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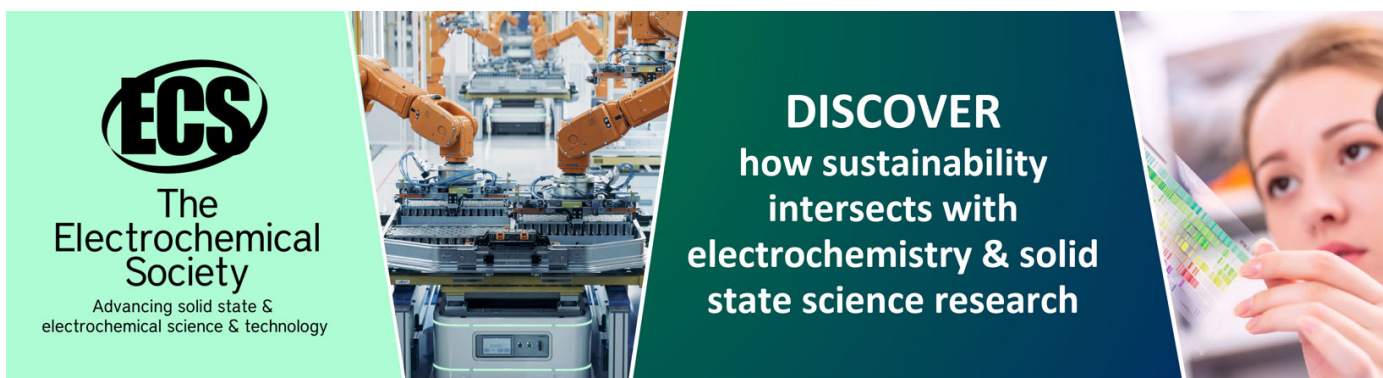
# Thermal conductivity of Taylor phase T-Al<sub>73</sub>Mn<sub>27</sub> complex metallic alloy

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## Thermal conductivity of Taylor phase T-Al<sub>73</sub>Mn<sub>27</sub> complex metallic alloy

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**Abstract.** Thermal conductivity coefficient,  $\kappa$ , of Taylor phase T-Al<sub>73</sub>Mn<sub>27</sub> complex metallic alloy with giant unit cell has been studied in the temperature interval from 2 K to 300 K.  $\kappa$  is relatively small in magnitude (comparable to that of thermal insulators), have a slope-change at about 50 K and increases up to 300 K. Such a low  $\kappa$  originates in complex structure: aperiodic in short length scale, that leads to frequent electron scattering and consequent low electron contribution to the thermal conductivity, while large lattice constant defines a small Brillouin zone that enhances *umklapp* scattering of extended phonons, and suppressing lattice thermal conductivity. Above ~100 K hopping of localized lattice vibrations gives an additional heat-carrying channel.

Complex metallic alloys (CMA) denote intermetallic phases with a giant unit cell containing from tens up to thousands atoms. The atoms inside the unit cell are arranged in clusters with the local icosahedral symmetry. In this paper we study thermal conductivity of the orthorhombic Al<sub>73</sub>Mn<sub>27</sub> compound first discovered by Hofmann [1] and later studied by Taylor [2,3], so it is often referred as the Taylor (T) phase. The structure is built of atomic layers stacked along *b* crystallographic axis, along which pentagonal columnar clusters are formed [4]. Therefore, they are considered to be approximants of the decagonal (*d*) Al-Mn phases. The unit cell of the T-Al<sub>73</sub>Mn<sub>27</sub> phase contains 156 atoms with many of the sites having either fractional occupation or mixed Al/Mn occupation, so that a great inherent chemical disorder exists on the lattice [5].

This study is a continuation of our previous investigation of the thermal conductivity of different families of CMAs [6-10], from which two conclusions can be drawn: (*i*) the thermal conductivity of CMAs is unusually low as compared to that of typical metallic alloys and (*ii*) the contribution of electrons to the thermal transport is significantly lower than that due to phonons over a wide temperature range. At the same time this study is a part of systematic investigation of thermal and electrical properties of *T*-Al<sub>73</sub>Mn<sub>23-x</sub>(Pd,Fe)<sub>x</sub> (0 < x < 6) alloys which are convenient for the research due to the strong variations of these properties with the composition.

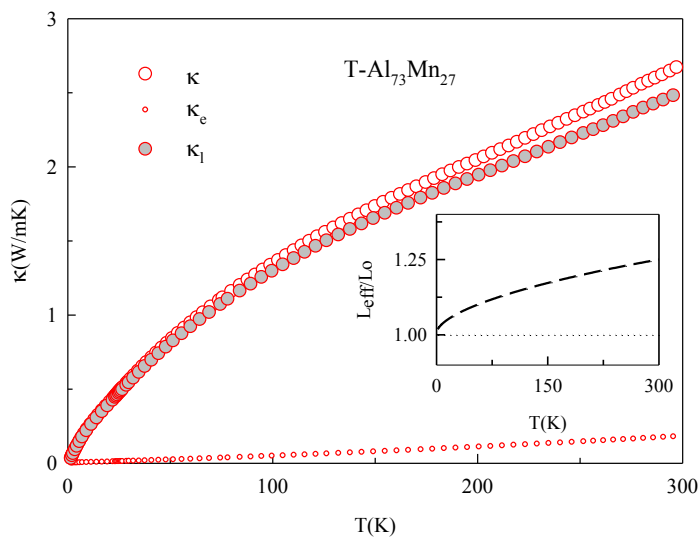
In what follows we first present some experimental details and the results for the thermal conductivity in T-Al<sub>73</sub>Mn<sub>27</sub> phase. Next, we separate the thermal conductivity into electron and lattice parts. There, the much smaller electron contribution was determined by the spectral conductivity

model. Further, the lattice contribution is analyzed by considering propagation of long-wavelength phonons within the Debye model and by a hopping of localized vibrations of a short wavelength. Finally, the results of a fitting procedure to experimental data are shown.

Polygrain ingot sample of desired composition was produced from constituent elements by levitation induction melting in a water-cooled copper crucible under an argon atmosphere. To obtain T-phase, parts of the sample was annealed in argon at 900 °C for up to 312 h, additionally at 930 °C for 3 h and subsequently quenched into water [5]. The annealed sample was single phase.

Thermal conductivity  $\kappa$  has been measured in the temperature interval from 2 to 300 K in liquid helium cryostat using an absolute steady-state heat-flow method. The thermal flux through the sample was generated by a 1 k $\Omega$  RuO<sub>2</sub> chip-resistor, glued to one end of the sample, while the other end was attached to a copper heat sink. The temperature gradient across the sample was monitored by a chromel – (gold+0.07 at.% Fe) differential thermocouple with the wires diameter of 25  $\mu$ m. Electrical resistivity  $\rho$  (conductivity  $\sigma = 1/\rho$ ) and the thermoelectric power  $S$  were measured in the same temperature range:  $\rho$  using the standard four-terminal technique, while  $S$  by a differential method with two identical thermocouples (chromel-gold + 0.07 at.% iron, 50  $\mu$ m of wire thickness), attached to the sample with silver paint.

The temperature dependence of the thermal conductivity  $\kappa(T)$  for the T-Al<sub>73</sub>Mn<sub>27</sub> is shown in figure 1.  $\kappa(T)$  shows characteristic behaviour for complex metallic alloys (e.g. Mg<sub>32</sub>(Al,Zn)<sub>49</sub> [11], Al<sub>74</sub>Pd<sub>22</sub>Mn<sub>4</sub>,  $\beta$ -Al<sub>3</sub>Mg<sub>2</sub> [12] and  $\epsilon$ -phases (Al-Pd-transition metal) [8-10]: relatively small in magnitude, change of slope at about 50 K and increases up to 300 K.



**Figure 1.** Temperature dependence of the thermal conductivity  $\kappa(T)$  between 2 and 300 K in T-Al<sub>73</sub>Mn<sub>27</sub>, electronic contribution,  $\kappa_e$ , calculated by the model of spectral conductivity, and estimated lattice contribution  $\kappa_l = \kappa - \kappa_e$ . The inset shows temperature dependence of the ratio of effective Lorentz number  $L_{eff}$  to the Lorentz number  $L_0$ .

At room temperature the magnitude of  $\kappa$  is 2.7 W/mK. Such small magnitude of thermal conductivity is the characteristic of thermal insulators like SiO<sub>2</sub> [13] and Zr/YO<sub>2</sub> [14]. The small value of  $\kappa$  has been found also in icosahedral quasicrystals *i*-Al-Pd-Mn [15,16] which is explained by (a) the low electronic density of states at Fermi level  $E_F$  (small contribution of electrons to thermal conductivity), and (b) lattice aperiodicity (that suppresses the lattice contribution to  $\kappa$ ). Similarly, the electrical conductivity of T-Al<sub>73</sub>Mn<sub>27</sub> is rather low compared to simple metals. In that sense, we apply the thermal conductivity model appropriate to systems with the long-scale lattice periodicity and the short-scale atomic clustering structure that has been described in details in ref. [6].

To estimate the electronic part to the thermal conductivity ( $\kappa_e$ ) we apply analysis based on the Kubo-Greenwood response theory [17,18]. The central quantity of this formalism is the spectral conductivity function  $\sigma_s(E)$  that incorporates both the band structure and the transport properties of the system. The analysis of the temperature dependence of the electrical conductivity  $\sigma(T)$  and the

thermoelectric power  $S(T)$  gives the shape of  $\sigma_S(E)$  in the vicinity of  $E_F$ . The details of the analysis, which it is a modified version of the procedure originally developed by Landau and Macia [19,20] and adjusted to suite the experimental data in this class of compounds, can be found in the reference [21]. Once calculated,  $\sigma_S(E)$  can be used to determine  $\kappa_e$  (for room-temperature values see table 1).

**Table 1.** Values at room temperature of: the electrical  $\sigma$ , and thermal conductivity,  $\kappa$ , the electronic contribution  $\kappa_e$  calculated by the model of spectral conductivity and the fit parameters for the lattice thermal conductivity  $\kappa_l = \kappa_D + \kappa_H$  (see text).

$\sigma$ ( $10^4 \Omega^{-1}m^{-1}$ )	$\kappa$ (W/mK)	$\kappa_e$ (W/mK)	$A$ ( $10^7 s^{-1}K^{-2}$ )	$\kappa_H^0$ (W/mK)	$E_a$ (meV)
1,97	2,69	0,18	5,6	4,8	17,7

It is interesting to consider the validity of the Wiedemann–Franz law (WFL)  $\kappa_{e0} = L_0 T \sigma$ , where  $L_0 = 2,44 \times 10^{-8} \Omega K^{-2}$  is the Lorenz number. Additionally, from the spectral conductivity model we can calculate the effective Lorenz number  $L_{eff} = \kappa_e / T \sigma$ . The ratio  $L_{eff} / L_0$  is given in the inset of Fig. 1: one can see that WFL is valid at the limit  $T \rightarrow 0$  only. Similar deviation from WFL in icosahedral quasicrystals is observed in ref. [22].

The lattice contribution,  $\kappa_l(T) = \kappa(T) - \kappa_e(T)$  is analyzed by considering propagation of long-wavelength phonons within the Debye model ( $\kappa_D$ ) and hopping of localized vibrations of a short wavelength ( $\kappa_H$ ). This picture assumes that large atomic clusters of icosahedral symmetry strongly suppress propagation of phonons in the lattice of complex metallic alloys, except acoustic phonons with long wavelength for which this material is an elastic continuum. Additionally, localized vibrations within the cluster substructure can participate in the heat transfer via thermally activated hopping. In the simplest model, hopping of localized vibrations is described by the single activation energy  $E_a$ , yielding a contribution to the thermal conductivity  $\kappa_H = \kappa_H^0 \exp(-E_a / k_B T)$  [7], where  $\kappa_H^0$  is a constant.

The thermal conductivity within Debye model is given by [6]:

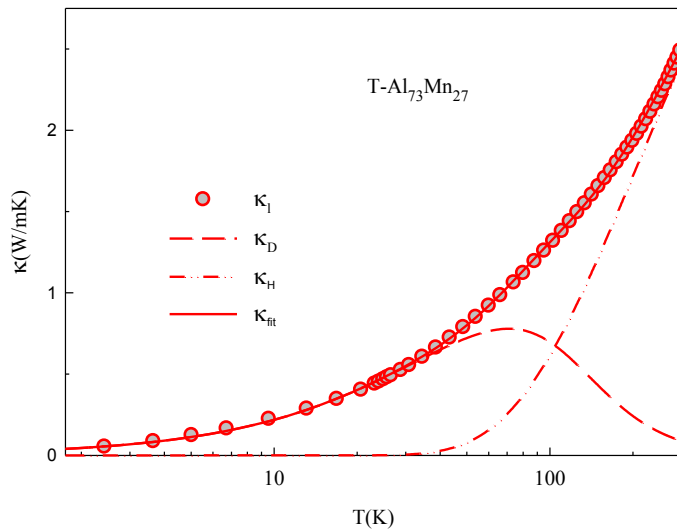
$$\kappa_D = C_D T^3 \int_0^{\theta_D/T} \tau(x) \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (1)$$

where  $C_D = k_B^4 / 2\pi^2 \bar{v} h^3$ ,  $\bar{v}$  is the average sound velocity,  $\theta_D$  the Debye temperature,  $\tau$  the phonon relaxation time,  $x = \hbar\omega / k_B T$ , and  $\hbar\omega$  is the phonon energy. Since the Debye temperature of the investigated T-Al<sub>73</sub>Mn<sub>27</sub> is not known, we have used  $\theta_D = 500 K$  reported for the related icosahedral *i*-Al–Pd–Mn quasicrystals [23]. Since our  $\kappa(T)$  data are available only up to 300 K, it turns out that the fit is insensitive to a slight change of  $\theta_D$ . The Debye constant  $C_D$  was also not taken as a free parameter, but was instead calculated by using  $\bar{v} = 4000 \text{ ms}^{-1}$ , a typical value for such complex structure [6]. The different phonon-scattering processes are incorporated into the relaxation time  $\tau(x)$  and we assume that Matthiessen's rule is valid,  $\tau^{-1} = \sum \tau_j^{-1}$ , where  $\tau_j^{-1}$  is a scattering rate related to the  $j$ -th scattering channel. In analogy to the  $\epsilon$ -phases in Al–Pd–Mn [6], we consider two dominant scattering processes in the investigated temperature interval. First, scattering of phonons on structural defects of stacking-fault type with the scattering rate

$$\tau_{sf}^{-1} = \frac{7}{10} \frac{a^2}{\bar{v}} \gamma^2 N_s \omega^2 \equiv A \omega^2 \quad (2)$$

where  $a$  is a lattice parameter,  $\gamma$  is the Grüneisen parameter and  $N_s$  is the linear density of stacking faults. The second scattering mechanisms are the *umklapp* processes with the phenomenological form of the scattering rate pertinent to complex metallic alloys [15],  $\tau_{um}^{-1} \propto \omega^\alpha T^{4-\alpha}$ . Thus for the total scattering rate we get  $\tau^{-1} = \tau_y^{-1} + \tau_{um}^{-1}$ .

Results of a fitting procedure of a relation  $\kappa_l(T) = \kappa_D(T) + \kappa_H(T)$  to experimental data are shown in figure 2. Parameters of the fitting procedure are given in table 1. From the figure 2, it is easy to see



**Figure 2.** Temperature dependence of the phonon thermal conductivity  $\kappa_l$  together with the Debye contribution  $\kappa_D$  and hopping contribution  $\kappa_H$  of T-Al<sub>73</sub>Mn<sub>27</sub> shown in log scale.

that Debye contribution  $\kappa_D(T)$  has a maximum at about 50 K while it becomes smaller at higher temperatures, a characteristic for the periodic structures that originates in phonon-phonon *umklapp* scattering processes. From the fitting parameter  $A$  we can obtain  $N_s$ : for typical values for the lattice parameter  $a \approx 1.5$  nm and the Grüneisen parameter  $\gamma \approx 2$ , we get  $N_s = 2 \mu\text{m}^{-1}$ . This micrometer-scale  $N_s$  value is comparable to those reported for  $\psi$ -Al-Pd-Mn [6],  $i$ -Al-Pd-Mn [24], and decagonal  $d$ -Al-Mn-Pd [25]. The parameter  $\alpha$  defines phonon scattering by *umklapp* processes in a phenomenological way. Fitting procedure gives  $\alpha = 1$ , so the frequency and temperature dependence of the *umklapp* term is  $\tau_{um}^{-1} \propto \omega T^3$ . Hopping contribution  $\kappa_H$  becomes significant above 100 K; obtained activation energy  $E_a$  is 17.7 meV and is smaller by factor 2 than  $E_a$  of  $\zeta$ -Al-Pd-Mn [6]. This smaller  $E_a$  value reflects the considerably less steep  $\kappa(T)$  increase at temperatures above 100 K for our samples compared to  $\zeta$ -Al-Pd-Mn. On the other side, the above  $E_a$  values correlate with the inelastic neutron and X-ray [6] scattering experiments on  $i$ -Al-Pd-Mn quasicrystals, where dispersionless vibrational states were identified for energies higher than 12 meV. Such states indicate localized vibrations and are considered to be a consequence of a dense distribution of energy gaps in the phonon excitation spectrum. Therefore, localized vibrations also appear to be present in the T-Al<sub>73</sub>Mn<sub>27</sub>, where their origin may be attributed to the cluster substructure of the giant unit cell.

To conclude, we have investigated thermal conductivity of T-Al<sub>73</sub>Mn<sub>27</sub> sample which show behavior typical for complex metallic alloys: relatively small value and change of slope at about 50 K. We have separated  $\kappa(T)$  into electron  $\kappa_e(T)$  and lattice (phonon)  $\kappa_l(T)$  parts. Electron contribution was determined by the spectral conductivity model, and it is much smaller than the lattice one, due to rather low electrical conductivity. The low level of the lattice thermal conductivity is determined by enhanced *umklapp* processes of phonon scattering (caused by large lattice constant and, consequently small Brillouin zone) and by inherent short- and middle scale size aperiodicity of the structure.

## Acknowledgements

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