

Development of Significantly Higher Efficiency Thermoelectric Devices Using Ultraconductor™ Polymers

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1 March 1998

Final Report

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13. ABSTRACT (Maximum 200 words)

ROOTS (Room Temperature Superconductors Inc) has demonstrated the feasibility of raising the efficiency of solid state thermoelectric (TE) devices by the application of Ultraconductor™ polymer films. The Ultraconductor material will provide a significant improvement in the overall figure of merit, Z, for existing and potential new TE devices used for cooling and thermal management.

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Contract: F29601-97-C-0125
Topic: BMDO97 007

FINAL REPORT

Development of Significantly Higher Efficiency Thermoelectric Devices Using Ultraconductor™ Polymers

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BMDO PHASE I FINAL REPORT

Contract: F29601-97-C-0125 Topic: BMDO97 007

Development of Significantly Higher Efficiency Thermoelectric Devices Using Ultraconductor™ Polymers

A. EXECUTIVE SUMMARY

The objective of this Phase 1 contract was to study the feasibility of using Ultraconductor polymer film to increase the efficiency of commercial thermoelectric (TE) devices.

That feasibility was successfully demonstrated by making definitive thermal measurements of fabricated arrangements of Ultraconductor films and by a corresponding mathematical model of the Ultraconductor used as a passive TE leg.

Both the model and the measurements show that efficiencies of present TE devices may be significantly increased by the use of Ultraconductor films. The degree of increase in the thermoelectric figure of merit, Z , ranges from 5% to 20%, using low value Ultraconductor films.

The degree of improved efficiency rises with lower operating temperature. Consequently, Ultraconductor materials extend the efficient operating range of existing TE devices into lower temperatures. The improvement in efficiency also increases with the degree of discrepancy between the Z factor for the positive (P) and negative (N) legs of a TE module. Such discrepancies exist in all present TE devices.

Additional improvements over and above these values are expected with the recently developed, 'enriched' Ultraconductor materials. Increased TE efficiency has particular value to three present Department of Defense cooling applications.

The Ultraconductor TE development will not only improve current devices, but also devices which use new active materials (such as superlattice and quantum well materials presently in development). The Ultraconductor application will also reduce the time to market for such materials, since P and N leg discrepancies are a common occurrence for newly developed thermoelectric materials. Consequently, Ultraconductors can provide a universal improvement for TE products.

The application of Ultraconductors to increase TE efficiency requires, in Phase II of the contract, the fabrication of thicker films with a high number of conducting regions. The breakthroughs required to ensure that development were accomplished under a concurrent 1996 - 1997 U.S. Air Force Small Business Innovation Research (SBIR) Phase II contract.

The Phase II proposal for Ballistic Missile Defense Organization (BMDO) is in preparation, to bring this application to commercial fruition.

B. VALUE OF THE DEVELOPMENT

Thermoelectric (TE) devices have high value for use in thermal management and electricity generation, where weight, size and robust, reliable long term operation are required. These are characteristics typical of Department of Defense, and commercial aerospace and space platforms, and for applications ranging from supercooled electronics to low cost power generation from waste heat.

Because the efficiency of TE devices are much lower than conventional cooling and generating systems, their application for a host of additional uses have been limited. Unfortunately, there have been no significant improvements in the efficiency of TE devices for two decades, until now.

The Ultraconductor application demonstrated in this contract provides a universal solution to increasing the efficiency, operating range, and application of TE devices. These benefits apply for all TE devices being commercially produced today, and also for advanced, new TE materials now in research.

B. 1. TECHNOLOGY

Ultraconductors are ambient temperature superconductors made of polymers. (Fundamental characteristics of the materials are reviewed in Appendix D.) Ultraconductors are usually prepared as thin (~ 10 - 40 microns) films.

The nature of the conductivity in Ultraconductor polymers is distinctive.

Like metals, the Ultraconductor polymer *material* is electrically neutral. Electrical conductivity occurs in the Ultraconductor film at discrete, stable regions, which are surrounded by dielectric polymer. These regions - macroscopic structures called 'channels' - are produced in select polymers by processing, resulting in the Ultraconductor material. In a recent USAF SBIR Contract examining near-term applications of these materials, these 1 - 2 micron diameter channels were shown to carry up to 100 ampere currents.

The electrical conductivity is normal to the plane of the film (in the Z (thin) axis), and very high¹.

At the same time, the thermal conductivity in these same regions is very low. Previous tests demonstrated that these channels violate the Wiedmann-Franz law by 7 orders of magnitude, providing the Ultraconductor with unique thermal advantages.

¹ Measurements of conductivity at ambient temperatures provide values of 10^{11} S/cm to 10^{24} S/cm and above (compared to copper, which is 10^5 S/cm). Between superconducting tin electrodes, at cryogenic temperatures, no measurable resistance is observed.

B. 2. INTRODUCTION: FEASIBILITY OF THE TE APPLICATION

The thermoelectric figure of merit, Z , is a function of two materials in a thermoelectric device. This is often approximated as the average of the individual figures of merit, z , defined as $z = \alpha^2 \sigma / \lambda$ where α is the Seebeck coefficient, λ is the thermal conductivity and σ is the electrical conductivity. Where Z is the average of z_1 and z_2 , it is clearly less than the better of z_1 or z_2 .

Because the materials used in TE devices typically have different individual figures of merit for each leg, this discrepancy results in an averaged, hence lower than optimum, Z for the device. This discrepancy reduces the efficiency of all known TE devices.

When a superconducting material is applied as a passive leg in a thermoelectric device, however, it can be shown that Z equals the z of the active leg². This effect enables the Z of the device to be increased to that of the highest z material.

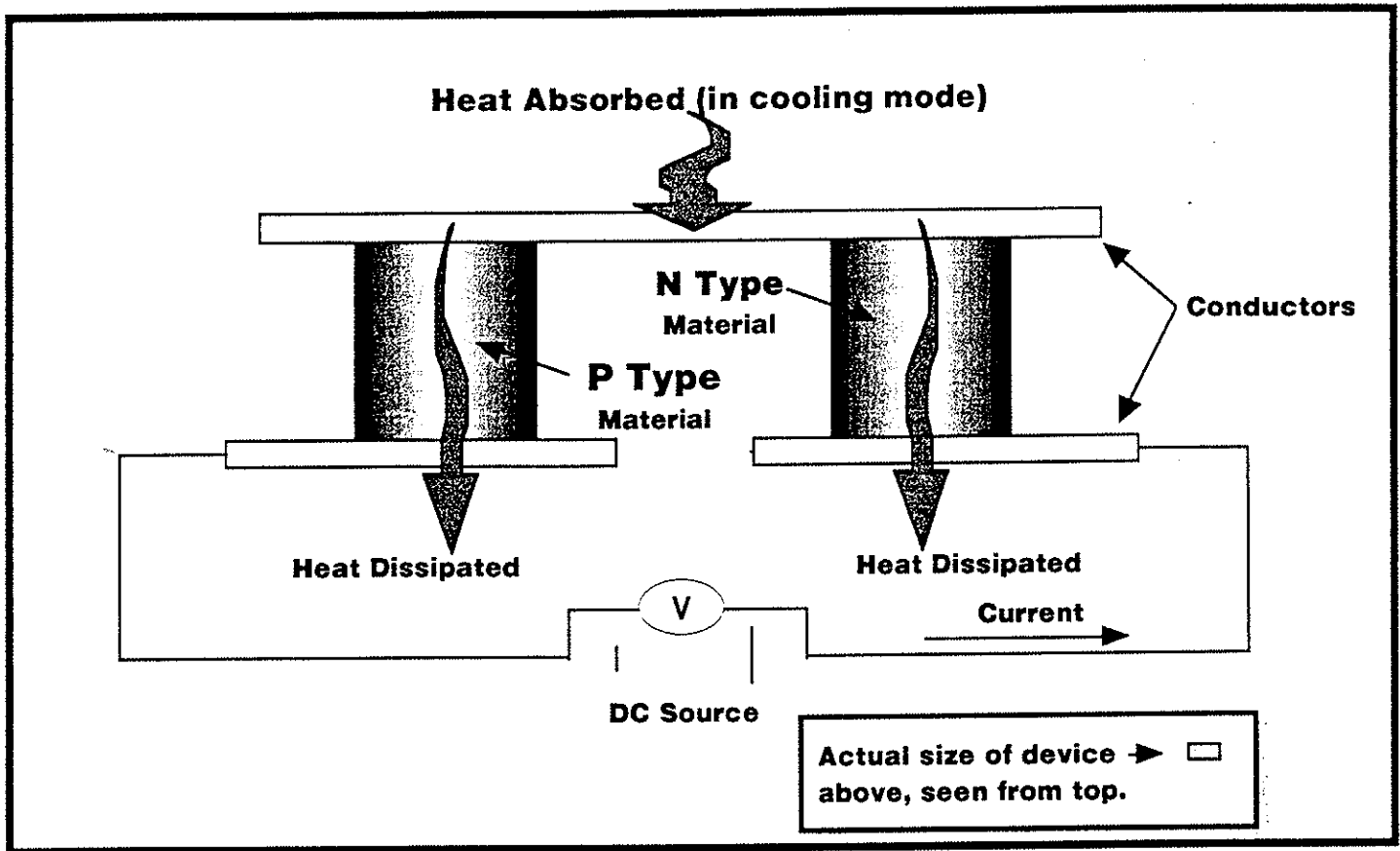
Until now, practical application of this effect has been limited by the fact that superconducting materials have needed to be maintained at cryogenic temperatures.

Because Ultraconductors do not require cryogenic temperatures, they appeared well suited, as a passive leg, to fulfilling the application at room temperature. In Phase 1, this effect was demonstrated. The Ultraconductor materials were shown to closely approximate an ideal superconductor in thermoelectric applications, over a wide temperature range, and with potentially high current densities.

Figure 1 shows the functioning of normal thermoelectric modules.

Figure 2 compares a normal module with an Ultraconductor thermoelectric module, showing an improvement of " Z " from 95% to 99%.

² *High Tc Superconductors as Passive Thermo-elements*; Journal of Physics D: Applied Physics 21 (1988) by H J Goldsmid, K Gopinathan, D N Matthews, K N R Taylor and C A Baird. (See Appendix C) This work was done in a magnetic field at liquid-nitrogen temperature.



**Figure 1:
Schematic of typical thermoelectric module in operation:
Cooling Mode**

In cooling (Peltier) mode the application of voltage causes the transport of heat from one surface (top) to the other (bottom), where it can be dissipated, as by heat sink. Reversing the voltage will reverse the direction of heat transport, causing the top surface to become heated.

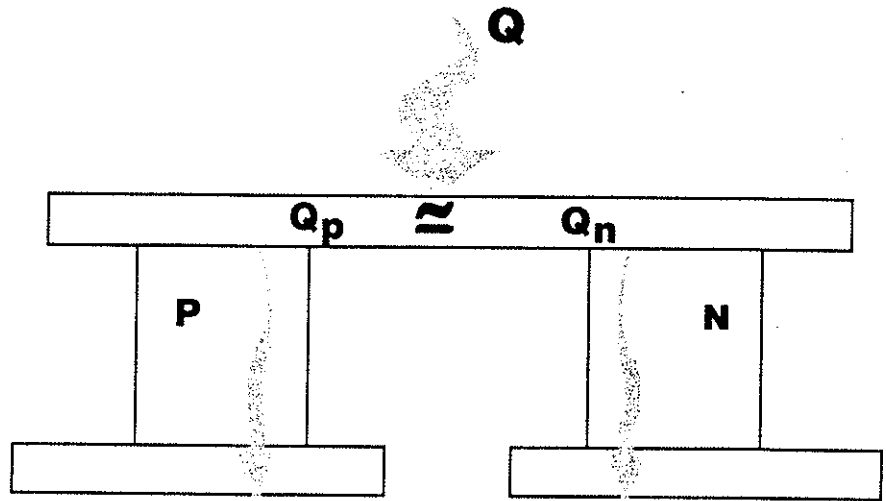
Application of heat to a similarly configured thermoelectric device will generate electricity (Seebeck mode).

The two materials of the thermoelectric module are semiconductors selected for their high thermoelectric merit. They are net positive (P) or net negative (N) materials, in order to complete the electric circuit in series.

The efficiency of the module is determined by the qualities of these materials, which is usually stated as a combined figure of merit, Z.

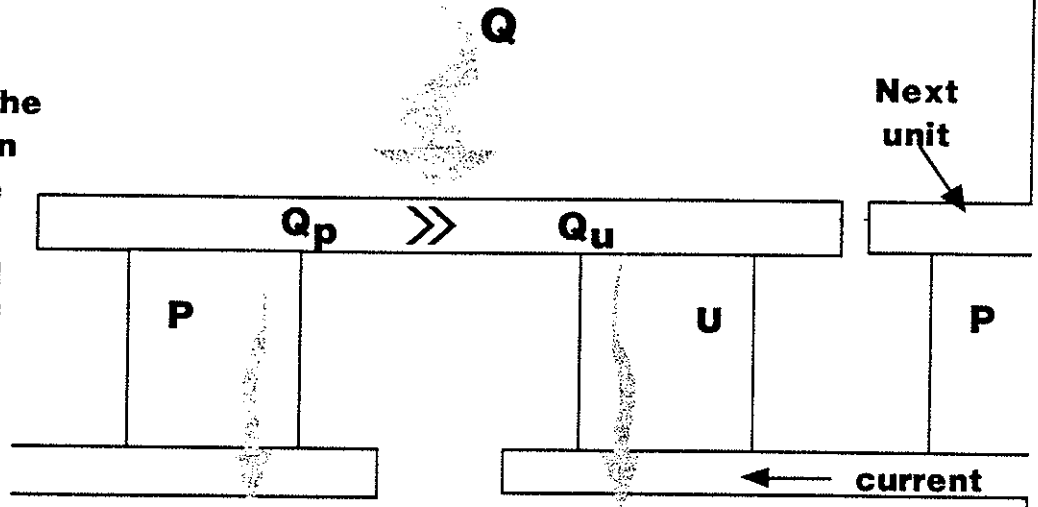
FIGURE 2. CONVENTIONAL VS. ULTRACONDUCTOR TE DEVICES

A. Normal TE Module, with two active (P and N material) legs. The figure of merit for the device is the average of the individual legs, which are not equal. If the figure of merit for the N leg, Z_n is equal to 0.9 of the P leg, Z_p , then Z for the entire device is 0.95.



B. Replacing one active leg with an Ultraconductor (U) leg raises the Z of the entire device by reducing the difference in merit between the two legs. Modeling the above case using an Ultraconductor leg showed an increase in the figure of merit for the device to $Z = 0.99$.

(In this case $I^2R_p \gg I^2R_u$.)



C. Comparison of Semiconductor vs Ultraconductor thermoelectric characteristics:

<u>Feature</u>	<u>Semiconductor</u>	<u>Ultraconductor</u>
Resistance (R)	Medium	Low
Thermal Conductivity (K)	Medium	Low
Seebeck Coefficient (S)	High	Zero

Ultraconductors enable exceptional improvements in thermoelectric device efficiency because they combine high electric conductivity, low thermal conductivity, and a zero Seebeck coefficient.

B. 3. MATHEMATICAL MODEL

Mathematical modeling for the Ultraconductor TE application followed the H. J. Goldsmid, et al, work, which reported a greatly improved Z factor can result from the use of superconductors as passive thermo-elements.

The standard theory applied to homogeneous materials. Under this contract the theory was expanded to analyze the Ultraconductor materials, in which electrical conduction is quasi one dimensional. (See Appendix A).

Consistent with the Goldsmid work, the results of modeling demonstrated that the Ultraconductor passive leg preserves better than 99% of the Z-factor of the active leg. The model assumed that the Ultraconductor met the following conditions:

- a) Contact resistance $r_c = 25$ mohms. This is the resistance at the interface of the Ultraconductor and the electrode, for each conducting region.
- b) The average distance between conducting regions must be less than 10 micron spacing, corresponding to a density of $10^9 / \text{sq cm}$.

Both conditions are achieved under present fabrication processing of Ultraconductor films. Condition a) (value of resistance) is achieved by "training" the Ultraconductor, by the application of a series of current pulses. Condition b) (density of conducting regions per cm^2) has also been achieved in thin films, and is expected in thick films, following the introduction of new concentration techniques, being implemented under our Air Force Phase 2 SBIR contract.

The above conditions ensure that the overall electrical conductivity does not detract from the thermoelectric performance.

The other significant factor required is low thermal conductivity, to prevent the loss of heat from the passive leg. The Ultraconductor polymer has normally low thermal conductivity, and the experiment below shows that this is not changed by the electrical conductivity.

That effect is not surprising in a superconductor, since the electron pairs carry no thermal energy.

B. 4. EXPERIMENTS

Overview

Under this contract, a measuring device was designed, constructed and operated, to confirm that the thermal conductivity of the polymer was not increased by electrical conductivity. Previously it had been shown, for individual conducting regions, that the Wiedmann-Franz law was violated by 7 orders of magnitude.

This experiment confirmed the measurement was unchanged for the bulk case. Consequently, the experiment verified that stacked film/substrate systems could be a practical approach to creating a prototype "leg".

The experiment demonstrated that the thermal conductivity of multiple layers of Ultraconductor is essentially what would be predicted for the same aggregate thickness of polymer. This shows the electrical conducting regions do not degrade the thermal resistivity of the material, and that with proper design the copper substrates interleaving the polymer do not create a thermal short circuit.

B. 4.a Thermal Conductivity Measurements of Ultraconductor Polymers

Thermal conductivity measurements were made of stacks of Ultraconductor Polysiloxane film-coated copper foils. The measuring apparatus employed two copper rods with foils sandwiched in between. The rods were encased in a thick polyethylene sleeve so that access to the various sections was readily available.

Thermocouples were placed so that the temperature difference across the foil stacks could be compared to the temperature difference across the upper rod. Since the thermal conductivity of copper is well known, a comparison of the relative temperature differences will give a value for the conductivity of the foil stack.

The polymer film thicknesses were in the range of 4 - 5 microns. A heating resistor was inserted into a cavity in the upper rod and connected to a power supply. The current to this resistor was adjusted so that the top part of the rod remained at room temperature.

The lower rod was immersed in an ice bath with a rotating magnetic stirrer to maintain a uniform temperature. The polyethylene sleeve was surrounded by a thick layer of foam rubber which blocked the flow of thermal energy from the environment into the copper rods. By monitoring the voltage supplied to the heating resistor and computing the thermal energy generated, an independent measure of thermal conductivity is obtained.

Measurements were made with stacks composed of 4, 8 and 12 polymer foils. The results averaged over the various measurements were in the range from 0.0031-0.0038 watt/(cm)(K).³ The published value for thermal conductivity of Polysiloxane is 0.0029 watt/(cm)(K).

B. 4.b. Electrical Resistance Measurements of Ultraconductor Polymers

The experimental setup used to make the thermal conductivity measurements was modified for the electrical resistance measurements. The measurements were made with a stack of 10 polymer foils in the test chamber.

³ The variation is due to the imprecision in determining the exact thickness of the individual polymer films.

Measurements were made with a Fluke VOM with a sensitivity of 10 milliohms. The polymer was first "trained" by pulsing the foil stack with increasing voltages until the average current during the pulse reached 50 amps⁴.

Prior to the training procedure the resistance across the stack was approximately 14 ohms. After the procedure the resistance dropped to 60 milliohms. This is an average of 6 milliohms per foil. This resistance is believed to be that of the contacting surfaces and not that of the Ultraconducting polymer.

Subsequently, the intermediate copper foils will be eliminated altogether in the application, utilizing instead thicker Ultraconductor films. The total resistance for the equivalent thickness of Ultraconductor polymer is likely to be dramatically lower than for the interleaved arrangement above.

B. 4.c. Fabrication of a Passive Leg

The use of an Ultraconductor passive leg as the commercial application requires that the polymers be fabricated with longer conduction paths than are presently made. The fundamental development steps for this have been achieved.

There is no theoretic limit to the length of the conducting structures. Investigations have demonstrated that their actual growth (and real length) depends upon the availability and abundance of superpolarons in the polymer. Methods for the manipulation and control of superpolarons in the material have consequently been one of the company's key development activities.

Several techniques have been developed which enable the concentration of superpolarons at 100 to 1000 times greater densities than that of the polymer samples which were used in the Phase I experiments. These concentrations are the key to making the thick Ultraconducting film required for the passive leg.

C. BENEFITS OF ULTRACONDUCTOR TE APPLICATION

Ultraconductors can improve the efficiency of current thermoelectric devices, by increasing the Z (figure of merit) by between 5% in the temperature range for which the device has been optimized (for example, 280 K), to over 20% outside this range (150 K). Consequently, the range of efficient operation for TE devices may be greatly extended, as well as increasing the efficiency in the normal range.

By improving the efficiency of thermoelectric devices, Ultraconductors increase their utility and value.

A significant feature of the Ultraconductor enhancement is that it is not limited to present day thermoelectric materials, but can optimize the efficiency of

⁴ This process increases the current carrying capacity of conducting regions in Ultraconductor films. It also decreases the contact resistance between the conducting channels and the metal surfaces making contact with the polymer.

new materials as they become available. This has particular significance in light of the promising research at several laboratories utilizing new quantum well and superlattice materials, which have been estimated to offer three to five times the thermoelectric efficiencies of present materials.

That increased efficiency has particular value to three present DoD cooling applications. The enhanced TE device can potentially be used as a bump up radiator device for supplementing mechanical heat pumps; for stepdown from high cryogenic temperatures, as used for shortwave infrared applications; and for supercooling electronics, especially for aerospace.

The use of Ultraconductor films as a passive leg does not require development of two matched (P and N) leg materials, as is typical of the present technology. The highest value material can be used immediately with the Ultraconductor film, providing 99% efficiencies of that higher value, rather than the average of the P and N leg materials, which must be developed in parallel.

This can speed the development and introduction of new materials in practical devices, and may also reduce the material costs of the final TE product.

In short, the Ultraconductor advance provides a universal solution for increasing the efficiency of present and future TE products.

D. COMMERCIALIZATION PATH

D.1 Commercial Impact of Thermoelectric Devices Featuring Ultraconductors

Annual worldwide sales of TE devices in 1996 totaled approximately \$130 million, and continue to rise at modest (1 to 5%) rates. The growth of the industry reflects the fact that the efficiencies of thermoelectric materials, and products, have been essentially unchanged for more than 20 years. In practical terms, present TE companies are able to claim a significant product advantage based upon an incremental advance of only 4 degrees Fahrenheit over their competitors.

Compared to conventional refrigeration and electric generation systems, present TE devices are approximately 3 times less efficient, and so have a limited competitive position.

Consequently, the real increase in efficiency provided by the Ultraconductor application, increases the utility and value of such systems in a range of applications. As TE efficiencies move toward the levels of standard technologies, their market value is dramatically increased, due to advantages of size, weight, and their solid state construction.

In addition, the application of Ultraconductor materials to TE devices represents the first product use of this exceptional material. The advent of products

containing ambient temperature superconductors is a watershed event in technology. Consequently, the value of the TE development may also be considered in light of the commercial implications of the launch of the technology.

A 1997 article in Scientific American, quoting a scientist, stated that a room temperature superconductor would "initiate a second industrial revolution". Superconductor applications already anticipated by world industries include exceptionally efficient power generation, transmission, distribution, and a host of superior electrical and magnetic products ranging from very high speed electronics to very large industrial motors. As an enabling technology - that is, one which enables development and design of entirely new products and technologies than exist today - Ultraconductors will have diverse and extensive impact across broad industrial sectors. The analogy is the development of the transistor.

Commercialization of the Ultraconductor TE device is envisioned as a two step program:

1. Application of the polymers in existing commercial devices, with active legs made of present thermoelectric materials. This may increase the Z factor by several per cent, which in the general market is a significant competitive advantage, and for military and airborne applications could be crucial.

2. Use of the Ultraconductors with new alloys such as those being developed by Dr. M. Dresselhouse at MIT, and by a team headed by Dr. J. P. Fleurial at JPL.

Typically, Ultraconductor products will be manufactured and sold under joint development or licensing agreement with corporate strategic partners. International corporations already manufacture and sell conventional versions of the products proposed. The largest have excellent market position, experience in the field, and significant capital resources.

Licensing or joint development agreements with these corporations will enable the experience and resources of these companies to accelerate each step of the development to market process. Competitive or simultaneous agreements, if acceptable, would further drive commercialization. Importantly, this approach enables our company to focus on core technology, and further development.

Such strategic alliances will reduce or eliminate duplicative start-up costs, allow parallel design and production cycles, reduce time-to-market, increase market penetration, and increase the speed with which industrial sectors can adopt and employ the new technology. They also ensure early technical and design feedback, essential to our own development approaches and objectives, a process already begun.

E. CONCLUSION

This Phase I program has demonstrated that as a component in a TE device, Ultraconductor materials can significantly enhance the efficiency, and broaden the utility of, present day commercial thermoelectric devices. This advantage translates into lower power consumption, wider operating ranges, or both.

In addition, as detailed in this report, the Ultraconductor application can increase the efficiency of any thermoelectric materials. The application is a universal solution, and so can speed the commercial utilization of other new thermoelectric materials presently in research.

The application marks a breakthrough in TE design which overcomes two decades of stagnation, and which may enable TE devices to be utilized in high value defense and commercial applications for which they were previously not suited. This expansion of TE operating potential may also make possible the eventual replacement of conventional cooling and generating systems over a broad range of applications.

A Phase II proposal is in preparation which will cover the design, preparation, characterization and testing of the thermal and electrical properties of Ultraconductors intended for use as advanced thermoelectric materials, in combination with thermoelectric materials currently in production and in development.

The Phase II objective will be to provide Ultraconductor passive legs in their standard form to commercial thermoelectric companies and labs, for testing of the advanced prototype devices prior to manufacture.

Appendix A. MATHEMATICAL MODEL

Technical Notes

References:

- Thermoelectric Conference 1996: Short course by Marlow Industries (TE96)
- HAES (Handbook of Applied Engineering Science)

$$Z = (S_p - S_n)^2 / [(r_p k_p)^{1/2} + (r_n k_n)^{1/2}]^2$$

TE96: Typical values for thermoelectric materials

$$\begin{aligned} S &= .0002 \text{ volts/K} & k &= .015 \text{ Watts/cm/K} \\ r &= .0013 \text{ ohm cm (N type material)} & \text{For } L &= .17 \text{ cm, } A = .14 \times .14 = .02 \text{ cm}^2 \\ R &= 0.011 \text{ ohms} \end{aligned}$$

With 2 active legs (using N type numbers) and using R instead of r (since r is not applicable to Ultraconductors)

$$D_a = \text{Denominator} = [(.011 \times .015)^{1/2} \times 2] = .0128 \times 2 = .0257$$

Passive leg: Ultraconductor equivalent to above

$$\begin{aligned} S &= 0 \\ k &= .0029 \text{ (HAES) Tbl 1-89: Polysiloxane Thermal conductivity} \\ &\text{W/cm.K } 0.0029 \\ R &= r_c / (d \times A), \text{ where } r_c \text{ is the contact resistance per channel, } d \text{ is the} \\ &\text{density of channels (number per sq. cm)} \end{aligned}$$

Case 1: No training; Present density for 10 micron film

$$\begin{aligned} r_c &= 1 \text{ ohm, } d = 100; R = 1 / (100 \times .02) = 0.5 \\ D_u &= \text{denominator} = [(.011 \times .015)^{1/2} + (0.5 \times .0029)^{1/2}] \\ &= .0128 + .038 = .051 \end{aligned}$$

This case shows that without training and at the present density the Ultraconductor will reduce the Z.

Case 2: Expected parameters with training and concentration

$$\begin{aligned} r_c &= 25 \text{ mohms} = .025 \text{ ohms} \\ d &= 10 \text{ micron spacing} = 10^3 / \text{cm} = 10^6 / \text{sq cm} \\ R &= r_c / (d \times A) = .025 / (10^6 \times .02) = 1.25 \times 10^{-6} \\ D_u &= [(.011 \times .015)^{1/2} + (1.25 \times 10^{-6} \times .0029)^{1/2}] \\ &= .0128 + (36.25 \times 10^{-10})^{1/2} = .0128 + 6.02 \times 10^{-5} \\ \% \text{ change in } D &= 6 \times 10^{-5} / .0128 = 4.7 \times 10^{-3} = 0.47 \% \end{aligned}$$

$Z_u = Z_a / (1.0047)^2 = Z_a \times 0.99$ where Z_a is for active legs with equal Z. Hence in Case 2, the Ultraconductor preserves 99% of the optimum Z.

Where the Z of the active legs are not equal, let this reduce Z_a by n%. In this case, substituting the Ultraconductor for the less efficient leg will improve Z_a by (n-1)%.

Appendix B

Illustration, next page:

ATOMIC FORCE MICROSCOPE SCANS OF ELECTRIC FIELD

These AFM images, produced by Parke Scientific, are of an Ultraconductor polymer film following processing to induce conductivity.

The first image (left) is a measurement of topology of a 100 micron square area of film. The probe is in resonant mode above the surface, and two frequency shift measurements are made at each scan point. The brightest regions are raised, about .5 microns (10% of the film thickness).

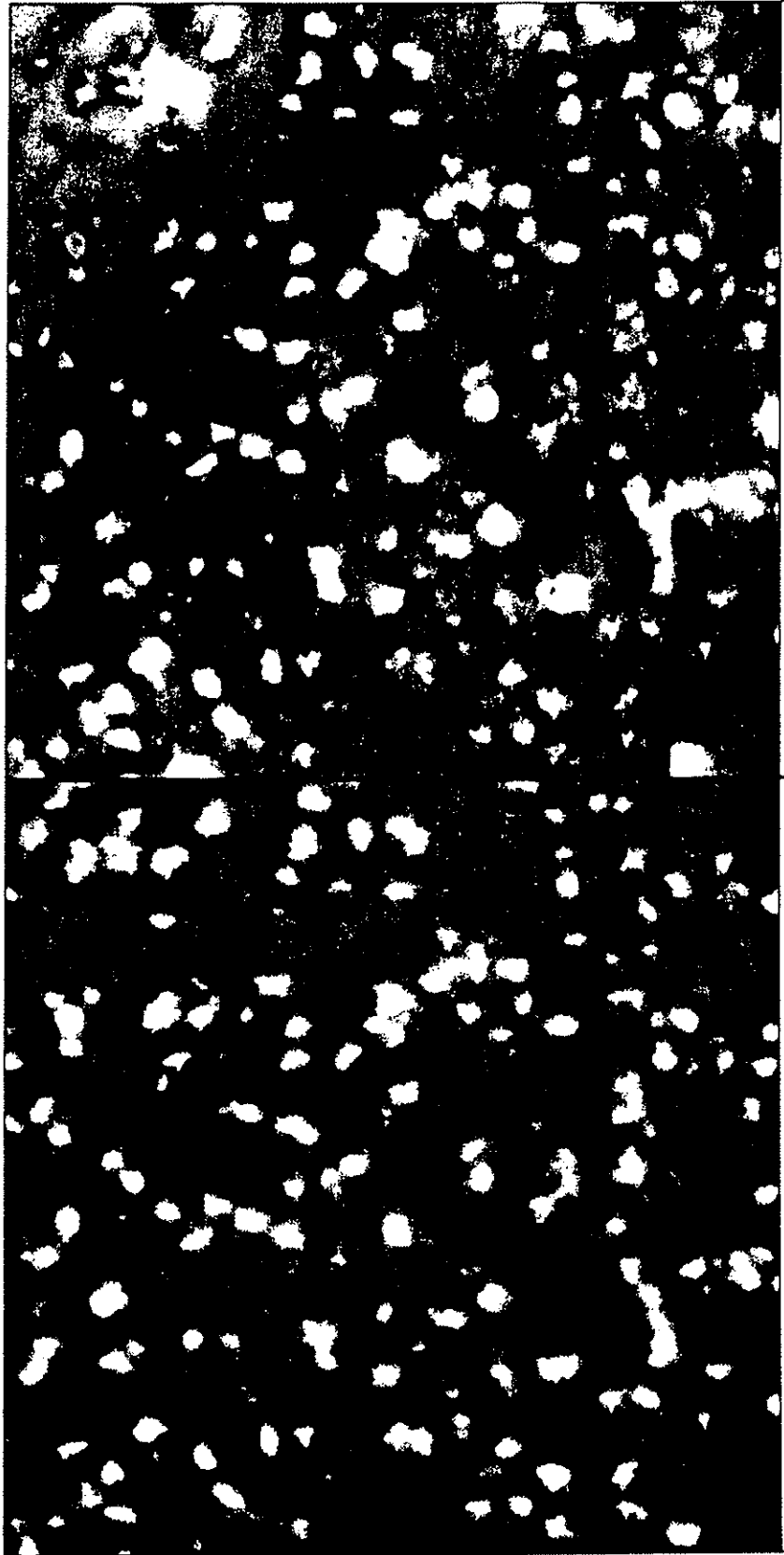
The second image (right) shows the electrostatic field measured at the probe tip, based on an alternating voltage applied to the substrate, and indicates a significant field change at the same points imaged in the topographic scan, the conducting channels.

Though not conclusive, (as these measurements were not simultaneously corroborated by other testing), it is thought that the lower brightness regions show channels, or aggregates of superpolarons, which are partially grown (eg; not entirely from surface to substrate), and hence are invisible to an electric probe.

The observation of (conducting) points in these images coincides with previous estimates of their distribution, made by sampling with electric probe. The topological features also correspond to the present model of channel structure and formation.

As a way of measuring the size and density of conducting points, AFM can be a valuable tool for monitoring the effect of process changes, making visible channel growth patterns, and enabling advanced experiments on the effects of local electric or magnetic fields.

RSTMAFM Images



0 100 μm 0 100 μm

Data type
Z range

Height
2.00 μm

Data type
Z range

20.0 Hz
Frequency

23vfm.000
23 Volts

Appendix C. Ultraconductor Scientific Overview and Process Sequence

The discovery of the fundamental phenomena emerged from an investigation in 1981 of anomalous conductivity (an undesirable feature) in a polymer dielectric (insulator). After several years of research, the original scientific team had successfully isolated, reproduced, and enhanced the effect. Subsequent research developed a body of data characterizing and measuring the phenomena, provided independent replication, and led to an understanding of the essential parameters for its creation.

Those specific conditions, necessary for a given polymer to become superconducting, are now well described. The polymers cannot be conjugated, but must be amorphous, viscous, polar elastomers. Specific chemical formula is not critical, *provided the polymer meets the physical criteria*. These preconditions, in combination with a sequential processing, create the phenomena.

The non-conjugation requires emphasis, to distinguish the conducting mechanism of Ultraconductors from other inherently conducting polymers. In Ultraconductors, conduction is not along the molecule; it occurs via free electrons held interstitially between molecules. These conducting electrons are 'suspended' in the electric field of molecular dipoles on the polymer molecular chains. The correlation of these charges results in the formation of discrete lattice-like structures formed of polymer molecular chains. As a result, Ultraconductors are more analogous to metals than conjugated polymers.

Like metals, the Ultraconductor polymer *material* is electrically neutral. Conducting electrons are not added charges (dopants), but electrons which have been separated by ionization of the polymer. Through a self-organization process, these electrons assume a quasi-one dimensional charge density state which potentiates pairing, and superconductivity. A quantum mechanical theory for the phenomena was completed in 1997.

Before describing the sequential process which induces the state of conductivity, it is necessary to introduce four key points of research:

- 1.) 'free' (ie: atomically dissociated) electrons can become stably suspended in certain polymers under explicit conditions;
- 2.) these electrons can interact with each other, and other charged elements in a polymer matrix, resulting in a self-organization of charge density;
- 3.) the charge density conditions resulting from this self-organization can create an electronically corresponding specific organization of polymer molecular chains; and
- 4.) the most energetically profitable state for the free electrons following this self-organization process is to be paired, and consequently, superconducting.

Let us review the actual process sequentially, for atactic polypropylene (PP). First, by definition, a dielectric polymer such as PP has no free electrons. When PP is

oxidized, however, the oxidation produces electric dipoles (C=O groups) on the molecular chain (total average concentration $\sim 10^{22}$ / cm³). (With other polymers, dipoles may already exist on the molecular chain, and oxidation is unnecessary.)

When the oxidized PP (OPP) is then irradiated with UV light, ionization occurs - that is, electrons are freed, and ions are created on the molecular chain. Normally, this ionization would reverse, and the electrons recombine. However, in a *polar media* it is possible for dipole groups to prevent this recombination, with the result that charges (such as electrons and ions) remain stably separated. The stabilization of separated charges due to electrolytic dissociation in polar solvents is well known. This is the case, for example, with NaCl in water: the H₂O dipoles maintain the charged elements (Na⁺ and Cl⁻) in solution separately. In the viscous OPP, the highly mobile molecular dipoles act in the same way, and surround and hold the freed electrons in their electric fields. These electrons, chemists say, are "solvated". Physicists call these solvated electrons "polarons".

At this stage, the polymer is now very different from the insulator it had been: positive dipole ends have been attracted to negatively charged free electrons; and those dipoles, together with positively charged ions ($\sim 10^{18}$ / cm³), are now present on the long molecular chains. ***Due to the high mobility of the polymer media, thermal motion of the polymer chains can move these randomly distributed charges relative to each other.*** One product of that movement is that polarons (an electron surrounded by polymer dipoles) collide.

It can be explicitly shown that two polarons together form a lower, and hence preferred, energy state, than solitary polarons: consequently, polarons which collide prefer to join. As they do, their attached electrons are brought together like pearls in a "sack". This event, repeated throughout the polymer over time, has enormous consequences on the organization of charge density and polymer chains.

As polarons join, multi-polaron units are formed, called 'superpolarons'. Their lengthening strings of electrons form a growing electronic potential valley. As this increasingly dense negative charge more strongly attracts the positively charged ions, and dipoles, their polymer molecular chains are drawn together, ultimately forming a corresponding shell, like a cocoon, around the electron string.

The surrounded electrons, in turn, are affected by the close ordering of dipoles and ions, become correspondingly condensed. The electronic system is quasi-one dimensional. In these conditions, the charge density in the quasi one-dimensional potential valley ($\sim 10^{21}$ electrons / cm³) must find an energetically stable state. This state is found to be achieved by electron pairing. This pairing is the fundamental superconducting state.

Appendix D.
BMDO-I CONTRACT SUMMARY CHRONOLOGY

June 97:

Work begins on design of rotating drum for laying down uniform layer of polymer in 1 - 5 micron range. Polymer solution to be sprayed onto 1/2 diameter, gold-plated copper discs. A blue dye which is soluble in toluene was obtained in order to analyze the uniformity of the spray pattern. Initial design would accommodate 15 copper discs.

July 97:

Participate in BMDO conference in Washington DC
(Jeff Bond, Ann Eskesen)

Participate in BMDO commercialization seminar in San Francisco -
(Dr. Peter Gerity, Tom Tucker, Barry Whalen)

Design work continues on the rotating drum device. An incandescent lamp is inserted into center of drum to heat the surface causing the solvent to evaporate more rapidly.

In parallel with the above another design is being analyzed to lay down a uniform layer of polymer on a disc. This design utilizes a disc at the base of a liquid-tight cylinder which is filled with polymer solution. The solution is heated and evaporates leaving a film on the disc. This design will work with thick or thin films. Using dyed solution to test for uniformity of film.

First thermal conductivity measurements made using a stack of thin copper foils with prepared polymer of polysiloxane obtained from the ROOTS Moscow laboratory. Foils measure 2 cm x 2 cm and have film of 4 - 5 microns. 4 foils used with simple Styrofoam container. Initial tests gave low values of conductivity. We believe that low results are due to contact resistance. between foils.

August 97:

Commercialization: discussion of strategic partnership with John Bass at Hi-Z (a thermoelectric company which was visited earlier). Program review visit by Waylon Gammill (program manager) and Pete Thomas of Aerospace Corporation: Presentation, Lab tour and discussions.

Improved setup for thermal conductivity experiment is made. Utilizes polyethylene casing and setup which compares temperature difference across copper rod to that across foil stack to assign a number for conductivity to polymer.

September 97:

Improvements made to thermal conductivity setup. First measurements were done this month. Measurements made with 4, 8 and 12 foils in the stack. The result for 4 foils was in the expected range for the published data on Polysiloxane. The value of thermal resistance for 8 foils was slightly below the range and for 12 well below.

Measurements with 8 and 12 foils stacks were repeated using moderate pressure to compress the foil stack. The new results fell within the expected range for 4 - 5 micron thick films of polysiloxane. It is theorized that the low values of thermal resistance obtained previously was due to the compression of the polymer stack due to the application of too much pressure.

October 97:

Initial measurements of the electrical resistance of a stack of 10 polymer foils was made using same setup as was utilized for the thermal measurements. The foam insulation was removed and the upper polyethylene sleeve was removed to facilitate the clamping of electrical leads to the upper and lower copper rods. A brass clamping bar was made to apply pressure to the foil stack. Measurements made with Fluke VOM, sensitivity 10 milliohms. Polymer was trained using voltage pulses in ever increasing size until 50 amp pulses are attained. Measured resistance across stack was 0.06 ohms or 6 milliohms per foil. Remainder of the time spent on analysis of ways to make passive leg 0.17 dia. and 0.17 long.

November 97:

This month devoted to writing the final report, modeling the various approaches to commercialization, and establishing discussions with commercialization partners for the Phase II Contract.

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