GERDA meeting,

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Zone refinement of 76Ge in Russia: an offer from IChHPS (Nizhny Novgorod)

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General scheme of 76GeO2 transformation

^{76}GeO2 of *4N grade*

[+ "wet" chemistry and/or metallurgical procedure]

↓

^{76}Ge of 6N grade

↓

^{76}Ge of 10N-11N after ZR/monozone

↓

HP^{76}Ge crystal pulling

Soviet program on HPGe detectors manufacture

The IChHPS participated in Soviet program on HPGe detectors manufacture (in the eighties and the beginning of nineties).

Fields of the responsibility inside the program:

- Wet chemistry (GeCl4 and GeH4)
- Metallurgical procedure including monozone refinement with productivity of ~ 5 kg/month
- Detector grade HPGe crystal growing (the EKZ 350 puller) with diameter up to D50 mm
- Development of complex of techniques for characterization of HPGe

Ge-76: zone refinement (ZR) in IChHPS

Estimated yield of Ge-76 after zone refinement is ~ 90%.

Purity of Ge after ZR is comparable to UMICORE's request;

Si and C content will be specified after testing

Metal after after 1st zone refinement (recoverable loss) will be purified again several times. Additional quantity of intrinsic germanium will be obtained.

Estimated productivity of zone refinement is ~ 4 kg/month

Unrecoverable loss of zone refinement is ~ 5% (after cutting procedure, sampling, and etching)

Element	Content, mass.%	Element	Content, mass.%
Al	$< 3*10^{-9}$	K	$< 6*10^{-7}$
B	$< 1*10^{-8}$	La	$< 7*10^{-9}$
Be	$< 2*10^{-8}$	Si	$< 2*10^{-5}$
Ca	$< 1*10^{-6}$	Au	$< 1*10^{-9}$
Cd	$< 3*10^{-7}$	Li	$< 1*10^{-7}$
Bi	$< 4*10^{-7}$	Eu	$< 8*10^{-9}$
Pb	$< 8*10^{-7}$	Na	$< 1*10^{-6}$
Mn	$< 5*10^{-8}$	Fe	$< 8*10^{-8}$
Ni	$< 7*10^{-7}$	Mg	$< 8*10^{-8}$
Co	$< 1*10^{-7}$	Ga	$< 1*10^{-8}$
Cr	$< 5*10^{-7}$	Zn	$< 1*10^{-5}$
Ag	$< 6*10^{-8}$	In	$< 6*10^{-7}$
Cu	$< 5*10^{-8}$	C	$< 5*10^{-6}$

Methods of characterization

After reduction (polycrystalline ingot):

- Resistivity measurements of ingots at RT → LN
- Definition of conductivity type (N/P)

After zone refinement (polycrystalline ingot with small single crystals/blocks) and after monozone refinement (slices):

- Hall effect measurements LN → LHe
- PTIS
- DLTS

After CZ growth of big single crystal (>= 2 cuttings of a boule):

- Resistivity measurements at LN along crystal
- Hall effect measurements LN in radial direction of slice
- DLTS (especially for N-type material !)
- Crystallographic examination (dislocation density)

Presentation of PTIS by the inventor

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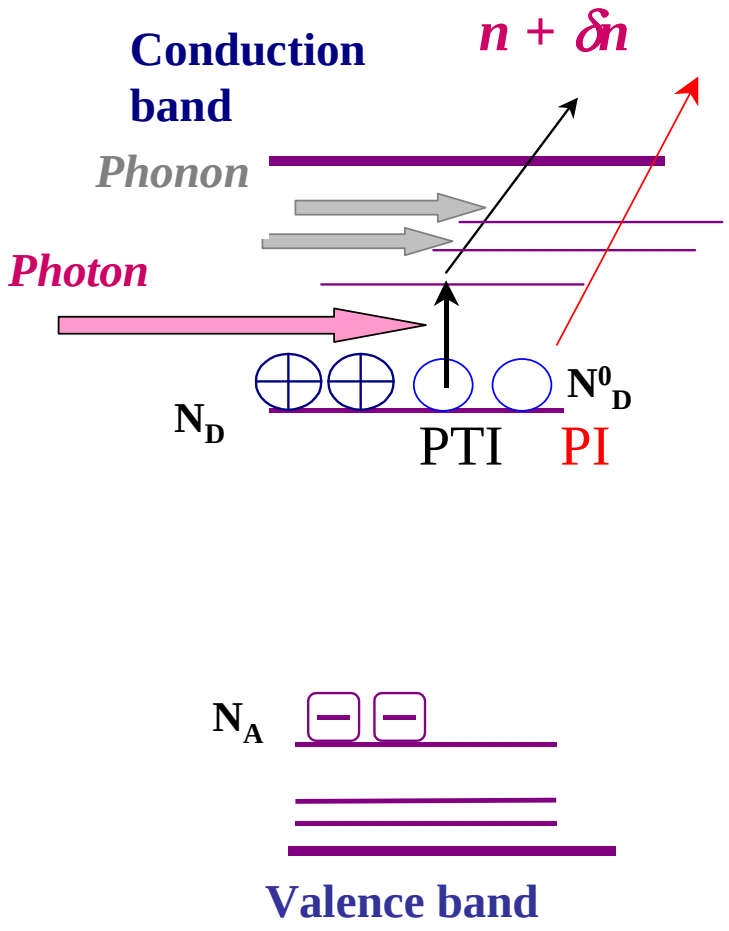
(Êîãàí . Èçâ.ÀÍ .1978.)



$$\sigma_{PTI} = \sigma_{abs.}(\nu_{g\to m}) \cdot I_m$$

σ - ñå÷åíèå ïîãëîùåíèÿ,

$\nu_{g\to m}$ – ÷àñòîòà $g\to m$ ïåðåõîäà,

I_m – âåðîÿòíîñòü òåðì è÷åñêîé èîíèçàöèè

$$I(E)=(1+E/kT)\exp(-E/kT)$$

$$\sigma_{PTI} / \sigma_{PI}(E_{ion.}) =$$

$$= I_m \cdot f_{g\to m} \cdot (E_{ion.}/\Gamma) \le 10^3$$

$\sigma_{PI}(E_{ion.})$- ñå÷åíèå ôîòîèîíèçàöèè ,

$E_{ion.}$- ýíåðãèÿ èîíèçàöèè,

Γ- øèðèíà ëèíèè ÔÒÈ,

$f_{g\to m}$ – ñèëà îñöèëëÿòîðà

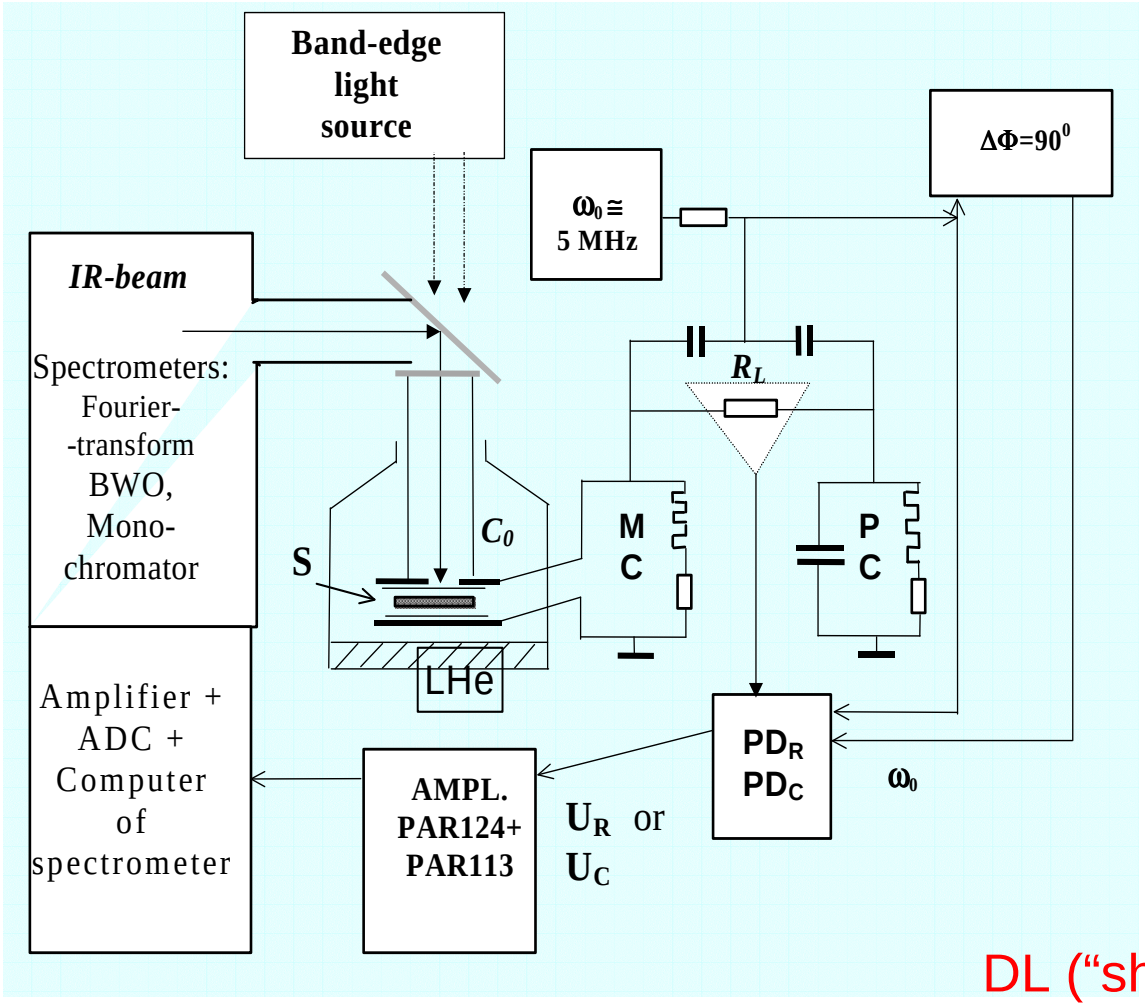
Methods of characterization

E.E.Haller after his job together with Soviet inventors of PTIS method wrote (E.E.Haller, Izvestiya of AS of USSR, Physics, 1978, Vol. 4, № 6, p.1131):

"Since the PTIS started to use, the growth of HPGe crystals transforms from "art in science" to routine business…"

Problems !!: fabrication of contacts which should work properly under LN and **LHe** temperature and don't introduce impurity into Ge under investigation

PTIS without Ohmic contacts
(B.A.Andreev, Nizhny Novgorod)



$(\delta C/C)_{min}=(2/Q)\cdot(P_N/P)$

$(\delta R/R)_{min}=2(P_N/P)$

Experiment

$(\delta C/C)_{min}= 8\cdot10^{-11}$

Theoretical limit

$(\delta C/C)_{min}= 3\cdot10^{-11}$

$(\delta R/R)_{min}=3\cdot10^{-9}$

для $P_N=(2/\pi)kT\Delta\Omega$

$T=300K \quad \Delta\Omega=1Hz$

$P=3mW$

DL ("shallow") ~ 10^8 atoms/cm^3

DL("deep") ~ 10^{-3} of DL("shallow")

Scheme of “cooling part” of the “contacts-free” PTIS set up (thanks to B.Andreev)

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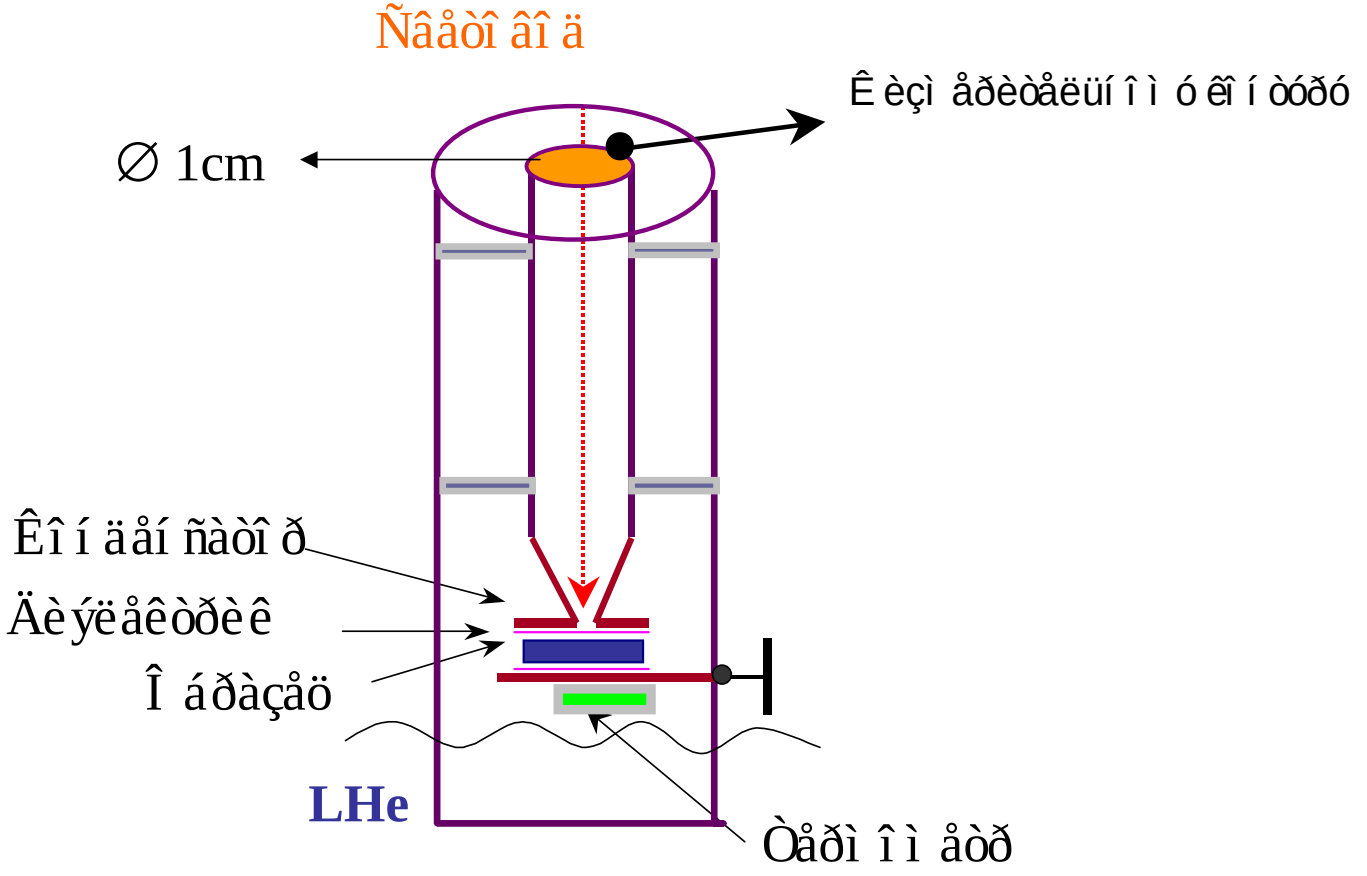


Storage of enriched material in the ICHPS

Depth of air-raid shelter under the building is about 1500 g/cm^2 (~ 15 m.w.e.) just under main building of the institute

Zone refinement at IChHPS: logistic

1) **By train.** Distance between Moscow and Berlin is 1800 km (it takes 25 hours) and 42 min by regular train Moscow-Berlin, Lichtenberg). Distance between Nizhny Novgorod and Moscow is 450 km (it takes 4 hours 50 min by express train, or about 7 hours by passenger train). Passenger train from Nizhy arrives Moscow at 6:00, and departure of train to Berlin is 8:32. In case of delay, there are metro stations (deep underground location) under railway stations in Moscow.

No transport container.

2) **By car.** There is autobahn of very good quality between Moscow and Brest (custom at boarder Byelorussia and Poland).

3) **By truck/train and a ferry.** Bring the material to St.Petersburg by truck/train (700 km from Moscow) and then

Transfer of technology/equipment to Germany

Mono zone refinement in IKZ?/Dresden?:

1) IChHPS will transfer the technology.

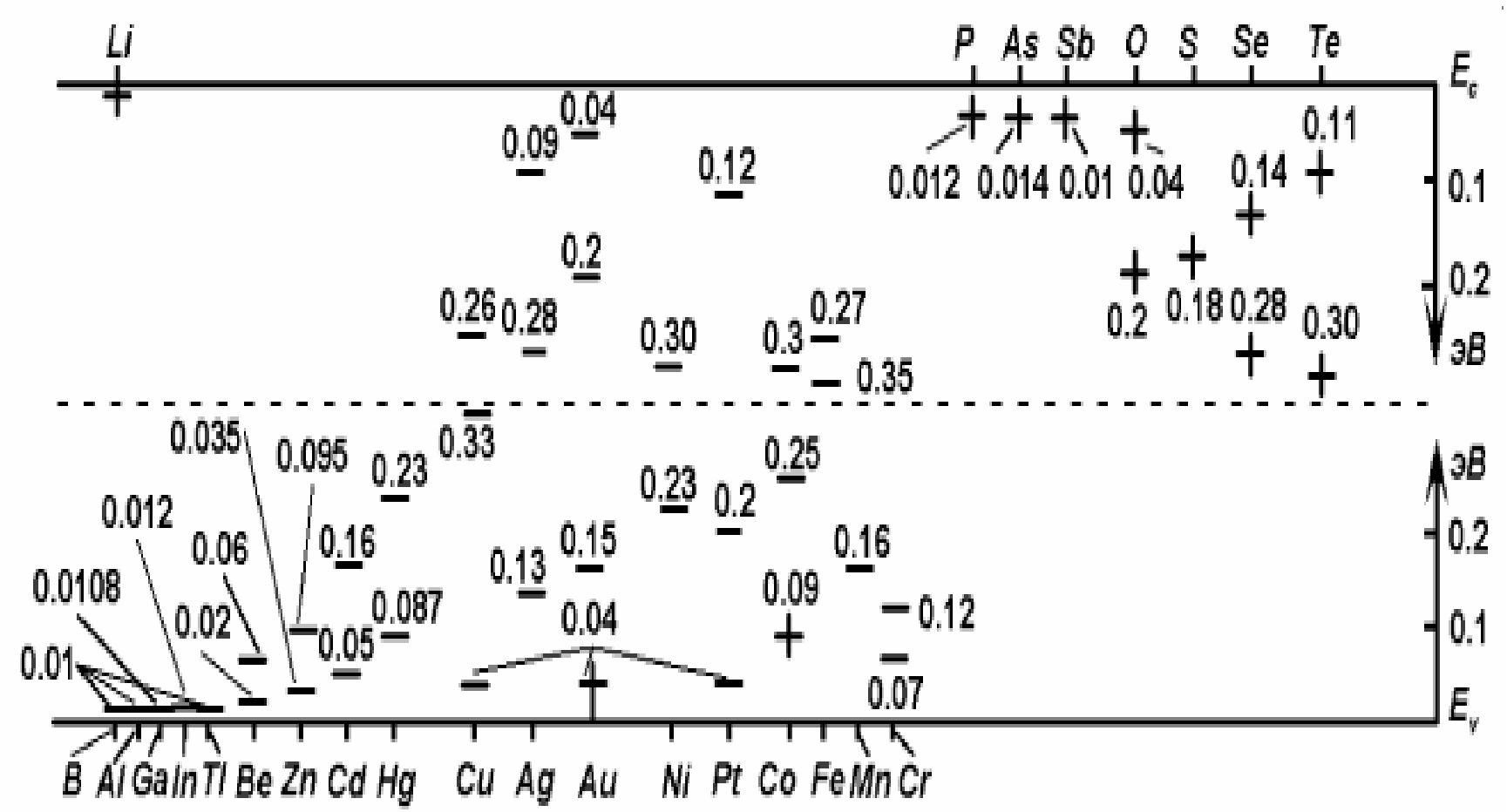
2) IChHPS will transfer part of their equipment to the IKZ (the boats).

The IKZ/Dresden? should buy a RF generator and a gas purification system (H2) + clean room.

1-2 specialists from Nizhny could be invited to Berlin?/Dresden? for quite a long time (8-12 months).

Backup slides

Donors (+) and acceptors (-) in Ge



Conversion of GeF4 → GeO2

Reduction procedure and mono-zone refinement can be done in the IChHPS. They demonstrated their capability concerning mono-zone refinement and pulling of boules for HPGe detector application (small size, 40 mm of diameter).

General scheme of the procedure (from semiconductor industry)

GeO_2 (< = 99.8%)

↓

GeO2 transformation to $GeCl_4$

↓

Extraction*

↓

Distillation

↓

Rectification

↓

$GeCl_4$ conversion to GeO2
(99.9999% & < 10 ppbw for electroactive metals)

⇓

Reduction GeO_2 ⇒ Ge metal

↓

Polyzone refinement of Ge
(up to 10^{13} impurities/cm^3)

⇓

Monozone refinement
(up to 10^{10} impurities/cm^3)

⇓

Crystal pulling (& cutting)
loading of furnace: 8 – 10 kg (D80-120 mm)