

# **Slow-positron beam studies of ZnSe and ZnTe compounds**

*(preliminary data)*

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# II-VI ternary compounds

- Wide gap: 1.5 eV (CdTe) ÷ 5.5 eV (BeSe):
  - light emitters
  - photodetectors
  - UV detectors in VIS and IR environment – astronomy, flame detectors, medical equipment
  - scintillators
  - heterojunction lasers
  - Mn chalcogenides  $Zn_{1-x-y}Be_xMn_ySe$  - magnetoelectronics
  - ...

# Blue-green laser

GaN: blue-violet laser, but hardly  $> 450$  nm

Green-blue laser ( $>450$  nm)

II- VI compounds

\* 1991 (M.A. Haase, APL 59, 1272)  
but  $\tau < 400$  h

Stress accumulation  
→ macroscopic defects  
in optically active zone

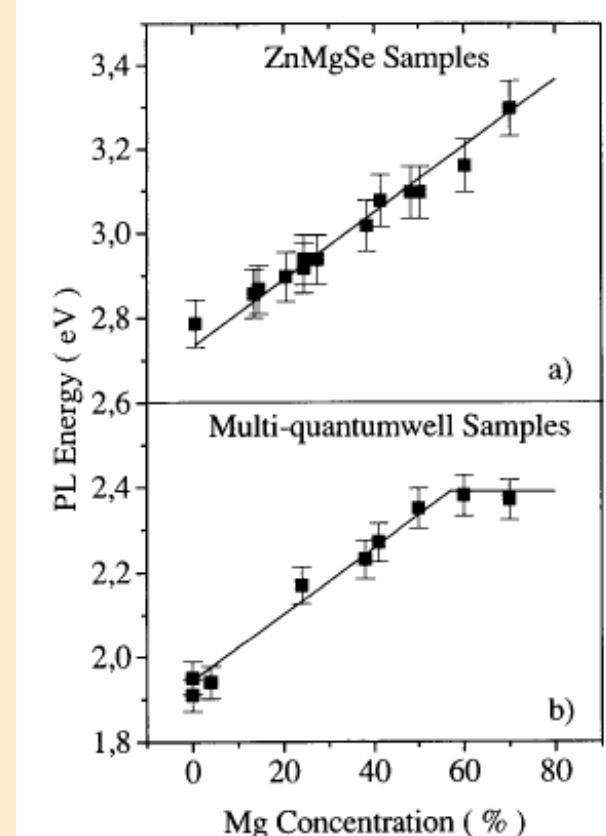


Fig. 2. (a) Energy of the near band edge PL data for the  $Zn_{1-x}Mg_xSe$  samples as a function of  $x$ . The solid line is a linear fit to the data that gives an energy gap variation of 7.8 meV per percent Mg content change. (b) PL peak energy for the  $ZnMgSe/ZnTe$  multi-quantum-well samples as a function of Mg content in the  $ZnMgSe$  layer. The fit gives the same energy dependence versus Mg content as in (a). The measurements were taken at 4.2 K, using an Ar laser line at 363.8 nm for excitation.

Type I-type II band offset transition of the  $ZnMgSe$ -- $ZnTe$  system  
S. O. Ferreira, H. Sitter, W. Faschinger, R. Krump and G. Brunthaler [J](#)

[ournal of Crystal Growth Volume 146, Issues 1-4, 1995, Pages 418-421](#)

# ZnSe ↔ ZnTe ↔ MgSe vs. GaN

Manufacturing Industry

## Blue-green semiconductor laser with 488 nm wavelength developed.(Optoelectronics)

[New Materials Asia](#), [March, 2008](#)



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RESEARCH

Nichia Corp, Japan, has developed a blue-green light-emitting semiconductor laser element whose centre wavelength is 488 nm in a continuous oscillation. It aims to start sample shipments of the laser in March 2008.

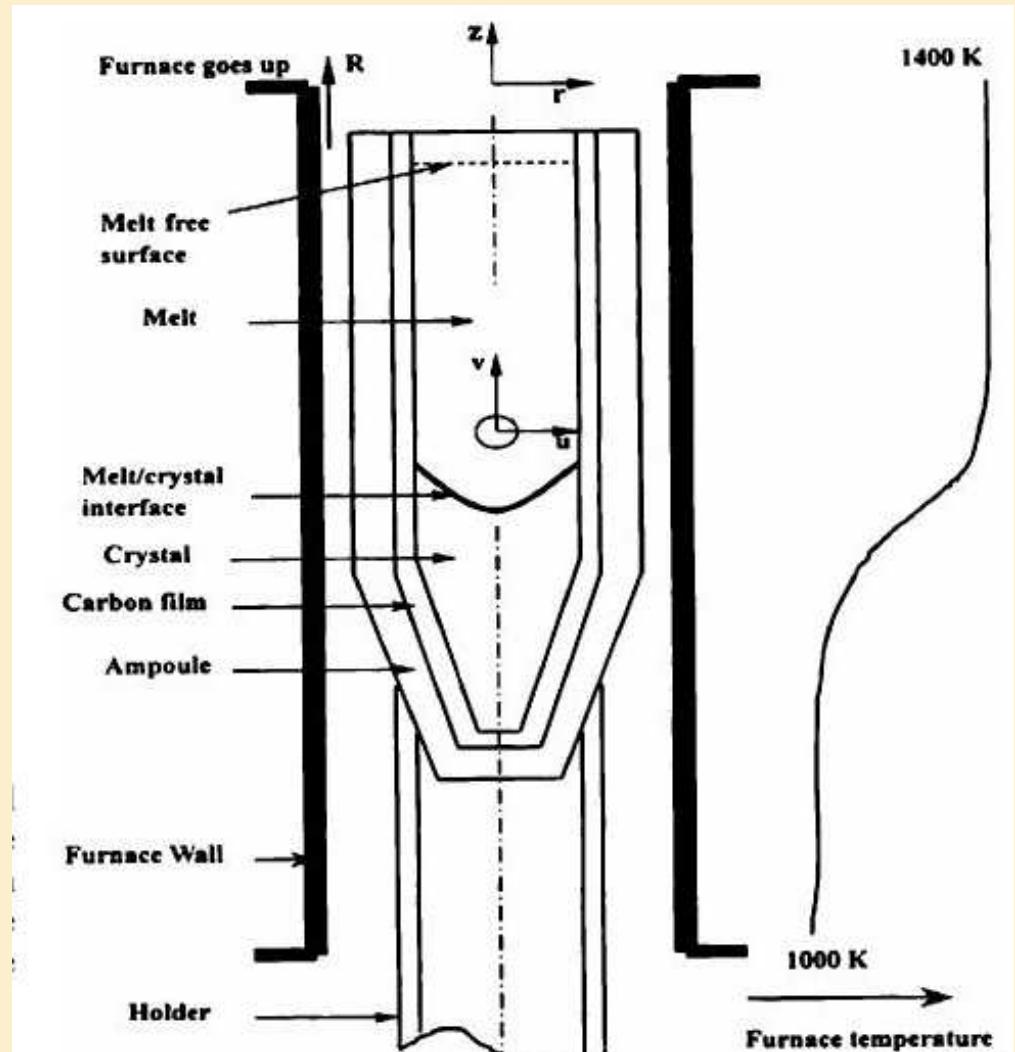
The luminous wavelength of the laser is the longest of all the products with a gallium nitride (GaN) semiconductor laser element.

# dopants

- **Beryllium:**
  - increase the lattice rigidity (covalent bonding)
  - better controlling the band gap and lattice constant to get matching with III-V etc.
  - UV detectors with 3 orders rejection rate vs VIS
- **Magnesium:**
  - tailoring band gap
- **Manganese:**
  - opto-magnetic applications

# II-VI ternary synthesis

- Thin films
  - metalloorganic chemical vapour deposition (MOCVD)
- Bulk:
  - Bridgman-Stockbarger technique



# Samples

- 1) ZnSe doped with Be, Mg, Mn,
- 2) ZnTe doped with Cr

From the melt (ZnSe + Be, Mg, Mn):

- 1) hydrostatic pressure  
10-13 MPa Ar  
1850 K 1.5 h + 2.7 mm/h
- 2) upper part removed, crushed,  
repeated
- 3) cut, mechanically polished  
and chemically etched

$Zn_xSe$ : Be 15% Mn 7%  
Be 5% Mn 15%  
Be 14% Mg 6%  
Be 6% Mg 14%

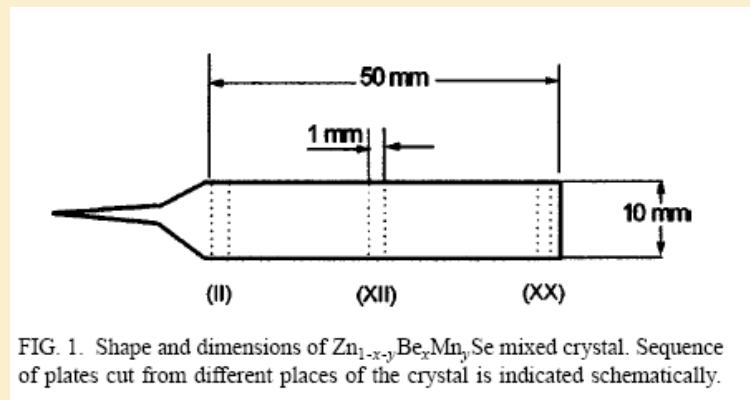
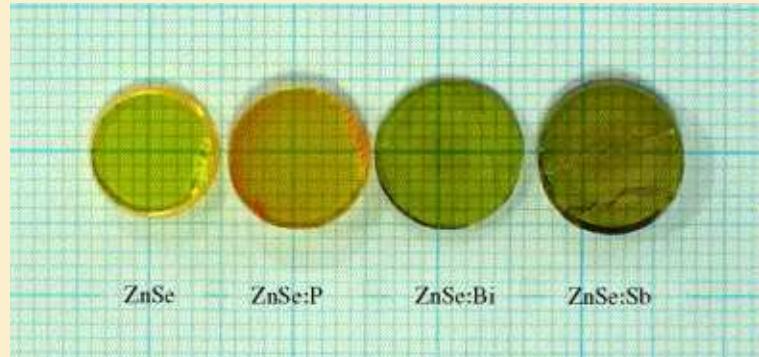


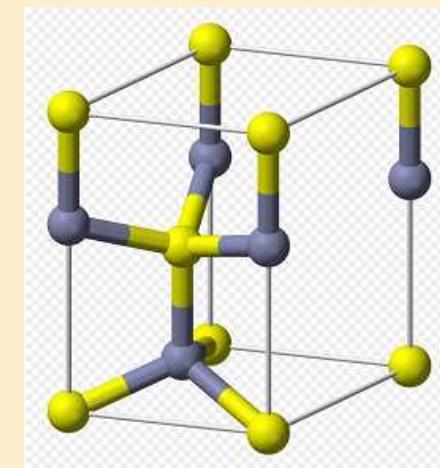
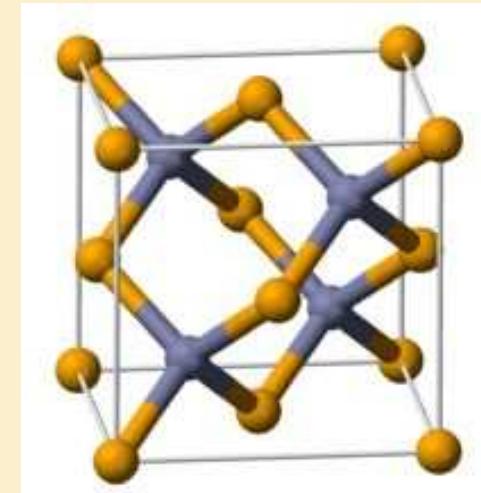
FIG. 1. Shape and dimensions of  $Zn_{1-x-y}Be_xMn_ySe$  mixed crystal. Sequence of plates cut from different places of the crystal is indicated schematically.



# Samples

## Features

- resistivity  $M\Omega \text{ cm}$ ,
- main defects: Zn - vacancies
- cubic (sphalerite) for  $\text{Mg} < 16\%$
- wurtzite for  $\text{Mg} > 16\%$
- non annealed in Zn vapour
- Slow growth – few defects ( $< 10^{15} \text{cm}^{-3}$ ) in undoped



# Photoluminescence

1)  $\text{Zn}_{0.94}\text{Mg}_{0.06}\text{Se}$

2.86 eV exciton line

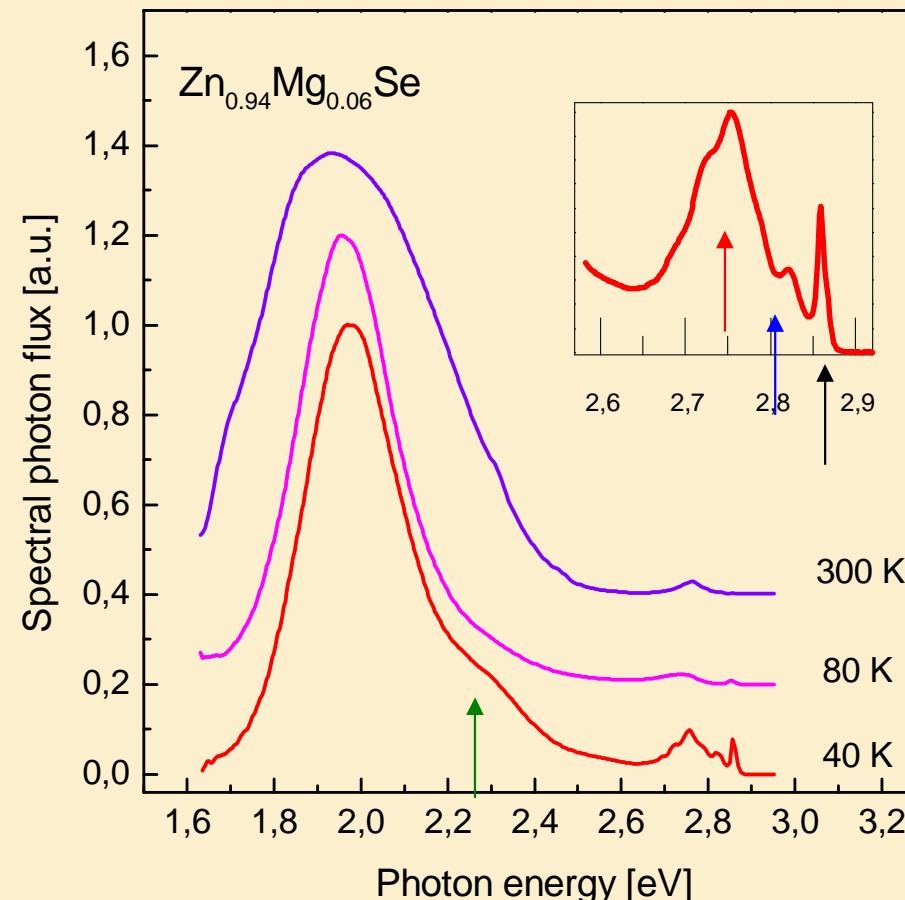
2.75 „edge emission”  
(shallow D-A pairs)

2.2 eV, 1.98 eV  
**deep level**  
emission bands

2.816 eV an exciton  
bound to „some” deep  
defect center

2.2 eV cation vacancy?

He-Cd, 325 nm  
55 mW



Nb. 2.2 eV emission disappears after 2 days annealing at 1230K in Zn vapour !

# Photoluminescence

1)  $\text{Zn}_{0.96}\text{Be}_{0.04}\text{Se}$

J. Appl. Phys. 103, 013501 (2008)

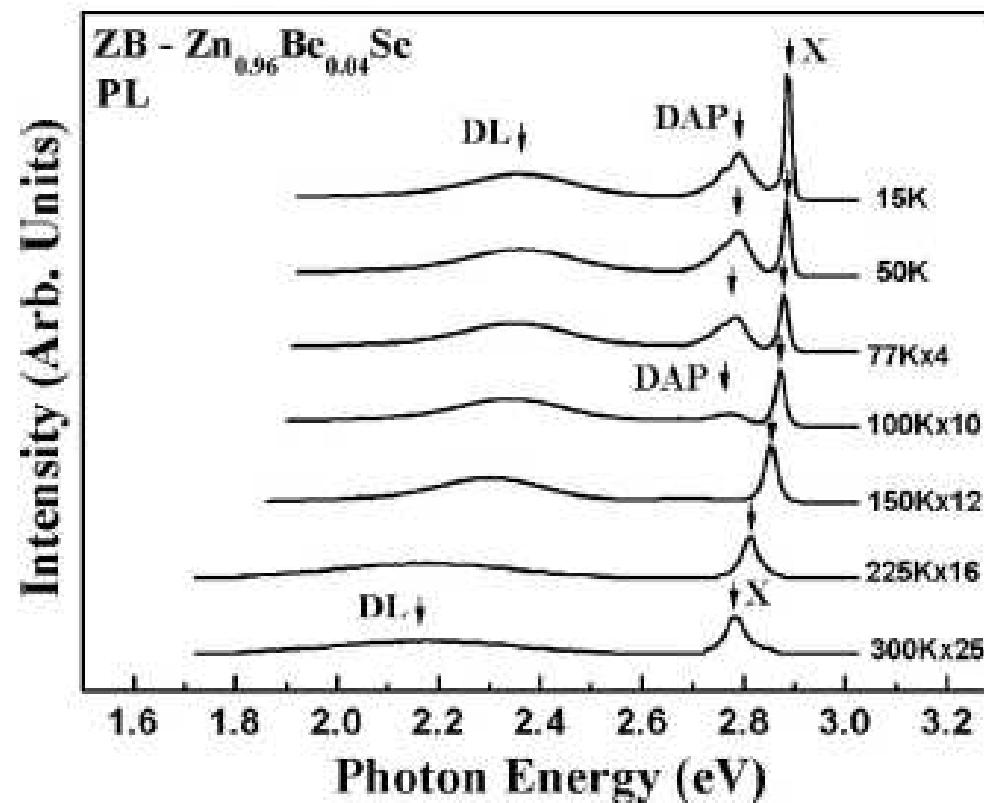


FIG. 1. The PL spectra of a  $\text{Zn}_{0.96}\text{Be}_{0.04}\text{Se}$  at several temperatures between 15 and 300 K.

Firszt et al.

# Photoluminescence

$\text{Zn}_{0.88}\text{Be}_{0.06}\text{Mg}_{0.06}\text{Se}$

093522-3 Dumcenco *et al.*

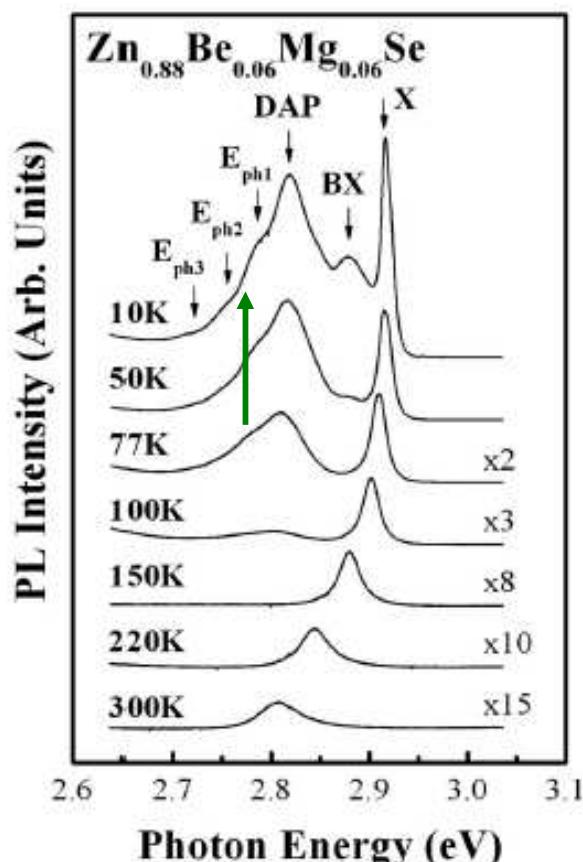


FIG. 2. The PL spectra of  $\text{Zn}_{0.88}\text{Be}_{0.06}\text{Mg}_{0.06}\text{Se}$  mixed crystal at several temperatures between 10 and 300 K. The band-edge excitonic line, free to band radiative recombination and DAP emission with clearly seen LO-phonon replicas are indicated by arrows.

$\text{Zn}_{0.68}\text{Be}_{0.06}\text{Mg}_{0.26}\text{Se}$

J. Appl. Phys. 103, 093522 (2008)

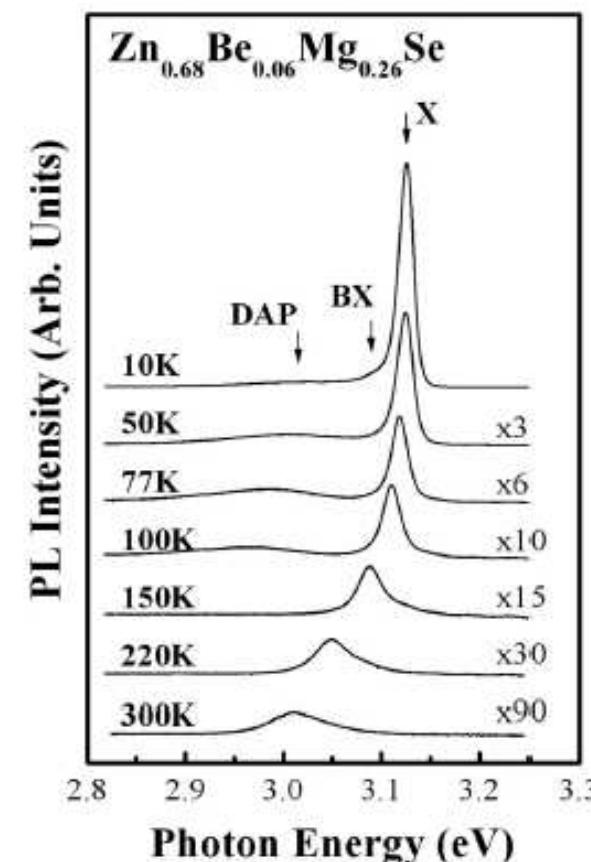


FIG. 4. The PL spectra of  $\text{Zn}_{0.68}\text{Be}_{0.06}\text{Mg}_{0.26}\text{Se}$  crystal at several temperatures between 10 and 300 K. The band-edge excitonic line, free to band radiative recombination and DAP emission are indicated by arrows.

# Previous positron studies

JOURNAL OF APPLIED PHYSICS

VOLUME 94, NUMBER 3

1 AUGUST 2003

## Defect characterization of ZnBeSe solid solutions by means of positron annihilation and photoluminescence techniques

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W. Paszkowicz

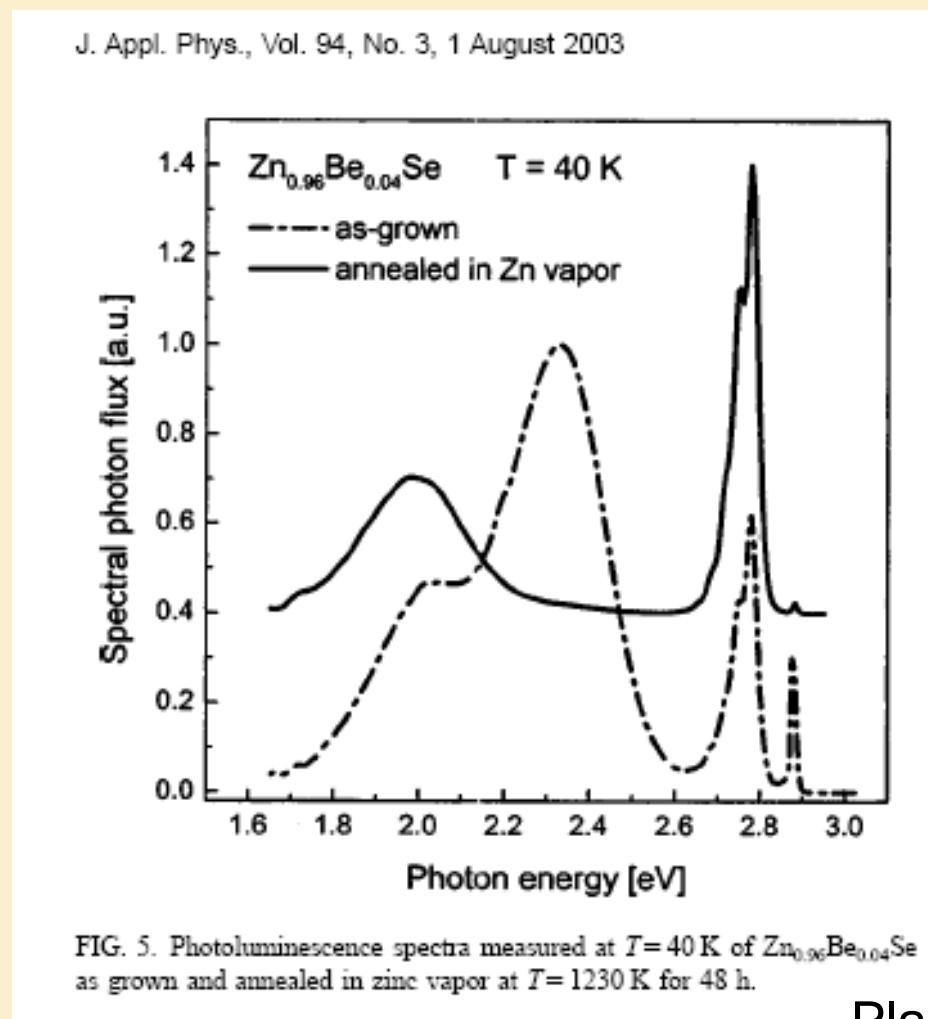
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# Photoluminescence

- $\text{Zn}_{0.96}\text{Be}_{0.04}\text{Se}$



Plazaola et al. 2003

# Photoluminescence

- $\text{Zn}_{1-x}\text{Be}_x\text{Se}$

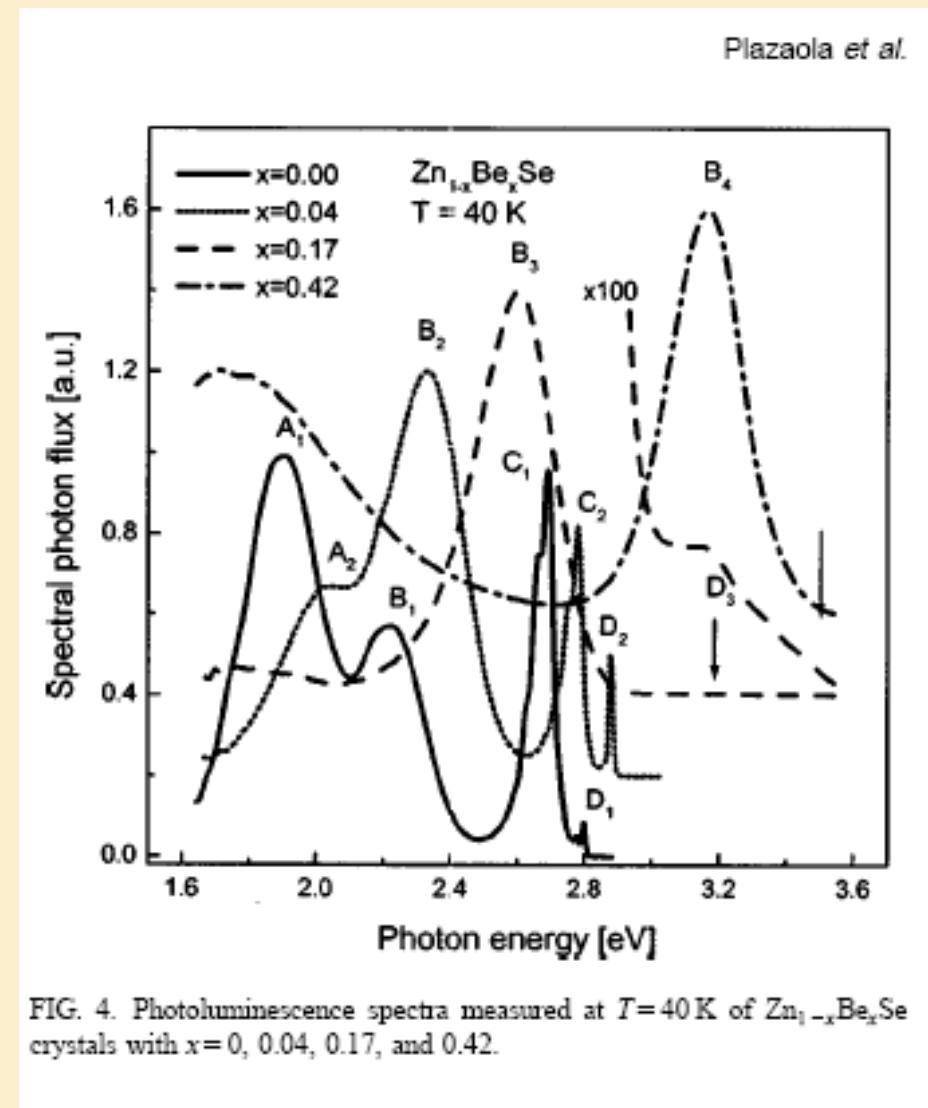


FIG. 4. Photoluminescence spectra measured at  $T=40 \text{ K}$  of  $\text{Zn}_{1-x}\text{Be}_x\text{Se}$  crystals with  $x=0, 0.04, 0.17$ , and  $0.42$ .

Plazaola *et al.* 2003

# Positron lifetime

Plazaola *et al.* 1649

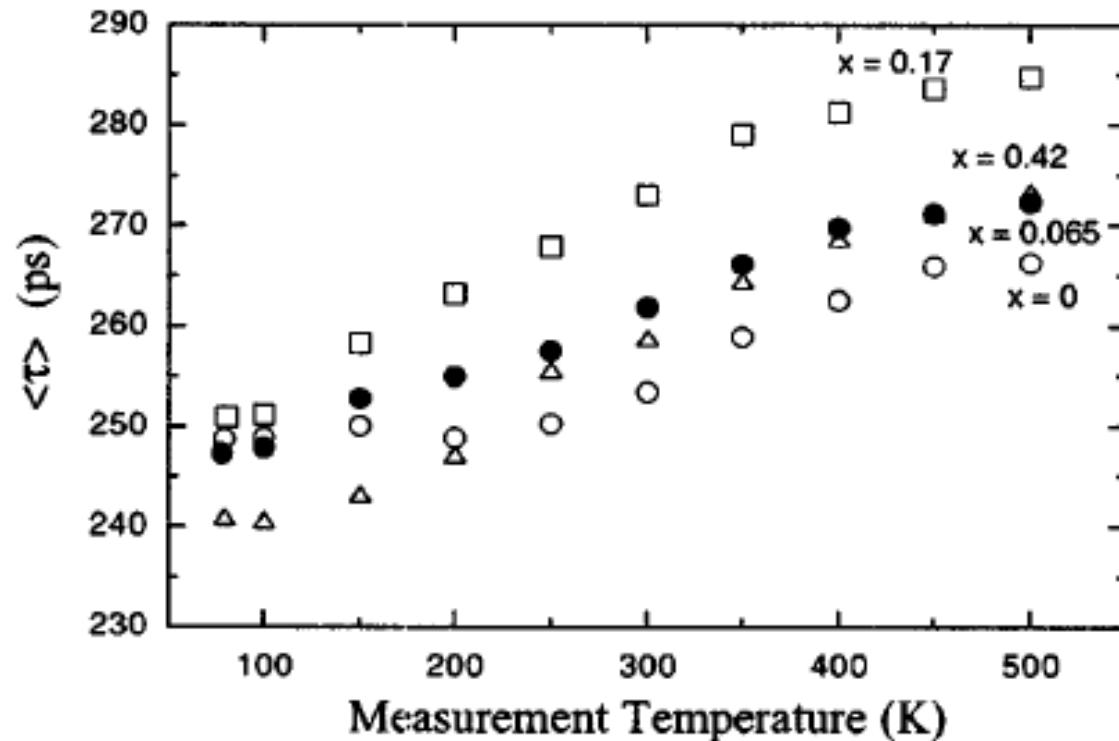
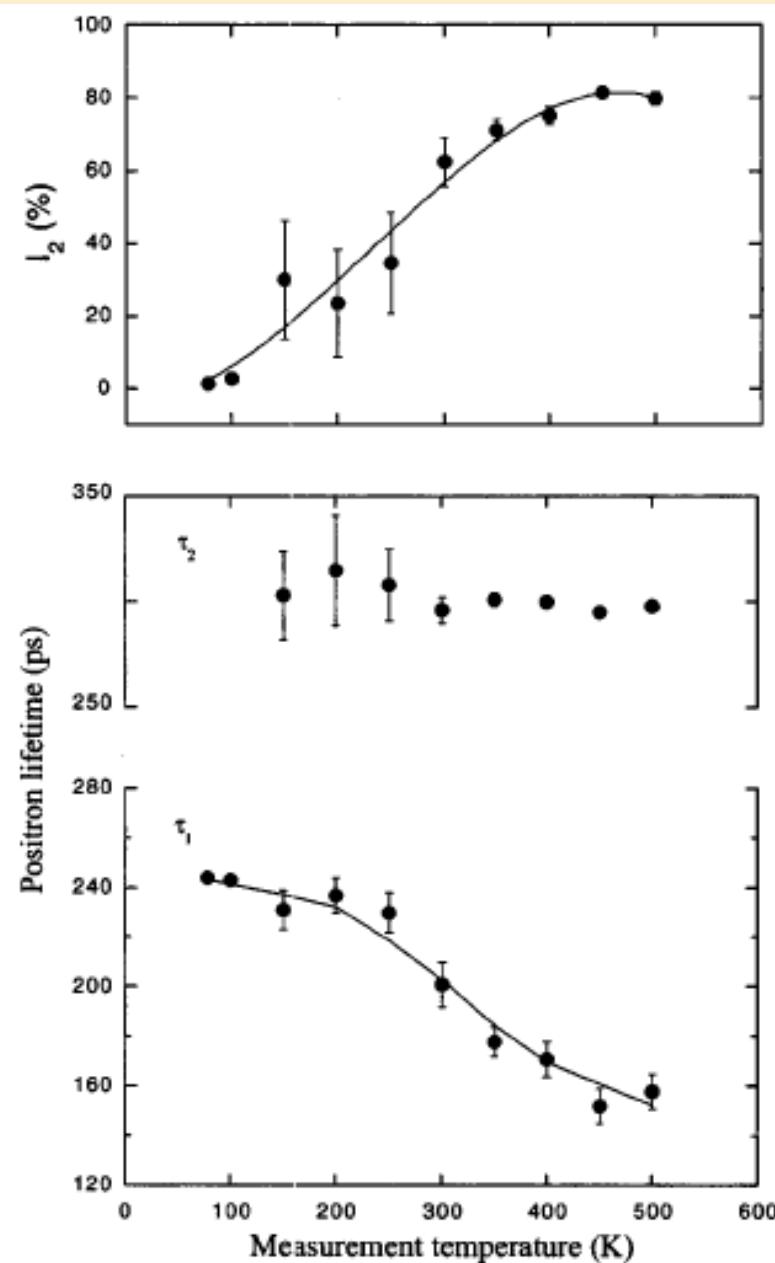


FIG. 1. Positron average lifetime  $\langle \tau \rangle$  vs the temperature for  $Zn_{1-x}Be_xSe$  crystals with  $x = 0$  (open circles), 0.065 (closed circles), 0.17 (squares), and 0.42 (triangles).

# Positron lifetime

Be -6.5%



J. Appl. Phys., Vol. 94, No. 3, 1 August 2003

TABLE I. Data for the  $Zn_{1-x}Be_xSe$  sphalerite structures used in the calculations. The structures simulated have lattice constant  $a$ .  $\tau_B$  corresponds to the theoretical bulk lifetimes calculated in bulk compound semiconductors.

$x$	$a$ ( $\text{\AA}$ )	Volume/atom ( $\text{\AA}^3$ )	$\tau_B$ (ps)
0	5.6675	22.76	250.5
0.0625	5.6304	22.31	246.8
0.15625	5.5817	21.74	242.1
0.25	5.5330	21.17	237.4
0.5	5.4031	19.72	225.5

TABLE II. Calculated lifetimes  $\tau_v$  in different types of neutral and unrelaxed vacancy-type defects in  $Zn_{1-x}Be_xSe$ .

$x$	$V_{\text{Zn}}$	$V_{\text{Be}}$	$V_{\text{Se}}$	$V_{\text{Zn}}V_{\text{Se}}$	$V_{\text{Be}}V_{\text{Se}}$
	$\tau_v$ (ps)	$\tau_v$ (ps)	$\tau_v$ (ps)	$\tau_v$ (ps)	$\tau_v$ (ps)
0	264.9		278.9	343.8	
0.0625	260.8	260.5	281.0	339.4	339.9
0.15625	255.3	255.1	275.8	333.6	333.9
0.25	252.1	250.1	270.5	330.8	328.3
0.5	240.3	238.4	262.3	317.7	315.8

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# Positron lifetime

$Zn_{1-x} Be_x Se$

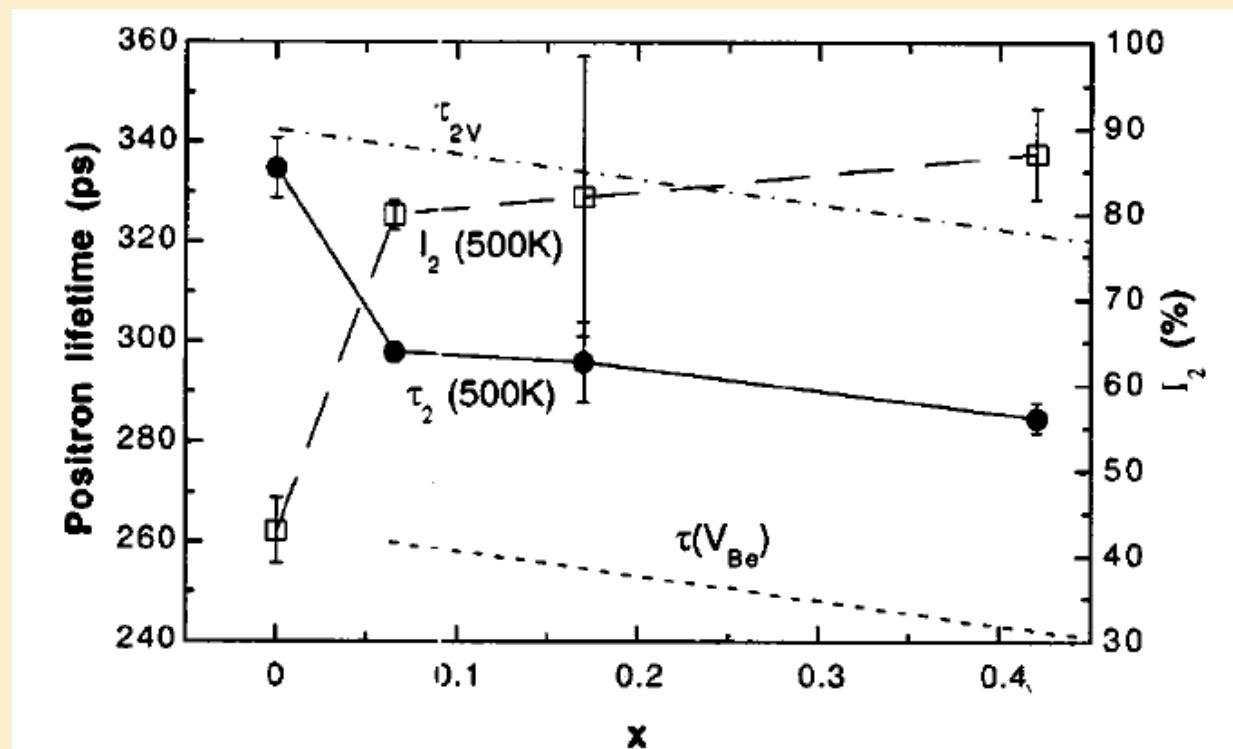


FIG. 3.  $\tau_2$  and  $I_2$  are the lifetime and intensity, respectively, of the second component measured at 500 K vs the Be content in the compound semiconductor. The continuous and broken lines correspond to fits of the theoretical positron lifetimes in monovacancies of Be and in divacancies, respectively.

divacancy relaxed inward  
monovacancy relaxed outward

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# Trento slow positron beam

$E=100 \text{ eV} - 25 \text{ keV}$   
spot < 5 mm

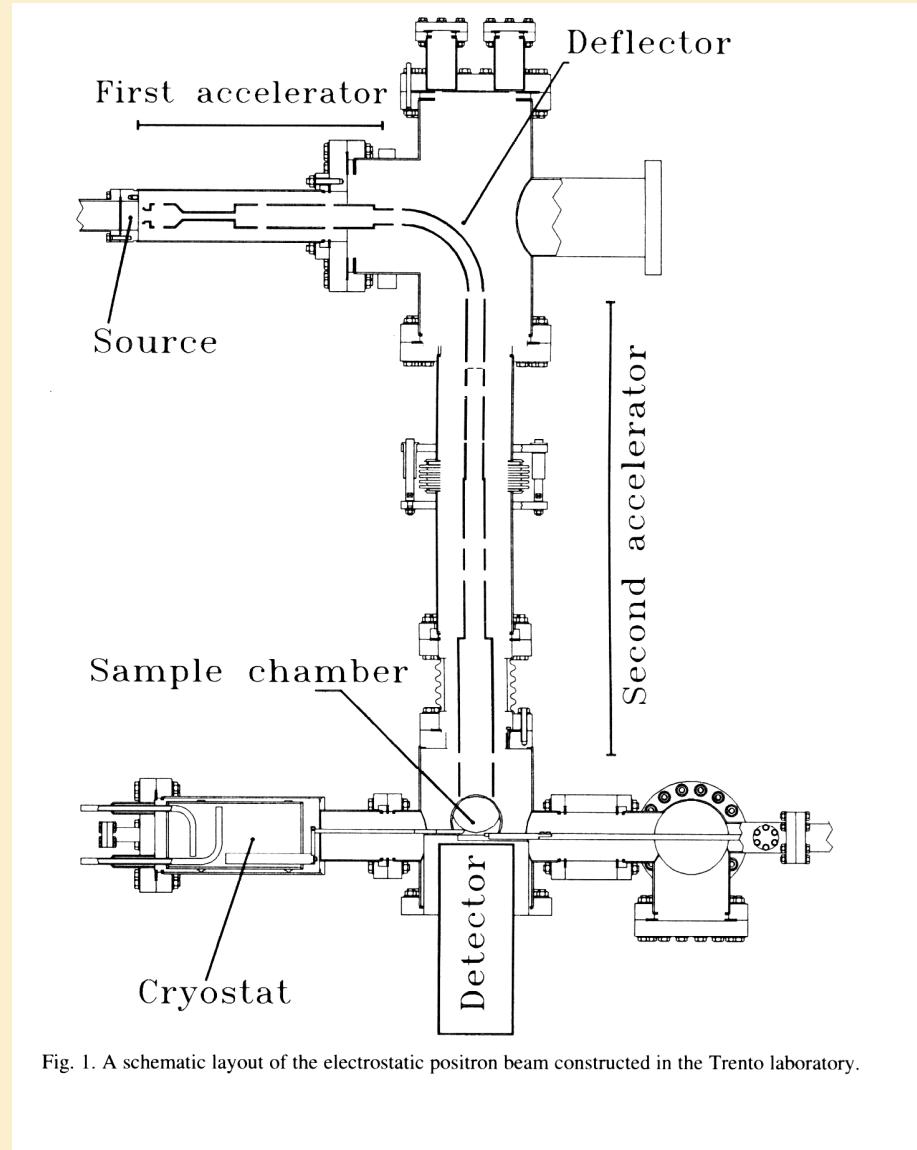
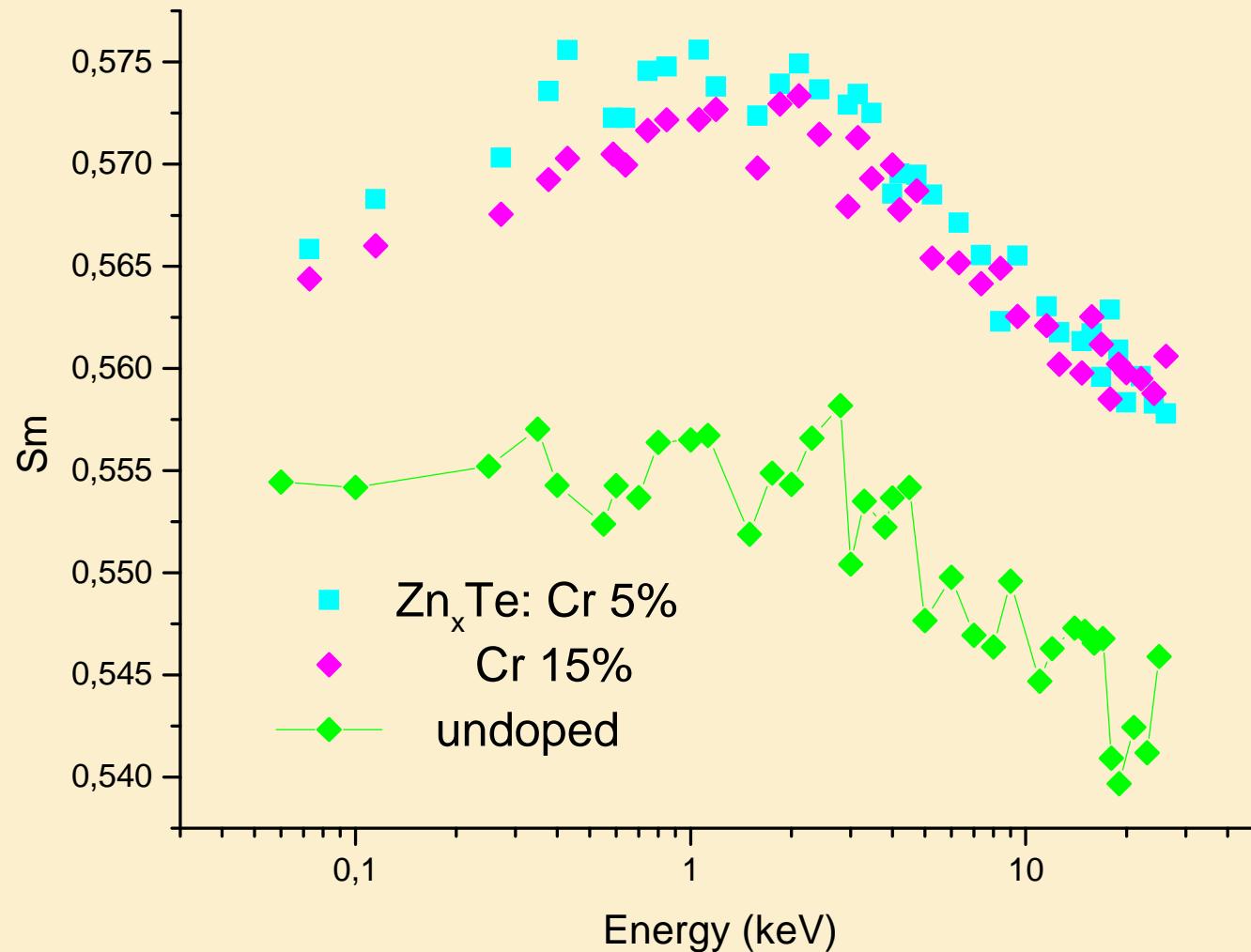
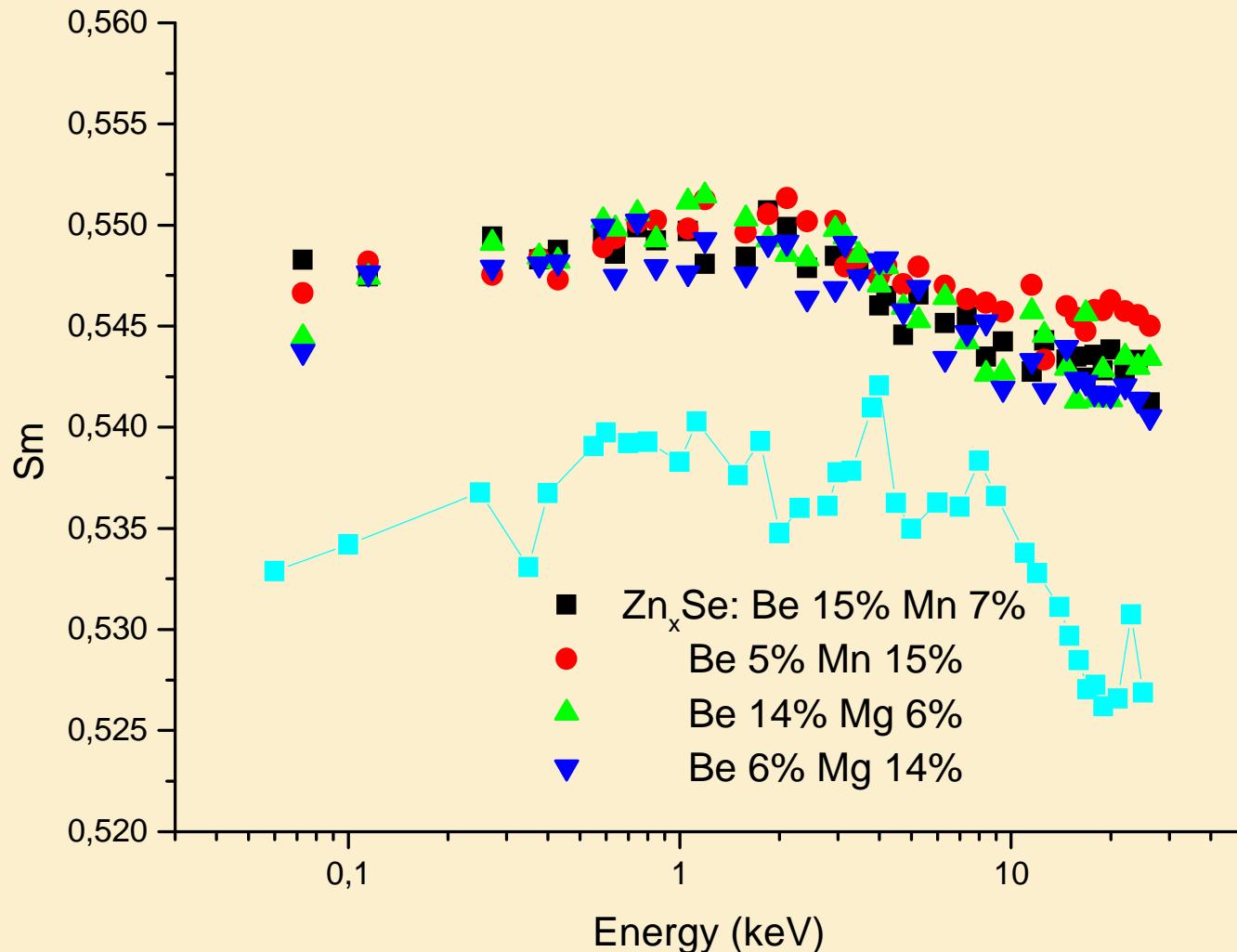


Fig. 1. A schematic layout of the electrostatic positron beam constructed in the Trento laboratory.

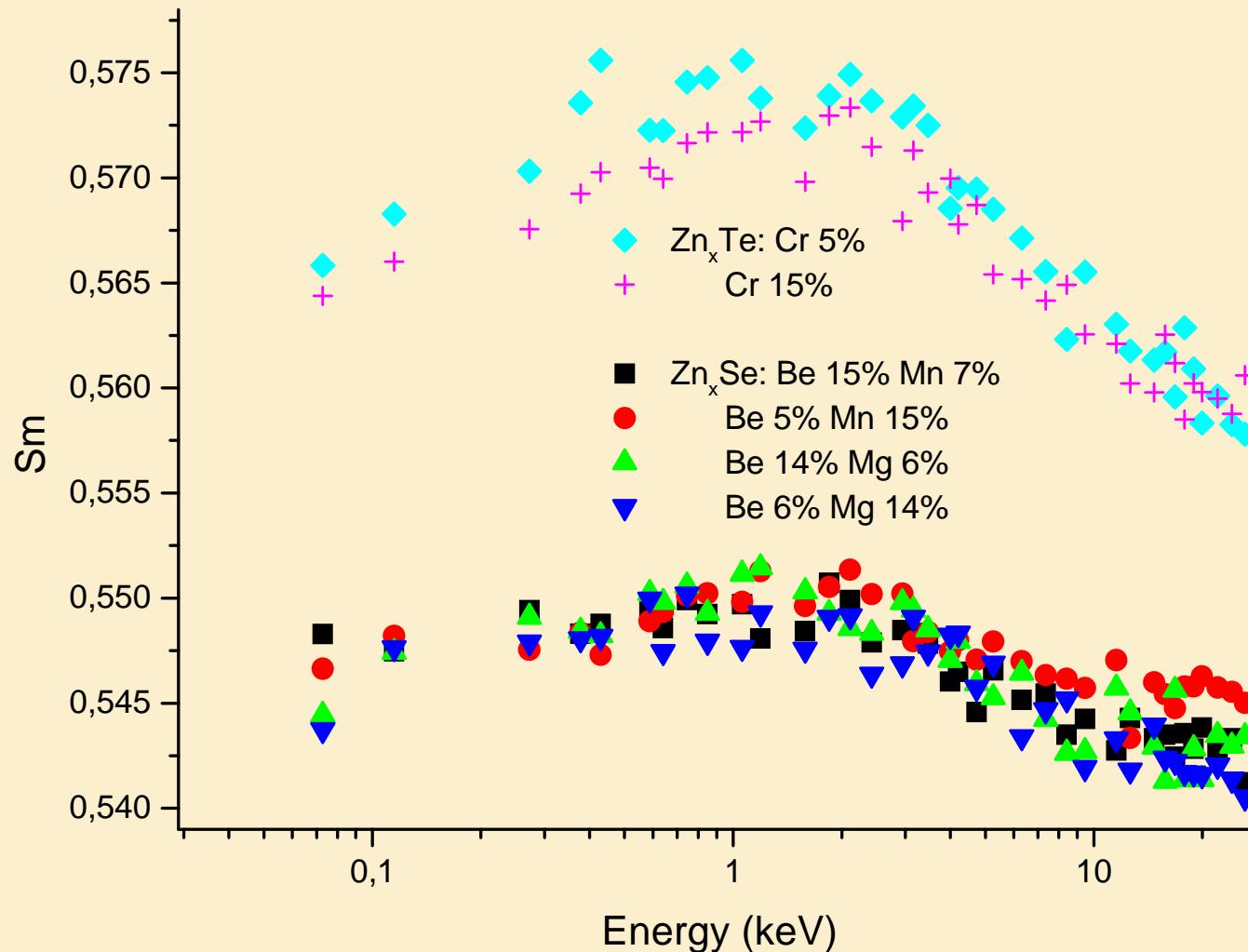
# Doppler broadening ZnTe



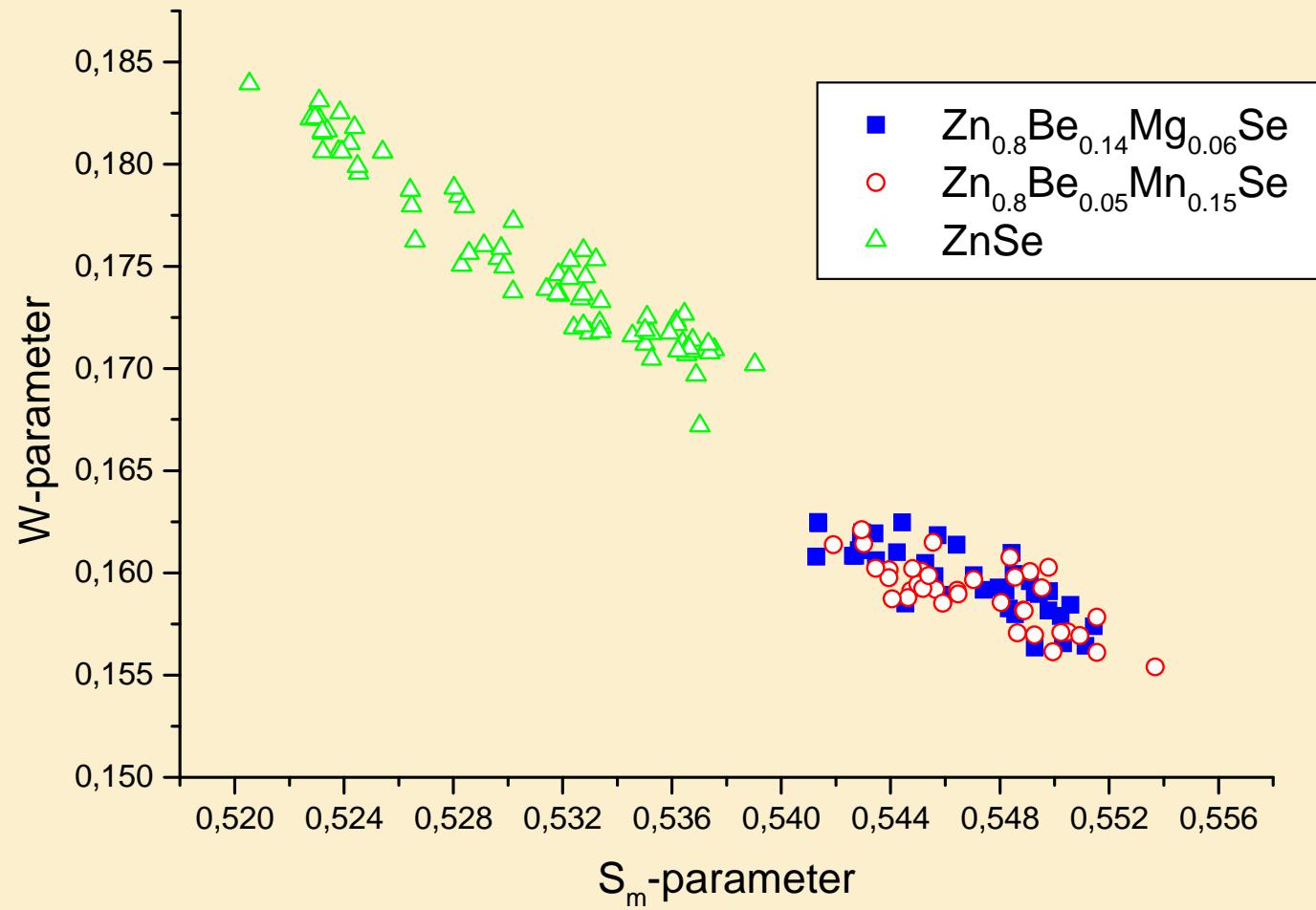
# Doppler broadening ZnSe



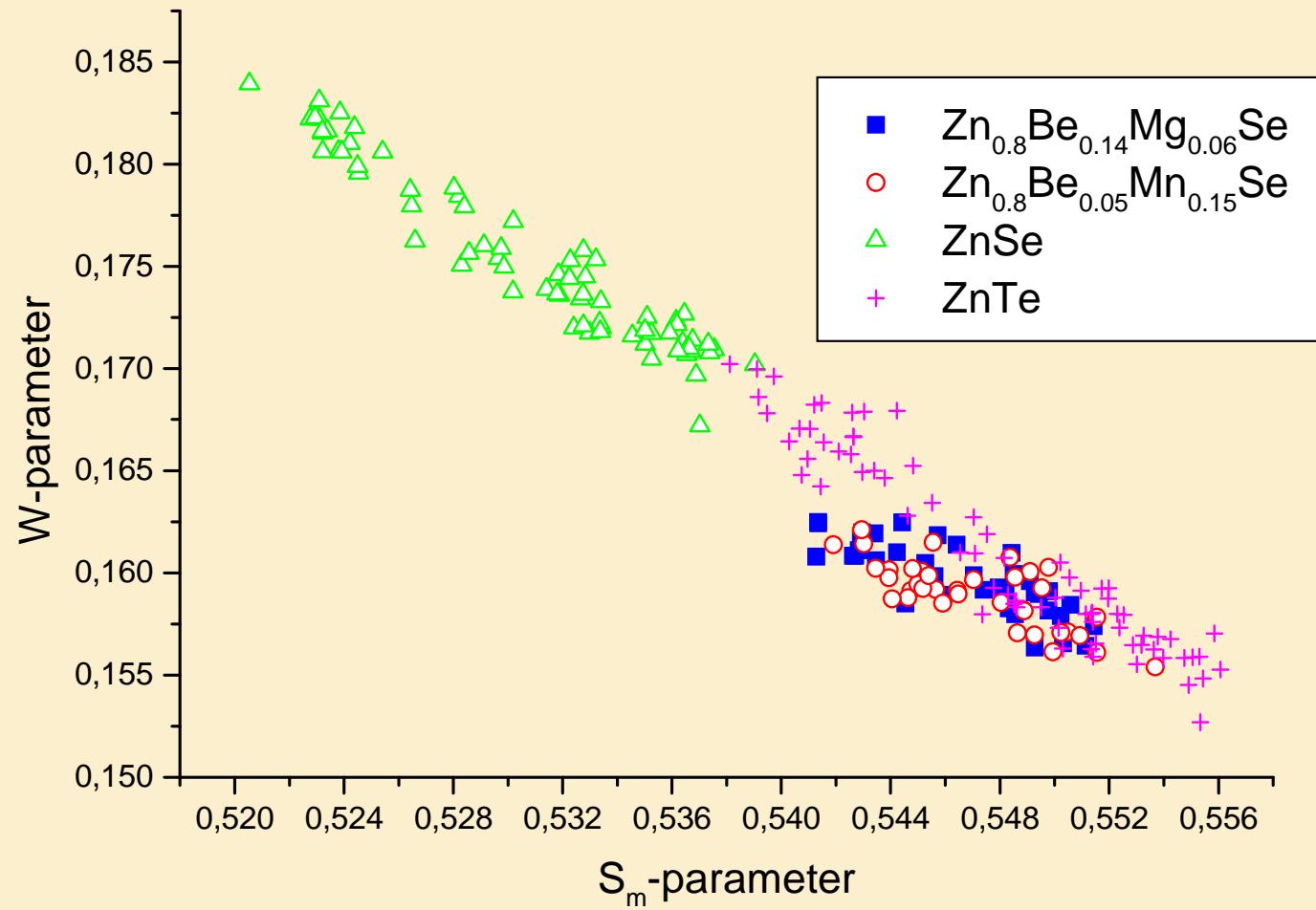
# Comparison ZnTe - ZnSe



# S-W curve



# S-W curve



# work in progress...

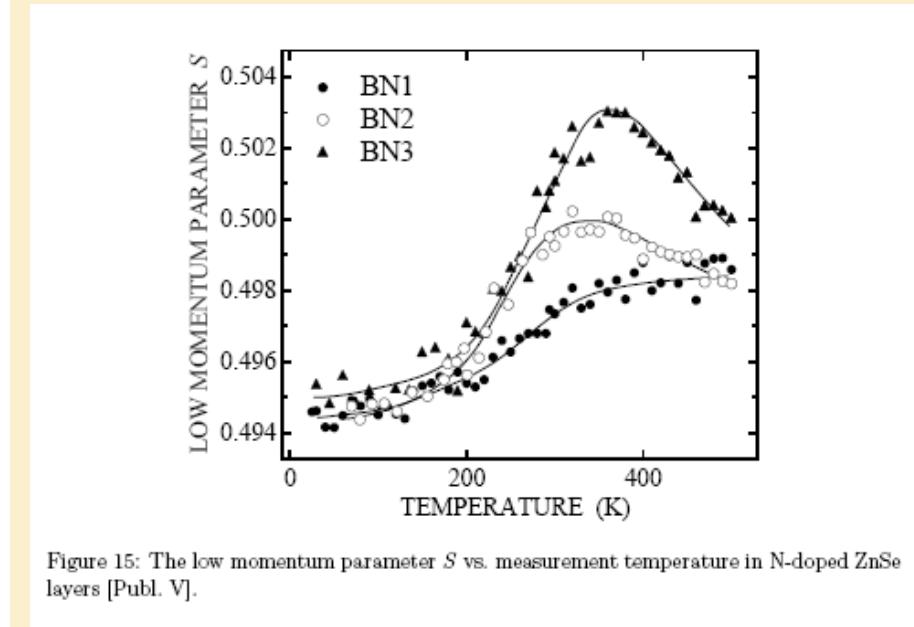
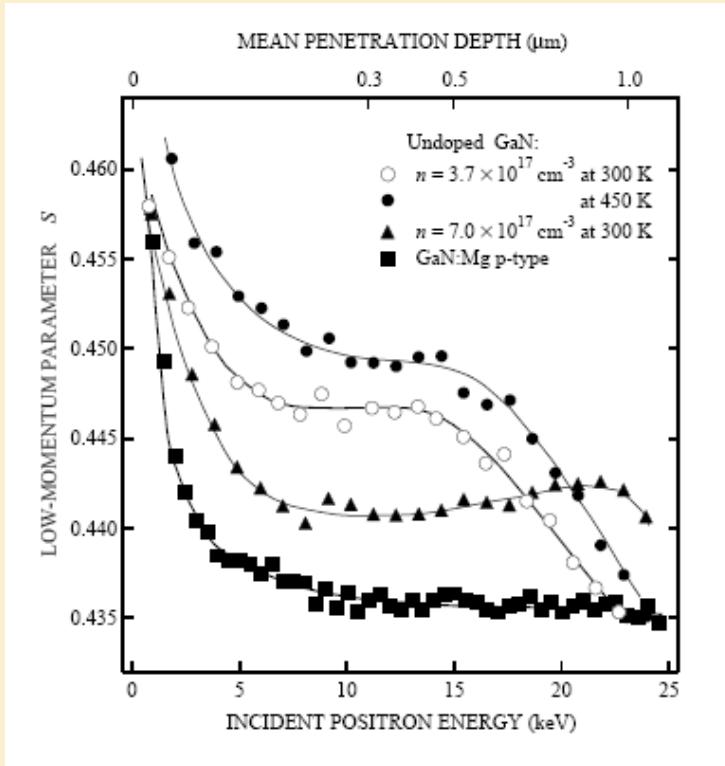


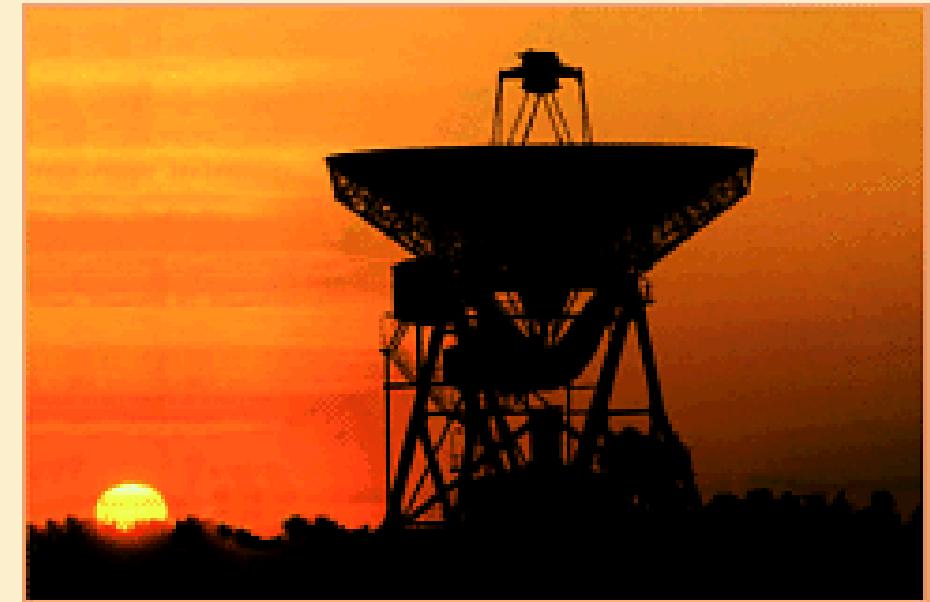
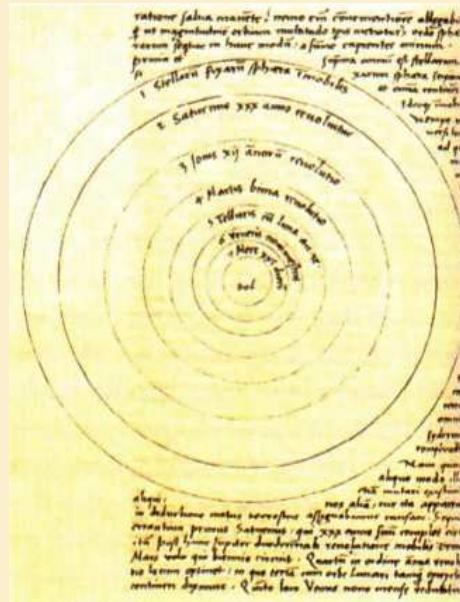
Figure 15: The low momentum parameter  $S$  vs. measurement temperature in N-doped ZnSe layers [Publ. V].

CHARACTERIZATION OF NATIVE VACANCIES  
IN EPITAXIAL GaN AND ZnSe  
SEMICONDUCTOR LAYERS BY POSITRON  
ANNIHILATION SPECTROSCOPY

- Temperature dependence
- Surface defects?
- Doppler coincidence
- Lifetime

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Thank you for the attention!

