

Phonon-enhanced thermoelectric power of Y–Al–Ni–Co decagonal approximant

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Abstract. We have investigated anisotropic electrical resistivity and thermoelectric power of the ypsilon-phase Al–Ni–Co (Y–Al–Ni–Co) decagonal approximant with composition Al₇₆Co₂₂Ni₂. The crystalline-direction-dependent measurements were performed along three orthogonal directions a^* , b and c of the Y–Al–Ni–Co unit cell, where (a , c) monoclinic atomic planes are stacked along the perpendicular b direction. Anisotropic electrical resistivity is low in all crystalline directions, appearing in the order $\rho_{a^*} > \rho_c > \rho_b$ and showing positive temperature coefficient typical of electron-phonon scattering mechanism. Thermopower shows electron-phonon enhancement effect. Anisotropic bare thermopower (in the absence of electron-phonon interactions) was extracted, appearing in the same order as the resistivity, $|S_{a^*}^{\text{bare}}/T| > |S_c^{\text{bare}}/T| > |S_b^{\text{bare}}/T|$.

Introduction

Decagonal quasicrystals (d -QCs) can be structurally viewed as a periodic stack of quasiperiodic atomic planes, so that d -QCs are two-dimensional quasicrystals, whereas they are periodic crystals in a direction perpendicular to the quasiperiodic planes. A consequence of the anisotropic structure are anisotropic magnetic and transport properties [1] (electrical resistivity, thermoelectric power, Hall coefficient, thermal conductivity), when measured along different crystalline directions. Here we report an experimental study of the anisotropic electrical resistivity and thermoelectric power of a complex metallic alloy Al_{13– x} (Co_{1– y} Ni _{y})₄ [2], known also as the ypsilon–Al–Ni–Co phase (Y–Al–Ni–Co), which is a monoclinic approximant to the decagonal phase with two atomic layers within one periodic unit along the stacking direction. We show that the thermopower exhibits an electron-phonon enhancement effect, as also observed in the related d -Al–Ni–Co quasicrystal [3].

Structural considerations and sample preparation

The Al_{13– x} (Co_{1– y} Ni _{y})₄ monoclinic phase belongs to the Al₁₃TM₄ (TM = transition metal) class of decagonal approximants. The structure of Al_{13– x} (Co_{1– y} Ni _{y})₄ with $x = 0.9$ and $y = 0.12$, corresponding to composition Al₇₅Co₂₂Ni₃, was first described by Zhang *et al.* [2]. Lattice parameters of the monoclinic unit cell (space group $C2/m$ (No. 12)) are $a = 17.071(2)$ Å, $b = 4.0993(6)$ Å, $c = 7.4910(9)$ Å, $\beta = 116.17^\circ$ and Pearson symbol $mC34-1.8$ with 32 atoms in the unit cell (8 Co/Ni and 24 Al), which are placed on 9 crystallographically inequivalent atomic positions (2 Co/Ni and 7 Al). Two of these are partially occupied (Al(6) by 90% and Al(6') by 10%). The structure of Al_{13– x} (Co_{1– y} Ni _{y})₄ is built up of one type of flat atomic layers, which are related to each other by a 2₁ axis, giving ~ 0.4 nm period along the [010] direction (corresponding to the periodic direction in the related d -Al–Ni–Co quasicrystal) and two atomic layers within one periodicity unit. Locally, the structure shows close resemblance to the d -Al₇₀Co₁₅Ni₅ quasicrystal [4], which also consists of only one type of a quasiperiodic layer, repeated by a 10₅-axis and giving the same ~ 0.4 nm period.

The single crystal used in our study was grown from an incongruent Al-rich melt of initial composition Al_{81.9}Co_{14.5}Ni_{3.6} by the Czochralski method using a native seed. The composition of the crystal (rounded to the closest integers) was Al₇₆Co₂₂Ni₂ and its structure matched well to the monoclinic unit cell of the Zhang *et al.* [2] model (who studied the composition Al₇₅Co₂₂Ni₃). In order to perform crystalline-direction-dependent studies, we have cut from the ingot three bar-shaped samples of dimensions $2 \times 2 \times 6$ mm³, with their long axes along three orthogonal directions. The long axis of the first sample was along [0 1 0] direction (designated in the following as b), which corresponds to the periodic direction in the related d -Al–Ni–Co quasicrystal. The (a , c) monoclinic plane corresponds to the quasiperiodic plane in d -QCs and the second sample was cut with its long axis along [001] (c) direction, whereas the third one was cut along the direction perpendicular to the (b , c) plane. This direction is

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designated as a^* (it lies in the monoclinic plane at an angle 26° with respect to a and perpendicular to c). The so-prepared samples enabled us to determine the anisotropic electrical resistivity and thermopower of the investigated monoclinic $\text{Al}_{76}\text{Co}_{22}\text{Ni}_2$ (abbreviated as Y–Al–Ni–Co in the following) along the three orthogonal crystalline directions.

Electrical resistivity

Electrical resistivity was measured between 300 and 2 K using the standard four-terminal technique and the $\rho(T)$ data are displayed in Fig. 1. The resistivity is the lowest along the b direction perpendicular to the atomic planes, where its room-temperature (RT) value amounts $\rho_b^{300\text{K}} = 25 \mu\Omega \text{ cm}$ and the residual resistivity is $\rho_b^{2\text{K}} = 10 \mu\Omega \text{ cm}$. The two in-plane resistivities are higher, amounting $\rho_c^{300\text{K}} = 60 \mu\Omega \text{ cm}$ and $\rho_c^{2\text{K}} = 29 \mu\Omega \text{ cm}$ for the c direction and $\rho_{a^*}^{300\text{K}} = 81 \mu\Omega \text{ cm}$ and $\rho_{a^*}^{2\text{K}} = 34 \mu\Omega \text{ cm}$ for the a^* direction. While ρ_b is considerably smaller than ρ_{a^*} and ρ_c by a factor of about 3, the two in-plane resistivities are much closer, $\rho_{a^*}/\rho_c \approx 1.3$. The above resistivity values, appearing in the order $\rho_{a^*} > \rho_c > \rho_b$, reveal that Y–Al–Ni–Co is good electrical conductor along all three crystalline directions. The strong positive temperature coefficient (PTC) of the resistivity along all three crystalline directions demonstrates predominant role of the electron-phonon scattering mechanism.

Thermoelectric power

The thermoelectric power (the Seebeck coefficient S) was measured between 300 and 2 K by applying a differential method with two identical thermocouples (chromel-gold with 0.07% iron), attached to the sample with silver paint, and the data are displayed in Fig. 2. Thermopower is negative for all three directions, suggesting that electron-type

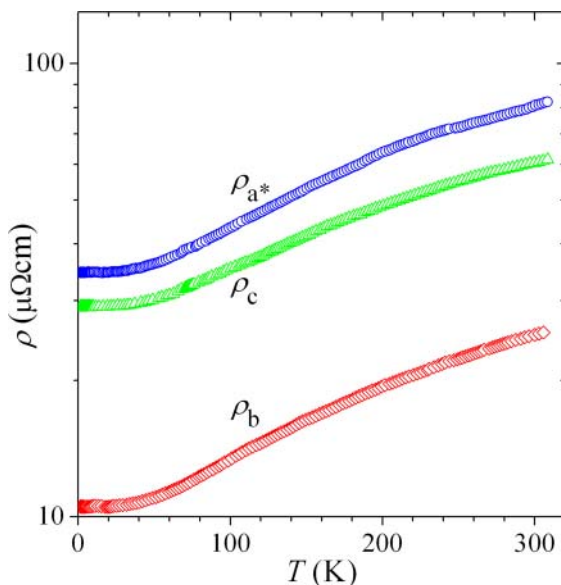


Fig. 1. (Color online) Temperature-dependent electrical resistivity of Y–Al–Ni–Co along three orthogonal crystalline directions a^* , b and c (note that the vertical scale is logarithmic).

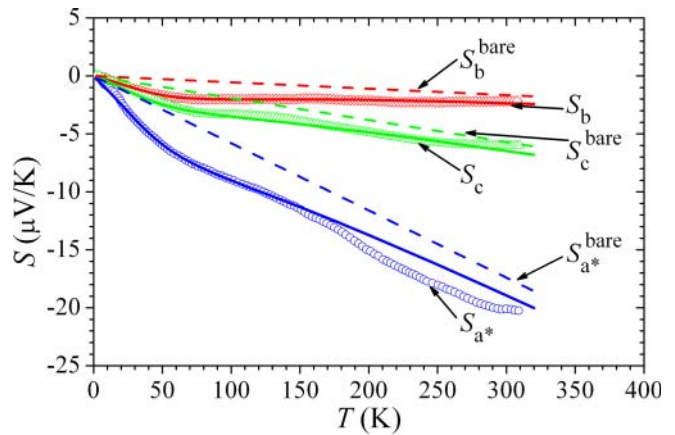


Fig. 2. (Color online) Temperature-dependent thermoelectric power (the Seebeck coefficient S) of Y–Al–Ni–Co along three orthogonal crystalline directions a^* , b and c . Solid curves are fits with Eqs. (1) and (3) and the fit parameters are given in Table 1. Bare thermopowers (in the absence of electron-phonon interactions) are shown by dashed lines.

carriers dominate the thermoelectric transport. The RT values are in the range between -2 and $-20 \mu\text{V/K}$ in the order $|S_{a^*}| > |S_c| > |S_b|$. The $S(T)$ characteristics for all directions are qualitatively similar, except for the variation in magnitude. In all cases, a change of slope is observed at about 70 K, where the low-temperature slope is higher than the high-temperature one. Nonlinearities in the thermopower in this temperature range are often associated with electron-phonon effects, which typically reach their maximum value at a temperature that is some fraction of the Debye temperature θ_D . The thermopower in all three directions extrapolates approximately linearly to zero upon $T \rightarrow 0$, a feature that is usually associated with metallic diffusion thermopower. These features allow comparing the $S(T)$ data from Fig. 2 to the behavior expected for the electron-phonon enhancement of diffusion thermopower, as observed in several metallic glasses [5] and also in the related $d\text{-Al}_{73}\text{Co}_{10}\text{Ni}_{17}$ quasicrystal [3]. The importance of phonons in the temperature-dependence of the thermopower of Y–Al–Ni–Co is analogous to the temperature-dependent electrical resistivity of this compound, where electron-phonon interaction represents the main scattering mechanism, leading to the PTC of the resistivity.

The electron-phonon enhancement of the diffusion thermopower can be written as [3, 5]

$$\frac{S}{T} = \frac{S^{\text{bare}}}{T} [1 + \lambda(T)], \quad (1)$$

where S^{bare} is the bare thermopower in the absence of the electron-phonon interaction and $\lambda(T)$ is the electron-phonon mass enhancement parameter given by [5]

$$\lambda(T) = \int_0^\infty d\omega \frac{\alpha^2 F(\omega)}{\omega} G\left(\frac{\hbar\omega}{k_B T}\right). \quad (2)$$

Here $\alpha^2 F(\omega)$ is the Eliashberg function and $G(\hbar\omega/k_B T)$ is a universal function, introduced by Kaiser [5]. Full treatment of the anisotropic thermopower should take into account the anisotropy of $\alpha^2 F(\omega)$, which is beyond our possibilities. To simplify the problem, we adopt the same approximation as applied before to the $d\text{-Al–Ni–Co}$ qua-

scrystal [3] using the Debye model, $\alpha^2 F(\omega) = C_D \omega^n$, with a cutoff frequency $\omega_D = k_B \theta_D / \hbar$, where the anisotropy is introduced phenomenologically through the orientation-dependent parameters C_D and n . Eq. (2) then becomes

$$\lambda(T) = C_D \int_0^{\omega_D} d\omega \omega^{n-1} G\left(\frac{\hbar\omega}{k_B T}\right). \quad (3)$$

Our fits of the anisotropic thermopower (solid curves in Fig. 2) could be made satisfactorily with $n = 2$, so that only C_D was varied for different crystalline directions. We observe that Eqs. (1) and (3) reproduce well the change of slope in the thermopowers at about 70 K. While the fits for the b and c directions are satisfactory up to the RT, the fit for the a^* direction is good up to 150 K, whereas it starts to deviate from the measured data at higher temperatures. At present we do not have an explanation for this deviation. The fit parameters are given in Table 1, where the value $\lambda(0) = C_D \omega_D^2 / 2$ is given instead of C_D (taking into account that $\lim_{T \rightarrow 0} G(\hbar\omega/k_B T) = 1$ in Eq. (3)). The Debye temperature was taken as $\theta_D = 320$ K. The bare thermopowers S^{bare} for all three crystalline directions are shown as dashed lines in Fig. 2.

The anisotropy of the so-extracted bare thermopowers can now be analyzed using the well-known expression derived from the linearized Boltzmann transport equation

$$S^{\text{bare}} = \frac{\pi^2}{3(-e)} k_B^2 T \left[\frac{\partial \ln \sigma(E)}{\partial E} \right]_{E=\zeta}. \quad (4)$$

where ζ is the chemical potential and $\sigma(E)$ is the spectral conductivity in the vicinity of the Fermi level. Since $\sigma(E)$ is not known, we made the following qualitative analysis. The geometry of our samples requested that we have experimentally measured the diagonal elements of the thermopower tensor in the Cartesian coordinate system $i = x, y, z$

$$S_{ii}^{\text{bare}} = \frac{\pi^2}{3(-e)} k_B^2 T \rho_{ii} \left[\frac{\partial \sigma_{ii}(E)}{\partial E} \right]_{E=\zeta}. \quad (5)$$

We assume that $\sigma(E)$ exhibits no sharp features in the vicinity of the Fermi level E_F , so that no singularities in its derivative are expected. Within the approximation that the derivative $(\partial \sigma_{ii}(E)/\partial E)_{E=\zeta}$ does not depend significantly on the crystalline direction, the magnitude of the thermopower in the direction i is predominantly determined by the magnitude of the resistivity ρ_{ii} in that direction. The geometry of our samples (their long axes were along three orthogonal directions a^* , b and c) and the direction of the electric field applied along their long axes imply that diagonal elements of the resistivity tensor $\rho_{xx} = \rho_{a^*}$, $\rho_{yy} = \rho_b$ and $\rho_{zz} = \rho_c$ were measured in our experiments. Since $\rho_{a^*} > \rho_c > \rho_b$ (Fig. 1), this requires bare thermopowers in the order $|S_{a^*}^{\text{bare}}/T| > |S_c^{\text{bare}}/T| > |S_b^{\text{bare}}/T|$. Figure 2 and Table 1 show that this was indeed observed experimentally. Here it should be emphasized that the above relation of the anisotropic thermopower to the anisotropic electrical resistivity is qualitative only. The microscopic origin of the anisotropy of any electron transport coefficient is the anisotropy of the Fermi surface, arising from the anisotropy of the elec-

Table 1. Fit parameters of the anisotropic thermopower using Eqs. (1) and (3).

crystalline direction	S^{bare}/T ($\mu\text{V}/\text{K}^2$)	$\lambda(0)$
a^*	-5.8×10^{-2}	1.0
b	-5.5×10^{-3}	5.0
c	-1.9×10^{-2}	1.6

tronic structure due to the specific atomic structural and chemical details of the crystalline lattice.

Conclusions

We have investigated anisotropic electrical resistivity and thermoelectric power of the Y–Al–Ni–Co decagonal approximant. Electrical resistivity is low in all three crystalline directions, with the RT values in the range 25–81 $\mu\Omega$ cm. There exists significant anisotropy between the in-plane resistivity and the resistivity along the perpendicular b direction by a factor about 3, whereas the anisotropy between the two in-plane directions a^* and c is much smaller. The anisotropic resistivity appears in the order $\rho_{a^*} > \rho_c > \rho_b$, so that b direction is the most electrically conducting one. Thermopower of Y–Al–Ni–Co is negative, suggesting dominant electron-type carriers, and shows electron-phonon enhancement effect that results in a change of slope in the Seebeck coefficient $S(T)$ at about 70 K for all three investigated crystalline directions. Bare thermopower (in the absence of electron-phonon interactions) was extracted and its anisotropy was analyzed within the frame of the linearized Boltzmann transport equation. Assuming that the spectral conductivity does not exhibit sharp features in the vicinity of the Fermi level and the derivative of the spectral conductivity does not depend significantly on the crystalline direction, the magnitude of the thermopower in a given direction is then predominantly determined by the magnitude of the resistivity in that direction. This suggests anisotropic bare thermopowers in the same order as the anisotropic electrical resistivity, $|S_{a^*}^{\text{bare}}/T| > |S_c^{\text{bare}}/T| > |S_b^{\text{bare}}/T|$, which was also observed experimentally.

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