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High Temperature Thermal Conductivity Measurements of Quasicrystalline $Al_{70.8}Pd_{20.9}Mn_{8.3}$

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ABSTRACT

We report measurements of the thermal conductivity on a potential high temperature thermoelectric material, the quasicrystal $Al_{70.8}Pd_{20.9}Mn_{8.3}$. Thermal conductivity is determined over a temperature range from 30 K to 600 K, using both the steady state gradient method and the 3ω method. Measurements of high temperature thermal conductivity are extremely difficult using standard heat conduction techniques. These difficulties arise from the fact that heat is lost due to radiative effects. The radiative effects are proportional to the temperature of the sample to the fourth power and therefore can lead to large errors in the measured thermal conductivity of the sample, becoming more serious as the temperature increases. For thermoelectric applications in the high temperature regime, the thermal conductivity is an extremely important parameter to determine. The 3ω technique minimizes radiative heat loss terms, which will allow for more accurate determination of the thermal conductivity of $Al_{70.8}Pd_{20.9}Mn_{8.3}$ at high temperatures. The results obtained using the 3ω method are compared to results from a standard bulk-thermal-conductivity-technique on the same samples over the temperature range, 30 K to 300 K.

INTRODUCTION

Thermoelectric devices are typically used in two distinct ways, either as a refrigerator or as an electric generator. For example, thermoelectric refrigerators can be used to cool electronics at room temperature, while thermoelectric generators are used to generate electricity at high temperatures, ~ 700 – 800 K, on deep space probes. These demands for thermoelectric devices require materials that are "thermoelectrically efficient" at the temperatures of use. Currently, Bi_2Te_3 and $Si_{1-x}Ge_x$ are the "thermoelectrically efficient" materials of choice in these respective applications.

A "thermoelectrically efficient" material is one in which the dimensionless figure of merit, ZT, is a maximum, where

$$ZT = \frac{S^2\sigma}{\kappa} T \qquad (1)$$

Here S is the Seebeck coefficient ,σ is the electrical conductivity and κ is the thermal conductivity. In order to increase the figure of merit, the numerator, which is also called the power factor, $S^2\sigma$, of Equation 1 should be made as large as possible and the denominator should be made as small as possible. We will mainly be concerned with measuring and minimizing the denominator or the thermal conductivity.

QUASICRYSTALS (POSSIBLE THERMOELECTRIC MATERIALS?)

Quasiperiodic structures, or quasicrystals, are non-crystalline materials with perfect long-range order, but with no three-dimensional periodicity ingredient, not even the underlying lattice of the incommensurate structures.[1] Theoretically, the results of quasiperiodicity could lead to interesting new transport properties within these structures. Since quasicrystals do not possess a typical lattice constant, and thus a very large number of atoms in a unit cell, they tend to have very low thermal conductivities. These thermal conductivities are on the order of an amorphous glass and exhibit a glass-like temperature dependence of the thermal conductivity.

The recent discovery[2] of a stable icosahedral phase in the Al-Mn-Pd system, $Al_{70.8}Pd_{20.9}Mn_{8.3}$, has lead to new opportunities in the study of the transport properties of these quasicrystals. Initially most of the studies performed on this material were related to its structual characteristics. Recently there has been some work done on the transport properties of these quasicrystals.[3] These results, suggest that the quasicrystal $Al_{70.8}Pd_{20.9}Mn_{8.3}$ may be a good high temperature thermoelectric.

We are not aware of any data on the thermal conductivity at higher temperature in the range of 300 K to 600 K, for these thermodynamically stable icosashedral AlPdMn quasicrystals. The thermal conductivity results from two different techniques, a standard steady-state temperature gradient method from 30 K to 300 K and a transient AC method "the 3-Omega method" from 30 K to 600 K, will be presented and discussed below.

EXPERIMENT

Quasicrystals were synthesized at Clemson University. Stoichiometric amounts of elemental Al, Pd, and Mn powders were weighed out in an argon atmosphere and subsequently mixed in a vibrating mill. The homogenized mixture was loaded into 1 cm pellet die and pressed to 6000 lbs. The pellet and zirconium were placed separately into an arc furnace, which was evacuated and refilled with argon. An arc was first established to the zirconium to getter any water within the arc furnace to reduce the chance of oxidation of the quasicrystal. The arc was then established to the sample pellet and maintained until the sample was completely melted. The sample was placed into an alumina crucible that was placed inside a quartz tubing vessel. The quartz vessel was placed into a resistive heating furnace and annealed to eliminate secondary phases. The sample was sectioned with a wire saw using boron carbide as a cutting agent. Left over sample sections were ball milled for powder X-ray diffraction measurements.

THERMAL CONDUCTIVITY MEASUREMENTS.

We employed a transient method (3ω-method) to determine the thermal conductivity of the quasicrystal over the temperature range, 30 K to 600 K, then compared this data with the data obtained from a standard temperature gradient method on the bulk crystal. The 3ω-method is a technique that involves reading an AC voltage at a frequency three times the driving frequency of the circuit and 60-80 dB lower than the driving signal. Our lock-in amplifier, with a built-in signal generator, provides the driving signal to the circuit and reads the 3-omega signal. The 3-omega signal is obtained by placing the sample into one arm of a Wheatstone bridge, then reading the difference of the voltage across the sample and the matching variable resistor (Figure 1). The DC output signal from the lock-in, which is a function of frequency, yields data leading to the thermal conductivity. One advantage that this technique has over a standard temperature gradient method in measuring thermal conductivity, is the insensitivity of the 3-omega method to radiation loss effects at high temperature.[4]

The sample was prepared as follows. The surface of the sample was polished to a mirror finish, and then a thin film of polyimide, several microns thick, was applied to the prepared surface of the quasicrystal. This film electrically isolates the heater/thermometer line from the substrate, which allows us to assume that all the power is input in the heater/thermometer line and not the sample. On top of the polyimide the heater/thermometer line is deposited through a shadow mask.

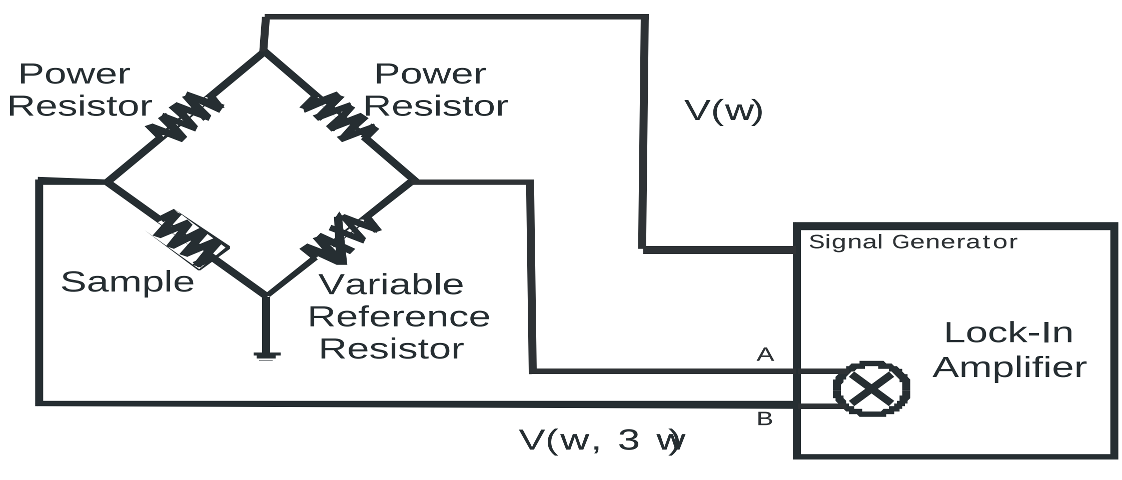

Fig.1 Schematic diagram of the circuit used in the 3-Omega method.

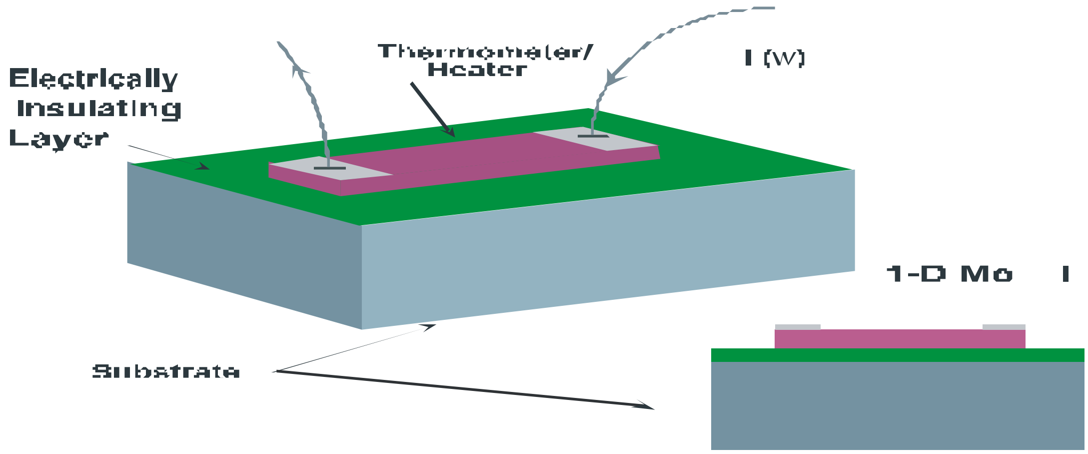

Fig.2 Sample Geometry

The material used in the line is nickel, because it has a reasonably large coefficient of resistance. This property of nickel provides for a more sensitive measure of the surface temperature oscillations that arise during the experiment (Figure 2).

The data analysis for our sample in principle requires the solution of Fourier's heat conduction Law for both layers with appropriate boundary conditions. Since our polyimide insulating layer is very thin, several microns, it is thermally bridged at low frequencies. In other words, since the thermal waves penetrate ~80-100 times this depth at low frequencies, it is assumed that we have a one layer problem. The derivation[5] of the functional dependence of the 3ω voltage on frequency for this one-dimensional problem is summarized below. The third harmonic AC voltage measured on the sample is

$$V_{3\omega,rms} = \frac{pV_{sample,rms} dR/dT}{4R_{sample}\sqrt{2\lambda\rho C_p}}\omega^{-1/2} \qquad (2)$$

Here ρ, C_p, and λ are the density, heat capacity and thermal conductivity of the material respectfully. p and dR/dT are the input power density and coefficient of resistance of the heater line. Thus, to obtain the thermal conductivity of the sample we plot the 3ω voltage versus the inverse square root of frequency and then take the slope of this line.

In Figure 4, the 3ω voltage, $V_{3\omega}$ is plotted as a function of the inverse square root of frequency, $\omega^{-1/2}$ at constant temperature, T. From this graph it is clear that there two distinct slopes, each of which contain information on the sample. In the high frequency limit the slope contains the physical information of the polyimide layer and in the low frequency limit the slope contains the information on the $Al_{70.8}Pd_{20.9}Mn_{8.3}$ quasi-crystal. With the data for heat capacity and density it is straightforward to obtain the thermal conductivity of the sample at each temperature.

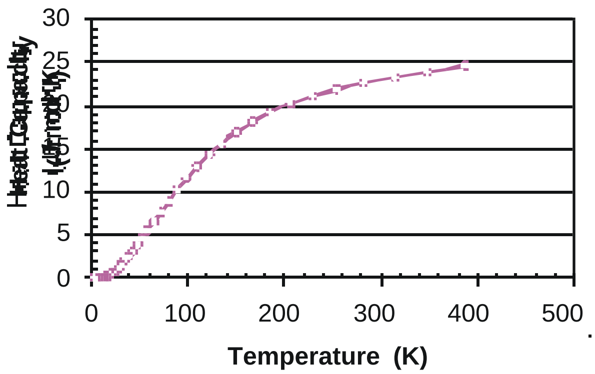

Fig. 3 Quasicrystal Heat Capacity. Above 400K the value is assumed to saturate at 3R

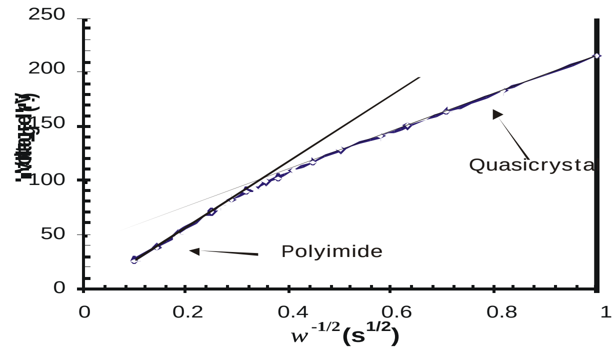

Fig.4 3-Omega voltage. Asymptotic lines provide the slope and therefore the thermal conductivity of the materials. Low frequency limit gives the thermal conductivity information of the quasicrystal. High frequency limit gives the information on the polyimide insulating layer.

The heat capacity data is shown in Figure 3. The density was taken as 0.069 atoms/A^3, at room temperature and an assumed linear coefficient of expansion of 1.2 x 10^{-5} (1/K). There are many possible errors involved in making thermal conductivity measurement with these two methods. Potential errors in the 3ω are: an error associated with the one-dimensional modeling of the thermal waves and a small error occurs in assuming that the electrically insulating layer is thermally bridged. The errors associated with these assumptions are thought to be relatively small, ~ 5-10%. The remaining error in the value of the thermal conductivity calculated from the 3ω method comes from the uncertainty in the various parameters in Equation 2.

The errors involved with temperature gradient methods are fairly well known, but we will enumerate them here again. Radiation loss is probably the best known cause of error in the temperature gradient method. This error is large at high temperatures but negligible at low temperatures. Care must be taken to minimize thermal conduction of heat through the various wires connecting the sample to the measurement apparatus. Finally there is an error in the measurement of the dimensions of the sample. All these errors combined contributed an uncertainty in the measurement in the low temperature regime of about 10%. In Figure 5 the thermal conductivity results are shown for the $Al_{70.8}Pd_{20.9}Mn_{8.3}$ quasicrystal over the temperature range, 10K-300K. In Figure 5, thermal conductivity results obtained from the 3ω-method and from the standard temperature gradient technique are shown for the temperature range, 10K-300K. The 3ω-data is ~10-15% higher than the temperature gradient method data over this range. In Figure 6, the thermal conductivity results are shown for the temperature range, 300-600 K. The results for the 3ω method generally agree with the Wiedermann-Franz approximation, but with a slightly higher slope and the same ~10-15% offset. The Wiedemann-Franz approximation is done assuming that the electronic contribution increases as $\sigma = \sigma_o + \alpha T$

and that the lattice portion is constant. The reasons for the discrepancy in the data between the Wiedemann-Franz approximation and 3ω over the low temperature range can be attributed to the uncertainties in the methods employed. Janot has predicted that thermal conductivity should increase as $T^{1.5}$, above room temperature.[6] Our data does not agree with this theory.

Another possible explanation for the difference in the data originates in the structure of the material itself. The technique used to synthesize the quasicrystal leaves many small voids in the sample. All of these voids take part in the conduction of heat in the standard temperature gradient method. Since the 3ω technique only samples a thin section at the surface of the sample, which has been polished to a mirror-like finish, it is thought that a smaller percentage, by volume, of these voids are being sampled, thereby increasing the thermal conductivity at least at low temperatures. Since, at low temperatures the data from the two methods matches in temperature dependence, it is thought that the effect of these voids is temperature independent. At high temperatures the effect of these voids is not clear.

Further investigation of high temperature thermal conductivity measurements in quasicrystalline systems is necessary. It is necessary to measure the high temperature electrical conductivity so that the electronic contribution can be determined. With this data, the assumptions of a constant lattice contribution and a linearly increasing conductivity can be determined. We have seen, however, that thermal conductivity increases at low temperature, peaks, experiences a flat plateau before it begins rising at higher temperatures. It is also

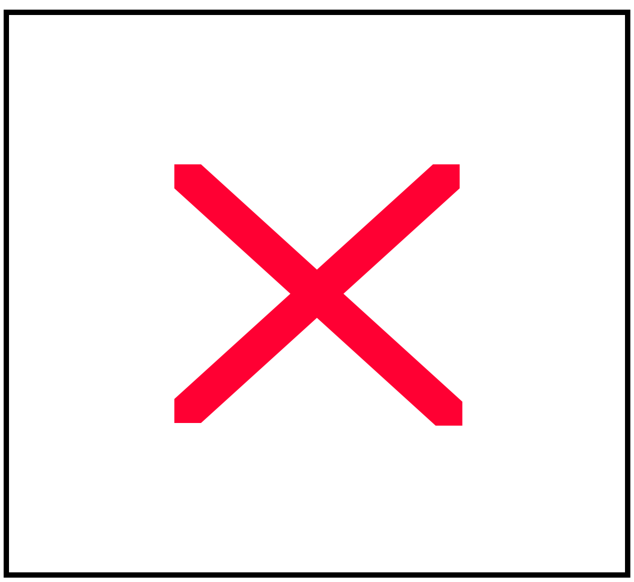

Fig.5 Low temperature thermal conductivity. The two methods coincide with a 13% offset.

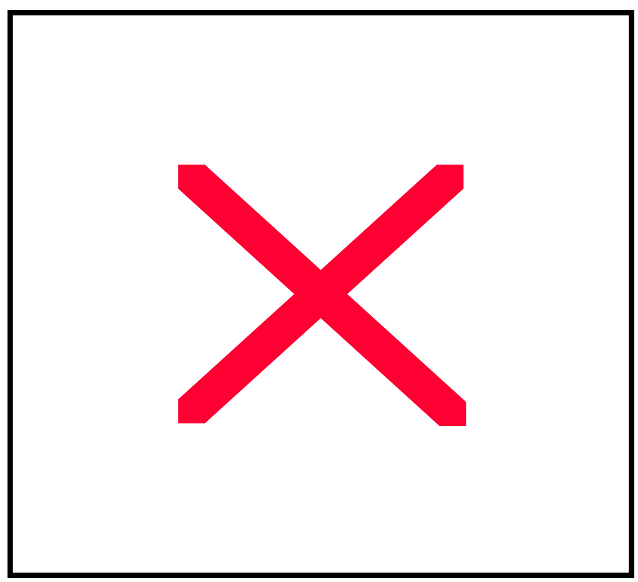

Fig.6 High Temperature thermal conductivity The 3-omega data follows the Wiedemann-Franz approximation with a slightly stronger temperature dependence. The hopping model thermal conductivity with a T^3/2 dependence is not seen.

encouraging to observe very good agreement of the two techniques within the overlap region of temperature, with each technique also yielding the same temperature dependence and similar absolute values.

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