Characterization of YbNi$_4$(P$_{1-x}$As$_x$)$_2$, $x = 0, 0.2$ single crystals grown by Czochralski method

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Abstract. We have investigated large single crystals of YbNi$_4$P$_2$ that were grown from a levitating melt by the Czochralski method. The new samples facilitate the determination of the absolute values of the electrical resistivity. Phase pure polycrystalline samples of the non-magnetic reference LuNi$_4$P$_2$ were prepared and the electrical resistivity was measured. Furthermore we have grown a single crystal of the As substituted compound YbNi$_4$(P$_{1-x}$As$_x$)$_2$, $x = 0.2$ and investigated the homogenity of the As distribution.

1. Introduction
YbNi$_4$P$_2$ has a Curie temperature of $T_C = 0.17$ K [1]. This is one of the lowest Curie temperatures ever observed among stoichiometric compounds [2]. The Curie temperature can be decreased even further in the substitution series YbNi$_4$(P$_{1-x}$As$_x$)$_2$. At $x \approx 0.1$ the rare case of ferromagnetic quantum critical point (FM QCP) occurs [3]. YbNi$_4$P$_2$ was found to be a Kondo lattice system with a Kondo temperature of $T_K \approx 8$ K revealed from specific heat measurements on powder samples. The occurrence of coherent Kondo scattering was observed in the resistivity which steeply decreases below 20K [1]. Resistivity measurements from 2 - 300 K on small Bridgman grown YbNi$_4$P$_2$ single crystals show an anisotropy between the $j \parallel c$ and the $j \perp c$-direction, which was explained by the presence of the crystalline electric field [4]. A further measurement on single crystals gave absolute values at 300 K of 90 $\mu$Ωcm for $j \parallel c$ and 160 $\mu$Ωcm for $j \perp c$-direction [3]. Until now, all reported resistivity measurements on single crystals were performed on crystals grown by the Bridgman method. This method yields thin needle shaped crystals of about 2 - 3 mm along the [001]–direction and of 0.5 - 0.7 mm in the perpendicular extension.

Here, we have investigated the electrical transport properties down to 1.8 K of single crystal samples which were cut from one large crystal. This single crystal had a conical shape with a diameter of 3 – 9 mm and a length of 14 mm. It belongs to a new generation of single crystals grown from a levitating melt by the Czochralski method [5].

In the past, samples of the substitution series YbNi$_4$(P$_{1-x}$As$_x$)$_2$ with As-contents up to $x = 0.13$ [3] have been investigated and the material was studied close to the ferromagnetic QCP. Until now, the T-$x$ phase diagram is incomplete due to a lack of samples with $x > 0.13$. To observe the emergence of Fermi liquid behaviour in the system, samples with these higher As concentrations are required. Using a seed from the new crystal generation, we have grown a
single crystal of the substituted compound \( \text{YbNi}_4\text{P}_2 \) with \( x = 0.2 \) with 16 mm in length and 3 – 6 mm in diameter. It turned out that the As distribution is homogeneous.

2. Experimental

An \( \text{YbNi}_4\text{P}_2 \) single crystal was grown by the Czochralski method from a Ni-P self-flux as described in [5]. The crystal structure was confirmed by powder X-ray diffraction (Cu \( \text{K}_\alpha \)). The chemical composition was checked by energy-dispersive X-ray spectroscopy (EDX). Upon investigating a polished surface by scanning electron microscopy and polarization microscopy an excellent homogenity of this surface and the absence of Ni-P flux-inclusions was found. The single crystal was oriented using the X-ray Laue back-scattering technique. From this crystal, samples for the electrical transport measurement were cut using a spark erosion device. The samples had initial dimensions of \( \approx 3 \text{ mm} \times 0.5 \text{ mm} \times 0.15 \text{ mm} \) and were oriented along the crystallographic main symmetry directions \([100]\), \([110]\) and \([001]\). Electrical transport measurements were performed between 1.8 and 300 K using the ACT option of a commercial PPMS (Quantum Design). The Czochralski method was also applied to grow a single crystal from a melt where 20 at\% of \( \text{P} \) was replaced by As. The crystal structure and the chemical composition were investigated by powder X-ray diffraction (PXRD) and EDX, respectively. Phase pure polycrystalline samples of the non-magnetic reference compound \( \text{LuNi}_4\text{P}_2 \) were prepared according to [6, 7]. PXRD measurements confirmed the \( \text{P}_{4}2_{1}/\text{mmm} \) tetragonal structure with lattice parameters \( a = 7.047(6) \, \text{Å} \) and \( c = 3.583(4) \, \text{Å} \), which is in agreement with the data published for polycrystalline samples [6]. PXRD data were refined using the General Structure Analysis System (GSAS) [8, 9].

3. Electrical resistivity \( \rho(T) \) of \( \text{YbNi}_4\text{P}_2 \)

For a tetragonal material Ohm's law reads

\[
\vec{j} = \begin{pmatrix} \sigma_a & \sigma_a \\ \sigma_a & \sigma_c \end{pmatrix} \vec{E}, \quad \rho = \frac{1}{\sigma}
\]

with \( \sigma_a \) being the isotropic conductivity in the basal plane and \( \sigma_c \) the conductivity along the \( c \)-direction for the electrical field \( \vec{E} \). The coordinates are chosen such that the \( z \)-axis is oriented along the crystallographic \( c \)-direction. Our Czochralski grown \( \text{YbNi}_4\text{P}_2 \) single crystals reproduce the temperature dependence of the reported data as shown in the main part of Fig. 1 and with them it is also possible to resolve the temperature dependence of the resistivity \( \rho_{[100]} \) and \( \rho_{[110]} \) of the in-plane directions. As expected according to Eqn. 1, the resistivity is isotropic in the \( a-a \) plane. We determined the absolute values at room temperature applying

\[
\rho(T) = \frac{ab}{II} U(T)
\]

with the width \( a \), the thickness \( b \) of the sample, the contact distance \( l \) and the applied constant current \( I \) and measured voltage \( U \). For \( j \parallel [001] \) we determined the resistivity \( \rho_{[001]}(300\text{K}) = 60\mu\Omega\text{cm} \), for \( j \perp [001] \) we found \( \rho_{[110]}(300\text{K}) = 70\mu\Omega\text{cm} \). The absolute value determined for the \([100]\)-direction agrees with that of the \([110]\)-direction. For comparison, the resistivity of the non-magnetic reference \( \text{LuNi}_4\text{P}_2 \) was measured and is shown in the inset of Fig. 1. For the determination of the absolute values, the measurement device \((U, I)\) as well as the geometry of the samples \((a, b, l)\) have to be considered as sources for uncertainties. In the resistivity measurement, the main contribution to the uncertainty comes from the geometry factors \( \Delta a/a \approx 3\%, \Delta b/b \approx 3\% \) and \( \Delta l/l \approx 1\% \). The uncertainty of the voltage \( \Delta U/U \) is between 1\% and 3\% for different temperatures. The uncertainty of the current \([10]\) with \( \Delta I/I \approx 5 \cdot 10^{-4}\% \) is negligible.
Figure 1. Left: Electrical resistivity $\rho$ as a function of temperature from 1.8K to 300K measured with current $j$ perpendicular ($j \parallel 100$ and $j \parallel 110$) and parallel to the crystallographic c-axis. The inset shows the electrical resistivity measured on a polycrystalline sample of LuNi$_4$P$_2$. The resistivity ratio was determined to be $\rho_{\text{poly}}(300\text{K})/\rho_{\text{poly}}(1.8\text{K}) = 7.4$. Right: Ratio of the normalized electrical resistivity $\rho_i$ of measurement $i$ divided by the average resistivity $\rho_{\text{av}}$ for the respective current direction as a function of temperature. The samples were thinned down in two steps from 0.15 ($i=1$, curve (1)) to 0.09 mm ($i=3$, curve (3)). In the inset, an oriented sample with the four platinum wire contacts prepared for the measurement is shown.

The aim of our optimization of the crystal growth process is to minimize the crystal defects. Indispensable is the use of high-purity starting materials. The contamination of the melt by crucible materials has to be avoided. Low growth rates avoid flux inclusions. Adjusting the temperature during the growth experiment reduces the evaporation of the elements and therefore a shift in the stoichiometry. At lowest temperatures, the scattering on crystal defects is the only contribution to the resistivity. Therefore, the resistivity ratio $R_{R_{1.8K}} = \rho(300\text{K})/\rho(1.8\text{K})$ is an indicator for the amount of crystal defects.

For 6 different samples, which were cut from the same single crystal, different $R_{R_{1.8K}}^{001}$ values between 11 and 17 were found. For the purest sample, we determined the absolute resistivity value to be $\rho_{001}(1.8\text{K}) = 3.5 \mu\Omega\text{cm}$. In the other case, if the current is perpendicular to the c-direction, $R_{R_{1.8K}}^{110}$ and $R_{R_{1.8K}}^{100}$, respectively, spread less for the 6 examined samples. The values are between 3.0 and 3.07. The absolute value is $\rho_{110}(1.8\text{K}) = 22.8 \mu\Omega\text{cm}$. The large variation in $R_{R_{1.8K}}^{001}$ can be caused by a misalignment of the four contacts for the current and voltage measurement. During the growth small-angle grain boundaries can evolve in a single crystal. They lead to the distortion of the lattice and enhance the residual resistivity. A further analysis by Laue method is required to clarify the origin of the variation of $R_{R_{1.8K}}^{001}$.

A common technique to improve the crystallinity of materials is annealing. An experiment at 800°C in an inert atmosphere for 5 days yields an increase of 25% of $R_{R_{1.8K}}^{001}$. Due to the large anisotropy for the different current directions, it is not clear if this improvement is the result of the annealing procedure or was caused by a slight misalignment of the contacts during the resistivity measurement. For further annealing studies with different parameters, well cut samples with a precise orientation are necessary. We investigated the influence of grinding and polishing to the residual resistivity ratio. Two samples cut from the single crystal were oriented along the [110] and the [001]-direction. They were thinned down in two steps from 0.15 to 0.09 mm and the respective temperature dependence of the resistivity $\rho_1, \rho_2, \rho_3$ (curves (1-3)) was measured and is shown on the left hand side of Fig. 1. We determined from our data for
each current direction the ratio \( \rho_i/\rho_{av} \) with 
\[
\rho_{av} = (\rho_1 \cdot \rho_2 \cdot \rho_3)^{1/3}
\]
to investigate if our polishing procedure causes stress and strain in the samples and therefore influences the sample quality. The right part of Fig. 1 shows that RR_{1,8K} slightly varies between the different thicknesses labelled by (1), (2), (3). For the current parallel to the \( c \)-direction, the polishing diminishes the value of \( \rho_{001}(1.8K) \). For the perpendicular direction, the opposite effect occurs. This result might be caused by the anisotropy of RR_{1,8K}. In the thinner sample the ideal current flow without a perpendicular component is approached. That means that the current is confined to the [001] or the [110]-direction and the respective perpendicular current component is reduced upon thinning down the sample. For the [001]-direction \( \rho_i \) becomes smaller for increasing \( i \) leading to a larger RR_{1,8K} and for the [110]-direction \( \rho_i \) becomes larger leading to a smaller RR_{1,8K} value. This investigation also demonstrates that the polishing procedure itself seems not to enlarge the number of crystal defects.

4. The substituted compound YbNi_{4}(P_{1-x}As_{x})_{2}, \( x = 0.2 \)

![Image](image_url)

**Figure 2.** Left: The YbNi_{4}(P_{1-x}As_{x})_{2}, \( x = 0, 0.2 \) crystals were grown from a levitating melt. The arrow mark the pulling direction of the seed (2) in the seed holder (1). The meniscus (4) marks the border between the grown sample (3) and melt (5) levitating in a cold copper crucible (6). The heating power is provided via a radio-frequency induction coil. The evaporation of the volatile elements was slowed down by applying an Ar pressure of 20 bar in the growth chamber; **Right, upper part:** The as grown sample with the nominal composition of YbNi_{4}(P_{0.8}As_{0.2})_{2}. The single crystal seed (1) consisted of YbNi_{4}P_{2} and was oriented along the [001]-direction. The determination of the As content of region (2) of the grown sample is shown in the lower part of the figure. The growth was terminated with a faster growth velocity leading to the incorporation of flux in part (3) of the sample; **Right, lower part:** The real As content \( y \) in the grown sample along two radial lines, A,B (black and grey symbols) was determined using EDX in dependence of the distance from the center of the sample.

The growth of the substituted compound by the Czochralski method Fig. 2, was done similarly to that reported in [5]. The liquidus temperature is measured during the growth experiments. Within the accuracy of the pyrometer \( \Delta T \approx \pm 50K \), no change compared to the stoichiometric compound was detected. The growth was started at about 1400°C using an YbNi_{4}P_{2} single crystal as the seed. After seeding, the sample was pulled with a rate of 0.3 mm/h. Such low growth velocities are necessary to obtain crystals without flux inclusions.
The distribution coefficient of As in the system $\kappa = c_{As}^l / c_{As}^s$ with the concentrations of As in the melt $c_{As}^l$ and in the solid $c_{As}^s$, respectively, is not known and does not necessarily have to be exactly one [11]. A deviation from $\kappa = 1$ would lead to the enrichment or depletion of As in the melt and an inhomogeneous As distribution in the grown crystal. The As distribution in the single crystal was investigated by EDX, and showed that the initial As:P ratio of the melt of 1:4 can be found all over in our sample except at the first part which is connected to the seed. The seed consisted of YbNi$_4$P$_2$ and over a length of about 2.5 mm the crystal structure included more and more As and the lattice adapted to the new lattice constants. The analysis along radial lines (Cut A,B) on polished surfaces shown in Fig. 2, yields a homogeneous As concentration from the center to the surface of the crystal. A part of the YbNi$_4$($P_{1-x}$As$_x$)$_2$, $x = 0.2$ sample was investigated by PXRD and the structure refinement yields an enlargement of the unit cell of $\Delta V/V = 0.0138$ compared to $x = 0$. The lattice constants of the tetragonal $P4_2/mnm$ structure are $a = 7.0803(5)$Å and $c = 3.6131(2)$Å.

5. Summary
The electrical resistivity was measured on Czochralski grown YbNi$_4$P$_2$ single crystals from 1.8 to 300 K and the absolute values at room temperature were determined to be $60 \mu \Omega \text{cm}$ for $j$ parallel to the $c$-direction and $70 \mu \Omega \text{cm}$ perpendicular. Comparing with the measurement on Bridgman grown samples [3], the data reproduce the temperature dependence of the resistivity but the absolute values differ. The resistivity ratio $RR_{1.8K}$ is strongly anisotropic. For $j$ parallel to the $c$-direction we found value between 11 and 17 for different samples. In the perpendicular directions, it is almost sample independent with values about 3. Polycrystalline LuNi$_4$P$_2$ samples, exhibit the resistivity characteristics of a non-magnetic metal. A single crystal of the substituted compound YbNi$_4$($P_{1-x}$As$_x$)$_2$ with $x = 0.2$ was grown. The phosphorous to arsenic ratio in the melt is maintained in the crystal. The As distribution is homogeneous throughout the whole sample. The enlargement of the unit cell is $\Delta V/V = 0.0138$ compared to $x = 0$.

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