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The Evolution of Nanothermoelectricity

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ABSTRACT

A personal review is presented. We review the renaissance in thermoelectric materials research that started in 1993 with the introduction of the nanostructure concept as a potential method to both increase the power factor and decrease the thermal conductivity and to even do both at the same time. The earliest work was limited to model systems for the demonstration of proof of principle. More recently the focus has evolved into demonstration of embedding the phenomena into bulk samples based on composites and superlattices. We here review this evolution of the nanothermoelectricity field. The resulting current activity is attracting many new researchers, industrial interest and the emergence of new ideas. We now look to the further development of these new ideas, and to the introduction of more new ideas and new approaches, as the field is now approaching the stage of commercial relevance.

INTRODUCTION

Thermoelectric materials entered an active growth period in the 1950s when doped semiconducting materials with good thermoelectric properties were produced that could be doped either n-type or p-type [1,2]. By about 1960, thermoelectric materials reaching values of $ZT = S^2\sigma T/\kappa \sim 1$ were achieved. In this early era, Bi_2Te_3, the main commercial thermoelectric material used until the present time, was developed. We then hit a 30 year period, from 1960-1990, when the thermoelectrics field saw much less activity. In the early 1990s, the French Navy and the US Navy both developed an interest to develop actual thermoelectric devices for energy utilization aboard submarines. Stimulated by their interest in thermoelectric materials for a specific application area, researchers were encouraged to look for new materials and new concepts to reinvigorate this research field and to stimulate interest in thermoelectricity.

At that time, I and my collaborator Professor Jean-Paul Issi at the Catholic University in Louvain la Neuve met in a nice restaurant near his university for discussions with John Stockholm from Paris whom we both knew quite well from French industry. John Stockholm brought with him to dinner a high official from the French Navy. The outcome of these dinner discussions led to two possible new research directions for advancing our knowledge, both involving promising new materials. The first research direction pointed to the examination of the many new materials that were uncovered during the 1960--1990 time frame that might have low thermal conductivity, and Jean-Paul Issi said that he would explore this idea and he took on this challenge. I took on the exploration of the second research direction of looking into nanoscale materials, which were basically unexplored before 1960, and although not much was known about them in 1990 regarding their possible relevance to thermoelectrics, it was a lot more than in 1960.

Not too much happened in the following year except for some rumblings on the topic of thermoelectric materials. Jean Paul Issi started looking at materials that were related to the newly discovered high T_c superconducting materials, but it turned out that most of the materials he investigated were not actual conductors, and were rather classified as semiconductors. This seemed promising for thermo-electricity. While the materials did indeed have low enough thermal conductivities to be of potential interest as thermoelectric materials, none had a large enough Seebeck coefficient S or a large enough power factor $S^2\sigma$ to be of great interest.

During this timeframe, I was very busy working on fullerenes and explaining their very complex IR and Raman spectra, involving more than 200 IR and more than 200 Raman spectral features. I was also very busy working with Riichiro Saito and Mitsutaka Fujita [3] on the forerunners of carbon nanotubes and showing that if a single wall carbon nanotube (SWNT) could actually be made, it could be either semiconducting or metallic, depending on the nanotube diameter and the orientation of the hexagons with respect to the nanotube axis. Since this was such a new concept at the time, we had to first convince ourselves and then to convince others that this concept could be correct. This activity kept me very busy with other interests.

While this was all going on, new students came to MIT in the fall every year looking for new research topics. One day a young man, Lyndon Hicks, a new young physics graduate student came around looking for a research project, and I suggested to him that we calculate the difference in the thermoelectric figure of merit ZT for an arbitrary two dimensional thermoelectric material in comparison to the three dimensional version of the same material. In about one week's time Lyndon Hicks returned with his solution, which predicted that an encouraging increase in ZT would occur as the thickness of the two dimensional (2D) thermoelectric materials got smaller. The results seemed so encouraging that we decided to write a short paper on the low dimensional thermoelectricity concept [4]. Since this was such a new topic, we had no idea where to publish our result. In the end we sent the manuscript to Physical Review B for lack of a more focused journal. The paper was readily accepted with not much comment.

Since the idea worked so well in 2D, we decided next to do the same calculation in 1D, for a putative quantum wire, and found that with additional quantum confinement, we got even better results, so we wrote a paper on the topic of a one dimensional thermoelectric material [5]. After sending the second paper off for publication, it seemed time to convince ourselves that these ideas made sense and we decided to consider the idea of quantum effects on the density of states of a real material. We decided on bismuth, because this was known to us as a good basic thermoelectric material for both electrons and holes. However, since bismuth is a semimetal in bulk form, the contribution to the Seebeck coefficient from the electrons in bulk bismuth canceled that for the holes. Nevertheless, the calculation showed that bismuth would be an attractive low dimensional thermoelectric material for both n-type and p-type material if it could be prepared as a semiconductor. Our calculations showed that a semimetal-semiconducting transition would occur as the size of one of the sample dimensions decreased to about 50 nm [6], which at that time was still large enough to think of making such a material in the form of a thin film or as a wire with facilities available to us.

Because of the rumblings about renewed interest in thermoelectric materials, the US Department of Defense held a workshop to which a few people working in the field were invited. At that conference I met Ted Harman of the MIT Lincoln Laboratory, who had a long time interest and background in the field of thermoelectric materials. It was through this conference that Lyndon Hicks and I started some collaboration with Ted Harman. It was through Harman's help that Lyndon Hicks in 1996 was able to implement his calculations on low dimensional thermoelectricity to show experimentally that the idea of nanostructures could under some circumstances lead to an enhancement in *ZT*, the thermoelectric figure of merit [4,7]. This 1996 thermoelectrics paper for a two dimensional experimental system [4,7] eventually had an impact on the thermoelectric research community and with time increasing numbers of people started to believe in this concept and to build on it.

Since the number of people working on thermoelectric materials at that time was small, and the concept was new, progress was slow. With time, workers in the thermoelectrics materials field started to show more interest in the potential of nanomaterials and started to invite me to talk about our work on the subject in departmental colloquia and at conferences on thermoelectricity. At a general seminar talk given by a visiting researcher, I stumbled upon the possibility of using mesoporous anodic alumina to make templates for the synthesis of bismuth nanowires, and I asked Jackie Ying who was a member of the Chemical Engineering Department at MIT for help with the implementation of this project. This idea was developed in the PhD thesis of Zhibo Zhang on the synthesis and properties of bismuth nanowires [8], and several publications on the subject resulted for bismuth and other materials [9-13]. Through these efforts, collaborations started with Gang Chen who was a junior faculty member of the Mechanical Engineering Department at Duke University interested in theoretical aspects of nanomaterials [14]. When he moved to UCLA, the collaboration was extended to Kang Wang of the UCLA Electrical Engineering Department and to Jean Pierre Fleurial who was a leader of the thermoelectric materials group at the Jet Propulsion Laboratory. This well-known group was stimulated by the nano-concept, and one of the young members of the group, Jeff Snyder, took an interest in this new research direction and eventually went on to make key discoveries of his own in the field, particularly when he later moved to CalTech and started his own independent research group [15].

THE MRS ERA

After joining forces with Gang Chen, we started a more serious and systematic study of the effects of nanostructuring on enhancing the figure of merit of thermoelectric materials, starting with bismuth nanowires [16]. Soon Joseph Heremans at the General Motors Research Laboratory joined forces on the project with a new method for preparing bismuth nanowires and new measurements of thermoelectric properties of Bi [17,18]. At the same time, thermal conductivity studies on the SiGe system started with Gang Chen at UCLA [19,20] and Elena Rogacheva started collaborating with us by studying thin films of the lead salts [21-23]. Because of his special expertise and interest, particular attention was given to the reduction of the thermal conductivity by Gang Chen, showing that what is most important for lowering the thermal conductivity is boundary scattering which was most sensitive to the interface density [24,25]. This consideration led to a concerted effort to introduce interfaces, and nanostructures with a high density of interfaces into bulk materials in order to produce macroscopic amounts of cooling or power generation.

Gang Chen's concept of interface introduction was implemented in conjunction with Professor Zhifeng Ren of Boston College and this concept started attracting attention [26] largely through the advent of the MRS Symposia series on thermoelectric materials which started around 2001 under the leadership of Terry Tritt and George Nolas [27]. The conceptual basis for the nanocomposite approach was generic and could be implemented in several common thermoelectric materials starting with p-type [28] and n-type [29] SiGe alloys, to produce bulk alloys of nano-structured material. The implementation of this concept was largely carried out by Gang Chen and Zhifeng Ren by starting from powders of nano-structured constituents which were rapidly hot pressed to form composite bulk materials containing a high density of nanostructures and large interface density. The particular study carried out on Bi_2Te_3, the most common bulk thermoelectric material, achieved a value of ZT=1.4 [30] and this work attracted attention. This work was then followed by related studies in several other materials systems and by other groups [31-36]. An excellent review of the status of these efforts was recently written by Austin Minnich [31].

LOOKING TO THE FUTURE

At the present time the field is very active internationally with many groups worldwide making important contributions to the field of nanothermoelectricity. There are now several viable approaches to producing nanostructured thermoelectric materials with values of ZT = 1.5 or thereabouts. By using a variety of materials systems, advanced nonstructural materials have been developed to cover temperature ranges from below room temperature to 1000° C. Attendance at MRS symposia and international conferences specifically devoted to thermoelectric materials has increased dramatically in the past 5 years as well as the industrial interest in the practical application of thermoelectric materials. Several approaches have been introduced which are having a major impact. The direct development of a high density of nanocomposite precipitates within a bulk thermoelectric material by chemical means has been successfully championed by the Kanatzidis group at Northwestern University [37]. Their work has been very impressive and has had a major impact on both the science and applications in this field. The Heremans group at Ohio State University has demonstrated the great impact of resonant states near the Fermi level on increasing ZT values, reaching values of ZT = 1.5 using only 2% Tl addition [38]. Although this concept was originally introduced for bulk materials, it might be further extended successfully in the future to nanosized constituents of bulk materials. The Johnson group in Oregon has taught us that superlattices with disordered constituents can produce amazingly low electrical conductivity [39], while the Snyder group at Caltech has shown [40] that a variety of thermoelectric materials can be used very effectively in many ways for practical thermoelectric systems. Asegun Henry and Gang Chen have looked into the contribution of specific phonons to the thermal conductivity of thermoelectric materials in accordance with their phonon mean free paths and wavelengths [41]. Such studies have been particularly useful in developing strategies to preferentially scatter phonons that actually carry most of the heat, and also in pointing out the differences between different thermoelectric materials in this regard. These studies on the thermal conductivity led to follow-up studies by Austin Minnich [42] showing that the phonons involved in ballistic heat transfer particularly in the low temperature regime are not well described by the Bolztmann equation and more detailed approached are needed [42]. Mona Zebarjadi has taken the concept of modulation doping in semiconductor physics and has both applied and extended this concept to thermoelectric materials from both an experimental and theoretical standpoint [43]. Celine Hin has shown the importance of site location for specific defects in thermoelectrics, insofar as a point defect can behave very differently if it is a vacancy or involves a specific impurity atom in a substitutional, antisite or interstitial location. Furthermore, she has been shown that an impurity atom can make a p-type or n-type carrier contribution to the electronic transport properties of a material depending on its specific site location [44]. Such information is valuable for materials synthesis designed specifically to improve explicit materials properties. Interesting works on half-Heusler compounds have also been carried out [45-47]. Depending on the temperature, structural arrangement, and dopant composition, these alloys exhibit a large Seebeck coefficient as well as a reasonably high electrical conductivity in the high temperature regime. These features make the half-Heusler compounds a very promising class of thermoelectric materials. Other compounds that are efficient at high temperature are the skutterudites. The skutterudites possess cage-like structures. When atoms are located into the interstitial cages of these materials, the lattice thermal conductivity can be substantially reduced compared to that of unfilled skutterudites [48]. These new concepts have invigorated the field and have brought in members of the next generation of young researchers. It now seems realistic to set a goal of reaching a *ZT* value of 2 by the end of this decade, which would likely have a major effect in stimulating the creation of several start-up companies and the generation of further scientific advances.

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REFERENCES

1. A.Yoffe, Adv. in Phys. **42**, 173 (1993).
2. H.J. Goldsmid, Thermoelectric Refrigeration, Plenum, New York, 1964.
3. R. Saito, M. Fujita, G. Dresselhaus, M.S. Dresselhaus, Electronic structures, Materials Science and Engineering B **19,** 185-191 (1993).
4. L.D. Hicks, M.S. Dresselhaus, Phys. Rev. B **47,** 12727 (1993).

5. L.D. Hicks, M.S. Dresselhaus, Phys. Rev. B **47**, 16631(1993).
6. L.D. Hicks, T.C. Harman, M.S. Dresselhaus, Appl. Phys. Lett. **63,** 3230 (1993).
7. L.D. Hicks, T.C. Harman, X. Sun, M.S. Dresselhaus, Phys. Rev. B **53,** R10493 (1996).
8. Z.B. Zhang, Fabrication, characterization and transport properties of bismuth nanowire systems, {Ph.D.} thesis, Massachusetts Institute of Technology, Department of Physics (February 1999).
9. X. Sun, Z. Zhang, M.S. Dresselhaus, Appl. Phys. Lett. **74,** 4005 (1999).
10. X. Sun, Z. Zhang, G. Dresselhaus, M.S. Dresselhaus, J.Y. Ying, G.Chen, Theoretical modeling of thermoelectricity in bismuth nanowires, in: T.M. Tritt, H.B. Lyon, Jr., G. Mahan, M.G. Kanatzidis (Eds.), Thermoelectric Materials. The Next Generation Materials for Small-Scale Refrigeration and Power Generation Applications: MRS Symposium Proceedings, Boston, volume, Vol. 545, Materials Research Society Press, Pittsburgh, PA, 1999, pp. 87-92.
11. T. Koga, T.C. Harman, S.B. Cronin, M.S. Dresselhaus, Phys. Rev. B **60**, 14286 (1999).
12. T. Koga, X. Sun, S.B. Cronin, M.S. Dresselhaus, Appl. Phys. Lett. **73**, 2950 (1998).
13. M.S. Dresselhaus, G. Dresselhaus, X. Sun, Z. Zhang, S.B. Cronin, T. Koga, Phys. Solid State **41**, 679 (1999).
14. M.S. Dresselhaus, G. Dresselhaus, X. Sun, Z. Zhang, S.B. Cronin, T. Koga, J.Y. Ying, G. Chen, Microscale Thermophysical Engineering **3**, 89 (1999).
15. G. S. Snyder and E. S. Toberer, NATURE Materials **7**, 105 (2008).
16. Y.-M. Lin, X.Sun, M.S. Dresselhaus, Phys. Rev. B **62**, 4610 (2000).
17. J.P. Heremans, C.M. Thrush, Y.M. Lin, S. Cronin, Z. Zhang, M.S. Dresselhaus, J.F. Mansfield, Phys. Rev. B **61**, 2921 (2000).
18. Y.M. Lin, O. Rabin, S.B. Cronin, J.Y. Ying, M.S. Dresselhaus, Appl. Phys. Lett. **81**, 2403 (2002).
19. T. Borca-Tasciuc, W. Liu, J. Liu, T. Zeng, D.W. Song, C.D. Moore, G. Chen, K.L. Wang, M.S. Goorsky, T. Radetic, R. Gronsky, T. Koga, M.S. Dresselhaus, Superlattices and Microstructures **28**, 199 (2000).
20. G. Chen, M.S. Dresselhaus, G. Dresselhaus, J.-P. Fleurial, T. Caillat, Recent developments in thermoelectric materials, in: M.J. Bevis (Ed.), International Materials Review, Vol. 48, Vol.~48, Institute of Materials Journals, 1 Carlton House Terrace, London SW1Y 5DB, 2003, pp. 45--66.
21. E.I. Rogacheva, I.M. Krivulkin, O.N. Nashchekina, A.Y. Sipatov, V.A. Volobuev, M.S. Dresselhaus, Appl. Phys. Lett. **78**, 3238 (2001).
22. E.I. Rogacheva, I.M. Krivulkin, O.N. Nashchekina, A.Y. Sipatov, V.V. Volubnev, M.S. Dresselhaus, Appl. Phys. Lett. **78**, 1661 (2001).
23. E.I. Rogacheva, T.V. Tavrina, O.N. Nashchekina, S.N. Grigorov, K.A. Nasedkin, M.S. Dresselhaus, Appl. Phys. Lett. **80**, 2690 (2002).
24. R. Yang, G. Chen, M.S. Dresselhaus, Phys. Rev. B **72**, 125418-1 (2005).
25. R. Yang, G. Chen, M.S. Dresselhaus, Nano Letters **5**, 1111 (2005).
26. M.S. Dresselhaus, G. Chen, M.Y. Tang, R.G. Yang, H. Lee, D.Z. Wang, Z.F. Ren, J.P. Fleurial, P.Gogna, New directions for nanoscale thermoelectric materials research, in: J. Yang, T.P. Hogan, R. Funahashi, G.S. Nolas (Eds.), Materials and Technologies for

Direct Thermal-to-Electric Energy Conversion: MRS Symposium Proceedings, Boston, December 2005, Vol. 886, Materials Research Society Press, Pittsburgh, PA, 2005, p 3.

27. T.M. Tritt, M.A. Subramanian, MRS Bulletin **31**, 188 (2006).
28. G. Joshi, H. Lee, Y. Lan, X. Wang, G. Xhu, D. Wang, R.W. Gould, D.C. Cuff, M.Y. Tang, M.S. Dresselhaus, G. Chen, Z.F. Ren, Nano Letters **8**, 4670 (2008).
29. X. Wang, H. Lee, Y. Lan, G. Zhu, G. Joshi, D. Wang, J. Yang, A.J. Muto, M.Y. Tang, J. Klatsky, S. Song, M.S. Dresselhaus, G. Chen, Z. Ren, Applied Physics Letter **93,** 193121 (2008).
30. B. Poudel, Q. Hao, Y. Ma, Y. Lan, A. Minnich, B. Yu, X. Yan, D. Wang, A. Muto, D. Vashaee, X. Chen, J. Liu, M.S. Dresselhaus, G. Chen, Z.F. Ren, Science **320**, 634 (2008).
31. A. Minnich, H. Lee, X.W. Wang, G. Joshi, M.S. Dresselhaus, Z.F. Ren, G. Chen, D. Vashaee, Physical Review B **80**, 155327 (2009).
32. J. Yang, Q. Hao, H. Wang, Y.C. Lan, Q.Y. He, A. Minnich, D.Z. Wang, J.A. Harriman, V.M. Varki, M.S. Dresselhaus, G. Chen, , Z.F. Ren, Phys. Rev. B **80**, 115329 (2009).
33. S.K. Bux, R.G. Blair, P.K. Gogna, H. Lee, G. Chen, M.S. Dresselhaus, R.B. Kaner, J.P. Fleurial, Advanced Functional Materials **19**, 2445 (2009).
34. G.H. Zhu, H. Lee, Y.C. Lan, X. Wang, D.W.G. Joshi, R. Blair, M. Tang, D. Vashaee, P. Gogna, Z. Ren, J. Fleurial, G. Chen, M.S. Dresselhaus, Physical Review Letters **102** 196803 (2009).
35. J. Baxter, Z. Bian, G. Chen, D. Danielson, M.S. Dresselhaus, A.G. Fedorov, T.S Fisher, C.W. Jones, E. Maginn, U. Kortshagen, A. Manthiram, A. Nozik, D.R. Rolison, T. Sands, L. Shi, D. Sholl, Y. Wu, Energy Environ. Sci. **2**, 559 (2009).
36. Y. Lan, B. Poudel, Y. Ma, D. Wang, M.S. Dresselhaus, G. Chen, Z. Ren, Nano Letters **9**, 1419 (2009).
37. M.G. Kanatzidis, The role of solid-state chemistry in the discovery of new thermoelectric materials, in: T.~M. Tritt (Ed.), Semiconductors and Semimetals: Recent Trends in Thermoelectric Materials Research II, Vol.~69, Academic Press, San Diego, CA, 2001, pp. 51--98.
38. J.P. Heremans, V. Jovovic, E.S. Toberer, A. Saramat, K. Kurosaki, A. Charoenphakdee, S. Yamanaka, G.J. Snyder, Science **521** (3588), 554, (2008).
39. C. Chiritescu, D. G. Cahill, N. Nguyen, D. Johnson, A. Bodapati, P. Keblinski, P. Zschack, Science **315 (5810),** 351 (2007).
40. G.J. Snyder, E.S. Toberer, Nature Materials **7(2),** 105 (2008).
41. A. Henry, G. Chen, Physical Review B **79(14)**, 144305 (2009).
42. A. J. Minnich, J. A. Johnson, A. J. Schmidt, K. Esfarjani, M. S. Dresselhaus, K. A. Nelson, G. Chen, Physical Review L, submitted.
43. M. Zebarjadi, G. Joshi, G. Zhu, B. Yu, A. Minnich, Y. Lan, X. Wang, M.S. Dresselhaus, Z. Ren, G. Chen, Nano Letters, in press (2011).
44. C. Hin, M.S. Dresselhaus, G. Chen, Applied Physics Letter, submitted.
45. C. Uher, J. Yang, S. Hu, D. T. Morelli, and G. P. Meisner, Phys. Rev. B **59**, 8615 (1999).
46. H. Hohl, A. P. Ramirez, C. Goldmann, G. Ernst, B. Wolfing, and E. Bucher, J. Phys.: Condens. Matter **11**, 1697 (1999).
47. K. Mastronardi, D. Young, C. C.Wang, P. Khalifah, R. J. Cava, and A. P. Ramirez, Appl. Phys. Lett. **74**, 1415 (1999).
48. G.S. Nolas, D.T. Morelli, T.M. Tritt, Annu. Rev. Mater. Sci. **29(89),** 116 (1999).