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Theoretical Aspects of Thermal Transport in Complex Metallic Alloys: A Generalization of the Wiedemann-Franz Law*

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Abstract. Motivated by a series of experimental facts regarding anomalous transport properties in certain complex metallic alloys in this work the use of a generalized expression for the Wiedemann-Franz law is proposed in order to properly reduce experimental data concerning the phonon contribution to the thermal conductivity in a systematic way.

Keywords: thermal conductivity, Wiedemann-Franz law, quasicrystal, complex metallic alloy

INTRODUCTION

In the study of the thermal transport properties of complex metallic alloys (CMAs) the Wiedemann-Franz law (WFL) is routinely applied in order to estimate the phonon contribution to the thermal conductivity, $\kappa_{ph}(T)$, by substracting to the experimental data, $\kappa_m(T)$, the expected electronic contribution, according to the expression

$$\kappa_{ph}(T) = \kappa_m(T) - L_0 T\sigma(T), \tag{1}$$

where T is the temperature, $L_0 = (\pi k_B/e)^2/3 = 2.44 \times 10^{-8}$ V K^{-2}, is the Lorenz number Sommerfeld's value, and $\sigma(T)$ is the electrical conductivity. In so doing, the ratio κ_e/κ_{ph}, where $\kappa_e(T)$ is the charge carriers' contribution to the thermal conductivity, has been determined for several CMA representatives at room temperature. The reported values cover a relatively wide interval, ranging from $\kappa_e/\kappa_{ph} \approx 2.6$ for the $(Al,Zn)_{51}Mn_{29}$ Bergman phase,[1] to $\kappa_e/\kappa_{ph} \approx 0.5$ and $\kappa_e/\kappa_{ph} \approx 0.01$ for AlReSi quasicrystalline approximant,[2] and AlPd(Mn,Re) icosahedral quasicrystals,[3,4] respectively. Keeping in mind that this ratio takes on values within the range 10–100 for conventional alloys, one realizes that the thermal transport of CMAs is largely dominated by phonons at room temperature, and that this unusual behavior becomes more significant as the structural complexity of underlying lattice progressively increases, approaching the long-range quasiperiodic limit. A similar trend was observed from a fitting analysis of the experimental curves to a slightly modified WFL version of the form

$$\kappa_{ph}(T) = \kappa_m(T) - (1+\varepsilon)L_0 T\sigma(T), \tag{2}$$

where the enhancement parameter ε takes on the values $\varepsilon = 0.3$, $\varepsilon = 0.43$, and $\varepsilon = 1.10$, for Ψ-AlPdMn,[5] O_1/O_2-AlCrFe,[6] and *i*-$Al_{64}Cu_{23}Fe_{13}$ alloys,[7] respectively. The convenience of adopting a Lorenz number value larger than the Sommerfeld's one was also reported from $\kappa_m(T)$ / $\sigma(T)$ fits indicating L_{QC} / $L_0 \approx 1.21$ for icosahedral AlCuFe samples at high temperatures within the temperature range 350–800 K.[8,9] On the basis of these results it seems then reasonable to revisit the standard approach based on the systematic application of the WFL as given by Eqs. (1) or (2). In particular, in this work we will propose the use of a generalized WFL of the form

$$\kappa_{ph}(T) = \kappa_m(T) - L(T)T\sigma(T), \tag{3}$$

which explicitly includes a temperature dependent Lorenz number, in order to properly reduce experimental data regarding $\kappa_{ph}(T)$ in a systematic way. In fact, since transport properties of most CMAs are quite unusual by the standard of common metallic alloys, it seems convenient to check up on the validity of this law for these materials, since our understanding of thermal properties in these materials should be substantially revised if it does not hold.[10–14]

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RESULTS AND DISCUSSION

Following previous works we consider a realistic model for the spectral conductivity close to the Fermi level, [15]

$$\sigma(E) = \bar{\sigma}\left\{\frac{\gamma_1}{(E-\delta_1)^2+\gamma_1^2}+\frac{\alpha\gamma_2}{(E-\delta_2)^2+\gamma_2^2}\right\}^{-1}, \quad (4)$$

which satisfactorily describes the electronic structure of several CMAs families in terms of a wide Lorentzian peak (related to the Fermi-surface Brillouin-zone interaction) plus a narrow Lorentzian peak (related to sp-d hybridization effects). This model includes six parameters, determining the Lorentzian's heights ($\bar{\sigma}/\gamma_i$) and widths ($\sim \gamma_i$), their positions with respect to the Fermi level, δ_i, and their relative weight in the overall structure, $\alpha > 0$. The parameter $\bar{\sigma}$ is a scale factor measured in $(\Omega \text{ cm eV})^{-1}$ units. Suitable values for these electronic model parameters can be obtained by properly combining *ab-initio* calculations of approximant phases with experimental transport data of CMAs within a phenomenological approach.[16,17,18]

Making use of Eq. (4) a closed analytical expression for the Lorenz function was obtained,[13]

$$L(T) \equiv \frac{\kappa_e(T)}{T\sigma(T)} = L_0\frac{\tilde{J}_{00}\tilde{J}_{20}+Q(\tilde{\beta})\tilde{\beta}^{-2}+\frac{7\pi^4}{15}\tilde{\beta}^{-4}}{\tilde{J}_{00}^2+\frac{2\pi^2}{3}\tilde{J}_{00}\tilde{\beta}^{-2}+\frac{\pi^4}{9}\tilde{\beta}^{-4}}, \quad (5)$$

where $Q(\tilde{\beta}) \equiv \pi^2(21\tilde{J}_{00}/5 + \tilde{J}_{20} - \tilde{J}_{11}^2)/3$, $\tilde{J}_{00} \equiv a_0 + a_4 q_0^{-1}\tilde{\beta}\zeta_H$, $\tilde{J}_{11} \equiv a_1 + 12a_3 q_0^{-1} f(\tilde{\beta})$, $\tilde{J}_{20} \equiv a_0 + 12a_4 q_0^{-1} f(\tilde{\beta})$, with $f(\tilde{\beta}) \equiv \tilde{\beta}^2(1-\tilde{\beta}\zeta_H)$, $\tilde{\beta} \equiv \sqrt{q_0\beta/2\pi}$, with $\beta \equiv (k_B T)^{-1}$, is a scaled variable and $\zeta_H(s,a) \equiv \sum_{k=0}^{\infty}(k+a)^{-s}$ is the Hurwitz Zeta function, which reduces to the Riemann Zeta function in the case $a = 1$. The coefficients q_0 and a_i were defined in Ref. 12 in terms of the spectral conductivity model parameters.

Taking into account the asymptotic limits

$$\lim_{\tilde{\beta}\to\infty}\tilde{\beta}\zeta_H = 1, \quad \lim_{\tilde{\beta}\to\infty}\tilde{\beta}^2(1-\tilde{\beta}\zeta_H) = 1/12, \quad (6)$$

Eq. (5) can be approximated in the intermediate temperature regime as

$$L(T) \approx L_0\frac{u^2+\bar{Q}bT^2+\frac{21}{5}b^2T^4}{u^2+2vbT^2+b^2T^4}, \quad (7)$$

where $\bar{Q} \equiv 26u/5 - 4v^2$, $b \equiv e^2L_0 = 2.44\ (\text{eV})^2\ \text{K}^{-2}$, and we have introduced the auxiliary coefficients

$$u \equiv \frac{\delta_1-\delta_2}{\delta_1\varepsilon_1^{-2}-\delta_2\varepsilon_2^{-2}}, \quad v \equiv \frac{(\delta_1-\delta_2)(\delta_1\varepsilon_2^2+\delta_2\varepsilon_1^2)}{\delta_1\varepsilon_2^2-\delta_2\varepsilon_1^2}, \quad (8)$$

expressed in terms of the $\sigma(E)$ model parameters, where $\varepsilon_i = \sqrt{\gamma_i^2+\delta_i^2}$.

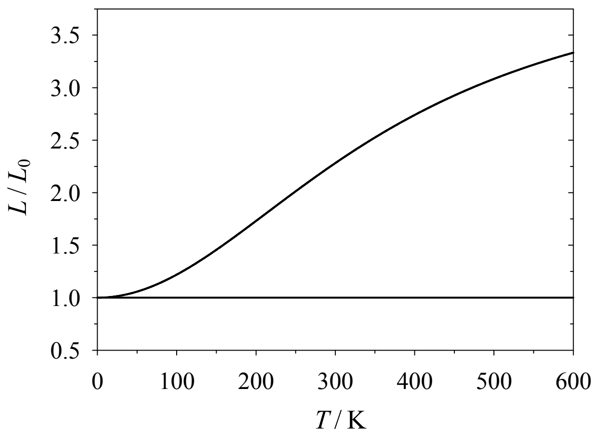

Figure 1. Temperature variation of the normalized Lorenz function. The WFL is obeyed at very low temperatures. At high temperatures $L(T)$ aproaches the asymptotic limit value 21/5. A significant enhancement of the Lorenz number with respect to the Sommerfeld's value takes place over a wide temperature range.

For the sake of illustration, we shall consider the thermal conductivity of the Ψ-AlPdMn complex phase (containing about 1500 atoms in the unit cell).[19] Following the phenomenological approach described in previous works,[16,17,18] the spectral conductivity model parameters can be determined from a simultaneous fitting analysis of the electrical conductivity $\sigma(T)$ and thermopower $S(T)$ curves reported in Ref. 19. In this way, we get $\alpha = 0.375$, $\gamma_1 = 0.028$ eV, $\gamma_2 = 0.040$ eV, $\delta_1 = 0.028$ eV and $\delta_2 = -0.057$ eV. Plugging these values into Eq. (8) the temperature dependence of the Lorenz function given by Eq. (7) can be explicitly determined (Figure 1). In the limit of low temperatures the WFL is satisfied, as expected, but as the temperature is progressively increased the Lorenz function also increases, in agreement with the experimental trends summarized in the previous section. As we see the $L(T)$ approaches an asymptotic limit in the limit of very high temperatures, so that the WFL is also obeyed in this case, but the limiting value is significantly larger than the Sommerfeld value L_0, in agreement with previous experimental reports.[8,20] Quite remarkably, a significant enhancement of the Lorenz number with respect to the Sommerfeld's value takes place over a wide temperature range.

The impact of the Lorenz's function temperature dependence in a proper analysis of the phonon contribution to the thermal conductivity is illustrated in Figure 2. In this figure we compare the measured thermal conductivity (including contributions from both charge carriers and phonons) with the phonon contribution derived from the application of the WFL by either assuming a constant value for the Lorenz number (Eq. (1), circles) or explicitly taking into account its temperature dependence according to Eq. (7) through the expression

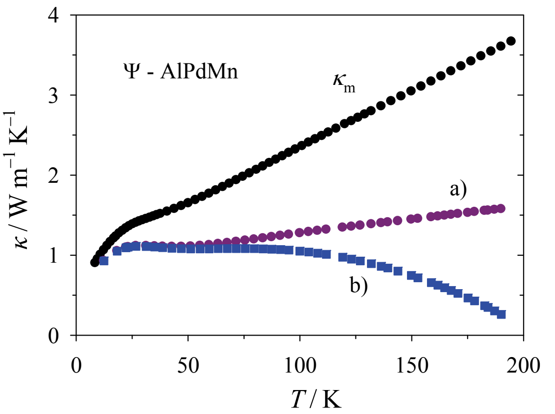

Figure 2. The phonon contribution to the thermal conductivity is derived by substracting to the experimentally measured thermal conductivity (κ_m, experimental data by courtesy of J. Dolinšek) the charge carrier contribution ($\sigma(T)$ was reported in Ref. 19) by assuming a) the validity of the WFL according to Eq. (1) (circles), or b) by considering a temperature dependent Lorenz function as given by Eq. (9) (squares).

$$\kappa_{ph}(T) = \kappa_m - L(T)\sigma(T)T. \tag{9}$$

One can clearly appreciate that the temperature dependences of the resulting $\kappa_{ph}(T)$ curves substantially differ in both cases. In fact, when one considers $L(T) \approx L_0$ one obtains an anomalous behavior, characterized by a smooth increase of the phonon contribution as the temperature increases. Conversely, when experimental data are properly corrected from the $L(T)$ enhancement effect one gets a physically sound phonon contribution to the thermal conductivity which steadily decreases with the temperature starting at $T = 100$ K, as expected on general physical principles involving phonon-phonon interactions.[21]

CONCLUSION

In this work we revisit the applicability of the WFL given by the expression $\kappa_e(T) = L_0 T\sigma(T)$ in CMAs. Spurred by a series of experimental facts, indicating significant enhancements of the Lorenz number with respect to the standard Sommerfeld's value, we propose the use of a generalized expression for the WFL which is characterized by a temperature dependent Lorenz number. On the basis of previous analytical calculations we obtain a suitable approximate expression for the $L(T)$ function in terms of a set of model parameters which can be derived from a fitting analysis to experimental transport curves corresponding to the electrical conductivity $\sigma(T)$ and thermoelectric power $S(T)$. As an illustrative example we derive the phonon contribution to the thermal conductivity for a Ψ-AlPdMn sample making use of Eqs. (1) and (9), respectively. Whereas the use of Eq. (1) leads to an anomalous temperature dependence of $\kappa_{ph}(T)$ (quite similar to those usually reported in the literature for these materials as recently reported in Refs. 22 and 23), the $\kappa_{ph}(T)$ curve obtained from Eq. (9) is physically well sound.

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SAŽETAK

Teorijski aspekti vođenja topline u kompleksnim metalnim legurama: Poopćenje Wiedmann-Frantzovog zakona

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Motivirano nizom eksperimentalnih činjenica u svezi anomalnih transportnih svojstava određenih kompleksnih metalnih legura u ovom radu je predložena upotreba generaliziranog izraza za Wiedemann-Franzov zakon. Cilj je da se na odgovarajući način sistematično reducira eksperimentalne podatke koji su relevantni za fononski doprinos toplinskoj vodljivosti.