SUMMARY REPORT ON ICT'99 – THE 18TH INTERNATIONAL CONFERENCE ON THERMOELECTRICS

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This paper summarizes selected highlights from the 18th International Conference on Thermoelectrics held 29 August – 2 September, 1999 in Baltimore, Maryland USA. 302 attendees (including 55 students) from all over the world delivered 116 oral and 90 poster presentations. Key highlights include development of the first quantum dot thermoelectric structures, novel clathrate compounds and advances in micropiles (small thermoelectric devices). A short report such as this can not do justice to recent progress in thermoelectrics

Introduction

The 18th International Conference on Thermoelectrics (ICT'99) was the best attended of any ICT to date (see Fig 1)[1]. The quality, variety and sophistication of the technical contributions indicate thermoelectrics is healthy as ever, even in the face of competition from emerging conversion technologies.

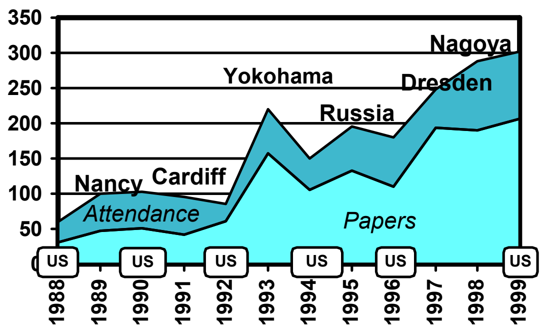

Fig. 1: ICT'99 was the largest to date.

The first 'quantum dot' thermoelectrics were reported, with ZT~2 at 500-700K. Clathrates have emerged as potential 'electron-crystal, phonon glass' materials. And rapid advances are being reported in 'micropile' technologies (very small thermoelectric devices) including a body-heat powered wrist watch and a thermoelectric motion sensor.

Based largely on what was heard and seen in Baltimore, errors, omissions and poor judgment are inevitable in this sort of report. The original authors deserve all credit for anything of interest reported here, and I take full responsibility for any errors in reporting.

Competition!

The ICT'99 organizers devoted a session to 'competing' energy conversion technologies including papers on AMTEC (Alkali Metal Thermal-to-Electric Converter), thermophotovoltaics, and thermoacoustics. The thermoacoustics presentation [Symko] included several excellent 'live' demonstrations.

The AMTEC paper by [**M.A. Ryan]** describes NASA's plan to use this emerging converter technology to replace the thermoelectric-based Radioisotope Thermoelectric Generators (RTGs) to power planetary exploration missions beyond the orbit of Mars. While not yet ready for near-term missions to Europa (in 2003) and Pluto (in 2004), AMTEC's efficiency of 12-18% is attractive.

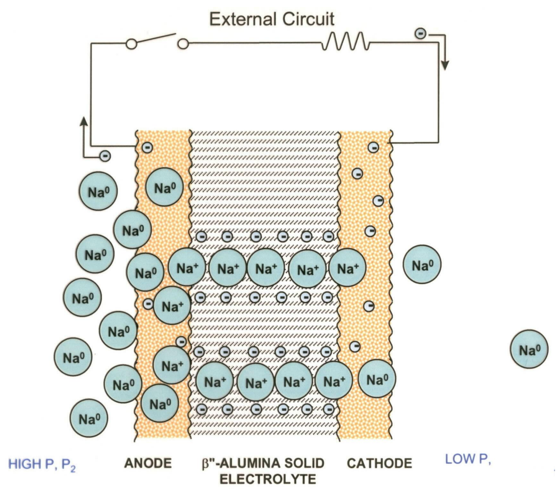

Fig. 2: AMTEC converts a Na pressure difference to electricity [Ryan].

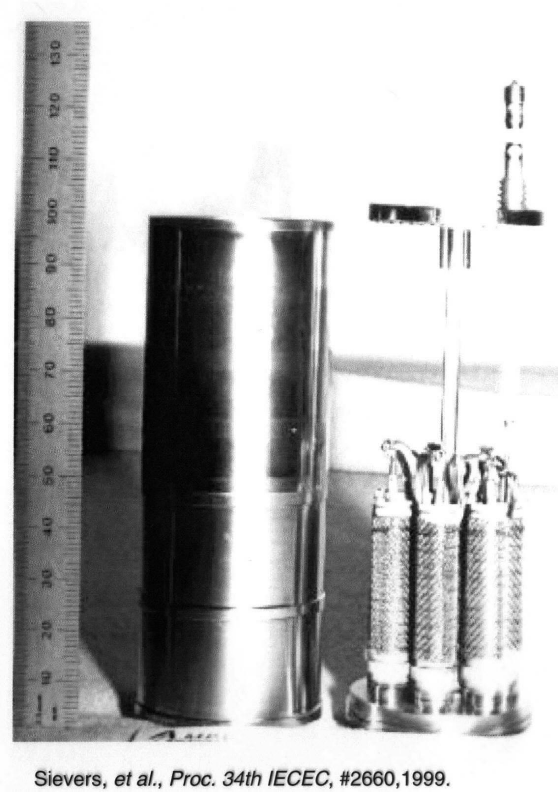

Fig. 3: A disassembled AMTEC cell. Na gas condenses at the top plate, flows through the central wick to the hot electrodes (bottom) to generate electricity [Ryan].

Another session was devoted to thermionic refrigeration. Analysis for a vacuum thermionic cooler by [**H.J. Goldsmid**] illustrates (Fig. 4) the potential to outperform thermoelectric coolers by a wide margin, at least near room temperature.

The key to vacuum thermionic cooling is finding a material with sufficiently low work function (0.3 eV), a prospect considered unlikely by [**G. Mahan**] who has instead focused on a multi-layer solid-state thermionics approach where the effective work function can be relatively easily controlled. In this approach, the boundary thermal resistance is key to high performance, so he has studied theoretically the effect of superlattice boundaries on phonon heat conduction. Contrary to prior studies, he finds short superlattice periods (i.e. lots of boundaries) do not appreciably lower the lattice thermal conductivity (Fig. 5).

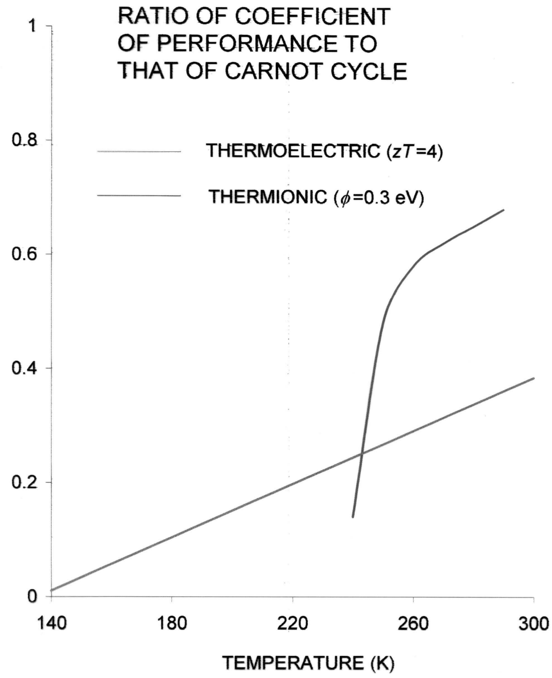

Fig. 4: Potential COP for vacuum thermionic coolers compared to advanced thermoelectrics [Goldsmid].

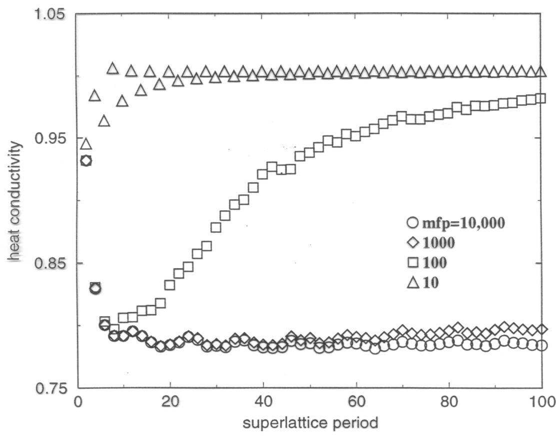

Fig. 5: Phonons with short mean-free-path (mfp) values are unaffected by the SL. As the SL period becomes very short, even long mfp phonons are less affected [Mahan].

Quantum Wells, Wires and Dots

Quantum confinement has been thought promising for increasing ZT values for some years, but now work is going beyond quantum wells to lower dimensional quantum wires and dots. A good example of the potential for Bi quantum wires is illustrated by [**S. Cronin**] in Fig. 6. Remarkably, fabricating (Fig. 7) and testing even individual nanowires (Fig. 8) now appears to be feasible.

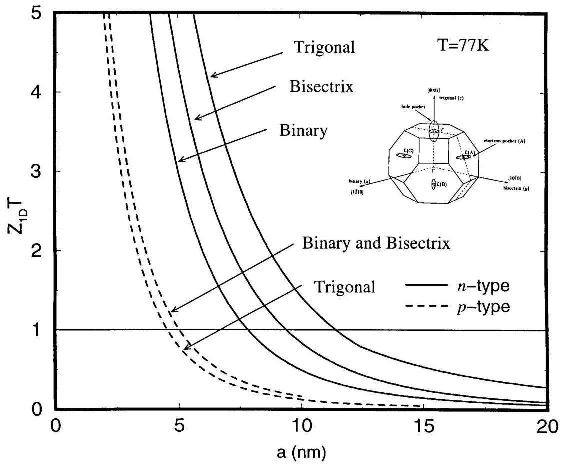

Fig. 6: Enhanced ZT values are expected in Bi nanowires of achievable dimensions [Cronin].

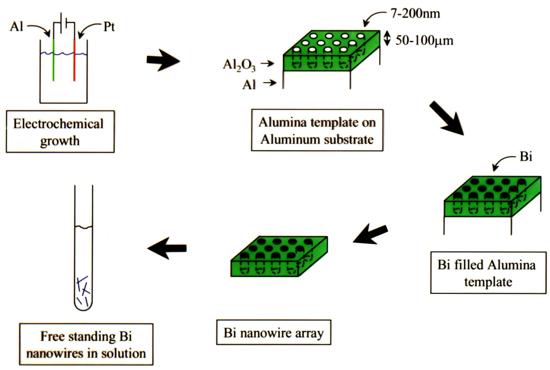

Fig. 7: Bi nanowire fabrication technique can yield either bundles of wires, or individual wires [Cronin].

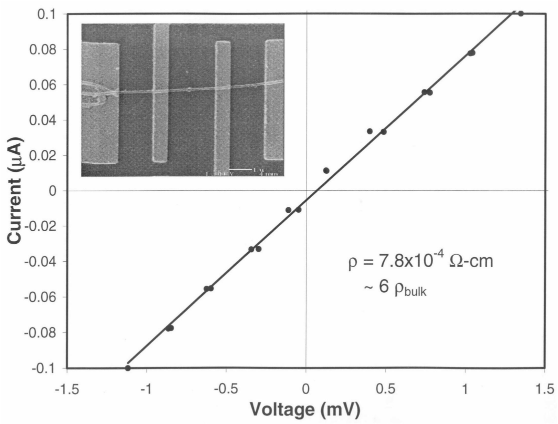

Fig. 8: 4 point resistivity measurement on a 70nm Bi nanowire fabricated as above [Cronin].

If 1-d wires are good, then zero dimensional dots should be better. A novel approach for making low dimensional structures based on opals was described by [**R. Baughman**]. This remarkable approach begins with highly uniform sized silica nano-sized spheres packed into a regular 3-d array, similar to natural opals. The voids between the spheres are then infiltrated with (for example) Bi and the silica spheres are removed with acid. The result is an 'inverse opal', a low density interconnected network of Bi, shown in Fig. 9. Depending on choice of materials and preparation methods, the resulting templates may exhibit features of dots, wires, or wells.

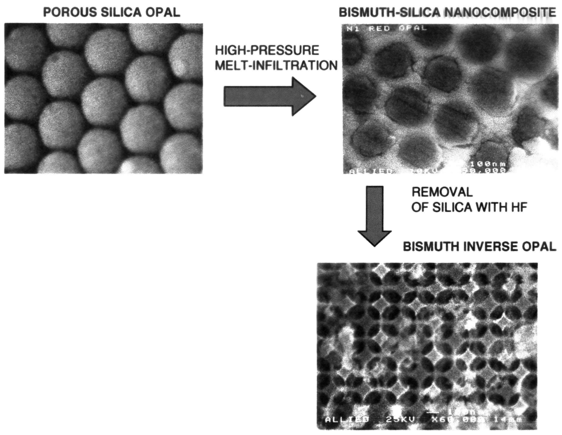

Fig. 9: One of many examples of the 'opal' approach to making low-dimensional structures [Baughman].

[**T. Harman**] has made a most remarkable material based on MBE growth of $PbSe_{0.98}Te_{0.02}/PbTe$, as shown in Fig. 10.

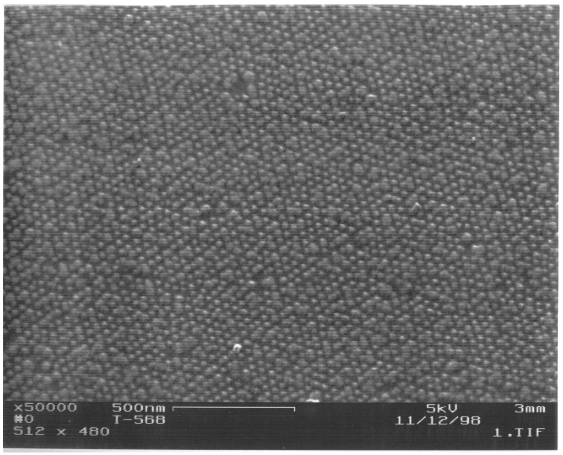

Fig. 10: FE-SEM image at 50,000x of a $PbSe_{0.98}Te_{0.02}/PbTe$ quantum dot superlattice structure. 7200 such layers were deposited, forming the first true 3D array of quantum dots. Each dot is in the shape of a pyramid roughly 20-30 nm on a side [Harman].

The pyramidal-shaped 'dots' of PbTe grow spontaneously (confined by the higher bandgap matrix material, PbSe) under appropriate conditions. The white images are individual dots with a density of about $9x10^{11}$ dots/cm^2. The resulting samples are thick enough (70 µm!) to use conventional measurement techniques. [Harman] reports ZT~1 near room temperature and ZT~2 at elevated temperatures (about 500-700 K), about twice as large as for bulk PbTe.

Bulk Materials: Skutterudites, Clathrates, Half-Heusler

Various bulk materials, including skutterudites, Half-Heusler compounds and others were well represented in Baltimore. But the clathrates, first proposed by Slack, seem particularly well suited as electron-crystals, phonon-glasses. [**G. Nolas**] of Marlow Industries listed 17 organizations collaborating on clathrate studies.

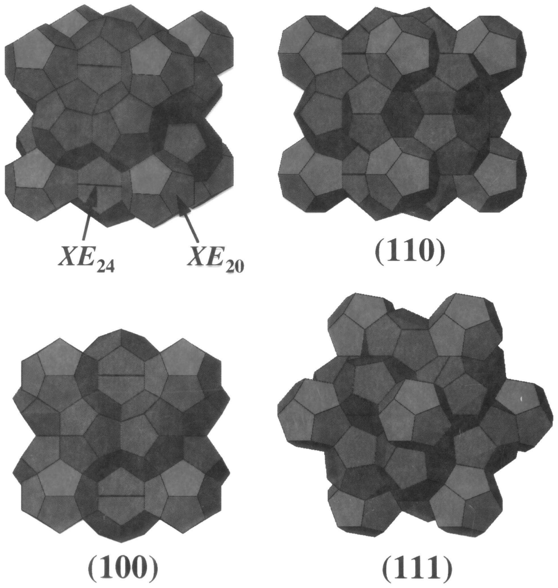

Fig. 11: Polyhedral views of clathrate X_8E_{46}-structure type, $Pm\bar{3}n$ [Nolas].

The crystal structure has large open cages which are evident in TEM images (Fig. 12). These cages are large enough to contain even large rare-earth atoms, with room to spare. The resulting 'rattling' of these heavy atoms in their cages is thought to be responsible for the remarkably low and glass-like temperature dependence of the thermal conductivity of compostions like $Sr_4Eu_4Ga_{16}Ge_{30}$ (Fig. 13).

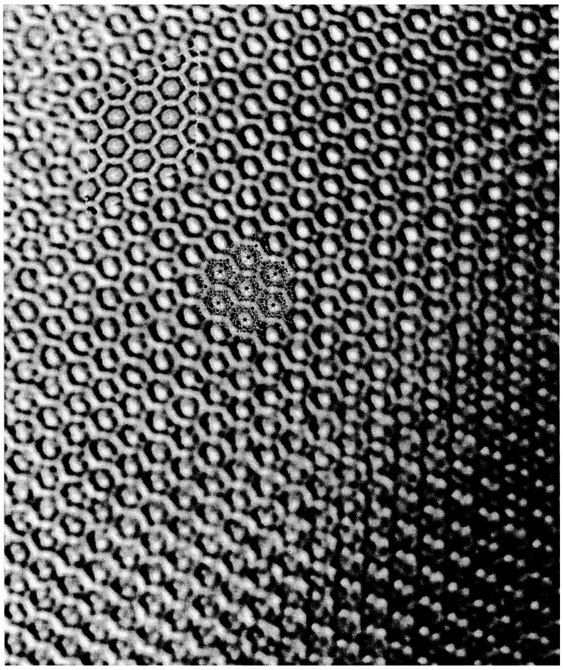

Fig. 12: TEM image of a highly regular clathrate surface. The diamond-shaped region in upper left and the seven hexagons near center are computer simulations of the ideal crystal structure [Nolas].

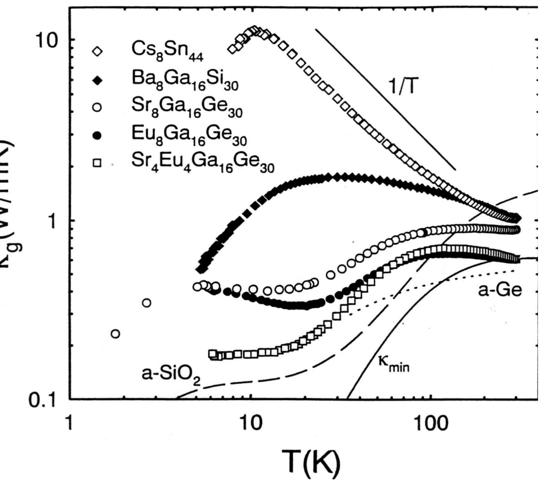

Fig. 13: Thermal conductivity of various clathrates, some of which exhibit nearly glass-like behavior [Nolas].

[**B. Sales**] has shown that for clathrate compounds (and some others) you can use room temperature ADP values (published x-ray data !) to estimate

a) Debye temperature
b) Velocity of Sound
c) Einstein frequency of rattler
d) Heat capacity vs temperature
e) mean free path of phonons
f) thermal conductivity

Atomic Displacement Parameters (ADP), are a measure of the deviation of atoms from their equilibrium positions. Typical atoms vibrate only a little bit, but 'rattlers' have lots of room to move and have large ADP values.

Table 1: ADP analysis - $LaFe_4Sb_{12}$ [Sales]

		From X-ray ADPs [2]	Other Data
Θ_{Debye}	K	299	305-320
$\Theta_{Einstein}$	K	79	80
v_s	m/s	2886	3007
$d_{rattler}$	Å	7.9	
$\kappa_{Lattice}$	W/cm-K	0.014	0.017

This method is significant because it allows one to estimate lattice thermal conductivity from published or easily obtained data.

Micropiles

The development of practical small-scale thermopiles must be regarded as one of the major developments of recent years in thermoelectricity.

In order to master the art of micropile fabrication, M. Kishi of Seiko Instruments has made a "Thermic" wrist-watch utilizing body heat to generate a few µW to power the watch. The entire micropile is about the size of a US dime, has about 1000 elements in series and generates 0.2V at 1 K temperature difference. 500 watches were built in the pilot run and sold for US$2,500-$3,000.

Using similar Bi_2Te_3-based, powder metallurgy fabrication techniques [**N. Elsner**], in this case for space applications (Fig. 14). D.T.S in Germany [**I. Stark**] employs an entirely different thin-film deposition technique to make an entire line of commercial sensors and miniature power generation devices.

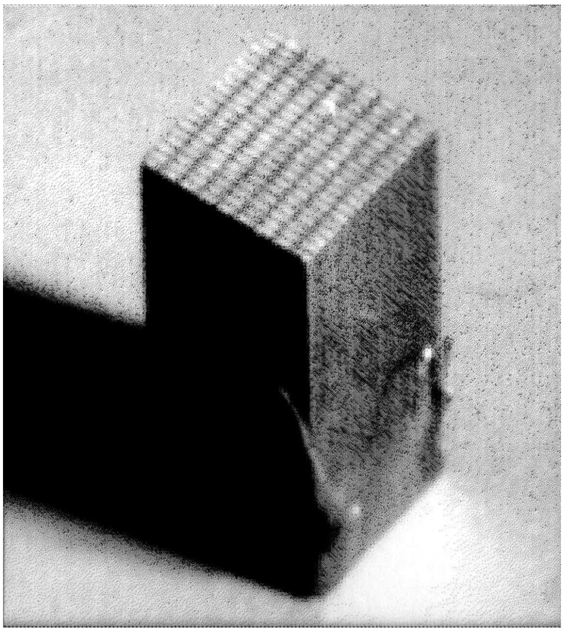

Fig. 14: Power generating micropile for space applications. 40 mW, 5V module contains 324 legs 0.015"x0.015"x0.09" in an 18x18 array [Elsner].

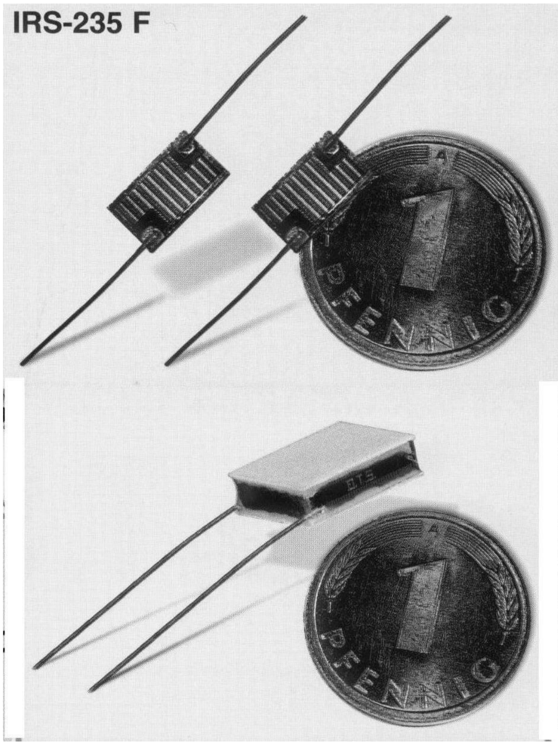

Fig. 15: D.T.S. manufactures miniature thermopile-based infrared sensors (above) and power generation modules (below). Devices are based on Bi_2Te_3 deposited on low thermal conductivity polyamide substrates.

[**F. Völklein**] is developing a variety of devices providing position-sensitive information from thermopiles. One of the more interesting devices is a thermoeletric-based motion detector (Fig. 16).

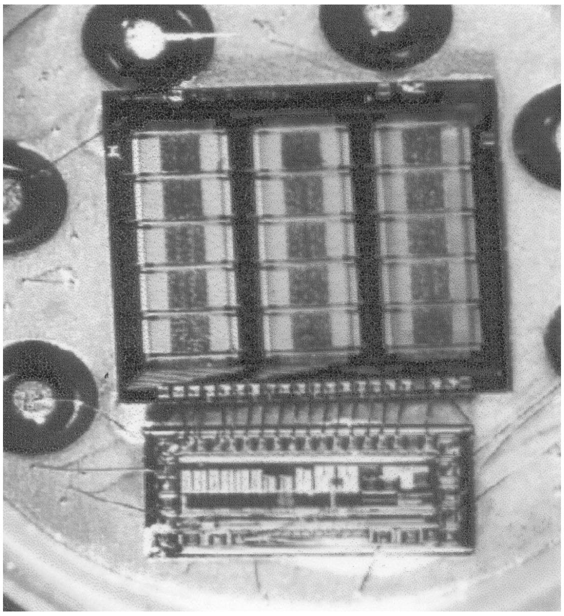

Fig. 16: A 5x3 array of infrared sensors can detect the motion of a person across a room, from their heat signature alone [Völklein].

A TE cooler operating at ΔT_{max} can temporarily be cooled to a lower temperature by increasing the applied current. It doesn't sound useful because eventually the Joule heating catches up with you. But what if you were only in contact with the TE cooler during that brief interval when it was especially cold? That is the idea behind MMC's MEMs cooler described by [**C. Hilbert**]. This marvel gangs together multiple TE modules, each with a tiny 'thermal switch' sequentially actuated to put your load temporarily in contact with the appropriate module. Cool.

Summaries and Overview

[**R. Chu**] from IBM gave an authoritative view of cooling needs for the computing industry. As chips become smaller and operate at higher speeds heat becomes increasingly important. Heat flux from computing modules was reaching hard to manage levels in the 1980s when much cooler CMOS technology replaced the older bipolar integrated circuit technology, as shown in Fig. 18

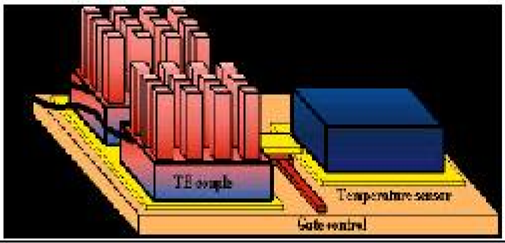

Fig. 17 Thermoelectric micro-electro-mechanical cooler achieves lower temperatures by a application of a transient current pulse, timed with a actuated thermal switch [Hilbert].

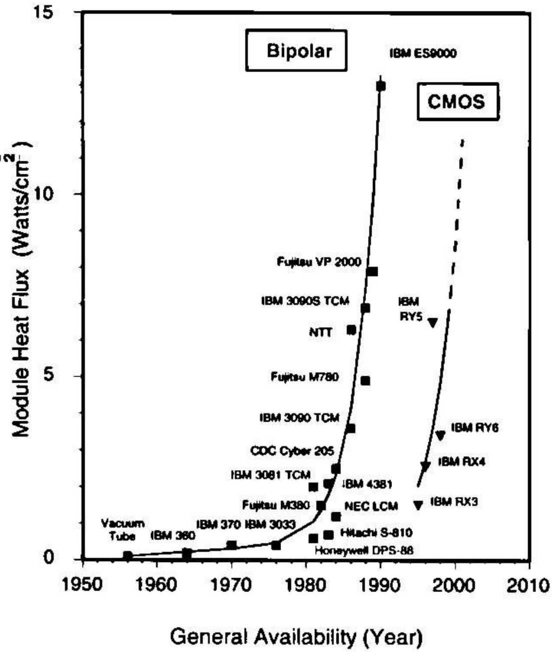

Fig. 18: Heat flux from computing modules over time. Heat generation is again reach levels requiring demanding and expensive thermal management solutions [Chu].

The primary concern of all this heat, of course, is the reliability of the system: heat accelerates failures. A second, but also important, factor is performance. CPU performance is strongly affected by the operating temperature. Colder means faster (Fig. 19). So far, thermoelectric coolers have played only a minor role in IBM thermal management strategies. But, with reduced cost and better system-leve integration the role or thermoelectrics may well increase in the future.

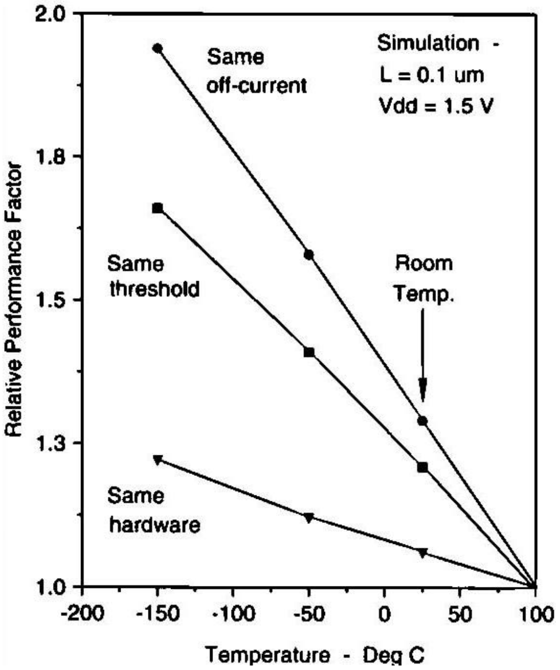

Fig. 19: Relative performance of computers as a function of the CPU operating temperature. [Chu].

The most dramatic way to improve the performance and reduce the cost of thermoelectric technology is, of course, to increase ZT. Several speakers were openly optimistic in this regard. Notably, Dr. Goldsmid expects to see significant advances in the coming year, either through achieving ZT of 2-3 directly or the equivalent cooling performance in some thermionic-type device.

Similar optimism was expressed by Dr. Larry Dubios from DARPA. Certainly the results presented at ICT'99, and summarized above, are evidence that renewed support of thermoelectric R&D in the US is yielding tangible results. Starting with modest support from the Army Research Office and Office of Naval Research in about 1993, basic R&D funding levels are now running at about US$8M-$9/year for thermoelectrics. From what I saw in Baltimore the scientific return on investment is looking quite good.

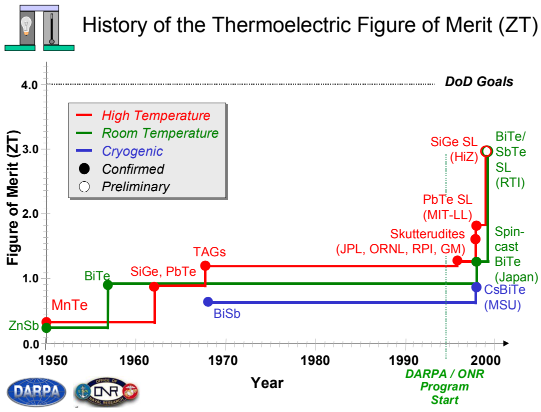

Fig. 20: The thermoelectric figure of merit changed very little from early 1960 to recent times, but there is now some sense that real advances in ZT have been, or soon will be realized [Dubios].

For details on any of the topics discussed in this paper please contact the indivual authors directly. Author contact information, the titles for these papers and the full agenda for ICT'99 can be found on the *ITS* Web site at http://www.its.org.

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References

1. Proc. of the 18th International Conference on Thermoelectrics, A. Ehrlich, Baltimore, MD USA, Aug. 29-Sept. 2, 1999, IEEE, Piscataway, NJ USA, to be published early 2000. Unless otherwise indicated, All references in this paper will appear in this Proceedings.

2. Braun and Jeitschko, J. Less-Common Metals, 72 (1980), 147.