May quasicrystals be good thermoelectric materials?

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(Received 12 June 2000; accepted for publication 11 September 2000)

We present a theoretical analysis of quasicrystals (QCs) as potential thermoelectric materials. We consider a self-similar density of states model and extend the framework introduced in [G. D. Mahan and J. O. Sofo, Proc. Natl. Acad. Sci. U.S.A. **93**, 7436 (1996)] to systems exhibiting correlated features in their electronic structure. We show that relatively high values of the thermoelectric figure of merit, ranging from 0.01 up to 1.6 at room temperature, may be expected for these systems. We compare our results with available experimental data on transport properties of QCs and suggest some potential candidates for thermoelectric applications. © *2000 American Institute of Physics.* [S0003-6951(00)03545-2]

During the last few years we have witnessed a growing interest in searching for high performance thermoelectric materials (TEMs).[1] The efficiency of thermoelectric devices depends on the transport coefficients of the constituent materials and it can be properly expressed in terms of the *figure of merit* (FOM) given by the dimensionless expression $\theta \equiv ZT = T\sigma S^2/(\kappa_e + \kappa_{\mathrm{ph}})$, where T is the temperature, σ is the electrical conductivity, S is the Seebeck coefficient and κ_e and κ_{ph} are the thermal conductivities due to the electrons and lattice phonons, respectively. The appealing question regarding what electronic structure provides the largest possible FOM was recently addressed by Mahan and Sofo[2] concluding that (i) the best TEM is likely to be found among materials exhibiting a sharp singularity (Dirac delta function) in the density of states (DOS) close to the Fermi level, and (ii), in that case, the effect of the DOS background contribution onto the FOM value may be quite dramatic: The FOM value being inversely proportional (in a marked nonlinear way) to the DOS value near the singularity.

Quite interestingly the electronic structure of *quasicrystalline alloys* may satisfy these requirements in a natural way. In fact, thermodynamically stable quasicrystals (QCs) of high structural quality[3] exhibit unusual composition and temperature dependences of their transport coefficients,[4] which resemble more semiconductorlike than metallic character.[5] Theoretical efforts aimed to understand these anomalous transport phenomena have rendered two main results: (i) the existence of *spiky features in the DOS* near the Fermi level,[6] and (ii) the presence of a *pronounced pseudogap at the Fermi level*.[7] The presence of a pseudogap has received strong experimental support during the last decade.[8,9] The physical origin of a spiky fine structure in the DOS may be related to the structural quasiperiodicity of the substrate via a hierarchical cluster aggregation resonance[10] or through *d*-orbital resonance effects.[11] These spiky features have remained quite elusive to experimental confirmation,[12] although some recent works support their possible physical existence.[13]

At first sight it may seem surprising to propose a metallic alloy as a suitable TEM. However, this possibility has been recently discussed by some authors on the basis of the peculiar transport properties of QCs.[14] In fact, their electrical conductivity[4]: (i) is remarkably low, (ii) it steadily increases as the temperature increases, and (iii) it is extremely sensitive to minor variations in the sample composition. This sensitivity to the sample stoichiometry is also observed in other transport parameters, such as the Hall or Seebeck coefficients, and resembles doping effects in semiconductors. Consequently, QCs are marginally metallic and should be properly located at the *borderline between metals and semiconductors*.[5] In addition, the *thermal conductivity* of QCs is *unusually low* for a metallic alloy and it is mainly determined by the lattice phonons (rather than the charge carriers) over a wide temperature range.[15] The low thermal conductivity of QCs is particularly appealing in the light of Slack's phonon-glass/electron-crystal description,[16] as properly highlighted by some recent studies on thermoelectric properties of QCs.[17]

Inspired by the above considerations, the aim of this letter is to provide a theoretical analysis on the use of QCs as potential TEMs. To this end, we will start by expressing the transport coefficients in the unified way[2,18]

$$\sigma(T) = \int_{-\infty}^{+\infty} dE \left(-\frac{\partial f}{\partial E} \right) \sigma(E), \tag{1}$$

$$S(T) = \frac{1}{e\sigma(T)T} \int_{-\infty}^{+\infty} dE \left(-\frac{\partial f}{\partial E} \right) (E-\mu)\sigma(E), \tag{2}$$

$$\kappa_e(T) = \kappa_0(T) - T\sigma(T)S^2(T), \tag{3}$$

where

$$\kappa_0(T) = \frac{1}{e^2 T} \int_{-\infty}^{+\infty} dE \left(-\frac{\partial f}{\partial E} \right) (E-\mu)^2 \sigma(E) \tag{4}$$

and e is the electron charge, $f(E,T)$ is the Fermi distribution, E is the electron energy, μ is the Fermi level and $\sigma(E)$ is the spectral conductivity, defined as the $T \to 0$ conductivity with the Fermi level at energy E. By expressing Eqs. (1)–(4) in terms of the scaled variable $x \equiv (E-\mu)/k_B T$, where k_B is the Boltzmann constant, the transport coefficients can be rewritten as

$$\sigma(T) = \frac{J_0}{4}, \quad S(T) = \frac{cJ_1}{J_0}, \quad \kappa_e(T) = \frac{c^2 T}{4} \left(J_2 - \frac{J_1^2}{J_0} \right), \tag{5}$$

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where $c \equiv k_B/e \simeq 87\,\mu\mathrm{V\,K}^{-1}$ and

$$J_n \equiv \int_{-\infty}^{+\infty} x^n \,\mathrm{sech}^2(x/2)\sigma(x)dx. \tag{6}$$

Substituting Eq. (5) into the FOM expression we get

$$\theta(x,T) = \frac{\xi}{1-\xi+A}, \tag{7}$$

where $\xi \equiv J_1^2/J_0 J_2$, and $A \equiv 4\kappa_{\mathrm{ph}}(T)/c^2 J_2 T$.

Making use of Eq. (7), Mahan and Sofo[2] found that the Dirac delta function is the only transport distribution function able to maximize the FOM, and also pointed out that when they tried two delta functions in the DOS they obtained lower θ values than with a single one. However, we have found that some interesting situations emerge when the positions of the delta functions and/or their relative strengths are *correlated*.

In fact, let us consider the case where the spectral conductivity can be described in terms of the two peak model given by

$$\sigma(E) \equiv \lambda_1 \delta(E-E_1) + \lambda_2 \delta(E-E_2), \tag{8}$$

where λ_i measure the strength of the δ peaks (in $\Omega^{-1}\,\mathrm{cm}^{-1}$ eV units) and E_i denote their position. The reasons supporting the suitability of our model are twofold. First, in order to make a meaningful comparison with experimental measurements the numerically calculated electronic structure should be modified in order to account for possible phason, finite lifetime and temperature broadening effects. In so doing, it is observed that most finer details in the DOS are significantly smeared out and only the most conspicuous peaks remain in the vicinity of the Fermi level at room temperature.[12] Second, two-band models seem to properly describe the overall temperature dependence of thermopower for realistic icosahedral QCs.[7,19,20] Then, by plugging Eq. (8) into Eq. (7) we get

$$\theta(x_1,x_2,T) = \frac{(x_1 u_1 + x_2 u_2)^2}{(x_1-x_2)^2 u_1 u_2 + a(u_1+u_2)}, \tag{9}$$

with $u_i \equiv \lambda_i\,\mathrm{sech}^2(x_i/2)$, and $a \equiv (4k_B/c^2)\,\kappa_{\mathrm{ph}}(T)$. Now, since QCs are characterized by a long-range quasiperiodic order based on the self-similarity of their structure, we will assume that the two-peak model DOS given by Eq. (8) satisfies the *self-similar transformation*

$$x_2 = \eta x_1 \equiv \eta x_1, \quad \lambda_2 = \eta \lambda_1, \tag{10}$$

where $\eta > 0$ is an inflation ($\eta > 1$) or deflation ($\eta < 1$) factor. Making use of Eq. (10) into Eq. (9) we obtain

$$\theta(x,T) = \eta[p^2(x) + \tilde{a}(T) q(x) \varphi^2(x)]^{-1}, \tag{11}$$

where

$$p(x) \equiv \frac{(1-\eta) r(x)}{1+r^2(x)}, \quad q(x) \equiv \frac{\eta + r^2(x)}{[1+r^2(x)]^2}, \tag{12}$$

$r(x) \equiv \eta \cosh(x/2)\mathrm{sech}(\eta x/2)$, $\varphi(x) \equiv x^{-1}\cosh(x/2)$ and $\tilde{a}(T) \equiv a(T)/\lambda_1$. The optimal electronic structure will be obtained from the extreme condition $\partial\theta/\partial x \equiv 0$, determining the proper positions and strengths of the δ peaks. In so doing, we obtain

TABLE I. Model parameters maximizing the figure of merit along with its corresponding optimum values at room temperature.

x_1	x_2	η	θ_{op} (300 K)
±0.758 58...	±0.758 58...	1.000 00...	
±1.244 04...	±4.106 09...	3.300 61...	0.35–1.60
±5.469 35...	±5.469 35...	1.000 00...	
±6.401 34...	±0.539 69...	0.084 31...	0.01–0.09

$$p^2(x) h(x) \frac{1-r^2(x)}{1+r^2(x)} + \tilde{a}\varphi^2(x)\left[q'(x) + 2q(x)\frac{\varphi'(x)}{\varphi(x)}\right] = 0 \tag{13}$$

with $h(x) \equiv \tanh(x/2) - \eta\tanh(\eta x/2)$, where the prime indicates derivative with respect to the x variable. In the limiting case $\eta = 1$ we have $p(x) = 0$, $q(x) = 1/2$, and $r(x) = 1$, so that Eq. (13) reduces to $\varphi'(x)/\varphi(x) = 0$, which in turn leads to $\tanh(x/2) = 2/x$, yielding the one peak solution $x_0 \simeq 2.399...$ previously obtained by Mahan and Sofo.[2] In this case Eq. (11) takes the form

$$\theta_{\mathrm{op}}(T) = \frac{8(x_0^2-4)}{\dfrac{b}{\lambda_1}\kappa_{\mathrm{ph}}(T)}. \tag{14}$$

Let us now consider the general case. A suitable solution of Eq. (13) for $\eta \neq 1$ is given by the choice $r^2(x) = 1$ and $q(x) = \varphi^{-2}(x)$ which, according to Eq. (11), leads us to the following expression for the optimal FOM:

$$\theta_{\mathrm{op}}(T) = \frac{4\eta}{(1-\eta)^2 + \dfrac{b}{\lambda_1}\kappa_{\mathrm{ph}}(T)}, \tag{15}$$

where $b \equiv (4/c)^2 k_B \simeq 0.182\,\mathrm{MeV\,K\,V^{-2}}$. The condition $r^2(x) = 1$ implies the self-similarity relationship $\eta\cosh(x/2) = \cosh(\eta x/2)$, meanwhile the condition $q\varphi^2 = 1$ leads us to the relationship $\eta = (2x\,\mathrm{sech}(x/2))^2 - 1$. By solving the system formed by these equations we obtain eight possible values for x which are listed in Table I, along with the corresponding η values. In Fig. 1 we compare the FOM curves corresponding to Eqs. (14) and (15) in terms of the auxiliary

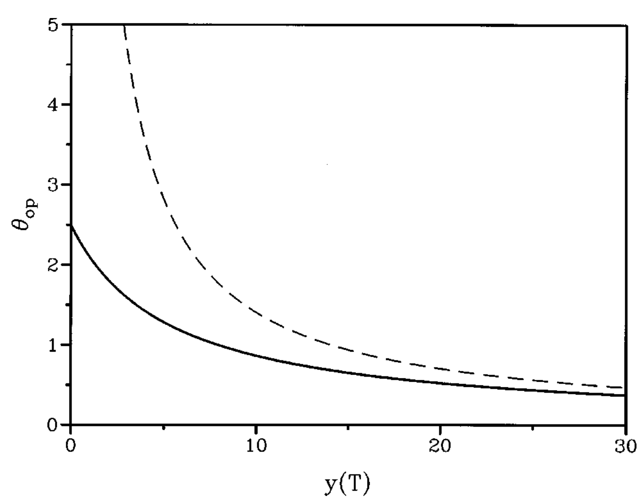

FIG. 1. Comparison between the optimal FOM obtained from the one peak model (dashed line) and the two peak model (solid line) in terms of the temperature dependent auxiliary parameter $y(T) = b\kappa_{\mathrm{ph}}/\lambda_1$. Both curves rapidly converge for high values of y. Note that the unphysical divergence of the Seebeck coefficient at low temperatures, which appears in the one peak model, is conveniently avoided in the two peak one.

TABLE II. Transport coefficient values at room temperature for different QCs, after: (a) Ref. 17, (b) Ref. 8, (c) Ref. 26, and (d) estimated.

Sample	σ (Ω^{-1} cm^{-1})	S (μV K^{-1})	κ (Wm^{-1} K^{-1})	θ (300 K)
AlCuRu	250[b]	27[b]	1.8[d]	0.003
AlCuFe	310[b]	44[b]	1.8[c]	0.01
AlCuRuSi	390[b]	50[b]	1.8[d]	0.02
AlPdMn	650[a]	80[a]	1.6[a]	0.08

parameter $y(T) \equiv b\kappa_{\rm ph}(T)/\lambda_1$. According to *ab initio* calculations, we can confidently take $10^2 \leqslant \lambda_1 \leqslant 10^3\ \Omega^{-1}\,\mathrm{cm}^{-1}\,\mathrm{eV}$.[7,19] Thus, from the experimental thermal conductivities given in Table II, we estimate the interval $3 \leqslant y(300\,\mathrm{K}) \leqslant 33$ as a physically plausible one. Then, making use of Eq. (15) we find that the best FOM (ranging from about $\theta_{\rm op}=0.3$ to $\theta_{\rm op}=1.6$) corresponds to a DOS model with $x_1=\pm 1.244...$, $x_2=\pm 4.106...$ and $\eta=3.3$. On the other hand, the DOS model determined by the values $x_1=\pm 6.401...$, $x_2=\pm 0.539...$ and $\eta=0.084...$ yields FOM values which are comprised in the interval $0.01 \leqslant \theta_{\rm op} \leqslant 0.09$. These FOM values are significantly high for a metallic alloy and compare well with the values obtained for other potential TEMs.[21]

How well do our obtained FOM values compare with experimental figures for QC samples? In Table II we list pertinent data obtained from the literature, and we can observe a continuous progression towards increasing values of θ(300 K) for higher quality QCs. In addition, the best FOM obtained so far is comparable to that obtained within our framework for the DOS structure given by $x_1=\pm 6.401...$, $x_2=\pm 0.539...$ and $\eta=0.084...$. Consequently, from the data listed in the last column of Table I, it seems reasonable to expect that, by a judicious choice of both sample composition and processing and annealing conditions, higher FOM values may be obtained. Although such a possibility is just a tentative one, we deem it is based on ground physical basis.

To conclude we propose two families of recently discovered QCs which may play a promising role as TEMs. The first one is the rare-earth based group of stable icosahedral phases in the system ZnMg(Y, Gd, Tb, Dy, Ho, Er).[22] The presence of *f*-type orbitals in these samples gives rise to the presence of *pronounced narrow peaks* in the DOS close to the Fermi level. Quite interestingly, the reported value of $\sigma(T)$ for these samples is one order of magnitude higher than those observed for other QC systems.[23] Another promising candidate might be the dodecagonal QC chalcogenide phase discovered in the TaTe system.[24] By all indications, these tellurides seem to have electrical properties being characteristic of small band gap semiconductors.[25]

In summary, in this work we provide a theoretical analysis on the use of QCs as potential TEMs by considering the role that self-similar correlated features in their electronic structure may play in their transport coefficients. In this way, we show that relatively high values of the FOM (ranging from 0.01 up to 1.6 at room temperature) may be expected and suggest two promising candidates for further studies.

The author warmly thanks T. Grenet, B. Harbrecht, C. Landauro, Z. M. Stadnik, A. L. Pope, A. P. Tsai, and T. M. Tritt for interesting comments and M. V. Hernandez for a critical reading of the manuscript. This work is supported by UCM through Project No. PR64/99-8510.

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