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LETTER TO THE EDITOR

THERMAL CONDUCTIVITY OF ICOSAHEDRAL i-$Al_{72}Pd_{19.5}Mn_{8.5}$ QUASICRYSTAL

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Dedicated to Professor Kseno Ilakovac on the occasion of his 70$^{\mathbf{th}}$ birthday

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Thermal, $K(T)$, and electrical conductivity, $\sigma(T)$, measurements of the polygrain icosahedral quasicrystal i-$Al_{72}Pd_{19.5}Mn_{8.5}$ are reported in the temperature range 10 K – 300 K. Electrical conductivity shows an anomalous behaviour with a minimum at 120 K and the room temperature value $\sigma_{RT} = 83000\ \Omega^{-1}\mathrm{m}^{-1}$. Thermal conductivity at a room temperature is $K_{RT} \approx 3.4$ W/mK, and by lowering temperature, $K(T)$ shows a broad minimum at 120 K, and a shallow maximum around 30 K. Temperature behaviour of thermal conductivity is explained by the Debye model in the temperature range below 50 K, and in the frame of the variable range hopping model above 120 K.

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First quasicrystals from the icosahedral i-Al-Pd-Mn family were fabricated in the early 1990's [1]. The absolute value and temperature behaviour of their electrical conductivity [2] are very sensitive to the composition and thermal treatment of the sample. Room-temperature values of electrical conductivity lie between $3 \times 10^4\ \Omega^{-1}\mathrm{m}^{-1}$ and $10^5\ \Omega^{-1}\mathrm{m}^{-1}$, while measured temperature gradients vary from positive to negative, with some intermediate cases which have minimum between 50 K and 100 K. Thermal conductivity of quasicrystals, in general, can be divided into three temperature regions. It is accepted that in the low-temperature region

($T < 1$ K), the main source of the phonon scattering are tunneling states (TLS) and boundary scattering [3–5]. Existence of tunneling states in quasicrystals is confirmed by acoustic measurements [6–8], although it is not clear whether or not tunneling states are an intrinsic characteristic of quasicrystals [7]. At temperatures between 10 K and 100 K, the existence of a plateau [3,9] and a shallow minimum [5,10,11] have been observed. Above 100 K, the increase of the value of thermal conductivity is common to all icosahedral quasicrystals.

The sample was prepared using the "self-flux" technique. In this technique, the ternary melt (the composition of which intersects the primary solidification surface of the quasicrystalline phase) is first slowly cooled, and then the remaining melt is decanted. The "self-flux" technique does not require large temperature gradients, so samples prepared by this technique have less strains than samples prepared by the the Bridgman or Czochralski techniques. In addition, quasicrystals grow via a series of stable thermodynamic steps, thus the time of growth can be almost arbitrarily long. The melt decanting ensures that samples are single-phased (a detailed description of the technique is given in Ref. [12]). The sample, in the shape of a rectangular prism, with dimensions 0.5 mm $\times$ 0.5 mm $\times$ 5 mm, was cut and polished from an as-grown sample. Electrical conductivity was measured by the standard four-contact method. Golden wires of 10 μm diameter were used as contact leads. We used the comparative method with constantan foil as a reference sample for measuring thermal conductivity. Temperature gradients across both samples (the reference and the investigated) were determined by 15 μm chromel-constantan differential thermocouples [13].

Figure 1 displays the measured thermal conductivity. The room temperature value is $K_{\mathrm{RT}} \approx 3.4$ W/mK. The position of the minimum of the thermal conductivity curve is at 120 K, which is higher than in the case of i-$\mathrm{Al_{70}Pd_{20}Mn_{12}}$ [10] (about 88 K), i-$\mathrm{Al_{62}Cu_{25.5}Fe_{12.5}}$ and i-$\mathrm{Al_{63}Cu_{25}Fe_{12}}$ [5] (about 85 K and about 90 K, respectively) or i-$\mathrm{Y_{8.6}Mg_{34.6}Zn_{56.8}}$ [11] (~ 65 K). The first step in the analysis of thermal conductivity data is the estimation of the electron contribution to thermal conduction. The only tool for this calculation is the Wiedemann-Franz law [14], $K_{\mathrm{e}} = L_0 \sigma T$, where L_0 is equal to 2.45×10^{-8} WΩ/K^2, while σ is the electrical conductivity and T is the temperature. If the only contribution leading to the rise in thermal conductivity, above approximately 100 K, is the electron contribution, one could expect equal values of $K/(\sigma T)$ for all quasicrystals. It was experimentally confirmed that for quasicrystals with higher value of conductivity σ, the ratio $K/(\sigma T$ is much closer to the value of L_0 than in the case of lower conductive quasicrystals [3–5,11,15]. From this it can be concluded that (i) not only electrons contribute to the rise of thermal conductivity of quasicrystals above 100 K and (ii) because of a very strong dependence of the ratio $K/(\sigma T)$ on conductivity σ, the electron contribution to thermal conductivity is much weaker than the quasillatice contribution.

The inset in Fig. 1 shows the electrical conductivity of i-$\mathrm{Al_{72}Pd_{19.5}Mn_{8.5}}$. The room temperature value of electrical conductivity is 8.3×10^4 $\Omega^{-1}\mathrm{m}^{-1}$, and is in the range of the room temperature values observed for other quasicrystals from

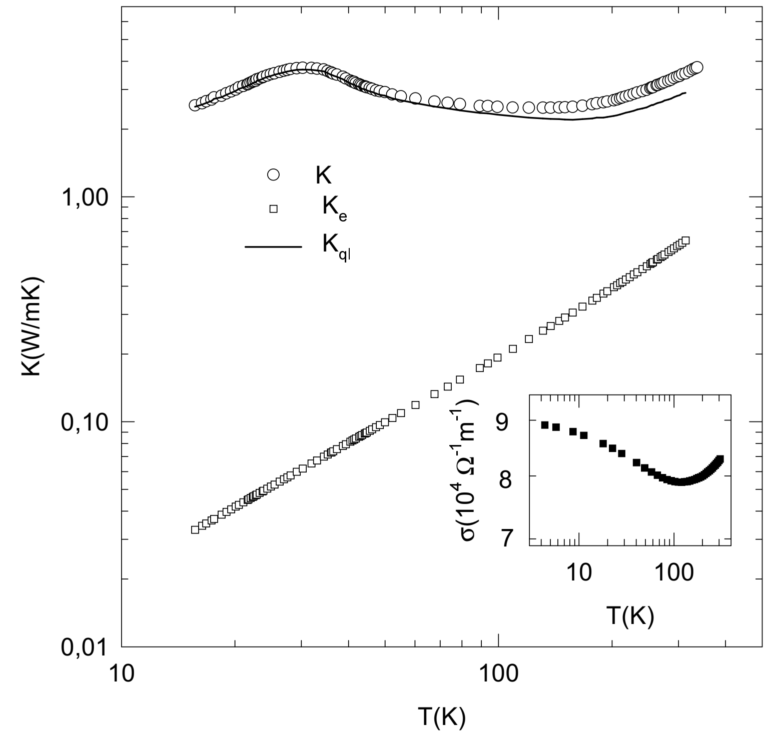

Fig 1. Thermal conductivity, $K(T)$, of i-$Al_{72}Pd_{19.5}Mn_{8.5}$ *(open circles). The open squares present the electron contribution, $K_e(T)$, to the thermal conductivity calculated using the Wiedemann-Franz law (see text), and the full line the quasilattice contribution to thermal conductivity, $K_{\rm ql}$, estimated by subtracting the electron contributin from the total thermal conductivity, $K_{\rm ql} = K - K_{\rm el}$. The inset shows the temperature behaviour of electrical conductivity, $\sigma(T)$ (full squares).*

the i-Al-Pd-Mn family [2]. But the temperature behaviour presented in the inset of Fig. 1 is not typical for other quasicrystals. Namely, in most quasicrystals electrical conductivity has a positive temperature gradient, while at lower temperatures (below 30 K) some have minima due to the quantum interference effects [2,16]. The electron contribution to thermal conductivity, K_e, calculated using the Wiedemann-Franz law and the measured electrical conductivity are shown in Fig. 1 by open squares. The quasilattice contribution to thermal conductivity, $K_{\rm ql}$ can be deduced by subtracting the electron contribution from the total thermal conductivity. It is presented by the full line in Fig. 1.

In periodic structures the lattice contribution to thermal conductivity is described by phonons. The concept of phonons implicitly includes the possibility of defining the unit cell and the parabolic interaction between atoms. In quasicrystals, one cannot find the repeating structural motive and thus the unit cell cannot be defined. However, calculations made using the Fibonacci chain [17], the archetypal one-dimensional quasicrystal, have shown existence of the acoustic branch in the long wavelength limit. This is not surprising because the long-wavelength phonons do not feel the underlying unordered structure. In three dimensions, there are no exact calculations of the dispersion curve, but from the neutron diffraction measurements [18] on quasicrystals from the i-Al-Pd-Mn family, it has been experimentally determined that for wave vectors with wave numbers smaller than 3 nm^{-1}, the acoustic branch is well defined. Following this argument, it can be concluded that in the long wavelength limit (the wave number of 3 nm^{-1} corresponds to the temperature of about 50 K), a Debye approach can be used to explain the low-temperature thermal conductivity data. In the Debye approximation, only acoustic vibrations are taken into account, and their thermal conductivity is given by the following integral [14]

$$K_{\mathrm{ql}}(T) = 3nk_B v^2 \left(\frac{T}{\Theta_D}\right)^3 \int\limits_0^{\Theta_D/T} \frac{x^4 \mathrm{e}^x}{(\mathrm{e}^x - 1)^2} \tau(x,T)\,\mathrm{d}x\,, \tag{1}$$

where n is the density of phonons, and is given by $k_D/(6\pi^2)$ (k_D is the Debye wave vector), k_B the Boltzmann constant, v the velocity of sound, Θ_D the Debye temperature and τ the phonon mean life time. Variable x is defined as the ratio $\hbar\omega/(k_B T)$, where ω is the phonon frequency and T the temperature. The value of sound velocity, $v = 3800$ m/s, is estimated as a mean value from two references [8,18], while the Debye temperature was set as a free parameter in the fitting procedure. It is reasonable to expect that the Debye temperature lies between 350 K and 550 K, as seen in other classes of quasicrystals [4,11,18–21]. To perform successful fitting, choosing the appropriate phonon scattering mechanisms is necessary. It is supposed that the scattering rates are mutually independent, and Matthiessen's rule can be applied, $\tau_{\mathrm{tot}}^{-1} = \sum \tau_i^{-1}$. τ_{tot}^{-1} is the total scattering rate, while τ_i^{-1} is the scattering rate of i^{th} scattering process. In the temperature range in which our measurements were done (above 15 K) there is no reason to take into account phonon scattering on tunneling states (TLS), which has been observed in quasicrystals from the i-Al-Pd-Mn [6,8] family. Moreover, the recent investigation of thermal conduction on i-$Y_{8.6}Mg_{34.6}Zn_{56.8}$ [15] above 0.1 K showed that phonon scattering on TLS is overwhelmed by "stacking-faults like defects" scattering mechanism, for which the scattering rate is given by [22]

$$\tau_{\mathrm{sf}}^{-1} = 0.7 \frac{a^2}{v_{\mathrm{ph}}} \gamma^2 \omega^2 N_s\,, \tag{2}$$

where a is the lattice constant, N_s the stacking-faults linear density, γ the Grüneisen parameter and ω the phonon frequency. The scattering of phonons on stacking-faults like defects competes with the structural scattering, or quasiumklapp scattering processes [17]. It has already been stated that the quasicrystal phonon dispersion relation is similar to the one for periodic crystals in the long wavelength limit. Outside the long-wavelength limit, the dispersion relation of quasilattice excitations is influenced by the quasicrystal structure through the forming of a hierarchy of gaps. This leads to quasiumklapp processes with the scattering rate, $\tau_{\mathrm{qu}}^{-1} \propto \omega^2 T^4$, which falls off much slower than the umklapp scattering rate in periodic crystals (exponential decrease). The combination of these two scattering processes gives a curve (the solid line in Fig. 2) which explains the K_{ql} results well bellow 40 K.

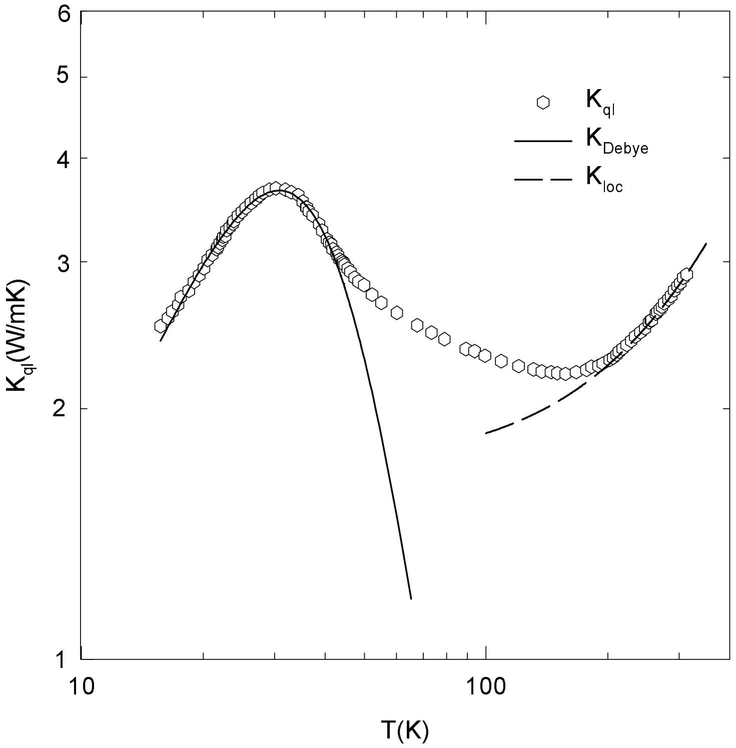

Fig. 2. Quasilattice part of thermal conductivity, K_{ql}, estimated by subtracting the electron contribution from the total thermal conductivity. The line, K_{Debye}, is a fit to the Debye model with stacking-like faults and structural scattering of phonons, and the dashed line is the contribution from the localized quasilattice vibrations, K_{loc}, in the frame of the variable-range hopping model (see text).

The Debye temperature obtained through the fitting procedure is 260 K, what is too low in comparision with Θ_D in other quasicrystals [4,11,19-21]. Investigations of specific heat below 40 K on quasicrystals from the i-Al-Cu-Fe family [20] (they are structurally similar to the i-Al-Pd-Mn) showed that below 40 K specific heat deviates from fully Debye-like behaviour. Moreover, in i-Al-Pd-Mn there is a possibility of a magnetic contribution to the specific heat. So, by applying the pure Debye model, we get an averaged value of the Debye temperature, which has to be smaller than the real Debye temperature. The fitting procedure, using Eq. (2) allowed a determination of N_S, the linear density of stacking faults. The Grüneisen constant, γ, for i-$Al_{72}Pd_{19.5}Mn_{8.5}$ was calculated from the Grüneisen constants of constituent elements [23], using the atomic formula ratios as weighting factors. In Ref. [23], several values of γ, calculated from different data, are given. The mean values for Al, Pd and Mn are 2.1, 2.3 and 1.7, respectively. The calculated Grüneisen constant of i-$Al_{72}Pd_{19.5}Mn_{8.5}$ is, therefore, 2.1. Due to a lack of the quasilattice constant value a, we have estimated it from the FCI quasilattice constant of a similar quasicrystal, i-$Al_{73}Pd_{19}Mn_{8}$, given in Ref. [12]. Its value is 0.6467 nm, and from it we can estimate that the value of a of our sample is in the interval (0.65 ± 0.04) nm. Using these values of the Grüneisen constant γ and the quasilattice constant a, the linear density of stacking faults is 1.4×10^6 m^{-1}. This is an order of magnitude smaller than in other Al-Pd-Mn icosahedral quasicrystals, and of the same order as in i-Al-Cu-Fe or i-Y-Mg-Zn [24].

The increase of thermal conductivity above approximately 100 K is a common property of all quasicrystals. The electron contribution to thermal conductivity, calculated using the Wiedemann-Franz law, increases throughout the whole temperature range (open squares in Fig. 1), but it is not the main contribution leading to the increase in the thermal conductivity curve. The model proposed by Janot [25] takes into account the high energy and the localized vibration modes, experimentally observed in quasicrystals by neutron diffraction [26]. In that model, the interaction between localized quasilattice vibrations and extended ones enables hopping of non-extended phonons. Taking into account structure inflation symmetry of an ideal icosahedral quasicrystal, the temperature behaviour of the thermal conductivity of localized phonon states assumes the power law, i. e., $K_{\rm loc} \propto T^n$, with $n = 1.5$. We have subtracted the Debye-model fit (solid line in Fig. 2) from the quasilattice thermal conductivity (open hexagons in Fig. 2). This difference, for temperatures above 200 K, has been fitted by the power law $K_{\rm loc} = A + BT^n$. The fitting procedure gave $n = 1.7$, which is close to the prediction of Janot's variable range hopping model. The fact that the position of the minimum of the thermal conductivity curve in our sample is relatively high compared to other icosahedral quasicrystals means a stronger localization of the high-energy quasilattice vibrations.

In conclusion, the measurements and analysis of thermal and electrical conductivity of icosahedral quasicrystal i-$Al_{72}Pd_{19.5}Mn_{8.5}$ are presented. Electrical conductivity has an atypical temperature behaviour for quasicrystals, showing a minimum around 120 K. The thermal conductivity curve shows typical temperature behaviour for quasicrystals: it has a shallow maximum at 30 K and a local minimum around 120 K. Below 50 K, the Debye approximation has been used, and the thermal conductivity curve shows a good agreement when using the stacking-like faults and structural scattering mechanisms. At higher temperatures, the model of variable range hopping of localized phonon states adequately explains the observed rise of thermal conductivity.

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TOPLINSKA VODLJIVOST IKOSAEDARSKIH KVAZIKRISTALA i-$Al_{72}Pd_{19.5}Mn_{8.5}$

Izvješćujemo o mjerenjima toplinske, $K(T)$, i električne, $\sigma(T)$, vodljivosti više-zrnatih ikosaedarskih kvazikristala i-$Al_{72}Pd_{19.5}Mn_{8.5}$ u području temperatura 10 K – 300 K. Električna vodljivost pokazuje anomalno ponašanje s minimumom na 120 K i vrijednošću $\sigma_{RT} = 83000\ \Omega^{-1}\mathrm{m}^{-1}$ na sobnoj temperaturi. Toplinska vodljivost na sobnoj temperaturi je $K_{RT} \approx 3.4$ W/mK, i ima plitak maksimum oko 30 K. Temperaturna se ovisnost toplinske vodljivosti objašnjava Debyevim modelom za temperature ispod 50 K, dok na osnovi modela preskakanja s promjenljivim dosegom iznad 120 K.