Anisotropic Thermal Conductivity of the 2D Single Quasicrystals: Al₆₅Ni₂₀Co₁₅ and Al₆₂Si₃Cu₂₀Co₁₅

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The anisotropic thermal conductivity of $Al_{65}Ni_{20}Co_{15}$ and $Al_{62}Si_3Cu_{20}Co_{15}$ single quasicrystals has been measured. While a nearly isotropic phonon contribution was observed, the electronic thermal conductivity is almost completely suppressed in the quasicrystalline plane in contrast to the periodic direction where the materials behave like the usual 3D alloy except for a markedly lower electronic contribution.

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The earlier measurements on the transport properties of quasicrystals were not so encouraging. The existence of large numbers of defects in quenched samples made it difficult to tell whether the similarity of their behavior to amorphous alloys is intrinsic or not. The discovery of stable quasicrystals¹ has brought some new hope to the investigation of the electronic properties inherent in quasicrystalline structures, since much fewer defects are expected in the stable phases. Especially, the success in growing single 2D quasicrystals of the AlCuCo (Ref. 2) and AlNiCo (Ref. 3) systems provides an opportunity to compare the physical properties of a quasicrystal with its crystalline counterpart in the same sample, which may be an important step toward an understanding of the electronic properties of the structure. Indeed, a striking anisotropy in the electrical resistivity, thermopower, and Hall coefficient was first observed in AlSiCuCo,^{4,5} and then in AlNiCo.⁶⁻⁸ Here we report the anisotropic thermal conductivity of these two materials. To our knowledge, this is the first such measurement in quasicrystals.

The details of the growth of Al₆₂Si₃Cu₂₀Co₁₅ single quasicrystals were reported in Ref. 9. The Al₆₅Ni₂₀Co₁₅ quasicrystals were grown by a method similar to that reported in Ref. 3. The quasicrystals of both materials were found to be well formed prisms with tenfold rotational symmetry and proved to be of single domain over the whole crystal, which usually was a few tenths mm in diameter and several mm in length. The general size of the AlNiCo single quasicrystals is larger than that of Al-SiCuCo, and the good quality of the samples was proved by the results of electron-diffraction patterns and x-raydiffraction peaks whose widths were only slightly wider than that for a good crystal. The AlNiCo quasicrystals were less defective than the AlSiCuCo as shown by the better quality of the diffraction pattern as well as by the better reproducibility of the transport properties of the former. dc and ac susceptibility measurements showed that both materials have a very small and weakly anisotropic temperature-independent susceptibility.¹⁰ The thermal conductivity was measured using a sweeping comparative method which we had successfully used for the measurements of small superconducting crystals.¹¹ The essence of the method consists in the comparison of the temperature distribution in a thermocouple bridge with and without the sample clamped in. The reliability of the method was proven by the results for oxide super-conductors¹¹ as well as by the present work for which we always obtained reproducible results when reloading the samples.

The quasicrystals were processed to form thin slices for experiments. Two AlNiCo samples and two AlSiCu-Co samples were measured between room temperature and 77 K. The dimensions of the four samples were, respectively, $0.68 \times 0.42 \times 0.15$, $1.16 \times 0.76 \times 0.21$, $0.38 \times 0.25 \times 0.08$, and $0.35 \times 0.20 \times 0.06$ mm³ in sequence of sample number. Figure 1 presents the thermal conductivity along the periodic direction, κ^c . While for AlSi-



FIG. 1. The thermal conductivity of $Al_{65}Ni_{20}Co_{15}$ and $Al_{62}-Si_{3}Cu_{20}Co_{15}$ single quasicrystals along the periodic direction.



FIG. 2. The thermal conductivity of $Al_{65}Ni_{20}Co_{15}$ and $Al_{62}-Si_{3}Cu_{20}Co_{15}$ single quasicrystals in the quasicrystalline plane.

CuCo the results are rather sample dependent, the Al-NiCo samples show quite reproducible and higher thermal conductivity, consistent with the better quality of the latter. The thermal conductivity in the quasicrystalline plane, κ^{qc} , is shown in Fig. 2. First, we notice that κ^{qc} for both materials is almost temperature independent. Since for an alloy of high resistivity, according to the Wiedemann-Franz law, the electronic thermal conductivity is nearly proportional to T, the independence of κ^{qc} on T should imply a negligible contribution from electrons. This is supported by the fact that the variation of κ^{qc} from sample to sample is much less sensitive than the variation of $\rho_0^{\rm gc}$. For example, the roomtemperature value of ρ^{qc} for sample 3 is 3 times larger than that for sample 1 (Table I), while the corresponding κ^{qc} changes only about 40%. A further support for the trivial contribution of electrons is the immunity of $\kappa^{\rm qc}$ to the temperature coefficient of electrical resistivity in the quasicrystalline plane, which is positive for Al-NiCo and negative for AlSiCuCo. The strong depression of the electronic thermal conductivity in the quasicrystalline plane is unusual. For example, according to the Wiedemann-Franz law, the electronic thermal conductivity for samples 1 and 2 should be more than 6 W m⁻¹K⁻¹ at room temperature, while κ^{qc} is actually

only $\sim 2.5 \text{ Wm}^{-1} \text{K}^{-1}$. As the Wiedemann-Franz law is based on the assumption that the relaxation time of electrons is isotropic and the same for electrical and thermal conduction, the breakdown of the law is indicative of the scattering in these 2D quasicrystals being quite different from the usual defect scattering. In the quasicrystals the scattering is more effective in thermal conduction than in electrical conduction. This feature should be characteristic of the quasicrystalline structure itself because a random distribution of disorder results in an isotropic scattering and the usual elastic defect scattering leads fairly well to the observation of the Wiedemann-Franz law.¹² Furthermore, for AlNiCo no evidence for disorder was visible in small-scale scanning tunneling microscopy images and full decagonal symmetry was realized on scales as small as 60 Å.¹³

At present it is too early to judge whether the temperature-independent phonon thermal conductivity is a common feature of 2D quasicrystals or whether it belongs only to these two materials. For a concentrated crystalline alloy solute scattering and electron scattering can also reduce the temperature dependence of the phonon component to practically a constant value.¹⁴ Supposing a temperature-independent phonon thermal conductivity, the combined contribution of phonons and electrons can be expressed by the modified Smith-Palmer formula¹⁴

$$\kappa^{c} = A(\rho_{0}^{c}/L_{0} + \rho_{i}^{c}/L)^{-1}T + B, \qquad (1)$$

where $\rho_{\delta}^{\epsilon}, \rho_{i}^{\epsilon}$ are the residual and intrinsic electrical resistivity along the tenfold axis, L_{0} is the Sommerfeld value of the electronic Lorenz function, and L is the intrinsic Lorenz function. The constant A is included to take into account the different relaxation times in thermal and electrical conduction. We see that in the quasicrystalline plane, A is approximately zero. In the periodic direction, however, the thermal conductivity κ^{c} is described well by relation (1), similar to many 3D crystalline concentrated alloys, except that the constant A is much lower than unity here. Assuming that the usual treatment in calculating L is still effective in the present case and taking the Debye temperature $\vartheta_{D} \sim 400$ K, ¹⁵ we may deduce the constants A and B as shown in Table I. As we already

TABLE I. The measured resistivity, the slope of thermal conductivity, and the calculated constants A and B according to Eq. (1) for Al₆₅Ni₂₀Co₁₅ and Al₆₂Si₃Cu₂₀Co₁₅ single quasicrystals.

Material	Sample	ρ_0^c ($\mu \Omega \mathrm{cm}$)	$\rho_i^c (300 \text{ K}) (\mu \Omega \text{ cm})$	$ ho_0^{\rm qc}$ ($\mu \Omega {\rm cm}$)	$\rho^{\rm qc}$ (300 K) ($\mu \Omega {\rm cm}$)	$\frac{d\chi^c/dT}{(W/m K^2)}$	A	<i>B</i> (W/m K)
AlNiCo	1	12.5 ^a	26.7	56.4 ^a	117	0.037	0.63	2.5
	2	8.8 ^a	30.7	48.2 ^a	120	0.037	0.64	2.5
AlSiCuCo	3	60.7 ^a	8.2	368 ^a	337	0.017	0.47	2.1
	4	76 ^b	8.2			0.012	0.40	1.7

^aExtrapolated value.

^bEstimated value.



FIG. 3. The variation of $d\kappa^c/dT$ and the constant A in Eq. (1) with the residual resistivity of the samples. The solid line represents the limit of elastic defect scattering: $d\kappa^c/dT = L_0/\rho_0$.

mentioned, the constant B represents the temperatureindependent phonon contribution along the tenfold axis. The constant A is nearly temperature independent, as can be seen from Fig. 1, and is easy to understand because the temperature dependence of ρ_i is greatly compensated by the temperature dependence of L. If we plot $d\kappa^{c}/dT$ and A against ρ_{0} (Fig. 3), we see that the constant A in all cases is substantially lower than unity. Furthermore, although we should not take the linear variation of A vs ρ_0 too seriously because the accuracy of the measurements was not good enough to determine the functional dependence, one thing is certain: A decreases with an increase of ρ_0 and tends to zero at a much lower value of ρ_0 than that expected from the usual model of defect scattering. These results contradict our understanding that ρ_0 represents the degree of disorder which contributes only to elastic scattering, and the observation that the Wiedemann-Franz law holds for arbitrary (elastic) scattering by impurities.¹² However, in the above discussion, we have completely ignored the strong anisotropy in the structural symmetry and electronic properties of the materials. We have taken into account only the resistivity in the periodic direction in Eq. (1), while actually the quasicrystalline structure may play an important role in reducing the electronic contribution to the thermal conductivity. This provides a possible explanation to the decrease of A with increasing ρ_0 which consists of some "defect-assisted" mixing of the contribution from the quasicrystalline plane into the periodic direction.

When we plot κ^{qc} against *B*, the phonon contribution to κ^c , we find that the variation follows roughly a straight line with slope not far from unity (Fig. 4). This not only proves a temperature-independent phonon con-



FIG. 4. The synchronous change of the constant B with the thermal conductivity in the quasicrystalline plane.

ductivity, but also shows that the phonon contribution to the thermal conductivity is nearly isotropic, in spite of the striking anisotropy of the structural symmetry, which may imply that the long-wavelength phonons play a more important role in the process.

In summary, we have made the first measurements of the anisotropic thermal conductivity of two 2D quasicrystals. While both materials show a nearly isotropic and temperature-independent phonon component, the electronic thermal conductivity is almost completely suppressed in the quasicrystalline plane and is markedly depressed along the periodic direction. This is indicative of a peculiar scattering mechanism, calling for more research work in both experiment and theory.

Finally, we should mention the difference between the present materials and the usual layered materials. In the latter case, the anisotropy comes from the much weaker bonding between the layers, which makes the materials quasi-2D systems. But in the present case, the materials behave in many ways like 3D systems. The electrical resistivity, thermopower, and mechanical properties show strong 3D bondings, which is supported by the isotropic phonon thermal conductivity of the materials. Therefore, our results present a unique example where a 3D electron system shows striking anisotropy in thermal conductivity due to the anisotropy of the structural symmetry.

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