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Decagonal Quasicrystals and Approximants: Two-Dimensional or Three-Dimensional Solids?

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Abstract: Crystallographic structures of decagonal quasicrystals (d-QCs) are traditionally described as a periodic stacking of atomic planes with quasiperiodic in-plane atomic order, so that d-QCs are considered to be two-dimensional (2D) quasicrystals, whereas they are periodic crystals in the third dimension. Similar stacked-layer structures are observed also in the periodic decagonal approximant phases. In this review paper, we consider the dimensionality of the chemical bonding network in the d-QCs and their approximants on the basis of electrical resistivity. By comparing the anisotropic resistivity along the stacking- and the in-plane directions of a series of decagonal approximants with different numbers of atomic layers within one periodicity unit

(the two-layer Y-Al-Co-Ni, the four-layer o-Al₁₃Co₄, Al₁₃Fe₄ and Al₁₃(Fe,Ni)₄, and the six-layer Al₄(Cr,Fe) and T-Al₃-(Mn,Fe)) and of a two-layer *d*-Al-Co-Ni decagonal quasicrystal, we show that universally, the stacking direction perpendicular to the atomic planes is always the most conducting one. Since the in-plane electrical resistivities are of the same order of magnitude as the resistivity along the stacking direction, this confirms the 3D character of the investigated solids. The stacked-layer description in terms of 2D atomic planes should therefore be regarded as a convenient geometrical approach to describe the complex structures of the *d*-QCs and their approximants, whereas their physical properties are those of true 3D solids.

Keywords: conducting materials · decagonal quasicrystals · electrical transport · intermetallic phases · quasicrystalline approximants

1. Introduction

The crystallographic structures of decagonal quasicrystals (d-QCs) and their periodic approximants are traditionally described as a periodic stacking of atomic planes with either quasiperiodic in-plane atomic order, in the case of d-QCs, or translationally periodic order, in the case of the approximants.^[1] Consequently, d-QCs are considered to be two-dimensional (2D) quasicrystals, whereas they are periodic crystals in the third dimension. Examples of the stacked-layer d-QC structures are d-Al-Co-Ni and d-Al-Co-Cu with two atomic layers within the periodicity length of about 0.4 nm along the stacking (10-fold) direction, d-Al-Co, d-Al-Ni and d-Al-Si-Cu-Co with four layers within the periodicity length of about 0.8 nm, d-Al-Mn, d-Al-Cr and d-Al-Mn-Pd with six layers within the periodicity length of about 1.2 nm, and d-Al-Pd and d-Al-Cu-Fe with eight layers within the periodicity length of 1.6 nm. Decagonal approximant phases are characterized by large unit cells but preserve the stacked-layer structure, with the periodicity lengths along the stacking direction almost identical to those of the d-QCs. The monoclinic Al13-x(Co1-vNiv)4 decagonal approximant,[2] known as the Y-phase of Al-Co-Ni (denoted as Y-Al-Co-Ni), comprises two atomic layers within one periodic unit. The $Al_{13}TM_4$ (TM = transition metal) family with TM = Co, Fe, Ru, Rh, Os represents four-layer approximant ${\rm phases},^{[3-7]}$ whereas the orthorhombic ${\rm Al}_4 TM$ phases, described by Deng et al.,^[8] and the orthorhombic Taylorphase^[9,10] T-Al₃Mn represent six-layer approximant structures. However, recent analysis of the chemical bonding in the orthorhombic o-Al₁₃Co₄ four-layer approximant by means of the electron localizability indicator (ELI)^[11,12] has led to a highly unexpected result that has put the traditional view of the Al₁₃TM₄ crystallographic structures in terms of atomic layers in question. Numerous covalentlike Co-Al and Al-Al bonds were found within the atomic layers as well as between the layers, revealing the

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formation of a three-dimensional (3D) bonding framework, contrary to the traditional consideration in terms of 2D atomic layers. This has suggested that the stackedlayer description is a convenient geometrical approach to describe the complex structure of the o-Al₁₃Co₄ phase, whereas its physical properties are those of a true 3D solid. In addition, elongated cavities along the stacking direction were identified in the 3D framework with the nearly linear Co-Al-Co "guest" atomic groups trapped inside. The ELI analysis has shown that the interactions within the Co-Al-Co group atoms (directed, covalent) differ from those between this group and the atoms of the framework (non-directed, ionic). While the covalent bonding between the Co-Al-Co atoms is strong, bonding of the Co-Al-Co group to the rest of the lattice is weaker. This unusual feature reveals analogy to the intermetallic clathrates, which also exhibit covalently bonded 3D networks with filler atoms in the cavities, interacting ionically with the host framework. The ²⁷Al NMR spectroscopic studies of the Al₁₃TM₄ four-layer approximant phases^[13,14] (the orthorhombic o-Al₁₃Co₄, the monoclinic Al₁₃Fe₄, its ternary derivative Al13(Fe,Ni)4, and the monoclinic Al₁₃Ru₄) confirmed the results of the bonding analysis and supported the unique bonding situation of Al in the nearly linear TM-Al-TM groups and the 3D nature of the bonding network.

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In this review paper, we consider the 3D nature of chemical bonding in the d-QCs and their approximants on the basis of electrical resistivity, which is highly sensitive to the dimensionality of the bonding network. The anisotropic electronic transport coefficients (the electrical resistivity, the thermoelectric power, the Hall coefficient, and the electronic thermal conductivity) depend on the dimensionality of the metallic bonding, whereas the charge localized on the covalent and ionic bonds does not participate in the electronic long-range transport. By comparing the anisotropic electrical resistivity along the stacking- and the in-plane directions of a series of decagonal approximants with different numbers of atomic layers within one periodicity unit and of a *d*-QC, we show the universality that the stacking direction perpendicular to the atomic planes is always the most conducting one. Since the in-plane electrical resistivities are of the same order of magnitude as the resistivity along the stacking direction, this confirms the 3D character of the investigated solids. The stacked-layer description in terms of 2D atomic layers should therefore be regarded as a convenient geometrical approach to describe the complex structures of the d-QCs and their approximants, whereas their physical properties are those of true 3D solids.

2. Samples Selection and Structural Considerations

Our analysis included the following phases: the Y-Al-Co-Ni two-layer approximant phase; the orthorhombic o- $Al_{13}Co_4$, the monoclinic $Al_{13}Fe_4$ and its ternary derivative $Al_{13}(Fe,Ni)_4$ four-layer approximant phases; the orthorhombic $Al_4(Cr,Fe)$ and the orthorhombic Taylor-phase T-Al₃(Mn,Fe) six-layer approximant phases and the *d*-Al-Co-Ni two-layer decagonal quasicrystal. Below we describe their structural features and sample preparation.

2.1. Y-Al-Co-Ni Two-Layer Approximant

The Al_{13-x}(Co_{1-y}Ni_y)₄ monoclinic phase^[2] belongs to the Al₁₃TM₄ class of decagonal approximants. Other members are monoclinic Al₁₃Co₄,^[15] orthorhombic Al₁₃Co₄,^[3] monoclinic Al₁₃Fe₄,^[4] monoclinic Al₁₃Os₄,^[7] Al₁₃Ru₄ (isotypical to Al₁₃Fe₄),^[5] and Al₁₃Rh₄ (also isotypical to Al₁₃Fe₄).^[6] 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 *C2m* (No. 12)) are *a*= 1.7071(2) nm, *b*=0.40993(6) nm, *c*=0.74910(9) nm, *β*= 116.17°, 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%). X-ray diffraction data revealed that the Al_{13-x}(Co_{1-y}Ni_y)₄ phase is identical to the

previously reported Y-phase, found as predominant phase in samples with compositions $Al_{75}Co_{20}Ni_5$ and $Al_{75}Co_{15}Ni_{10}$.^[2,16] The structure of $Al_{13-x}(Co_{1-y}Ni_y)_4$ is built up of flat atomic layers of a single type, which are related to each other by a 2₁ axis, giving ≈ 0.4 nm period along the [010] direction (corresponding to the periodic 10-fold direction in the related *d*-Al-Co-Ni quasicrystal) and two atomic layers within one periodicity unit. Locally, the structure shows close resemblance to the *d*-Al₇₀Co₁₅Ni₁₅ quasicrystal,^[17] which also consists of only one type of quasiperiodic layer, repeated by a 10₅-axis and giving the same ≈ 0.4 nm period.

The single crystal used in our study was grown 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. model.^[2] In order to perform crystalline-direction-dependent studies, we cut from the ingot three bar-shaped samples of dimensions $2 \times 2 \times 6$ mm, with their long axes along three orthogonal directions. The long axis of the first sample was along the [010] direction (designated in the following as b), which corresponds to the periodic 10-fold direction in the related d-Al-Co-Ni quasicrystal. The (a,c) monoclinic plane corresponds to the quasiperiodic plane in the d-QC and the second sample was cut with its long axis along the [001] (c) direction, whereas the third one was cut along the direction perpendicular to the (b,c) plane. This direction is designated as a^* (it lies in the monoclinic plane at an angle 26° with respect to *a* and perpendicular to *c*). Anisotropic physical properties (the magnetic susceptibility, the electrical resistivity, the thermoelectric power, the Hall coefficient, and the thermal conductivity) of our monoclinic Al₇₆Co₂₂Ni₂ (abbreviated as Y-Al-Co-Ni in the following) were reported recently.^[18]

2.2. o-Al₁₃Co₄ Four-Layer Approximant

According to the original structural model of the o-Al₁₃Co₄ phase by Grin et al.,^[3] the lattice parameters of the orthorhombic unit cell (space group Pmn2, Pearson symbol *oP*102) are a = 0.8158 nm, b = 1.2342 nm, and c =1.4452 nm with 102 atoms in the unit cell distributed over 10Co and 28Al crystallographic sites. Within the traditional stacked-layer description, the structure corresponds to a four-layer stacking along [100], with flat layers at x =0 and x = 1/2 and two symmetrically equivalent puckered layers at x = 1/4 and 3/4, giving ≈ 0.8 nm period along [100]. All lattice sites of the original model are fully occupied. Based on a recent more precise crystal structure determination, Grin et al.^[12] have proposed a new model of the o-Al₁₃Co₄, where some sites of the original model are split, yielding partial occupation of the sites Al(14) and Al(25)-Al(32) (nine altogether) in the new model with the probabilities 0.715, 0.576, 0.516, 0.6, 0.351, 0.554, 0.192, 0.305, and 0.399, respectively.

The o-Al₁₃Co₄ single crystal used in our study was grown by the Czochralski technique and the growth details are described elsewhere.^[19] Three bar-shaped specimens of dimensions $2 \times 2 \times 7$ mm were cut from the parent crystal with their long edges along [100] (*a*), [010] (*b*), and [001] (*c*) crystallographic directions, where *a* is the pseudo 10-fold direction of the o-Al₁₃Co₄ structure. Anisotropic physical properties of the o-Al₁₃Co₄ phase (the magnetic susceptibility, the electrical resistivity, the thermoelectric power, the Hall coefficient and the thermal conductivity) were reported recently.^[20]

2.3. Al₁₃Fe₄ and Al₁₃(Fe,Ni)₄ Four-Layer Approximants

According to the original structural model of $Al_{13}Fe_4$ by Grin et al.,^[4] lattice parameters of the monoclinic unit cell (space group C2m, Pearson symbol mC102) are a =1.5492 nm, b = 0.8078 nm, c = 1.2471 nm, and $\beta = 107.69^{\circ}$ with 102 atoms in the unit cell distributed over 5Fe and 15 Al crystallographic sites. All lattice sites are fully occupied except the site Al(2), which shows partial occupation of 0.92 ± 0.02 . The structure can be described as a fourlayer stacking along [010], with flat layers at y=0 and y=1/2 and two symmetrically equivalent puckered layers at y = 1/4 and 3/4, giving ≈ 0.8 nm period along [010]. Based on a recent high-resolution X-ray diffraction study, the structural model of Al₁₃Fe₄ has been refined.^[21] The atomic coordinates of the refined model are within 3 e.s.d. (estimated standard deviation) equal to the atomic coordinates of the original model, whereas the occupancy of the position Al(15) (which corresponds to the partially occupied position Al(2) of the original model) was found to be within one e.s.d., so that all lattice sites of the refined model are fully occupied. Thus, in comparison with many other members of the $Al_{13}TM_4$ family, the $Al_{13}Fe_4$ reveals a nearly completely ordered crystal structure.

The Al₁₃(Fe,Ni)₄ phase is a ternary solid solution of Ni in Al₁₃Fe₄ with the maximum solubility of Ni 8.9 at. %.^[22] The chemical composition of the Al₁₃(Fe,Ni)₄ single crystal used in our investigations was Al_{76.5}Fe_{21.3}Ni_{2.2}. The introduction of a small quantity of Ni atoms into the structure of the ternary extension Al₁₃(Fe,Ni)₄ (about 2 at. %in our case) creates positional and substitutional disorder within the more or less perfect Al₁₃Fe₄ structure, so that the Al₁₃(Fe,Ni)₄ can be viewed as a disordered variant of the structurally well ordered Al₁₃Fe₄.

The Al₁₃Fe₄ and Al₁₃(Fe,Ni)₄ single crystals used in our study were grown by the Czochralski technique and the details of preparation are described elsewhere.^[19] Three bar-shaped samples of dimensions $1 \times 1 \times 8$ mm were prepared for each compound, with their long edges along three orthogonal directions. The long edge of the first sample was along the [010] stacking direction (designated in the following as *b*), which corresponds to the periodic 10-fold direction in the related *d*-QCs. The (*a,c*) monoclinic plane corresponds to the quasiperiodic plane in the

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d-QCs and the second sample was cut with its long edge along the [001] (*c*) direction, whereas the third one was cut along the direction perpendicular to the (*b,c*) plane. This direction is designated as a^* (it lies in the monoclinic plane at an angle 17.69° with respect to *a* and perpendicular to *c*). The anisotropic physical properties of Al₁₃Fe₄ and Al₁₃(Fe,Ni)₄ (the magnetic susceptibility, the electrical resistivity, the thermoelectric power, the Hall coefficient, and the thermal conductivity) were reported recently.^[21]

2.4. Al₄(Cr,Fe) Six-Layer Approximant

The Al₄(Cr,Fe) compound belongs to the class of bodycentered orthorhombic phases Al₄TM, which coexist with the d-QC having a period of 1.25 nm along its periodic 10-fold direction (corresponding to the *a* axis of Al₄TM).^[8] The Al₄TM phase has been so far observed in no less than six different Al-TM alloys, so that it must be a common structure to this class of alloys. The Al₄TM structure can be described as a periodic repetition of a sequence P'FPp'fp of six atomic layers stacked within one periodicity length of 1.25 nm along a, showing close structural relationship to the six-layer Al-TM d-OCs with the same periodicity. The block P'FP is composed of a flat layer F at x = 0 and a puckered layer P at $x \approx a/6$, whereas the puckered layer P' is in mirror-reflecting position across the F layer. The block p'fp equals the block P'FP translated by (a/2, b/2, c/2).

The single crystal used in our study was grown by the Czochralski method using a native seed. The composition of the sample (rounded to the closest integers) was Al₈₀Cr₁₅Fe₅ and its structure could be assigned to the orthorhombic phase described by Deng et al.,^[8] with the following crystallographic parameters: Pearson's symbol oI366-59.56, space group Immm (No. 71), unit cell parameters a = 1.2500(6) nm, b = 1.2617(2) nm, c = 3.0651(8) nm and 306.44 atoms in the large unit cell. Due to body centering, the primitive unit cell contains only half as many atoms. Cr and Fe atoms are not differentiated crystallographically. In order to examine anisotropy of transport properties, we prepared three bar-shaped samples of dimensions $2 \times 2 \times 8$ mm with their long axes along the three crystallographic directions of the orthorhombic unit cell. The [100] direction (designated in the following as a) corresponds to the periodic direction in the d-QC, whereas the [010] (b) and [001] (c) directions lie within the atomic planes (corresponding to the quasiperiodic directions in the d-QC). The anisotropic physical properties (the magnetic susceptibility, the electrical resistivity, the thermoelectric power, the Hall coefficient, and the thermal conductivity) of our Al₈₀Cr₁₅Fe₅ (abbreviated as Al₄(Cr,Fe) in the following) were reported recently.^[23]

2.5. T-Al₃(Mn,Fe) Six-Layer Approximant

The binary Taylor-phase T-Al₃Mn orthorhombic approximant to the decagonal phase, and its ternary extensions T-Al₃(Mn,Pd) and T-Al₃(Mn,Fe), are all structurally isomorphic. The structure of the binary T-Al₃Mn was first solved by Hiraga et al.,^[10] whereas the model of T-Al₃-(Mn,Pd) with composition Al_{72,3}Mn_{24,5}Pd_{3,2} was reported by Klein et al.^[24] Within the Klein model, the T-Al₃-(Mn,Pd) phase is described as an independent ternary phase structurally similar to binary T-Al₃Mn, whereas Balanetskyy et al.^[25] have reported that this phase is not an independent ternary phase, but a ternary solid solution of Pd in the binary T-Al₃Mn. The same consideration holds for the ternary solid solution T-Al₃(Mn,Fe). The structure of the Taylor phase is built of two atomic layers within the (a,c) planes stacked along the *b* pseudo-10-fold crystallographic direction, a flat layer F and a puckered layer composed of two sublayers P1 and P2. The layers are located at $y \approx 0.25, 0.38$, and 0.43, and there are six layers within one periodic unit. The orthorhombic unit cell (space group Pnma) contains 156 atoms and the lattice parameters of the binary T-phase are^[9] a = 1.48 nm, b=1.24 nm, and c=1.26 nm (the values for the T-Al₃-(Mn,Pd) and T-Al₃(Mn,Fe) solid solutions are very similar). Most of the lattice sites show either fractional occupation (the sites are too close in space to be occupied simultaneously) or mixed TM/Al occupancy, so that there exists structural and chemical disorder in the lattice. The majority of the atoms are clustered in the form of pentagonal prisms and antiprisms.

The T-phase in the Al-Mn-Fe system is stable at high temperatures only, similar to the T-phase in the binary Al-Mn system. It is observed at room temperature (RT) only in rapidly quenched materials. On the other hand, the T-phase in the Al-Mn-Pd system remains stable also at lower temperatures. From this point of view, the Tphase in the Al-Mn-Fe system is more similar to the binary T-phase in the Al-Mn system than to the ternary one in the Al-Mn-Pd system. The reason is probably the fact that the similarity between the manganese and iron atoms is higher than the similarity between the manganese and palladium atoms; iron is just beside manganese in the periodic table. It was also reported that the Al₇₃Mn₂₁Fe₆ composition behaves special since additional annealing of the quenched T-Al₇₃Mn₂₁Fe₆ Taylor phase resulted in a transformation to the decagonal phase.^[26]

Our study was performed on a single crystal T-Al_{72.5}Mn_{21.5}Fe_{6.0} grown by the Czochralski technique. Three rectangular bar-shaped samples of dimensions $2 \times 1 \times 1$ mm were cut from the parent crystal, with their long axes along the *a*, *b*, and *c* crystallographic directions. The anisotropic physical properties (the magnetic susceptibility, the electrical resistivity, the thermoelectric power, the Hall coefficient, and the thermal conductivity) of our T-

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Al_{72.5}Mn_{21.5}Fe_{6.0} samples (abbreviated as T-Al₃(Mn,Fe) in the following) were reported recently.^[27]

2.6. d-Al-Co-Ni Two-Layer Decagonal Quasicrystal

The quasiperiodic plane of the *d*-Al-Co-Ni structure is perpendicular to the [00001] 10-fold direction and contains 20 directions (including the opposite ones) that correspond to the positions of 10 2-fold axes.^[28,29] These 2fold axes belong to two sets, sometimes called 2 and 2' (denoted crystallographically as the sets $\langle 10000 \rangle$ and $\langle 10\bar{1}00 \rangle$, respectively), which are not equivalent to each other but rotated by 18° with respect to the other set. The angle between two neighboring 2-fold directions of a given set amounts to 36°. The quasiperiodic plane with the 20 2-fold directions is shown in Figure 1, where the directions of set 2 are given by solid lines and those of the set 2' by dashed lines. The particular directions [01000] of set 2 and [10 $\bar{1}00$] of set 2', which are perpendicular to each other, are shown in bold.

The centimeter-size single crystal was grown by the Czochralski method. The electron probe microanalysis (EPMA) measurements yielded the average composition of $Al_{69,7}Co_{10,0}Ni_{20,3}$ with a standard deviation of 0.2 at.% for each component. This composition is close to the Nirich limit of the quasicrystal stability region. Details of the sample preparation and characterization by X-ray transmission topography and other techniques are published elsewhere.^[30] The radial elemental distribution was found absolutely homogeneous within the error of EPMA.

We cut from the parent crystal three rectangular bars of dimensions $10 \times 2 \times 2$ mm, with the long edges of the



Figure 1. The quasiperiodic plane of the *d*-Al-Co-Ni structure with the 20 2-fold directions, where the directions of set 2 are given by solid lines and those of set 2' by dashed lines. The particular directions [01000] of set 2 and $[10\overline{1}00]$ of set 2', which are orthogonal to each other and were employed as the measurement directions, are shown in bold.

parallelepipeds directed along three orthogonal crystallographic directions, the [00001] 10-fold direction, the [01000] 2-fold direction and the [$10\overline{1}00$] 2'-fold direction (the last two are shown in bold in Figure 1). The anisotropic physical properties (the magnetic susceptibility, the electrical resistivity, the thermoelectric power, the Hall coefficient, and the thermal conductivity) of the investigated *d*-Al_{69.7}Co_{10.0}Ni_{20.3} samples (abbreviated as *d*-Al-Co-Ni in the following) were determined recently.^[31]

3. Electrical Resistivity

In an anisotropic crystal, the electrical conductivity σ (the inverse resistivity $\sigma = \rho^{-1}$) is a second-rank tensor, relating the current density \bar{j} to the electric field \bar{E} via the relation $j_i = \sum_i \sigma_{ij} E_j$, where i,j=x,y,z denote crystalographic directions in a Cartesian coordinate system. The tensorial ellipsoid exhibits the same symmetry axes as the crystalographic structure. In the following we shall present the anisotropic electrical resistivity of the investigated compounds measured along three orthogonal crystallographic directions, the stacking directions within the atomic planes and two directions within the atomic planes. On the graphs, the resistivity along the stacking direction will be denoted by an additional label S. The temperature-dependent resistivity measurements were performed by a standard four-terminal technique.

3.1. Y-Al-Co-Ni Two-Layer Approximant

Electrical resistivity of Y-Al-Co-Ni was measured between 300 and 2 K and the $\rho(T)$ data along the three crystallographic directions are displayed in Figure 2. The resistivity is the lowest along the stacking b direction perpendicular to the atomic planes, where its RT value amounts to $\rho_b^{300K} = 25 \ \mu\Omega \text{cm}$ and the residual resistivity is $\rho_b^{2K} = 10 \ \mu\Omega \text{cm}$. The two in-plane resistivities are higher, amounting to $\rho_c^{300K} = 60 \ \mu\Omega \text{cm}$ and $\rho_c^{2K} = 29 \ \mu\Omega \text{cm}$ for the c direction and $\rho_{a*}^{300K} = 81 \ \mu\Omega \text{cm}$ and $\rho_{a*}^{2K} = 34 \ \mu\Omega \text{cm}$ for the a^* direction. While ρ_b is 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 $\rho_b < \rho_c < \rho_{a*}$ (even the inequality $\rho_b \ll \rho_c < \rho_{a*}$ may be considered to hold), reveal that Y-Al-Co-Ni is a good electrical conductor along all three crystallographic directions. The ratios of the resistivities along different crystallographic directions vary little over the whole investigated temperature range of 300-2 K, amounting at RT to $\rho_{a*}/\rho_b \approx 3.2$, $\rho_c/\rho_b \approx 2.5$, and $\rho_{a*}/\rho_{c} \approx 1.3$. The strong positive temperature coefficient (PTC) of the resistivity along all three crystallographic directions demonstrates the predominant role of the electron-phonon scattering mechanism, so that the resistivity is of Boltzmann type.

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Figure 2. Temperature-dependent electrical resistivity of Y-Al-Co-Ni along three orthogonal crystallographic directions a^* , b, and c.^[18] The stacking direction perpendicular to the atomic layers is denoted by S.

3.2. o-Al₁₃Co₄ Four-Layer Approximant

The $\rho(T)$ data of o-Al₁₃Co₄ along the three crystallographic directions are displayed in Figure 3. The resistivity is the lowest along the stacking *a* direction perpendicular to the atomic planes, where its RT value is $\rho_a^{300K} = 69 \,\mu\Omega$ cm and the residual resistivity is $\rho_a^{300K} = 47 \,\mu\Omega$ cm. The two in-plane resistivities are higher, $\rho_b^{300K} = 169 \,\mu\Omega$ cm and $\rho_b^{2K} = 113 \,\mu\Omega$ cm for the *b* direction and $\rho_c^{300K} = 180 \,\mu\Omega$ cm and $\rho_c^{2K} = 129 \,\mu\Omega$ cm for the *c* direction. The anisotropy of the two in-plane resistivities is small, amounting at RT to $\rho_c^{300K} / \rho_b^{300K} = 1.07$, whereas the anisotropy to the stacking direction is considerably larger, $\rho_c^{300K} / \rho_a^{300K} = 2.6$ and $\rho_b^{300K} / \rho_a^{300K} = 2.5$. The anisotropic resistivities thus appear in the order $\rho_a < \rho_b < \rho_c$ (even the inequality $\rho_a \ll \rho_b < \rho_c$ may be considered to hold). The PTC of the resistivity along all three crystallographic directions demonstrates the predominant role of the electron-phonon scattering mechanism and that the resistivity is of Boltzmann type.

3.3. Al₁₃Fe₄ and Al₁₃(Fe,Ni)₄ Four-Layer Approximants

The $\rho(T)$ data along the three crystallographic directions of Al₁₃Fe₄ are shown in Figure 4*i*, and those of Al₁₃-(Fe,Ni)₄ are shown in Figure 4*ii*. For both compounds, the anisotropic resistivity appears in the order $\rho_b < \rho_{a*} < \rho_c$, so that the resistivity is lowest along the stacking *b* direction perpendicular to the atomic planes. The anisotropy between the two in-plane directions *a*^{*} and *c* is also substantial.



Figure 3. Temperature-dependent electrical resistivity of $o-Al_{13}Co_4$ along three orthogonal crystallographic directions *a*, *b*, and *c*.^[20] The stacking direction perpendicular to the atomic layers is denoted by S.



Figure 4. Temperature-dependent electrical resistivity of (*i*) $AI_{13}Fe_4$ and (*ii*) $AI_{13}(Fe,N)_4$ along three orthogonal crystallographic directions a^* , b, and c.^[21] The stacking direction perpendicular to the atomic layers is denoted by S.

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The resistivities of the two compounds exhibit different temperature dependence. Al₁₃Fe₄ exhibits small residual resistivities $\rho(T \rightarrow 0)$, amounting at 2 K to $\rho_{a*}^{2K} = 11 \ \mu\Omega \text{cm}$, $\rho_b^{2K} = 2.5 \ \mu\Omega \text{cm}$ and $\rho_c^{2K} = 14 \ \mu\Omega \text{cm}$, and large PTC of the resistivity along all three crystallographic directions, demonstrating the important role of the electron-phonon scattering mechanism. At 300 K, the revalues $\rho_{a*}^{300K} = 268 \,\mu\Omega \text{cm},$ sistivities reach the $\rho_b^{300K} = 88 \ \mu\Omega \text{cm}$ and $\rho_c^{300K} = 576 \ \mu\Omega \text{cm}$. In contrast, the residual resistivities of Al₁₃(Fe,Ni)₄ are much larger — $\rho_{a^*}^{2K} = 286 \ \mu\Omega \text{cm}, \rho_b^{2K} = 81 \ \mu\Omega \text{cm}, \text{ and } \rho_c^{2K} = 548 \ \mu\Omega \text{cm}$ and the PTC of the resistivity is small for all three crystallographic directions. The 300 K resistivity values of Al₁₃- $(Fe,Ni)_4$ are almost the same as those of $Al_{13}Fe_4$. The marked difference between the residual resistivities of the two compounds can be explained by the presence of quenched structural disorder in Al₁₃(Fe,Ni)₄ and its absence in Al₁₃Fe₄. Within the relaxation-time approximation, the electrical resistivity of a solid is proportional to the inverse relaxation time τ of the conduction electrons between two scattering events, $\rho \propto 1/\tau$. Assuming a nonmagnetic solid, the relaxation rate contains two terms, $1/\tau = 1/\tau_0 + 1/\tau_{ph}$, where $1/\tau_0$ describes elastic scattering of electrons by quenched defects and $1/\tau_{ph}$ is due to electron-phonon inelastic scattering. In a perfect structure, the absence of quenched disorder implies $1/\tau_0 = 0$, whereas the phonon rate vanishes in the limit $T \rightarrow 0$, so that the total rate $1/\tau$ vanishes at zero temperature and the residual resistivity approaches zero in this limit. In the presence of quenched disorder, $1/\tau_0 \neq 0$ and the residual $T \rightarrow 0$ resistivity is non-zero. In the structurally well-ordered Al₁₃Fe₄, the amount of quenched disorder is small, yielding small residual resistivities and large PTC due to the high density of phonons in the lattice that are at the origin of the PTC. The large non-zero residual resistivity of $Al_{13}(Fe,Ni)_4$ is, on the other hand, a consequence of quenched disorder in this compound. The strong anisotropy of the residual resistivity suggests that the amount of quenched disorder depends on the crystallographic direction. Structural disorder also explains the small PTC of the resistivity in this compound, as the disorder suppresses propagation of phonons. However, the nonzero PTC of the resistivity in the disordered Al₁₃(Fe,Ni)₄ demonstrates that structural disorder does not suppress the phonons completely, but some phonons are still excited, though their density is considerably less than that in the structurally well-ordered $Al_{13}Fe_4$.

3.4. Al₄(Cr,Fe) Six-Layer Approximant

The anisotropic electrical resistivity of Al₄(Cr,Fe) is displayed in Figure 5. The resistivity is the lowest along the stacking *a* direction perpendicular to the atomic planes. ρ_a shows a PTC in the whole investigated temperature interval and a RT value of $\rho_a^{300K} = 297 \,\mu\Omega$ cm. The resistivities within the atomic planes are higher and exhibit quali-



Figure 5. Temperature-dependent electrical resistivity of Al₄(Cr,Fe) along three orthogonal crystallographic directions *a*, *b*, and *c*.^[23] Solid curves are the fits with Equation 2. The stacking direction perpendicular to the atomic layers is denoted by S.

tatively different temperature-dependencies with a broad maximum, where the temperature coefficient is reversed. ρ_b exhibits a maximum at about 125 K with the peak value 375 $\mu\Omega$ cm and the RT value $\rho_b^{300K} = 371 \,\mu\Omega$ cm. The resistivity ρ_c is the highest; its maximum value of 413 $\mu\Omega$ cm occurs at 100 K, and its RT value is $\rho_c^{300K} = 407 \,\mu\Omega$ cm. At RT, the ratios of the resistivities amount $\rho_c/\rho_a = 1.37$, $\rho_b/\rho_a = 1.25$, and $\rho_c/\rho_b = 1.10$. The resistivity of Al₄(Cr,Fe) is thus qualitatively different from the Boltzmann-type PTC resistivities of Y-Al-Co-Ni, o-Al₁₃Co₄, Al₁₃Fe₄, and Al₁₃(Fe,Ni)₄. In the following we review the theoretical consideration of this non-Boltzmann behavior.^[23]

The orthorhombic symmetry of the Al₄(Cr,Fe) phase implies that the conductivity tensor σ_{ij} is diagonal in the

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basis of the crystallographic directions *a*, *b*, and *c*. The geometry of our samples (their long axes were along the three crystallographic directions) and the direction of the electric field applied along their long axes imply that diagonal elements $\sigma_{xx} = \sigma_a$, $\sigma_{yy} = \sigma_b$, and $\sigma_{zz} = \sigma_c$ were measured in our experiments. The temperature dependence of each of these elements can be analyzed using the theory of slow charge carriers by Trambly de Laissardière et al.,^[32] which applies to any diagonal element of the conductivity tensor (in ref. [32], σ_{xx} is considered, but *x* can be any crystallographic direction).

According to the theory of slow charge carriers, the semiclassical (Bloch-Boltzmann) model of conduction breaks down when the mean free path of charge carriers is smaller than a typical extension of their wave function. This situation is realized for sufficiently slow charge carriers (where low electronic velocity is a consequence of weak dispersion of the electronic bands) and leads to a transition from a metallic to an insulating-like regime when scattering by defects or temperature effects increases. According to the Einstein relation, the conductivity σ depends on the electronic density of states (DOS) $g(\varepsilon)$ and the spectral diffusivity $D(\varepsilon)$ within the thermal interval of a few $k_B T$ around the Fermi level ε_F . In the case of slowly varying metallic DOS around ε_F , it is permissible to replace $g(\varepsilon)$ by $g(\varepsilon_F)$. It was shown^[32] that the diffusion constant can be written as $D = v^2 \tau + L^2(\tau)/\tau$, where v is the electronic velocity, τ the relaxation time, and $L^2(\tau)$ is the non-ballistic (non-Boltzmann) contribution to the square of spreading of the quantum state at energy ε due to diffusion, averaged on a time scale τ . $L(\tau)$ is bound by the unit cell length and saturates to a constant value already for short averaging time. The dc conductivity of the system in the crystallographic direction j can be written as

$$\sigma_j = \sigma_{Bj} + \sigma_{NBj} = e^2 g(\varepsilon_F) v_j^2 \tau_j + e^2 g(\varepsilon_F) \frac{L_j^2(\tau_j)}{\tau_j}, \qquad (1)$$

where σ_{Bj} is the Boltzmann contribution and σ_{NBj} is the non-Boltzmann contribution. The relaxation rate τ^{-1} will generally be a sum of a temperature-independent rate τ_0^{-1} due to scattering by quenched defects and a temperature-dependent term due to scattering by phonons τ_p^{-1} . The anisotropy of the atomic structure implies that the phonon spectrum will also be anisotropic, so that the relaxation rate will generally depend on the crystallographic direction, $\tau_j^{-1} = \tau_0^{-1} + \tau_{pj}^{-1}$. In the simplest case, τ_{pj} can be phenomenologically written as a power-law of temperature, $\tau_{pj} = \beta_j / T^{\alpha_j}$, at least within a limited temperature interval. Assuming that $L_j^2(\tau_j)$ can be replaced by its limiting value, a constant L_j^2 , Equation 1 yields a minimum in the conductivity σ_j as a function of τ_j or temperature (or equivalently, there is a maximum in the resistivity $\rho_j = \sigma_j^{-1}$) under the condition $\tau_j = L_j / v_j$. Above the resistivity

tivity maximum, the non-Boltzmann contribution prevails and the resistivity exhibits a nonmetallic negative temperature coefficient (NTC), whereas below the maximum, the resistivity exhibits a metallic PTC due to dominant Boltzmann contribution. The resistivity maxima, as observed for ρ_b and ρ_c in Figure 5, can thus be considered as a consequence of crossover from dominant ballistic conductivity at low temperature to dominant non-ballistic conductivity at high temperatures due to small velocities of the charge carriers.

Defining $A_j = e^2 g(\varepsilon_F) v_j^2 \tau_0$, $B_j = e^2 g(\varepsilon_F) L_j^2 / \tau_0$, and $C_j = \tau_0 / \beta_j$, Equation 1 can be rewritten as

$$\sigma_j = \frac{A_j}{1 + C_j T^{\alpha_j}} + B_j \left(1 + C_j T^{\alpha_j} \right) \tag{2}$$

that contains four crystallographic-direction-dependent fit parameters A_j , B_j , C_j and a_j (the last two always appear in product $C_i T^{a_i}$). In the regime of dominant scattering by quenched defects, $\tau_0/\tau_{pj} = C_j T^{a_j} \ll 1$, normally realized at low temperatures, expansion of Equation 2 yields the low-temperature form of the conductivity $\sigma_i = \sigma_i^0 - \sigma_1 T^{a_i}$ (provided that $A_i > B_i$). This can be viewed as a generalized Bloch-Grüneisen law that yields a metallic PTC resistivity. In the other extreme of dominant phonon scattering, $\tau_0/\tau_{pj} = C_j T^{a_j} \gg 1$, normally realized at high temperatures, Equation 2 yields the high-temperature form of the conductivity as $\sigma_i = \sigma_2 T^{\alpha_i}$, resulting in an insulatorlike NTC resistivity. The relative magnitudes of A_i , B_i , and $C_i T^{\alpha_i}$ coefficients thus determine the temperature dependence of the resistivity within a given temperature range, which can either be in the metallic or insulatinglike regimes, or at a crossover between these two regimes (in which case the resistivity exhibits a maximum). Since these coefficients depend on the electronic structure of the investigated compound $(g(\varepsilon_F) \text{ and } v_i)$, its crystallographic details (L_i) , defect concentration (τ_0) , and phononic spectrum (τ_{pi}) , they are specific to a given structure and sample purity.

The fits of the resistivities with Equation 2 are displayed in Figure 5 as solid curves, and the fit parameters can be found in Table III of ref. [23]. The fits are excellent for all three crystallographic directions. Here it should be mentioned that a maximum in the resistivity at low temperatures is also predicted by the theory of weak localization,^[33] frequently used to analyze the temperature-dependent resistivity of icosahedral quasicrystals. Weak localization is considered to introduce small temperature-dependent correction to the Boltzmann conductivity due to spin-orbit and inelastic scattering processes of electrons. However, while the validity of the weak localization concept is restricted to low temperatures, the theory of slow charge carriers of Equation 2 is applicable at all temperatures and does not involve any electron localization.

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3.5. T-Al₃(Mn,Fe) Six-Layer Approximant

The $\rho(T)$ data of our single-crystalline T-Al₃(Mn,Fe) along the three orthogonal crystallographic directions are displayed in Figure 6. All resistivities show NTC, since they increase with decreasing temperature. The resistivity



Figure 6. Temperature-dependent electrical resistivity of $T-Al_3-(Mn,Fe)$ along three orthogonal crystallographic directions *a*, *b* and *c*.^[27] Solid curves represent the fits with Equation 3. The stacking direction perpendicular to the atomic layers is denoted by S.

is lowest along the stacking b direction perpendicular to atomic planes, where RT the value is the $\rho_b^{300K} = 441 \ \mu\Omega cm$ and the 2 K resistivity is $\rho_b^{2K} = 601 \ \mu\Omega cm$, yielding the increase upon cooling of $(\rho_b^{2K} - \rho_b^{300K}) / \rho_b^{300K} = 40\%$. The two in-plane resistivities ρ_a and ρ_c are higher, $\rho_a^{300K} = 501 \,\mu\Omega$ cm and $\rho_a \quad \text{and} \quad \rho_c \\
\rho_a^{2K} = 740 \,\mu\Omega \text{cm},$ with an increase of $(\rho_a^{2K} - \rho_a^{300K})/\rho_a^{300K} = 48\%$, whereas $\rho_c^{300K} = 490 \ \mu\Omega \text{cm}$ and $\rho_c^{2K} = 709 \ \mu\Omega \text{cm}$ yield an increase of $(\rho_c^{2K} - \rho_c^{300K}) / \rho_c^{300K} = 45\%$. Considering the experimental error to be about 5% (originating mainly from the uncertainty in the samples' geometric parameters), no pronounced anisotropy between the two in-plane directions, a and c, can be claimed, whereas the anisotropy to the stacking b direction is significant, though still small (at 300 K, the ρ_b value is 10% less than that of ρ_a and ρ_c).

The temperature-dependent resistivity of $T-Al_3(Mn,Fe)$ can again be analyzed using the model of slow charge carriers, as expressed by Equations 1 and 2. The NTC of the resistivity reveals that the system is in the non-Boltzmann (non-ballistic) regime, so that Equation 2 simplifies into

$$\sigma_j = B_j (1 + C_j T^{a_j}). \tag{3}$$

The fits using Equation 3 are shown by solid curves in Figure 6 and the fit parameters can be found in Table I of ref. [27]. Excellent fits down to the lowest investigated temperature of 2 K demonstrate that the degree of structural and chemical disorder in the T-Al₃(Mn,Fe) samples

is large enough that the system is in the non-Boltzmann regime within the whole investigated temperature range.

3.6. d-Al-Co-Ni Two-Layer Decagonal Quasicrystal

The $\rho(T)$ data of d-Al-Co-Ni decagonal quasicrystal, measured between 340 and 2 K along the 10, 2, and 2' crystallographic directions, are shown in Figure 7*i*, whereas the resistivities normalized to their 340 K values, ρ/ρ_{340K} , are shown in Figure 7*ii*. The resistivity is again the lowest along the stacking (10-fold) direction, whereas there is no anisotropy between the two in-plane directions. At 340 K, $\rho_2 \approx \rho_{2'} = 303 \pm 4 \,\mu\Omega \text{cm}$, whereas $\rho_{10} = 36 \,\mu\Omega \text{cm}$, yielding the anisotropy factor $\rho_O / \rho_{10} = 8.4$ (where the index "Q" is conveniently used for both inplane directions). The normalized in-plane resistivities in Figure 7*ii* overlap perfectly, demonstrating that they exhibit identical temperature dependence and the tiny differences in their absolute values can be accounted for by constant scaling factors due to geometrical error in the determination of the samples' length and cross section.



Figure 7. (*i*) Temperature-dependent electrical resistivity of *d*-Al-Co-Ni, measured along 10, 2, and 2' crystallographic directions. (*ii*) The resistivities normalized to their 340 K values, ρ/ρ_{340K} .^[31] The index Q is conveniently used for the 2 and 2' in-plane directions. The stacking (10-fold) direction perpendicular to the atomic layers is denoted by S.

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The resistivities exhibit metallic PTC for all three investigated directions. The PTC is large for the periodic 10-fold direction, giving fractional increase between 2 and 340 K by $R_{10} = (\rho_{10}^{340K} - \rho_{10}^{2K})/\rho_{10}^{340K} = 26\%$. For the two in-plane directions, the fractional increase is much smaller, amounting to $R_Q = (\rho_Q^{340K} - \rho_Q^{2K})/\rho_Q^{340K} \approx 2\%$. Another marked difference between the in-plane and the periodic resistivities is their temperature dependence. While ρ_{10} exhibits a linear-like increase upon heating at temperatures above the low-temperature saturated region, the in-plane resistivities show a tendency to exhibit maximum or at least leveling off at temperatures close to RT in their much weaker temperature dependence.

4. Discussion and Conclusions

The anisotropic electrical resistivity of the investigated stacked-layer decagonal approximants (the two-layer Y-Al-Co-Ni, the four-layer o-Al₁₃Co₄, Al₁₃Fe₄ and Al₁₃-(Fe,Ni)₄, and the six-layer Al₄(Cr,Fe) and T-Al₃(Mn,Fe)) and the two-layer d-Al-Co-Ni decagonal quasicrystal shows that the stacking direction perpendicular to the atomic planes is always the one with the highest conductivity. The electrical resistivity is highly sensitive to the dimensionality of the bonding network in the lattice. In electronic long-range transport, the conduction electrons will preferentially move along connected paths of uniform charge density. High conductivity along a given crystallographic direction can be expected along the direction in which structurally ordered atomic chains with metallic bonding propagate. Any disorder (static quenched impurities, partially or mixed-populated lattice sites, and dynamic disorder due to lattice vibrations) will decrease the electrical conductivity. The observed universality that the conductivity of the investigated stacked-layer structures is always the highest along the stacking direction perpendicular to the atomic planes confirms the metallic character along the stacking direction. Since the in-plane electrical resistivities are of the same order of magnitude as the resistivity along the stacking direction, this confirms the 3D character of the investigated solids (recall that, for a true 2D solid, the in-plane resistivity should be orders of magnitude lower than the perpendicular resistivity). The stacked-layer description of decagonal quasicrystals and their periodic approximants in terms of 2D atomic planes should, therefore, be regarded as a convenient geometrical approach to describe their complex structures, whereas their physical properties are those of true 3D solids.

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