

# Radiation-induced defect reactions in oxygen-doped Ge crystals

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*In collaboration with*

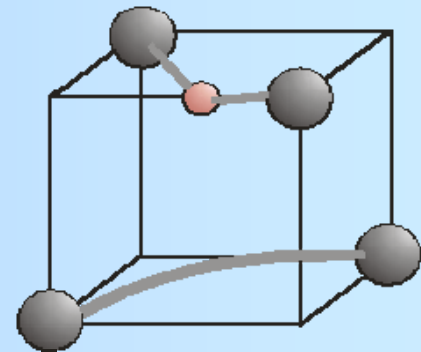
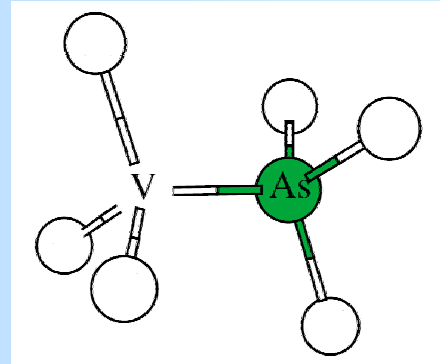
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# Outline

- **Recent DLTS results on the electronic properties of radiation-induced defects in Ge crystals – short summary**
- **Experimental details**
- **Isochronal annealing study of radiation-induced defects in Ge: Bi, O crystals**
- **DLTS studies of properties and annealing behaviour of radiation-induced defects in Ge: Sb, O crystals**
- **Infrared absorption study of transformations of oxygen-related LVMs in electron-irradiated Ge:O crystals**

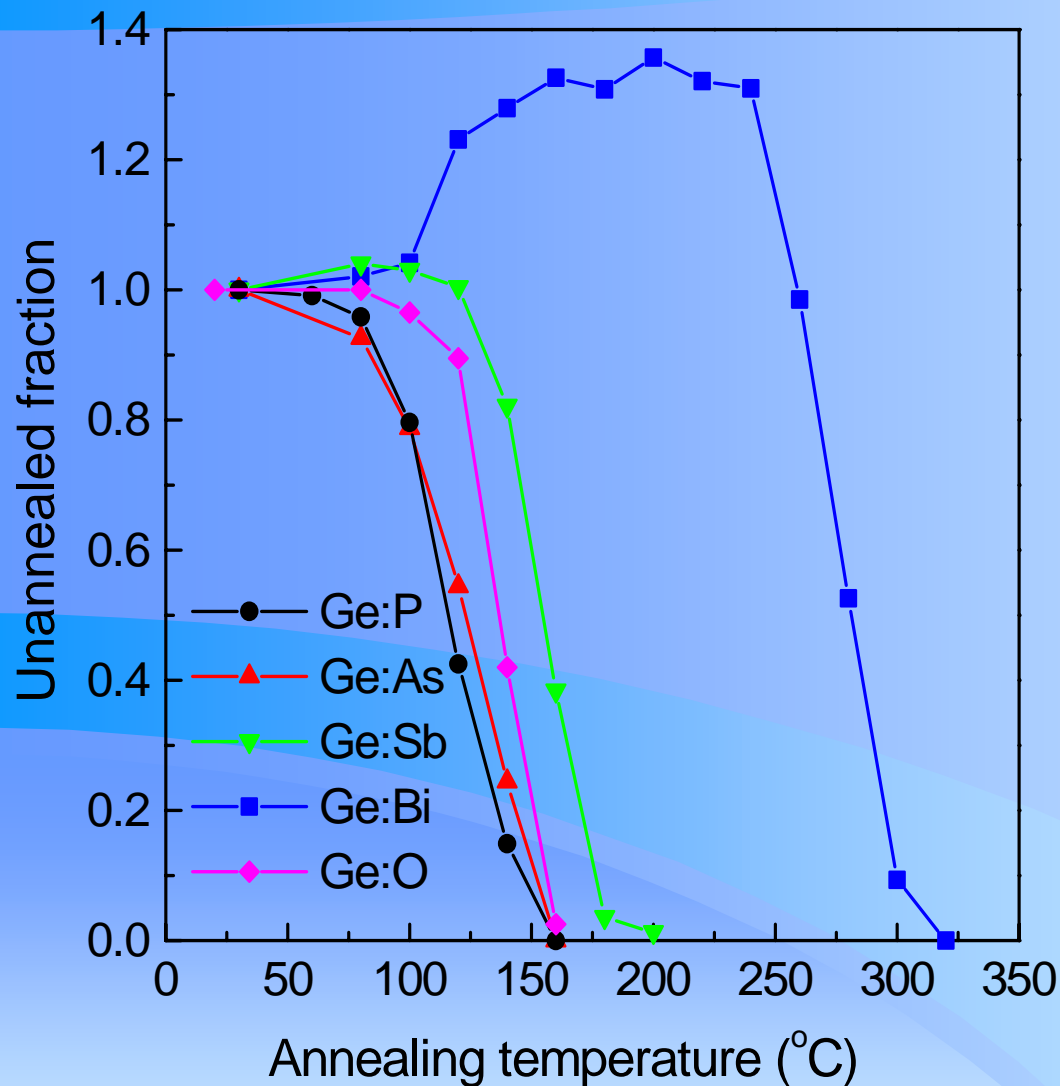
# Electronic properties of vacancy-related radiation-induced defects in Ge crystals – DLTS studies

$V_2$ 0.29	$VO^{-/-}$ 0.26	$VBi^{-/-}$ 0.265	$VSb^{-/-}$ 0.295	$VAs^{-/-}$ 0.245	$VP^{-/-}$ 0.225
	$VO^{0/-}$ 0.33	$VBi^{0/-}$ 0.31	$VSb^{0/-}$ 0.31	$VAs^{0/-}$ 0.33	$VP^{0/-}$ 0.35
			$VSb^{0/+}$ 0.09		
170°C	135°C	270°C	160°C	130°C	125°C



- **Vacancy donor pair (E centre) in P, As, Sb & Bi doped Ge**  
*Phys Rev B 70, 235213 (2004); JAP 95 4078 (2004)*
- **Vacancy-oxygen centre in Ge**  
*APL 81, 1821 (2002); Phys Stat Sol C 0, 702 (2003)*

# Isochronal annealing behaviour of dominant vacancy-related defects in gamma-irradiated n-type Ge crystals



Changes in normalized concentrations of the dominant electron traps in gamma-irradiated oxygen-lean Ge crystals doped with P, As, Sb Bi and in an O-doped Ge sample upon 30-min isochronal annealing. The trap concentrations were determined from DLTS measurements.

# Experimental details

## I) Samples

n-type Ge crystals doped with P, As, Sb, Bi and O; a) oxygen-rich Ge;  $[O_i] \approx (1-1.6) \times 10^{17} \text{ cm}^{-3}$ ;  $[Sb] \approx 4 \times 10^{14}$  and  $(1-2) \times 10^{15} \text{ cm}^{-3}$ ,  $[Bi] \approx 1.5 \times 10^{14}$  and  $3 \times 10^{15} \text{ cm}^{-3}$ ; b) oxygen-lean Ge,  $[O_i] \leq 5 \times 10^{15} \text{ cm}^{-3}$ ;  $[D^+] = (1-20) \times 10^{14} \text{ cm}^{-3}$ .

## II) Irradiation

a) Fast electrons (4 or 6 MeV in energy) @ RT,  $F = 1.5 \times 10^{15} \text{ cm}^{-2}$ ; b)  $^{60}\text{Co}$  gamma rays @ RT.

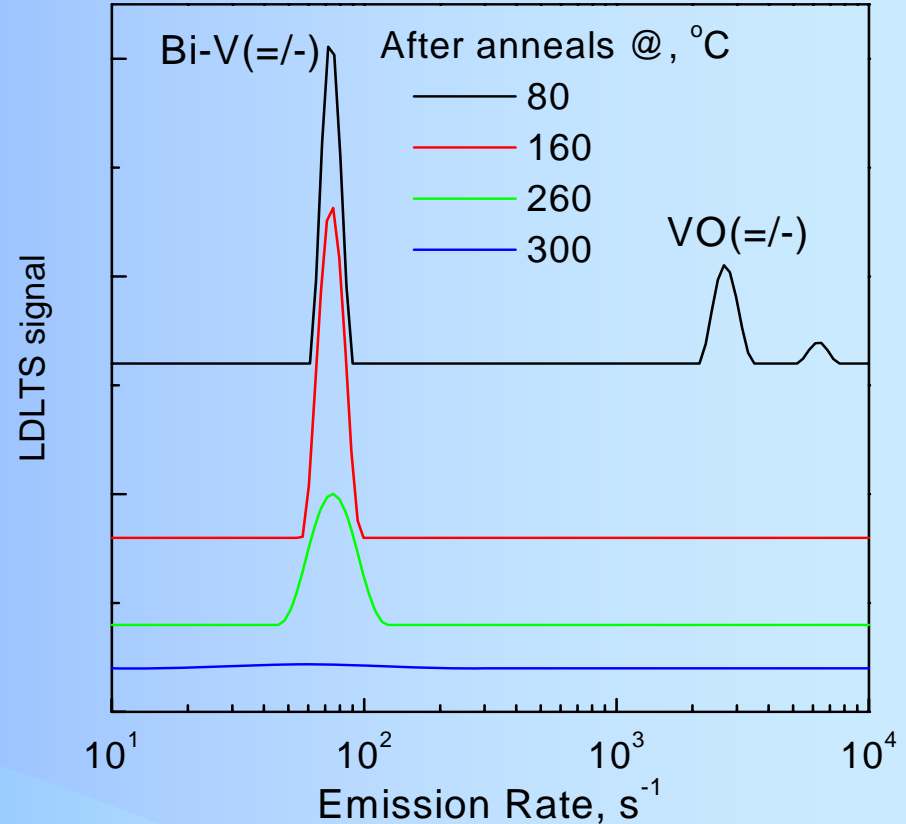
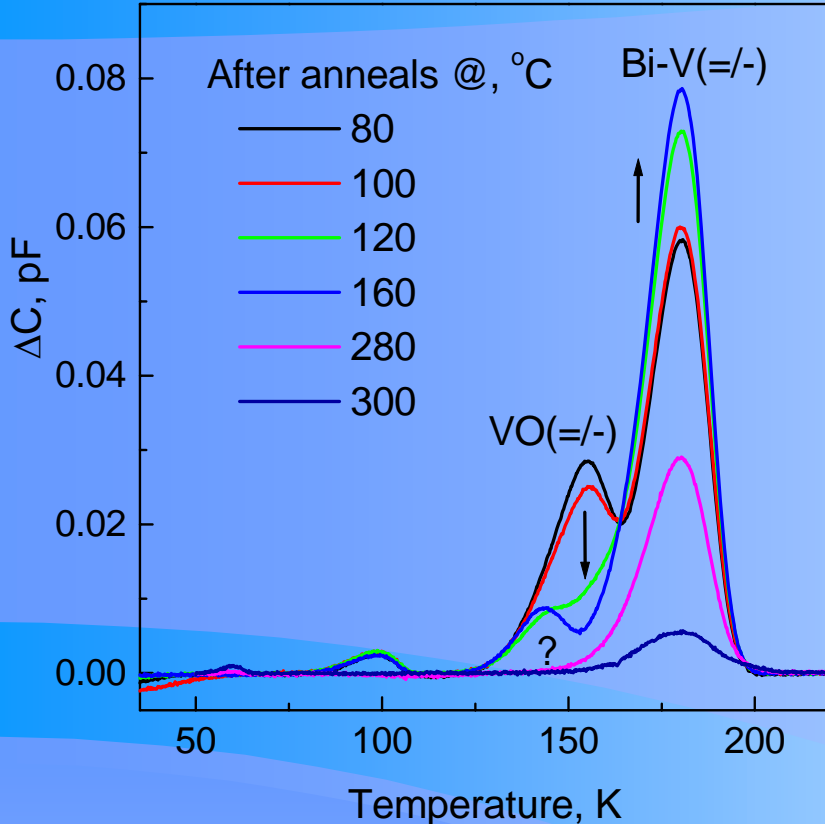
## III) Processing and Measurements

Au Schottky diodes prepared by thermal evaporation of Au on the surface etched in a 1HF+10HNO<sub>3</sub> mixture; a) IV and CV; b) DLTS and Laplace DLTS measurements @ 30 to 300 K.

## IV) Annealing

a) 30-min isochronal anneals in the temperature range 80-360°C with 20°C increments; b) Isothermal anneals at 60, 75 and 90°C in a nitrogen gas ambient

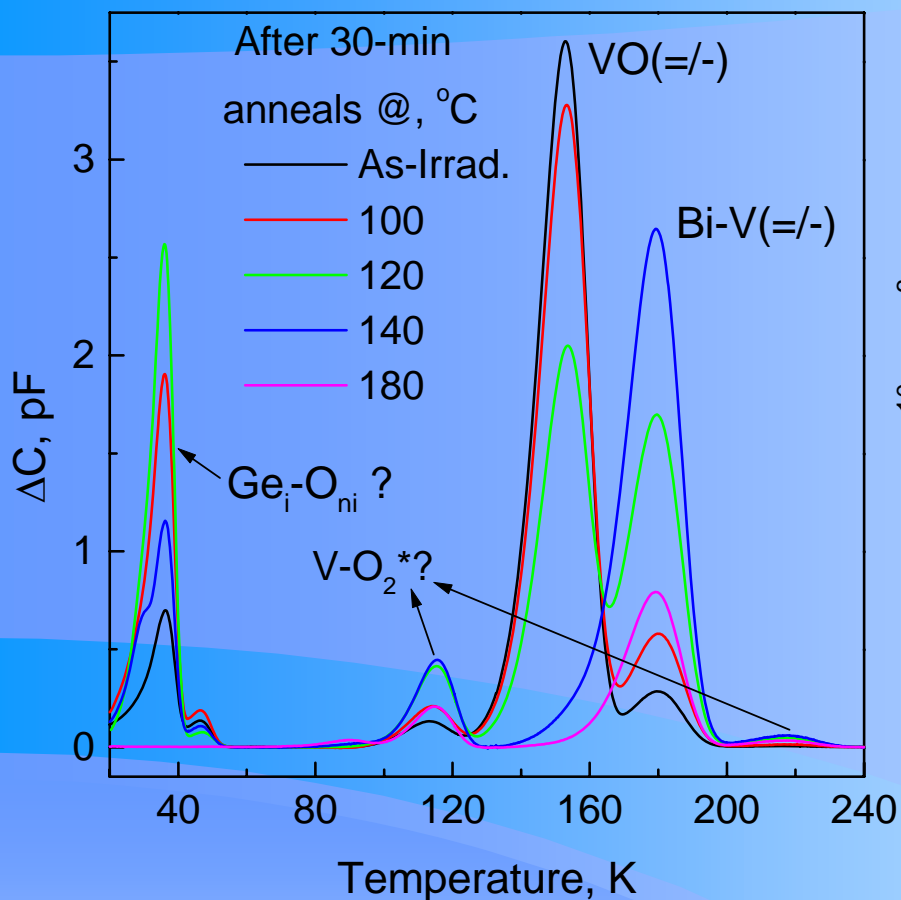
# Defect transformations upon isochronal annealing of gamma-irradiated Ge:Bi, O crystals



DLTS spectra for a Bi-doped  $\{[Bi] = 1.5 \cdot 10^{14} \text{ cm}^{-3}, [O_i] < 5 \cdot 10^{15} \text{ cm}^{-3}\}$  Ge sample after gamma-irradiation and subsequent 30 min isochronal annealing. Measurement settings:  $e_n = 80 \text{ s}^{-1}$ ,  $t_p = 1 \text{ ms}$ , and bias  $-5.0 \rightarrow -0.5 \text{ V}$  for all spectra.

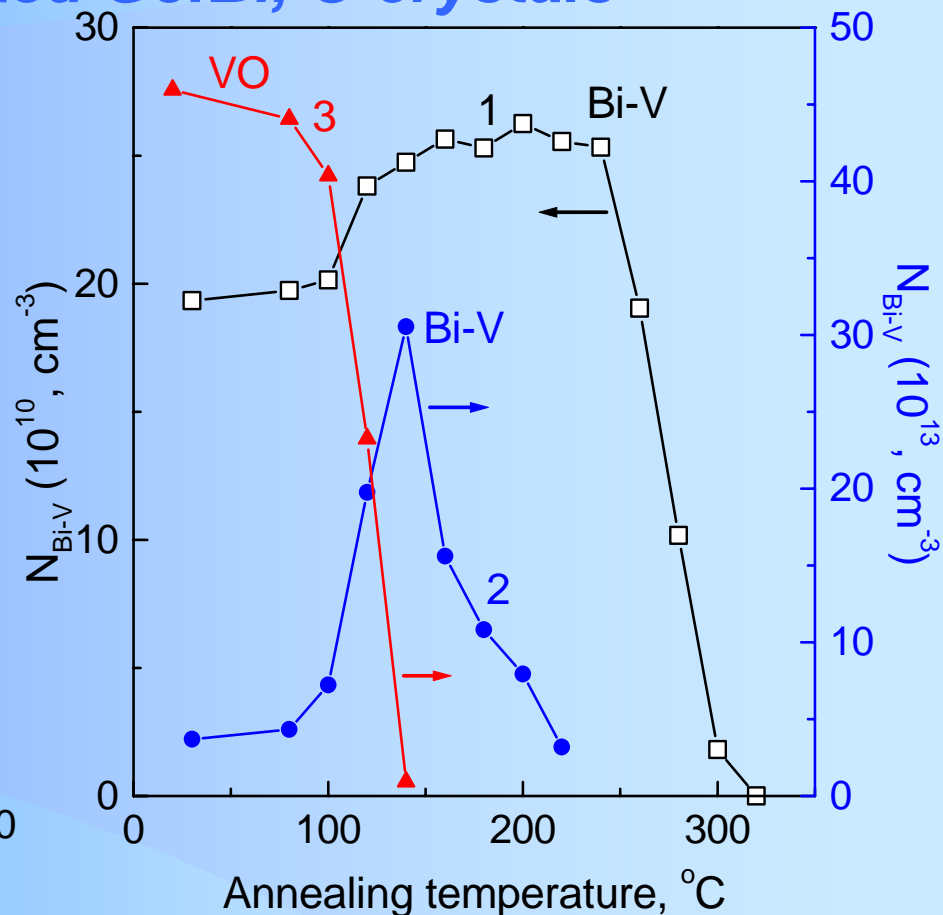
LDLTS spectra at 179 K for a Bi-doped  $\{[Bi] = 1.5 \cdot 10^{14} \text{ cm}^{-3}, [O_i] < 5 \cdot 10^{15} \text{ cm}^{-3}\}$  Ge sample after  $\gamma$ -irradiation and subsequent 30 min isochronal annealing. Measurement settings:  $t_p = 1 \text{ ms}$  and bias sequence  $-5.0 \rightarrow -0.5 \text{ V}$  for all spectra.

# Defect transformations upon isochronal annealing of electron-irradiated Ge:Bi, O crystals



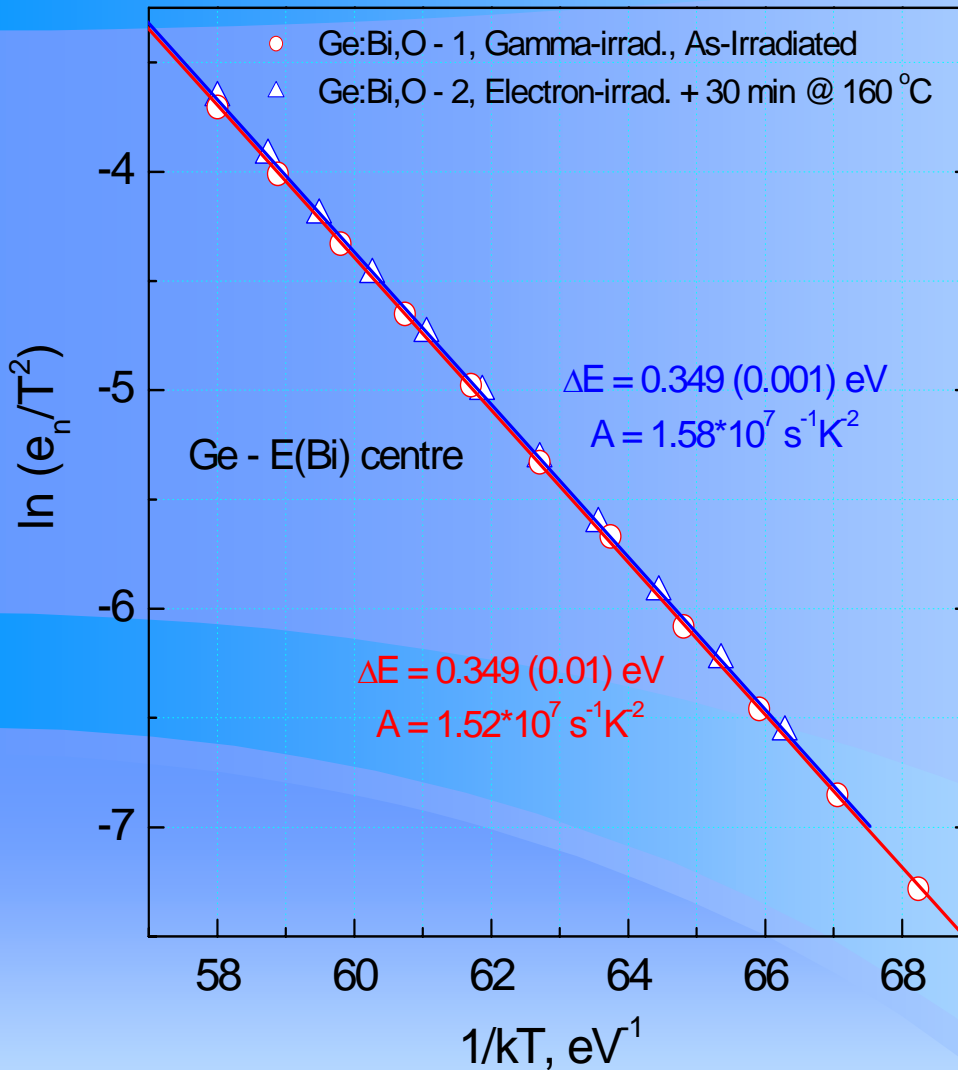
DLTS spectra for a (Bi+O)-doped  $\{[Bi] \approx 3 \cdot 10^{15} \text{ cm}^{-3}, [O_i] \approx 1.6 \cdot 10^{17} \text{ cm}^{-3}\}$  Ge sample after  $e^-$ -irradiation and subsequent 30 min isochronal annealing.

Measurements:  $e_n = 80 \text{ s}^{-1}$ ,  $t_p = 1 \text{ ms}$ , bias  $-5.0 \rightarrow -0.5 \text{ V}$



Changes in concentrations of the VO and Bi-V in irradiated Ge crystals upon 30-min annealing. (1)  $[Bi] \approx 1.5 \cdot 10^{14} \text{ cm}^{-3}$ ,  $[O_i] < 5 \cdot 10^{15} \text{ cm}^{-3}$ ,  $^{60}\text{Co}$  irradi.; (2,3)  $[Bi] \approx 3 \cdot 10^{15} \text{ cm}^{-3}$ ,  $[O_i] \approx 1.6 \cdot 10^{17} \text{ cm}^{-3}$ ,  $e^-$ -irrad.

# Defect transformations upon isochronal annealing of an electron-irradiated Ge:Bi, O crystal



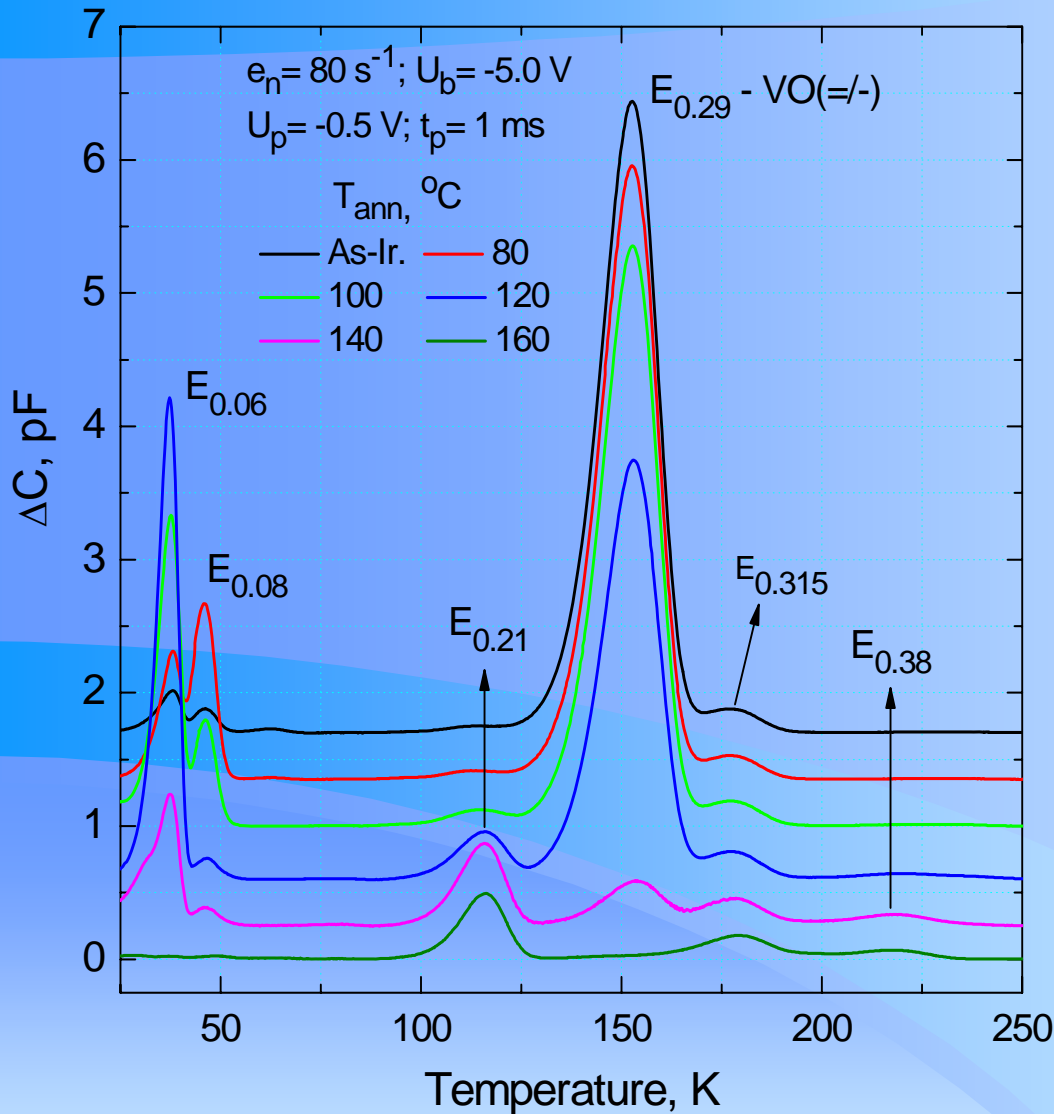
Arrhenius plots of  $T^2$ -corrected electron emission rates from the doubly negatively charged state of the Bi-V centre in two irradiated Ge:Bi,O crystals. The electron emission rates have been derived from Laplace DLTS measurements.



# Defect reactions occurring upon isochronal annealing of irradiated Ge:Bi, O crystals: an analysis of the DLTS results

- *Capture of vacancies by impurities in Ge.* There is strong evidence that in n-type Ge at  $T \sim 300$  K the single vacancy is negatively charged (Sieleman, 1998). Therefore, the positively charged donor provides a much more attractive capture site for the vacancy than neutral  $O_i$  by almost an order of magnitude. Ratio of concentrations of A to E centres after irradiations depend on the ratio of concentrations of  $O_i$  to group V donor atoms.
- *Mechanism of annealing of the A centre in Ge.* An increase in the concentration of Bi-V centres upon annealing in the temperature range 100-150 °C can be linked with a decrease in the concentration of the VO centres in the same range. The results obtained indicate that there is a release of vacancies from the A centre which are subsequently trapped by the Bi impurity atoms to form the Bi-V E centre. It can be suggested that the dissociation is the preferable mechanism of A centre annealing in Ge.
- *Interaction of interstitial- and vacancy-related centers in Ge.* A sharp decrease in the concentration of the Bi-V centre in electron-irradiated oxygen-rich Ge samples in the temperature range 150-200 °C can be associated with an interaction of the E centres with some mobile particles. It can be suggested that these mobile particles are Ge self-interstitials, which are released from some oxygen-related traps ( $O_i$ ,  $O_{2i}$ ) at  $T \geq 140$  °C. It appears that the  $Ge_i-O_{ni}$  centres are responsible for the peaks, which are observed in the range of 20-50 K in the DLTS spectra of irradiated oxygen-rich Ge samples. The traps, which give rise to these peaks, disappear upon annealing at  $T \geq 140$  °C.

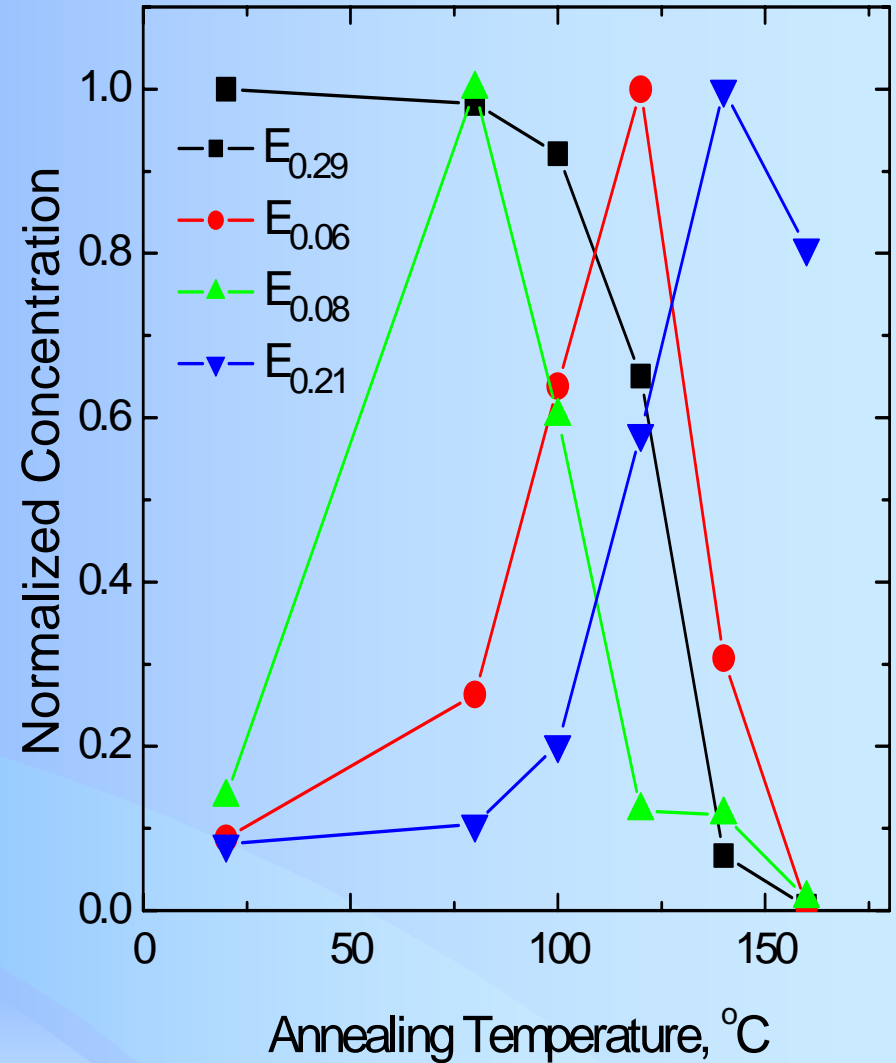
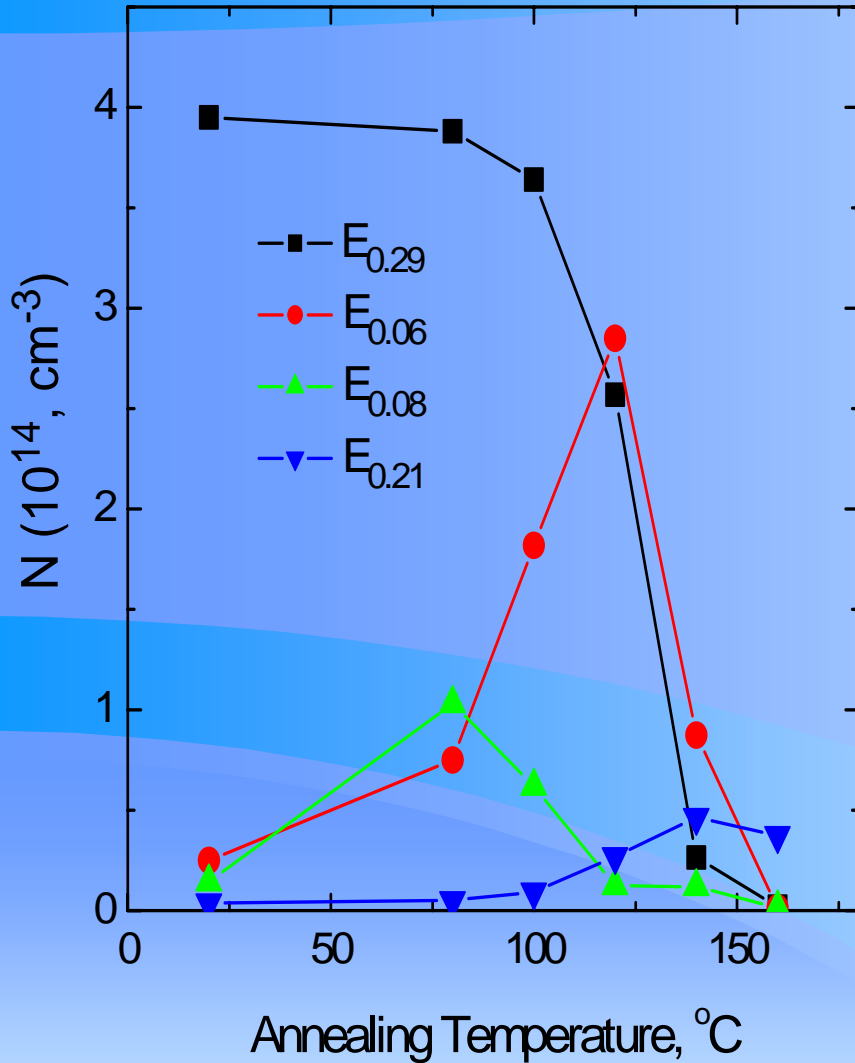
# Defect transformations upon isochronal annealing of electron-irradiated Ge:Sb, O crystals



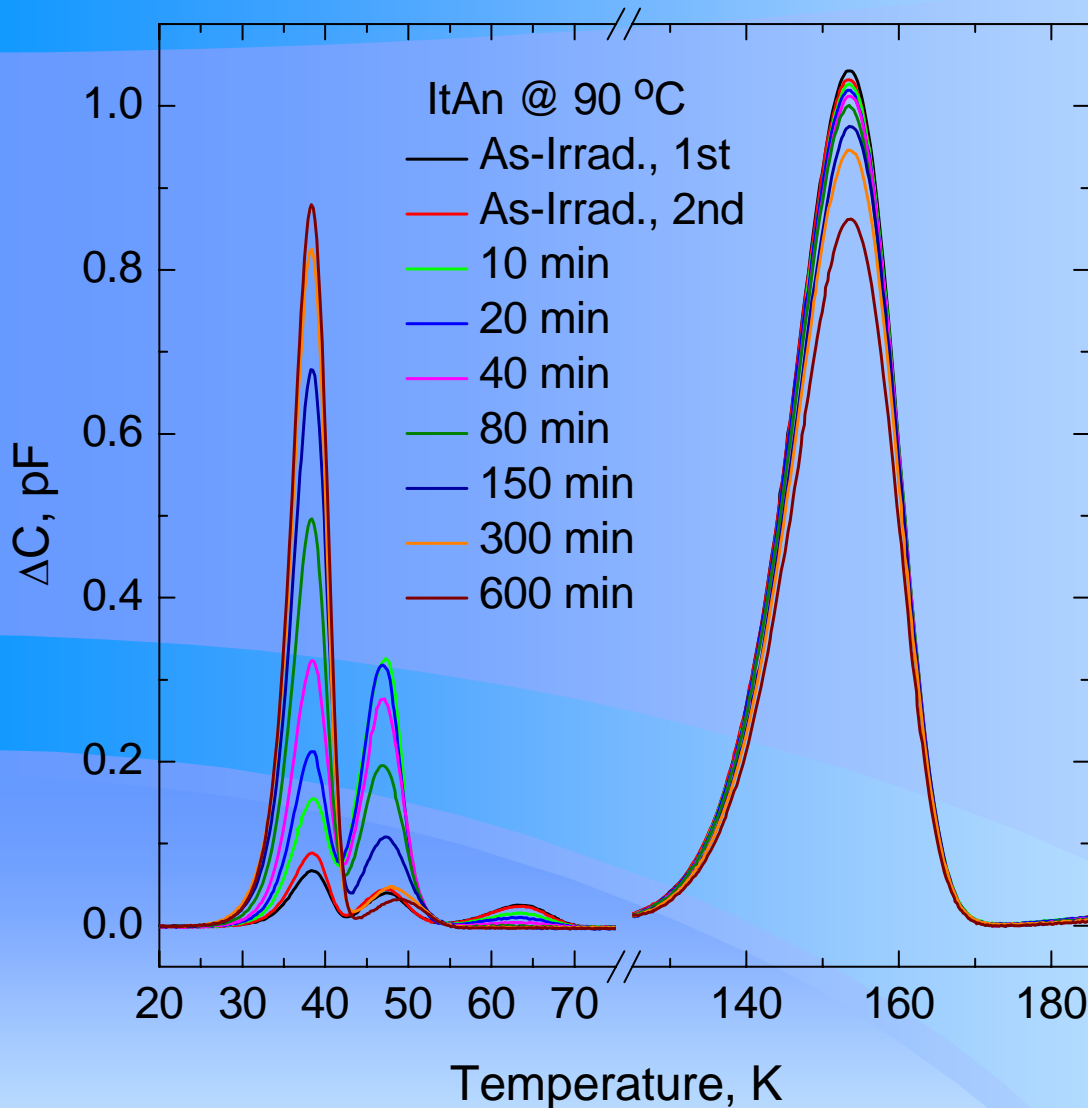
DLTS spectra for a (Sb+O)-doped  $\{[\text{Sb}] \approx 1.5 \cdot 10^{15} \text{ cm}^{-3}, [\text{O}_i] \approx 1.0 \cdot 10^{17} \text{ cm}^{-3}\}$  Ge sample after the irradiation with 4 MeV electrons ( $F = 1.5 \times 10^{15} \text{ cm}^{-2}$ ) and subsequent 30 min isochronal annealing.

Measurements:  $e_n = 80 \text{ s}^{-1}$ ,  $t_p = 1 \text{ ms}$ , bias  $-5.0 \rightarrow -0.5 \text{ V}$ .

# Defect transformations upon isochronal annealing of electron-irradiated Ge:Sb, O crystals



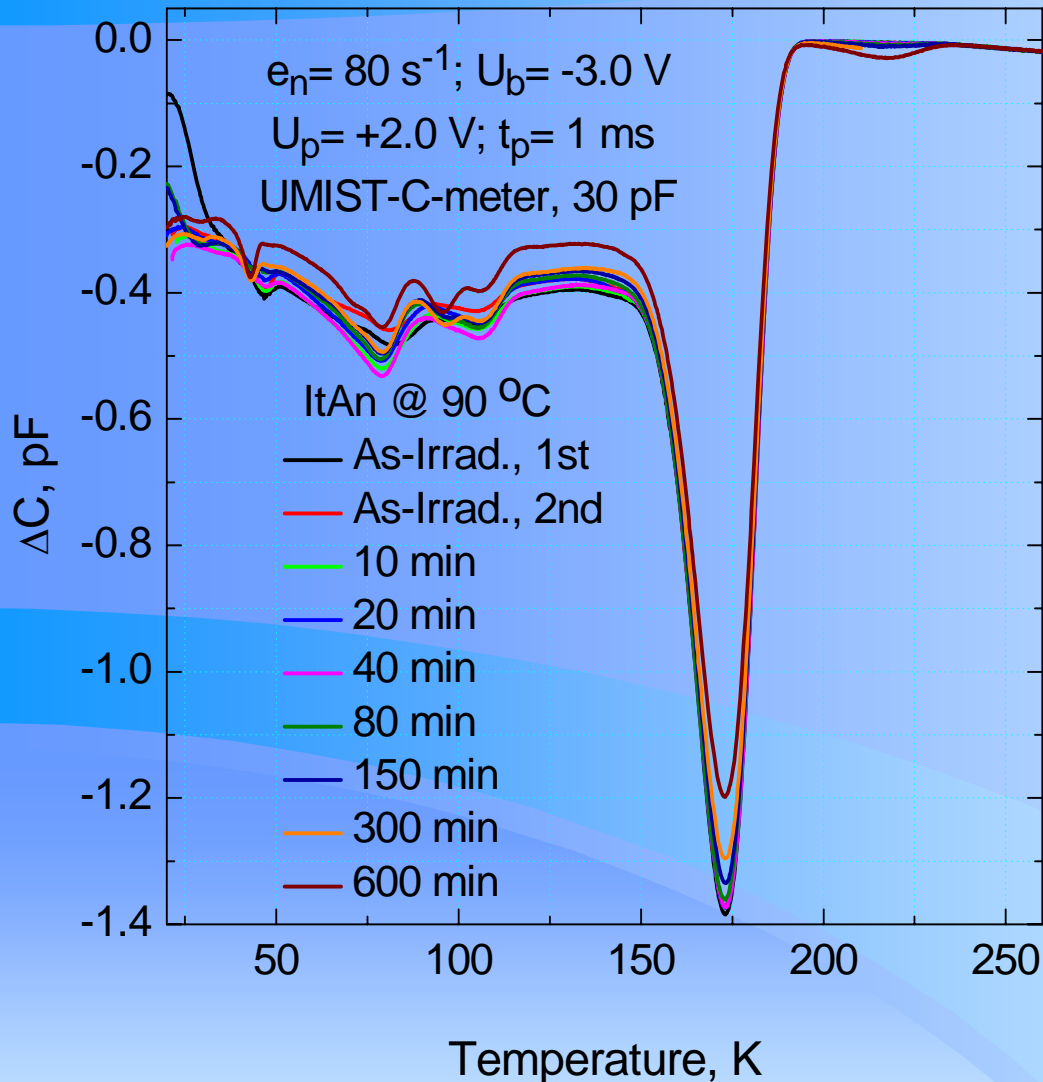
# Defect transformations upon isothermal annealing of electron-irradiated Ge:Sb, O crystals



DLTS spectra for a (Sb+O)-doped  $\{[Sb] \approx 4 \cdot 10^{14} \text{ cm}^{-3}, [O_i] \approx 1.0 \cdot 10^{17} \text{ cm}^{-3}\}$  Ge sample after the irradiation with 4 MeV electrons ( $F = 2 \cdot 10^{14} \text{ cm}^{-2}$ ) and subsequent isothermal annealing at 90 °C.

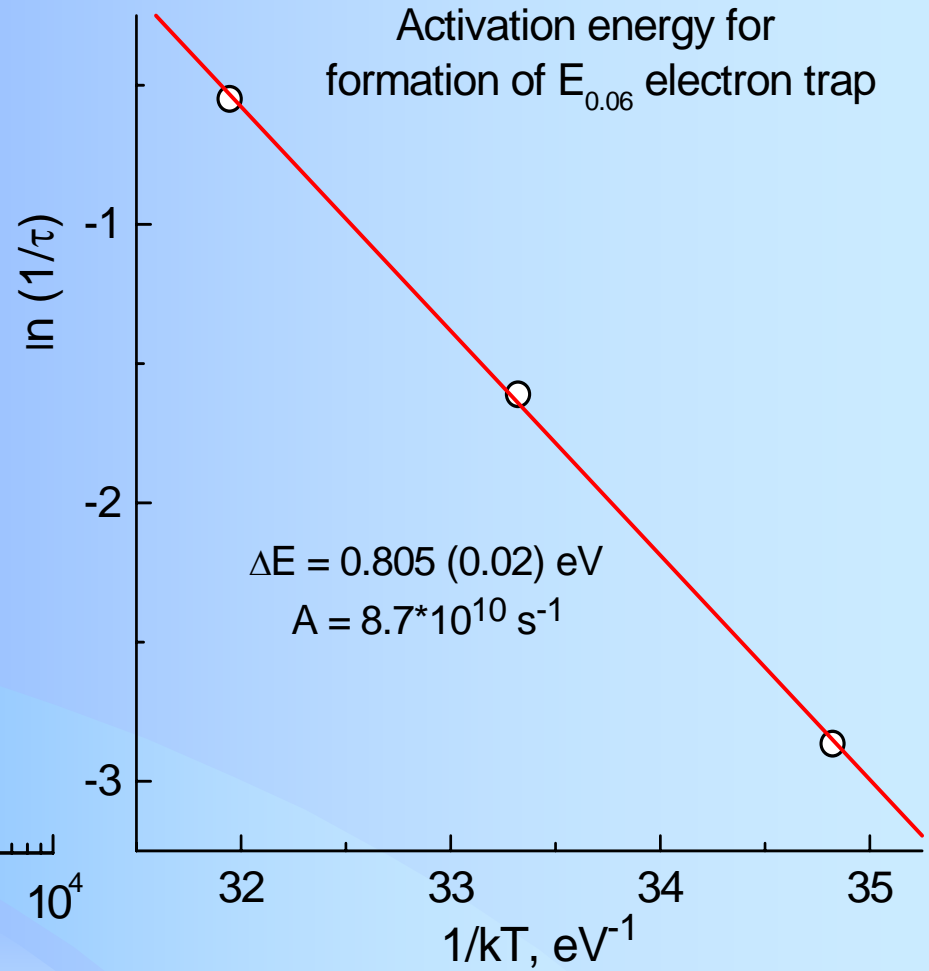
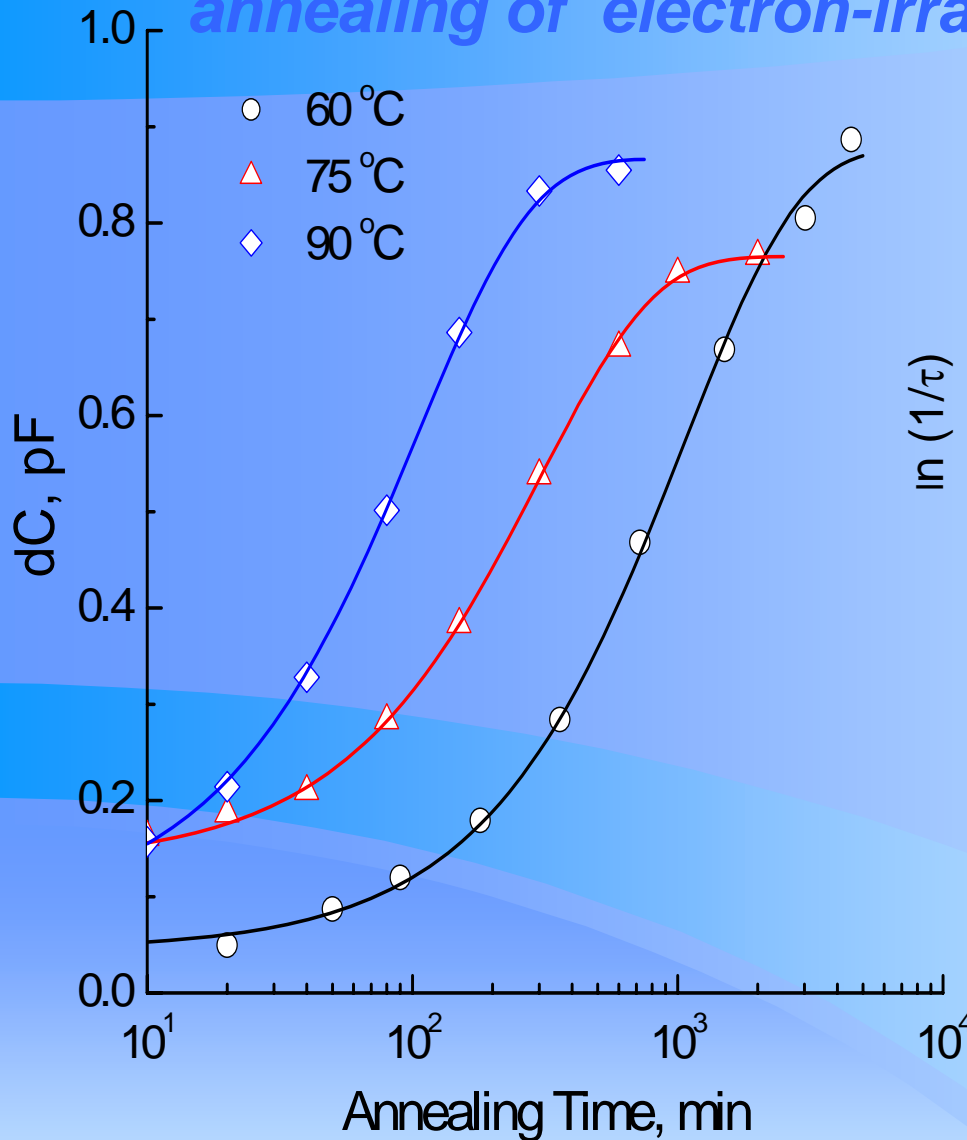
Measurements:  $e_n = 80 \text{ s}^{-1}$ ,  $t_p = 1 \text{ ms}$ , bias  $-5.0 \rightarrow -0.5 \text{ V}$ .

# Defect transformations upon isothermal annealing of electron-irradiated Ge:Sb, O crystals

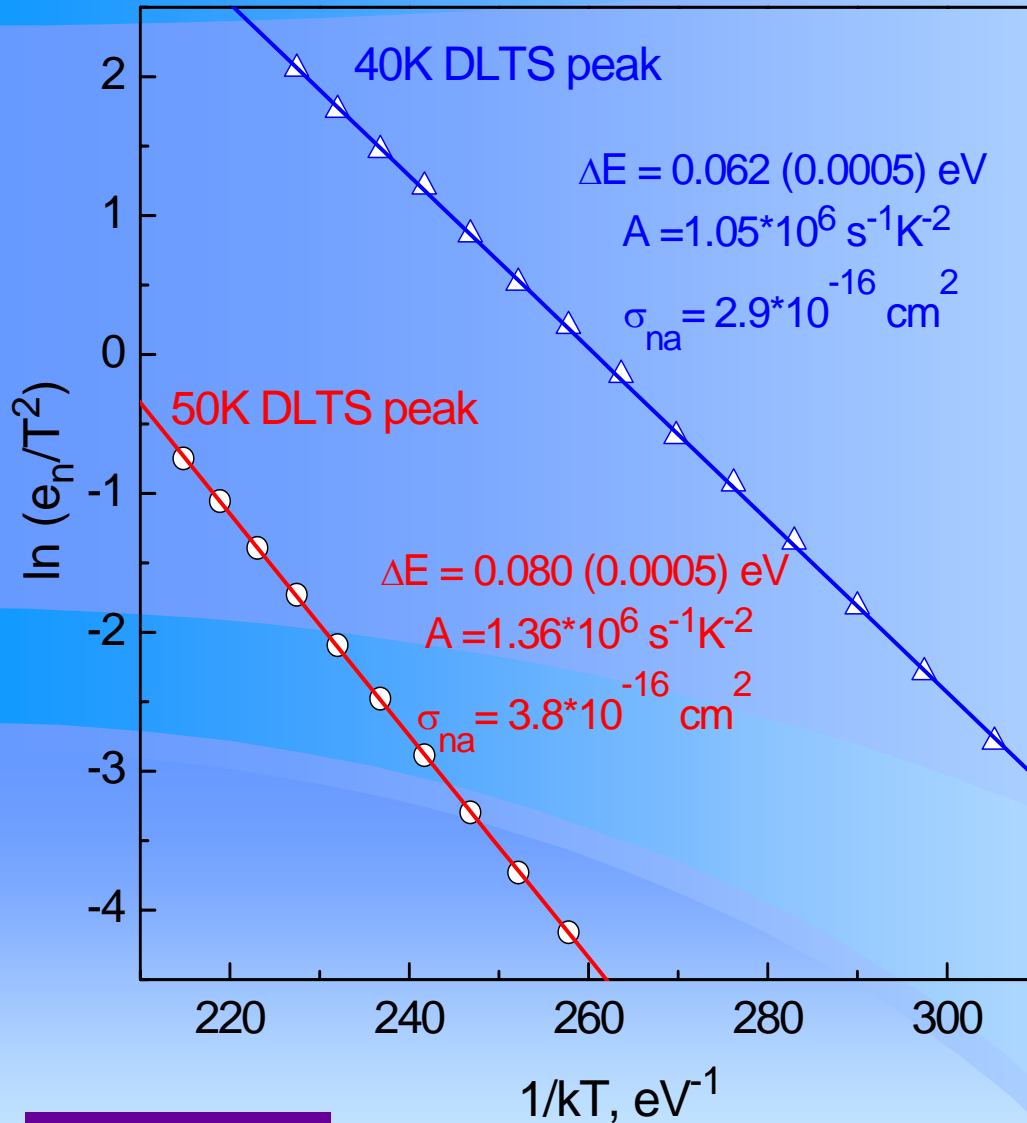


DLTS spectra for a (Sb+O)-doped  $\{[\text{Sb}] \approx 4 \cdot 10^{14} \text{ cm}^{-3}, [\text{O}_i] \approx 1.0 \cdot 10^{17} \text{ cm}^{-3}\}$  Ge sample after the irradiation with 4 MeV electrons ( $F = 2 \cdot 10^{14} \text{ cm}^{-2}$  and subsequent isothermal annealing at 90 °C. Measurements:  $e_n = 80 \text{ s}^{-1}$ ,  $t_p = 1 \text{ ms}$ , bias  $-3.0 \rightarrow +2.0 \text{ V}$ .

# Formation kinetics of the $E_{0.06}$ trap upon isothermal annealing of electron-irradiated Ge:Sb, O crystals

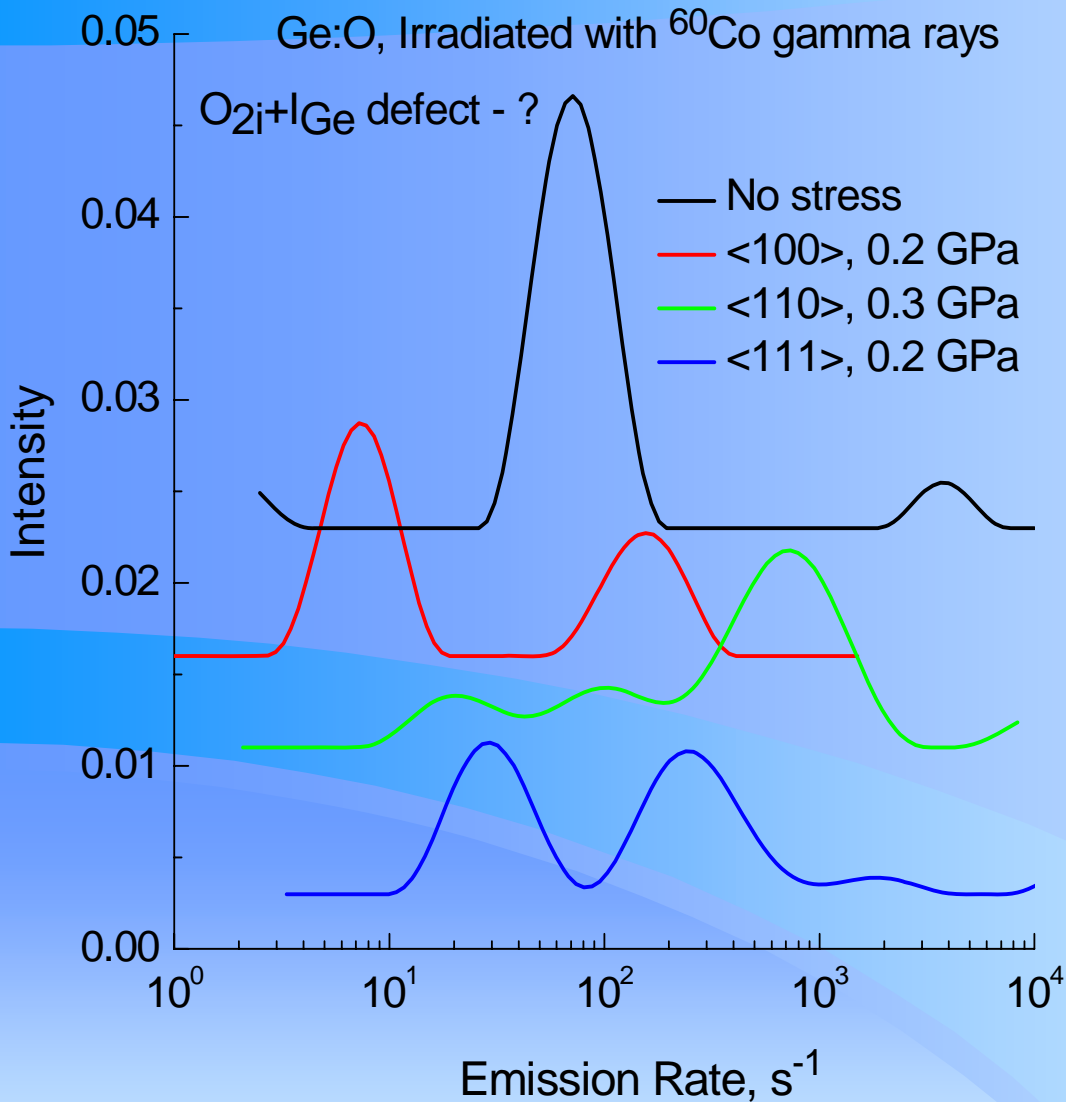


# Electronic properties of $I-O_{ni}$ defects



It has been inferred from the analysis of direct measurements of capture cross sections and changes in the concentration of free electrons upon the formation of  $E_{0.06}$  and  $E_{0.08}$  traps that the traps are related to  $E(-/0)$  states of the corresponding defects.

# Symmetry of the $E_{0.06}$ defect



Splitting pattern under application of uniaxial stress indicates that the corresponding defect has orthorhombic-I ( $C_{2v}$  point group) symmetry.



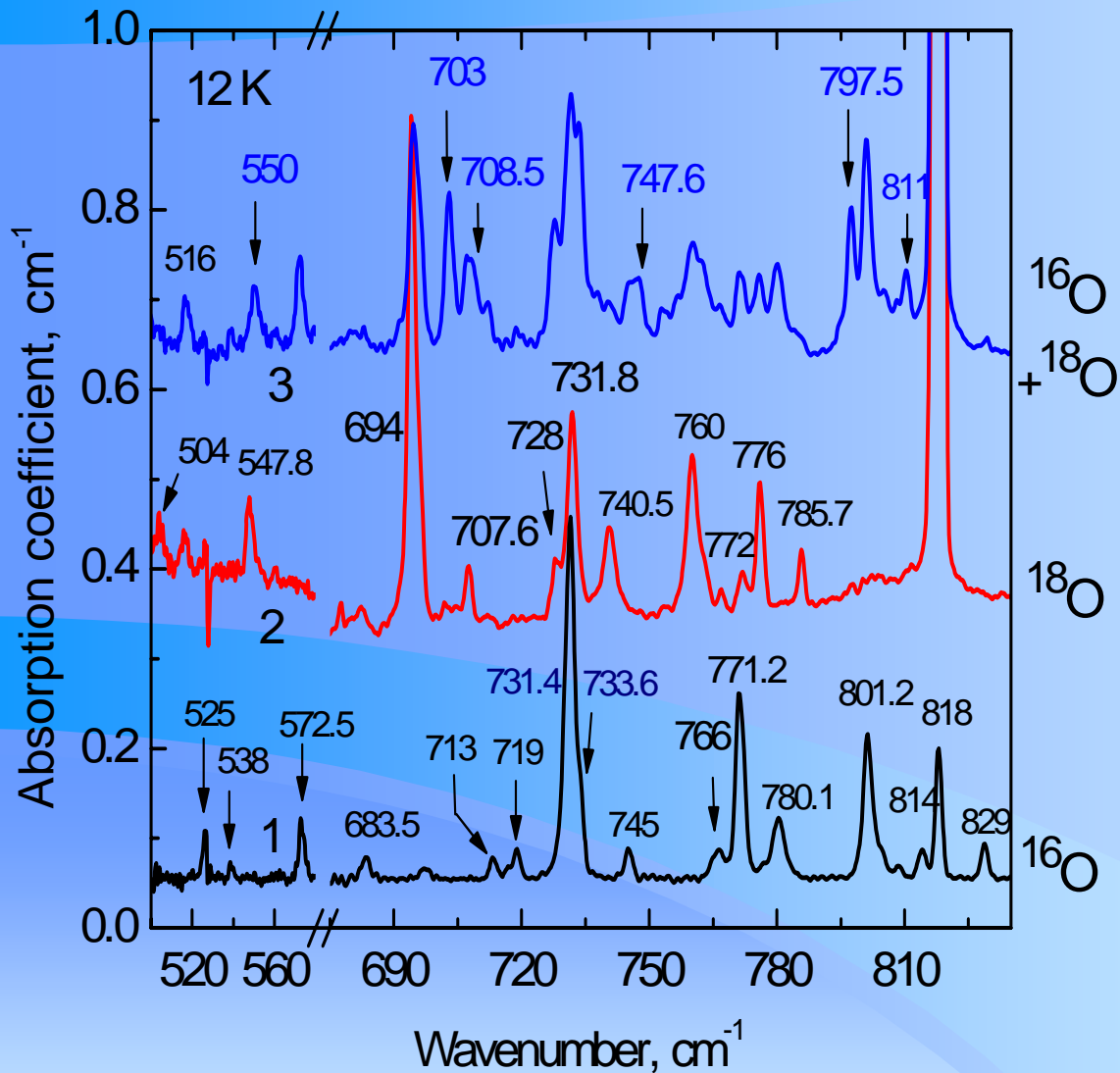
# The $E_{0.06}$ and $E_{0.08}$ traps in electron- and gamma-irradiated oxygen-rich Ge crystals: observations

- *Formation conditions and kinetics.*
  - a) The traps have been observed only in irradiated oxygen-rich Ge crystals.  $\Rightarrow$  Oxygen atoms and radiation-induced defects are constituents.
  - b) Immediately after electron irradiation at room temperature the concentration of the traps is very small. The traps are formed upon long storage of the irradiated samples at room temperature or upon heat-treatments at  $T > 330$  K. The activation of formation of the dominant  $E_{0.06}$  trap is 0.8 (0.02) eV.
  - c) Vacancy-oxygen centres have been observed immediately after the electron irradiations at RT and there are no significant changes in the concentration of A centres upon the first stages of formation of the  $E_{0.06}$  and  $E_{0.08}$  traps. The maximum achievable concentration of the  $E_{0.06}$  trap is close to the concentration of A centres.  $\Rightarrow$  The traps are related to complexes of self-interstitial and oxygen atoms.
- *Electronic properties and symmetry of the  $E_{0.06}$  and  $E_{0.08}$  traps.*
  - a) It has been inferred from the analysis of direct measurements of capture cross sections and changes in the concentration of free electrons upon the formation of  $E_{0.06}$  and  $E_{0.08}$  traps that the traps are related to  $E(-/0)$  states of the corresponding defects.
  - b) it has been found from the analysis of Laplace DLTS measurements under uniaxial stress that the  $E_{0.06}$  trap possess orthorhombic-I ( $C_{2v}$  point group) symmetry.

# The $E_{0.06}$ and $E_{0.08}$ traps in electron- and gamma-irradiated oxygen-rich Ge crystals: speculations

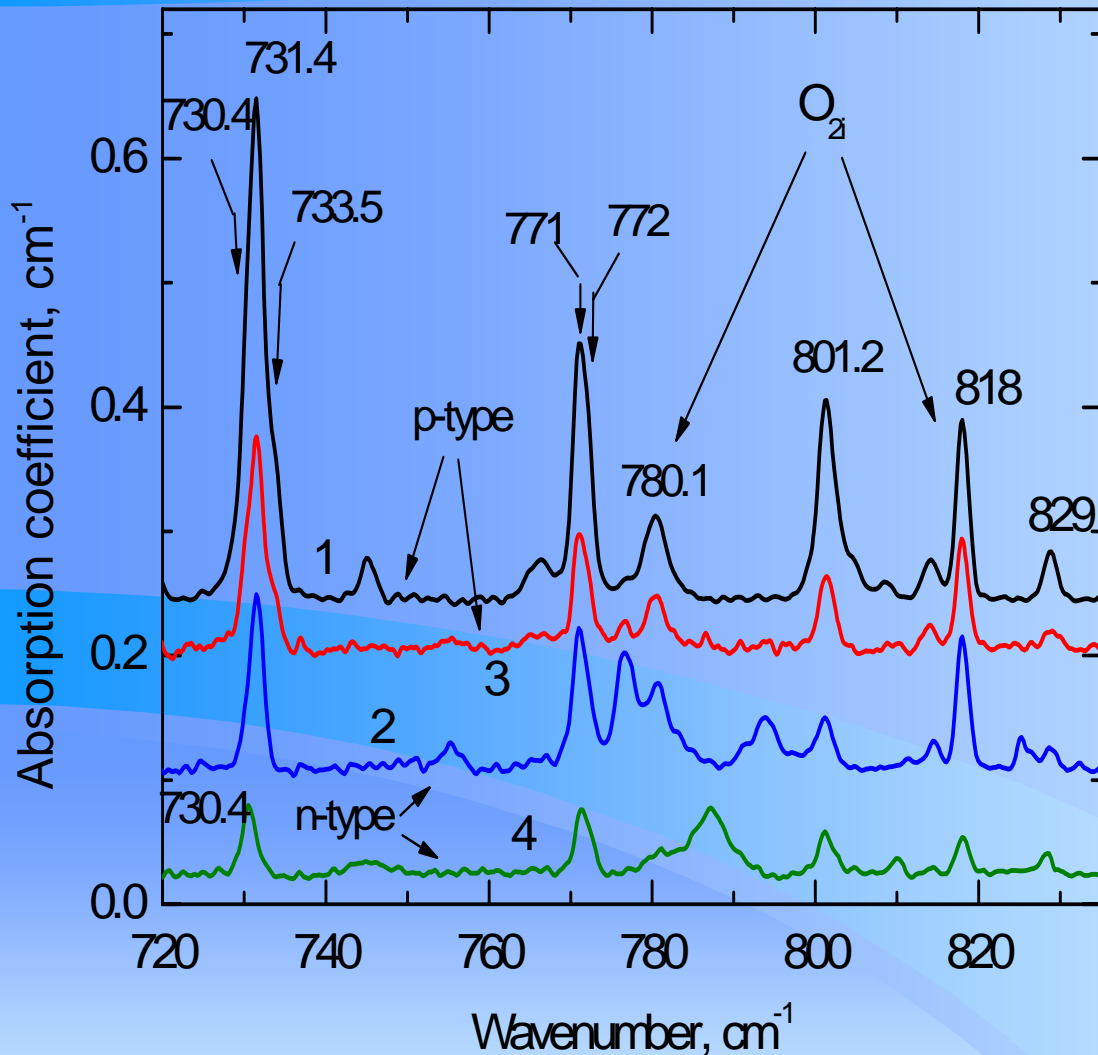
- *Interaction of self-interstitials with oxygen-related centers in Ge.*
- It can be suggested that the  $E_{0.06}$  trap is related to a complex of one self-interstitial and two interstitial oxygen atoms ( $\text{IO}_{2i}$ ).
- Immediately after electron irradiation at RT self-interstitials are trapped by interstitial oxygen atoms. The  $\text{IO}_i$  centre does not exhibit deep energy levels in the gap. However, the existence of shallow levels or deep donor level in the lower part of the gap is not ruled out.
- The  $\text{IO}_i$  centres can migrate at temperatures higher than 330 K. The activation energy of the migration is 0.8 eV.
- The mobile  $\text{IO}_i$  centres can be captured by interstitial oxygen atoms, that results in the formation of  $\text{IO}_{2i}$  complexes. This complex has a  $E(-/0)$  level at about  $E_c - 0.06$  eV and posses orthorhombic-I ( $C_{2v}$  point group) symmetry.
- *Help from Exeter is needed to approve or reject these speculations!*

# Defect transformations upon isochronal annealing of electron-irradiated Ge:O crystals: IR absorption study



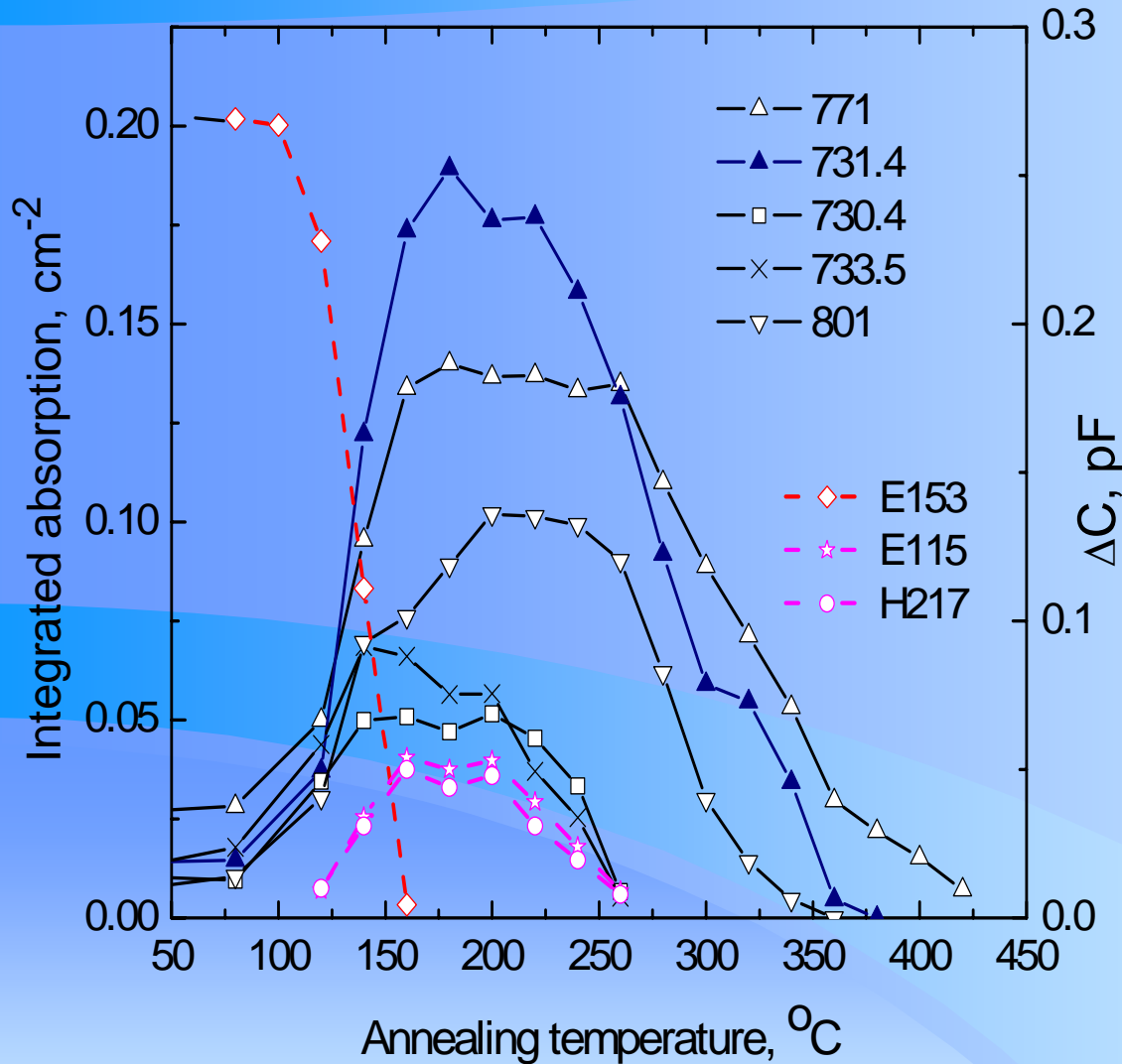
Absorption spectra at 12 K for Ge crystals after irradiation with 6 MeV electrons ( $F = 1.3 \times 10^{17} \text{ cm}^{-2}$ ) and subsequent annealing for 30 min at 160 °C: (1) Ge:<sup>16</sup>O ( $\rho = 4 \text{ } \Omega \cdot \text{cm}$ ,  $[\text{O}_i] = 2.3 \times 10^{17} \text{ cm}^{-3}$ ), (2) Ge:<sup>18</sup>O ( $\rho = 1,2 \text{ } \Omega \cdot \text{cm}$ ,  $[\text{O}_i] = 4.3 \times 10^{17} \text{ cm}^{-3}$ ) and (3) Ge:<sup>16</sup>O+<sup>18</sup>O ( $\rho = 0.9 \text{ } \Omega \cdot \text{cm}$ ,  $[\text{O}_i] = 5.4 \times 10^{17} \text{ cm}^{-3}$ ,  $[\text{O}_i] = 4.2 \times 10^{17} \text{ cm}^{-3}$ ).

# Defect transformations upon isochronal annealing of electron-irradiated Ge:O crystals: IR absorption study



Absorption spectra in the spectral regions of 700-825 cm<sup>-1</sup> at 12 K for Ge:<sup>16</sup>O crystals doped with (1 and 2) Sb, (3) Ga и (4) TDDs (created by a heat-treatment at T=350 °C for 200 h), after irradiation with electrons and subsequent anneals for 30 min at (1,3,4) 160 °C or (2) 300 °C. Fluences of irradiation were: 1 and 2 -  $1.3 \times 10^{17}$  cm<sup>-2</sup>, 3 -  $5 \times 10^{16}$  cm<sup>-2</sup>, and 4 -  $1.1 \times 10^{16}$  cm<sup>-2</sup>.

# Defect transformations upon isochronal annealing of electron-irradiated Ge:O crystals: IR absorption study



Development of infrared absorption bands at 731, 771 and 801 cm<sup>-1</sup> and magnitudes of DLTS peaks due the A centre (E153 trap) and an electron trap (E115) and a hole trap (H217), which are formed simultaneously with the disappearance of the A centre, upon 30 min isochronal annealing of electron-irradiated Ge:<sup>16</sup>O samples.