~~To appear in:~~
XIIth International Conference on Thermoelectrics
edited by K. ~~Ta~~ Matsuura
held November 9-11, 1993
Yokohama, Japan

pp. 126 - 131

Thermoelectric Materials of the Future

Cronin B. Vining

Jet Propulsion Laboratory/California Institute of Technology,
Pasadena, CA 91109

ABSTRACT

Today, more than ever before, means must be found to apply the full power of modern materials science to the important problem of efficient and environmentally friendly energy conversion devices. Applications ranging from high value-added aerospace power generation to consumer-oriented conveniences such as picnic baskets must be made smaller, more efficient, more economical, and perhaps most importantly, more compatible with the environment. Fortunately, the growth of materials science presents a variety of new experimental and theoretical techniques with the potential to crack the ZT barrier and usher in a new generation of high performance thermoelectric technology. From Kondo materials, thin-films and quantum wells to novel binary and ternary semiconductors, the number of recent suggestions is almost overwhelming. This paper surveys various possibilities and discusses several key experimental and theoretical questions which need to be resolved.

INTRODUCTION

In principle, thermoelectric devices can be as efficient as any existing mechanical energy conversion device. Achieving high efficiencies would be as revolutionary to energy sciences as the development of the transistor was to electronics. Such dreams may seem strange today, but the rapid rise to prominence of semiconductor technology in the 1950's inspired confidence. It seemed to some that not only vacuum tubes, but turbines and compressors also would become obsolete. Major efforts were undertaken around the world, particularly in the Soviet Union. Such was the enthusiasm of the time that by 1961 several dozen facilities in the United States were making major investments in thermoelectric research [1]. In 1959 Zener considered 35% efficiency a "conservative goal" for a thermoelectric generator [2].

Needless to say, efficient thermoelectric technology is not yet available. But we have learned a few things since 1959. We know why SiGe has the thermoelectric performance it has [3, 4, 5, 6]. We know why Bi_2Te_3 has the performance it has [7]. We also know about entire families of materials and variations of materials which were entirely unknown in 1960. But one thing has not changed: there still is no fundamental reason why *all* thermoelectric materials have such poor performance [8].

Such predictions are fraught with uncertainty, but there are in fact so many untested possibilities that radically improved thermoelectric performance is, at the very least, plausible. Plausible enough that in a recent science fiction novel Arthur C. Clark suggests "a spin off from the superconductor revolution that ups efficiency several times" will be discovered in the near future [9]. More than merely fiction, such dreams can also be used to motivate a vigorous search for new thermoelectric materials. As a part of the search, this paper attempts to survey the types of materials which might improve thermoelectric performance by several times and bring the dreams of Zener and Clark slightly closer to reality.

NEW APPROACHES

For convenience, the various approaches to next generation thermoelectric materials have been grouped into categories: conventional semiconductors, unconventional semiconductors, heterostructures (including quantum wells) and metals. The boundaries between the categories are somewhat arbitrary, but there are important differences in the factors influencing the thermoelectric performance in each case. The following sections describe the major approaches.

CONVENTIONAL SEMICONDUCTORS

The term "conventional semiconductors" is intended to imply that the transport mechanisms in these materials are well described by traditional semiconductor theory. The most common thermoelectric materials (based on Bi_2Te_3, PbTe or SiGe) all fall into this category. So, the selection criteria for such a material is essentially the same as described by Ioffe [10]. Before discussing particular new materials a very brief overview of the selection criteria is given.

Conventional Selection Criteria

Conventional theory for a single band semiconductor indicates the optimum thermoelectric figure of merit ZT ($ZT= \alpha^2\sigma T/\lambda$, where α is the Seebeck coefficient, σ is the electrical conductivity, λ is the thermal conductivity and T is the temperature) depends on the carrier scattering mechanism and a material parameter

$$\beta = T^{\frac{5}{2}} m_{eff}^{\frac{3}{2}} \frac{\mu}{\lambda_{ph}} \qquad (1)$$

where m_{eff} is the carrier effective mass, μ is the carrier mobility and λ_{ph} is the lattice contribution to the thermal conductivity [11]. The single most important effect of a two band semiconductor is that thermal excitation of minority carriers above about $4kT \gtrsim E_g$ rapidly suppresses the Seebeck coefficient. For operation at room temperature, this implies a band gap of at least 0.1 eV is required.

A large value for β is typically an indicator of the potential for high ZT values. Ideally, β depends only weakly on doping level so measurements on an unoptimized sample can provide some indication of the ZT values expected of optimally doped samples. This assumption should be used with some caution, however. For example, β for undoped SiGe is about 3 times greater than β for optimally doped SiGe, mostly due to a drop in the carrier mobility.

Still, β reflects the usual expectations from conventional theory: high mobility, low lattice thermal conductivity and high effective mass are desired. For new materials, however, even these few properties are usually unavailable. Fortunately, some insight can be gained from the composition and crystal structure alone. Slack has discussed the role of the crystal structure in determining the lattice thermal conductivity [12] and more recently, the importance of the electronegativity difference in determining carrier mobility [13]. Heavy atoms and large unit cell sizes contribute to low thermal conductivity values and small electronegativity differences appear to be important to achieve high carrier mobility values. Unfortunately, more detailed theoretical considerations are seldom of much value when considering really new materials.

Binary Compounds

Several semiconductors involving only elements from columns IIIA to VIA are known to have ZT up to about 1, and slightly higher. These include materials based on BiSb, Bi_2Te_3, PbTe, and SiGe. Indeed, almost all compounds based strictly on elements from the right-hand portion of the periodic table have been examined sufficiently to conclude that probably none of them is likely to have really large ZT values. There are few possible exceptions even within this narrow class, but these will be discussed later because by conventional criteria they are not promising at all.

Fortunately, there are many more semiconductors known. Almost every binary system between a metal and an elements from column IIIA-VIA exhibits at least one compound with semiconducting or insulating properties. It is difficult to rule out *any* of these compounds *a priori*, but for most of them enough literature is available to suggest that high ZT values are unlikely. Even today, however, there still remain more than a simple binary compounds which have yet to be sufficiently characterized.

In recent years, several groups have been examining various novel semiconductors for their thermoelectric properties. In the 1980's JPL, Sandia, Thermotrex (then called Thermo Electron), General Atomics and General Electric performed studies on B_4C, $La_{3-x}S_4$, and $La_{3-x}Te_4$ [14, 15] resulting in thermoelectric properties comparable to (although not yet superior to) state of the art SiGe alloys. This work lay a foundation for examining even more novel semiconductors. The list of possible thermoelectric materials examined experimentally in recent years at JPL is now rather long and includes: B_4C, $La_{3-x}S_4$, $La_{3-x}Te_4$, Ru_2Si_3 [16], Ir_3Si_5, $IrSi_3$ [17], Ru_2Ge_3 [18], Re_3Ge_7, $Mo_{13}Ge_{23}$, $Cr_{11}Ge_{19}$, $CoGe_2$ [19], $RuSb_2$, $IrSb_2$ [20], $IrSb_3$, and $CoSb_3$ [21].

Silicides have received attention [22] because their high melting points and low vapor pressures make them attractive for high temperature applications. Several of these, such as Os_2Si_3 and $OsSi_2$, probably deserve further study. Ru_2Si_3, for example, appears to have the potential for quite high ZT values if suitable doping and preparation techniques can be identified.

Although known for some years, the $Mg_2(Si,Ge,Sn)$ system has received renewed interest in recent years [23] and ZT values as high as 1.68 have been reported [24]. While such high ZT values must be confirmed, these materials do appear to be at least comparable to current materials.

$RuAl_2$ and $RuGa_2$ are interesting because they are semiconductors even though each of the elements involved are clearly metallic [25]. Examples such as these show the difficulty of predicting even the occurrence of semiconducting behavior.

Like most diborides TiB_2, ZrB_2, and HfB_2 have metal-like resistivity values (<10 $\mu\Omega$-cm), but these three diborides have relatively large Hall coefficient values (>2×10^{-3} cm^3/C) [26]. The large Hall coefficient values correspond to less than one carrier per atom, which has been confirmed by electronic structure calculations indicating a minimum in the density of states near the Fermi level [27]. These diborides are interesting because even though the carrier concentration is about $1\text{-}3\times10^{21}$ cm^{-3} and the electronic states at the Fermi level are predominantly d-states, the mobility values remain quite appreciable (>200 $cm^2/V\text{-}s$). Reasonable ZT values may result if some method can be found to create a true energy gap in these materials.

Slack has recently surveyed basically all the known binary compounds and has tabulated about 28 known binary compounds which meet certain criteria thought to be required for a good thermoelectric material [13]. The thermoelectric properties of most of these materials are essentially unknown. Among those he identifies as most promising are: $IrSb_3$, Re_6Te_{15}, and Mo_6Te_8.

Ternary and More Complex Compounds

The compounds described above are all binary compounds, or solid solutions between binary compounds. And even though several binary compounds with considerable promise for thermoelectric applications remain to be studied, more complex materials may prove even more promising.

True ternary compounds, in which each of three elements occupies distinct crystallographic sites, have hardly been examined for thermoelectric properties even though there are vastly more ternary compounds compared to the number of binary compounds. A few systems have begun to be studied, however, and some of these are described below.

Marchuk et al [23] indicate $Mn_4Al_3Si_5$ may be of interest based on its unusual transport properties. The Hall coefficient (R_H) is

small such as found in metals, but the magnitude of the Seebeck is much larger than typical of metals. At about 600 K, the Seebeck coefficient reaches a relatively large maximum value of $|S|_{max}$~100 μV/K and has a negative sign. On the other hand, R_H actually passes through zero at about 700 K. Below 700 K even the signs of the Hall and Seebeck coefficients do not agree. Although the reported results yield only ZT< 0.2, these unusual transport properties deserve closer study since they present a challenge to conventional analysis.

Rules for the occurrence of semiconducting behavior have been described by Dashevsky for another class of ternary compounds with the composition ABC with A=Ti, Zr, Hf, V, Nb, and B=Fe, Ru, Os, Co, Rh, Ir, Ni, Pd or Pt, and C=Sn or Sb [28]. Several of these compounds have already been shown to exhibit attractive thermal conductivity and power factor values. Given the high metal content of these compounds (67%), the occurrence of semiconducting behavior at all is of some interest.

Macklin and Moseley have surveyed available literature on the copper oxide based high temperature superconductors [29, 30], a class of materials for which much literature is available.. They concluded that the highest ZT achieved was about 0.06. Mason's analysis indicates significant improvement in ZT for the copper oxides is unlikely, unless the thermal conductivity can be substantially reduced [31]. The basic problem with these materials is that they have relatively low carrier mobilities.

UNCONVENTIONAL SEMICONDUCTORS

The band-conduction picture treats each of the electrons as essentially independent of the other electrons as well as the independent of the phonons. The independent electron assumption is not always sufficient and transport in many semiconductors is not well described by the conventional criteria described above. While the best thermoelectric materials known are well described by conventional band-conduction, some unconventional materials actually have reasonable ZT values in spite of ranking very low by conventional evaluation criteria.

Polaron conductors, for example, are characterized by relatively low carrier mobility values but can exhibit quite substantial ZT values. In a polaronic conductor, the presence of a charge carrier distorts (i.e. polarizes) the surrounding lattice. The coupled motion of a charge carrier with its associated lattice distortion is called a polaron.

n-type β-$FeSi_2$ is a polaronic semiconductor. Conventional estimates suggest that β for n-type β-$FeSi_2$ is about 50 times smaller than β for n-type SiGe alloys [22]. But ZT_{max}≈0.4 for n-type β-$FeSi_2$, less than 3 times smaller than ZT for SiGe. So β-$FeSi_2$ actually has much higher ZT values than expected by conventional criteria. A major appeal of $FeSi_2$ as a thermoelectric material is its low cost. For this reason, considerable work has been devoted to this material, by Birkholz's group [32] in Germany and by Matsubura [33]and several other groups in Japan.

Another intriguing polaronic conductor is B_xC, which has ZT values as large as 0.4-0.5 at high temperatures [15]. This, and several related boron-rich solids, are characterized by small mobility values (about 1 $cm^2/V\text{-}s$ or less) which increase with increasing temperature, high carrier concentration (10^{21} cm^{-3}), and large Seebeck values (100-300 μV/K) which also increase with temperature. Seebeck values are much larger than expected from conventional theory.

The boron carbides are refractory materials composed of light elements and have poor carrier mobilities and relatively high carrier concentration. By conventional judgment, these materials should have high thermal conductivity, low power factor and negligible ZT values. In fact, they have ZT values within a factor of 2-3 of state of the art materials. Further study of thermoelectric effects in materials with strong electron-phonon coupling, such as boron carbide and iron disilicide, appears promising.

Strongly interacting electron systems are also appealing. For example, Slack has suggested that $U_3Pt_3Sb_4$ may be of interest [34]. This, and a number of isostructural compounds such as

$Ce_3Pt_3Bi_4$, represents an entirely new class of semiconductor known as a "heavy fermion semiconductor." The name "heavy fermion" reflects the unusual electronic properties of these materials, which behave as if the carriers have effective masses many times greater than typical of ordinary semiconductors. The theory of heavy fermion semiconductors is only now being worked out, but the formation of an energy gap is associated with the *f*-orbitals from the lanthanide or actinide element [35].

While much remains unknown about heavy fermion materials, they typically have enhanced Seebeck coefficients due to the large effective mass of the carriers. A recent survey of heavy fermion materials identified several candidate compounds which may be of interest, including $(Ce_{1-x}La_x)Ni_2$, $(Ce_{1-x}La_x)In_3$, $CePd_3$, and $CeInCu_2$ [36].

As a final example of unconventional semiconductors, consider organic materials and polymers in particular. Some organic conductors exhibit such extraordinary properties that perhaps closer attention is justified. Polyacetylenes, for example, have been doped to conductivity values higher than many good metals [37] and even higher values may yet be possible. At lower doping and conductivity levels, Seebeck values over 1000 μV/K have been observed [38]. The low cost and great chemical variability of organic conductors make them attractive candidates, even though competitive ZT values have not been observed to date in these materials.

HETEROSTRUCTURES

The advent of modern semiconductor fabrication techniques enables the manufacture of materials and structures with properties never previously possible. But today, theoretical and experimental attempts to apply these techniques to engineering the thermal and thermoelectric properties of materials is still in its infancy.

At low temperatures and in small conductors, quantum effects become very important and both the Seebeck coefficient and thermal conductance become quantized in this regime [39]. This type of study on very simple and well controlled quantum point contacts provides confidence that theory is capable of describing transport under even very extreme conditions. Now, attention is turning to more complex systems.

Several reports have appeared studying both experimental and theoretical aspects of thermopower in heterostructures, but only a few specifically address the thermoelectric figure of merit. Anatychuk et al. discuss non-equilibrium between the carrier temperature and the lattice temperature in small thermoelements [40]. Balmush et al. [41] and Dashevsky et al. [42] have extended the conventional description of p-n junctions to conditions with temperature gradients and including non-linear effects such as the Benedicks emf.

Moizhes and Nemchinsky [43] have described a novel inhomogeneous materials approach. Energy barriers are placed in the current path which allow carriers above the Fermi level to pass and block the passage of carriers below the Fermi level. In this scheme, the Seebeck coefficient and figure of merit are improved in the direction perpendicular to the plane of the energy barriers. Each of these studies describe unique and potentially significant methods of achieving higher ZT values.

Particularly noteworthy, however, are calculations by Hicks and Dresselhaus on the thermoelectric figure of merit in one [44] and two [45] dimensional quantum well structures. They estimate that two dimensional quantum well structures of Bi_2Te_3-based materials may have thermoelectric figure of merit values up to 13 times greater than found in analogous bulk materials. Another factor of 2 improvement may be possible in a one dimensional structure.

The enhancements suggested by Hicks and Dresselhaus are based on modifying the electronic density of states. Other beneficial effects are also possible with heterostructures, such as mobility enhancements and increased phonon scattering.

METALS

Metals generally have low Seebeck values due to their high degeneracy and for this reason are routinely considered to be poor thermoelectric materials. There is really nothing to be done with low Seebeck materials because the Weidemann-Franz law does place an upper limit on ZT:

$$ZT \le \frac{S^2}{L_o\left(\frac{k}{e}\right)^2} \qquad (2)$$

where L_o is a constant between 2 and 4. Even under the most favorable circumstances (λ_{ph}=0, acoustic scattering and nondegeneracy), the Seebeck coefficient must be at least 122 μ V/K to reach ZT=1. So, if S cannot exceed 122 μV/K then no further examination is required.

There is no proof, however, that metals *must* have low Seebeck coefficient values. Indeed, solid solutions of metals with different valences can have surprisingly large Seebeck values. $Cu_{0.5}Ni_{0.5}$, for example, reaches S=73 μV/K at 1200 K [46]. If simple, random metal alloys can have Seebeck values this large, can engineered systems such as metallic multilayers be designed with enhanced values? At present, there appears to be no experimental or theoretical evidence for Seebeck enhancement in metallic multilayer systems. But it seems unlikely that the random atomic arrangement of alloys is actually the best of all possible atomic arrangements. Theoretical studies in this area are of considerable interest.

VERY LOW TEMPERATURES

Kapitulnik has suggested that large ZT values may be realized at very low temperatures [47]. In conventional terms, $\lambda_{ph} \sim T^3$ at very low temperatures so β approaches infinity as $T \to 0$. With proper control of the carrier concentration to yield high Seebeck coefficient values, certain materials are thought to be capable of providing efficient cooling at temperatures below 4 K. Experimental verification of this prediction could provide a practical alternative for refrigeration at very low temperatures, but more importantly would demonstrate the principle that very large ZT values are actually possible.

SUMMARY

This survey illustrates that there are a great many materials which have not been evaluated for thermoelectric performance. There will be considerable disagreement about ranking which of these options are the most promising or selecting which option to pursue first. Also, there can be no denying that most of these materials will turn out to have low ZT. But the shear number and variety of possibilities suggests real progress is reasonably likely.

Progress, however, will not be easy. The technical skills required to pursue preparation of bulk samples, for example, are rather different from the skills required to prepare good quality superlattices. New preparation and measurement techniques are needed so that many materials and structures can be studied. Also, new analytical techniques are needed to ensure that promising options are not eliminated prematurely and to ensure that too much effort is not wasted pursuing dead ends.

A particularly difficult challenge in the evaluation of new ideas is the "horizon effect." If ample data and reliable models are available, the "horizon" is far away and one can see quite far into the future. Materials such as SiGe and Bi_2Te_2 have quite distant horizons and we can see rather clearly that only limited improvements (certainly less than ZT=2) are possible for these materials, even in principle. For most of the suggestions described in this survey, however, the horizon is much closer and predictions are much less reliable.

It could be, for example, that high quality samples of Mo_6Te_8 will behave as conventional semiconductors, but have poor mobility values. Or it could be that the mobility values are not small, in which case further studies are warranted. This is the "horizon effect": it is absolutely impossible to know the results of good experiments before they are performed. Progress demands performing the studies anyway and proceeding even when most of the results are discouraging. Typically, sponsors will be the first to become discouraged and it will be critical to remind them that success depends on examining *many* ideas.

The potentially enormous impact of high efficiency thermoelectric devices on the environment and economy, combined with the large number of possible new thermoelectric materials suggests an exciting future for thermoelectric research and development. As the examples discussed here suggest, however, the greatest challenge is not the generation of plausible ideas, but the rapid and accurate evaluation of those ideas.

ACKNOWLEDGMENT

The work described in this paper was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

REFERENCES

[1] P.E. Snyder, Chemical and Engineering News, March 13, 1961, pp.102-112.

[2] C. Zener, *Proc. 13th Annual Power Sources Conf.*, 28-30 April, 1959 (US Army Signal Research and Development Laboratory, Fort Monmouth, NJ, 1959).

[3] C. B. Vining, "A model for the high-temperature transport properties of heavily doped n-type silicon-germanium alloys," J. Appl. Phys., 69(1), pp. 331-341 (1991).

[4] C. B. Vining, "A model for the high temperature transport properties of heavily doped p-type silicon-germanium Alloys," *Modern Perspectives on Thermoelectrics and Related Materials*, MRS Symp. Proc. Vol. 234, edited by D.D. Allred, C.B. Vining, and G.A Slack, (Materials Research Society, Pittsburgh, Pennsylvania, 1991) 95-104.

[5] D.P. White and P.G. Klemens, "Thermal conductivity of thermoelectric $Si_{0.8}Ge_{0.2}$ alloys," J. Appl. Phys. 71(9) (1992) 4258-4263.

[6] G.A. Slack and M.A. Hussain, "The maximum possible conversion efficiency of silicon-germanium generators," J. Appl. Phys. 70(5) (1991) 2694-2718.

[7] J.P. Fleurial, "Thermal and electrical transport properties modeling of Bi_2Te_3-based alloys," *XI Int. Conf. on Thermoelectrics*, ed. K. R. Rao (University of Texas at Arlington, Arlington, Texas, 1992) 276-280.

[8] C. B. Vining, "The thermoelectric limit ZT~1: fact or artifact," *XI Int. Conf. on Thermoelectrics*, ed. K. R. Rao (University of Texas at Arlington, Arlington, Texas, 1992) 276-280.

[9] C.A. Clark, *The Ghost from the Grand Banks* (Bantam Books, New York, 1990).

[10] A.F. Ioffe, *Semiconductor Thermoelements and Thermoelectric Cooling*, (Infosearch, London, 1957).

[11] D.M. Rowe and C.M. Bhandari, *Modern Thermoelectrics* (Reston Publishing Co., Reston, VA, 1983).

[12] G.A. Slack, "The thermal conductivity of nonmetallic solids," Sol. St. Phys. 34 (1974) 1-71.

[13] G.A. Slack, "New materials and performance limits for thermoelectric cooling," *Handbook of Thermoelectrics*, ed. D.M. Rowe (CRC Press, London, to be published).

[14] D. Emin, "Icosahedral boron-rich solids as refractory semiconductors," *Novel Refractory Semiconductors*, MRS Symp. Proc. Vol. 97, edited by D. Emin, T. L. Aselage, and C. Wood, (Materials Research Society, Pittsburgh, Pennsylvania, 1987) 3-16.

[15] C. Wood, "Refractory semiconductors for high temperature thermoelectric energy conversion," *Novel Refractory Semiconductors*, MRS Symp. Proc. Vol. 97, edited by D. Emin, T. L. Aselage, and C. Wood, (Materials Research Society, Pittsburgh, Pennsylvania, 1987) 335-346.

[16] C.B. Vining and C.E. Allevato, "Intrinsic thermoelectric properties of single crystal Ru_2Si_3," *Xth Int. Conf. on Thermoelectrics*, ed. D.M. Rowe, (Babrow Press, Cardiff, UK, 1991) 167-173.

[17] C.E. Allevato and C.B. Vining, "Phase diagram and electrical behavior of silicon-rich iridium silicide compounds," J. Alloys and Compounds, in press.

[18] A. Borshchevsky and J.P. Fleurial, "Properties of semiconducting Ru_2Ge_3," *XIIth Int. Conf. on Thermoelectrics*, this conference.

[19] T. Caillat, A. Borshchevsky, and J.P. Fleurial, "Search for new high temperature thermoelectric materials," *27th Intersociety Energy Conversion Conference* (Society of Automotive Engineers, 1992) 3.499-3.503.

[20] T. Caillat, A. Borshchevsky, and J.P. Fleurial, "Investigations of several new advanced thermoelectric materials," Thermoelectric properties of a new semiconductor: $RuSb_2$," *28th Intersociety Energy Conversion Conference* (American Chemical Society, 1993) 1.245-1.248.

[21] T. Caillat, A. Borshchevsky and J.P. Fleurial, "Novel transition metal compounds with promising thermoelectric properties," *XIIth Int. Conf. on Thermoelectrics*, this conference.

[22] C.B. Vining, "Thermoelectric properties of silicides," *Handbook of Thermoelectrics*, ed. D.M. Rowe (CRC Press, London, to be published).

[23] N. D. Marchuk, V. K. Zaitsev, M. I. Fedorov, A. E. Kaliazin, "Thermoelectric properties of some cheap n-type materials," *8th Int. Conf. on Thermoelectric Energy Conversion*, edited by H. Scherrer and S. Scherrer (Institute National Polytechnique de Lorraine, Nancy, France, 1989) 210-214.

[24] Y. Noda, H. Kon, Y. Furukawa, I.A. Nishida, and K. Masumoto, "Temperature dependence of thermoelectric properties of $Mg_2Si_{0.6}Ge_{0.4}$," Materials Trans., JIM, 33(9) (1992) 851-855.

[25] J. Evers, G. Oehlinger, and H. Meyer, "Semiconducting behavior of $RuGa_2$," Mat. Res. Bull. 19 (1984) 1177-1180.

[26] H. J. Juretschke and R. Steinitz, "Hall effect and electrical conductivity of transition-metal diborides," J. Phys. Chem. Solids 4 (1958) 118-127.

[27] V.M. Anshchik and N.N. Dorozhkin, "Electronic Structure of TiB_2 and ZrB_2," Phys. Stat. Sol. (b) 160 (1990) 173-177.

[28] Z. M. Dashevski, L.L. Dudkin, V.B. Eliseev and R.V. Skolozdra, "New materials for thermoelectric generators," *Xth Int. Conf. on Thermoelectrics*, ed. D.M. Rowe, (Babrow Press, Cardiff, UK, 1991) 186-190.

[29] W. J. Macklin and P. T. Moseley, "On the use of oxides for thermoelectric refrigeration," Mat. Sci. and Engin. B7 (1990) 111-117.

[30] W. J. Macklin and P. T. Moseley, "Reply to comment on 'On the use of oxides for thermoelectric refrigeration'," Mat. Sci. and Engin. B10 (1991) 260.

[31] T. O. Mason, "Comment on 'On the use of oxides for thermoelectric refrigeration'," Mat. Sci. and Engin. B10

(1991) 257-260.

[32] U. Birkholz, E. Gross, M. Riffel, H. Toth, U. Stohrer and W. Wittmer, "Measurement of the efficiency of a HMS-$FeSi_2$ Thermoelectric Generator," *XIth Int. Conf. on Thermoelectrics*, ed. K.R. Rao (University of Texas at Arlington, Arlington, Texas, 1992) 51-54.

[33] K. Matsubara, T. Miki, K. Nagao, K. Kishimoto, O. Nakanshi, O. Ueda, and K. Jujii, "Characterization and thermoelectric properties of new β-$FeSi_2$ ceramics developed by a RF-plasma processing in O_2 and SiH_4 gases," *XIth Int. Conf. on Thermoelectrics*, ed. K.R. Rao (University of Texas at Arlington, Arlington, Texas, 1992) 24-27.

[34] G.A. Slack, "Some new materials for thermoelectric cooling," *1st National Thermogenic Cooler Conference*, ed. S. Horn (Center for Night Vision and Electro-Optics, Fort Belvoir, Virgina, 17 September 1992) 171-195.

[35] P. S. Riseborough, "Theory of the dynamic magnetic response of $Ce_3Bi_4Pt_3$: A heavy fermion simiconductor," Phys. Rev. **B45**(24) (1992) 13984-13995.

[36] B. Louie and R. Radebaugh, "Survey of heavy fermions for thermoelectric refrigeration," *1st National Thermogenic Cooler Conference*, ed. S. Horn (Center for Night Vision and Electro-Optics, Fort Belvoir, Virgina, 17 September 1992) 140-170.

[37] A. B. Kaiser, "Metallic behavior in highly conducting polymers," Synthetic Metals, **45** (1991) 183-196.

[38] C. O. Yoon, B. C. Na, and Y. W. Park, "Thermoelectric power and conductivity of the stretch-oriented polyacetylene film doped with $MoCl_6$," Synthetic Metals, **41-43** (1991) 125-128.

[39] L. W. Molenkamp, T. Gravier, H. van Houten, O. J. A. Buijk, and M. A. A. Mabesoone, "Peltier coefficient and thermal conductance of a quantum point contact," Phys. Rev. Lett. **68**(25) (1992) 3765-3768.

[40] L. I. Anatychuk, L.P. Bulat, D.D. Nikirsa, and V.G. Yatsyuk, "Influence of size effects on the properties of cooling thermoelements," Sov. Phys. Semicond. **21**(2) (1987) 206-207.

[41] I.I. Balmush, Z.M. Dashevskii, and A.I. Kasiyan, "Distribution of potentials in a p-n junction semiconductor structure in the presence of a temperature gradient," Sov. Phys. Semicond. **20**(8) (1988) 968-969.

[42] Z.M. Dashevsky, A.I. Kasiyan, and N.V. Kolomoets, "Thermoelectric properties of p-n junctions and heterojunctions," *Eight International Conference on Thermoelectric Energy Conversion*, (Insitut National Polytechnique de Lorraine, 1989) 200-204.

[43] B. Y. Moizhes and V. A. Nemchinsky, "Nontraditional methods of improvement of the thermoelectric figure-of-merit based on size effects," *Xth Int. Conf. on Thermoelectrics*, ed. D.M. Rowe, (Babrow Press, Cardiff, UK, 1991) 232-235.

[44] L. D. Hicks and M. S. Dresselhaus, "Thermoelectric figure of merit of a one-dimensional conductor," Phys. Rev. **B47** (1993) 16631-16634.

[45] L. D. Hicks and M. S. Dresselhaus, "Effect of quantum-well structures on the thermoelectric figure of merit," Phys. Rev. **B47** (1993) 12727-12731.

[46] C. Y. Ho, M. W. Ackerman, and K. Y. Wu, "Thermal conductivity of copper-nickel and silver-palladium alloy systems," Thermal Conductivity **14**, edited by P. G. Klemens and T. K. Chu. (Plenum Press, New York, 1976) 233-244.

[47] A. Kapitulnik, "Thermoelectric cooling at very low temperatures," Appl. Phys. Lett **60**(2) (1992) 180-182.