90th anniversary of Czochralski method

1885-1953
In 2006 we celebrate the 90th anniversary of Czochralski pulling method. Professor Jan Czochralski invented this method during the investigations of the crystallization rate of metals. In the fifties of the twentieth century his method was adopted for growing large single crystals of semiconductors on an industrial scale. Moreover, a large group of applicable oxides are grown using Czochralski method. Also the number of single crystals of intermetallic compounds is quickly growing thanks to this method.

The Institute of Electronic Materials Technology (ITME)
• Professor Jan Czochralski was born on October 23, 1885 in Kcynia, in part of Poland at that time under the Prussian domination, as the eighth child of the Polish craftsmen Franciszek Czochralski and Marta from the Suchomski family. The Czochralskis were carpenters for many generations.

• Jan completed teachers' seminar in Kcynia according to the wish of his father. He was already interested in chemistry during his school days. However, he did not accept his matriculation certificate due to poor grades.

• Lack of this certificate unable him to continue his education. For some time he worked in Krotoszyn in a drugstore.
At the end of 1904 he went to Berlin and began to work in the drugstore of Dr. A. Herbrand in Altglienicke, the districts of Berlin. Later he worked for a short period in the laboratory of Kunheim and Co. in Niederschönweide near Berlin and then in Allgemeine Elektrizitäts-Gesellschaft (AEG). The job in Kabelwerk Oberspree and the two years spent in their research laboratories prepared him to become head of the laboratory of steel and iron research. This laboratory dealt with the checking the quality and purity of metals and alloys and was engaged in the refinement of copper. Simultaneously he attended lectures on chemistry at the Charlottenburg Polytechnic near Berlin. From 1911 to 1914 he was an assistant of Wichard von Möllendorff with whom he published his first paper devoted to the crystallography of metals, dislocation theory (Zeitschrift des Vereines Deutcher Ingenieure 57 (1913) 931-5, 1014-20).

KABELWERK OBERSPREE RESEARCH LABORATORIES, JAN CZOCHRALSKI (FAR LEFT).
Jan Czochralski married in 1910 Marguerit Haase, a pianist of Dutch origin, the daughter of a rich owner of houses. They had three children: two daughters – Leonia (1914) and Cecilia (1920,) and a son Borys (1918).
• In 1916 professor Jan Czochralski invented a method for measuring the crystallization velocity of metals. The method was invented by accident and through Czochralski careful observations.

• The idea of this method is based on pulling a crystal from the melt. The grown during the experiment crystals as metallic wires were single crystals.

• The results of Czochralski studies were published in several papers, The first one was published in Zeitschrift für Physikalische Chemie 92, 219 (1918), in German.

• This new technique allowed to obtain the good quality single crystals of pure metals like Sn, Pb, Zn. After the II World War the Czochralski method was adopted by the Americans G.K. Teal and J.B. Little from Bell Telephone Laboratories for growing large single crystals of semiconductors on an industrial scale (Growth of germanium single crystals, Phys. Rev. 78, 647 (1950) and Bull. Amer. Phys. Soc. 25, 16 (1950)).
Franfurt on Mein

• In 1917 Jan Czochralski moved to Frankfurt on Mein and organized the Laboratory of Metal Science. Several valuable scientific papers and patents were developed there. Among the patents was the highly famous patent on a tin-free bearing alloy for railways, called metal B, patented in 1924 and bought by many countries all over the world, including USA, France and England.
• He also pioneered investigations of the anisotropy of the hardness of single crystals (works between 1913 and 1923), which are of great importance for the plastic treatment of materials.
• In 1919 Czochralski was among the scientists who founded the German Society for Metal Science and in 1925 he became its president.

Warsaw

• When Poland regained independence he accepted in 1929 the invitation of the President of Poland, Ignacy Mościcki. Czochralski obtained his first honorary doctorate of the Faculty of Chemistry at the Warsaw University of Technology. It enabled him to take the position of a professor there.

The Czochralski’s house in Warsaw
THE POLISH PRESIDENT IGNACY MOŚCICKI (FAR RIGHT) VISITING CZOCHRALSKI’S LABORATORY. JAN CZOCHRALSKI (SECOND FROM THE LEFT).
After the II World War due to his connections with Germans Czochralski was suspected of collaboration and even arrested. The suspicion was continued to date of his death, but up to now there is no evidence for his collaboration. In fact professor Czochralski helped the National Army and many people during the war time. Czochralski returned to Kcynia and to the chemistry and to production of cosmetics and household chemicals.

He died on April 22, 1953 in Poznań due to heart disease and was buried in Kcynia.

Professor Jan Czochralski was outstanding metallurgist, chemist and crystallographer, whose crystal growth method allowed dynamic development of the modern science and technology. However, after the war he was almost forgotten, especially in Poland.

After the political changes in Poland the Tenth European Crystallographic Meeting, organized in Wroclaw in 1986, was dedicated to Professor Jan Czochralski to commemorate the seventieth anniversary of the discovery of the Czochralski method.

Since its foundation in 1991, the Polish Society for Crystal Growth commemorates him in the form of Czochralski Lecture, which is delivered as the opening lecture of every Polish Crystal Growth Conference by a distinguished scientist with recognized contribution in crystal growth related fields. In 1998 this Society changed its name to Czochralski Polish Society for Crystal Growth.
The Czochralski’s house in Kcynia
„Margowo”
Professor Czochralski started the crystal growth of metals by immersion of a narrow capillary in the crucible with melt. In capillary a small nucleus of crystal was formed. Slow pulling out of the melt allowed to obtain metallic monocrystalline wires with diameters of about 1 mm and lengths up to 150 mm. The crystal growth using the Czochralski method is continuously improved and developed.

In the Solid State Department of the Institute of Physics University of Silesia modification of the Czochralski method from the levitating melt was applied. Growing single crystals of intermetallics in crucibles degrades their purity and quality due contact with the material of the crucible particularly when the sample contains high reactivity of rare earths. The applied crucibleless method allows to obtain a relative optimal quality of single crystals of rare earth intermetallics.
RTX intermetallics

GdPdAl - Berg-Barrett topography

ZrNiAl

TiNiSi
The two layers of the structure of GdPdAl (4 unit cells) at level $z=0.5$ (a) and $z=0$ (b); only inter-layer bonds are exhibited. The arrows indicate the movement of the Al-atoms and the shortening of the bonds upon cooling (strongly exaggerated).
GdPdAl [105]

Temperature (K)

Electrical resistivity (µΩm)

$T_c = 48 \, \text{K}$

$T_N = 24 \, \text{K}$

$180 \, \text{K}$
$\theta = 67 \text{ K}$

$C = 7.9 \text{ emuK/mole}$

$\mu_{\text{eff}} = 7.94 \mu_B/\text{f.u.}$

$1/\chi = (T-\theta)/C$
$\chi_{ac}'$ (arb. u.)

Temperature (K)

GdPdAl [105]
### Lattice Parameter vs. Temperature

**DyPdAl**

**Cal (Θ₀ = 225K)**

**Exp**

#### Lattice Parameter $a$ [Å]

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#### Unit Cell Volume [Å³]

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**DyPdAl fit (Θ₀ = 225K)**

**Experimental**
DyPdAl

Resistivity (µΩm)

Temperature (K)

25 K

17 K
HoPdAl

Cal ($\Theta_d=225$K)

Exp

Lattice parameter $a$ [Å]

Temperature [K]

Lattice parameter $c$ [Å]

Volume [Å$^3$]

Temperature [K]
<table>
<thead>
<tr>
<th>Compound X (IIIA group)</th>
<th>Crystal structure V (Å³)</th>
<th>Pd 4d $\Gamma_{FWHM}$ (eV)</th>
<th>Compound X (IVA group)</th>
<th>Crystal structure V (Å³)</th>
<th>Pd 4d $\Gamma_{FWHM}$ (eV)</th>
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</thead>
<tbody>
<tr>
<td>GdPdAl (143pm)</td>
<td>TiNiSi 240.4</td>
<td>2.2</td>
<td>GdPdSi (118 pm)</td>
<td>β – GdPdSi 455.0</td>
<td>2.4</td>
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<tr>
<td>GdPdGa (135pm)</td>
<td>Co₂Si 240.3</td>
<td>1.7</td>
<td>GdPdGe (122 pm)</td>
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<td>2.1</td>
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<td>GdPdIn (167pm)</td>
<td>Co₂Si 223.0</td>
<td>1.3</td>
<td>GdPdSn (140 pm)</td>
<td>Co₂Si 264.9</td>
<td>1.9</td>
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</tbody>
</table>

\[ d = M \cdot n/V \]

(M – molecular mass of the GdPdX compound,

n – number of molecules per unit cell volume,

V - unit cell volume)
Binding energy (eV)

Intensity (arb. u.)

Pd 4d  Gd 4f  Gd 5p

GdPdSi  GdPdIn
Berg-Barrett topography of the Gd$_7$Pd$_3$ single crystal
Berg-Barrett topography of the Gd$_7$Pd$_3$ single crystal
Berg-Barrett topography of the Gd$_7$Rh$_3$ single crystal
Gd$_7$Rh$_3$

Gd$_7$Pd$_3$
Gd₇Rh₃

Lattice parameter a (Å)

- exp
- cal (Θ_D=160K)

Lattice parameter c (Å)

Volume (Å³)

Temperature (K)

Gd₇Pd₃

Lattice parameter a (Å)

- exp
- cal (Θ_D=160K)

Lattice parameter c (Å)

Volume (Å³)

Temperature (K)
\[ \rho(T) = 27 + 0.005T^2 \]

\[ \rho(T) = 130 + 0.022T^2 \]

\[ \rho(T) = 60 + 0.022T^2 \]

\[ \rho(T) = 27 + 0.015T^2 \]
The figure shows the thermoelectric power, $S$, as a function of temperature, $T$, for two samples: Gd$_7$Rh$_3$ (a) and Gd$_7$Pd$_3$ (b). The diagrams depict $\Delta T \parallel c$ and $\Delta T \parallel a$ for each sample.

For Gd$_7$Rh$_3$ (a), the thermoelectric power $S$ is shown with a peak at $T_N$, indicating a phase transition. The temperature range is from 0 to 300 K.

For Gd$_7$Pd$_3$ (b), the thermoelectric power $S$ is shown with a peak at $T_c$, also indicating a phase transition. The temperature range is from 0 to 350 K.
\[
\chi^{-1} = (T - 176)/58.4
\]

\[
\mu_{\text{eff}} = 8.2 \mu_B
\]
<table>
<thead>
<tr>
<th></th>
<th>c/a</th>
<th>a/a\textsubscript{Gd}</th>
<th>c/c\textsubscript{Gd}</th>
<th>V/V\textsubscript{Gd}</th>
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<tr>
<td>GdPdAl(I)</td>
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<td>2</td>
<td>0.7</td>
<td>2.78</td>
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<tr>
<td>GdPdAl(II)</td>
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<td>1.96</td>
<td>0.71</td>
<td>2.75</td>
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<tr>
<td>Gd\textsubscript{7}Rh\textsubscript{3}</td>
<td>0.63</td>
<td>2.72</td>
<td>1.09</td>
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<tr>
<td>Gd\textsubscript{7}Pd\textsubscript{3}</td>
<td>0.63</td>
<td>2.75</td>
<td>1.09</td>
<td>2.75</td>
</tr>
</tbody>
</table>

\[ \mu_{\text{eff}} = g_J \mu_B \sqrt{J(J+1)} \left[ 1 + A N(E_F) \frac{g_J - 1}{g_J} \right] \]

- \( g_J \) – the Lande factor
- \( J \) – the total quantum number
- \( N(E_F) \) – the density of states at the Fermi energy
- \( A \) – the exchange interaction
Acknowledgments

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