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14. ABSTRACT 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					
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Final Report

ONR Award Number: N00014-97-1-0157

Project Title: Novel Thermoelectric Materials

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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, $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$. 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 $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$, 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 (ρ), the thermal conductivity (κ), 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 $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ 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 $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ 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
Christopher Jones, PhD 1999, employed full time at Bell Labs, Lucent Technologies
Kristin Poduska, PhD 2001, postdoctoral position at York University, Toronto, Canada
Christopher 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_3As_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. Ijiri, F.J. DiSalvo, and H. Yamane, J. Solid State Chem. **122**, 143 (1996)
3. “Substitution in Ce_2TSi_3 Intermetallic Compositions with $T = (\text{Cr}, \text{Mn}, \text{Fe}, \text{Co}$ or $\text{Ni})_x(\text{Pd}$ or $\text{Au})_{1-x}$ ”, 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: $\text{CePd}_{0.63}\text{Ge}_{1.37}$ and $\text{CeAu}_{0.75}\text{Ge}_{1.25}$ ”, C.D.W. Jones, R.A. Gordon, F.J. DiSalvo, R. Pöttgen, and R.K. Kremer, J. Alloys Comp. **260**, 50 (1997)

5. "Thermoelectric Materials: Solid State Synthesis", M.G. Kanatzidis and F.J. DiSalvo, Naval Research Reviews **68**, Issue 4, 14 (1996)
6. "Thermoelectric Properties of $R_x\text{Ce}_{1-x}\text{Pd}_3$ ($R = \text{Y}, \text{La}_{0.5}\text{Y}_{0.5}, \text{Nd}$)", Y. Ijiri and F.J. DiSalvo, Phys. Rev. B **55**, 1283 (1997)
7. "Specific Heat and Heavy-Fermionic Behavior in $\text{Ce}_8\text{Pd}_{24}\text{M}$ ($M = \text{Ga}, \text{In}, \text{Sn}, \text{Sb}, \text{Pb}$ and Bi)", B.K. Cho, R.A. Gordon, C.D.W. Jones, F.J. DiSalvo, J.S. Kim, and G.R. Stewart, Phys. Rev. B **57**, 15191 (1998)
8. "Solid State Chemistry", F.J. DiSalvo, Solid State Commun. **102**, 79 (1997)
9. "Synthesis and X-Ray Crystal Structure of $\text{K}_4\text{PbTe}_3 \cdot 2(\text{en})$ ", C.D.W. Jones, F.J. DiSalvo, and R.C. Haushalter, Inorg. Chem. **37**, 821 (1998)
10. "Comparisons of Electrical, Magnetic and Low Temperature Specific Heat Properties in Group 13 and Group 14 $\text{Ce}_8\text{Pd}_{24}\text{M}$ Compounds ($M = \text{B}, \text{Al}, \text{Ga}, \text{In}$ and $\text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$)", C.D.W. Jones, R.A. Gordon, B.K. Cho, F.J. DiSalvo, J.S. Kim, and G.R. Stewart, Physica B **262**, 284 (1999)
11. "Thermoelectric Properties of the Doped Kondo Insulator: $\text{Nd}_x\text{Ce}_{3-x}\text{Pt}_3\text{Sb}_4$ ", C.D.W. Jones, K.A. Regan, and F.J. DiSalvo, Phys. Rev. B **58**, 16057 (1998)
12. "Modification of the Thermoelectric Properties of CePd_3 by the Substitution of Neodymium and Thorium", K.J. Proctor, C.D.W. Jones, and F.J. DiSalvo, J. Phys. Chem. Solids **60**, 663 (1999)
13. "Electronic Structure and Bonding in Ce Nitride Compounds: Trivalent versus Tetravalent Cerium", G.A. Landrum, R. Dronskowski, R. Niewa, and F.J. DiSalvo, Chem.-Eur. J. **5**, 515 (1999)
14. "Intermediate Valence Behavior of Yb in $\text{Yb}_2\text{Ni}_{12}(\text{P}, \text{As})_7$ ", B.K. Cho, F.J. DiSalvo, J.S. Kim, G.R. Stewart, and S.L. Bud'ko, Physica B **253**, 40 (1998)
15. " $\text{Ce}_3\text{Cu}_x\text{Pt}_{3-x}\text{Sb}_4$: Modifying the Properties of a Kondo Insulator by Substitutional Doping", C.D.W. Jones, K.A. Regan, and F.J. DiSalvo, Phys. Rev. B **60**, 5282 (1999)
16. "Czochralski Growth and Thermoelectric Properties of Single Crystalline Ce_2CoSi_3 ", K.J. Proctor, C.D.W. Jones, and F.J. DiSalvo, J. Alloys Comp., submitted.
17. "Single-Crystal Growth and Thermoelectric Properties of $\text{Ce}_5\text{Cu}_{19}\text{P}_{12}$ ", K.J. Proctor and F.J. DiSalvo, Mater. Res. Soc. Symp. Proc. **545**, 171 (1999)
18. "Thermoelectric Cooling and Power Generation", F.J. DiSalvo, Science **285**, 703 (1999)

19. "Synthesis and Structural Characterization of Ba_2CdTe_3 ", Y.C. Wang and F.J. DiSalvo, J. Solid State Chem. **148**, 464 (1999)
20. "Thermoelectric Properties of the Intermediate Valent Cerium Intermetallic $\text{Ce}_2\text{Ni}_3\text{Si}_5$ Doped with Pd, Co, and Cu", K.J. Proctor, K.A. Regan, A. Littman, and F.J. DiSalvo, J. Alloys Comp. **292**, 124 (1999)
21. "Pressure-Tuning in the Search for Improved Thermoelectric Materials", D.A. Polvani, J.F. Meng, C.D.W. Jones, F.J. DiSalvo, and J.V. Badding, Mater. Res. Soc. Symp. Proc. **545**, 259 (1999)
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24. "Crystal Structure of $\text{Tm}_2\text{Ni}_{12}\text{P}_7$ ", T.P. Braun and F.J. DiSalvo, J. Alloys Comp. **307**, 111 (2000)
25. "Transport Properties of Intermetallic Thulium Compounds", T.P. Braun and F.J. DiSalvo, J. Alloys Comp. **305**, 43 (2000)
26. "Bismuth Selenide Iodide", T.P. Braun and F.J. DiSalvo, Acta Crystallogr. C **56**, e1-e2 (2000)
27. "Synthesis and Characterization of SrBi_2Se_4 ", Y.C. Wang, R. Hoffmann, and F.J. DiSalvo, J. Solid State Chem. **256**, 230 (2001)
28. "Exploring Complex Chalcogenides for Thermoelectric Applications", Y.C. Wang and F.J. DiSalvo, 2000 MRS Meeting, San Francisco.
29. "Structure and Physical Properties of BaCu_2Te_2 ", Y.C. Wang and F.J. DiSalvo, J. Solid State Chem. **256**, 44 (2001)
30. "Structure and Physical Properties of CeSbTe ", Y.C. Wang, K.M. Poduska, R. Hoffmann, and F.J. DiSalvo, J. Alloys Comp. **314**, 132 (2001)
31. "Structure and Properties of the Stannides CeAuSn , $\text{Ce}_3\text{Rh}_4\text{Sn}_{13}$, and $\text{Ce}_3\text{Ir}_4\text{Sn}_{13}$ ", D. Niepmann, R. Pöttgen, K.M. Poduska, F.J. DiSalvo, H. Trill, and B.D. Mosel, Z. Naturforsch. **56b**, 1 (2001)

32. "Structural Studies of a Cubic, High-temperature (α) Polymorph of Pb_2GeS_4 and the Isostructural $\text{Pb}_{2-x}\text{Sn}_x\text{GeS}_{4-y}\text{Se}_y$ Solid Solution", K.M. Poduska, L. Cario, F.J. DiSalvo, K. Min, and P.S. Halasyamani, J. Alloys Comp., accepted.
33. "Structure Determination of $\text{La}_3\text{CuGeS}_7$ and $\text{La}_3\text{CuGeSe}_7$ ", K.M. Poduska, F.J. DiSalvo, K. Min, and P.S. Halasyamani, J. Alloys Comp., accepted.