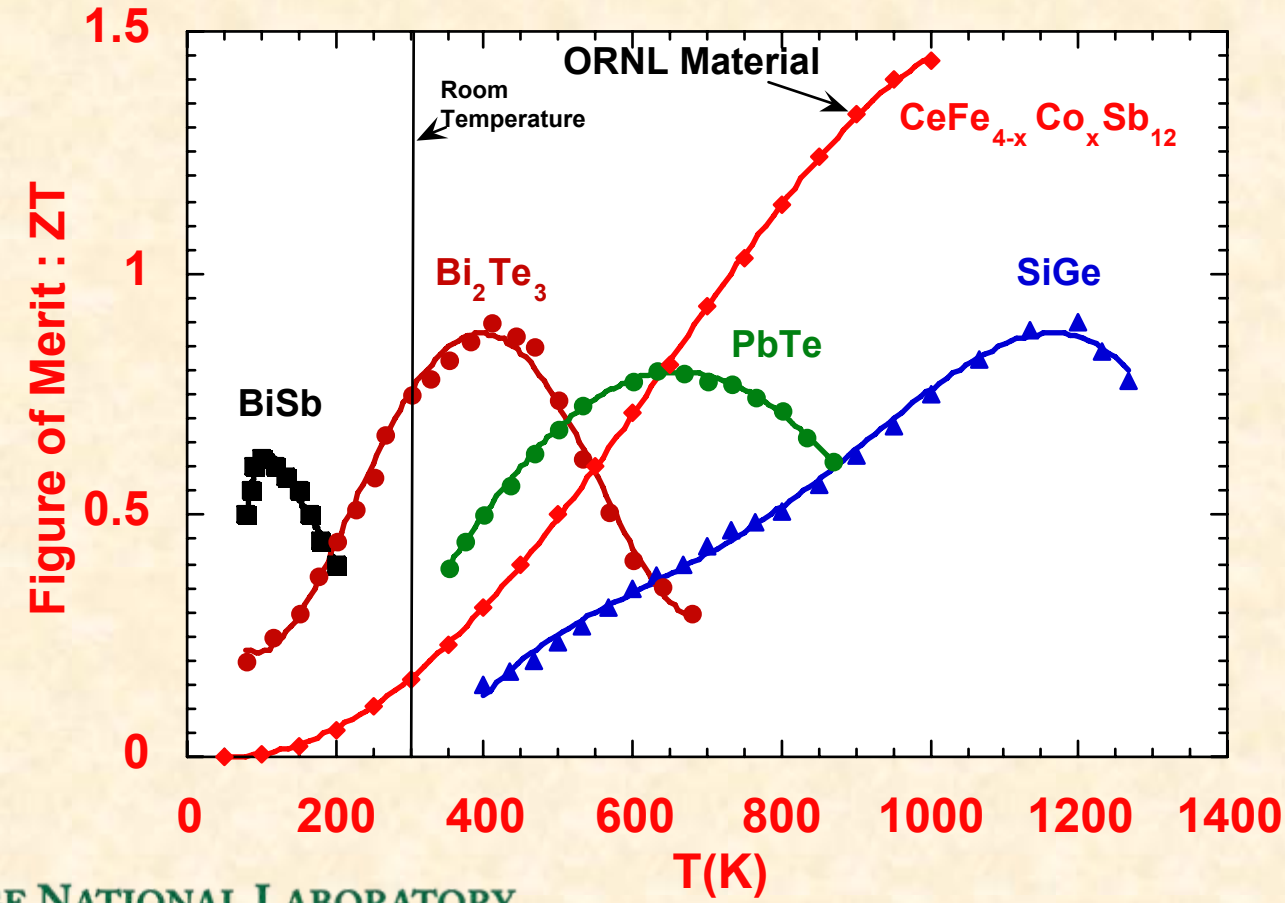
or $S > 156\ \mu V/K$

"Best" Thermoelectrics Among Mixed Valence Intermetallics

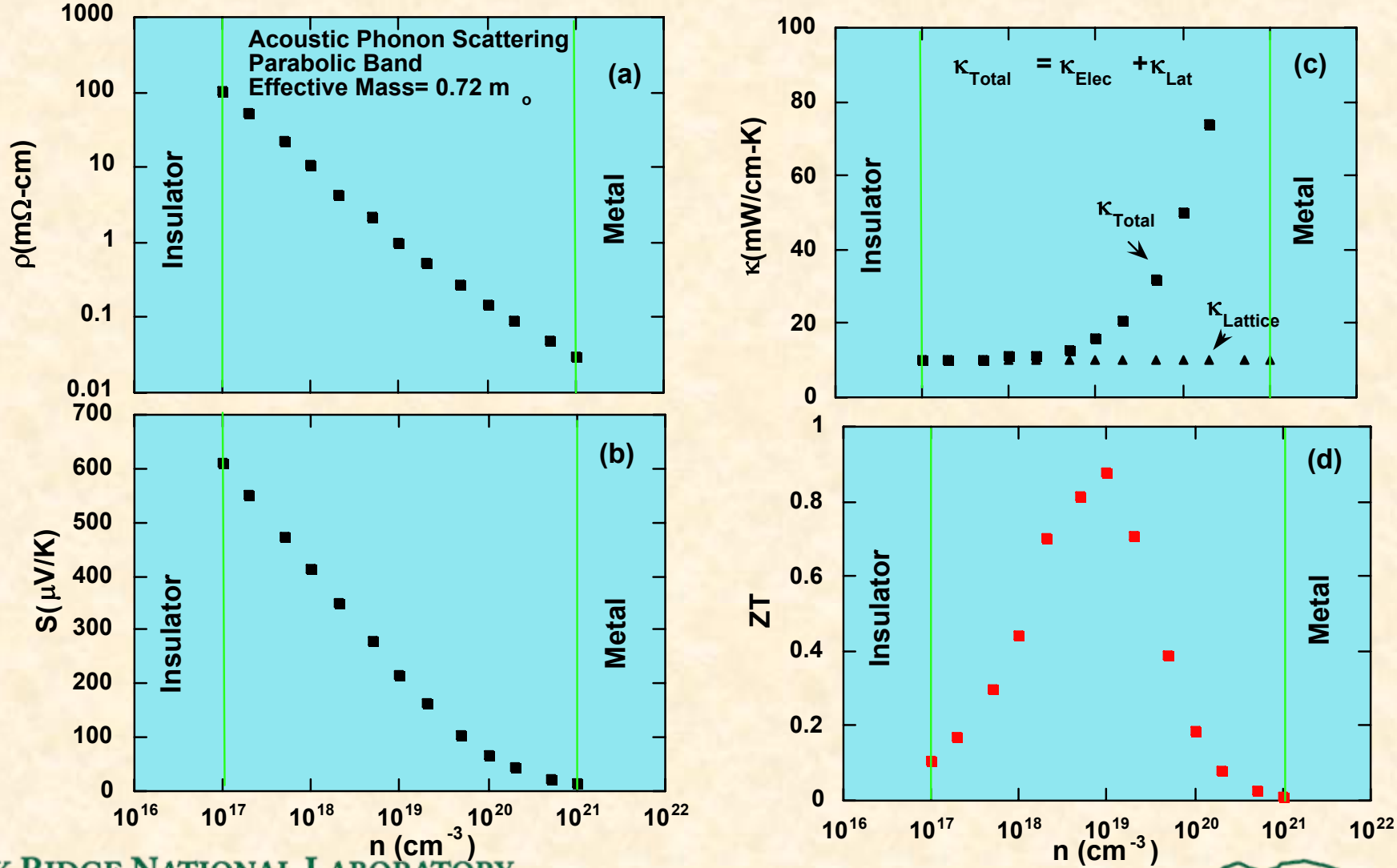
(Physics Today, March 1997)



"State-of-the-art" Thermoelectric Materials



Why finding a "good thermoelectric" (ZT > 1) is hard! ZT = $T S^2/\kappa\rho$ (Physics Today, March1997)



New Classes of Promising Metalloid Thermoelectric Materials (bulk) Most ZT values good above room temp:

- Filled skutterudites, e.g. $CeFe_4Sb_{12}$, $Yb_x CoSb_3$ - ZT ≈ 1.2, T≈ 600-900K
- Half-Heusler Alloys: e.g. TiNiSn, ZrNiSn

  ZT ≈ 0.7 , 800 K
- Semiconducting Clathrates, e.g $Sr_8Ga_{16}Ge_{30}$, ZT ≈ 1 , T ≈700 K
- Complex Bi chalcogenides $CsBi_4Te_6$, ZT≈0.8 , T = 225 K
- Cubic Ag-Pb-Sb-Te bulk compounds-may have ≈ epitaxial nanocrystal inclusions, ZT ≈ 2.2 at 800 K

Another Approach: Thin Films, Wires and Superlattices

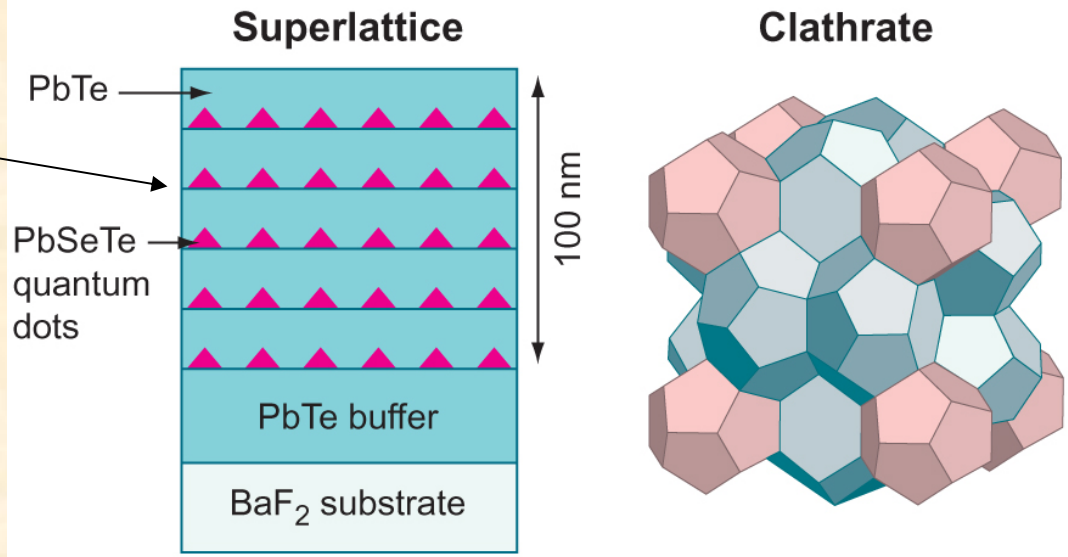
Proposed by Dresselhaus group starting ≈1993

Lower dimensionality can result in:

- Enhancement in density of states near Fermi energy which leads to larger Seebeck coefficient
- Exploit anisotropic Fermi surfaces in cubic multivalley semiconductors
- In nano-structured superlattices, boundary scattering can effect phonons more than electrons (or holes)

PbTe Superlattice with PbSeTe nanodots grown with Molecular Beam Epitaxy has ZT≈2 at room temperature

Harman et al. *Science 297 (2002) 2229*



Promising new materials. (**Left**) Nanoengineered thermoelectric materials of this kind are prepared with molecular beam epitaxy. (**Right**) In this model clathrate crystal structure, the cubic crystal structure is composed of two types of polyhedra that consist of clusters of 20 or 24 atoms. In self-assembled structures of this type, nature does the nanoengineering.

ZT ≈ 2.2 Bulk Sample of $AgPb_{18}SbTe_{20}$ (Kanatzidis group- *Science, Feb 2004)*

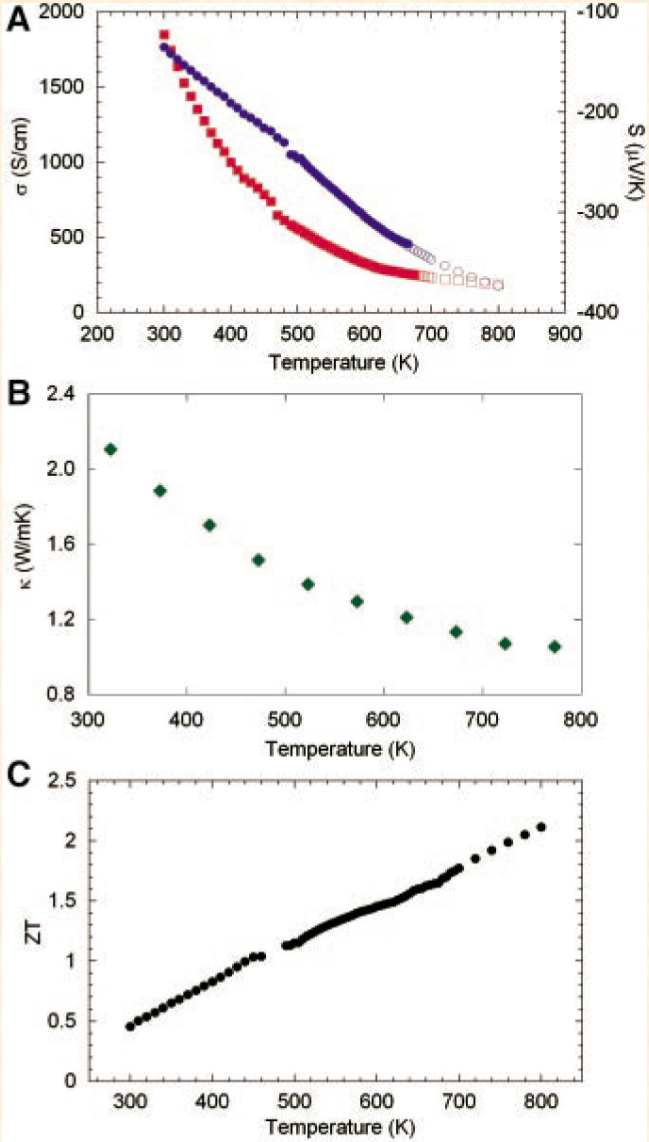


Fig. 3. Variable-temperature charge transport and thermal transport data for $AgPb_{18}SbTe_{20}$: (**A**) Electrical conductivity (σ) and thermopower *(S)*. (**B**) Total thermal conductivity (κ) in the range 300 to 800 K. The data were obtained as described in (*19*). (**C**) Thermoelectric figure of merit, *ZT*, as a function of temperature.

High ZT values may be related to nanocrystal inclusions. Implication: It may be possible to reproduce the high ZT values of MBE films using bulk processing techniques!

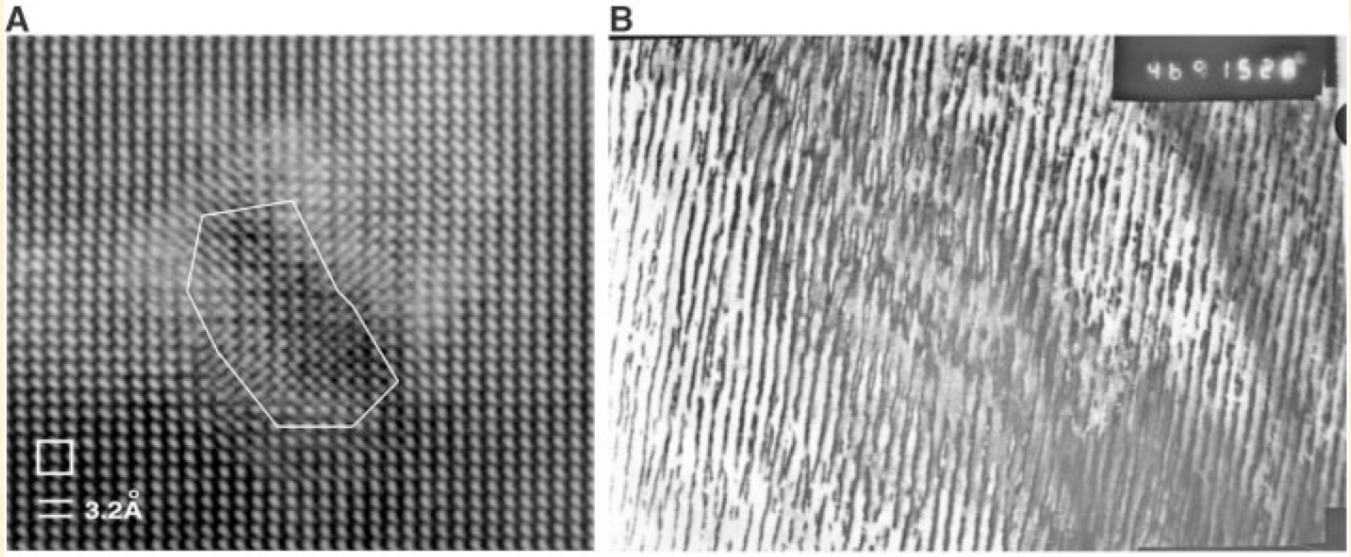


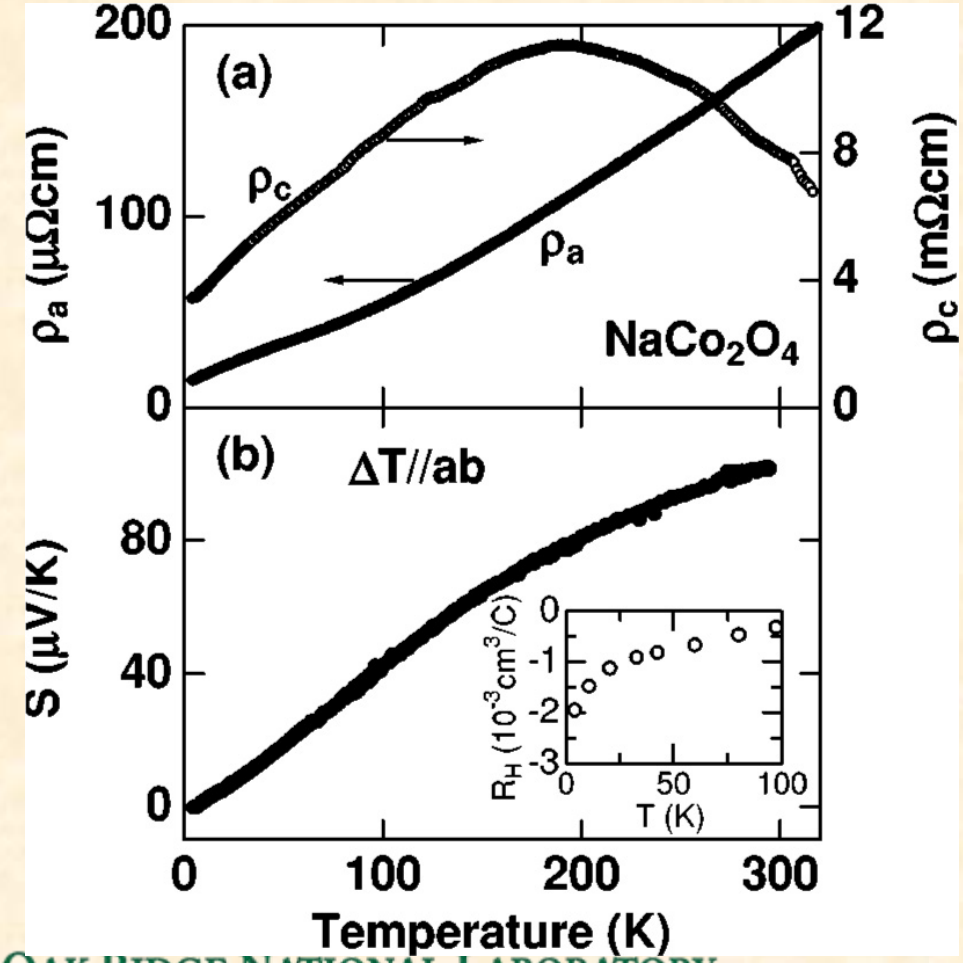
Fig. 4. (**A**) TEM image of a $AgPb_{18}SbTe_{20}$ sample showing a nano-sized region (a "nanodot" shown in the enclosed area) of the crystal structure that is Ag-Sb–rich in composition. The surrounding structure, which is epitaxially related to this feature, is Ag-Sb–poor in composition with a unit cell parameter of 6.44 Å, close to that of PbTe. (**B**) Compositional modulations over an extended region of a $AgPb_{10}SbTe_{12}$ specimen. The spacing between the bands is ~20 to 30 nm. In essence, the observed compositional modulation is conceptually akin to the one found in the artificial PbSe/PbTe superlattices (*15*). In the latter, the compositional modulation exists at least along the stacking direction.

Recent Interest in Na_xCoO_2 Materials as Thermoelectrics

Terasaki et al. Phys. Rev. B56, R12685 (1997)

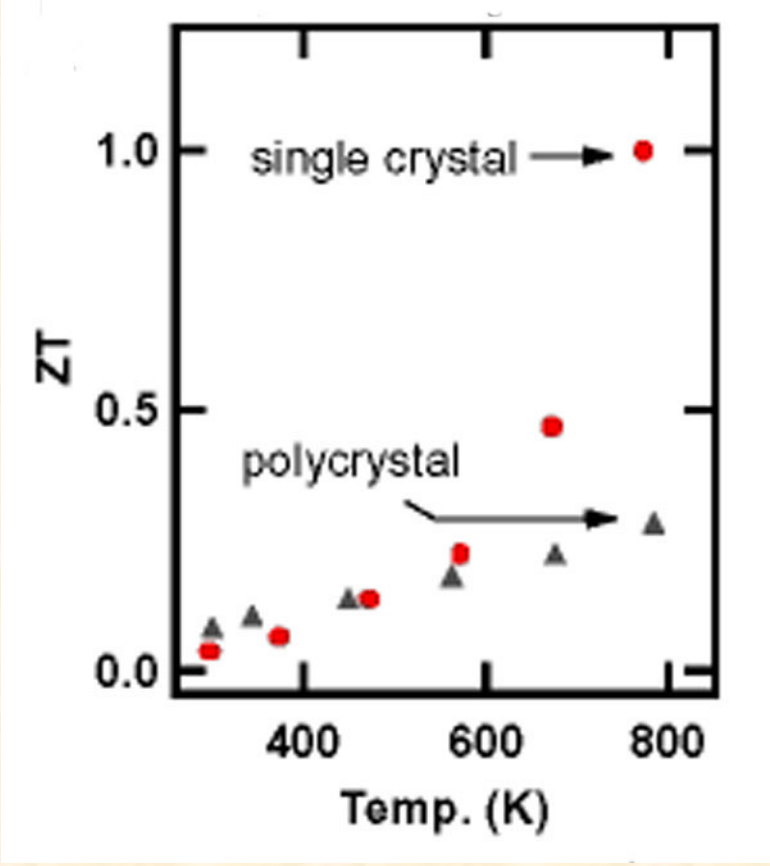
- This material violates most of the "traditional rules" for finding a good thermoelectric (heavy atoms, small electronegativity differences, no magnetic elements)
- However oxides are attractive since they are stable in air at elevated temperatures

Data on $Na_{0.7}CoO_2$ from Terasaki's Original Paper. Good oxide thermoelectric ! Violates "conventional wisdom"



Oxides are very intriguing as thermoelectrics for power generation : relatively cheap and stable in air

Na_xCoO_2 Crystals Have Good Thermoelectric Properties at High Temperatures ! Why?

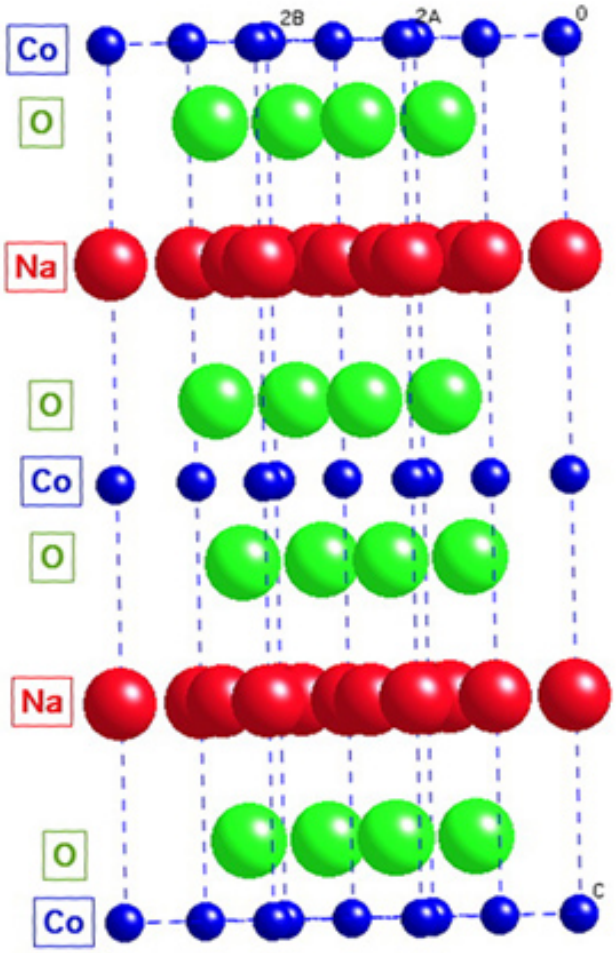


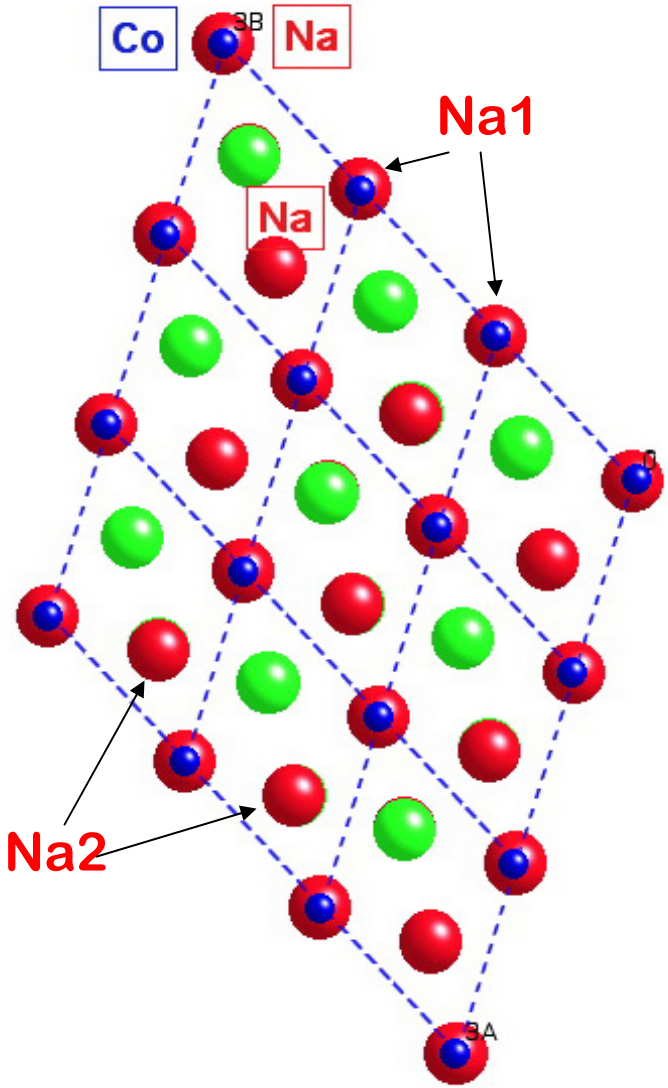
K. Fujita et al.
Jpn. J. Appl. Phys.
40 (2001) 4644

Layered Hexagonal Structure of $Na_{0.75}CoO_2$

Mixed Co Valence 3.25

Two Partially Occupied Na Sites (Na1 ≈ 0.25,Na2 ≈ 0.5)





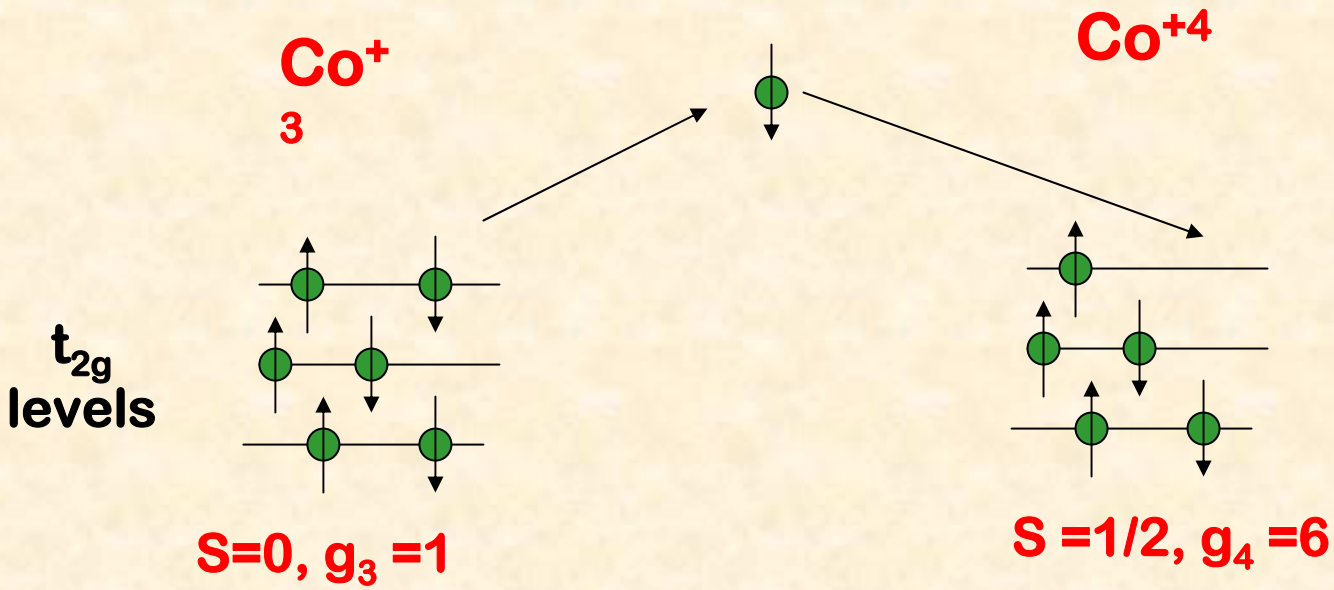
Is this structure important for a good CoO_2 based thermoelectric material ? Apparently YES since several other layered hexagonal Cobalt oxides also have high ZT values :

$Bi_{2-x}Pb_xSr_2Co_2O_y$

$Ca_3Co_4O_9$

$TlSr_2Co_2O_y$

Possible origin of high Thermopower in Hexagonal CoO_2 Layers: Entropy current as carrier moves between Co^{+3} and Co^{+4} configurations.



Thermopower at high temperature due to configurational Entropy Current Calculated By:

Koshibe et al. *PRB* **62**, *6869 (2000)*

$S = -k_B/e \ln\{(g_3/g_4) (x/1-x)\}$,
where x is fraction of Co^{4+} ions

TABLE I. The ratio g_3/g_4 in Eq. (13) in the cases (i)–(v). The obtained values of thermopower Q at $x=0.5$ are also presented.

	Co^{3+}	Co^{4+}	g_3/g_4	$Q(x=0.5)$
(i)	HS	HS	15/6	-79 μV/K
(ii)	HS+LS	HS	16/6	-84 μV/K
(iii)	LS	HS+LS	1/12	214 μV/K
(iv)	LS	LS	1/6	154 μV/K
(v)	HS+LS+IS	HS+LS+IS	34/36	5 μV/K

References

- *"Recent Trends in Thermoelectric Materials"* Semiconductor and Semimetals, Edited by Terry Tritt, Volumes 69,70,71, Academic Press (2001)
- T. C. Harman et al. *Science* 297 (2002) 2229
- K. F. Hsu et al. *Science* 303 (2004) 818
- R. Venkatasubramanian et al. *Nature* 413 (2001) 597
- B. C. Sales *Science* 295 (2002) 1248
- G. Mahan, B. Sales and J. Sharp, *Physics Today, March 1997, p.42*

Power Point Presentation Available at www.cemg.ornl.gov