

Heat Conduction in Complex Metallic Alloys*

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Abstract. Thermal conductivity, κ , of ϵ -phase $\text{Al}_{73}\text{Pd}_{25}\text{Fe}_2$ and "Bergman phase" Mg-Al-Zn is presented, which resembles the features common to all complex metallic alloys: relatively low value, shallow local maximum or change of slope at approximately 50 K, and a rise above 100 K. The electron contribution, κ_{el} , is calculated using Wiedemann-Franz law, while the calculation of the phonon thermal conductivity, κ_{ph} , below 50 K is calculated employing Debye model. The sum of the two does not explain the experimental data at higher temperatures (above 100 K). This discrepancy is analyzed in three competitive ways: assuming an increase of an effective Lorenz number, taking into account the hopping of localized lattice vibrations, and employing a "bipolar diffusion effect", known from the theory of semiconductors. While the results of the former two approaches confirm other findings in literature, "bipolar diffusion effect" needs to be adopted for the specific electron structure of complex metallic alloys.

Keywords: thermal conductivity, Wiedemann-Franz law, Debye model, localized lattice vibrations, bipolar diffusion

INTRODUCTION

The term "complex metallic alloys (CMA)", which are considered here, relates to intermetallics with giant unit cells comprising hundreds or even thousands of atoms. From the point of view of application, potentialities of CMAs are rather notable: hydrogen-storage, great hardness and low wetting properties, resistance to oxidation, and good plasticity above room temperature being only some of them. Low thermal conductivity (comparable to those of amorphous insulators)^{1,2,3} makes them good candidates for thermal coating applications, while combined with relatively high electrical conductance and thermoelectric power indicate a possible use in thermoelectric conversion.

Two length scales are important in CMAs: long-range periodic and short-range cluster-like ones. Periodicity favors the presence of acoustical phonons extended throughout the structure, but a small first-Brillouin-zone volume (due to large unit cells) leads to their frequent *umklapp* scatterings,⁴ which eventually reduces the lattice contribution to the thermal conductivity of CMAs. The peculiar structure affects also the electronic properties: in CMA a pseudogap in the elec-

tronic density of states exists as a consequence of Hume-Rothery stabilization and hybridization,⁵ and is observed experimentally.⁶ Experimental electronic transport properties (electrical resistivity and thermoelectric power) are well explained within the pseudogap model,^{7,8} while calculations of the electronic thermal conductivity imply that an effective Lorenz number can exceed L_0 ($L_0 = 2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$).^{8,9}

The temperature dependence of the thermal conductivity of CMAs resembles that of amorphous insulators: for low-temperature region (typically between 1 K and 10 K) the thermal conductivity follows a power law ($\kappa(T) \propto T^n$, $n < 3$). At moderate temperatures (10 K $< T < 100$ K) the thermal conductivity generally saturates or has a broad and shallow maximum. Above $T \approx 100$ K, the thermal conductivity rises again and its origin is still an open question. Generally, several mechanisms can be involved: (i) non-monotonic temperature dependence of the effective Lorenz number ($L_{\text{eff}} > L_0$) enhances the electronic contribution to the thermal conductivity, (ii) the inter-cluster hopping of localized lattice vibrations,^{1,2,3,10} (iii) an anomalous increase of the lattice specific heat at high temperatures,¹¹ or (iv) due to pseudo-gap in electronic density of states, one can define

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"valence" and "conduction" band in which electrons and holes conduct the heat independently of one another.¹²

In this paper we present the thermal conductivity of two complex metallic alloys: an ϵ -phase of composition $\epsilon\text{-Al}_{73}\text{Pd}_{25}\text{Fe}_2$, and the "Bergman phase" Mg-Al-Zn, with a special attention given to the increase of thermal conductivity at high temperatures.

EXPERIMENTAL

The samples of $\epsilon\text{-Al}_{73}\text{Pd}_{25}\text{Fe}_2$ are polycrystalline, produced by levitation induction melting in a water-cooled copper crucible (see Ref. 3 and references therein). They had been annealed for 114 h at 750 °C and then water quenched. The structural characterization was performed by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM), showing that the sample was pure, not contaminated by secondary phases. The sample abbreviated as "Bergman phase" was grown by the Bridgman method and has the chemical composition of $\text{Mg}_{36.3}\text{Al}_{32.0}\text{Zn}_{31.7}$ (fractions of atoms expressed in percents) that corresponds to $\text{Mg}_{29.4}(\text{Al,Zn})_{51.6}$ (for more details, see Ref. 13). The sample used for measurements was cut from a Bridgman monocrystalline ingot and had the form of a rectangular prism with dimensions 2 mm \times 2 mm \times 7 mm, and the long axis parallel to the [1 0 0] crystal direction. This was also the direction of heat flow in the transport measurements. Due to the cubic symmetry, however, no orientation-dependence of the transport coefficients is to be expected.

The samples investigated are rod-shaped and one-dimensional approximation can be used for experimental determination of the thermal conductivity: $P_Q/A = \kappa \Delta T/l$, where P_Q , A , κ are the thermal flux, sample

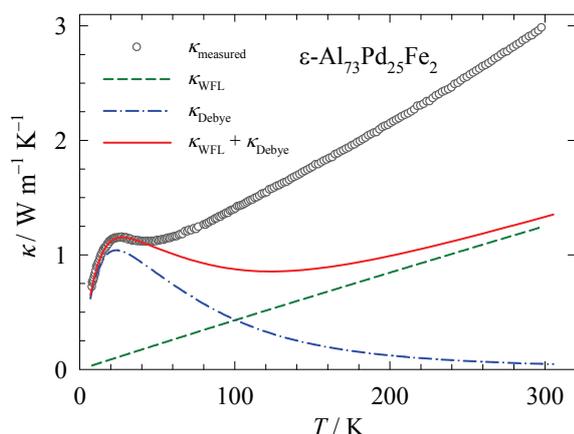


Figure 1. Measured thermal conductivity (open symbols) of $\epsilon\text{-Al}_{73}\text{Pd}_{25}\text{Fe}_2$. Dashed line is electron contribution to the thermal conductivity calculated by Wiedemann-Franz law (see text), while dot-dashed line is Debye contribution, calculated by Eq. (2). Solid line is the sum of these two.

cross section, and the thermal conductivity coefficient, respectively, while ΔT is the temperature drop along the sample length l . We use an absolute measurement method, where the sample heater is glued directly to the sample, the other end of which is thermally anchored to a heat sink, *i.e.* the sample-holder body. As the heater, we use a RuO_2 chip-resistor. The heat power through the sample (P_Q) is supposed to be equal to the electrical power P_E of the chip-resistor ($P_E = UI$, where U is the voltage drop, and I the current). The sample and the chip-resistor are glued with IMI 7031 varnish, in order to provide as good as possible a thermal contact between each other. The IMI 7031 varnish is also used to anchor the sample thermally to the heat sink. The temperature drop across the sample is monitored with a 25 μm differential thermocouple of chromel-gold with the fraction of iron atoms of 0.07 % its length being 20 cm.

RESULTS AND DISCUSSION

The open symbols on Figures 1 and 2 show the thermal conductivities of $\epsilon\text{-Al}_{73}\text{Pd}_{25}\text{Fe}_2$ and "Bergman phase", respectively. At $T \approx 30$ K, $\kappa(T)$ of $\epsilon\text{-Al}_{73}\text{Pd}_{25}\text{Fe}_2$ has a shallow local maximum, and for $T > 50$ K rises again; the room-temperature value being 3 W / m K. On the other hand, the thermal conductivity of "Bergman phase" does not have any local maximum, while the room temperature value is 24 W / m K.

The solid lines represent the fit obtained from the following equation:

$$\kappa_0(T) = \kappa_{\text{WFL}}(T) + \kappa_{\text{Debye}}(T), \quad (1)$$

where $\kappa_{\text{WFL}}(T)$ represents Wiedemann-Franz law which

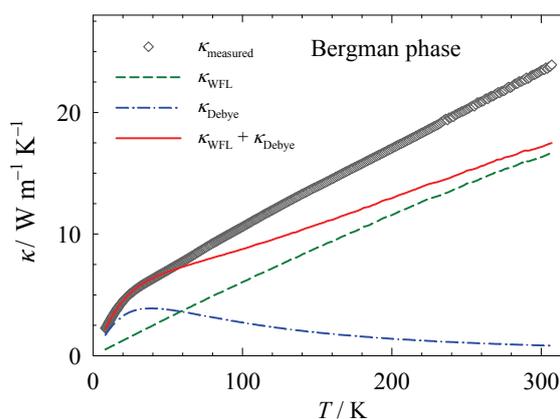


Figure 2. Measured thermal conductivity (open symbols) of "Bergman phase". Dashed line is electron contribution to the thermal conductivity calculated by Wiedemann-Franz law (see text), while dot-dashed line is Debye contribution, calculated by Eq. (2). Solid line is the sum of these two.

relates the electronic thermal with electrical conductivity $\sigma(T)$ and the temperature T in metals: $\kappa_{\text{WFL}}(T) = L_0 \sigma(T) T$ ($L_0 = 2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$ is the Lorenz number). The data of electrical conductivity for both samples is given elsewhere.^{3,13}

The phonon thermal conductivity is described by a general formula $\kappa_{\text{ph}} = (1/3)C_{\text{ph}}v_{\text{ph}}l_{\text{ph}}$, where C_{ph} , v_{ph} , l_{ph} are the phonon heat capacity, the mean group velocity, and the mean free path, respectively. For an exact calculation of these parameters, the calculation of phonon dispersion relation is needed. In the case of approximant phases of Al-TM-Si (TM denotes the transition metals: Re, Mn, Cu, and Fe), it shows the existence of three well defined acoustic phonon branches, with numerous optical ones, due to many atoms in a unit cell.¹⁴ At low energies, the density of states of acoustic phonons follows the Debye model. The upper limit of energy where the Debye model is still valid in CMA is around 5 meV $\approx 50 \text{ K} \cdot k$. The Debye model gives the following formula for the phonon thermal conductivity:

$$\kappa_{\text{Debye}}(T) = C_{\text{D}} T^3 \int_0^{\theta_{\text{D}}/T} \tau(x) \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (2)$$

where $C_{\text{D}} = k^4 / 2\pi^2 v_{\text{s}} h^3$ (v_{s} is a sound velocity), θ_{D} the Debye temperature, $\tau(x)$ the phonon relaxation time and $x = \hbar\omega/kT$, where $\hbar\omega$ is the phonon energy.

The different phonon-scattering processes are incorporated into the relaxation time $\tau(x)$ and we assume that Matthiessen's rule is valid, *i.e.* $\tau^{-1} = \sum \tau_i^{-1}$, where τ_i^{-1} is a scattering rate related to the i -th scattering channel. At the temperature range used, we consider two dominant scattering processes: (i) the scattering of phonons on structural defects of stacking-fault type with the scattering rate $\tau_{\text{sf}}^{-1} \propto \omega^2 \propto x^2 T^2$, and (ii) the *quasiumklapp* processes. In QCs and approximants, the *umklapp* scattering can be described by a power-law frequency and temperature dependence of the scattering rate $\tau_{\text{qu}}^{-1} \propto x^2 T^4$ (see Ref. 4). Many different power-law expressions, such as $\tau_{\text{qu}}^{-1} \propto x^3 T$, $\tau_{\text{qu}}^{-1} \propto x^2 T^2$, can be found in the literature,^{1,2,15} so that we assume a phenomenological form of the scattering rate, $\tau_{\text{qu}}^{-1} \propto x^{\alpha} T^4$. The Debye temperatures for several quasicrystalline and approximant phases are determined experimentally using specific heat data,^{16,17} and generally they range between 350 K and 500 K. Since our $\kappa(T)$ available data reach only up to 300 K, it turned out that the fit was insensitive to a slight change of the value of θ_{D} , so that a fixed $\theta_{\text{D}} = 500 \text{ K}$ was used. The Debye constant C_{D} was also not taken as a free parameter, but was instead calculated using $v_{\text{s}} = 4000 \text{ m/s}$, a value determined for the *i*-Al-Pd-Mn quasicrystal from ultrasonic data.¹⁷

Above approximately 50 K, the measured data start to deviate from the fits, as already observed in

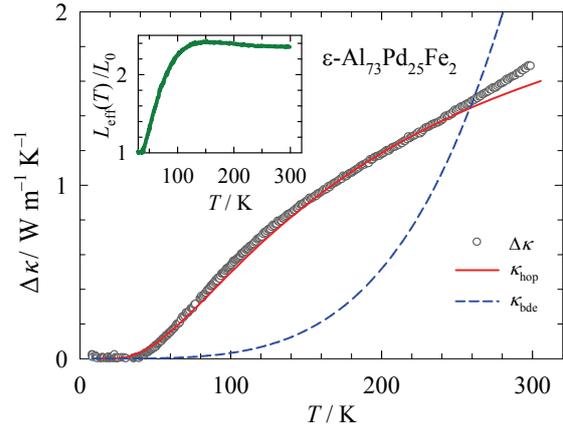


Figure 3. Main panel: Difference between measured thermal conductivity and $\kappa_{\text{WFL}}(T) + \kappa_{\text{Debye}}(T)$ for $\epsilon\text{-Al}_{73}\text{Pd}_{25}\text{Fe}_2$. Solid line is a fit to Eq. (3), while dashed line to $\kappa_{\text{bde}}(T) \propto T^4$ (see text). Inset: Ratio of the effective (L_{eff}) and Lorenz number (L_0), under assumption that the whole $\Delta\kappa(T)$ originates from increased electron contribution to the thermal conductivity (see text).

other thermal conductivity data.^{1,2} The difference ($\Delta\kappa(T)$) between the measured thermal conductivity and $\kappa_0(T)$, defined by Eq. (1), is shown by open symbols on Figures 3 and 4 for $\epsilon\text{-Al}_{73}\text{Pd}_{25}\text{Fe}_2$ and "Bergman phase", respectively. There is no clear and unique explanation for this deviation. We consider the following approaches:

(i) The effective Lorenz number L_{eff} exceeds L_0 , which leads to an enhanced electron contribution to the thermal conductivity $\kappa_{\text{el}}(T) = L_{\text{eff}}(T) \sigma(T) T$. Assuming $\Delta\kappa(T) = \kappa_{\text{el}}(T)$, $L_{\text{eff}}(T)$ can be calculated, and is shown on insets of Figures 3 and 4 for $\epsilon\text{-Al}_{73}\text{Pd}_{25}\text{Fe}_2$ and

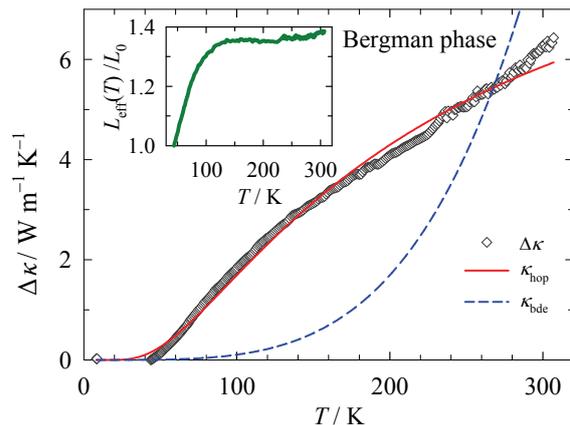


Figure 4. Main panel: Difference between measured thermal conductivity and $\kappa_{\text{WFL}}(T) + \kappa_{\text{Debye}}(T)$ for "Bergman phase". Solid line is a fit to Eq. (3), while dashed line to $\kappa_{\text{bde}}(T) \propto T^4$ (see text). Inset: Ratio of the effective (L_{eff}) and Lorenz number (L_0), under assumption that the whole $\Delta\kappa(T)$ originates from increased electron contribution to the thermal conductivity (see text).

"Bergman phase", respectively. In both cases $L_{\text{eff}}(T)$ resembles the theoretical predictions by Maciá and Rodríguez-Oliveros⁹ quite well.

(ii) Localized lattice vibrations within the cluster substructure can participate to the heat transport via the thermally-activated hopping. In the simplest way, the hopping of localized vibrations is described by the mean activation energy E_a , contributing to the thermal conductivity as

$$\kappa_{\text{hop}}(T) = \kappa_{\text{hop},0} \exp(-E_a / kT), \quad (3)$$

where $\kappa_{\text{hop},0}$ is a constant.¹⁰ Fits to Eq. (3) are shown as solid lines on Figures 3 and 4, with parameters $E_a \approx 32$ meV for $\varepsilon\text{-Al}_{73}\text{Pd}_{25}\text{Fe}_2$, and $E_a \approx 16$ meV for "Bergman phase". These values of the activation energy correspond well to the energy of optical phonons in calculated phonon dispersion for Al-TM-Si approximants,¹⁴ and with other analyses of the thermal conductivity data of CMA.^{1,2}

(iii) Another explanation for $\Delta\kappa(T)$ has been proposed recently.¹² It employs a "bipolar diffusion effect" based on two-band model, known from the semiconductor theory, in which electrons and holes are assumed to conduct independently in the conduction and valence bands. An extension of the theory of semiconductors to CMAs is based on the existence of a pseudogap in electron dispersion, although this assumption is a crude simplification of the real electronic structures in CMA. Anyhow, the thermal conductivity in the "bipolar diffusion effect" is given by the following formula

$$\kappa_{\text{bde}}(T) = \frac{\sigma_e \sigma_h}{\sigma_e + \sigma_h} (\alpha_e - \alpha_h)^2 T^3, \quad (4)$$

$\sigma_{e,h} = K_{0(e,h)}$, and $\alpha_{e,h} = (1/eT) K_{1(e,h)} / K_{0(e,h)}$, with

$$K_{n(e,h)} = \int (\varepsilon - \mu)^n \sigma_{e,h}(\varepsilon) (-\partial f_{\text{FD}} / \partial \varepsilon) d\varepsilon$$

where ε , μ , $\sigma_{e,h}(\varepsilon)$, and f_{FD} denote energy, chemical potential, spectral conductivity, and Fermi-Dirac distribution function, respectively. In the simplest case, the spectral function can be modeled with a quadratic function $\sigma_{e,h}(\varepsilon) = a_{e,h}(\varepsilon - \mu)^2 + b_{e,h}(\varepsilon - \mu)$, leading to $\kappa_{\text{bde}}(T) \propto T^4$. (Note that a symmetrical spectral function would give $\kappa_{\text{bde}}(T) = 0$.) Dashed lines on Figures 3 and 4 show $\kappa_{\text{bde}}(T) \propto T^4$, implying that this model is not fully applicable for these two cases; modifications of it are needed that would take into account the real electronic structure of CMA.

In conclusion, we have presented experimental data of the thermal conductivity of two complex metallic alloys (ε - and Bergman phase). An analysis that includes solely Wiedemann-Franz and Debye law is not valid for

high temperatures, indicating the presence of other heat conductance channel(s). It is analyzed in three competitive ways: assuming an increase of the effective Lorenz number, taking into account the hopping of localized lattice vibrations, and employing a "bipolar diffusion effect", known from the theory of semiconductors. While the results of the former two approaches confirm other findings in literature, "bipolar diffusion effect" needs to be adopted for the specific electron structure of complex metallic alloys.

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SAŽETAK**Transport topline u kompleksnim metalnim legurama****Ante Bilušić,^{a,b} Igor Smiljanić,^b Željko Bihar,^b Denis Stanić^b i Ana Smontara^b**^a*Odjel za fiziku, Prirodoslovno-matematički fakultet, Sveučilište u Splitu, Nikole Tesle 12,
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Prikazane su toplinske vodljivosti ε -faze $\text{Al}_{73}\text{Pd}_{25}\text{Fe}_2$ i "Bergmanove faze" Mg-Al-Zn koje imaju svojstva zajednička kompleksnim metalnim spojevima: relativno malu vrijednost toplinske vodljivosti, plitak lokalni maksimum ili promjenu nagiba na približno 50 K te porast iznad 100 K. Doprinos elektrona je izračunat Wiedemann-Franzovim zakonom, dok je za proračun doprinosa fonona za temperature niže od 50 K korišten Debye-ov model. Njihov zbroj ne objašnjava eksperimentalne podatke za više temperature (iznad 100 K), za što su ponuđena tri kompetitivna modela: povećanje efektivnog Lorenzovog broja, preskoci lokaliziranih titrajnih stanja rešetke te "učinak bipolarne difuzije", poznat iz teorije poluvodiča. Dok rezultati prva dva pristupa potvrđuju ostale rezultate iz literature, "učinak bipolarne difuzije" ipak treba biti prilagođen specifičnostima elektronske strukture kompleksnih metalnih legura.