UNIVERSITY
OF APPLIED SCIENCES
MUNICH

Temperature dependent FTIR analysis for the LVM band of the ($^{14}N_{As}$-V_{Ga}) complex in gallium arsenide

Laboratory
of
Solid State Physics

Project work

of

Nicola Kovač

FK06, MNM

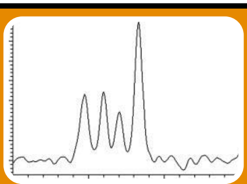
Structure

Theoretical basics

- Vibrations of molecules, crystals and defects
- Vibrational spectroscopy
- Infrared spectroscopy

Experimental setup and enforcement

- Aim of the work
- Experimental apparatus and samples
- Enforcement



Measuring results

- Discussion and evaluation

Outlook

- Piezospectroscopy

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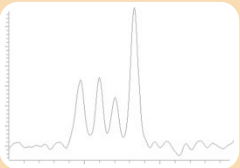

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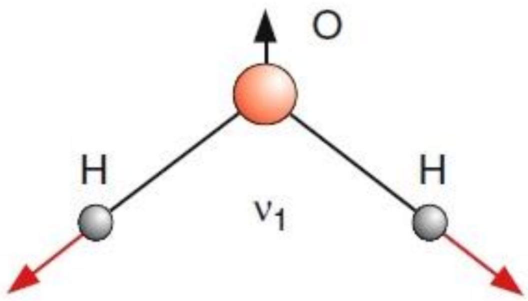
Molecular and crystal vibrations

- Definition: Time periodic changes of bond lengths and angles
- System motion = Interference of maximum (3*N*-6) normal vibrational modes

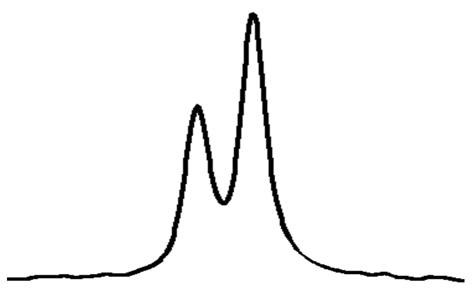


Molecular and crystal vibrations

- Definition: Time periodic changes of bond lengths and angles
- System motion = Interference of maximum (3*N*-6) normal vibrational modes
- In spectroscopy:

  Measurement of energetic transitions between

  vibronic states ⇒ **Bands** in spectrum



- Requirements:
  - existing dipole moment $\vec{\mu}(\vec{r})$
  - Transition dipole moment

$$\vec{R}_{mn}(\vec{r}) = \left.\frac{d\vec{\mu}}{d\vec{r}}\right|_0 * \int \psi_n^* \vec{r} \psi_m dV \neq 0$$

⇒ temporally changing dipole moment $\vec{\mu}$ ⇒ **infrared active band**

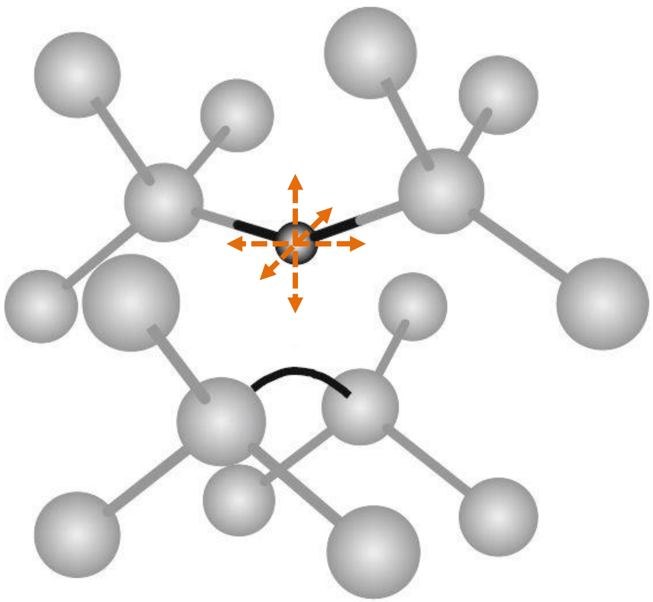
Defect vibrations

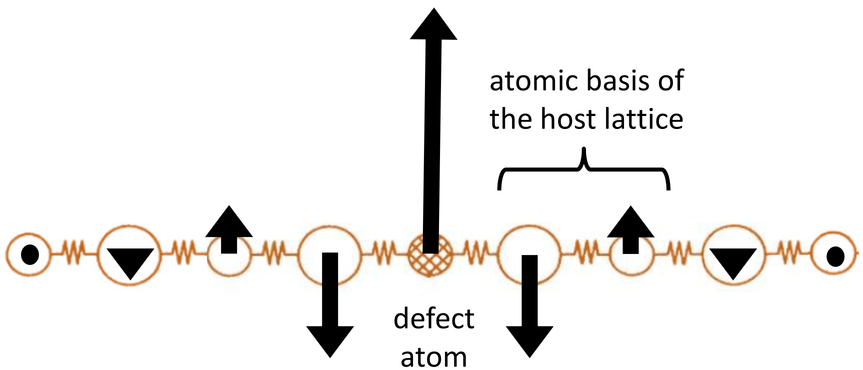
Defects in crystal alter e. g.

– lattice structure (periodicity, symmetry, …)
– lattice potential
– energy bands and states
– **lattice vibrations** (shape and frequency)

↳ among them: non-propagating vibrations concentrated at the defect position

⇒ **localized** (lattice/defect) **vibrational modes (LVM)**





Measurement of atomic vibrations

Vibrational spectroscopy

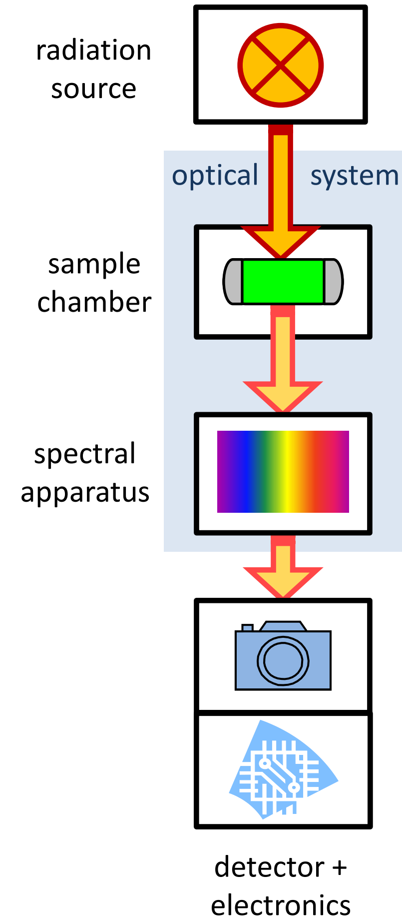
Raman spectroscopy

Spectral range: VIS

Experimental technique: scattering

Infrared spectroscopy

Spectral range: IR (= NIR, MIR, FIR)



cosmic radiation	γ-rays	X-rays	UV	VIS	Near IR	Mid IR	Far IR	micro waves	radio waves

$\tilde{\upsilon}$ (cm^{-1})	10^{10}	10^{8}	10^{6}	25000	14200	4000	650	12	0.05
λ (nm)	10^{-4}	10^{-2}	1	400	700	2500	15400	830000	2×10^{8}

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Experimental technique: scattering

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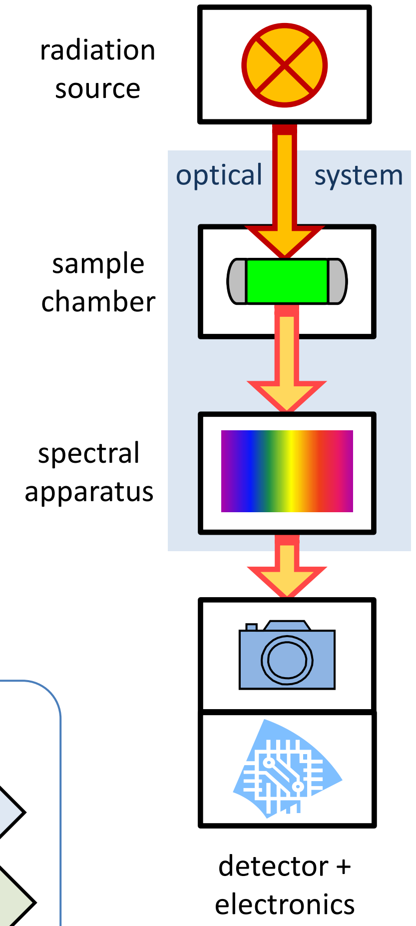
Spectral range: IR (= NIR, MIR, FIR)

Exp. technique:

- transmission
- reflection
- emission

Spectrometer technique:

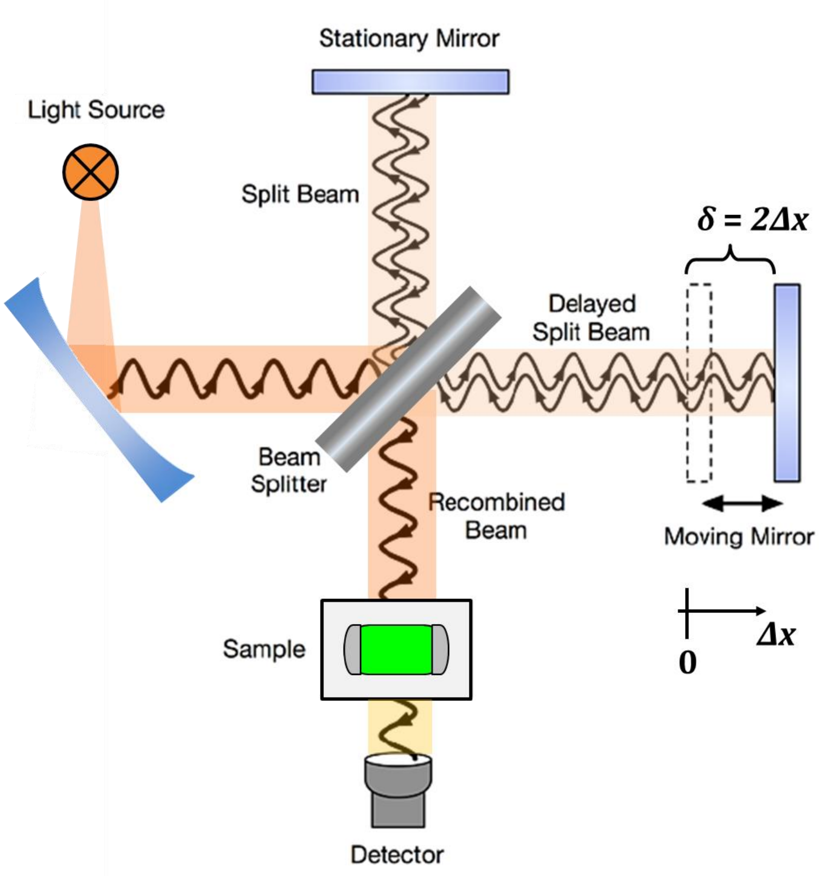
non-dispersive	filter
dispersive	prism/grating + slit
Fourier	interferometer + Fourier analysis



FTIR spectroscopy

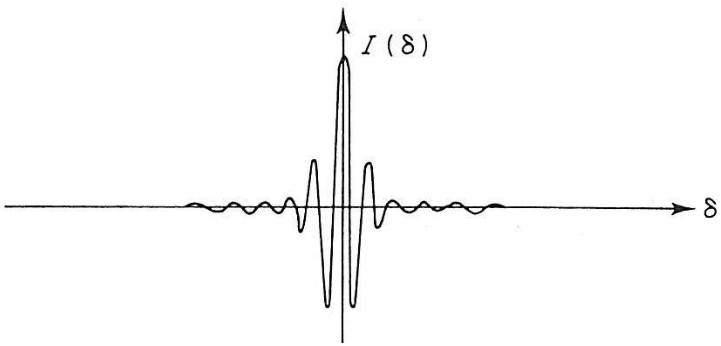
Main component:

Michelson interferometer



Measuring results:

a) direct: Interferogram $\tilde{I}(\delta)$



FT

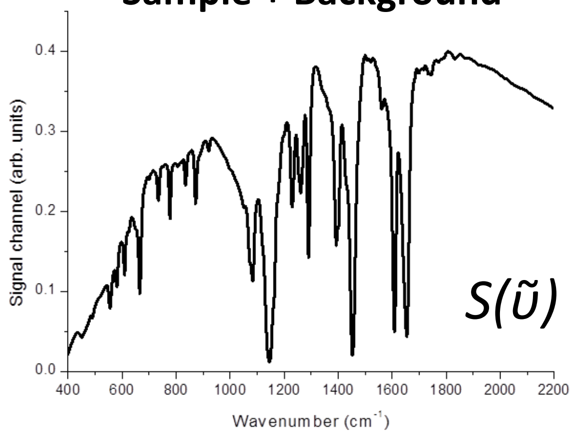
b) indirect: Spectrum *S(ũ)*

$$S(\tilde{\upsilon}) = \int_{-\infty}^{\infty} \tilde{I}(\delta) * e^{-i*2\pi*\tilde{\upsilon}*\delta} d\delta$$

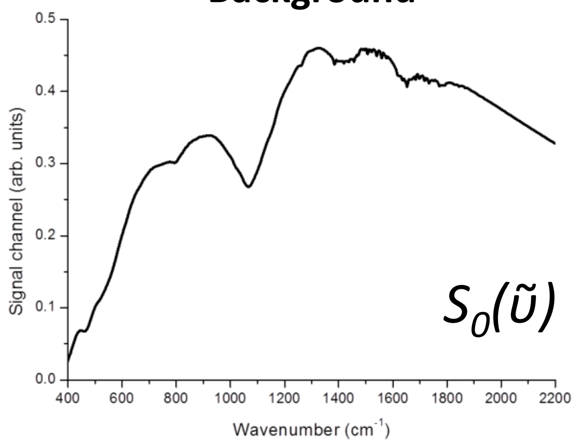
Practise: $S(j) = \sum_{n=0}^{N-1} \tilde{I}(n) * e^{-i*2\pi*\frac{j*n}{N}}$

FTIR spectroscopy

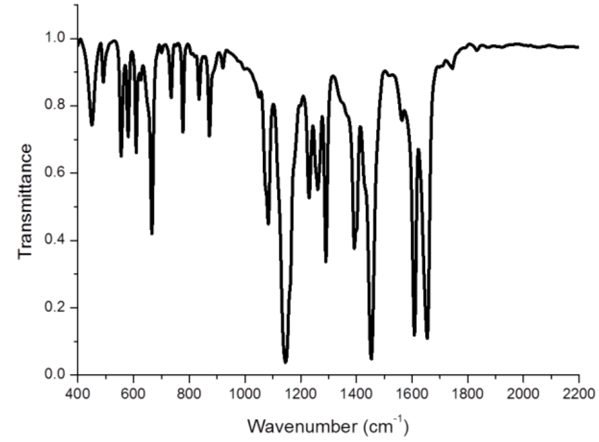
Sample + Background



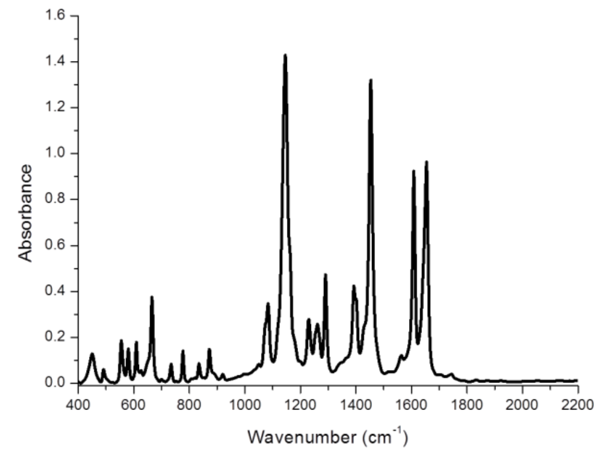
Background



Transmission



Absorbance



$$T = \frac{S(\tilde{\upsilon})}{S_0(\tilde{\upsilon})}$$

$$\mathcal{A} = -lg(T)$$

$$\mathcal{A} \sim c$$

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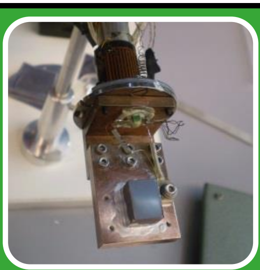

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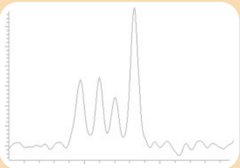

Measuring results

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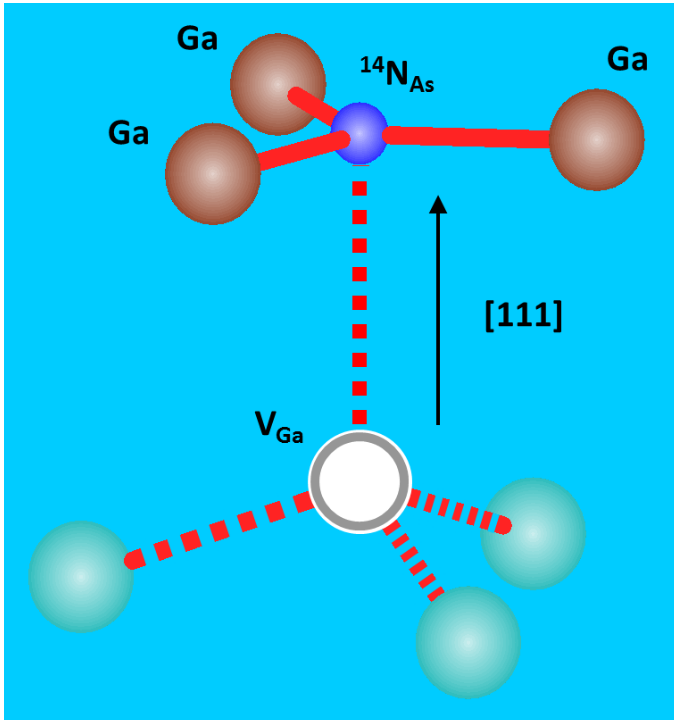
Aim of the work

($^{14}N_{As}$- V_{Ga}) complex

- First investigations in GaAs by Alt *et al.*
- Defect inside the Ga-As bond
  - ➢ $^{14}N_{As}$ atom + Ga vacancy
- quasi-plane structure of the N-Ga_3 molecule

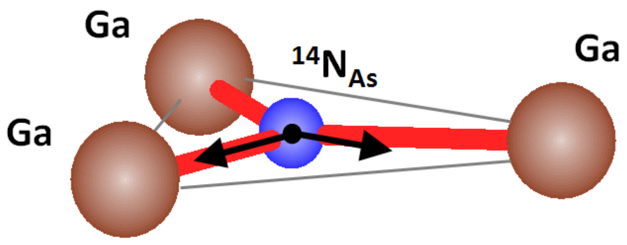


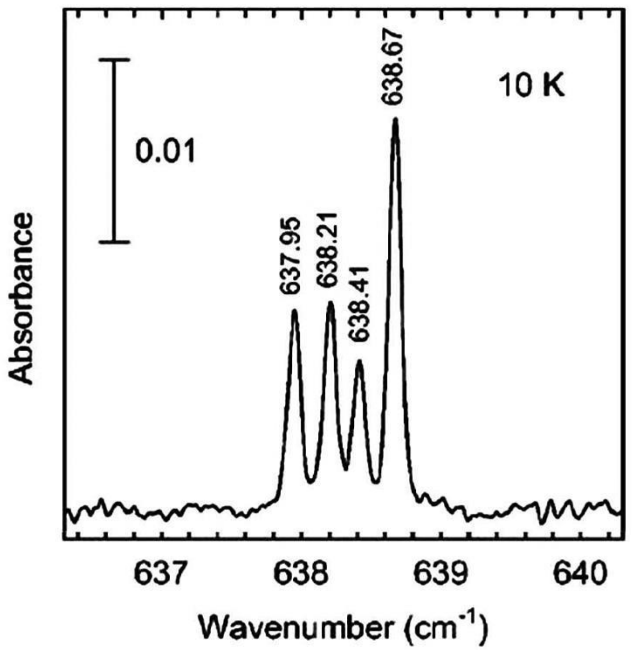
Aim of the work

($^{14}N_{As}$- V_{Ga}) complex

- First investigations in GaAs by Alt *et al.*
- Defect inside the Ga-As bond
  - ➢ $^{14}N_{As}$ atom + Ga vacancy
- quasi-plane structure of the N-Ga_3 molecule
- LVM band at $\tilde{\upsilon}$ = 638 cm^{-1}
  - ➢ 2D vibration ∥ Ga_3 plane
  - ➢ Fine structure due to isotopic mass effect

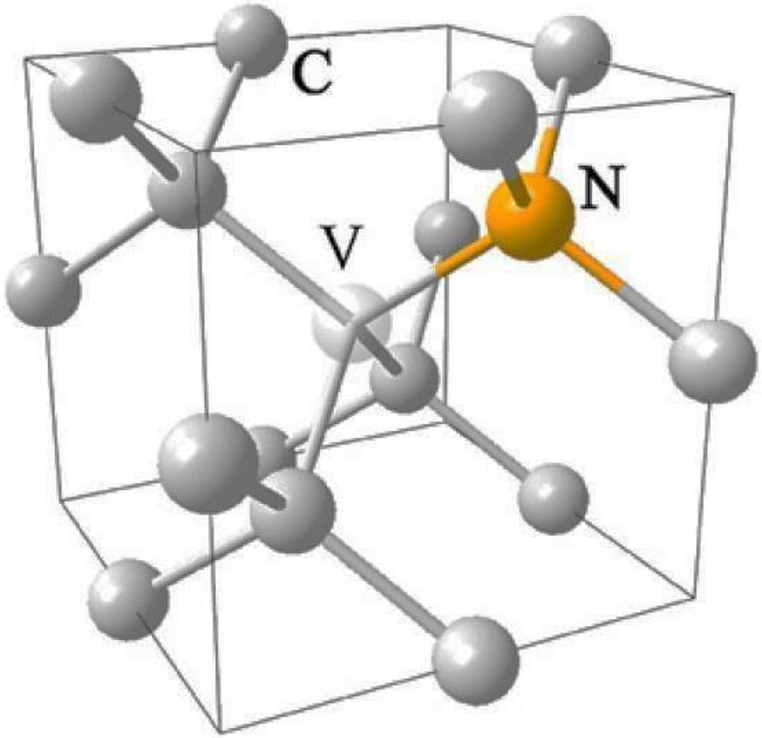
Configuration	Mode (Degen.)	Calculated frequency [cm^{-1}]
$^{14}N\ ^{71}Ga_3$	*E* (2)	637.95
$^{14}N\ ^{71}Ga_2\ ^{69}Ga_1$	*A'* (1)	638.43
	A'' (1)	637.95
$^{14}N\ ^{71}Ga_1\ ^{69}Ga_2$	*A'* (1)	638.19
	A'' (1)	638.67
$^{14}N\ ^{69}Ga_3$	*E* (2)	638.67





Aim of the work

Structural analogue:



NV^{-} defect in diamond

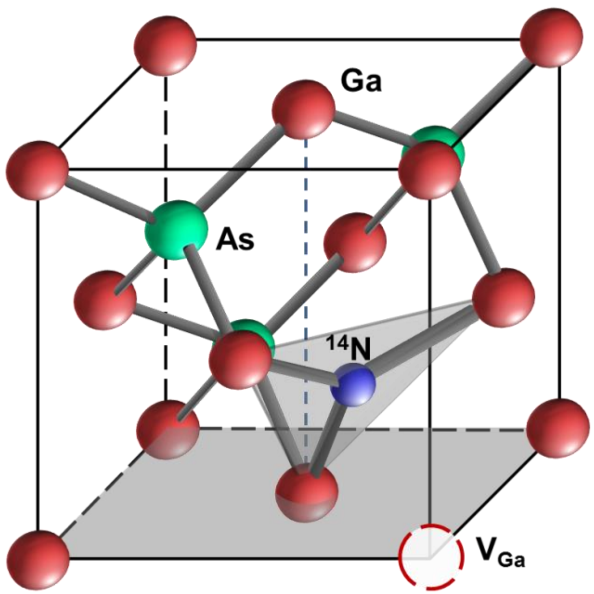
- Investigation for nearly 50 years
- Special feature:

  Manipulability of long-lived electronic spin ground states as well as optically excitable electronic transitions

  ⇒ predestined basic component for future **quantum technology**

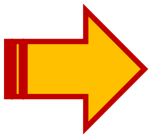
⇒ same defect behaviour in GaAs?

Aim of the work



NV complex in GaAs is mainly **unexplored** up to now

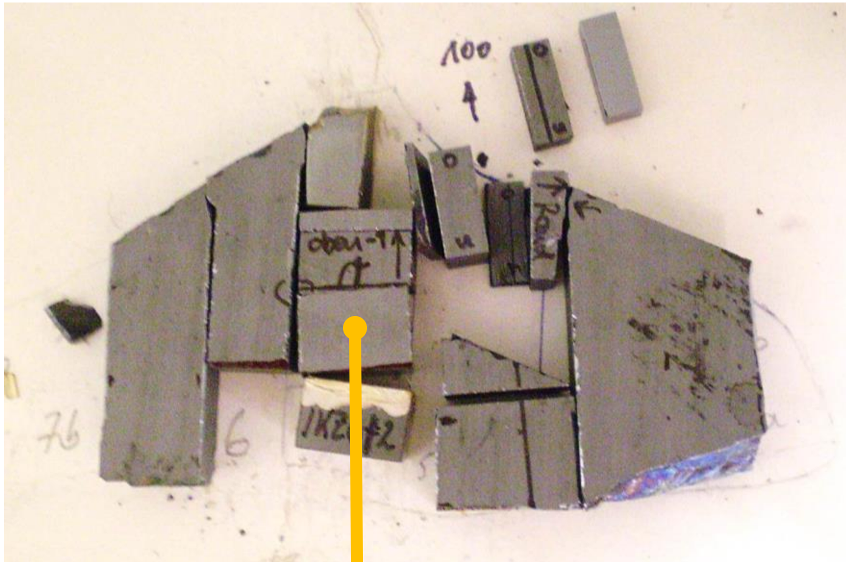
⇒ **basic spectroscopic research** as well as **continuous characterization** required!



My job: FTIR spectroscopy at different external perturbations

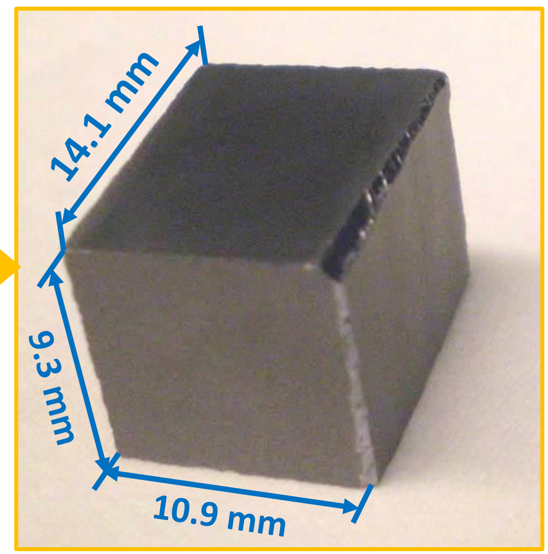
- **varying temperature** **(project work)**
- mechanical stress (master thesis)
- ...

Investigated GaAs samples

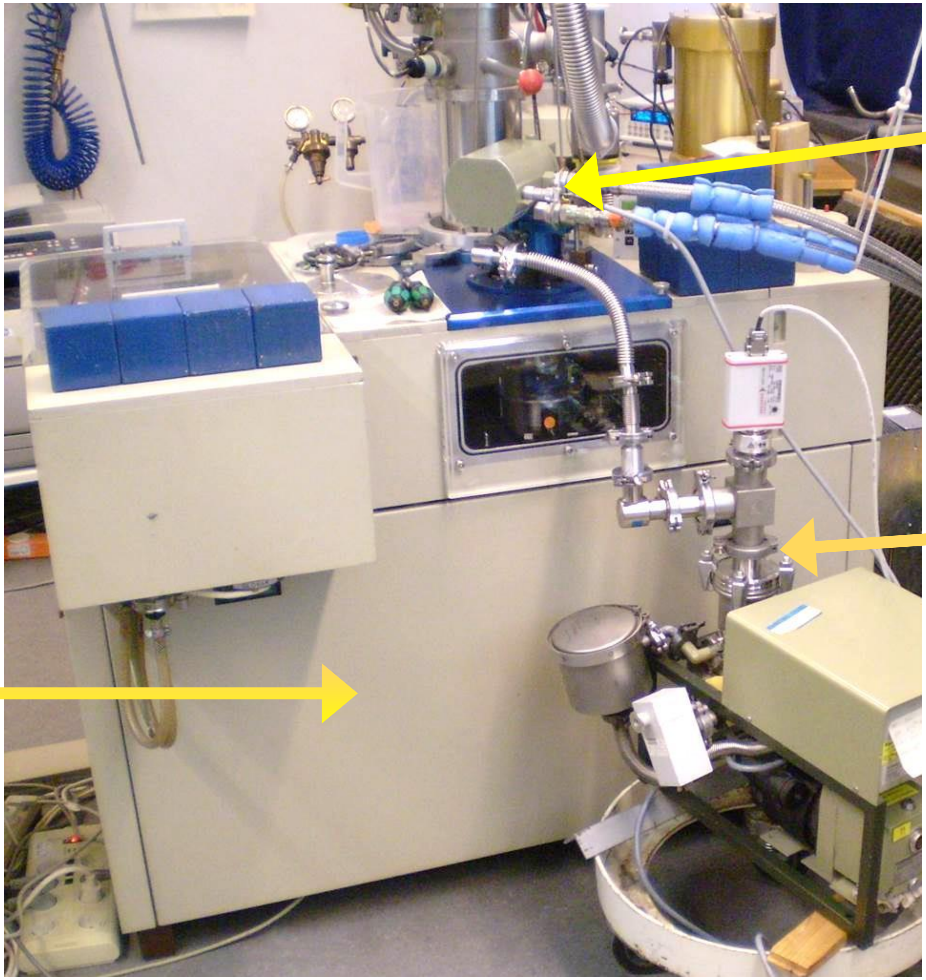


Prefabricated sample of a GaAs ingot:

- grown by the vertical gradient freeze technique under N_2 atmosphere
- doping with C and O



Experimental setup

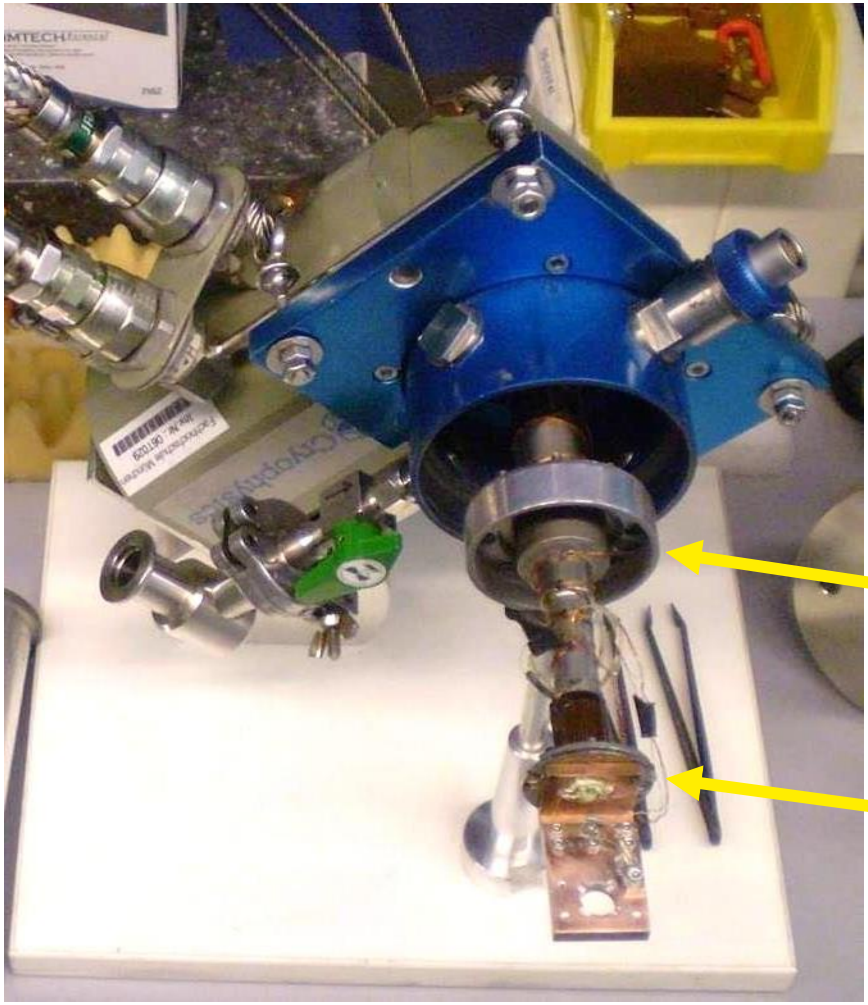


FTIR spectrometer „IFS 113v" (Bruker)

Helium refrigerator cryostat (CTI-Cryogenics)

Turbo molecular pumping station (Pfeiffer Balzers)

Experimental setup - cryostat

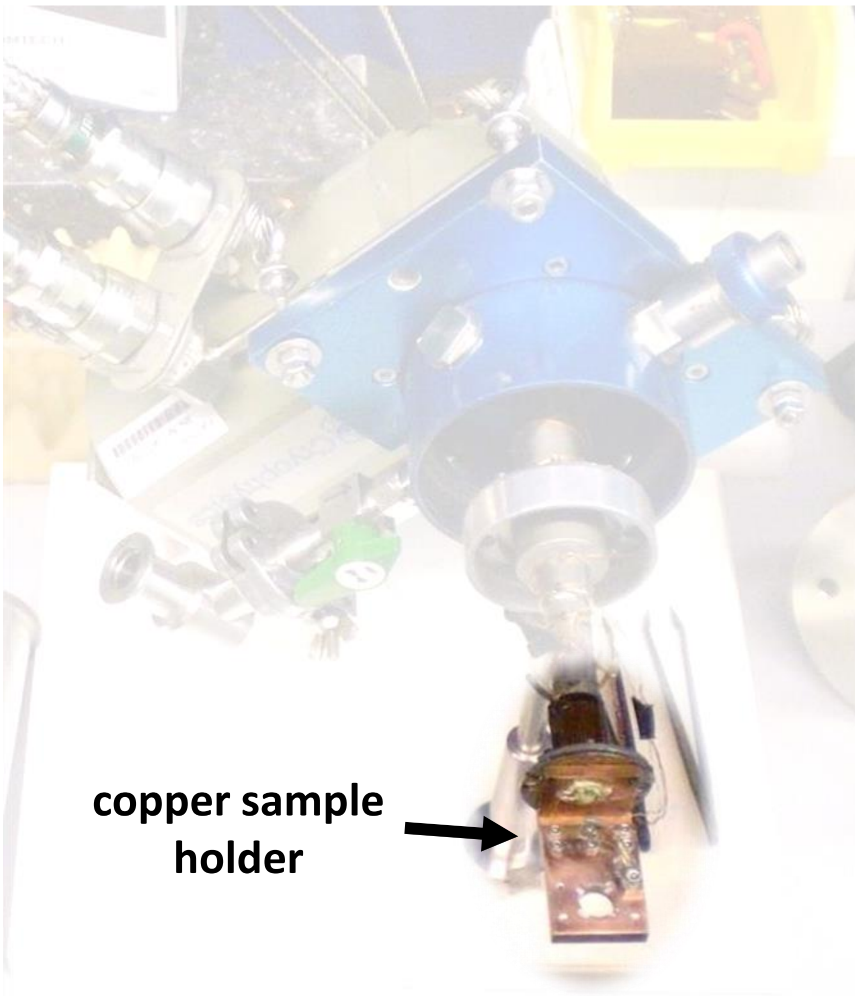


- Two-stage Gifford-McMahon refrigerator (GMR)
  - ➢ Cooling process: periodic compression and expansion of He gas
  - ➢ two combined GMRs

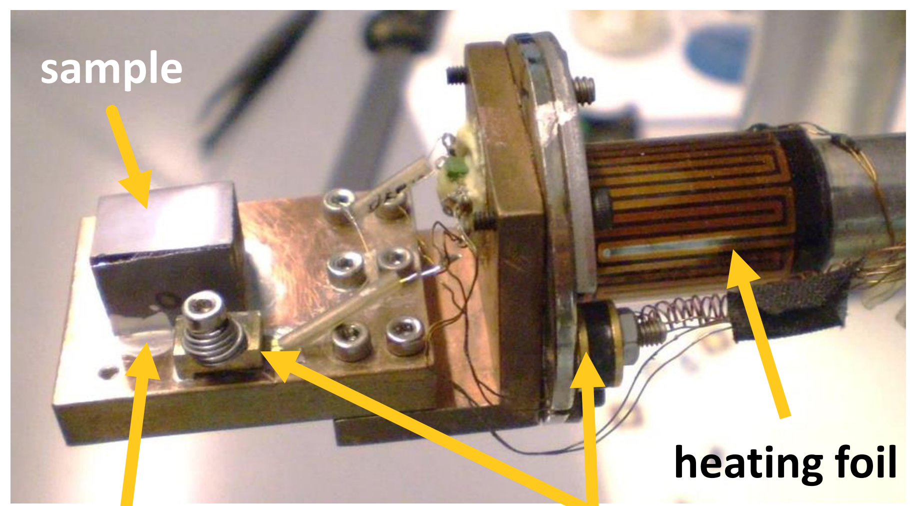
first cold stage (≈ 35 K)

second cold stage (≈ 8 K)

Experimental setup - cryostat



- Copper sample holder at the second cold stage
- Sample mounting with conductive silver glue
- Temperature control through sensors and heating foil



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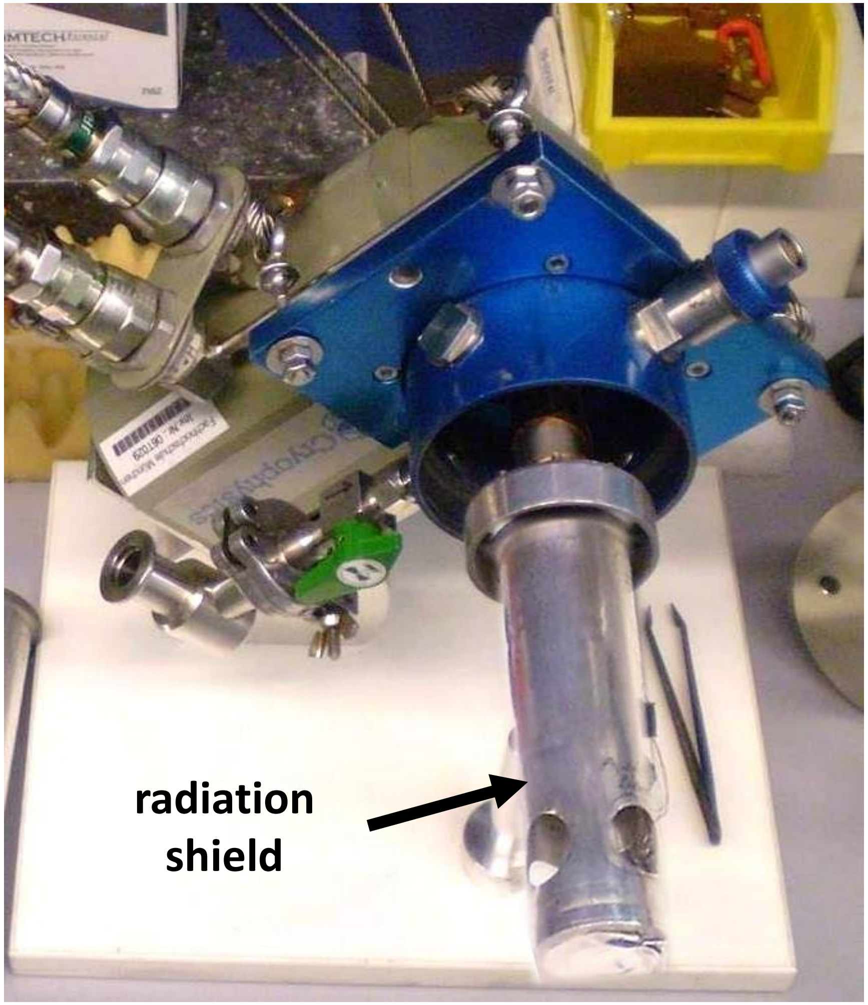
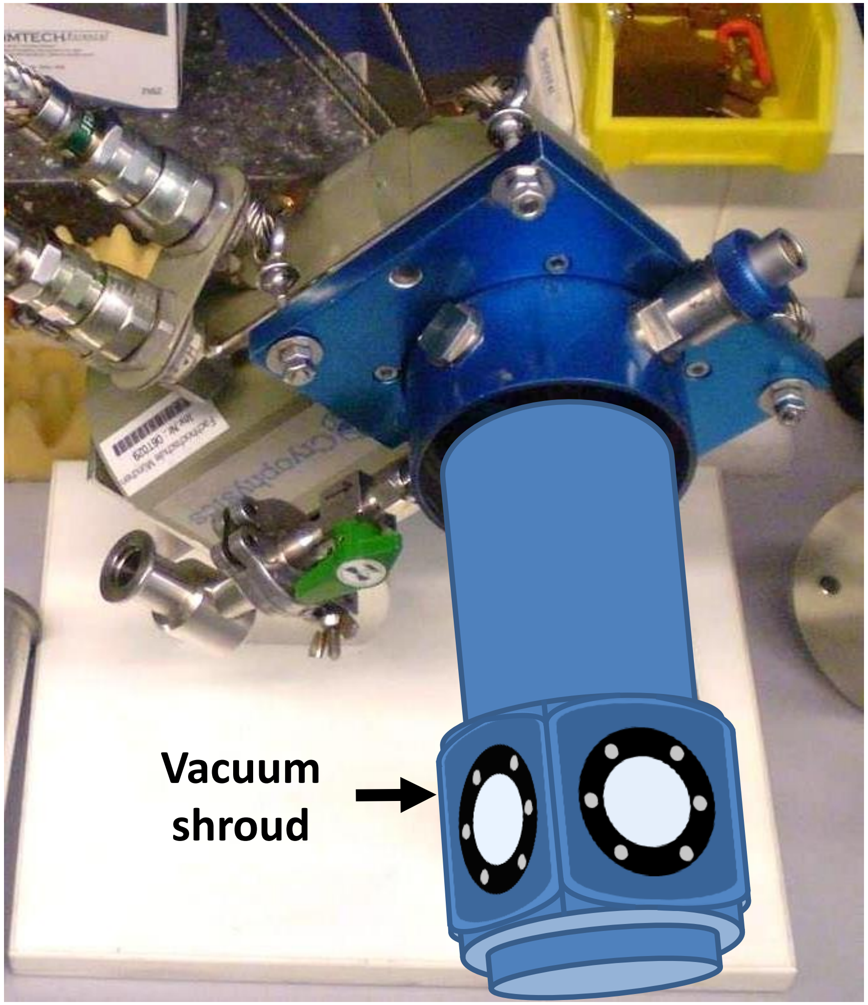
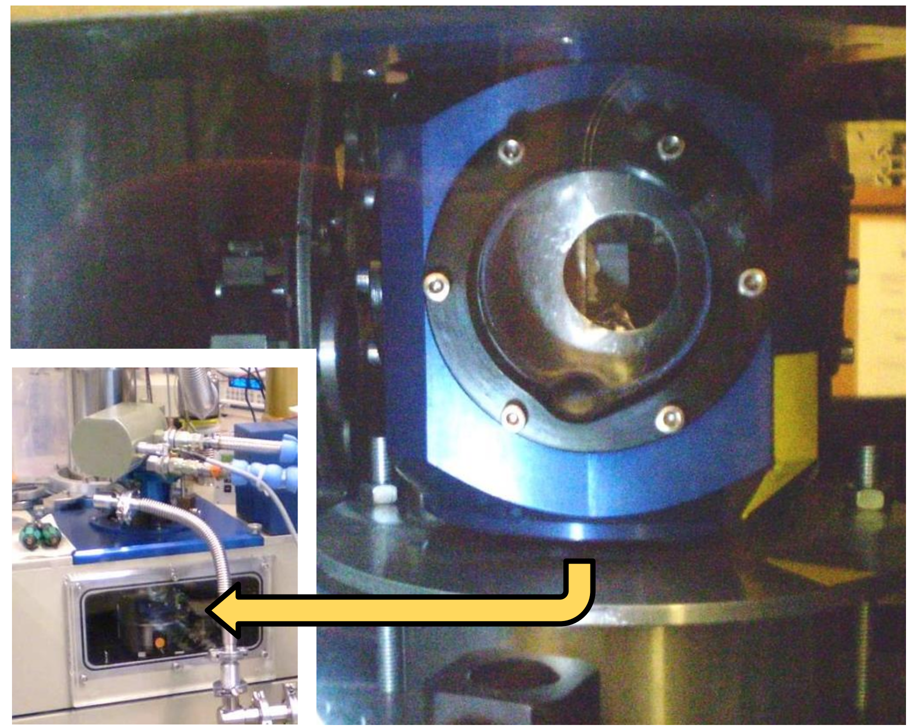


– Protection from heat radiation by a radiation shield at the first cold stage

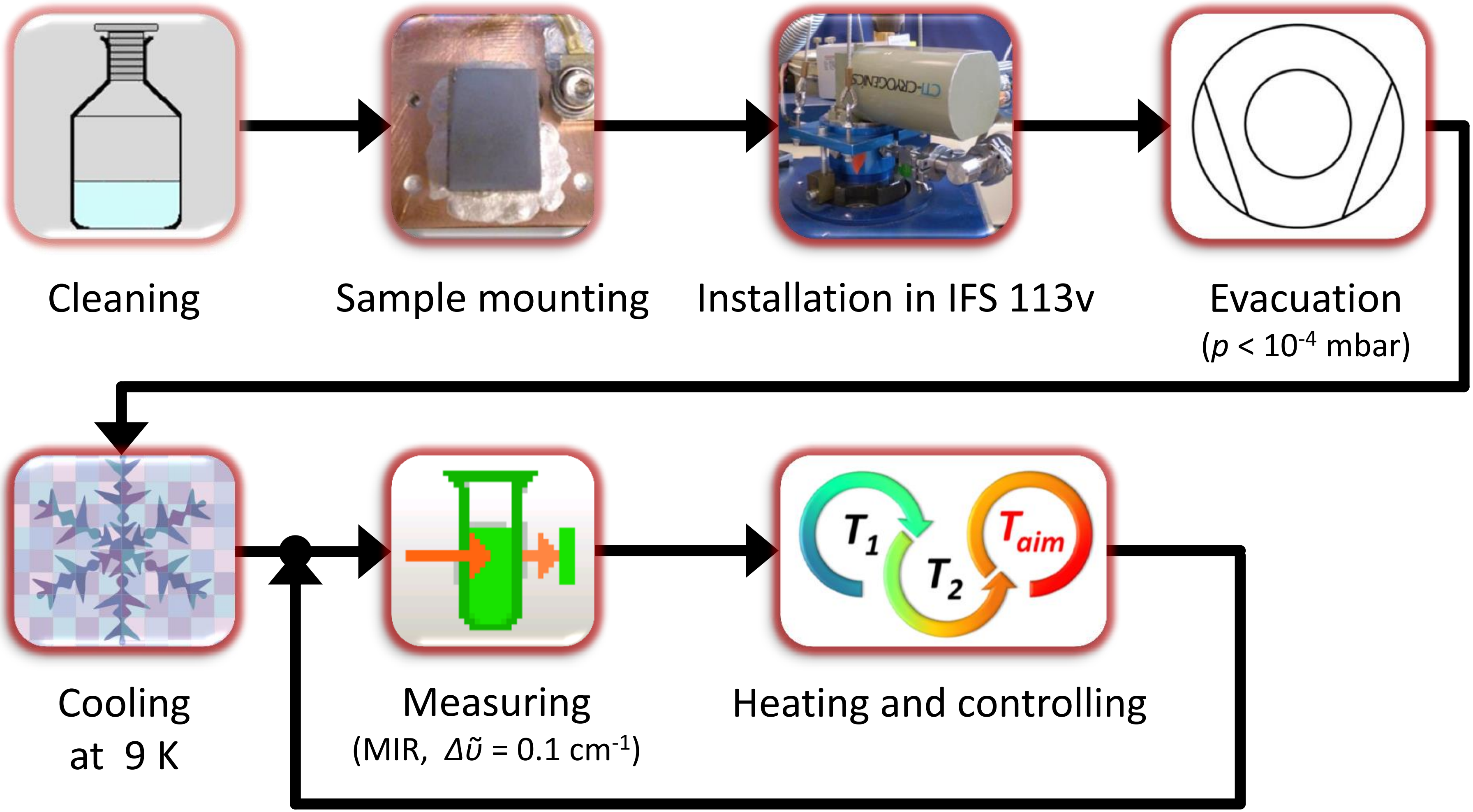
Experimental setup - cryostat



- Protection from heat radiation by a radiation shield at the first cold stage
- Vacuum shroud for evacuation



Experimental enforcement



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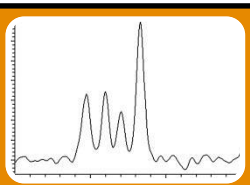

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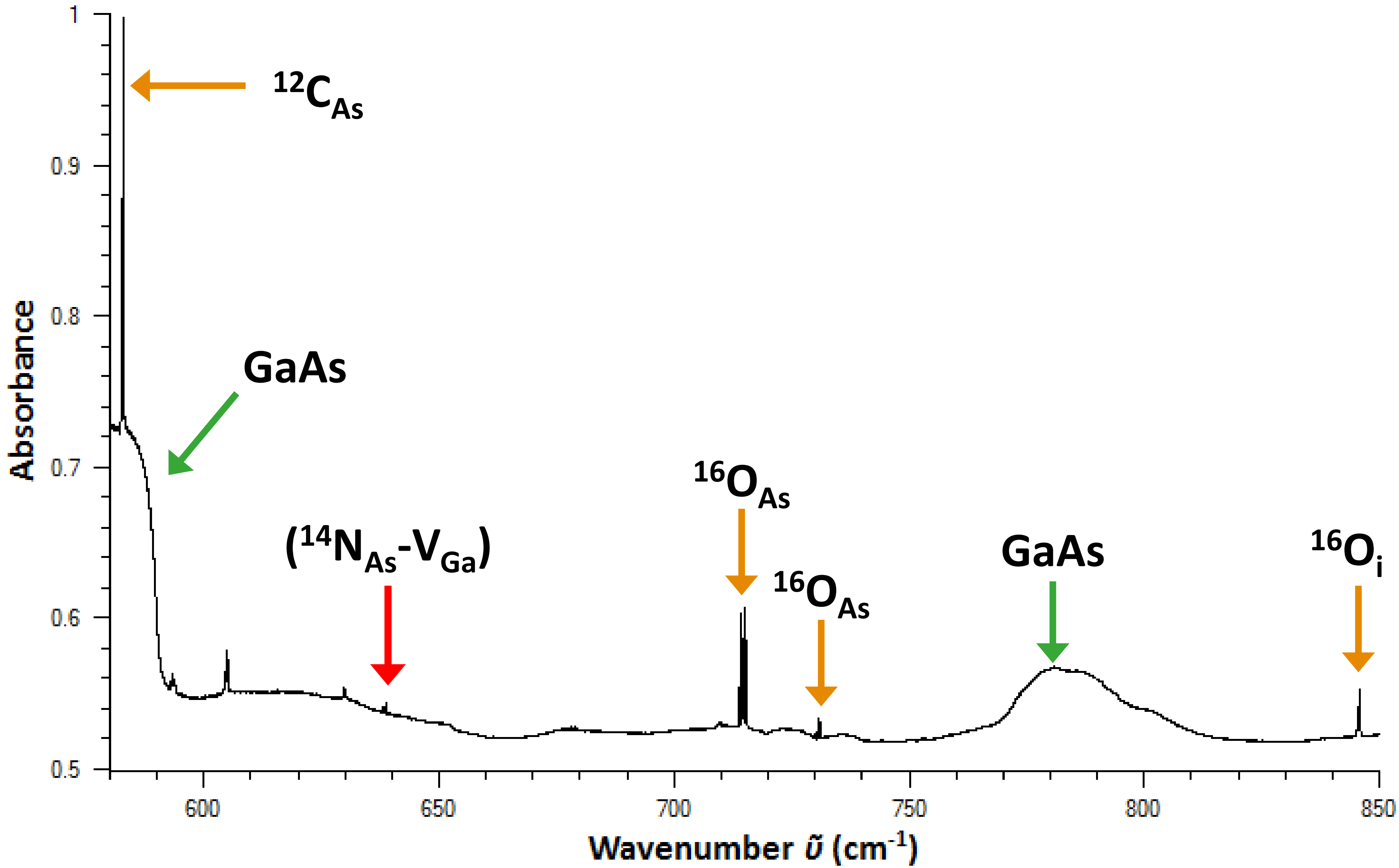
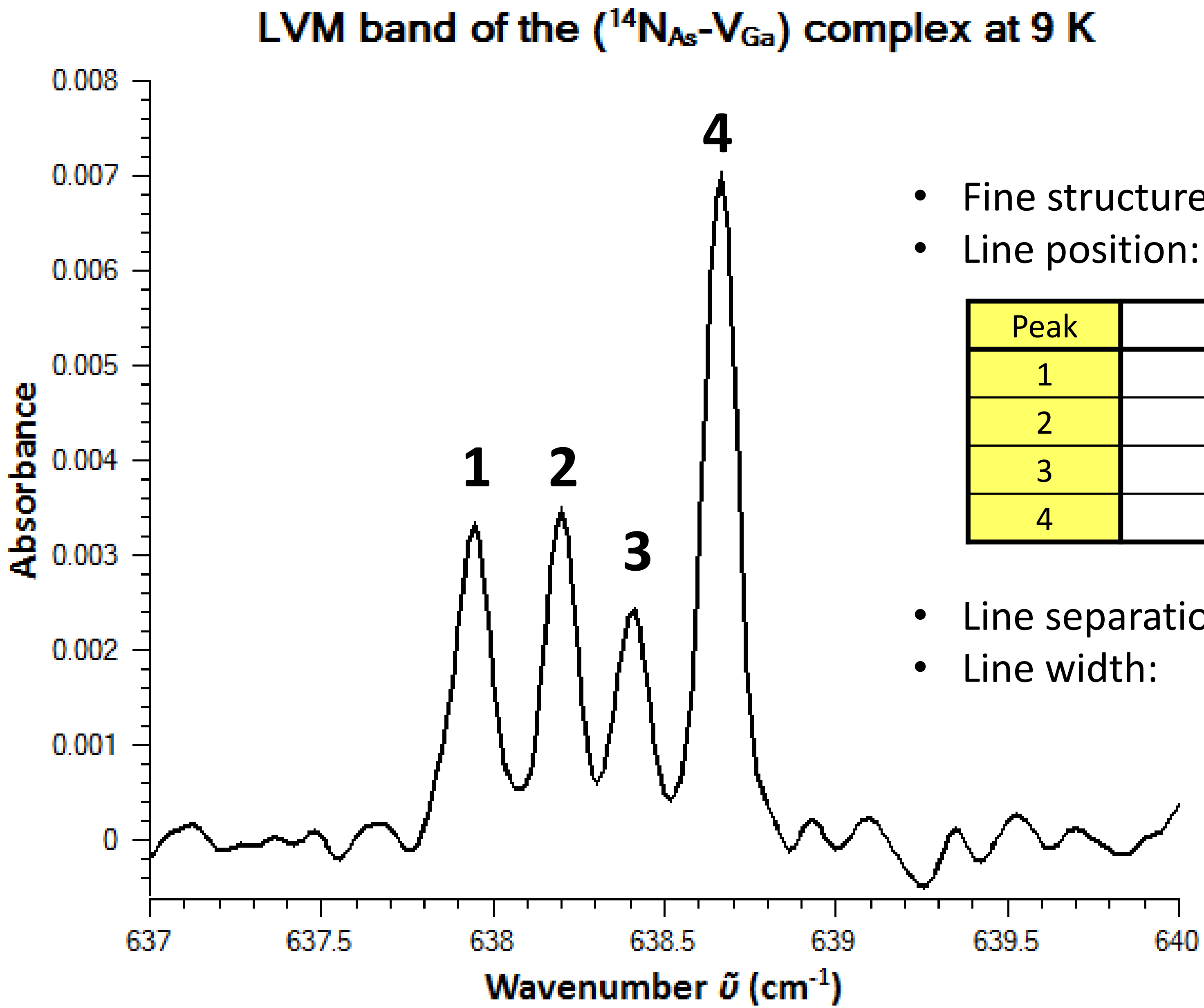
Absorbance spectrum at 9 K



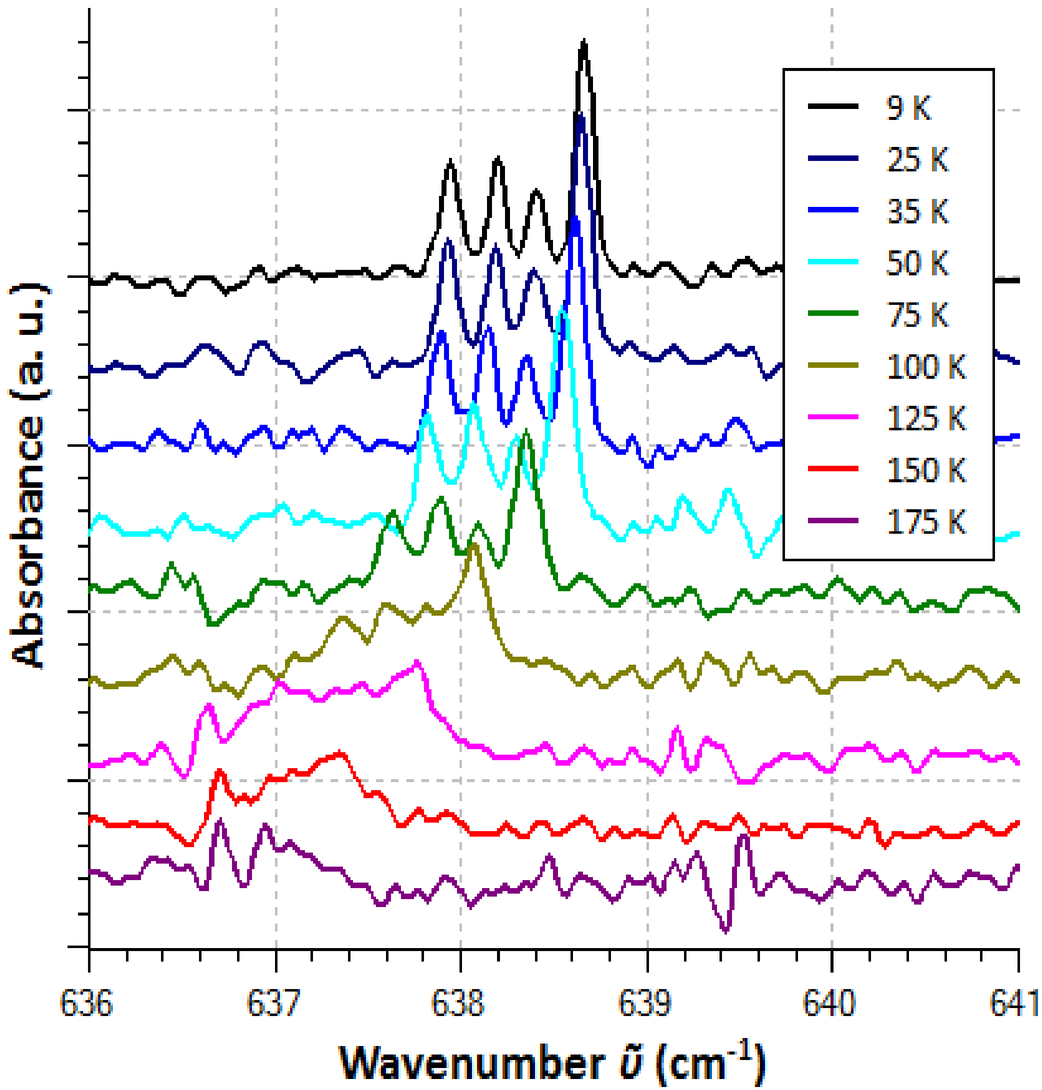


- Fine structure: quadruplet
- Line position:

Peak	$\tilde{\upsilon}$ (cm^{-1})
1	637.94 ± 0.02
2	638.20 ± 0.02
3	638.41 ± 0.02
4	638.67 ± 0.02

- Line separation: ≈ 0.2 cm^{-1}
- Line width: 0.11 cm^{-1}

LVM band of the ($^{14}N_{As}$-V_{Ga}) complex in GaAs at different sample temperatures

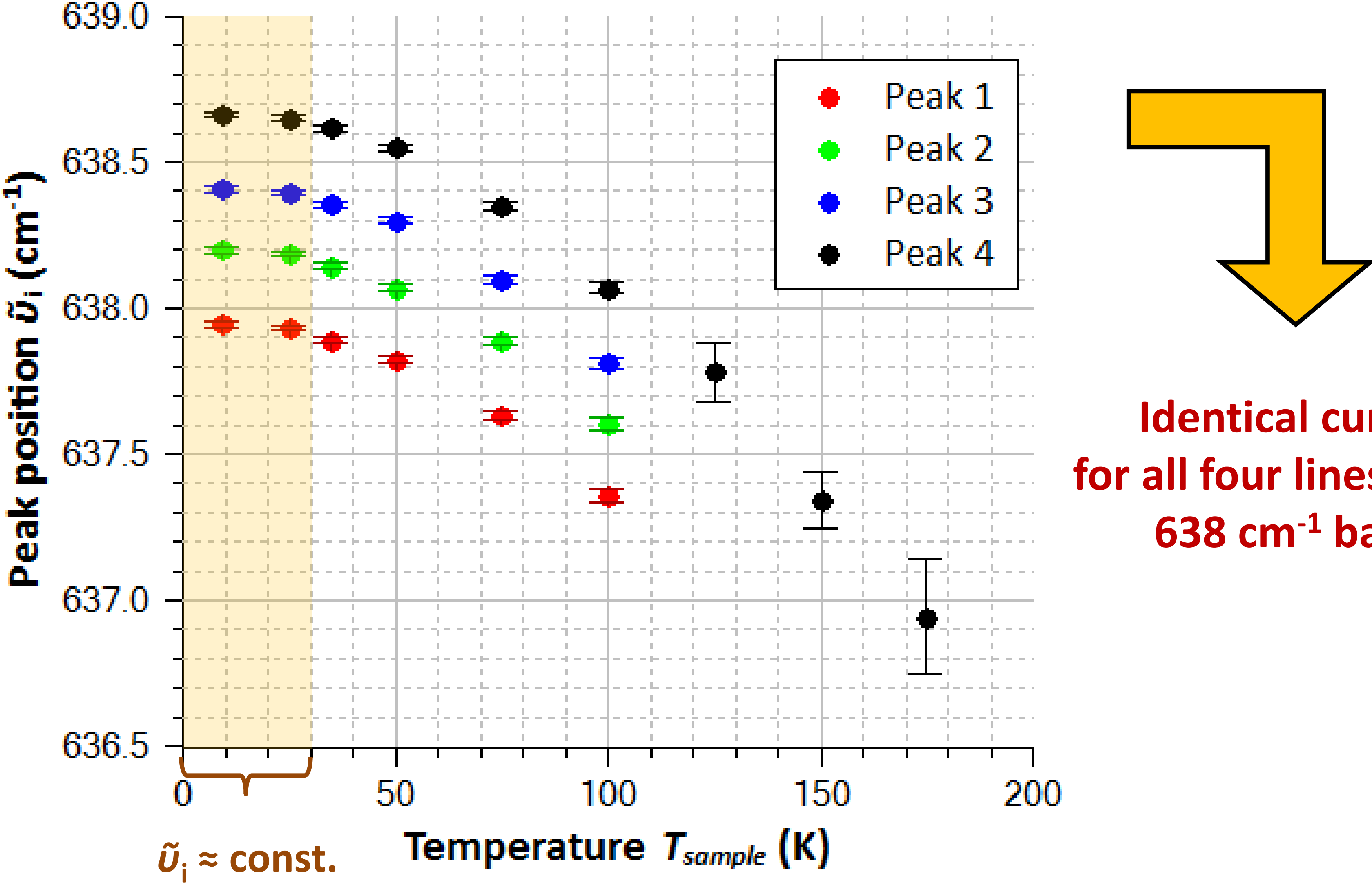


T_{sample} ↗

$\tilde{\upsilon}_{Peak}$	$FWHM_{Peak}$	$\mathcal{A}_{Peak}$
↘	↗	↘

Reason:
Interaction between defect mode and phonon

Temperature dependence of the 638 cm^{-1} band in GaAs



Identical curves for all four lines of the 638 cm^{-1} band

Theoretical model of temperature dependent line shift:

$$\tilde{\upsilon}_{Peak}(T) = \tilde{\upsilon}_{Peak}(T = 0\ K) + \frac{\delta\tilde{\upsilon}}{e^{h*c*\tilde{\upsilon}_0/k_B*T} - 1}$$

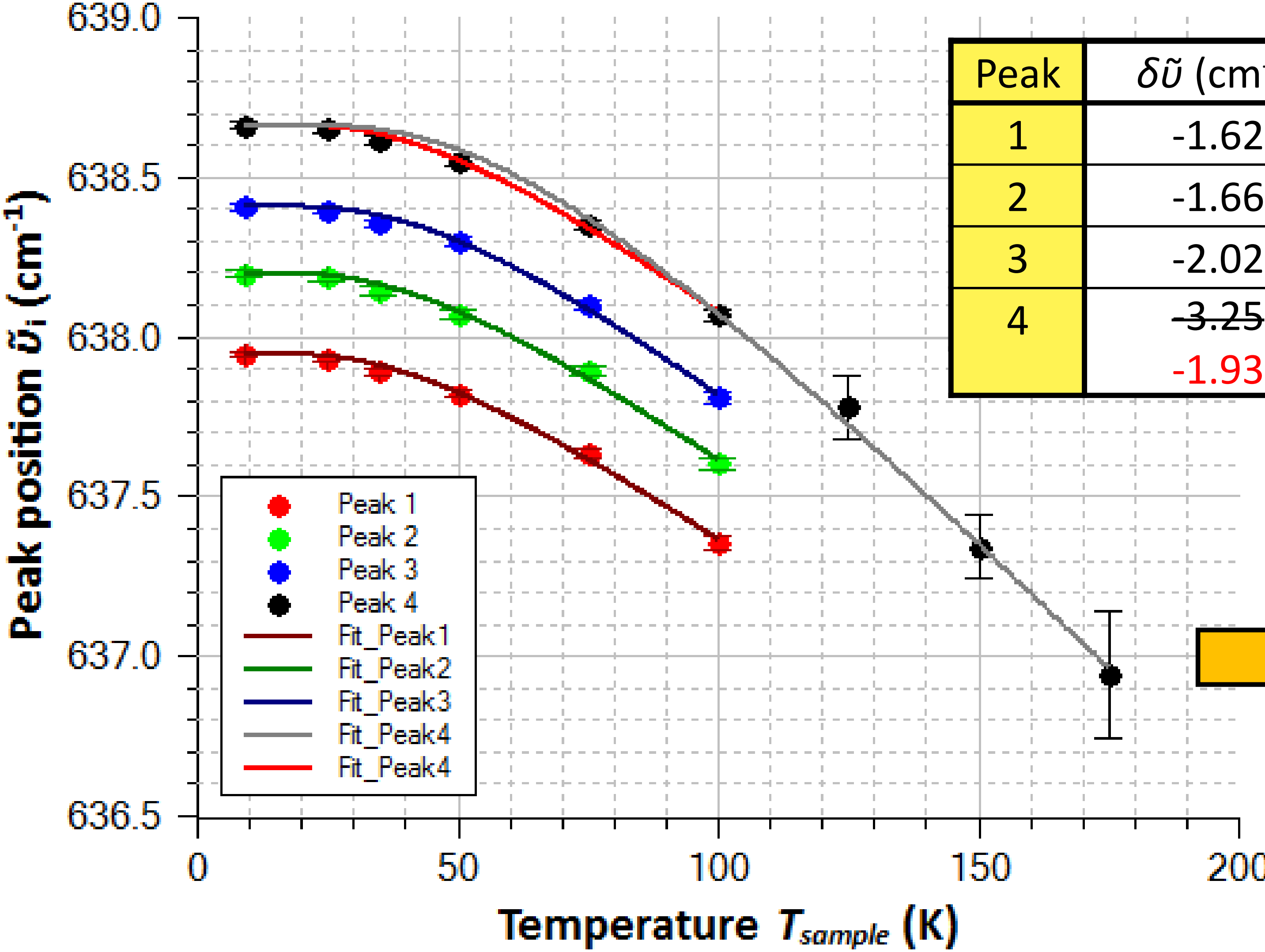
with $\tilde{\upsilon}_{Peak}$ = peak position

$\delta\tilde{\upsilon}$ = phonon coupling parameter

$\tilde{\upsilon}_0$ = frequency of the interacting phonon

Determination of $\delta\tilde{\upsilon}$ und $\tilde{\upsilon}_0$ with curve fitting

Temperature dependence of the 638 cm^{-1} band in GaAs



Peak	$\delta\tilde{\upsilon}$ (cm^{-1})	$\tilde{\upsilon}_0$ (cm^{-1})
1	-1.62	92.54
2	-1.66	93.52
3	-2.02	103.22
4	~~-3.25~~ -1.93	~~129.95~~ 100.98

Summary

<u>Obtained results for the 638 cm^{-1} band:</u>

– Quantity of temperature dependent
    - line shift and
    - line broadening

  ⇒ Limitation of useable sample temperature range to $T < 80$ K for further spectroscopy

– Identical behaviour of all vibrational modes

– Phonon coupling parameters

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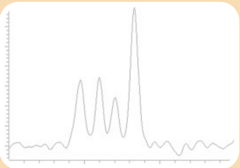

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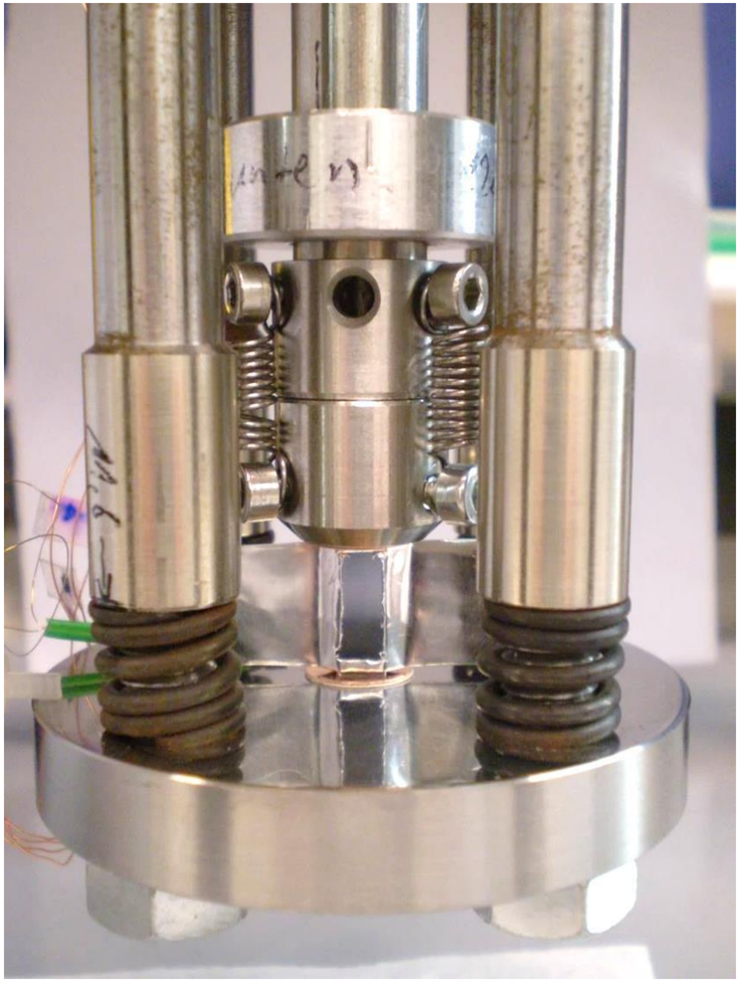
Outlook – master thesis

Investigation of the ($^{14}N_{As}$-V_{Ga}) complex under mechanical stress through **FTIR-based piezospectroscopy**

- Analysis while applying an uniaxial stress up to 0.15 GPa
- Crystal deformation ⇒ alteration of lattice potential ⇒ shift and splitting of absorption bands
- Gain of information about
  - defect structure,
  - symmetry,
  - …



Bibliography

See references in:

- Kovač N.: *Temperaturabhängige FTIR-Analyse der LVM-Bande des ($^{14}N_{As}$-V_{Ga})-Komplexes in Galliumarsenid*. Project work, University of Applied Sciences Munich, 2016

Thank you for your attention!

I'm happy to take questions.