Do quasicrystals follow Wiedemann–Franz's law?

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In this work we present a theoretical study on the thermal and electrical conductivities of quasicrystals. By considering a realistic model for the spectral conductivity we derive closed analytical expressions for the transport coefficients which allow us to study the temperature dependence of the Lorenz ratio $L(T)=\kappa_e(T)/T\sigma(T)$ at different temperature regimes. We conclude that quasicrystals closely follow Wiedemann–Franz's law over a wide temperature range. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1488696]

According to Wiedemann–Franz's law (WFL) in most materials thermal and electrical conductivities are mutually related, over certain temperature ranges, through the relationship $\kappa_e(T)/\sigma(T)=\mathcal{L}_0 T$, where $\kappa_e(T)$ gives the contribution to the thermal conductivity due to the charge carriers, $\sigma(T)$ is the electrical conductivity, T is the temperature, and $\mathcal{L}_0 =(k_B/e)^2\ \eta_0$ is the Lorenz number, where k_B is the Boltzmann constant, e is the electron charge, and η_0 is a constant whose value depends on the nature of the sample. Thus, for metallic systems $\eta_0=\pi^2/3$, and we get the Sommerfeld's value $\mathcal{L}_0=2.44\times 10^{-8}\ \mathrm{W\,\Omega\,K^{-2}}$, while for semiconductors described by Maxwell–Boltzmann statistics we have $\eta_0 \simeq 2$.[1] The WFL has a broad range of validity, and usually holds for arbitrary band structures provided that the change in energy during an electron collision is small compared with k_BT. Then, elastic processes dominate the transport coefficients, and the carriers motion determines both the electrical and thermal currents.[2] Quasicrystals (QCs) are well-ordered metallic alloys exhibiting a broad collection of anomalous transport properties,[3–5] resembling more semiconductor-like than metallic character.[6] Thus, a proper classification of these materials, able to account for both their peculiar electronic structure and their related transport properties, remains elusive.[7] In addition, it has been reported that Ohm's law holds in high quality icosahedral QCs,[8] hence, opening the question regarding what other fundamental laws may also be followed by these materials. From a fundamental viewpoint it seems then quite pertinent to ascertain whether one may expect the WFL to hold in the case of QCs as well. Furthermore, the study of the WFL validity range is also crucial in order to test the working hypothesis usually made when estimating the phonons contribution to the thermal conductivity, $\kappa_{\mathrm{ph}}(T)$, by substracting to the experimental data, $\kappa_{\mathrm{mes}}(T)$, the electronic contribution according to the expression $\kappa_{\mathrm{ph}}=\kappa_{\mathrm{mes}}-\mathcal{L}_0 T\sigma$. In fact, were the WFL not valid for QCs, several conclusions about the phonon dynamics in these materials should be substantially revised, an important question which has been scarcely considered in the literature.[9] Unfortunately, the high electrical resistivity of QCs currently prevents an accurate experimental evaluation of the Lorenz number for these materials.[10,11] The main goal of this work is then to theoretically estimate the validity of WFL for QCs, providing some physical insight aimed to spur subsequent experimental research. To this end, we will derive closed analytical expressions for both the transport coefficients and the Lorenz ratio $L(T)=\kappa_e(T)/T\sigma(T)$, hence, extending the few numerical results previously reported.[12,13] By studying the dependence of the analytical $L(T)$ function on the temperature we conclude that *QCs closely obey the Wiedemann–Franz's law* over a wide temperature range.

To date, theoretical efforts aimed to understand the unusual transport phenomena of QCs have focused on the existence of a pronounced pseudogap at the Fermi level[14–16] and the possible presence of a dense set of nested peaks in the density of states (DOS).[17–19] At the time being, the very existence of such peaks remains controversial.[20–22] In any event, 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.[7] These considerations convey us to reduce the number of sharp spectral features necessary to capture the main physics of the transport processes. In previous works we have considered simple models for the electronic structure of QCs, evaluating the possible effects of their main features on different transport coefficients.[23–25] In this work, we shall consider a realistic model for the spectral conductivity of QCs based on recent *ab initio* band structure calculations.[12,13] 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 to properly fit the experimental $\sigma(T)$ and $S(T)$ curves.[13] Accordingly, we shall consider the following model for the spectral conductivity:

$$\sigma(E)\equiv A[L_1(E)+L_2(E)]^{-1}, \tag{1}$$

where the parameter A is expressed in $\Omega^{-1}\ \mathrm{cm}^{-1}\ \mathrm{eV}^{-1}$ units and the Lorentzians

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$$L_i(E)=\frac{\gamma_i}{\pi}[\gamma_i^2+(E-\mu-\delta_i)^2]^{-1}, \quad (2)$$

characterize the height, $(\pi\gamma_i)^{-1}$, and position, δ_i, of each spectral feature with reference to the Fermi level, μ. Following previous works[23–26] we will start by expressing the transport coefficients in the unified way

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

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

$$\kappa_e(T)=\kappa_0(T)-T\sigma(T)S^2(T), \quad (5)$$

where

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

$f(E,T)$ is the Fermi distribution, and E is the electron energy. By expressing Eqs. (3)–(6) in terms of the scaled variable $x\equiv\beta(E-\mu)$, with $\beta\equiv(k_BT)^{-1}$, the transport coefficients we are interested in can be written as[23,24]

$$\sigma(T)=\frac{J_0}{4}, \quad (7)$$

$$\kappa_e(T)=\frac{c^2T}{4}\left(J_2-\frac{J_1^2}{J_0}\right), \quad (8)$$

where $c\equiv k_B/e$, and we have introduced the integrals

$$J_n(\beta)\equiv\int_{-\infty}^{+\infty}x^n\,\mathrm{sech}^2(x/2)\sigma(x)dx. \quad (9)$$

Expressing $\sigma(x)=c_0P_4(x)/P_2(x)$, with

$$P_4(x)\equiv\beta^{-4}x^4-2\beta^{-3}n_3x^3+\beta^{-2}n_2x^2-2\beta^{-1}n_1x+n_0,$$

$$P_2(x)\equiv\beta^{-2}x^2-2\beta^{-1}q_1x+q_0, \quad (10)$$

where $c_0\equiv\pi A(\gamma_1+\gamma_2)^{-1}$, $n_3\equiv\delta_1+\delta_2$, $n_2\equiv\varepsilon_1^2+\varepsilon_2^2+4\delta_1\delta_2$, $n_1\equiv\delta_2\varepsilon_1^2+\delta_1\varepsilon_2^2$, $n_0\equiv\varepsilon_1^2\varepsilon_2^2$, $q_0\equiv\varepsilon\varepsilon_1^2\varepsilon_2^2(\gamma_1+\gamma_2)^{-1}$, $q_1=(\gamma_1\delta_2+\delta_1\gamma_2)(\gamma_1+\gamma_2)^{-1}$, with $\varepsilon_i^2\equiv\gamma_i^2+\delta_i^2$, and $\varepsilon\equiv\gamma_1\varepsilon_1^{-2}+\gamma_2\varepsilon_2^{-2}$, we can rewrite Eq. (9) in the form

$$J_nc_0^{-1}=\int_{-\infty}^{\infty}\left[\sum_{k=0}^{2}a_k\beta^{-k}x^{n+k}+\frac{Q_{n+1}(x)}{P_2(x)}\right]\mathrm{sech}^2(x/2)dx, \quad (11)$$

where $a_0=2q_1a_1+n_2-q_0$, $a_1=2(q_1-n_3)$, $a_2=1$, and $Q_{n+1}(x)\equiv a_3\beta^{-1}x^{n+1}+a_4x^n$, with $a_3=2q_1a_0-q_0a_1-2n_1$, and $a_4=n_0-q_0a_0$. Making use of the integrals

$$\int_{-\infty}^{\infty}\mathrm{sech}^2(x/2)dx=4,\quad \int_{-\infty}^{\infty}x^2\,\mathrm{sech}^2(x/2)dx=\frac{4\pi^2}{3},$$

$$\int_{-\infty}^{\infty}x^4\,\mathrm{sech}^2(x/2)dx=\frac{28\pi^4}{15},\quad \int_{-\infty}^{\infty}x^l\,\mathrm{sech}^2(x/2)dx=0,\ (l\ \text{odd})$$

we obtain

$$J_0c_0^{-1}=4\pi^2\beta^{-2}/3+a_3\beta^{-1}H_1+a_4H_0+4a_0,$$
$$J_1c_0^{-1}=4\pi^2a_1\beta^{-1}/3+a_5H_1+a_3\beta G_0,$$
$$J_2c_0^{-1}=28\pi^4\beta^{-2}/15+a_6\beta H_1+a_5G_0\beta^2+4\pi^2a_0/3, \quad (12)$$

where $a_5\equiv 2a_3q_1+a_4$, $a_6\equiv 2a_5q_1-a_3q_0$, $G_0\equiv 4-q_0H_0$, and we have introduced the auxiliary integrals

$$H_k(\beta)\equiv\int_{-\infty}^{\infty}\frac{x^k}{P_2(x)}\mathrm{sech}^2(x/2)dx. \quad (13)$$

In order to evaluate these integrals we shall expand the function $P_2^{-1}(x)$ in Taylor series around the Fermi level to get

$$H_0\simeq\frac{4}{q_0}\left(1+\frac{\pi^2}{3}\frac{4q_1^2-q_0}{q_0^2}\beta^{-2}\right),$$
$$H_1\simeq\frac{8\pi^2q_1\beta^{-1}}{3q_0^2}\left(1+\frac{14\pi^2}{5}\frac{2q_1^2-q_0}{q_0^2}\beta^{-2}\right). \quad (14)$$

By plugging Eqs. (14) into Eqs. (12) and (7), keeping $\mathcal{O}(\beta^{-2})$ terms, we finally arrive to

$$\sigma(T)=c_0(\xi_0+\xi_1e^2\mathcal{L}_0T^2), \quad (15)$$

where $\xi_0\equiv(\gamma_1+\gamma_2)\varepsilon^{-1}$, and $\xi_1\equiv[4q_1(q_1\xi_0-n_1)+q_0(n_2-\xi_0)]q_0^{-2}$. Now, let us consider the electronic contribution to the thermal conductivity. To this end, we can express

$$J_1=\frac{8\pi^2}{3}c_0\left(\xi_2\beta^{-1}+\frac{2\pi^2}{3}\xi_3\beta^{-3}\right), \quad (16)$$

where $\xi_2\equiv(q_1n_0-q_0n_1)q_0^{-2}$, and $\xi_3\equiv 21a_5q_1q_0^{-4}(2q_1^2-q_0)/5$. By plugging Eqs. (16) and (12) into Eq. (8), keeping $\mathcal{O}(\beta^{-4})$ terms, we obtain

$$\kappa_e(T)=c_0\mathcal{L}_0T\{\xi_0+4bT^2[\xi_4-\xi_2\mathcal{F}(T)]\}, \quad (17)$$

where $b\equiv e^2\mathcal{L}_0$, $\xi_4\equiv 21/20+a_6\xi_3/a_5$, and we have introduced the auxiliary function

$$\mathcal{F}(T)=\frac{\xi_2+4\xi_3bT^2}{\xi_0+\xi_1bT^2}. \quad (18)$$

Making use of Eqs. (15) and (17) we finally obtain the following expression for the Lorenz ratio:

$$L(T)=\mathcal{L}_0\frac{\xi_0+4bT^2[\xi_4-\xi_2\mathcal{F}(T)]}{\xi_0+\xi_1bT^2}. \quad (19)$$

Since $\mathcal{F}(T\to 0)=\xi_2/\xi_0$, we have $L(T\to 0)=\mathcal{L}_0$, so that theoretically QCs exactly obey the WFL in the low temperature limit. On the other hand, in the regime of high temperatures we have $L(T\to\infty)=4\mathcal{L}_0(\xi_1\xi_4-4\xi_2\xi_3)\xi_1^{-2}$. Then, in the high temperature regime the WFL may be satisfied or not depending on the electronic structure of the sample. For the sake of illustration, we will take $\gamma_1=1.35$ eV, $\gamma_2=0.04$ eV, $\delta_1=-0.44$ eV, $\delta_2=-0.01$ eV, and $A=955.11\Omega^{-1}$ cm^{-1} eV^{-1}, as determined from a fit to experimental $\sigma(T)$ and $S(T)$ curves for i-AlCuFe QCs.[13] In Fig. 1 we show the variation of the Lorenz ratio with the temperature as determined from the analytical expression (19). The WFL is closely followed in the low temperature range up to $\sim$30 K, as it can be seen in the inset. A progres-

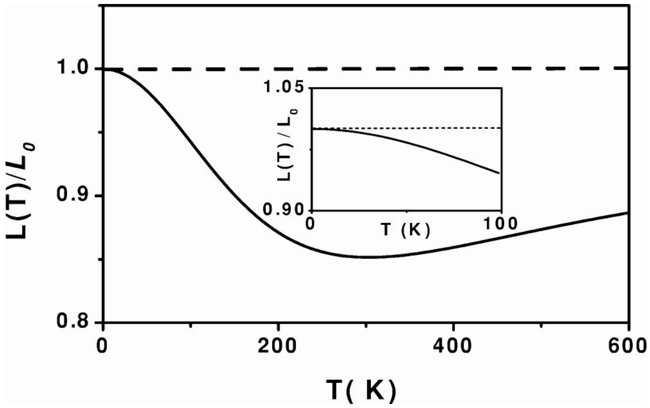

FIG. 1. Temperature dependence of the normalized Lorenz ratio $L(T)/\mathcal{L}$, as obtained from the analytical expression Eq. (19). The inset shows the low temperature behavior.

sive deviation from the ideal behavior is observed as the temperature increases until a broad minimum is reached at $T_{\mathrm{min}} \simeq 300$ K. The position of this minimum takes place at a temperature four times higher than that reported for typical metals like copper ($\sim$80 K).[27] This shift towards higher values may be interpreted as indicating that electron-phonon interaction processes become relevant at higher energies in QCs, as compared to those occurring in metals. Finally, the Lorenz ratio curve smoothly approaches to the asymptotic limit $L(T \to \infty) = 0.92\mathcal{L}_0$ as the temperature is further increased. This value is significantly close to the ideal limit $L(T)/\mathcal{L}_0 = 1$, in agreement with recent measurements of the thermal conductivity of i-AlPdMn samples in the temperature range 300–600 K.[11] From the overall behavior of the $L(T)/\mathcal{L}_0$ curve we then conclude that QCs should closely follow the WFL at low temperatures, while they reasonably follow it at high temperatures, depending on the electronic structure of the considered sample.

In summary, making use of a realistic model for the spectral conductivity, we have derived analytical expressions for the thermal and electrical conductivities, and Lorenz ratio. Our theoretical prediction is that QCs do follow the WFL in a way analogous to that observed for usual metallic or semiconducting systems, hence, supporting the common procedure of substracting to the experimental thermal conductivity data the electronic contribution as given by the WFL in order to get suitable information about the phonon dynamics. In light of these results, experimental work, aimed to estimate whether the Lorenz ratio given by Eq. (19) properly applies to a broad collection of quasicrystalline samples, seems quite appealing.

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[1] See, for example, G. D. Mahan and M. Bartkowiak, Appl. Phys. Lett. **74**, 953 (1999).
[2] J. M. Ziman, *Electrons and Phonons* (Clarendon, Oxford, 1960), p. 270; N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders College, Cornell, 1976), p. 255.
[3] Ö. Rapp, in *Physical Properties of Quasicrystals*, Springer Series in Solid-State Physics 126, edited by Z. M. Stadnik (Springer, Berlin, 1999), p. 127.
[4] T. Grenet, in *Quasicrystals Current Topics*, edited by E. Belin-Ferré, C. Berger, M. Quiquandon, and A. Sadoc (World Scientific, Singapore, 2000), p. 455.
[5] S. Legault, B. Ellman, J. O. Ström-Olsen, L. Taillefer, S. Kycia, T. Lograsso, and D. Delaney, in *New Horizons in Quasicrystals: Research and Applications*, edited by A. I. Goldman, D. J. Sordelet, P. A. Thiel, and J. M. Dubois (World Scientific, Singapore, 1997), p. 224.
[6] R. Tamura, A. Waseda, K. Kimura, and H. Ino, Phys. Rev. B **50**, 9640 (1994); T. Klein, C. Berger, D. Mayou, F. Cyrot-Lackmann, Phys. Rev. Lett. **66**, 2907 (1991); A. Carlsson, Nature (London) **353**, 353 (1991).
[7] Z. M. Stadnik, D. Purdie, Y. Baer, and T. A. Lograsso, Phys. Rev. B **64**, 214202 (2001); Z. M. Stadnik, in *Physical Properties of Quasicrystals*, Springer Series in Solid-State Physics 126, edited by Z. M. Stadnik (Springer, Berlin, 1999), p. 257.
[8] T. Klein and O. G. Symko, Phys. Rev. Lett. **73**, 2248 (1994).
[9] See, for instance, D. Mayou, in *Physical Properties of Quasicrystals*, Springer Series in Solid-State Physics 126, edited by Z. M. Stadnik (Springer, Berlin, 1999), p. 445.
[10] K. Giannò, A. V. Sologubenko, M. A. Chernikov, H. R. Ott, I. R. Fisher, and P. C. Canfield, Phys. Rev. B **62**, 292 (2000).
[11] P. S. Davis, P. A. Barnes, C. B. Vininig, A. L. Pope, B. Schneidmiller, T. M. Tritt, and J. Kolis, Mater. Res. Soc. Symp. Proc. **626**, Z5.4.1 (2000).
[12] H. Solbrig and C. V. Landauro, Physica B **292**, 47 (2000); C. V. Landauro and H. Solbrig, Mater. Sci. Eng., A **294–296**, 600 (2000).
[13] C. V. Landauro and H. Solbrig, Physica B **301**, 267 (2001).
[14] J. Friedel, Helv. Phys. Acta **61**, 538 (1988); T. Fujiwara and T. Yokokawa, Phys. Rev. Lett. **66**, 333 (1991).
[15] T. Klein, O. G. Symko, D. N. Davydov, and A. G. M. Jansen, Phys. Rev. Lett. **74**, 3656 (1995); D. N. Davydov, D. Mayou, C. Berger, C. Gignoux, A. Neumann, A. G. M. Jansen, and P. Wyder, *ibid.* **77**, 3173 (1996).
[16] E. Belin, Z. Dankhazi, A. Sadoc, Y. Calvayrac, T. Klein, and J. M. Dubois, J. Phys.: Condens. Matter **4**, 4459 (1992).
[17] T. Fujiwara, S. Yamamoto, and G. Trambly de Laissardière, Phys. Rev. Lett. **71**, 4166 (1993); G. Trambly de Laissardière and T. Fujiwara, Phys. Rev. B **50**, 5999 (1994); **50**, 9843 (1994); G. Trambly de Laissardière and D. Mayou, *ibid.* **55**, 2890 (1997).
[18] J. Hafner and M. Krajčí, in *Physical Properties of Quasicrystals*, Springer Series in Solid-State Physics 126, edited by Z. M. Stadnik (Springer, Berlin, 1999), p. 209.
[19] C. Janot and M. de Boissieu, Phys. Rev. Lett. **72**, 1674 (1994); C. Janot, Phys. Rev. B **53**, 181 (1996).
[20] R. Escudero, J. C. Lasjaunias, Y. Calvayrac, and M. Boudard, J. Phys.: Condens. Matter **11**, 383 (1999).
[21] M. Krajčí and J. Hafner, J. Phys.: Condens. Matter **13**, 3817 (2001).
[22] E. S. Zijlstra and T. Janssen, Europhys. Lett. **52**, 578 (2000).
[23] E. Maciá, Phys. Rev. B **64**, 094206 (2001).
[24] E. Maciá, Appl. Phys. Lett. **77**, 3045 (2000).
[25] E. Maciá, Phys. Rev. B **61**, 8771 (2000).
[26] F. S. Pierce, S. J. Poon, and B. D. Biggs, Phys. Rev. Lett. **70**, 3919 (1993).
[27] Z. A. Xu, Y. Zhang, N. P. Ong, K. Krishana, R. Gagnon, and L. Taillefer, Physica C **341–348**, 1833 (2000).