High-temperature thermal transport properties of a single-grain decagonal $Al_{74}Ni_{10}Co_{16}$ quasicrystal

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Thermal transport properties have been determined for a decagonal $Al_{74}Ni_{10}Co_{16}$ quasicrystal in the temperature range 373–873 K. Differential scanning calorimetry and a laser flash method were employed in the determination of heat capacity and thermal diffusivity, respectively. Thermal conductivity was determined from the product of diffusivity, heat capacity, and density. A high degree of anisotropy was observed between the aperiodic and periodic axes. The anisotropic heat flow is described using the thermal ellipsoid model. The model was applied to a surface oriented 45° to the major axes and substantiated from bulk measurements obtained from a sample cut along this orientation. Within this temperature range, the thermal transport of this two-dimensional quasicrystal may be described in a manner similar to anisotropic metallic single crystals.

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INTRODUCTION

Since the initial discovery of quasicrystals, several stable quasiperiodic intermetallic phases have been found.[1,2] Of particular interest are the stable decagonal quasicrystals, which consist of a periodic stacking of tenfold quasiperiodic planes. This unique structure allows one to study quasicrystalline and crystalline properties comparatively along different directions within the same sample. Studies of this type may provide important clues toward understanding the unusual properties of quasiperiodic materials.

It is well known that thermal transport in quasicrystals is anomalously low compared with intermetallic crystalline phases. These properties are often attributed to electron localization and the existence of a pseudogap in the electronic density of states at the Fermi level.[2,3] Since decagonal quasicrystals are only quasicrystalline in two dimensions, it is not surprising that significant anisotropic transport properties have been reported;[4–7] however, to date, studies of the Al-Ni-Co decagonal system have been limited to temperatures below 300 K. A study of the high-temperature thermal transport properties complements existing low-temperature results and provides useful information toward practical applications of quasicrystals. In this paper we report on high-temperature thermal diffusivity and heat capacity data for decagonal (d)-$Al_{74}Ni_{10}Co_{16}$ over the temperature range of 373–873 K. The thermal conductivity was calculated as a function of temperature over this range.

EXPERIMENT

A large ($0.8\ \mathrm{cm}^3$) single-grain decagonal $Al_{74}Ni_{10}Co_{16}$ quasicrystal was grown using a flux growth technique.[8] The sample possessed a rodlike morphology, with the c axis parallel to the length of the rod and 10-side growth facets oriented normal to the c axis, reflecting the decagonal symmetry of the quasicrystal structure. Samples with parallel faces of approximately 10 mm in diameter and 1 mm in thickness were cut by electrodischarge machining and used for diffusivity measurements. The aperiodic and periodic sample surfaces are perpendicular to the periodic c axis and the aperiodic radial axes, respectively. Experiments were also performed on a sample surface oriented 45° from the c axis, i.e., the sample's normal axis is halfway between the periodic axis and the aperiodic plane. Figure 1 illustrates how the samples were cut from the single-grain ingot. The samples will hereon be referred to as periodic, aperiodic, and 45°, as indicated in Fig. 1. Pieces of the remaining single grain adjacent to the harvested samples were cut and ground into powder for x-ray analysis and heat capacity measurements. The structural quality of the sample used in this study is comparable, based on powder x-ray diffraction data, to the sample having the same nominal composition described by Fisher *et al.*[8]

Diffusivity measurements on these samples were made using the laser flash method. Samples were coated with a thin layer of graphite (10 to 30 μm) to reduce the reflection of background radiation. A monochromatic laser ($\lambda=628$ nm) is used to irradiate the front surface of the sample with a 1 ms pulse. The temperature profile of the opposite surface is monitored using a liquid-nitrogen-cooled InSb infrared detector. The detector output is transferred to a digital storage oscilloscope. Calibration of the scope enables quantitative determination of the sample's temperature as a function of time. Irradiation of the aperiodic sample and periodic sample provides bulk thermal diffusivity data along an aperiodic radial axis and the periodic c axis, respectively. The thermal diffusivity, α, can be calculated from the temperature rise profile using

$$\alpha=1.38L^2/\pi^2 t_{1/2}, \tag{1}$$

where L is the thickness of the sample and $t_{1/2}$ is the time

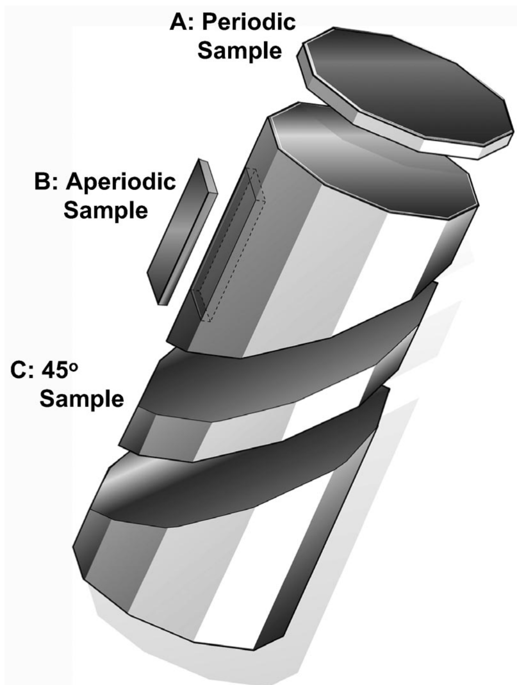

FIG. 1. Schematic representation of how samples were cut from the single grain *d*-Al-Ni-Co quasicrystal. A is the periodic sample, B is the aperiodic sample, and C is the 45° sample.

required for the heat pulse to reach one-half the maximum value. The thermal conductivity, κ, is related to the diffusivity, α, by the following equation:

$$\kappa = \alpha \rho C_p, \tag{2}$$

where C_p is the molar heat capacity ($\mathrm{J\,mol^{-1}\,K^{-1}}$) and ρ is density ($\mathrm{g\,cm^{-3}}$).

Density measurements were made at room temperature using Archimedes' technique. Measurements of heat capacity were made using a Perkin Elmer Pyris 7 differential scanning calorimeter. The sample was ground into a powder and placed in a platinum crucible. An empty platinum crucible was used as a reference. Heating and cooling rates were 5 K/min.

RESULTS AND DISCUSSION

Results of the diffusivity characterization for the three orientations are shown in Fig. 2. Thermal diffusivity through the aperiodic sample is comparable to data previously reported for icosahedral quasicrystals.[3,9] A clear anisotropy is seen among the samples. Measurements of the periodic sample show thermal diffusivities nearly an order of magnitude larger than the corresponding aperiodic specimen over the observed temperature range.

Figure 3 shows the molar heat capacity as determined by differential scanning calorimetry (DSC). At lower temperatures these data appear to be a continuation of the heat capacity data recently reported for *d*-Al-Ni-Co.[10] At higher temperatures, the heat capacity continually increases up to about 800 K. This trend is consistent with that reported by Edagawa and Kajiyama for both decagonal Al-Cu-Co and icosahedral Al-Pd-Mn quasicrystals.[11]

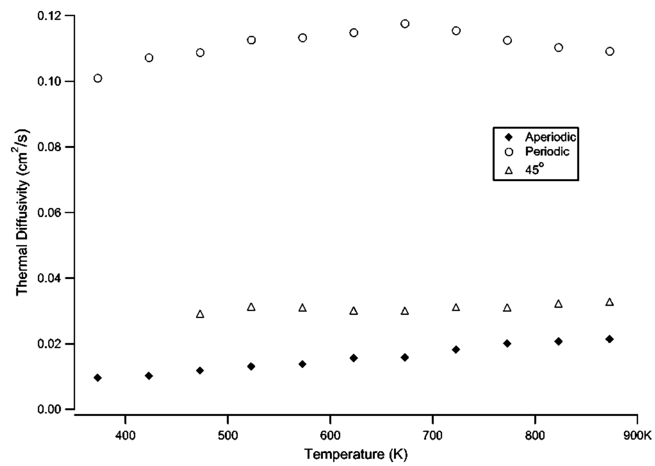

FIG. 2. Bulk thermal diffusivity for the *d*-Al-Ni-Co quasicrystal through different directional axes.

The sample density, ρ, was measured at room temperature as 4.01 g/ml. The thermal conductivity was calculated for each sample using the density, heat capacity, and diffusivity values; the results are shown in Fig. 4. Again, at low temperatures, our data appear consistent with previously reported low-temperature measurements on *d*-Al-Ni-Co.[4,7] Additionally, the trend in the aperiodic data set is comparable to results reported for icosahedral Al-Cu-Fe over the same temperature range; however, the values are about 2.4 times higher.[3] The values for thermal conductivity are much lower than one would expect for a typical metal. For comparison, at 373 K the thermal conductivity through the periodic axis is approximately an order of magnitude lower than that of pure aluminum (~237 W/m K), while the thermal conduction through the aperiodic plane is nearly two orders of magnitude less.

Thermal conductivity was also determined for the 45° sample. These data are compared to a theoretical thermal transport model. For an isotropic crystal, we would expect isotropic spherical thermal diffusion under the assumption of a free-electron gas; however, since diffusion through our ma-

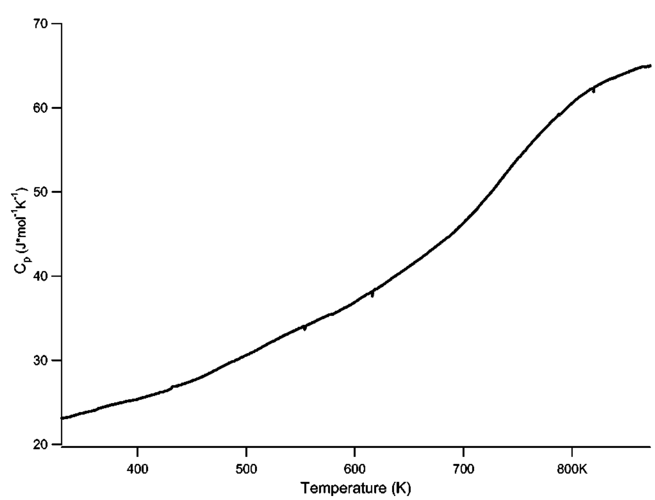

FIG. 3. DSC heat capacity measurement for the *d*-Al-Ni-Co quasicrystal.

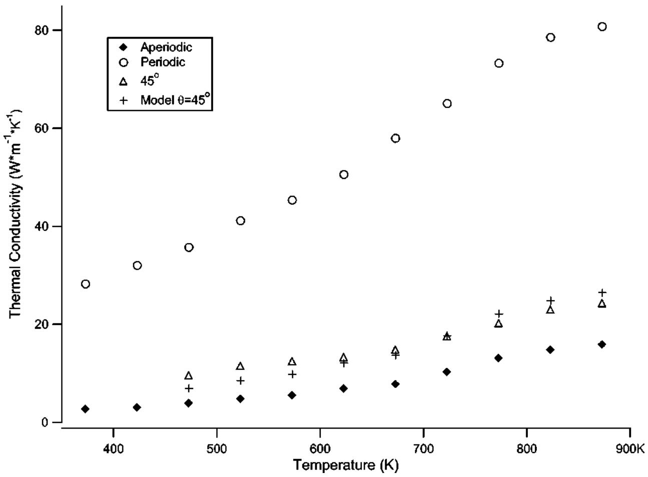

FIG. 4. Thermal conductivity for the *d*-Al-Ni-Co quasicrystal. Values calculated using the thermal ellipsoid model (θ=45°) show very good agreement with experimental data from the 45° sample.

terial is clearly anisotropic, the thermal ellipsoid model was employed. From this model, thermal conductivity at a given temperature is calculated using

$$\frac{1}{\kappa_\theta}=\frac{1}{\kappa_a}+\left(\frac{1}{\kappa_p}-\frac{1}{\kappa_a}\right)\cos^2\theta, \tag{3}$$

where κ_p is the measured conductivity through the periodic axis, κ_a is the measured conductivity though an aperiodic axis, and $\kappa\theta$ is the predicted conductivity through a sample having a normal axis at an angle, θ, relative to the periodic axis. For this work θ=45°. This model was first developed by Voigt[12] and was successfully used by Bridgman[13] to describe anisotropic conductivity in metallic single crystals. A more detailed description of this model has been given elsewhere.[14,15]

As seen in Fig. 4, the thermal ellipsoid model shows very good agreement with the experimental data collected for the 45° sample. The model assumes a linear relationship between temperature and thermal conductivity, in which scattering is proportional to the square of the amplitude of the atomic vibrations about their equilibrium lattice sites. The fact that the model describes the quasicrystal so well suggests that a free-electron gas may be a valid assumption at higher temperatures. A Debye temperature, θ_D, for *d*-Al-Ni-Co of about 400 K has been independently reported by Martin *et al.*[5] and Inaba *et al.*[10] As our measurements were obtained above θ_D, Drude-type behavior is not an unreasonable assumption. Although when considering the clear anisotropy in thermal transport behavior, it appears that the periodic axis is greatly favored. These trends in the thermal conductivity may be explained in terms of charge carriers and the mean free time of carrier collisions.

The electrical conductivity, σ, may be written as

$$\sigma=\frac{ne^2\tau}{m^*}, \tag{4}$$

where n is the carrier density, m^* is the effective mass, e is the charge on an electron, and τ is the mean free time between collisions. Theoretical analyses by Macia concluded that quasicrystals reasonably follow the Wiedemann-Franz law at high temperatures.[16] This allows us to derive the following relationship for thermal conductivity:

$$\kappa_{\rm el}=\mathrm{Lo}\frac{ne^2\tau T}{m^*}, \tag{5}$$

where $\kappa_{\rm el}$ is the electronic contribution to thermal conductivity and Lo is the Lorentz number. While our measured data represent the total thermal conductivity, we have assumed that over our temperature range the phonon contribution is negligible; therefore, $\kappa_{\rm el}\approx\kappa_{\rm total}$.

Equation (5) implies that for a given temperature, $\kappa_{\rm el}\propto\tau$. If the mean free time were independent of the sample axis direction, one would expect the thermal conductivities of the periodic and aperiodic samples to increase with temperature at the same rate; however, when comparing the two samples, we notice that the periodic sample has a much higher rate of increase than does the aperiodic sample. We have ascribed this difference to anisotropy of the carrier mean free time. While the number density of the charge carriers increases independent of direction, the carrier mean free time is substantially shorter along the aperiodic axes. This leads to the observed anisotropy in the rate of increase in thermal conductivity and also accounts for the overall anisotropy seen between the periodic and aperiodic samples.

The agreement of the thermal ellipsoid model with the data obtained from the 45° sample demonstrates that the high-temperature anisotropic transport properties of the two-dimensional quasicrystal may be described in the same manner as those in an anisotropic metallic crystal. Additionally, the successful prediction of transport properties across the 45° sample using a vector-based model suggests that the transport mechanisms of the quasicrystalline plane are not coupled with those of the periodic *c* axis.

CONCLUSIONS

In this work we present high-temperature thermal transport data for the decagonal Al-Ni-Co system. Heat capacity, density, and thermal diffusivity are experimentally measured and employed in the calculation of thermal conductivity. A high degree of anisotropy in thermal transport between the periodic and aperiodic directions was observed. The thermal ellipsoid model was employed to predict thermal transport behavior through a sample cut with a normal axis 45° from the periodic *c* axis. Experimental data collected on such a sample shows excellent agreement with predicted values. This suggests the validity of a Drude free-electron model at high temperatures. The observed rate of change in thermal conductivity with temperature is much higher along the periodic axis, possibly due to a longer carrier mean free time along the periodic direction.

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