CROATICA CHEMICA ACTA
CCACAA, ISSN 0011-1643, e-ISSN 1334-417X
Croat. Chem. Acta **83** (1) (2010) 101–105.
CCA-3398

Original Scientific Paper

Anisotropic Transport Properties of the $Al_{13}Fe_4$ Decagonal Approximant*

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RECEIVED JANUARY 06, 2010; REVISED JANUARY 20, 2010; ACCEPTED JANUARY 21, 2010

Abstract. We have investigated electrical resistivity, thermoelectric power and thermal conductivity of the $Al_{13}Fe_4$ monoclinic approximant to the decagonal quasicrystal. The crystallographic-direction-dependent measurements were performed along the a^*, b and c directions of the monoclinic unit cell, where (a^*,c) atomic planes are stacked along the perpendicular b direction. The electronic transport exhibit significant anisotropy. The stacking b direction is the most conducting direction for the electricity and heat. The anisotropic thermopower reflects complicated structure of the anisotropic Fermi surface that contains electron-like and hole-like contributions.

Keywords: electrical resistivity, thermal conductivity, anisotropy, $Al_{13}Fe_4$, complex metallic alloys

INTRODUCTION

A basic question in the physics of quasicrystals (QCs) is whether quasiperiodicity of the structure influences the physical properties of a solid in a fundamental way by introducing qualitatively new phenomena or the unusual properties are rather a consequence of complex local atomic order with no direct relationship to the quasiperiodicity. In order to elucidate this question, decagonal quasicrystals (d-QCs) are of particular importance due to the fact that their structure can be 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. Physical properties of d-QCs can be consequently studied along the quasiperiodic and periodic crystallographic directions on the same sample. A consequence of the structural anisotropy of d-QCs are anisotropic thermoelectrical properties (electrical resistivity ρ,[1–3] thermoelectric power S,[4] and thermal conductivity κ[5,6]), when measured along the quasiperiodic and periodic directions. The electrical resistivity generally shows positive temperature coefficient (PTC) at metallic values along the periodic direction, whereas the resistivity in the quasiperiodic plane is considerably larger and exhibits negative temperature coefficient (NTC) and sometimes also a maximum somewhere below room temperature (r.t.). The degree of anisotropy of the transport coefficients is related to the structural details of a particular decagonal phase, depending on the number of quasiperiodic layers in one periodic unit.[7,8] The most anisotropic case are the phases with just two layers, realized in d-Al-Ni-Co and d-Al-Cu-Co, where the periodicity length along the periodic axis is about 0.4 nm and the resistivity ratio at room temperature amounts typically $\rho_Q/\rho_P \approx 6–10$.[1–3] Other d phases contain more quasiperiodic layers in a periodic unit and show smaller anisotropies. In d-Al-Co, d-Al-Ni and d-Al-Si-Cu-Co there are four quasiperiodic layers with periodicity about 0.8 nm and the room temperature anisotropy is $\rho_Q/\rho_P \approx 2–4$.[4] d-Al-Mn, d-Al-Cr and d-Al-Pd-Mn phases contain six layers with the periodicity of about 1.2 nm and the anisotropy amounts $\rho_Q / \rho_P \approx 1.2–1.4$, whereas d-Al-Pd and d-Al-Cu-Fe phases with eight layers in a periodicity length of 1.6 nm are close to isotropic. While the origin of the anisotropic electron transport coefficients is the anisotropic Fermi surface, the anisotropy of which originates from the specific stacked-layer crystal structure of the d-QC phases and the chemical decoration of the lattice. Approximant phases are

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* Presented at the EU Workshop "Frontiers in Complex Metallic Alloys", Zagreb, October 2008.
Dedicated to Professor Boran Leontić on the occasion of his 80th birthday.

** Authors to whom correspondence should be addressed. (E-mail: ppopcevic@ifs.hr, ana@ifs.hr) characterized by large unit cells, which periodically repeat in space with the atomic decoration closely resembling that of d-QCs. Atomic layers are again stacked periodically and the periodicity lengths along the stacking direction are almost identical to those along the periodic direction of d-QCs. Moreover, atomic planes of approximants and d-QCs show locally similar patterns, so that their structures on the scale of near-neighbor atoms closely resemble each other. Decagonal approximants thus offer valid comparison to the d-QCs.

Recently, the anisotropic transport properties (electrical resistivity, thermoelectric power, and thermal conductivity), measured along three orthogonal crystallographic directions, were reported for three decagonal approximant phases of increasing structural complexity comprising two, four and six atomic layers in the unit cell. The first was the Y-phase of Al-Ni-Co compound,[9] which belongs to the $Al_{13}TM_4$ (TM = transition metal) class of complex intermetallics and is a monoclinic approximant to the decagonal phase with two atomic layers within one periodic unit of ≈ 0.4 nm along the stacking direction and a relatively small unit cell, comprising 32 atoms. The second was the orthorhombic *o*-$Al_{13}Co_4$ decagonal approximant,[10] also belonging to the $Al_{13}TM_4$ class of intermetallics, but comprising four atomic layers within one periodic unit of ≈ 0.8 nm along the stacking direction and a larger unit cell comprising 102 atoms. The third was the $Al_4(Cr,Fe)$[11,12] compound belonging to the class of orthorhombic Al_4TM phases first described by Deng *et al.*,[13] which are approximants to the decagonal phase with six atomic layers in a periodic unit of 1.25 nm and 306 atoms in the giant unit cell. Common to all these phases is strong anisotropy of the transport properties between the stacking and in-plane directions, where the crystals show the highest conductivity for both the electricity and heat along the stacking direction (corresponding to the periodic direction in d-QCs), whereas the in-plane anisotropy is considerably smaller, yet significant.

In this paper we present anisotropic transport properties of another decagonal approximant phase from the $Al_{13}TM_4$ class of complex intermetallics, the monoclinic $Al_{13}Fe_4$. It comprises four atomic layers within one periodic unit of ≈ 0.8 nm along the stacking direction and a unit cell comprising 102 atoms and the crystals can be grown to the highest structural perfection within the $Al_{13}TM_4$ class.

EXPERIMENTAL

The $Al_{13}Fe_4$ single crystal used in our study was grown by the Czochralski technique and the details of preparation are described elsewhere.[14] The structure of investigated compound matched well to the monoclinic unit cell of the Grin *et al.* model.[15] In order to perform crystallographic-direction-dependent studies, we have cut from the ingot of each compound three bar-shaped sample of dimensions $1 \times 1 \times 8$ mm^3, with their long axes along three orthogonal directions. The long axis of the first sample was along the [010] stacking direction (designated in the following as *b*), which corresponds to the periodic direction in the related d-QCs. The (*a*,*c*) monoclinic plane corresponds to the quasiperiodic plane in d-QCs 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 of 17° with respect to *a* and perpendicular to *c*). For each sample, the orientation of the other two crystallographic directions was also known. The so-prepared samples enabled us to determine the anisotropic physical properties along the three orthogonal directions of the investigated monoclinic $Al_{13}Fe_4$. Electrical resistivity, ρ, was measured between 300 and 2 K using the standard four-terminal technique.[16] The thermoelectric power (the Seebeck coefficient *S*) was measured by using a standard temperature-gradient technique[17] in the same temperature range. Thermal conductivity, κ, was measured along the *a**, *b* and *c* directions using an absolute steady-state heat-flow method.[18] The thermal flux through the samples was generated by a 1 kΩ RuO_2 chip-resistor, glued to one end of the sample, while the other end was attached to a copper heat sink. The temperature gradient across the sample was monitored by a chromel-constantan differential thermocouple.

RESULTS AND DISCUSSION

The electrical resistivity $\rho(T)$ data along the three crystallographic directions are displayed in Figure 1 for

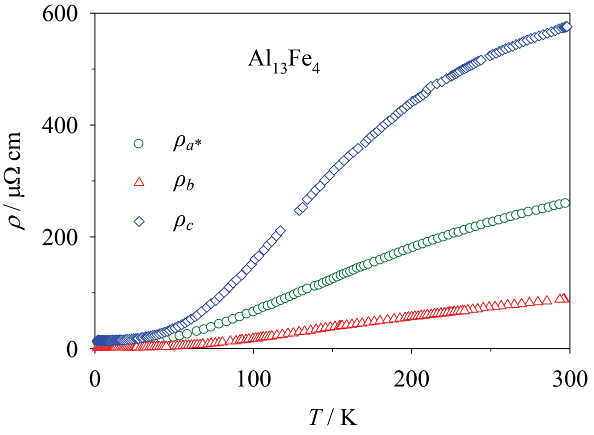

Figure 1. Temperature-dependent electrical resistivity of $Al_{13}Fe_4$ along three orthogonal crystallographic directions *a**, *b* and *c*.

$Al_{13}Fe_4$. The anisotropic resistivities appear in the order $\rho_b < \rho_{a*} < \rho_c$, so that the resistivity is the 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. The resistivities of the $Al_{13}Fe_4$ exhibits small residual resistivities $\rho(T \rightarrow 0)$, amounting at 2 K $\rho_{a*}^{2\text{ K}} = 11$ μΩ cm, $\rho_b^{2\text{ K}} = 2.5$ μΩ cm and $\rho_c^{2\text{ K}} = 14$ μΩ cm, and large PTC of the resistivity along all three crystallographic directions, demonstrating an important role of the electron-phonon scattering mechanism. At room temperature, the resistivities reach the values $\rho_{a*}^{\text{r.t.}} = 268$ μΩ cm, $\rho_b^{\text{r.t.}} = 88$ μΩ cm and $\rho_c^{\text{r.t.}} = 576$ μΩ cm. 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, $1/\tau = 1/\tau_0 + 1/\tau_{\text{ph}}$, where $1/\tau_0$ describes elastic scattering of electrons by quenched defects and $1/\tau_{\text{ph}}$ 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 is zero in this limit. In the presence of quenched disorder, $1/\tau_0 \neq 0$ and the residual $\rho(T \rightarrow 0)$ resistivity is nonzero. In the structurally well-ordered $Al_{13}Fe_4$, 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 strong anisotropy of the residual resistivity suggests that the amount of quenched disorder depends on the crystallographic direction. Quenched disorder also explains the small PTC of the resistivity in this compound, as the disorder suppresses propagation of phonons.

The thermopower data, measured along the three crystallographic directions *a**, *b* and *c*, are displayed in Figure 2 for $Al_{13}Fe_4$. The thermopowers along different crystallographic directions exhibit maxima, cross each other and also change sign. Assuming that the electronic DOS does not exhibit sharp features in the vicinity of the Fermi energy E_F, such complicated behavior may originate from (i) specific details of the anisotropic Fermi surface that contains electron-like and hole-like parts and (ii) anisotropic electron-phonon interactions, due to the high density of phonons (as also evident from the strong PTC of the resistivity of $Al_{13}Fe_4$). Quantitative analysis requires knowledge of the anisotropic Fermi surface and the anisotropic phonon spectrum of the solid.

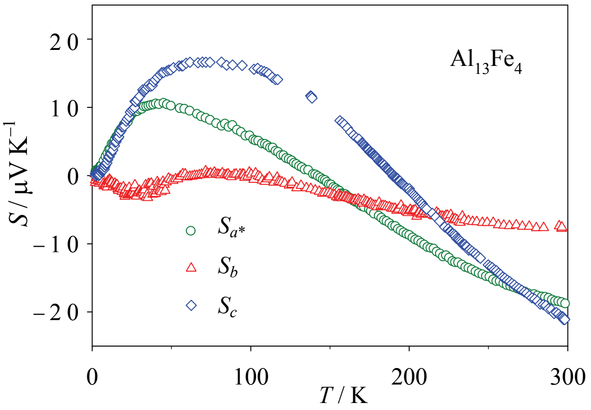

Figure 2. Temperature-dependent thermoelectric power (the Seebeck coefficient *S*) of $Al_{13}Fe_4$ along three orthogonal crystallographic directions *a**, *b* and *c*.

The total thermal conductivity $\kappa(T)$ along the three crystallographic directions is displayed in Figure 3 for $Al_{13}Fe_4$. In all three directions, $\kappa(T)$ shows a typical phonon *umklapp* maximum at about 35 K. The thermal conductivity shows large anisotropy in the order $\kappa_b > \kappa_{a*} > \kappa_c$, being the highest along the stacking *b* direction, whereas the in-plane conductivities κ_{a*} and κ_c are lower and show smaller, yet significant anisotropy. Since the electrical conductivity $\sigma(T) = \rho^{-1}(T)$ of $Al_{13}Fe_4$ (Figure 1) is also the highest along *b*, this material is the best conductor for both the electricity and heat along the stacking *b* direction perpendicular to the (*a*,*c*) atomic planes. The phononic contribution $\kappa_{\text{ph}} = \kappa - \kappa_{\text{el}}$ can be estimated by subtracting the electronic contribution κ_{el} from the total conductivity κ using the Wiedemann-Franz (WF) law, $\kappa_{\text{el}} = \pi^2 k_B^2 T\sigma(T)/3e^2$, and the measured electrical conductivity data $\sigma(T)$. Here it is important to recall the validity of the WF law,[19] which is valid under the condition of dominant elastic scattering of the electrons, usually realized at high temperatures $T > \theta_D$ (*e.g.*, for typical metals, the WF law is valid already at room temperature). At low temperatures, the WF law is valid for solids where only the residual electrical resistivity (due to elastic scattering by quenched defects) is observed. Inspecting electrical resistivities of $Al_{13}Fe_4$ from Figure 1, we observe that the residual

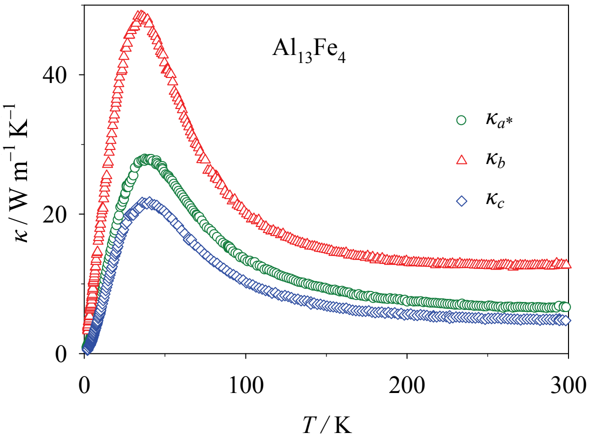

Figure 3. Total thermal conductivity κ of $Al_{13}Fe_4$ along three orthogonal crystallographic directions *a**, *b* and *c*.

resistivity is very small, and the WF law can be used only at high temperatures, such as room temperature and above. For that reason we present in the following the analysis of κ_{el} and κ_{ph} of $Al_{13}Fe_4$ only at the room temperature. We obtain the following electronic thermal conductivity values at room temperature (r.t.): $\kappa_{\mathrm{el}}{}^{a^*} = 2.8$ W m^{-1} K^{-1}, $\kappa_{\mathrm{el}}{}^{b} = 8.3$ W m^{-1} K^{-1} and $\kappa_{\mathrm{el}}{}^{c} = 1.3$ W m^{-1} K^{-1}, whereas the total conductivities are $\kappa_{a^*} = 6.7$ W m^{-1} K^{-1}, $\kappa_b = 12.8$ W m^{-1} K^{-1} and $\kappa_c = 4.7$ W m^{-1} K^{-1}. This gives the ratios $(\kappa_{\mathrm{el}}{}^{a^*}/\kappa_{a^*})_{\mathrm{r.t.}} = 0.42$, $(\kappa_{\mathrm{el}}{}^{b}/\kappa_b)_{\mathrm{r.t.}} = 0.65$ and $(\kappa_{\mathrm{el}}{}^{c}/\kappa_c)_{\mathrm{r.t.}} = 0.28$, which are similar values as those obtained for the disorder $Al_{13}(Fe,Ni)_4$,[20] where the residual resistivity is the dominant part of the total resistivity within the investigated temperature range 2–300 K, so that the WF law should be a good approximation to κ_{el}. For the investigated structurally ordered $Al_{13}Fe_4$, the residual resistivities are very small, and the WF law can be used only at high temperatures, such as room temperature and above.

Hint: Recently, the transport properties of the T-$Al_3Mn(Fe,Pd)$ complex metallic alloys were analysed within the Kubo Greenwood response theory, where the central quantity is spectral conductivity function.[21–22] The same formalism might consistently explain the reordered data of the $Al_{13}Fe_4$.

CONCLUSION

We have investigated electrical resistivity, thermoelectric power, and thermal conductivity of the $Al_{13}Fe_4$ monoclinic approximant to the decagonal quasicrystal. The electronic transport exhibits significant anisotropy. The stacking *b* direction was found to be the most conducting direction for the electricity and heat. As the electrical and thermal conductivities of the related Y-Al-Ni-Co and *o*-$Al_{13}Co_4$ decagonal approximants are also the highest along the stacking direction, this feature appears to be a common property of the $Al_{13}TM_4$ family of complex intermetallics. The anisotropic thermopower reflects complicated structure of the anisotropic Fermi surface that contains electron-like and hole-like contributions. The anisotropy of the Fermi surface is at the origin of the anisotropic transport properties.

The $Al_{13}Fe_4$ decagonal approximant phase from the $Al_{13}TM_4$ family of intermetallics exhibits anisotropic transport properties qualitatively similar to the d-Al-Ni-Co type decagonal quasicrystals. The approximants and the d-QCs have both in common the structural detail that atomic planes are stacked periodically. The stacked-layer structure appears to be at the origin of the anisotropic transport properties, whereas the in-plane structural details seem to be of marginal importance for the anisotropic transport properties of these stacked-layer intermetallic compounds.

Acknowledgements. This work was done within the activities of the 6th Framework EU Network of Excellence "Complex Metallic Alloys" (Contract No. NMP3-CT-2005-500140). P. P., and A. S. acknowledge support of the Ministry of Science, Education and Sports of the Republic of Croatia through the Research Project No. 035-0352826-2848.

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SAŽETAK

Anizotropna transportna svojstva $Al_{13}Fe_4$ dekagonalnog aproksimanta

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Istraživani su električna otpornost, termostruja i toplinska vodljivost legure $Al_{13}Fe_4$ koja je monoklinski aproksimant dekagonalne kvazikristalne faze. Provedena su mjerenja transportnih svojstava duž tri glavna smjera monoklinske jedinične ćelije *a**, *b* i *c.* Transport naboja je izrazito anizotropan. Najvodljiviji smjer za elektricitet i toplinu je smjer slaganja *b.* Anizotropija termostruje, posljedica je složenosti anizotropne Fermijeve površine koja se sastoji od elektronskih i šupljinskih doprinosa.