

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/3742193>

Potential of quasicrystals and quasicrystal approximants for new and improved thermoelectric materials

Conference Paper · September 1997

DOI: 10.1109/ICT.1997.667184 - Source: IEEE Xplore

CITATIONS

3

READS

206

5 authors, including:



T.M. Tritt

Clemson University

371 PUBLICATIONS 14,818 CITATIONS

[SEE PROFILE](#)



Rhonda M. Stroud

United States Naval Research Laboratory

477 PUBLICATIONS 12,009 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



Thermophysical Properties [View project](#)



Great Jobs in Condensed Matter Physics & Astronomy @ Clemson University [View project](#)

Potential of Quasicrystals and Quasicrystal Approximants for New and Improved Thermoelectric Materials.

Terry M. Tritt^{1,2}, M. L. Wilson*, A. L. Johnson, S. LeGault³ and R. Stroud⁴

¹Department of Physics and Astronomy, Clemson University, Clemson SC

²Materials Science and Engineering Department, Clemson University, Clemson SC

³McGill University, Department of Physics and Astronomy, Montreal Canada

⁴Naval Research Laboratory, Washington D.C.

Abstract:

The focus of our research revolves around a search for new thermoelectric materials with improved performance over present materials. We have performed preliminary experiments to assess the potential of quasicrystalline materials for thermoelectric applications. The investigation of known classes of quasicrystals and quasicrystal approximants is important for potential thermoelectric materials as well as a search for entirely new phases of these materials. The advantage of quasicrystals is that their electrical conductivity (and possibly their thermoelectric power) can be manipulated through variation of their composition, synthesis or annealing conditions without sacrificing their usually low thermal conductivity. Quasicrystalline materials exhibit characteristics which are suggestive of Slack's idea of a phonon-glass, electron-crystal material for thermoelectric applications. We will present some of our results of resistivity, thermopower, and thermal conductivity on measurements to show the potential of these materials. A more thorough investigation of this class of materials and a systematic search for new quasicrystalline and related compounds might very well yield new materials for thermoelectric devices

Introduction:

Over the past 30 years, alloys based on the Bi_2Te_3 [($\text{Bi}_{1-x}\text{Sb}_x$)₂($\text{Te}_{1-x}\text{Se}_x$)₃] and $\text{Si}_x\text{Ge}_{1-x}$ have been extensively studied and optimized for their use as thermoelectric materials both for cooling (Bi_2Te_3) and power generation (SiGe) applications.^{1,2,3} Improvement over the past decade in Bi_2Te_3 , in particular, has been relatively minor with the thermoelectric figure of merit ZT relatively constant at $ZT=1$. Due to this slow progress, recent research has focused on the investigation of new classes of materials as advanced thermoelectric systems.⁴ Material classes currently under investigation include skutterudites,^{5,6,7,8} quantum-well materials,^{9,10} superlattice structures^{11,12} and low-dimensional systems.¹³

This recent activity has also been driven by advanced military and civilian applications that

demand higher performance thermoelectric materials and systems operating at temperatures down to -100 K. In particular, cryoelectronics and "cold computing" are emerging fields requiring reliable low-maintenance cooling and refrigeration technology. Sloan states that "speed gains of 30% - 200% are achievable in some CMOS computer processors" where "cooling is the fundamental limit to electronic system performance."¹⁴ In addition, a limitation to cellular phone technology using superconducting narrow-band spectrum dividers is the lack of reliable refrigeration.

The potential of a material for thermoelectric applications is determined by the material's dimensionless figure of merit, $ZT = (\alpha^2\sigma/\lambda)T$, where α is the Seebeck coefficient, σ the electrical conductivity, λ the total thermal conductivity ($\lambda = \lambda_L + \lambda_E$; the lattice and electronic contributions respectively) and T the temperature. In most materials, α increases while σ decreases as the carrier concentration is lowered. This results in the ability to tune the power factor ($\alpha^2\sigma$) through control of the carrier concentration. In most materials the power factor is a maximum near a carrier concentration of $10^{19}/\text{cm}^3$, resulting in the feature that most thermoelectric materials are heavily doped semiconductors. High mobility carriers are most desirable, so as to have the highest possible electrical conductivity yet, still retain a low carrier concentration.

While $\alpha^2\sigma$ can be maximized through chemical doping, λ_{tot} is not so easily tuned. The electronic thermal conductivity, λ_E is tied to σ through the Wiedemann-Franz Law ($\lambda_E/\sigma = L_0T$, $L_0 = \text{Lorentz number} \sim 2.3 \times 10^{-8} \text{ W}\Omega/\text{K}^2$). Therefore, while doping may increase σ , and hence λ_E , doping is also known to lower λ_L , leading to unknown changes in λ_{tot} . State-of-the-art thermoelectric materials have a $ZT \approx 1$. This value has been a practical upper limit for more than 30 years, yet no theoretical or thermodynamic reason exists for why it can not be larger.

In 1995, Glen Slack published a paper describing the chemical characteristics of materials which might be candidates for good thermoelectric materials.^{15,16} The candidate material needs to be a narrow bandgap semiconductor with high mobility carriers. Typically this requires strong covalent bonding between elements with a small difference in electronegativity. This has led to a thorough search of materials containing at least one element from the lower right section of the periodic table. Additionally, at lower thermal conductivity, the Seebeck coefficient and electrical conductivity (both in the numerator of ZT) are strong functions of the doping level and chemical composition, which must therefore be optimized for good thermoelectric performance.

The thermal properties of complex materials can often be modified by chemical doping. Understanding these various effects and selecting optimization strategies, however, can be an exceedingly difficult problem. In complex materials there are often many possible degrees of freedom.

Quasicrystals as thermoelectric materials:

Prior to 1983, single-crystals were defined as solids composed of a unit-cell repeated translationally throughout the crystal. This translational order required that the crystal contain either 2-, 3-, 4-, or 6-fold rotational symmetry so a unit cell can be repeated throughout space and have all space be filled. Quasicrystals break this rule in that they display a "forbidden" structural symmetry, typically 5-, 8-, 10- or 12-fold symmetry.^{17,18,19} Rather than typical translational order evident in crystals, quasicrystals exhibit long-range positional order. Quasicrystals are argued to grow by means of local matching rules governing the orientation of new atoms, by which single-domain crystals can be formed. In these single-domain crystals, the position of all atoms in the lattice is uniquely determined, yet no repeating pattern exists. This positional order gives rise to observation of sharp X-ray diffraction lines similar to those of conventional single crystals.^{20,21}

Icosahedral (S-fold symmetric) quasicrystals form the largest family of quasicrystalline materials with over 60 members known.^{*} Of these systems 12 can be grown as stable, single-domain, macroscopic crystals of large enough size (~1 mm³) to perform 'intrinsic' transport measurements. Most icosahedral quasicrystals are composed of icosahedral metal clusters known as Pauling triacontahedra (containing 44 atoms) or Mackay icosahedra (containing 54 atoms). These clusters are then arranged with additional linking atoms in a non-repeating pattern to form a quasicrystal. In some cases these clusters are arranged in a repeating pattern, resulting in a material known as a

quasicrystalline approximant. Most of the understanding of electronic and phonon structure, and precision knowledge of atomic positions in quasicrystalline materials are actually determined from measurements on and calculations of stable approximant phases. One such approximant Al₅CuLi₃ is a bcc lattice of Pauling triacontahedra containing a total of 180 atoms per unit cell. This is actually a small approximant lattice, phases with lattice constants of up to 100 Å, containing over 50,000 atoms per unit cell, are known.²²

For the best thermoelectric material, Slack suggested it should behave as a "phonon-glass, electron-crystal". It would have the thermal properties of a glass and the electronic properties of a crystal. Quasicrystals, which were discovered in 1984 by Shechtman et. al.,²³ seem to possess properties usually associated with both crystalline and amorphous materials.^{24,25} Single-domain quasicrystals exhibit the low thermal conductivity of amorphous materials in all the cases that have been studied and yet have electrical properties ranging from "dirty" metals to semiconductors. The advantage of quasicrystals is that one can vary the electrical conductivity (and possibly tune this thermoelectric power) by varying the composition or defect concentration without sacrificing the low lattice thermal conductivity. For these reasons, a systematic search through the different classes of existing and proposed quasicrystals is underway to develop new materials for thermoelectric applications; and possibly the phonon-glass, electron-crystal suggested by Slack.

Published data on the thermopower of quasicrystals is rather scarce with values ranging from -30 μV/K to +50 μV/K. While moderately large, these values are currently not large enough for thermoelectric application. However, we take interest in the fact that nearly this entire variability can be found in a single quasicrystalline system, AlCuFe. This may allow for both the n- and p-type legs in a thermoelectric device to be fabricated from the same system. For example, at 300 K iron-rich Al_{62.5}Cu_{24.5}Fe₁₃ has α = +45 μV/K, while iron-poor Al_{62.5}Cu_{26.5}Fe₁₁ has α = -30 μV/K.²⁶ This variance in stoichiometry is intrinsic to quasicrystals since they do not require a rigid chemical formula for stability. The elements in the crystal can typically be changed by a few atomic percent without changing the structure of the crystal. Lacking a unique empirical chemical ratio makes these crystals easy to dope, resulting in high tunability of the thermal and electrical properties. 62.5 24.5 13 26.5 11

In the search for new thermoelectric materials, we are investigating the resistance and thermopower of multi-domain stable icosahedral phase quasicrystals. Of the twelve stable icosahedral

quasicrystals, data will be presented for $\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$, $\text{Al}_{70}\text{Pd}_{20}\text{Re}_{10}$, $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$, and $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$.

Experimental:

In determining the thermoelectric-figure-of-merit, several properties of the material must be quantified; thermal conductivity, electrical conductivity, and thermopower. Of these quantities, the thermal conductivity is one of the most difficult to control. Thermal conductivity is the sum of the lattice (phonon) and electronic contribution of the thermal conductivity. The electronic thermal conductivity is essentially the lower limit for the total thermal conductivity of an electrically conducting system. Consequently, it is always desirable to search for a system possessing a low lattice thermal conductivity in order for the total thermal conductivity to be as low as possible.

The thermoelectric figure of merit is inversely proportional to λ . Hence, low values of λ greatly enhance the potential of a material for thermoelectric application. While few studies of the thermal conductivity have been made on stable icosahedral quasicrystalline compounds, most materials examined have λ_{phonon} below about $2 \text{ W/m}\cdot\text{K}$ at temperatures below 150 K.

Thermal conductivity data for three multi-domain quasicrystalline materials; $\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$, $\text{Al}_{70}\text{Pd}_{20}\text{Re}_{10}$, and $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$ are presented in Figure 1. AlPdRe and AlCuFe display nearly indistinguishable measurements of λ_{tot} yet, as will be discussed below, their electrical conductivities differed by more than a factor of 2, [Figure 2]. These thermal conductivity values resemble those of amorphous glasses which typically have $\lambda_{\text{tot}} \sim 1 \text{ W/m}\cdot\text{K}$.²⁷

Estimations of the electronic thermal conductivity using the Wiedemann-Franz law yields $\lambda_{\text{e}} \cong 0.03 \text{ W/m}\cdot\text{K}$, assuming L_0 is $\sim 2.3 \times 10^{-8} \text{ W}\Omega/\text{K}^2$ at 150 K. This corroborates the idea that the majority of the total thermal conductivity in these samples is from lattice contributions.

The electrical properties of these materials are also related to their unique structure. Nearly all stable single-domain quasicrystals display semimetallic resistive behavior with $\rho(300\text{K})$ between 0.1 and $10 \text{ m}\Omega\cdot\text{cm}$. At low temperatures, the resistivity increases by a factor from 1 to 20 times the room temperature resistivity. These data imply that some quasicrystals have a band gap of less than 0.2 eV .² Previous studies have related this observed band gap to a pseudogap formed from localization at the Fermi level. Thus, conduction at low temperatures is best described using models of weak localization and strong electron-electron scattering. Localization in these materials is enhanced by improved crystallinity of the sample. Consequently, as crystal quality is improved (evidenced by sharper x-ray or electron diffraction spots) the resistivity increases significantly.^{28,29} This is contrary to typical observations for a metallic crystal. Consequently, the resistivities measured on high-quality single-domain samples provide a maximum limit to the resistivity in a tuned material.

Resistivity in quasicrystals is also reported to increase as the atomic number of the alloy increases. This is described in studies of single domain $\text{Al}_{70}\text{Cu}_{20}\text{Fe}_{10}$, $\text{Al}_{70}\text{Cu}_{20}\text{Ru}_{10}$ and $\text{Al}_{70}\text{Cu}_{20}\text{Os}_{10}$ quasicrystals.³⁰ Consequently, many avenues exist by which the conductivity of a quasicrystal can be tuned.

AlPdRe has a large room temperature resistivity (approximately $10 \text{ m}\Omega\cdot\text{cm}$) which increases rapidly as the temperature is lowered

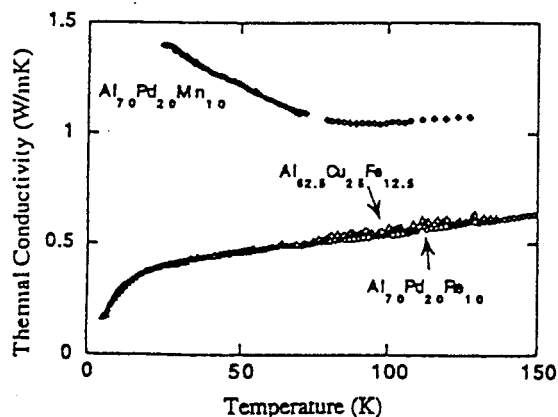


Figure 1: Thermal conductivity for AlPdRe , AlPdMn , and AlCuFe quasicrystals.

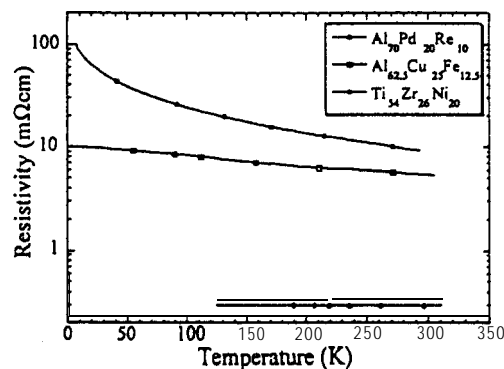


Figure 2: Resistivity vs. temperature for AlPdRe , AlCuFe , and TiZrNi quasicrystals.

AlPdRe has a large room temperature resistivity (approximately $10 \text{ m}\Omega\text{cm}$) which increases rapidly as the temperature is lowered [FIGURE 2]. AlCuFe, however, has a room temperature resistivity of about $5 \text{ m}\Omega\text{cm}$ which only increases by a factor of two at 10 K. TiZrNi which displays the lowest resistivity, is virtually temperature independent for the range studied. This trend of lower overall resistivity correlating with a smaller temperature dependence of the resistivity is commonly found in quasicrystals, and some argue this is a universal property of these systems? While the conductivity of the AlPdRe and AlCuFe samples appear to be too small for good thermoelectric materials, the TiZrNi sample does have a large enough conductivity to be of interest being $-3.4 (\text{m}\Omega\text{cm})^{-1}$.

For AlCuFe quasicrystals we find a thermopower of $+12 \mu\text{V/K}$ which is in the range of the previously published data (Figure 3). AlPdRe on the other hand, is found to have a very large thermopower for a quasicrystal $+55 \mu\text{V/K}$ and to be fairly constant near room temperature. This high thermopower over a broad temperature range is desirable for a widely useful low temperature thermoelectric cooling system. TiZrNi, while having the best conductive properties of the three systems studied has the lowest thermopower. AlPdMn also has a very large thermopower at room temperature, $\alpha = +61 \mu\text{V/K}$.

The variability and sensitivity of the thermopower to slight changes in the structure are also borne out through band structure calculations^{3,4,32} and photoemission measurements.³³

Summary:

At least a few of the challenges that are evident in relation to the potential of the quasicrystal

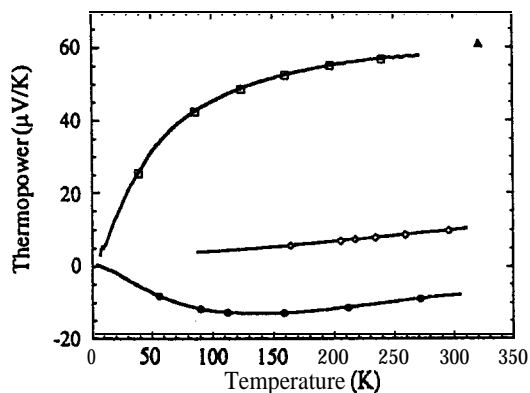


Figure 3: Thermoelectric power vs. temperature for AlPdRe (□), AlCuFe (◇), TiZrNi (△), and AlPdMn (●).

class of materials for utilization in thermoelectric applications lie in achieving a higher thermoelectric power and a higher carrier mobility. One very important point should be made. Researchers are just beginning to thoroughly investigate the coupled thermal and electronic transport properties of these materials. Very little thermopower, thermal conductivity and carrier mobility data exist for any particular class of quasicrystals. Most of the research performed on these systems to date has been related to the structure, which is of course very reasonable given their complex nature.

Quasicrystals show potential as a new class of thermoelectric materials. The intrinsic chemical variability of these crystals allows for a high degree of tunability of their thermal and electrical properties. This should lead to a broad range within this class of materials. Known quasicrystals have thermal conductivities approaching that of an amorphous glass, yet their electrical conductivity is more akin to a small gap semimetal. These characteristics broadly meet Slack's "phonon-glass, electron-crystal" model. The sensitivity of the sign of the thermopower to elemental concentration raises hope that n- and p-type thermoelectrics could be found in the same material. Although the quasicrystals form a rather large class of compounds, for each quasicrystal, there also typically exists at least one conventionally ordered quasicrystalline approximant phase. These approximants will also be investigated for their potential as thermoelectric materials since they are known to have similar electrical and thermal properties to their related quasicrystals.¹

Much more research must be done and an extensive data base must be established on the electrical and thermal properties of this large group of materials. Then, possibly, a much clearer indication of the potential of these materials can be established.

References:

- ¹ H. J. Goldsmid, *Electronic Refrigeration*, (Pion Limited Publishing, London, (1986).
- ² *CRC Handbook of Thermoelectrics*, edited D. M. Rowe, CRC Press, Boca Raton (1995).
- ³ C. W. Wood, Rep. Prog. Phys. 51, 459-539 (1988).
- ⁴ Terry M. Tritt, Science, 272, 1276 (1996).
- ⁵ B. C. Sales, D. Mandrus and R. IS. Williams, Science, 272, 1325 (1996).
- ⁶ G. A. Slack and V. G. Toukala, Jour. Appl. Phys. 76, 1635 (1994); G. Nolas, et al., Jour. Appl. Phys., 79, 4002 (1996); D. T. Morelli, et al., Phys. Rev. B 51 9622 (1995).

- ⁷T. M. Tritt, *et al.*, Jour. Appl. Phys., 79, 8412 (1996).
- ⁸Baoxing Chen, *et al.*, Phys. Rev. B **55** 1476 (1997).
- ⁹L. D. Hicks and M. S. Dresselhaus, Phys. Rev. B. 47, 12727 (1993).
- ¹⁰L. D. Hicks, *et al.*, Phys. Rev. B. 53, R10493 (1996).
- ¹¹R Venkatasubramanian, Proc. of the XIII International Conference on Thermoelectrics, AIP, p 40-44 (1995).
- ¹²R Venkatasubramanian, 1997 Spring MRS Abstracts, 29 1 (1997).
- ¹³T. M. Tritt, *et al.*, submitted to 1997 MRS Symposium Q (San Francisco, CA).
- ¹⁴J. Sloan, Superconductor Industry, Fall 1996, p30 (1996).
- ¹⁵G. A. Slack, in CRC Handbook of Thermoelectrics, Rowe ed. 1995, ref. 2, p 407.
- ¹⁶G. A. Slack, in Solid State Physics, 34 1 (1979), ed. by F. Seitz, D. Turnbull, and H. Ehrenreich, Academic Press, New York.
- ¹⁷S. J. Poon, Advances in Physics, 41, 303-363 (1992).
- ¹⁸C. Janot, *Quasicrystals*, Clarendon Press, Oxford.
- ¹⁹A. I. Goldman and K. F. Kelton, Reviews of Modern Physics, 65, 213 (1993).
- ²⁰P. A. Bancel, Phys. Rev. Lett. 63, 2741 (1989).
- ²¹C. A. Guryan, *et al.*, Phys. Rev. Lett. 62, 2409 (1989).
- ²²T. L. Daulton and K. F. Kelton, Philos. Mag. B 66, 37 (1992).
- ²³D. Shechtman, *et al.*, Phys. Rev. Lett. 53, 1951 (1984).
- ²⁴S. Legault, *et al.*, Conference Proceedings "New horizons in Quasicrystals: Research and Applications", August 19-23, 1996, Iowa State University, Ames, Iowa.
- ²⁵A. Perrot, *et al.*, Proceedings of the 5th International Conference on Quasicrystals, World Scientific, 1995, p. 588.
- ²⁶F.S. Pierce, *et al.*, Phys. Rev. Lett. 70, 39 19 (1993).
- ²⁷M.A. Chemikov, A. Bianchi, and H.R. Ott, Phys. Rev. B 51, 153 (1995).
- ²⁸T. Klein, C. Berger, D. Mayou, and F. Cyrot-Lackmann, Phys. Rev. B 66, 2907 (1991).
- ²⁹R. Tamura, A. Waseda, K. Kimura, and H. Ino, Phys. Rev. B 50, 9640 (1994).
- ³⁰Y. Honda, K. Edagawa, S. Takeuchi, A.-P. Tsai and A. Inoue, Jpn. J. Appl. Phys. 34, 2415 (1995).
- ³¹G. Kasner, H. Schwabe and H. Böttger, Phys. Rev. B 51, 10454 (1995).
- ³²S.E. Burkov, A.A. Varlamov and D.V Livanov, Phys. Rev. B 53, 11504 (1996).
- ³³U. Mizutani, Y. Yamada, T. Takeuchi, K. Hashimoto, E. Belin, A. Sadoc, T. Yamauchi and T. Matsuda, J. Phys: Conds. Matter 6, 7335 (1994).