Hall effect in the Y-Al-Ni-Co and \( o-Al_{13}Co_4 \) decagonal approximants

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Abstract. The Hall effect in Y-Al-Ni-Co and \( o-Al_{13}Co_4 \) single crystals has been investigated for all combinations of the electrical current and magnetic field directions and in the temperature interval from 90 to 380 K. In these intermetallics the Hall coefficient \( R_H \) exhibits well defined anisotropy and only weak temperature dependence. \( R_H \) is negative electron-like or zero for the magnetic field perpendicular to the plane that corresponds to the quasiperiodic plane in decagonal quasicrystals, and is positive hole-like or zero for the magnetic field parallel to this plane. The results for the anisotropy of \( R_H \) are well correlated to the anisotropy of \( R_H \) in \( d-Al-Ni-Co \) and \( d-Al-Cu-Co \) quasicrystals. Therefore, the anisotropy in both crystalline and quasicrystalline samples originates from the specific stacked-layer structure and the chemical decoration of the lattice. The investigated anisotropic \( R_H \) in Y-Al-Ni-Co was reproduced theoretically by calculation using Boltzmann transport theory, \textit{ab-initio} calculated anisotropic Fermi surface, and isotropic relaxation time approximation.

The monoclinic Y-Al-Ni-Co phase and orthorhombic \( Al_{13}Co_4 \) phase belong to the \( Al_{13}TM_4 \) (TM = transition metal) group of complex metallic compounds and are approximants to the decagonal quasicrystals (\( d-QCs \)). While decagonal quasicrystals can be structurally viewed as a periodic stack of quasiperiodic atomic planes, their approximant phases are characterized by large unit cells which periodically repeat in space with the atomic decoration closely resembling that of \( d-QCs \). Moreover, atomic layers of the approximant phases correspond to the quasiperiodic atomic planes of \( d-QC \) in the sense that they show locally similar patterns, which means that their structures on the scale of near-neighbor atoms closely resemble each other. Further, the periodicity lengths along the stacking direction of these layers in the approximant phases are almost identical to those along the periodic direction of \( d-QCs \). Decagonal approximants thus offer valid comparison to the \( d-QCs \).

A consequence of the anisotropic structure of both \( d-QCs \) and their approximants are anisotropic electrical and thermal transport properties (electrical resistivity, thermoelectric power, Hall coefficient, thermal conductivity) when measured along different crystalline directions [1]. The anisotropy of the Hall coefficient \( R_H \) of \( d-QCs \) [2,3] is especially intriguing, being positive hole-like \( (R_H > 0) \) for the magnetic field lying in the quasiperiodic plane, whereas it changes sign to negative \( (R_H < 0) \) for the field along the periodic direction, thus becoming electron-like. This \( R_H \) anisotropy was reported for the \( d-Al-Ni-Co \), \( d-Al-Cu-Co \) and \( d-Al-Si-Cu-Co \) and is considered to be a universal feature of \( d-QCs \).
However, the lack of translational periodicity within the quasi-periodic layers prevents any quantitative theoretical analysis of these anisotropic properties in d-QCs. At the same time, for the approximant phases to the decagonal phase theoretical simulations are straightforward to perform and they can give us information for the microscopic origin of this anisotropy in general. Therefore, in this article we present a brief overview of our experimental results and \textit{ab-initio} calculation obtained up to now for the anisotropic Hall coefficient for the Y-Al-Ni-Co [1,4] and o-Al\textsubscript{13}Co\textsubscript{4} [5] complex metallic alloys.

The single crystals used in our study were grown by the Czochralski technique [6]. The structure of the Y-Al-Co-Ni (Al\textsubscript{76}Ni\textsubscript{22}Co\textsubscript{2}) matched well to the monoclinic unit cell of the Zhang et al. model [7] and the structure of the o-Al\textsubscript{13}Co\textsubscript{4} matched well to the orthorhombic unit cell of the Grin et al. model [8]. The monoclinic Y-Al-Ni-Co phase has two atomic layers within one periodic unit of $\approx 0.4$ nm along the stacking [010] direction and a relatively small unit cell, comprising 32 atoms, and o-Al\textsubscript{13}Co\textsubscript{4} complex metallic compound has four atomic layers within one periodic unit of $\approx 0.8$ nm along the [100] stacking direction and a unit cell comprising 102 atoms.

In order to perform crystalline-direction-dependent studies, we have cut from the ingots of each alloy three bar-shaped samples of dimensions $1 \times 1 \times 7\ mm^3$, with their long axes along three orthogonal directions. For each sample the long sides of the bar are perpendicular to other two orthogonal directions. The three orthogonal directions are equal to $a$ and $c$ crystallographic directions for both alloys, and to $a$ direction for orthorhombic Al\textsubscript{13}Co\textsubscript{4} alloy. For monoclinic Y-Al-Co-Ni the third orthogonal direction denoted as $a^*$ lies in the monoclinic plane at an angle 26° with respect to $a$, and is perpendicular to $c$ and $b$.

The Hall effect measurements were performed by the five-point method using standard ac technique in magnetic fields up to 1 T and in the temperature interval from 90 to 380 K. The temperature-dependent Hall coefficient $R_H = E_j/j_B B_z$ of Y-Al-Ni-Co and o-Al\textsubscript{13}Co\textsubscript{4}, for all combinations of the current and magnetic field directions, is displayed in figure 1.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Anisotropic temperature-dependent Hall coefficient $R_H = E_j/j_B B_z$ of monoclinic Y-Al-Ni-Co (a) and o-Al\textsubscript{13}Co\textsubscript{4} (b) for different combinations of the current $j_x$ and magnetic field $B_z$. The superscript on $R_H$ denotes the direction of magnetic field. Note that the stacking direction for Y-Al-Ni-Co and o-Al\textsubscript{13}Co\textsubscript{4} are $b$ and $a$ directions, respectively.}
\end{figure}

The $R_H$ values are typical metallic in the range $10^{-10}\ m^3\ C^{-1}$ (with the experimental uncertainty of $\pm 0.1\times10^{-10}\ m^3\ C^{-1}$). For each alloy the six $R_H$ sets of data form three groups of two practically identical $R_H$ curves, where the magnetic field in a given crystallographic direction yields, in accordance with the Onsager relations [9], the same $R_H$ for the current along the other two crystallographic directions in the perpendicular plane. For each alloy $R_H$ exhibits a pronounced anisotropy and a weak temperature...
dependence that tends to disappear at higher temperatures, as is typical for the metallic systems. The anisotropic values of $R_H$ at 300 K are collected in table 1. The comparison of these results to the results for $d$-QCs will be discussed later after the presentation of a theoretical analysis of the Hall effect.

**Table 1.** Experimental and calculated values of the anisotropic Hall coefficient $R_H = E_y/j_x B_z$ of Y-Al-Ni-Co and $o$-Al$_{13}$Co$_4$ for various directions of the current $j_x$ and magnetic field $B_z$ at 300 K. Average values for a particular field and two current directions are given.

|                | $R_H$ ($10^{-10}$ m$^3$/C) |
|----------------|-----------------------------|
|                | Experiment | Theory | Experiment | Theory |
| $B_z$          | $j_x$       |         | $B_z$       | $j_x$   |         |
| $a^*$          | $b$, $c$    | 8.5     | $a$         | $b$, $c$| -6.5    |
| $b$            | $a^*$, $c$  | 0       | $b$         | $a$, $c$| 3.5     |
| $c$            | $a^*$, $b$  | 4.5     | $c$         | $a$, $b$| -0.6    |

A quantitative theoretical analysis of the anisotropic Hall coefficient requires knowledge of the anisotropic electronic band structure i.e. the Fermi surface. The calculations of the band structure were performed for two similar structural models (original [7] and relaxed [4]) for Y-Al-Co-Ni and for two similar structural models (original [8] and new [5]) for $o$-Al$_{13}$Co$_4$. It is out of scope of the present article to go into minor differences connected with the different models, and here we present the results for relaxed Y-Al-Ni-Co and original $o$-Al$_{13}$Co$_4$. The *ab-initio* calculation of the band structure was performed within the framework of the density functional theory by applying Wien97 code [10] and ABINIT code [11]. The calculated Fermi surfaces visualized by using the *xcrysden* program [12], are presented in figure 2. It is transparent that the Fermi surfaces are highly anisotropic for both Y-Al-Co-Ni and $o$-Al$_{13}$Co$_4$, which is at the origin of the experimentally observed anisotropy in the electronic transport coefficients along different crystallographic directions.

![Figure 2](image)

**Figure 2.** (Color online) Fermi surface in the first Brillouin zone, calculated *ab-initio* for (a) the relaxed model of Y-Al-Ni-Co and (b) for original model for $o$-Al$_{13}$Co$_4$. Orientation of the reciprocal-space axes $a^*$, $b^*$ and $c^*$ is also shown.

The theoretical Hall coefficient was calculated by means of the Boltzmann semiclassical theory as implemented in the BoltzTraP code [13] by applying the band structure calculated *ab-initio* as described above, and for the same set of combinations of the current and field directions as the
experimental ones in figure 1. The results are shown in figure 3 and table 1. For both complex intermetallic compounds, the six theoretical $R_H$ sets of data form three groups of two similar $R_H$ curves, where the magnetic field in a given crystalline direction yields similar values of the coefficient for the current along the other two crystalline directions in the perpendicular plane. For Y-Al-Ni-Co there exist some temperature-dependent differences within each group, where the temperature dependence originates from the Fermi-Dirac function. The main objection to the theoretical analysis is that it assumes a single (band independent) and isotropic scattering time which can be canceled out in the actual calculations.

![Figure 3](image-url) (Color online) Theoretical anisotropic Hall coefficient, calculated ab-initio for (a) the relaxed Y-Al-Ni-Co model [4] and (b) the old $o$-Al$_{13}$Co$_4$ model [7]. $R_H$ was calculated for the same set of current and field directions as employed in the experimental measurements of the Hall coefficient shown in figure 1. The superscript on $R_H$ denotes the direction of the magnetic field. Note that the stacking direction for Y-Al-Ni-Co and $o$-Al$_{13}$Co$_4$ are $b$ and $a$ directions respectively.

From figures 1 and 3 and table 1 it can be concluded that the theoretical Hall coefficient, calculated for the relaxed Y-Al-Ni-Co phase reproduces well the experimental features of the anisotropic Hall coefficient in this alloy. For $o$-Al$_{13}$Co$_4$ compound the theory gives too large values for all combinations of directions. However, the theory reproduces well the order of appearance of the anisotropic Hall coefficient (the theoretical order $R_H^b > R_H^c > R_H^a$ matches the experimental one) and the crystallographic-direction-dependent change of sign $R_H^b > 0$ and $R_H^a < 0$.

In conclusion, the origin of the anisotropic Hall coefficient in Y-Al-Ni-Co and $o$-Al$_{13}$Co$_4$ is the anisotropic Fermi surface, the anisotropy of which in turn originates from the specific stacked-layer structure and the chemical decoration of the lattice. The theory reproduces the experimental results quantitatively for Y-Al-Ni-Co and only qualitatively for $o$-Al$_{13}$Co$_4$. There is almost complete analogy between the $R_H$ anisotropy of Y-Al-Ni-Co and $o$-Al$_{13}$Co$_4$ on the one side and d-QCs on the other. In d-QCs $R_H > 0$ for the field lying in the quasiperiodic plane (corresponding to the in-plane coefficients $R_H^a > R_H^b > R_H^c$ of Y-Al-Ni-Co and $R_H^a > R_H^b$ of $o$-Al$_{13}$Co$_4$), whereas $R_H$ changes sign to negative for the field along the periodic direction (corresponding to $R_H^b < 0$ of Y-Al-Ni-Co and $R_H^a < 0$ of $o$-Al$_{13}$Co$_4$). This suggests that long-range quasiperiodicity of the structure is of marginal importance (if it is of any at all) for the anisotropy in d-QCs, which originates from the stacked-layered structure and the complex local atomic order on the scale of nearest-neighbor atoms.
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