We examined a large number of rare earth intermetallic compounds in the search for materials with improved thermoelectric efficiency. After an extensive study of those compounds that displayed large thermopowers due to intermediate valence effects, we concluded that attainable efficiencies in this class of compounds were unlikely to surpass that of currently available Bi$_2$Te$_3$ devices. We then turned our attention to semi-conducting systems. An analysis of the current theories suggests that complex materials of cubic symmetry have the potential to exhibit significantly improved efficiencies. Synthesis experiments to explore this conjecture were undertaken and novel materials discovered. However, in the project period there was not enough time to fully explore this new hypothesis.
Final Report

ONR Award Number: N00014-97-1-0157

Project Title: Novel Thermoelectric Materials

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Date: April 13, 2001
Novel Thermoelectric Materials: Final Report

This award was for work performed in the period November 1996 to November 2000 under grant number N00014-97-0157. The award funded research aimed at finding materials with higher thermoelectric figure of merit than for the currently used device material, Bi$_0.5$Sb$_1.5$Te$_3$. We explored two major classes of materials: rare earth based intermetallic compounds and small band gap semiconductors. Although no new materials were discovered that had a higher figure of merit than Bi$_0.5$Sb$_1.5$Te$_3$, a detailed examination of the best theoretical models of complex semiconducting materials, combined with our synthetic explorations, have produced a set of clear objectives for the structural characteristics that should lead to better materials. One hopes that such work will be funded in the future.

Our research in rare earth materials began with the observation that a small number of such compounds have abnormally high thermopower for metallic compounds. Those few compounds had a common characteristic: they displayed intermediate valent (IV) behavior. We synthesized many of the known, as well as some new, IV materials and measured their electrical and thermal properties. We also explored the effects of alloying (or doping) on those properties. In particular the properties measured were typically the electrical resistivity ($\rho$), the thermal conductivity ($\kappa$), the thermopower ($S$) and the magnetic susceptibility. The latter is diagnostic for IV behavior and the first three properties are essential in determining the Thermoelectric figure of merit: $ZT = S^2T/\rho\kappa$. Maximum $ZT$ for Bi$_0.5$Sb$_1.5$Te$_3$ occurs at room temperature and has a value near 1.0. This produces cooling efficiencies of about $1/3$ that attainable with typical home refrigerators. If $ZT$ could be increased to 4, purely electronic devices could be made that have the same efficiency as home refrigerators, but would not use freons, make noise, etc.

Despite synthesizing and characterizing a large number of different rare earth compounds, we were unsuccessful in finding any materials with a $ZT$ larger than approximately 0.2. Since we had explored all of the known IV materials and found a few new ones as well, we concluded that such materials were unlikely candidates to produce $ZT > 1$. Thus our search shifted to the family of small band gap semiconductors, of which Bi$_0.5$Sb$_1.5$Te$_3$ is a member. On the basis of the well developed theory of thermoelectric effects, we pointed out that band degeneracy is an important, often overlooked, parameter in determining the $ZT$. In fact all known materials with $ZT$ near 1 have significant band degeneracy, usually near 6. But much larger band degeneracies are possible, up to 48 in some cubic systems. If it were possible to increase the degeneracy from 6 to 48 without changing other features of the semiconductor, then $ZT > 4$ would be possible. However, such high band degeneracy is most likely to occur in materials with large, complex cubic unit cells. Such materials are relatively rare and none of the known materials of this class are suitable, since the band gaps are too large.

Consequently, during the last year and a half of the award period, we set out on a search for novel materials that would have the required large unit cells. While we made some progress in preparing new compounds with large unit cells having high symmetry, none
were cubic. Our short foray into this area of complex semiconductor compounds has
convinced us that this is a promising route to higher ZT, but clearly much more synthetic
effort will be required to find the new class of materials that will display all the necessary
characteristics for high ZT.

A complete technical summary of all our work can be found in the publications resulting
from our work. These are listed at the end of the report.

Finally, it is important to mention that the research was performed by undergraduate,
graduate and post doctoral students as part of their professional training. The list below
gives the names of individuals supported in the period of this award and current status of
each of those students:

Undergraduates:
Kimberly Regan – currently a graduate student in Chemistry at Princeton University
Josh Bales – currently finishing junior year at Cornell

Graduate Students:
Kevin Proctor – PhD 2000, employed full time at Intel Corp.
Ying Wang – PhD 2000, employed full time at KLA-Tencor
Chistopher Jones, PhD 1999, employed full time at Bell Labs, Lucent Technologies
Kristin Poduska, PhD 2001, postdoctoral position at York University, Toronto, Canada
Chritopher Hoffman – currently finishing fourth year in graduate school
Thomas Reynolds – currently finishing second year in graduate school

Postdoctoral Students:
Thomas Braun, employed full time at Cornell Information Technologies

Technical Publications resulting from work supported by this award:

1. "Physical Properties of CePd$_3$As$_2$", R.A. Gordon, F.J. DiSalvo, and R. Pöttgen,
   J. Alloys Comp. 236, 86 (1996)

2. "Structural, Magnetic and Electrical Properties of the New Ternary CePdIn$_2$", Y.

3. "Substitution in Ce$_2$TSi$_3$ Intermetallic Compositions with T = (Cr, Mn, Fe, Co or
   Ni)$_x$(Pd or Au)$_{1-x}$", R.A. Gordon, C.J. Warren, M.G. Alexander, F.J. DiSalvo, and R.
   Pöttgen, J. Alloys Comp. 248, 24 (1997)

4. "Magnetic Behavior of Two AlB$_2$ Related Germanides: CePd$_{0.63}$Ge$_{1.37}$ and
   CeAu$_{0.75}$Ge$_{1.25}$", C.D.W. Jones, R.A. Gordon, F.J. DiSalvo, R. Pöttgen, and R.K. Kremer,
   J. Alloys Comp. 260, 50 (1997)


