Theoretical prospective of quasicrystals as thermoelectric materials

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In this work we present a theoretical study on the possible use of quasicrystals as potential thermoelectric materials. By considering a suitable model for the spectral conductivity we show that high values of the thermoelectric figure of merit, beyond the practical upper limit $ZT=1$, may be expected for certain quasicrystalline alloys. We also study their performance at different working temperature ranges, favoring low temperature thermoelectric applications for these materials. By comparing our analytical results with available experimental data on the transport coefficients of different quasicrystalline families, we suggest the icosahedral Cd-Yb and the dodecagonal Ta-Te binary phases as two promising candidates for further research.

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I. INTRODUCTION

Thermodynamically stable quasicrystals[1,2] (QC's) exhibit quite unusual transport properties. In fact, a broad collection of different transport anomalies have been reported during the last decade, progressively leading to a condensed matter *paradigm evolution* for this new class of ordered structures.[3] Thus, anomalous behaviors in the temperature dependence of electrical conductivity,[4] Seebeck coefficient,[5–7] and thermal conductivity[8–10] strongly suggest that quasicrystalline alloys are marginally metallic and should be properly located at the *border line* between metals and *semiconductors.*[11] When considered from the perspective of current trends in the search for novel high performance thermoelectric materials (TEM's),[13] the peculiar position of these alloys is quite appealing. In particular, the question regarding whether the different purported anomalies in the transport properties of QC's may be properly balanced to obtain promising materials for thermoelectric applications arises in a natural way. From a theoretical point of view, such a possibility has been discussed by Cyrot-Lackmann who focused on the role of the phonon drag contribution of quasi-Umklapp processes in QC's.[14] At the same time, after a systematic investigation of electrical and thermal transport properties of different quasicrystalline materials, Tritt and collaborators recently proposed the *i*-AlPdMn system as a potential candidate for small scale thermoelectric refrigeration and power generation applications.[15]

Motivated by these promising results we have recently provided a *theoretical analysis* on the possible use of QC's as potential TEM's. In that work we considered self-similarly correlated features in their electronic structure and estimated their possible effects on the different transport coefficients.[16] The aim of this work is to further elaborate these preliminary results in order to gain an additional theoretical insight which may contribute to guide subsequent experimental research. To this end, we shall consider a *realistic model* for the *spectral conductivity* of QC's based on recent *ab initio* band structure calculations by Landauro and Solbrig.[17,18] In this way, we will show that high values of the figure of merit (FOM), well beyond the practical upper limit $\theta=1$, may be expected at different temperature regimes. By comparing experimental data, available in the literature, with the obtained analytical results we offer a quantitative estimation on the suitability of different QC's as potential good TEM's, and suggests two promising candidates deserving a more detailed experimental study, namely: the icosahedral cadmium ytterbium,[19] and the dodecagonal tantalum telluride binary phases.[20]

The paper is organized as follows. In Sec. II we present the physical motivations supporting our proposal of QC's as suitable thermoelectric materials, briefly reviewing the most relevant experimental results concerning the anomalous transport properties of QC's. In Sec. III, we introduce our model for the spectral conductivity. Afterwards, in Sec. IV, we present our approach for studying the transport coefficients of quasicrystalline alloys, and obtain closed analytical expressions for the FOM. Section V is devoted to discuss the obtained analytical results in the light of some pertinent experimental data reported to date. Finally, in Sec. VI we summarize the main conclusions of this work.

II. PHYSICAL MOTIVATIONS

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* given by the dimensionless expression

$$\theta \equiv ZT = \frac{T\sigma S^2}{\kappa_e + \kappa_{\rm ph}}, \tag{1}$$

where T is the temperature, $\sigma(T)$ is the electrical conductivity, $S(T)$ is the Seebeck coefficient and $\kappa_e(T)$ and $\kappa_{\rm ph}(T)$ give the contribution to the thermal conductivity due to the electrons and lattice phonons, respectively. Accordingly, the FOM depends on the electronic and vibrational structure of the sample as well as on the working temperature of the device.

At first sight it may seem surprising to propose a *metallic* alloy as a suitable TEM. However, such a proposal makes sense due to the peculiar transport properties of QC's. In fact, their electrical conductivity:[4] (i) is remarkably low (ranging from 100 to 5000 Ω^{-1} cm^{-1} at room temperature), (ii) it steadily *increases* as the temperature increases up to the highest temperatures of measurement ($T\simeq 900$ K),[21,22] 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, like the Hall or Seebeck coefficients, and resembles doping effects in semiconductors. In addition, (i) the temperature dependence of the Seebeck coefficient:[5–7] is clearly nonlinear, exhibiting well-defined extrema in most instances, (ii) small variations in the chemical composition give rise to sign reversals in the $S(T)$ value, (iii) for a given sample stoichiometry it shows a strong dependence on the heat treatments applied to the sample,[15] and (iv) $S(T)$ has large values when compared to those of disordered metallic systems.[23] Therefore, the situation is quite different from that observed in amorphous materials, where the $S(T)$ curve is dominated by electron diffusion yielding a linear temperature dependence. Therefore, the *electronic transport properties* of quasicrystalline alloys exhibit unusual composition and temperature dependences, resembling more semiconductorlike than metallic character.[11] In fact, it has been recently pointed out that the electrical conductivity of icosahedral QC's may be strongly dependent on the bonding nature of icosahedral clusters, so that small changes in the cluster structure may induce a metallic-covalent bonding conversion.[12]

Furthermore, the *thermal conductivity* of QC's 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.[8,10] Thus, for most icosahedral phases the thermal conductivity at room temperature is comparable to that of zirconia ($\sim 1-2$ W m^{-1} K^{-1}).[9] This low thermal conductivity of QC's is particularly remarkable in the light of Slack's phonon-glass/electron-crystal proposal for promising TEM's,[24] and it has considerably spurred the interest on the potential application of QC's as TEM's from an experimental viewpoint. In fact, one of the main advantages of QC's over other competing TEMs is that one can try to modify both the electrical conductivity and the thermoelectric power, without losing the low thermal conductivity, by properly varying the sample stoichiometry.[15] What is the physical origin for such an interesting behavior?

III. ELECTRONIC STRUCTURE MODEL

Theoretical efforts aimed to understand these unusual transport phenomena have rendered two main results concerning the electronic structure of QC's. The first one refers to the presence of a *pronounced pseudogap at the Fermi level*. The second one concerns the existence of *spiky features* in the density of states (DOS) near the Fermi level. The presence of a pseudogap was predicted in order to explain the stability of QC's,[25] and its physical existence has received strong experimental support during the past decade.[6,26–30] The existence of a spiky fine structure of the electronic DOS (over an energy scale of about 10 meV) was obtained in self-consistent *ab initio* calculations.[31,32] The physical origin of such peaks may stem from the structural quasiperiodicity of the substrate via a hierarchical cluster aggregation resonance[33] or through *d*-orbital resonance effects.[34] These spiky features have remained quite elusive to experimental confirmation,[35–38] although some recent works provide some support to their possible physical existence.[39,40] Thus, although the presence of a dense set of spiky features in the DOS might have a profound effect on the transport properties of QC's, significantly contributing to explain some unusual behaviors in both the electrical conductivity[41] and the thermopower in terms of band structure effects,[42] at the time being the question about their very physical existence is far from being definitively settled.

Quite interestingly, however, a number of basic results coming from the TEM's research arena clearly indicate that this is a quite relevant issue. In fact, conventional empirical searches have shown that all good TEM's are small-band-gap semiconductors or semimetals whose FOM sensitively depends on the *number of band extrema* near the Fermi level, so that most promising candidates should exhibit multiple peaks and valleys in their electronic band structure. Thus, it has been argued that the high performance observed in the Bi_2Te_3 samples may be due to this effect.[43] From this perspective, the purported convenience of a multipeaked DOS to explain the unusual transport properties in QC's,[41,42] provides additional support for considering QC's as suitable TEM's.

The point here is that numerical simulations predict the presence of a *dense set of nested peaks*, while in order to make a meaningful comparison between experimental measurements and numerically calculated electronic structures one should take into account 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.[35] These considerations convey us to reduce the number of sharp spectral features necessary to capture the main physics of the transport processes. To this end, a fruitful approach has been recently introduced by Landauro and Solbrig.[17] According to these authors the spectral resistivity, $\rho(E)$, corresponding to *i*-AlCuFe phases can be satisfactorily modeled by means of just two basic spectral features, namely, a wide and a narrow Lorentzian peaks. Quite remarkably, this simple model is able, not only to reproduce the results previously obtained from detailed *ab initio* calculations, but also to properly fit the experimental $\sigma(T)$ and $S(T)$ curves corresponding to the *i*-$Al_{62.5}Cu_{25}Fe_{12.5}$ QC.[18]

Motivated by these results, in this work we shall extend our previous work by considering the following model for the spectral conductivity (defined as the $T\rightarrow 0$ conductivity with the Fermi level at energy E):

$$\sigma(E) \equiv \lambda_1 \delta(E-E_1) + \lambda_2 \delta(E-E_2). \tag{2}$$

The spectral conductivity is then characterized by the presence of two main spectral features, corresponding to dips of depth λ_i (in Ω^{-1}cm^{-1}eV units) located at the energies E_i. It is worth noticing that in our previous treatment,[16] we assumed that the $\sigma(E)$ function should closely resemble the overall structure of the DOS, so that we consider δ peaks rather than dips as the most relevant spectral features of the $\sigma(E)$ curve. However, according to the detailed numerical study performed in Refs. 17 and 18 the relationship between

the DOS and the spectral conductivity is not so simple. In particular, it has been shown that a dip in the $\sigma(E)$ curve can correspond with a peak in the DOS. Since the conductivity spectrum depends on the diffusivity of the electronic states as well as the DOS structure, this behavior is likely to be related to the peculiar nature of critical electronic states.[44–46] Consequently, in the light of these results, we consider a two-dip model as a more adequate physical description. Without loss of generality we can take the depth of one of the dips as a reference value, say λ_1. In this way we have three free parameters in our model, E_1, E_2, and $\lambda \equiv \lambda_2/\lambda_1 > 0$. In the following section we will analytically study the dependence of the FOM in terms of these free parameters.

IV. ANALYTICAL TREATMENT

Following previous works[6,41] we will start by expressing the transport coefficients in the unified way[47]

$$\sigma(T) = \int_{-\infty}^{+\infty} dE \left(-\frac{\partial f}{\partial E} \right) \sigma(E), \tag{3}$$

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

$$\kappa_e(T) = \kappa_0(T) - T\sigma(T)S^2(T), \tag{5}$$

where

$$\kappa_0(T) = \frac{1}{e^2 T} \int_{-\infty}^{+\infty} dE \left(-\frac{\partial f}{\partial E} \right) (E-\mu)^2 \sigma(E), \tag{6}$$

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. By expressing Eqs. (3)–(5) 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[48]

$$\sigma(T) = \frac{J_0}{4}, \quad S(T) = \frac{cJ_1}{J_0}, \quad \kappa_e(T) = \frac{c^2 T}{4} \left(J_2 - \frac{J_1^2}{J_0} \right), \tag{7}$$

where $c \equiv k_B/e \simeq 87\ \mu \mathrm{V\,K}^{-1}$, and we have introduced the auxiliary integrals[16]

$$J_n \equiv \int_{-\infty}^{+\infty} x^n \,\mathrm{sech}^2(x/2)\sigma(x)dx. \tag{8}$$

Substituting Eq. (7) into Eq. (1) we get

$$\theta(x,T) = \frac{\xi}{1-\xi+A}, \tag{9}$$

where

$$\xi \equiv \frac{J_1^2}{J_0 J_2}, \quad A \equiv \frac{4\kappa_{\mathrm{ph}}(T)}{c^2 J_2 T}. \tag{10}$$

Making use of Eq. (9), within the framework of the Boltzmann approach, Mahan and Sofo[48] found that the Dirac delta function is the only transport distribution function able to maximize the FOM. Consequently, they suggested that the best TEM is likely to be found among materials exhibiting a sharp singularity (Dirac delta function) in the DOS close to the Fermi level. We have recently extended this result by considering the influence of a self-similar pair of δ-like spectral features in the spectral conductivity on the transport coefficients.[16] Now, we shall consider the general case where the model expression for the spectral conductivity depends on three free parameters. Then, by plugging Eq. (2) into Eqs. (9) and (10) we get

$$\theta(x_1,x_2,\lambda,T) = \frac{(x_1u_1+\lambda x_2u_2)^2}{(x_1-x_2)^2\lambda u_1u_2 + a(T)(u_1+\lambda u_2)}, \tag{11}$$

with

$$u_i \equiv \mathrm{sech}^2(x_i/2), \quad a(T) \equiv \frac{b}{\lambda_1}\kappa_{\mathrm{ph}}(T), \tag{12}$$

and $b \equiv 4k_B/c^2 \simeq 0.0455\ \mathrm{MeV\,K\,V}^{-2}$. For a given temperature, the optimal electronic structure will be obtained from the extreme condition $\nabla\theta = 0$, determining the proper positions and depths for the different spectral features. In so doing, we obtain

$$2x_2D - N[a + u_1(x_1-x_2)^2] = 0, \tag{13}$$

$$2(1-x_1\varphi_1)D - N[2(x_1-x_2)\lambda u_2 - \varphi_1[a + \lambda u_2(x_1-x_2)^2]] = 0, \tag{14}$$

$$2(1-x_2\varphi_2)D + N[2(x_1-x_2)u_1 + \varphi_2[a + u_1(x_1-x_2)^2]] = 0, \tag{15}$$

where we have defined

$$N \equiv x_1u_1 + \lambda x_2u_2, \tag{16}$$

$$D \equiv a(u_1+\lambda u_2) + \lambda u_1u_2(x_1-x_2)^2, \tag{17}$$

and $\varphi_i \equiv \tanh(x_i/2)$. Unfortunately, this set of coupled transcendental equations cannot be easily solved, so that in order to gain some physical insight into the problem we will consider a simpler situation given by the condition $x_2 \equiv -x_1 = -x$. This relationship describes a symmetric electronic structure around the Fermi level. Quite interestingly, recent *ab inito* calculations indicate that such kind of electronic structure may satisfactorily capture the essential ingredients describing the electrical conductivity of some realistic icosahedral QC's.[17,18] Accordingly, we can confidently expect that the results obtained below may be quite representative for these samples. Making use of the above mentioned assumption, expression (11) simplifies to

$$\theta(x,\lambda,T) = \frac{(1-\lambda)^2}{4\lambda + a(T)f^2(x)(1+\lambda)}, \tag{18}$$

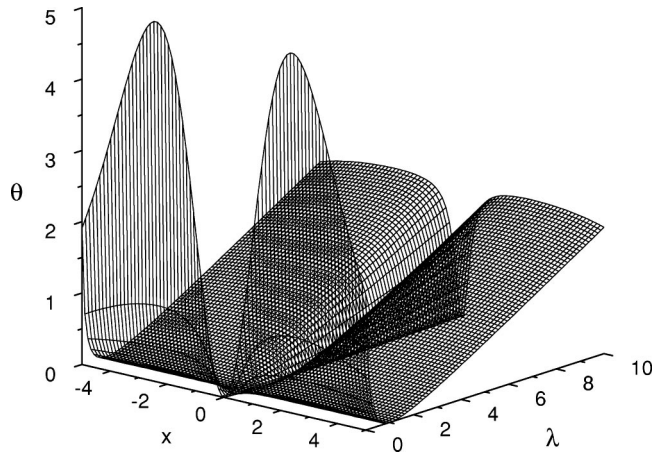

FIG. 1. 3D plot showing the most relevant topological features of the $\theta(x,\lambda)$ surface. We have taken $\kappa_{\rm ph}=1.5$ W m^{-1}K^{-1}. See the text for more details.

where $f(x)\equiv x^{-1}\cosh(x/2)$, and we have explicitly made use of the condition $x\neq 0$. In so doing, we are not losing relevant physical information, since the case $x=0$ corresponds to the trivial minimum $\theta=0$. Another trivial solution, yielding $\theta=0$ occurs if both dips have exactly the same depth ($\lambda=1$). Now, the extreme condition $\nabla\theta=0$ leads to the following relationships:

$$\tanh(x/2)=2/x, \tag{19}$$

$$4(1+\lambda)+a(T)(3+\lambda)f^2(x)=0. \tag{20}$$

Noticeably, Eq. (19) can be solved exactly, and its solution, namely, $x_0=\pm 2.399\ldots$, coincides with that previously obtained by Mahan and Sofo in their study of the DOS single-peak model.[48] On the other side, since $a(T)$ remains always positive, it is clear that Eq. (20) cannot be solved for any physically acceptable combination of the remaining parameters.

In order to get a clearer picture of the overall dependence of the FOM on the free parameters x and λ, in Fig. 1 we display the surface $\theta(x,\lambda)$ for the particular choices $k_{ph}=1.5$ W m^{-1} K^{-1} (which can be considered as a representative upper limit for the quasilattice contribution to the thermal conductivity[8,10]) and $\lambda_1\simeq 0.2$ MeV Ω^{-1}m^{-1} (a suitable value, as reported in Refs. 17 and 18). By inspecting the plot we can appreciate two distinct regions in the parameter space landscape, which are separated by the absolute minimum ($\theta=0$) defining a valley along the line $\lambda=1$. One side of this valley ($\lambda<1$) is characterized by the presence of two pronounced hills, symmetrically located around the Fermi level value $x=0$. The maxima associated to these hills naturally occur at the previously obtained value x_0, where the FOM peaks at about $\theta\simeq 5$, a really high value indeed. Conversely, the other side of the valley ($\lambda>1$) exhibits a remarkably smoother appearance, characterized by two inclined plains with an almost constant positive slope, which suddenly merge at the groove extending along the $x=0$ axis. From the overall topological structure of the $\theta(x,\lambda)$ surface shown in Fig. 1 one realizes that the highest values of the

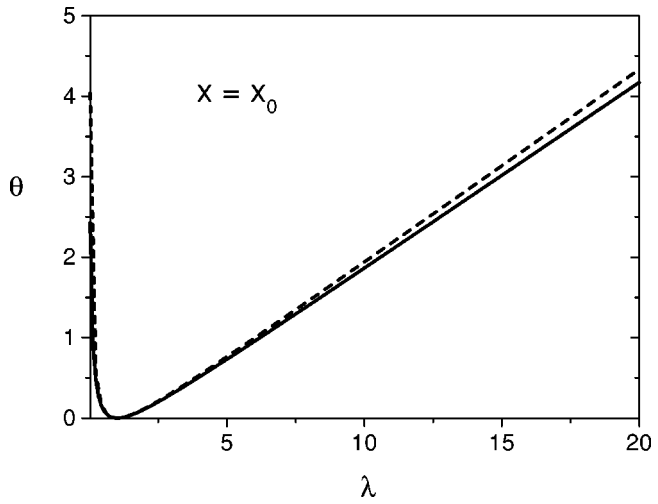

FIG. 2. Plot of the optimal figure of merit corresponding to the slice $x=x_0$ in the landscape shown in Fig. 1. We have taken $\kappa_{\rm ph}=2$ Wm^{-1}K^{-1} (solid line) and $\kappa_{\rm ph}=1$ Wm^{-1}K^{-1} (dashed line). See the text for more details.

FOM will be contained in the transversal planes slicing the peaks of the hills in the parameter space landscape, i.e., those determined by the condition $x=\pm x_0$. Then, by substituting the solution of Eq. (19) into Eq. (18) above, we get the following expression for the optimal FOM:

$$\theta_{op}(x_0,\lambda,T)=\frac{(1-\lambda)^2}{4\lambda+\dfrac{b'}{x_0^2-4}(1+\lambda)\kappa_{\rm ph}(T)}, \tag{21}$$

where $b'\equiv b/\lambda_1\simeq 0.2275$ mW^{-1} K. In Fig. 2 we plot the resulting curve for two different values of the thermal conductivity. It is worth noticing that significantly high values for the FOM (well above the practical upper limit $ZT=1$) could be reached for reasonable values of the parameter λ, measuring the relative depths of the spectral conductivity dips. In fact, values of λ close to 10 may be expected for AlCuFe QC's,[17,18] suggesting that values around $\theta_{op}\simeq 2$ may be potentially attained in that case. These theoretical FOM values are remarkably high for a metallic alloy and even exceed the values obtained for usual non-metallic TEM's like, for example, $LaFe_3CoSb_{12}$ skutterudites[49] ($\theta\simeq 1.4$ at 600 K), Y_2O_3 porous ceramics[50] ($\theta\simeq 1$ at 950 K), Tl_2SnTe_5 semiconductors[51] ($\theta\simeq 0.85$ at 400 K) or half-Heusler LnPdSb structures[52] ($\theta\simeq 0.06$ at 300 K). On the other hand, depending on the adopted model parameters the θ_{op} values may differ by several orders of magnitude. This fact agrees with the purported sensitivity of the transport properties of QC's to minor variations in the electronic structure of the sample as a consequence of slight stoichiometric changes.

V. DISCUSSION

How well do our theoretically estimated high FOM values compare with current experimental figures for QC samples? To this end, in Table I we list relevant transport coefficient measurements, as reported in the literature, along with the

TABLE I. Transport coefficients values at room temperature for different QC's.

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	640[a]	85 [a]	1.6[a]	0.08

[a]Reference 15.
[b]Reference 27.
[c]Reference 9.
[d]Estimated.

corresponding FOM values at room temperature. From the listed data we can appreciate a progressive trend towards increasing values of θ(300 K) resulting from the acquisition of higher quality, appropriate QC's. Quite promisingly, the best FOM reported so far[15] compares well with some of the most conservative figures obtained in our theoretical prospective study; i.e., those corresponding to the points located around the $\lambda=1$ valley in the parameter space (see Figs. 1 and 2). Consequently, it seems reasonable to expect that, by a judicious choice of both sample composition and processing and annealing conditions, higher FOM values, comparable to the figures currently obtained for good TEM's (or even better) may be ultimately reached by following a systematic research. Although such a possibility is just a tentative one, we deem it is based on ground physical basis, particularly if one keeps in mind the purported sensitivity of the relevant transport coefficients to different preparation techniques.[15] In this regard, the recent measurement of Seebeck coefficients reaching values typical of semiconducting materials (100 μ V K^{-1} for $Al_{70}Pd_{20.4}Re_{8.6}$ at room temperature) is quite encouraging,[53] although the exceedingly low values of the electrical conductivity of these quasicrystalline samples (40–100 Ω^{-1}cm^{-1}), yielding θ values below 0.01, still prevent their possible consideration for thermoelectrical applications.

In a previous work, we suggested that the rare-earth based group of stable icosahedral phases in the system (Gd,Tb,Dy,Ho,Er)MgZn may play a promising role as TEM's.[16] Although the subtle effects stemming from the interaction of the charge carriers with a quasiperiodic distribution of local magnetic moments due to $4f$ atoms are far from being fully understood, our proposal was mainly based on the very existence of f type orbitals in these samples, giving rise to the presence of peaked narrow bands in the DOS. Depending on the precise contribution of these narrow bands to the spectral conductivity around the Fermi level, either $\lambda \ll 1$ or $\lambda \gg 1$ values may be obtained. Then, if these narrow bands are located relatively close to the optimal x_0 value (say, $|E_i-\mu|\sim 0.1$ eV), significantly high values for the FOM may be expected, as it is inferred from the topology of the $\theta(x,\lambda)$ surface shown in Fig. 1. Unfortunately, recent experimental work clearly indicates that this favorable scenario does not take place in the actual samples considered to date. In fact, significant advances in the growth of large

TABLE II. Transport coefficients values at room temperature for different rare-earth based quasicrystalline samples, after Ref. 59.

Sample	σ (Ω^{-1}cm^{-1})	S (μV K^{-1})	κ (Wm^{-1}K^{-1})	θ (300 K)
TbMgZn	4880	6	5.0	0.0003
HoMgZn	5400	8	5.5	0.0006
YMgZn	5710	8	5.5	0.0007
ErMgZn	6170	7	4.5	0.0007

single-grain RE-ZnMg QC's have allowed for the study of transport properties without the unwanted effects of grain boundaries and second phases upon the measured quantities.[54–56] The reported values of the electrical conductivity for these samples are about one order of magnitude higher than that observed in the other quasicrystalline systems, ranging from $\sigma\simeq 5400$ to $\sigma\simeq 6200$ Ω^{-1}cm^{-1} at room temperature.[55,57–59] On the other hand, thermal conductivity measurements for single-grain RE based quasicrystalline samples range from $\kappa\simeq 5.5$ to $\kappa\simeq 4.5$ W m^{-1} K^{-1} at room temperature.[59,60] When taking these figures along with the rather low Seebeck coefficient values (6–8 μV K^{-1}) recently reported,[59] typically metallic FOM values [below $\theta(300\ \mathrm{K})\simeq 0.001$] are obtained, as we list in Table II. This unsatisfactory situation probably results from the actual location of the narrow f bands in the electronic structure of this QC family. In fact, recent calculations for the electronic structure of closely related hexagonal RE-ZnMg compounds indicate that these bands may be located quite far from the Fermi level position (namely $|E_i-\mu|\sim 5$–6 eV; i.e., $x \approx 200$), thus having a subsidiary role in the related transport properties.[61] Although it is difficult to assess the significance that these results, obtained for crystalline samples, may have for quasicrystalline alloys, it is clear that by considering the transport measurements report to date as a whole, and properly balancing them, QC's belonging to the RE-MgZn family should be classified as poor metals rather than marginally metallic materials near the border line with semiconducting ones. Although it is now clear that RE-MgZn compounds are not as promising as it was originally thought, the recently discovered stable icosahedral QC's in the binary Cd-Yb system[19] may well do the job, since in that case the f orbitals of the Yb may be located closer to the Fermi level,[62,63] as it has been confirmed by recent *ab-initio* band structure calculations of periodic approximants.[64]

Another promising candidate might be found in the dodecagonal QC chalcogenide phase discovered in the TaTe system.[20] By all indications, these tellurides seem to have electrical properties being characteristic of small bandgap semiconductors. In fact, since their resistivities at room temperature are similar to those of semimetals (about 1–10 mΩ cm) and they seem to exhibit a complex electronic structure near the Fermi level, these tellurides may have promising thermoelectrical properties.[65]

Once we have discussed those aspects related to the electronic structure we shall briefly estimate the most appropriate *working temperature ranges* of interest. To this end, under the reasonable assumption that the electronic structure it is

not severely affected by temperature effects well below the Debye temperature, we impose to Eq. (21) the extreme condition $d\theta_{op}/dT \equiv 0$ to get

$$\frac{d\theta_{op}}{dT} = \theta_{op}^2 \frac{b'}{4-x_0^2} \frac{1+\lambda}{(1-\lambda)^2} \left(\frac{d\kappa_{ph}}{dT} \right). \tag{22}$$

As expected, for a given electronic structure, the most appropriate working temperatures are those determined from the extreme condition $d\kappa_{ph}/dT = 0$, effectively minimizing the quasilattice thermal conductivity. Now, we recall that the overall behavior of the thermal conductivity in QC's is quite sensitive to the microstructure of the sample. Thus, for poly-grained QC's, the $\kappa_{ph}(T)$ monotonically increases with T, showing a marked tendency to saturation for temperatures above 10–20 K, and exhibiting a *characteristic plateau* with $\kappa_{ph} \simeq 1$ W m^{-1}K^{-1}, from about 25 to 55 K.[8] On the contrary, the lattice thermal conductivity of single-grained AlPdMn QC's first increases with increasing T, it reaches a well defined *maximum* ($\kappa_{ph} \simeq 1.3$ W m^{-1}K^{-1}) at about 20 K, followed by a *broad minimum* ($\kappa_{ph} \simeq 1.1$ W m^{-1}K^{-1}) located between 50–90 K, and then it smoothly increases with further increasing T.[8,10,15] A similar behavior exhibiting a well defined maximum ($\kappa_{ph} \simeq 2.7$ W m^{-1}K^{-1}) at 25 K and a shallow minimum ($\kappa_{ph} \simeq 2.5$ W m^{-1}K^{-1}) at 65 K, has been recently reported for a single-grained YMgZn QC sample.[60] These experimental data suggest that both poly-grained QC's and single-grained QC's may satisfy the $d\kappa_{ph}/dT = 0$ condition through a certain temperature range. For single-grained samples this range would correspond to the broad minimum interval, meanwhile for poly-grained ones it would be placed along the plateau region, where the phonon thermal conductivity is not only low, but also almost constant. These considerations seem to indicate that QC's may exhibit their higher thermoelectric performance at relatively low working temperatures [see the $\theta(x_0, \lambda)$ curve corresponding to the dashed line in Fig. 2], somewhere placed in the broad interval $T^* \simeq 70 \pm 20$ K.

VI. CONCLUSIONS

In this work we provide a theoretical analysis on the use of QC's as potential TEM's by considering a suitable two-dip model for the spectral conductivity and evaluating its influence on the transport coefficients. In this way, we show that high values of the FOM, well above the $\theta = 1$ practical limit may be expected by a judicious choice of both sample composition and processing conditions. Depending on the microstructure of the quasicrystalline samples (strongly influencing their related thermal conductivities) these materials could efficiently operate at room temperature. Therefore, possible thermoelectrical application of QC's may be found as new materials for small scale refrigeration and micro power generators. From the theoretical prospective study presented in this work, a systematic research on the transport properties of the icosahedral cadmium-ytterbium and the dodecagonal tantalum telluride binary phases, aimed to improve the FOM values observed to date, would be interesting. At present the available information on the transport properties of this families is quite scarce, particularly regarding their thermal conductivity and thermoelectric power. Nonetheless, I understand that pertinent measurements may be performed in a near future.[65,66] Our theoretical estimations also suggest that good quality, single grained QC's may exhibit a good thermoelectric performance at liquid nitrogen temperatures. Consequently, these materials may be potentially used in several applications of industrial interest like, for example, cooling for cryoelectronic and infrared detectors or cold computing.[67] Experimental research aimed to check such possibilities would be appealing.

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