

Heat Transport in Aluminum-Based Quasicrystals *i*-AlPdMn, *i*-AlCuFe, and *d*-AlCoNi

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Abstract: We present a semi-quantitative model used to analyze thermal conductivity data of single-grain aluminum-based icosahedral *i*-AlPdMn and *i*-AlFeCu, and decagonal *d*-AlCoNi quasicrystals in the quasiperiodic plane. The analysis is based on the validity of the Wiedemann–Franz law and applicability of the Debye model of quasilattice thermal conductivity at low temperatures, where the main phonon

scattering centers are assumed to be structural defects in the form of the stacking faults and phenomenological quasilattice klappp. At high temperature, electron and quasilattice contributions underestimate the data. This has motivated us to consider two possible additional heat-carrying channels: the activation of localized lattice vibrations and modifications of the Wiedemann–Franz law.

Keywords: low-temperature physics · quasicrystals · thermal conductivity · Wiedemann–Franz law

1. Introduction

Quasicrystals are a form of condensed matter that differs from the other two — crystalline and amorphous — by possessing long-range quasiperiodic translational and non-crystallographic orientational order.^[1] For example, icosahedral quasicrystals exhibit diffraction patterns with fivefold symmetry axes, while diffraction patterns of decagonal quasicrystals exhibit tenfold symmetry axes. This particular character of the structure raises the question of how the dynamics of quasilattices are best described and whether the aperiodicity implies that the vibration spectra of quasicrystals are similar to those of amorphous materials.

A particular characteristic of amorphous materials is the existence of tunneling states^[2] modeled by structural configurations of the atoms which are almost degenerate in energy. These states are separated by low potential barriers through which “tunneling” is possible, and their influence on physical properties is significant in the sub-Kelvin temperature range. The thermal conductivity is the physical quantity that reveals the nature of lattice vibration. The phonon scattering on tunneling states leads to $\kappa(T) \propto T^2$ dependence at low temperature, that is, in quasicrystals described in refs. [3, 4]. Although other experiments do not confirm tunneling states as relevant phonon scattering centers,^[5] ultrasonic attenuation data^[6–8] still confirm their presence in quasicrystals, indicating that low-temperature lattice excitations are similar to those of amorphous materials.

In this work we present the study of the heat transport in aluminum-based quasicrystals with different symmetries (icosahedral and decagonal), covering the temperature range between 2 K and 300 K. After subtracting the

electron contribution, the low-temperature quasilattice contribution was analyzed using the Debye thermal conductivity model, which fails to reproduce the experimental data above approximately 50 K. For that temperature range we have employed two competitive models: one where the activation of localized lattice vibration is taken into account, and the other that considers modifications of the Wiedemann–Franz law in quasicrystals.

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2. Sample Selections and Experimental Details

For our study we chose the following samples: icosahedral (*i*) quasicrystals $\text{Al}_{72}\text{Pd}_{19.5}\text{Mn}_{8.5}$ (abbreviated as *i*-AlPdMn) and $\text{Al}_{64}\text{Cu}_{23}\text{Fe}_{13}$ (*i*-AlCuFe), and the decagonal quasicrystal (*d*) $\text{Al}_{70}\text{Co}_{10}\text{Ni}_{20}$ (*d*-AlCoNi).

2.1. *i*-AlPdMn Icosahedral Quasicrystals

The samples of *i*-AlPdMn were grown in the Ames Laboratory by I.R. Fisher and P.C. Canfield from the ternary melt via a “self-flux” technique.^[9] The quasicrystals grown by this technique have a composition of $\text{Al}_{72}\text{Pd}_{19.5}\text{Mn}_{8.5}$ as measured by electron microprobe analysis (EMPA), with an estimated error of approximately 0.5 at.% for each element.^[9] The samples show a high degree of structural order, as demonstrated by X-ray transmission and electron-diffraction.^[9] For the transport measurements, a bar of dimensions $0.5 \times 0.6 \times 5.9 \text{ mm}^3$ was cut from a well-formed very large ingot, using a wire saw. Transport properties (electrical resistivity, thermopower, and thermal conductivity) and transmission electron microscopy (TEM) experiments of icosahedral $\text{Al}_{72}\text{Pd}_{19.5}\text{Mn}_{8.5}$ were reported recently.^[10,11]

2.2. *i*-AlCuFe icosahedral quasicrystals

The single-crystal icosahedral quasicrystals with composition $\text{Al}_{64}\text{Cu}_{23}\text{Fe}_{13}$ were grown by the Czochralski technique at the Himeji Institute of Technology by Y. Yokoyama.^[12] This composition was chosen because of its superior thermal stability (any secondary-phase precipitates in the as-grown material disappeared upon annealing^[13]), so that it is considered to represent the ideal icosahedral composition. The crystal was pulled out of the molten alloy of composition $\text{Al}_{57.7}\text{Cu}_{37.7}\text{Fe}_{3.5}\text{Si}_{1.1}$ (where Si was added to restrain crystallization of $(\text{Al} + \text{Cu})_{13}\text{Fe}_4$) and the growth direction was parallel to the threefold symmetry axis. The investigated single-crystal *i*-AlCuFe has an almost phason-free quasicrystalline structure and shows superior quasicrystallinity on both macro- and microscopic scales.^[14] The sample was shaped in the form of a prism, with dimensions $3.9 \times 1.5 \times 1.4 \text{ mm}^3$. Intrinsic electrical, magnetic, and thermal properties of icosahedral $\text{Al}_{64}\text{Cu}_{23}\text{Fe}_{13}$ were reported recently.^[15]

2.3. *d*-AlCoNi Decagonal Quasicrystals

The single crystal of *d*- $\text{Al}_{70}\text{Co}_{10}\text{Ni}_{20}$ was grown by the Czochralski method in the laboratory of P. Gille at LMU, Munich.^[16] The EMPA measurements yielded the average composition of $\text{Al}_{69.7}\text{Co}_{10.6}\text{Ni}_{20.3}$ with a standard deviation of 0.2 at.% for each component. This composition is close to the Ni-rich limit of the quasicrystal stability region. The characterization by X-ray transmission indicates a superior structural quality of the material.^[16] The radial ele-

mental distribution was found absolutely homogeneous within the error of EMPA. In order to perform transport measurements in the quasiperiodic direction, we have cut, from the parent crystal, a rectangular bar of dimensions $10 \times 2 \times 2 \text{ mm}^3$, with the long axis oriented in the quasiperiodic plane. Intrinsic transport and magnetic properties of decagonal $\text{Al}_{70}\text{Co}_{10}\text{Ni}_{20}$ were determined recently.^[17,18]

2.4. Experimental

Since the samples investigated are rod-shaped, one-dimensional approximation can be used for experimental determination of the thermal conductivity: $P_Q/A = \kappa \Delta T/l$, where P_Q , A , and κ are the thermal flux, sample cross section, and thermal conductivity coefficient, respectively, and ΔT is the temperature drop along the sample length l . We use a specially designed, laboratory-made cryostat,^[19] applying 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, that is, the sample-holder body. We use a RuO_2 chip-resistor as the heater. 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 the best possible thermal contact between them. 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 differential, chromel–gold thermocouple with the fraction of iron atoms of 0.07%. Its dimensions are 20 cm in length and 25 μm in diameter. As shown in refs. [20] and [21], heat losses due to radiation and conduction through the contact wires can be neglected with this set-up at temperatures below 300 K. The experimental thermal conductivity data were taken in temperature steps. The electrical resistivity was measured on the same specimens using the standard dc four-terminal technique using a laboratory-made cryostat designed for the measurement of the electrical resistivity and the thermoelectric power in the temperature range between 1.5 K and 325 K.^[20,22] During the experiment, the temperature was sweeping not faster than 5 Kelvin per hour.

3. Thermal Conductivity

The thermal conductivity of quasicrystals consists of quasi-lattice ($\kappa_{\text{ql}}(T)$) and electronic contribution ($\kappa_{\text{el}}(T)$). The approach to the determination of the electronic thermal conductivity and that of quasi-lattice thermal conductivity is quite different. In the case of electrons, the problem is normally regarded as one of calculating the effective Lorenz number, $L(T) = \kappa_{\text{el}}(T)/\sigma(T) \cdot T$, where electrical conductivity, $\sigma(T) = \rho(T)^{-1}$, is taken from the

measurements that should cover the same temperature range as that of the thermal conductivity. Thus, the information on the electrical conductivity is essential if the thermal conductivity is to be successfully analyzed. On the other hand, the quasi-lattice thermal conductivity is treated as an entity in itself. One normally calculates the electronic thermal conductivity as accurately as possible, so that the quasi-lattice conductivity, under assumption of their mutual independence, is obtained by subtracting the electronic from the total conductivity, $\kappa_{\text{ql}}(T) = \kappa(T) - \kappa_{\text{el}}(T)$.

3.1. A Semi-Quantitative Analysis of Thermal Conductivity Data

In what follows, we present a study of thermal conductivity combined with the electrical resistivity data of the single crystals *i*-AlPdMn, *i*-AlCuFe and *d*-AlCoNi.

A semi-quantitative model of thermal conductivity appropriate to quasicrystals was used previously in the investigations of AlCrFe approximant^[23,24] and AlPdMn quasicrystalline phases.^[25,26] According to that model, thermal conductivity parameter $\kappa(T)$ is divided into three terms

$$\kappa_{\text{el}}(T) = \kappa_{\text{el}}(T) + \kappa_{\text{ql}}(T) = \kappa_{\text{el}}(T) + \kappa_{\text{Debye}}(T) + \kappa_{\text{hop}}(T) \quad (1)$$

where $\kappa_{\text{hop}}(T)$ is the contribution important at higher temperatures only ($T > 100$ K), and comes from the hopping of localized vibrations.

The simplest way to estimate the electronic contribution to the thermal conductivity $\kappa_{\text{el}}(T)$ is the Wiedemann–Franz law that follows from the Drude theory

$$\kappa_{\text{el}}(T) = L_0 T / \rho(T) \quad (2)$$

where $L_0 = 2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$ is the Lorenz constant. The assumption of the validity of Equation 2 in the whole temperature range is rather crude; even for metals, it holds only within elastic electron scattering limit (i.e., for very low and very high temperatures, as compared to the Debye temperature). Calculation of the effective Lorenz number $L(T)$ for the intermetallic Al₃(Mn,Pd) phases^[26,27] and quasicrystals^[15] has shown that its “relaxation-time-approximation” value, L_0 , has correction parameter c of the order of 10%. For that reason a slight modification of the Wiedemann–Franz law is assumed:

$$\kappa_{\text{el}}(T) = (1 + c)L_0 T / \rho(T) \quad (2a)$$

The parameter c may also be considered as a compensating factor for the experimental error in the resistivity $\rho(T)$ data, which is of the same order of magnitude. Note that Equation 2 does not include the temperature dependence of the effective Lorenz number. The physically

more appropriate way to calculate electronic contribution $\kappa_{\text{el}}(T)$ is within Kubo–Greenwood formalism, which employs the spectral conductivity $\sigma(\epsilon)$.^[15,26,28–30] This requires, in addition to the knowledge of the electrical conductivity $\sigma(T)$, the knowledge of the thermopower $S(T)$ of the system. In the limit of zero temperature, the spectral conductivity model predicts $L(T \rightarrow 0) \rightarrow L_0$. The upper limit for the effective Lorenz number is reached for $T \rightarrow \infty$, being $L \rightarrow (21/5)L_0$ for icosahedral quasicrystals.^[28] Between these two temperature extremes, $L(T)$ in general rises monotonically. The spectral conductivity model suggests that instead of the Wiedemann–Franz law given in Equation 2, one should use its modified form

$$\kappa_{\text{el}}(T) = L(T)T / \rho(T) \quad (2b)$$

The quasi-lattice contribution, calculated as $\kappa_{\text{ql}}(T) = \kappa(T) - \kappa_{\text{el}}(T)$, could be analyzed by considering two contributions: 1) the propagation of long-wavelength acoustic phonons within the Debye model which is, at low temperature, applicable for non-crystals too since only long-range acoustic phonons that are not affected by underlying non-periodicity are excited, and 2) hopping of localized vibrations within the icosahedral cluster substructure, which participate in the heat transfer via thermally activated hopping. In the simplest model, hopping of localized vibrations is described by mean activation energy E_a , yielding a contribution to the thermal conductivity

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

where κ_{hop}^0 is a constant. The Debye thermal conductivity is related to the phonon mean free path l and the specific heat C ^[31]

$$\kappa_{\text{Debye}}(T) = \frac{1}{3} \bar{v} \cdot \int_0^{\theta_D/T} l(x) \cdot C(x) dx = \frac{k_B}{2\pi^2 \bar{v}} \left(\frac{k_B}{\hbar} \right)^3 \cdot T^3 \cdot \int_0^{\theta_D/T} \tau(x) \cdot \frac{x^4 \cdot e^x}{(e^x - 1)^2} dx \quad (4)$$

where \bar{v} is the average sound velocity, θ_D the Debye temperature, τ the phonon relaxation time, and $x = (\hbar\omega/k_B T)$ with $\hbar\omega$ being the phonon energy. The different phonon-scattering processes are incorporated into the relaxation time $\tau(x)$. We assume that different scattering mechanisms are independent (i.e., Matthiessen’s rule is valid), $\tau^{-1} = \sum \tau_j^{-1}$, where τ_j^{-1} is a scattering rate related to the j -th scattering channel. In analogy to the AlCrFe approximants^[24] and AlPdMn quasicrystalline phases,^[25,32] it is appropriate to consider two dominant scattering processes. The first one follows from

$\kappa(T) \propto T$ for $T < 10$ K. We assign such temperature dependence to the phonon scattering on structural defects of stacking-fault type with the scattering rate $\tau_{\text{sf}}^{-1} \propto x^2 T^2$ (note that, since $x^2 \propto \omega^2 T^{-2}$, τ_{sf}^{-1} does not show an explicit temperature-, but frequency-dependence

$$\tau_{\text{sf}}^{-1} = \frac{7a^2\gamma^2 N_s}{10v_{\text{mean}}} \omega^2 \quad (5)$$

where N_s , a , and γ are the linear density of stacking faults, lattice, and the Grüneisen parameter, respectively. The second important scattering process should be responsible for maximum/plateau appearance at $T \approx 20 - 30$ K. It is the *umklapp*-type process with the phenomenological form of the scattering rate pertinent to quasicrystals,^[11,24,25] $\tau_{\text{qu}}^{-1} \propto x^\alpha T^\beta$. The corresponding frequency and temperature dependence of the *quasi-umklapp* scattering rate is

$$\tau_{\text{qu}}^{-1} \propto \omega^\alpha T^{\beta-\alpha} \quad (6)$$

where the exponents α and β are determined from the fit, paying attention to reproduce a maximum/plateau region of the quasilattice thermal conductivity as good as possible. Assuming the validity of Matthiessen's rule, the total scattering rate of phonons in quasicrystals within the Debye model is

$$\tau^{-1} = \tau_{\text{sf}}^{-1} + \tau_{\text{qu}}^{-1} \quad (7)$$

3.2. *i*-AlPdMn

The thermal conductivity of *i*-AlPdMn quasicrystal is shown in the main panel of Figure 1. The room-temperature value is relatively low and typical for quasicrystals: $\kappa(300 \text{ K}) \approx 4.3 \text{ W/mK}$. By lowering the temperature, the thermal conductivity first reaches a local minimum at $T \approx 100$ K where $\kappa \approx 2.2 \text{ W/mK}$, then starts to rise until $T \approx 23$ K and $\kappa \approx 3.8 \text{ W/mK}$, and falls again at lower temperatures. The inset in Figure 1 shows the electrical resistivity data of *i*-AlPdMn. The room-temperature value is $\rho(300 \text{ K}) \approx 1220 \mu\Omega \text{ cm}$. It depends non-monotonically on the temperature, with a maximum at $T \approx 120$ K. Such temperature behaviour comes from the scattering of the conduction electrons on the ones localized around diluted magnetic manganese atoms (this model of electron scattering is known as the Korringa–Gerritsen model).^[33]

Quantitative analysis of the thermal conductivity of *i*-AlPdMn is presented in the main panel of Figure 2. The electron contribution, denoted as the dash-double-dot line, is calculated using the Wiedemann–Franz law (Equation 2), and contributes at most 10% at room temperature. It is then subtracted from the measured thermal conductivity; the resulting data we assign to the quasilattice contribution. Notice the importance of the proper de-

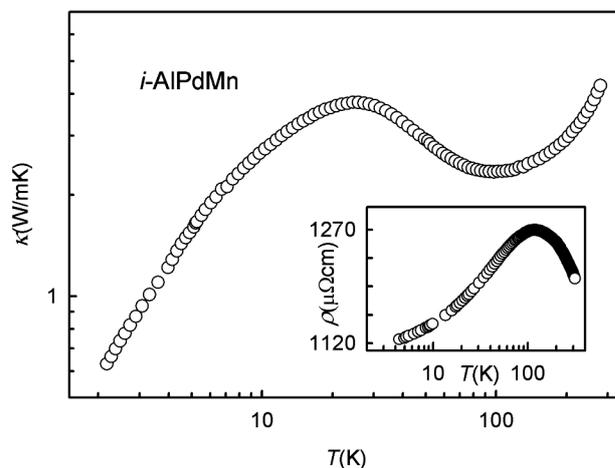


Figure 1. Temperature-dependent thermal conductivity, $\kappa(T)$, of the single grain *i*-AlPdMn. The inset shows the temperature-dependent electrical resistivity $\rho(T)$.^[10,11]

termination of the electronic contribution. It is specifically related to the low-temperature region where the Debye model is applied. However, the electron thermal conduction calculated by the Wiedemann–Franz law contributes less than 1% at low temperature (see Table 1), and any enhanced electron heat conduction due to the Wiedemann–Franz law violation does not affect $\kappa_{\text{qlatt}}(T)$ very much. We tested different cut-off temperature limits

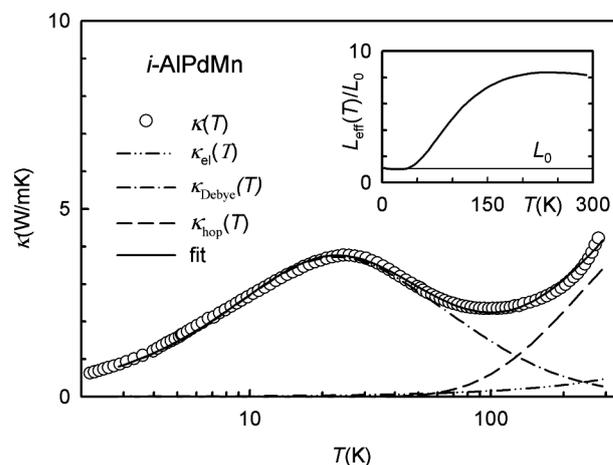


Figure 2. Temperature-dependent thermal conductivity $\kappa(T)$ with the fit to the total $\kappa(T)$, of the single crystal *i*-AlPdMn. Three contributions to the total $\kappa(T)$, electronic $\kappa_{\text{el}}(T)$, Debye $\kappa_{\text{Debye}}(T)$ and hopping $\kappa_{\text{hop}}(T)$, are shown separately.^[11] Inset: Ratio of the effective (L_{eff}) and Lorenz number (L_0), under assumption that the whole difference between measured thermal conductivity and $\kappa_0 = \kappa_{\text{el}}(T) + \kappa_{\text{Debye}}(T)$ originates from increased electron contribution to thermal conductivity.

Table 1. Comparison of thermal conductivity measured (κ) and calculated by the Wiedemann - Franz law (κ_{el}) at $T = 20$ K for *i*-AlPdMn, *i*-AlCuFe, and *d*-AlNiCo quasicrystals.

Sample	$\kappa(T = 20 \text{ K})$ [W/mK]	$\kappa_{\text{el}}(T = 20 \text{ K})$ [W/mK]	$\frac{\kappa_{\text{el}}(T = 20 \text{ K})}{\kappa(T = 20 \text{ K})}$
<i>i</i> -AlPdMn	3.7	3.4×10^{-2}	0.9 %
<i>i</i> -AlCuFe	0.9	1.2×10^{-2}	1.3 %
<i>d</i> -AlNiCo	2.9	1.8×10^{-1}	6.3 %

($T_{\text{cut-off}}$) where the Debye model can still be applied, and concluded that $T_{\text{cut-off}} \approx 50$ K is the proper choice. The choice of $T_{\text{cut-off}}$, and especially that of α and β , affects the values and temperature dependence of $\kappa_{\text{hop}}(T)$. The average sound velocity \bar{v} that enters in Equation 4 is provided by ultrasonic data,^[34] giving $\bar{v} = 4000 \text{ m}\cdot\text{s}^{-1}$. The fit of the quasilattice data to Equations 4, 5, 6, and 7 results in the following parameters: for the exponents of the empirical quasi-*umklapp* scattering rate (Equation 6) we obtain $\alpha = 2$ and $\beta = 4$, while for the linear density of stacking-fault-like defects we can estimate the order of magnitude only: $N_s = 0.1 - 1 \mu\text{m}^{-1}$. This uncertainty arises from the vagueness in the Grueneisen parameter calculation from the data available in the literature.^[35,36] The calculated Debye contribution is presented as the dash-dot line in Figure 2.

Above $T \approx 50$ K we have to introduce a new heat-carrying channel, since the sum of the Debye and the Wiedemann-Franz contributions cannot reproduce the experimental data. We propose two possible contributions:

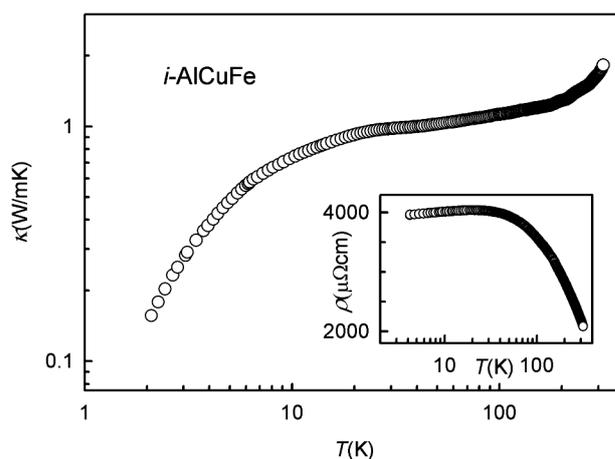
1) The first one is the hopping of the localized vibrations that exist in the icosahedral clusters. The probability of their jumps from site to site rises with temperature, which in the most general case can be described with the activation law given by Equation 3. The obtained fit is shown as the dashed line in Figure 2, with the calculated mean activation energy $E_a \approx 23$ meV. This result correlates with the inelastic neutron (INS)^[37-39] and X-ray^[40] scattering experiments on *i*-AlPdMn quasicrystals, where dispersionless vibrational states are identified for energies higher than 12 meV. Such dispersionless states indicate localized vibrations and are considered to be the consequence of a dense distribution of energy gaps in the phonon excitation spectrum of quasicrystals. The total fit curve $\kappa_{\text{el}}(T) + \kappa_{\text{Debye}}(T) + \kappa_{\text{hop}}(T)$ is presented by the solid line in Figure 2.

2) The other possible heat-carrying channel is electrons, whose thermal conductivity is, in that case, strongly underestimated by the Wiedemann-Franz law (Equation 2). Assuming that all the excess of the thermal conductivity above $T \approx 50$ K is due to the enhanced electron heat conduction, one is able to determine an effective Lorenz number $L(T)$. The calculated $L(T)/L_0$ is presented in the inset of Figure 2. At $T \approx 250$ K it reaches the local maximum of $L(T)/L_0 \approx 8.4$, exceeding the theoretically predicted extreme $L(T)/L_0$ for icosahedral quasicrystals.^[28] From that we conclude that the rise of the thermal con-

ductivity above $T \approx 50$ K can be attributed to both the hopping of localized lattice vibrations and to the enhanced effective Lorenz number.

3.3. *i*-AlCuFe

The thermal conductivity $\kappa(T)$ and the electrical resistivity $\rho(T)$ of *i*-Al₆₄Cu₂₃Fe₁₃ have been measured along the threefold symmetry direction and are displayed in Figure 3. The thermal conductivity value is low in the whole temperature interval investigated from 2 to 300 K, with a room-temperature value $\kappa_{300\text{K}} = 1.7 \text{ W/mK}$. This value is surprisingly low for an alloy of regular metals and is even lower than the thermal conductivity of known thermal (and electrical) insulators, that is, amorphous SiO₂ with $\kappa(300 \text{ K}) = 2.8 \text{ W/mK}$.^[41] The electrical resistivity (inset in Figure 3) exhibits a negative temperature coefficient with a room-temperature value $\rho_{300\text{K}} = 2200 \mu\Omega\text{cm}$ and $\rho_{4\text{K}} = 3950 \mu\Omega\text{cm}$. At 20 K, $\rho(T)$ has a weakly pronounced maximum with the peak value $\rho_{20\text{K}} = 4040 \mu\Omega\text{cm}$. The analysis of electrical resistivity together with the thermopower data obtained on the same specimen^[15] shows that the Fermi energy is located at the minimum of the pseudogap in the spectral conductivity $\sigma(T)$. All this gives evidence that we are dealing with an icosahedral quasicrystalline sample of exceptional quality,

**Figure 3.** Temperature-dependent thermal conductivity, $\kappa(T)$, of the single-crystalline *i*-AlCuFe. The inset shows the temperature-dependent electrical resistivity $\rho(T)$.^[15]

so that its transport properties may be considered as intrinsic to the *i*-AlCuFe phase. The thermal conductivity $\kappa(T)$ data were analyzed by means of Equations 1–7 using the Debye temperature estimated from specific heat data $\theta_D \approx 560$ K^[42] and mean sound velocity $\bar{v} = 4000$ m·s⁻¹ from ultrasonic data.^[37] $\kappa_{el}(T)$ is determined by the Wiedemann–Franz law (Equation 2); both $\kappa(T = 20$ K) and $\kappa_{el}(T = 20$ K) are given in Table 1. Similarly to *i*-AlPdMn, due to rather small electron contribution at low temperatures, the fit to the Debye model is not much affected by the model used for $\kappa_{el}(T)$ determination. The total fit, together with the electronic ($\kappa_{el}(T)$), Debye ($\kappa_{Debye}(T)$) and hopping ($\kappa_{hop}(T)$) contributions are shown separately in Figure 4.

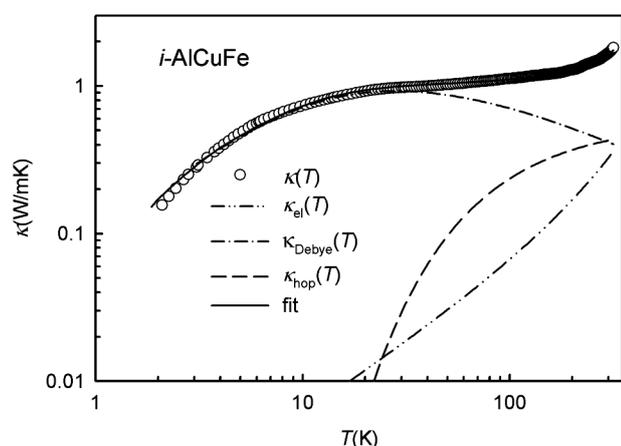


Figure 4. Thermal conductivity $\kappa(T)$ with the fit to the total $\kappa(T)$, of the single crystal *i*-AlCuFe. The three contributions to the total $\kappa(T)$, electronic $\kappa_{el}(T)$, Debye $\kappa_{Debye}(T)$ and hopping $\kappa_{hop}(T)$, are shown separately.^[15]

The room temperature value of the electronic contribution calculated by the Wiedemann–Franz law (Equation 2) amounts $\kappa_{el,300K} = 0.69$ W/mK, so that at room temperature the electrons carry at least 40% of the total heat. The Debye contribution exhibits a maximum at about 30 K and declines above, whereas the hopping contribution becomes significant at elevated temperatures. The activation energy for hopping was determined as $E_a = 6.3$ meV. The parameters α and β define phonon scattering by quasi-*umklapp* processes in a phenomenological way (Equation 4). The fit-determined $\alpha = 3.2$ and $\beta = 4.0$ values yields the frequency and temperature dependence of the quasi-*umklapp* term $\tau_{qu}^{-1} \propto \omega^{3.2} T^{0.8}$, indicating similarity to the modified quasi-*umklapp* scattering rate $\tau_{um}^{-1} \propto \omega^3 \cdot T$, used for the analysis of thermal conductivity of *i*-ZnMgY quasicrystals.^[5] Here it should be mentioned that the Debye and hopping contributions slightly compensate each other in the fit procedure, so that the

parameter values characterizing κ_{Debye} and κ_{hop} should be considered at the qualitative level only.

As in the case of *i*-AlPdMn, one can assume that excess of the measured thermal conductivity to $\kappa_{el}(T) + \kappa_{Debye}(T)$ above $T \approx 30$ K originates in the increased electron contribution. In that case the effective Lorenz number $L(T)$ can be estimated giving $L(T)/L_0 = 2.1$ at room temperature,^[15] that falls within the limit predicted in ref. [28].

3.4. *d*-AlCoNi

The thermal conductivity $\kappa(T)$, measured in quasiperiodic plane is shown in Figures 5 and 6, while the inset of Figure 5 gives the resistivity data $\rho(T)$ measured in the quasiperiodic plane as well. It exhibits metallic behavior, with the fractional increase amounting to $\rho^{300K} - \rho^{2K}/\rho^{300K} \approx 2\%$.^[43] Note that the value of electrical resistivity is an order of magnitude smaller as compared to *i*-AlPdMn and *i*-AlCuFe, but still hundred times larger than that of copper. The thermal conductivity $\kappa(T)$ shows an initial fast increase at low temperatures up to about 30 K. Above that temperature, $\kappa(T)$ exhibits a wide, shallow maximum up to 100 K, and grows only insignificantly upon further heating, reaching the room temperature value of $\kappa = 5$ W/mK. The dashed line represents the fit obtained from the following equation:

$$\kappa_0(T) = \kappa_{el}(T) + \kappa_{Debye}(T) \quad (8)$$

where the electronic thermal conductivity $\kappa_{el}(T)$ is estimated using Equation 2 and the phonon thermal conductivity is calculated within the Debye model using Equa-

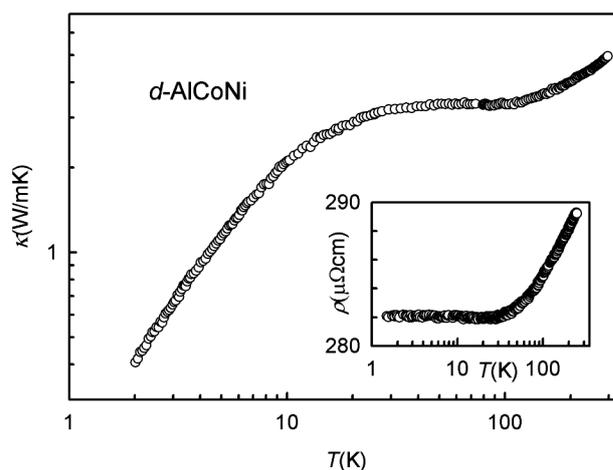


Figure 5. Temperature-dependent thermal conductivity, $\kappa(T)$, of *d*-AlCoNi measured in the quasiperiodic plane. Inset: the temperature-dependent electrical resistivity $\rho(T)$, measured in the quasiperiodic plane.^[17,18]

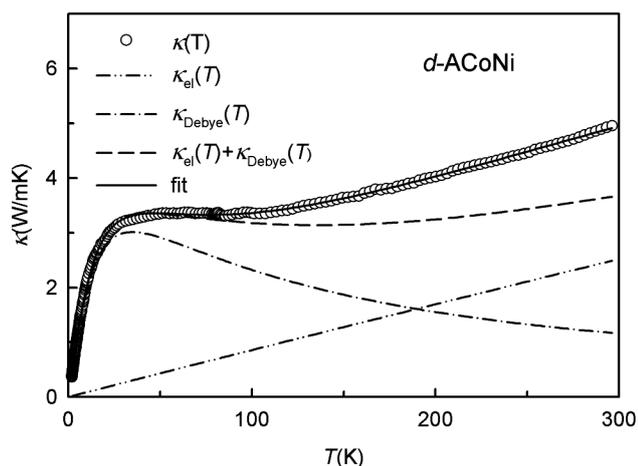


Figure 6. Temperature-dependent thermal conductivity $\kappa(T)$ with the fit to the total $\kappa(T)$ of the single crystal *d*-AlCoNi. The three contributions to the total $\kappa(T)$ — electronic $\kappa_{\text{el}}(T)$, Debye $\kappa_{\text{Debye}}(T)$, and $\kappa_0 = \kappa_{\text{el}}(T) + \kappa_{\text{Debye}}(T)$ — are shown separately.^[42]

tions 4–7, giving parameters $\alpha = 3$ and $\beta = 4$. We use Debye temperature $\theta_{\text{D}} = 545$ K determined from the specific heat measurements^[18] and the mean sound velocity $\bar{v} = 4900 \text{ m}\cdot\text{s}^{-1}$ calculated from the resonant ultrasound spectroscopy.^[44] As in previous cases of *i*-AlPdMn and *i*-AlCuFe, $\kappa_{\text{el}}(T)$ at low temperature contributes a few percents only (Table 1). Accordingly, any enhanced electron contribution to the heat conduction does not affect further calculations much. Above approximately 60 K, the measured data start to deviate from the fits, as already observed in the other thermal conductivity data.^[24,25] The difference ($\Delta\kappa(T)$) between the measured thermal conductivity and $\kappa_0(T)$, defined by Equation 8, is shown in Figure 7. In order to explain this deviation we again consider two approaches 1) The effective Lorentz number $L(T)$ exceeds L_0 , which leads to an enhanced electron contribution to thermal conductivity (Equation 2b). Assumption $\Delta\kappa(T) = \kappa_{\text{el}}(T)$ enables calculation of $L(T)$, which is shown in the inset of Figure 7. It resembles the theoretical predictions given in ref. [27]. 2) Contribution of localized lattice vibrations (Equation 3) is shown in Figure 7 as the dashed line, with the parameter $E_a \approx 25 \text{ meV}$.^[45] This value of the activation energy corresponds well to the energy of optical phonons in the calculated phonon dispersion for AlTMSi approximants,^[46] and with other analyses of the thermal conductivity data of quasicrystalline phases.^[24,32]

4. Discussion and Conclusions

The thermal conductivity of quasicrystals exhibits some general features regardless of the underlying type of quasicrystal lattice. The most noticeable is its relative low

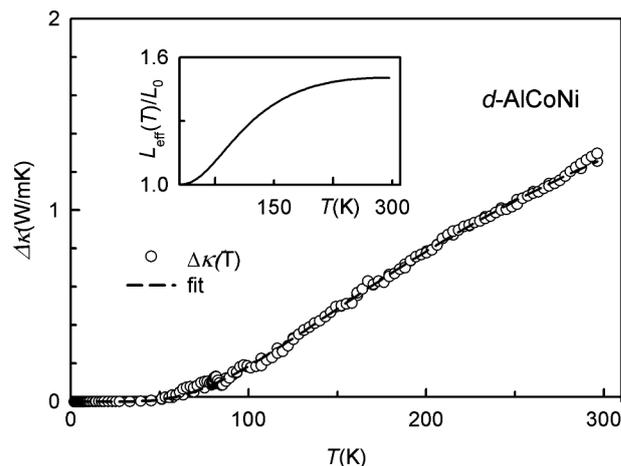


Figure 7. Difference between measured thermal conductivity and $\kappa_{\text{el}}(T) + \kappa_{\text{Debye}}(T)$ for the single crystal *d*-AlCoNi. Solid line is the fit to $\kappa_{\text{hop}}(T) = \kappa_{\text{hop},0} \cdot \exp(-E_a/k_B T)$. Inset: Ratio of the effective (L_{eff}) and Lorenz number (L_0), under assumption that the whole difference between the measured thermal conductivity and $\kappa_0 = \kappa_{\text{el}}(T) + \kappa_{\text{Debye}}(T)$ originates from an increased electron contribution to the thermal conductivity (see text).

value, that is, at room temperature, comparable to that of the best thermal insulators. The temperature variation of the thermal conductivity follows this general pattern: going from the low temperatures, the thermal conductivity first, rather slowly, increases ($\kappa(T) \propto T$ above 1 K), then reaches either a shallow maximum or a plateau at the temperature of several tens of Kelvin, while it starts to rise again above $T \approx 100$ K. The $\kappa(T) \propto T$ dependence between 2 K and 10 K we attribute to long wave-length acoustical phonon scattering on the structural defects similar to the stacking faults. Other studies assign the phonon scattering at the low-temperature to a declination of structural defects, which originate from close packing in 3D of icosahedra and icosidodecahedra.^[47,48] On the basis of the thermal conductivity data only, it is hard to distinguish which of the two defects really does take part in phonon scattering, since both of them lead to the same temperature dependence of the thermal conductivity. The structural study of *i*-AlPdMn presented in this work show, the existence of stacking faults.^[11] The appearance of maxima at $T \approx 20$ K should be an intrinsic feature of the thermal conductivity in quasicrystals. The reason is the presence of hierarchy of energy gaps in the acoustical vibrational spectrum of quasicrystals^[49] that leads to quasi-*umklapp* phonon scattering and to the decrease of the thermal conductivity with rising temperature. However, in some cases instead of maxima a plateau appears what is noticed in the fitting procedure as non-uniqueness of the quasi-*umklapp* scattering rate. This comes from differences in vibration spectra suggesting that ab initio calculations should be employed in order to determine the

form of quasi-*umklapp*. The problem of determining the electron contribution is the one of the essential requirements for the thermal conductivity analysis of quasicrystals. Although widely used, the Wiedemann–Franz law is not simply applicable even for metals. The most accepted approach to modified Wiedemann–Franz law is, as already described in previous text, via the spectral conductivity model, that predicts a strong enhancement of the electron heat conduction at elevated temperatures and its saturation to 4.2 times the value predicted by Wiedemann–Franz law as $T \rightarrow \infty$.^[28] An alternative calculation of Vekilov and co-workers^[50] resulted with the conclusion that WFL in quasicrystals is valid only at temperatures much higher than the Debye one. However, experiments suggest that the thermal conductivity of quasicrystals increases above $T \approx 100$ K, which can be attributed at least partially to enhanced electron heat conduction. Complementary contribution to such thermal conductivity rise has its origin in quasilattice, made of clusters where localized atomic vibrations easily occur. As the temperature rises, these localized states have more thermal energy that enables their jumps between clusters, creating a new heat-carrying channel.

In conclusion, in this work we have described a semi-quantitative procedure for the analysis of the thermal conductivity of quasicrystals. It takes into account two heat carriers: electrons, whose contribution is calculated by the Wiedemann–Franz law where a modified Lorenz number is temperature independent and can differ by around 10% from the Lorenz number valid in metals; and quasilattice vibrations for which, at the low temperature limit, we use the Debye approximation, while at high temperatures we apply the model of activation conductivity of localized vibrations. The procedure explains the measured data very well, giving physically plausible fitting parameters comparable, at least in order of magnitude, with the results of other experiments (e.g., the linear density of stacking faults, excitation energy of localized vibrations). At present the main disadvantage of the procedure is that it still does not incorporate the temperature dependence of the effective Lorenz number.

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