Intermetallic Compounds PdIn and PdGa: Comparative Study of Transport Properties

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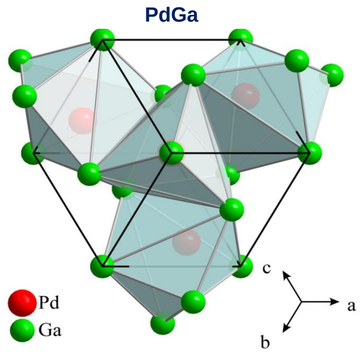
Abstract

The bulk transport properties of single-crystalline bimetallic PdIn have been investigated in correlation with previously studied PdGa. Both compounds are promising for selective catalysis. It's known that the bulk is influencing the properties of the surface, so knowledge of the bulk properties of the material is important to connect catalytic properties of the surface to the structural and electronic properties of the bulk. For that purpose we have determined the transport properties (electrical resistivity, thermoelectric power and Hall coefficient) of single crystal of PdIn. The temperature behavior of electrical resistivity, Hall coefficient and thermoelectric power clearly demonstrates stronger metallic like properties of PdIn and rather complicate temperature dependent interplay of electron-phonon interactions in case of PdGa.

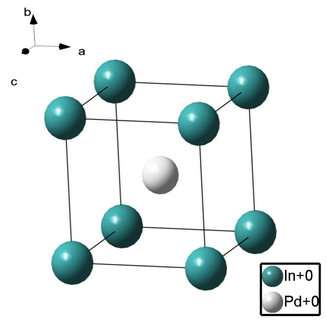
STRUCTURE

PdGa

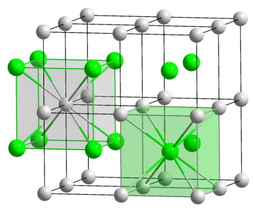


- PdGa is a cubic phase crystallizing in the FeSi type of structure, which may be considered as strongly distorted NaCl type.
- The first coordination shell of Pd or Ga, respectively, consists exclusively of atoms of the other kind and may be described as distorted monocapped trigonal prism [1].
- This structural arrangement makes the Pd atoms well separated by the surrounding Ga shell, fulfilling the requirement of the active-site isolation for the catalytic selectivity.

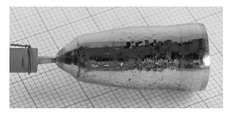
PdIn



- PdIn is forming the structure sometimes called B2 type structure [2] where the centred atoms and cornered atoms are different such as in CsCl structure.



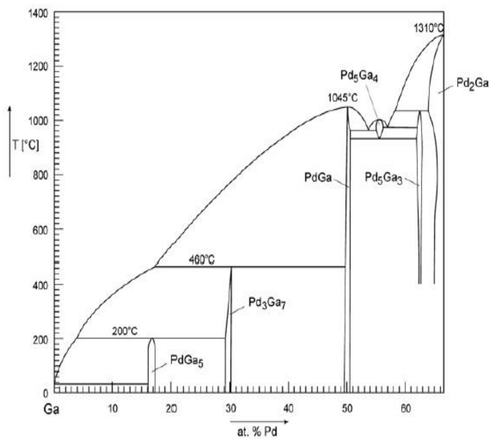
SAMPLES



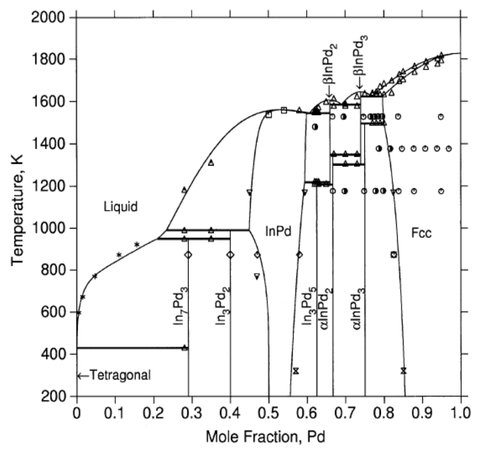
- A centimeter-size PdIn and PdGa, oriented single crystals were grown using the Czochralski method [3] by the group of Peter Gille from Ludwig-Maximilians-Universität München.
- For the measurements, three rectangular bars were cut from the parent crystall of approximatelly dimensions 7×1×1 mm^3, with their long axes along the [111] crystallographic direction.
- Due to the cubic symmetry of the PdIn structure, no anisotropy of the bulk physical properties of tensorial character is expected.

Phase diagrams

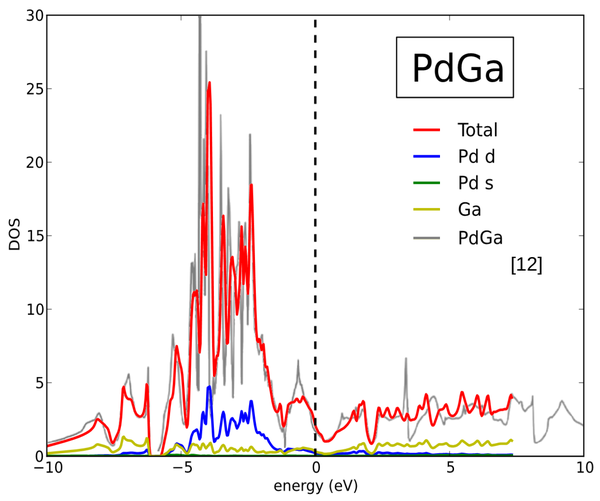
PdGa

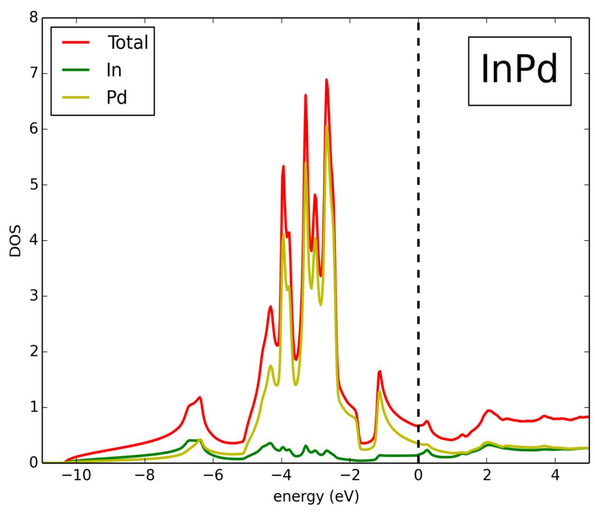


InPd

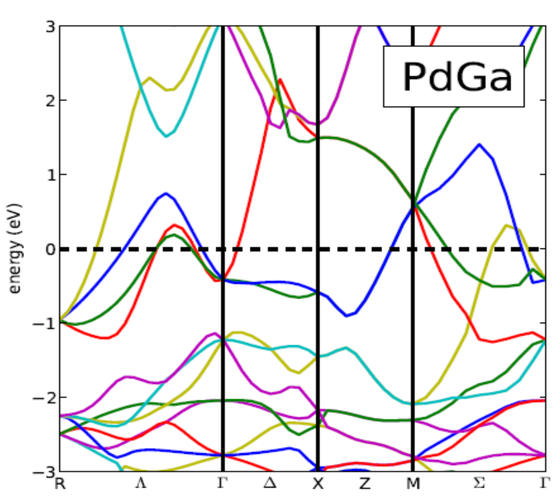


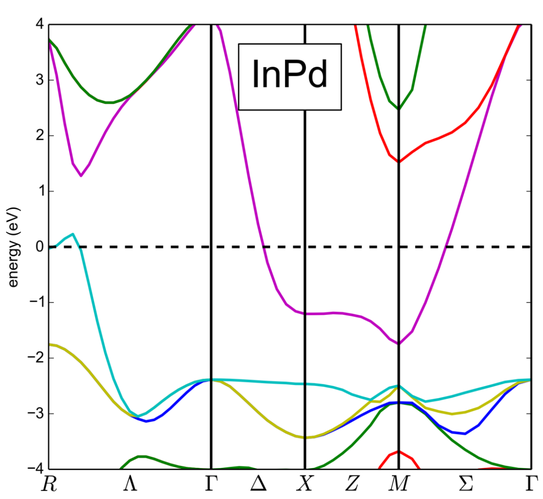
DENSITY OF STATES





ENERGY BANDS





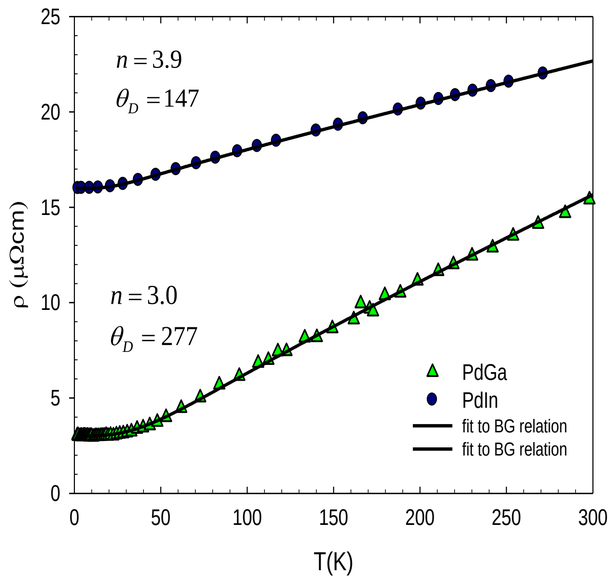
EXPERIMENTAL

- Electrical resistivity was measured by a standard four-terminal technique between 300 and 2 K.
- The thermoelectric power was measured between 320 and 2K by applying a differential method with two identical thermocouple (chromel-gold with 0,07 % iron) attached to the sample with silver paint.
- The Hall-coefficient measurements were performed by the five-point method in the temperature range between 360 and 90K.
- All measurements were performed using the laboratory-made cryostat.

ELECTRICAL RESISTIVITY

- The temperature dependent electrical resistivity of the intermetalic PdGa and PdIn can be well approximated by the Boltzmann theory using Bloch-Grüneisen relation:

$$\rho(T) = \rho_0 + C\left(\frac{T}{\theta_D}\right)^n \int_0^{\theta_D/T} \frac{x^n}{(e^x - 1)(1 - e^{-x})} dx$$



- Away from the low-*T* limit, approx. above 30 K, the resistivity increases linearly with temperature, where the positive temperature coefficient demonstrates predominant role of the electron–phonon inelastic scattering mechanism in the temperature dependence of ρ.
- The saturation of ρ to a constant plateau in the limit T→0 is due to quenched defects in the structure.
- The resistivity values are typical metallic, therefore, both materials PdGa and PdIn can be considered as good metallic conductors.

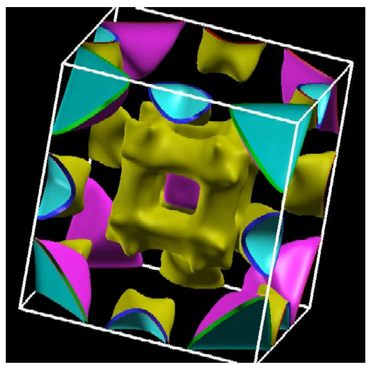
sample	ρ^{RT}[μΩcm]	ρ_0[μΩcm]	θ_D [K]	S^{RT}[μVK^{-1}]	R_H^{RT}[x10^{-10} m^{3}C^{-1}]
Pd	10,5[4]	0.02[6]	290[4].	-10[5]	-0.006[7]
PdGa	15[6]	3[6]	267[6]	-3,65[6]	+1,6[6]
PdIn	22	16	243[8]	+2,3	+0.8

The room temperatureelectrical resistivity (ρ^{RT}), thermopower (S^{RT}) and Hall coefficient (R_H^{RT}) together with residual resistivity (ρ_{res}^0) and Debye tempetarature (Θ_D) for pure Pd, PdGa and PdIn, respectively.

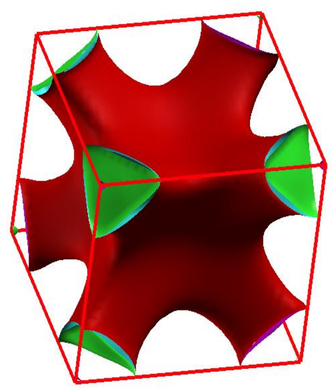
- The DFT calculations of electronic properties of PdGa and InPd presented were carried out using the Wien2k program with LAPW (the full potential linearized augmented plane wave method).
- In this approach, the generalized gradient approximation was used for the exchange correlation potential.
- Fermi surfaces are visualisated using the XCrySDen program.

FERMI SURFACE

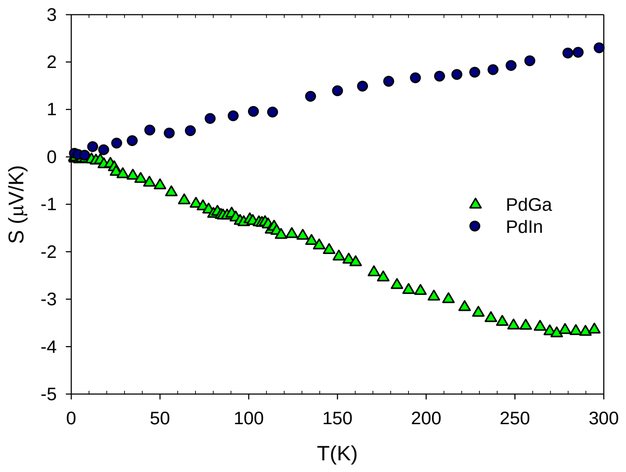
PdGa



InPd

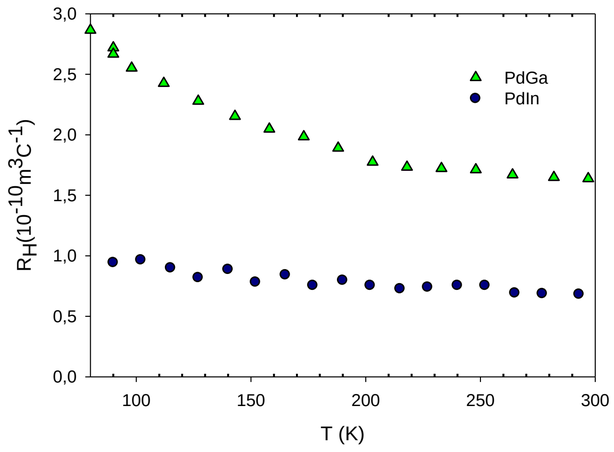


THERMOELECTRIC POWER



- In case of the PdGa sample the thermopower is small, with absolute value of few μV/K, and negative.This implies electrons to be considered as the majority charge carriers.
- On the other hand, the PdIn shows thermopower that is small, positive and rather smooth within the temperature measuring range.
- Thermopower of PdIn has the same sign as Hall effect. That is not true for PdGa where several hole-like and electron-like bands are crossing Fermi level and whose contributions end up with different sign for thermopower and Hall effect.

HALL COEFFICIENT



- Both samples exhibit the positive RT values that increase upon cooling.
- Due to the metallic values, this small increase in case of PdGa sample can be attributed to the temperature-dependent changes of the Fermi surface we noted in thermopower review. The positive sign suggests that holes are the majority charge carriers, whereas the negative thermopower offers the opposite conclusion that the charge is carried by the electrons.
- This apparent contradiction for PdGa sample can be resolved by considering the details of the Fermi surface which consists of several electron-like and hole-like parts .
- In case of the PdIn sample, the small variation in temperature dependence ofR_H is probably due to the anisotropy of electron scattering times.

CONCLUSION

- **The temperature behavior of resistivity, Hall coefficient and thermoelectric power clearly demonstrates stronger metallic like properties of PdIn and small temperature dependent interplay of electron-phonon interactions in case of PdGa.**
- **The present comparative study demonstrates stability and suitability of the surface and the bulk under reaction conditions in order to assign the observed catalytic properties to the electronic and geometric properties of the complex metallic phase.**
- **This work complements the determination of anisotropic bulk physical properties of the $Al_{13}Co_4$ [7], $Al_{13}Fe_4$ [8] and PdGa [3] complex intermetallics used as selective and stable catalysts in the semi-hydrogenation of acetylene.**

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