Compatibility factor of segmented thermoelectric generators based on quasicrystalline alloys

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In this work we present a prospective study on the possible use of certain quasicrystalline alloys in order to improve the efficiency of segmented thermoelectric generators. To this end, we obtain a closed analytical expression for their compatibility factor [G. J. Snyder and T. S. Ursell, Phys. Rev. Lett. 91, 148301 (2003)]. By comparing our analytical results with available experimental data we conclude that a promising high temperature material, compatible with benchmark thermoelectric materials, can be found among AlPdMn based icosahedral quasicrystals.

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The efficiency of a thermoelectric device depends on the transport properties of the constituent materials and the temperature difference between the hot and cold sides, which sets its Carnot upper limit. Evaluation of new materials for thermoelectric applications is usually made in terms of the dimensionless figure of merit,

\[ ZT = \frac{s \alpha^2 T}{\kappa_e + \kappa_{ph}}, \]

where \( T \) is the temperature, \( s(T) \) is the electrical conductivity, \( \alpha(T) \) is the Seebeck coefficient, \( \kappa_e(T) \) is the charge carrier contribution to the thermal conductivity, and \( \kappa_{ph}(T) \) is the lattice contribution to the thermal conductivity. When considering segmented devices one should also consider the compatibility factor defined by

\[ s = \frac{\sqrt{1 + ZT} - 1}{\alpha T}, \]

since materials with dissimilar \( s \) values cannot be efficiently combined in that case. The thermoelectric compatibility of several materials of current technological interest has been recently reviewed, concluding that a semimetallic material with high \( p \)-type thermopower is required for development of segmented generators.\(^2\)

In the last few years it has been progressively realized that quasicrystals (QC)s deserve some attention as potential thermoelectric materials (TEMs), since they naturally fulfill the Slack’s requirements for a material belonging to the “electronic crystal/phonon glass” class.\(^3-7\) Quite interestingly, relatively high, positive thermopower values (+100 \(-120 \mu \text{V} \text{K}^{-1}) have been reported for representatives of the icosahedral AlPdMn and AlPdRe families in the temperature range 300–600 K.\(^8-10\) The main aim of this paper is to show that, by a judicious choice of sample’s stoichiometry,\(^11\) suitable candidates for a high temperature material, compatible with PbTe, (AgSbTe\(_2\))\(_{0.15}\)(GeTe)\(_{0.85}\) (TAGS) or skutterudites, may be found among the AlPd(Re, Mn) quasicrystalline alloys.

To this end, let us start by briefly summarizing some relevant experimental data. In Tables I and II we list the figure of merit and compatibility factors of different QCs as reported in the literature. At room temperature we observe that the largest \( s \) values are comparable to those observed in usual TEMs, like Bi\(_2\)Te\(_3\) or SiGe (\( s \approx 1 \text{V}^{-1})\).\(^2\) At higher temperatures the most promising QC is i-AlPdMn, which exhibits an \( s \) factor larger than those reported for SiGe (\( s \approx 1 \text{V}^{-1})\) and PbTe (\( s \approx 1.2 \text{V}^{-1})\), and approaches that of TAGS (\( s \approx 2.7 \text{V}^{-1})\) at \( T=550 \text{K} \). On the other hand, the \( s \) factor corresponding to AlPdRe samples is larger at room temperature (where it exhibits a lower \( ZT \) value) than it is at higher temperatures (albeit it exhibits a larger \( ZT \) value). This result highlights the importance of properly balancing the \( ZT \) and \( s \) contributions in designing optimized devices.

In order to gain some theoretical insight into this question we obtain a closed analytical expression for the compatibility factor within the Kubo-Greenwood framework.\(^15\) The central information quantities are the kinetic coefficients,

\[ \mathcal{L}_c(T) = (-1)^{ij} \int \sigma(E)(E - \mu)^{ij-2} \left( -\frac{\partial f}{\partial E} \right) dE, \]

where \( f(E, \mu, T) \) is the Fermi-Dirac distribution function. In this formulation all the microscopic details of the system are included in the \( \sigma(E) \) function. As a first approximation we will assume \( \mu(T) = E_F \). Then, by expressing (3) in terms of the scaled variable \( x = (E - \mu)/k_B T \), the transport coefficients can be written as\(^6,16\)

\[ \sigma(T) = \frac{J_0}{4}, \]

\[ \alpha(T) = -\frac{k_B J_1}{|e| J_0}, \]

\[ \kappa_e(T) = \frac{k_B T}{4e^2} \left( J_2 - \frac{J_1^2}{J_0} \right), \]

where we have introduced the reduced kinetic coefficients,

\[ J_n(T) = \int x^n \sigma(x) \text{sech}^2(x/2) dx. \]

In previous works\(^16-18\) it has been shown that the experimental \( \sigma(T) \) and \( \mathcal{L}(T) \) curves of several QCs can be consistently described in terms of the two-Lorentzian spectral conductivity function.\(^19,20\)
TABLE I. Room temperature thermopower, figure of merit, and compatibility factors for samples belonging to different quasicrystalline families.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ref.</th>
<th>$\alpha$ ((\mu\text{V K}^{-1}))</th>
<th>$ZT$</th>
<th>$s$ (V(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCuFe</td>
<td>12</td>
<td>+44</td>
<td>0.01</td>
<td>0.38</td>
</tr>
<tr>
<td>AlCuRuSi</td>
<td>12</td>
<td>+50</td>
<td>0.02</td>
<td>0.66</td>
</tr>
<tr>
<td>CdYb</td>
<td>13</td>
<td>+16</td>
<td>0.01</td>
<td>1.04</td>
</tr>
<tr>
<td>AlPdRe</td>
<td>14</td>
<td>+95</td>
<td>0.07</td>
<td>1.21</td>
</tr>
<tr>
<td>AlPdMn</td>
<td>5</td>
<td>+85</td>
<td>0.08</td>
<td>1.54</td>
</tr>
</tbody>
</table>

\[
\sigma(E) = \frac{B}{\pi} \left[ \frac{\gamma_1}{(E - \delta_1)^2 + \gamma_1^2} + A \frac{\gamma_2}{(E - \delta_2)^2 + \gamma_2^2} \right]^{-1},
\]

(8)

where $B$ is a scale factor expressed in $\Omega^{-1}$ cm\(^{-1}\) eV\(^{-1}\) units, and the Lorentzian peaks are characterized by their height, $(\gamma_i)^{-1}$, and their position, $\delta_i$, with reference to the Fermi level. The overall behavior of this curve agrees well with the experimental results obtained from tunneling and point contact spectroscopy measurements, where the presence of a dip feature of small width (20–60 meV, narrow Lorentzian), superimposed onto a broad (0.5–1 eV, broad Lorentzian), asymmetric pseudogap has been reported.\(^{21–25}\) The relative importance of each spectral feature in the overall electronic structure is tuned through the weight factor $A$ in Eq. (8).

Making use of Eq. (8) into Eq. (7) we get\(^{16}\)

\[
\begin{pmatrix}
  J_0 \\
  J_1 \\
  J_2
\end{pmatrix} = 4 \sigma_0 \begin{pmatrix}
  1 & 0 & 0 & 0 & 0 & J_0 \\
  0 & 2 \xi_1 & 0 & 2 \xi_3 & 0 & 2 J_1 \\
  \frac{\pi^2}{3} & 0 & \frac{21}{5} \xi_2 & 0 & \frac{\pi^2}{3} J_2 & 0
\end{pmatrix}
\times
\begin{pmatrix}
  1 \\
  bTk_B \\
  bT^2 \\
  b^2T^3k_B \\
  b^2T^4 \\
  b^2T^5k_B \\
  b^2T^6
\end{pmatrix},
\]

(9)

where $\sigma_0 = \sigma(T = 0)$ is the residual electrical conductivity, and $b = e^2L_0$, where $L_0 = \pi^2k_B^2/3e^2 = 2.44 \times 10^{-8}$ V\(^2\) K\(^{-2}\) is the Lorenz number. The phenomenological coefficients $\xi_i$ as well as the parametric functions $j_i = j_i(\xi_3, \xi_1)$, are directly related to the sample’s electronic structure. In particular, we have\(^{17}\)

\[
\xi_i = \left. \frac{1}{2} \left( \frac{d \ln \sigma(E)}{dE} \right) \right|_{E_F},
\]

(10)

so that, according to Mott’s expression, $\xi_1$ can be derived from the low temperature slope, $\alpha$, of the experimental $\alpha(T)$ curve as\(^{18}\)

\[
\xi_1^{\exp} = -20.5 a[\mu\text{V K}^{-2}] \text{ (eV)}^{-1}.
\]

(11)

Making use of Eq. (9) into Eqs. (4)–(6) and Eqs. (1) and (2) we get

\[
s = -Q \left[ \sqrt{\frac{1}{1 - R}} - 1 \right] \text{ V}^{-1},
\]

(12)

where

\[
Q(T) = \frac{P_0}{2bT^2P_1},
\]

(13)

\[
R(T) = \frac{2P_1}{Q(P_2 + \Psi)},
\]

(14)

$\psi(T) = \kappa_{ph}(T)/\sigma_0L_0T$, and we have introduced the polynomials

\[
P_0(T) = 1 + (2\xi_1^2 + \Omega)y + \xi_1\Omega^2 + J_0y^3,
\]

(15)

\[
P_1(T) = \xi_1 + \xi_1y + j_1y^2,
\]

(16)

\[
P_2(T) = 1 + \frac{21}{5}(2\xi_1^2 + \Omega)y + j_2y^2.
\]

(17)

where

\[
\Omega = \frac{1}{2} \left( \frac{d^2\ln \sigma(E)}{dE^2} \right)_{E_F},
\]

(18)

measures the curvature of $\sigma(E)$ at the Fermi level.\(^{17}\) At a given temperature Eq. (12) can be regarded as a parametric function of the different phenomenological coefficients, i.e., $s(\xi)$. We note that the thermal conductivity of QCs is mainly determined by the lattice contribution rather than the charge carriers in the considered temperature range.\(^{26}\) Therefore, we can confidently assume $\kappa_{ph} \approx k$ in Eq. (14), where $k = \kappa_e + \kappa_{ph}$ is the experimentally measured total thermal conductivity.

In Fig. 1 we compare the room temperature compatibility factors of $i$-AlPdRe [$\kappa = 0.7$ W m\(^{-1}\) K\(^{-1}\), $\sigma_0 = 30$ (\(\Omega\) cm\(^{-1}\)) and $i$-AlPdMn [$\kappa = 1.6$ W m\(^{-1}\) K\(^{-1}\), $\sigma_0 = 740$ (\(\Omega\) cm\(^{-1}\)), (Ref. [5]) as a function of $\xi_1$. These curves are derived from Eqs. (12)–(17) with $\Omega=400$ (eV)\(^{-2}\) (Ref. 17); $\xi_1 = -2910$ (eV)\(^{-1}\), $\xi_2 = 17000$ (eV)\(^{-2}\), $J_0 = 10^5$ (eV)\(^{-4}\), $J_1 = 130000$ (eV)\(^{-4}\), and $J_2 = -30000$ (eV)\(^{-4}\). In order to check the feasibility of the adopted model parameters we have determined the value of the $\xi_1$ coefficient corresponding to the
 prospective residual conductivities, determining the curves is due to the significant difference between their respective residual conductivities, determining the $\Sigma$ value in Eq. (14). In the inset of Fig. 1 we plot the corresponding $ZT(\tilde{\xi})$ curves, which exhibit a deep minimum, flanked by two maxima. According to Eq. (2), both $ZT$ and $s$ vanish at $\tilde{\xi}_0 = +5.76$ (eV)$^{-1}$. Consequently, QCs can exhibit $p$-type ($\tilde{\xi}_1 < \tilde{\xi}_0$) or $n$-type ($\tilde{\xi}_1 > \tilde{\xi}_0$) thermopowers depending on the $\tilde{\xi}_1$ value which, according to Eq. (10), is very sensitive to the sample’s electronic structure near $E_F$. In fact, the electronic structure of QCs is characterized by the presence of a narrow pseudogap in the density of states close to the Fermi level. Thus, when $E_F$ is located at the left (right) of the pseudogap’s minimum $\tilde{\xi}_1$ takes negative (positive) values, and its magnitude is directly related to the $\sigma(E)$ slope. Therefore, the $\tilde{\xi}_1$ value can be controlled by changing the sample stoichiometry, hence shifting $E_F$ in a scale of a few meV. In this way, we can confidently expect that larger values of the room temperature compatibility factor, close to $s = 2.0$ (eV)$^{-1}$ may be attained in AlPdMn QCs with $\xi_1 = -15$ (eV)$^{-1}$. In addition, a significant enhancement of the $s$ factor is expected for AlPdMn QCs at higher temperatures, as it is shown in Fig. 2. The value $s(\xi_1^{\text{exp}}) = 3.7$ (eV)$^{-1}$ (dotted line) is better than that reported for both TAGS and skutterudites at $T = 550$ K. Nonetheless, we should keep in mind that our rigid band model, which does not take into account the temperature dependence of $E_F$, will be hardly applicable at temperatures beyond the Debye one ($\Theta_D = 450$ K for AlPdMn). Further experimental and theoretical work is then appealing in order to fully exploit the unusual transport properties of quasicrystalline alloys in thermoelectric devices.

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FIG. 1. (Color online) Room temperature dependence of the compatibility factor (main frame) and the thermo-electric figure of merit (inset) as a function of the phenomenological coefficient $\tilde{\xi}_1$ for i-AlPdRe (dashed line), and i-AlPdMn (solid line).

FIG. 2. (Color online) Dependence of the compatibility factor as a function of the phenomenological coefficient $\tilde{\xi}_1$ for i-AlPdRe with $\kappa = 1.2$ Wm$^{-1}$ K$^{-1}$ at $T = 660$ K (dashed line), and AlPdMn with $\kappa = 2.1$ Wm$^{-1}$ K$^{-1}$ at $T = 550$ K (solid line) (Ref. 5).
469 (2002).


