

Local Structure Analysis of Germanium in the Optical Fiber

Junji IIHARA, Sumitomo Electric Industries, LTD., Analysis Technology Research Center

junji-iihara@sei.co.jp

The optical fiber is essential to the mass high-speed optical communication. Optical signals are transmitted in the optical fiber core region by the waveguide structure. To control the refractive index, GeO_2 and/or F are doped to SiO_2 glasses. The transmission losses, relating to the glass structure, are required to be suppressed to low levels. They, however, increase with increasing the GeO_2 concentration. We, therefore, have studied the GeO_2 - SiO_2 glass structure with focus on the local structure of Ge against the GeO_2 concentration.

The figure shows XANES spectra of the GeO_2 - SiO_2 glasses with different GeO_2 concentrations. The spectral shapes are quite similar to each other but the absorption edge is shifted to the higher energy side according to the refractive index difference (n).

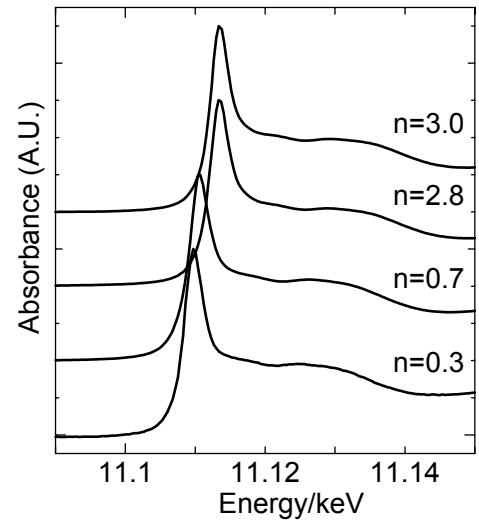


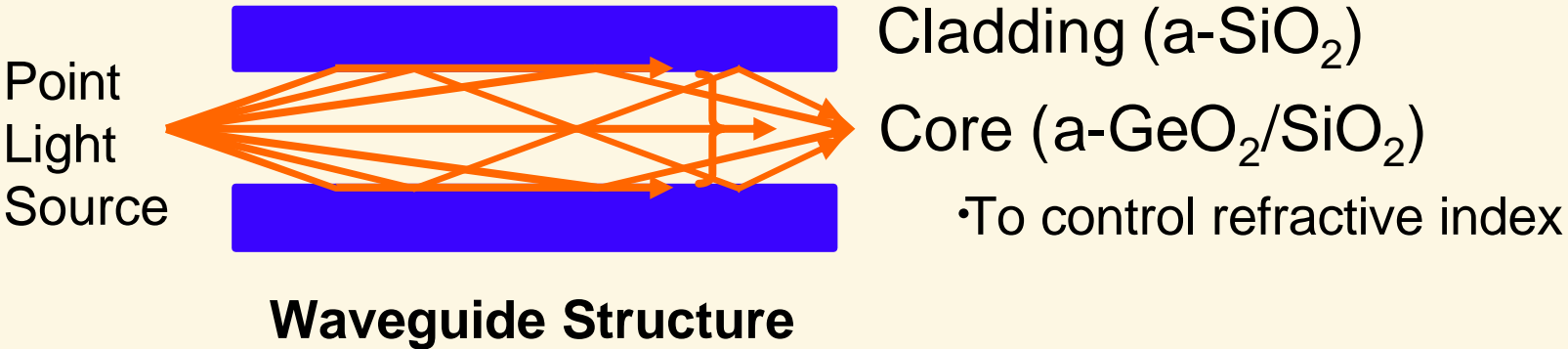
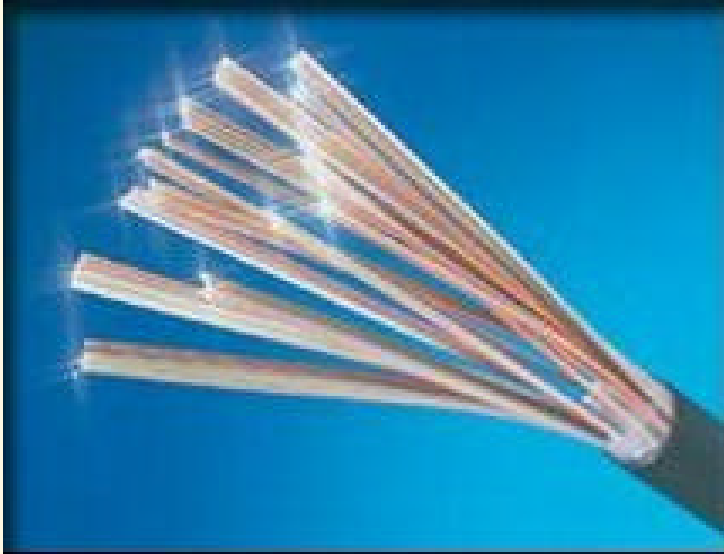
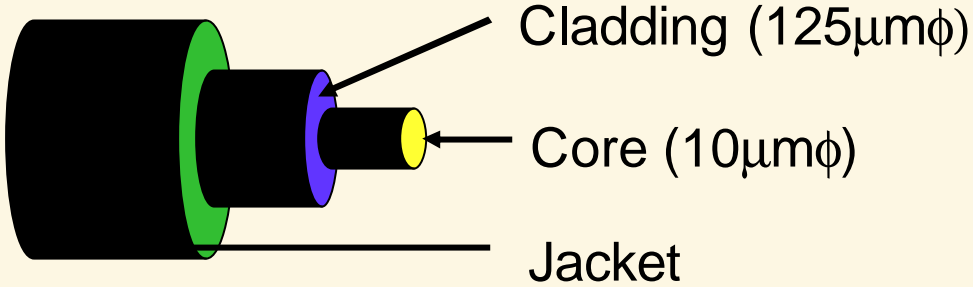
Figure The Ge-K XANES spectral change with the refractive index difference (n) of GeO_2 - SiO_2 glasses.

LOCAL STRUCTURE ANALYSIS OF GERMANIUM IN THE OPTICAL FIBER

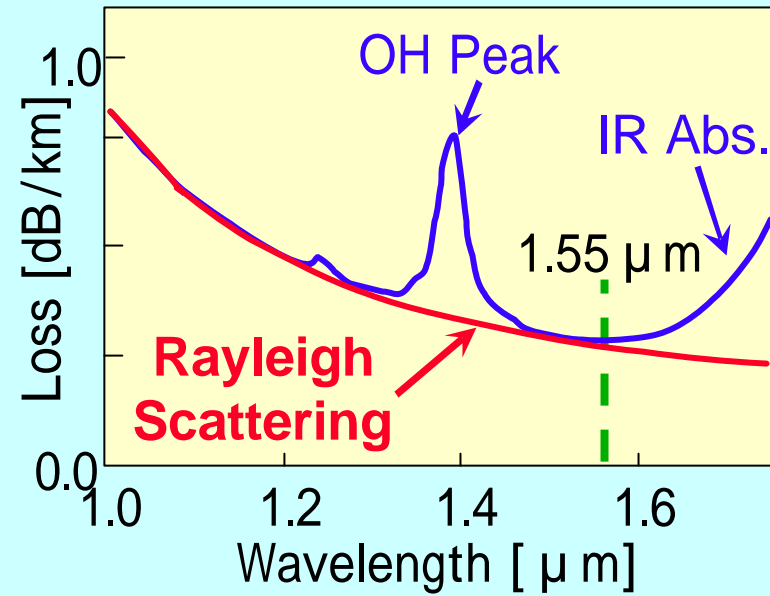
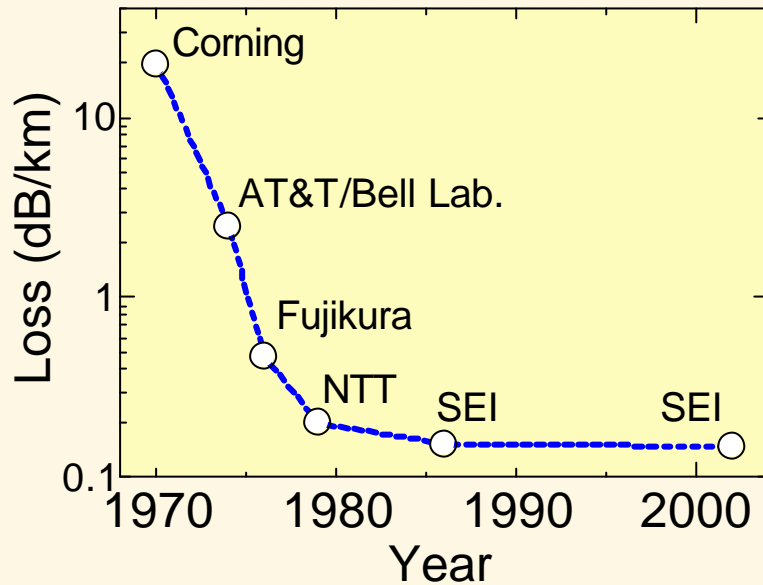
1. Introduction
2. Theoretical analysis of Ge XANES
3. Conclusion

Junji Iihara (junji-iihara@sei.co.jp)

Sumitomo Electric Industries, Ltd.
Analysis Technology Research Center



Lowering the Loss of Optical Fiber



Rayleigh Scattering

IR Absorption



Structure

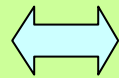
Impurities

Limit

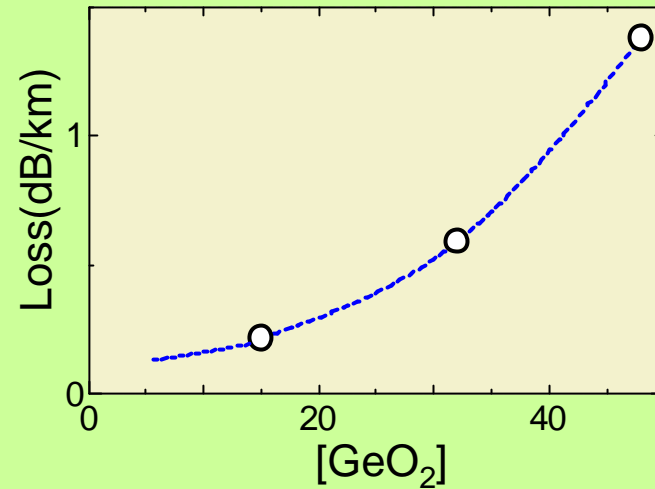
GeO₂ doped SiO₂ glass

Loss [GeO₂]

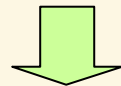
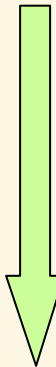
[GeO₂]



Structure



Ge metal cluster observed by TEM

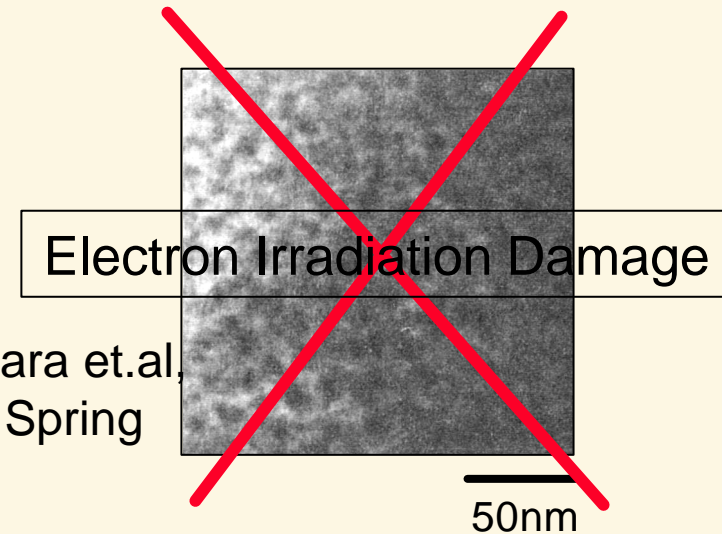


Useful Method?

Verification

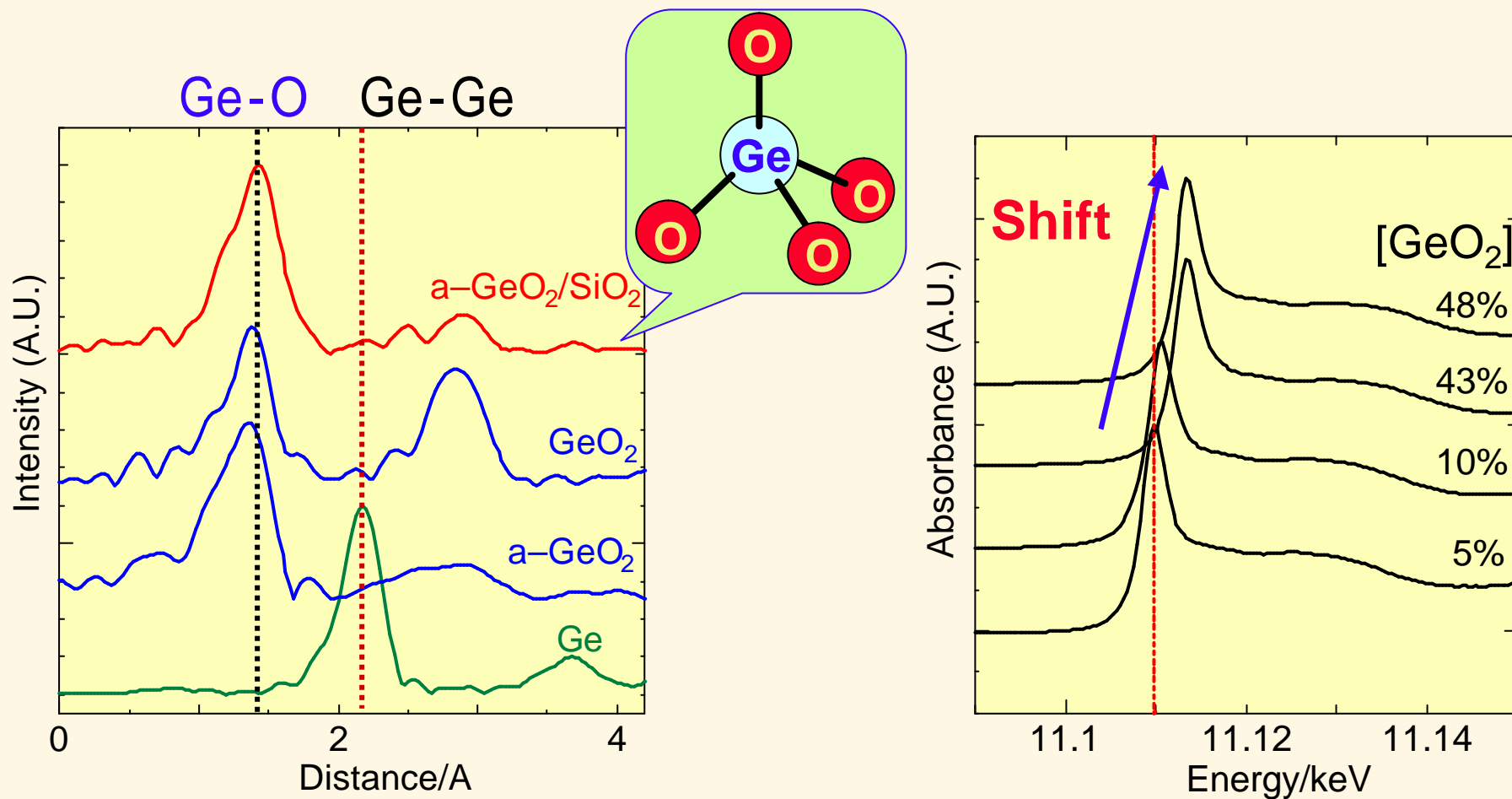
XAFS Method

Ge metal cluster was denied.



Ishikawa, Iihara et al.
JSAP 2001 Spring

H. Hosono et al.,
J. Appl. Phys. 80, 3115 (1996)



•1st Neighbor : Oxygen, Coordination Number ~ 4
•XANES Peak : Shift to Higher Energy by [GeO₂]

Theoretical analysis of XANES energy shift

1. Selection of XANES analysis method
2. XANES simulation for some models

Identification of XANES

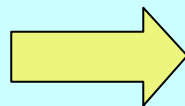
•Fingerprinting Method →

Preparation of Standard Specimen is impossible

•Simulation Method

Selection of Calculation Method

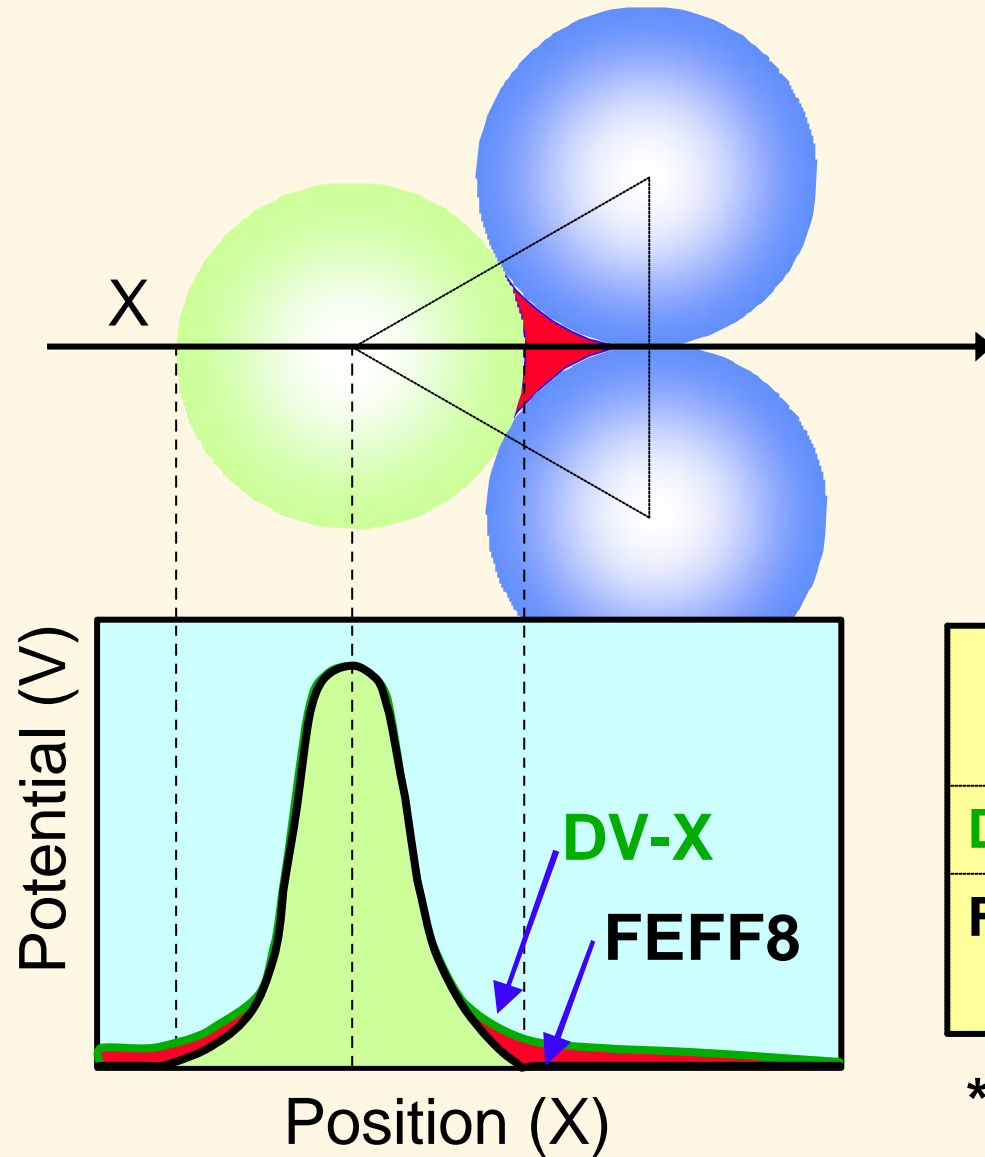
FEFF8
DV-X



Test calculation for
GeO₂, Metallic Ge

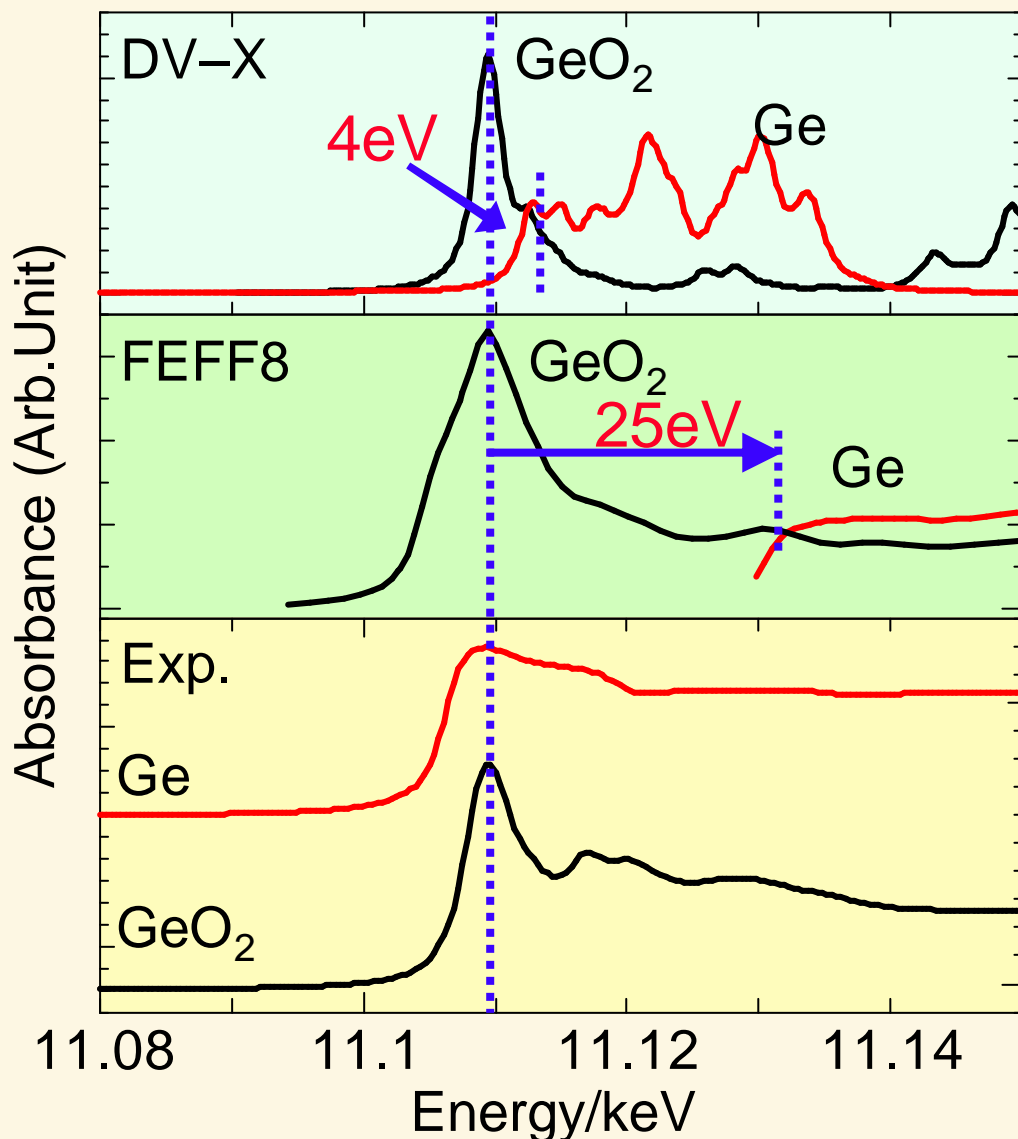
Object

•XANES Energy Shift



	Inter-electron repulsive potential
DV-X *	Exact
FEFF8	Approximate (Muffin-Tin)

*Discrete Variational X_α method



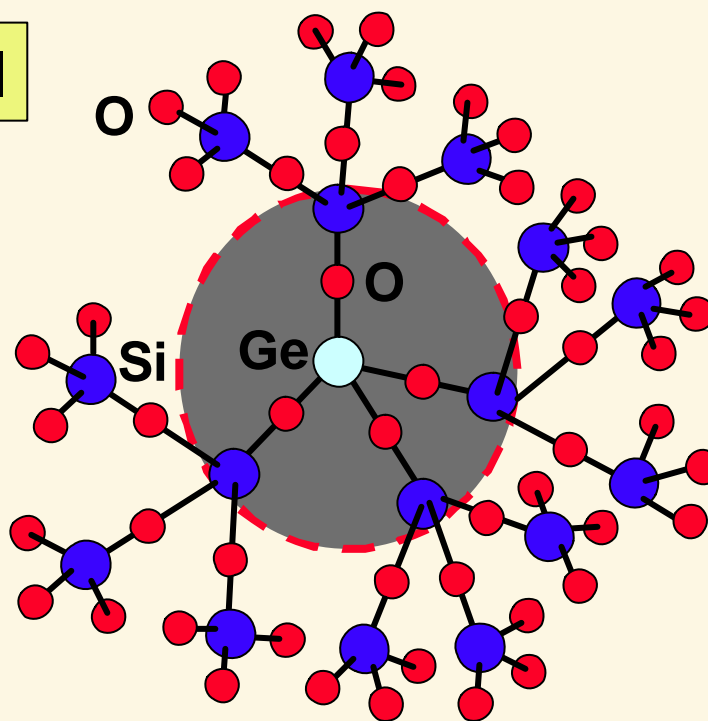
Relative Energy Difference

DV-X < FEFF8

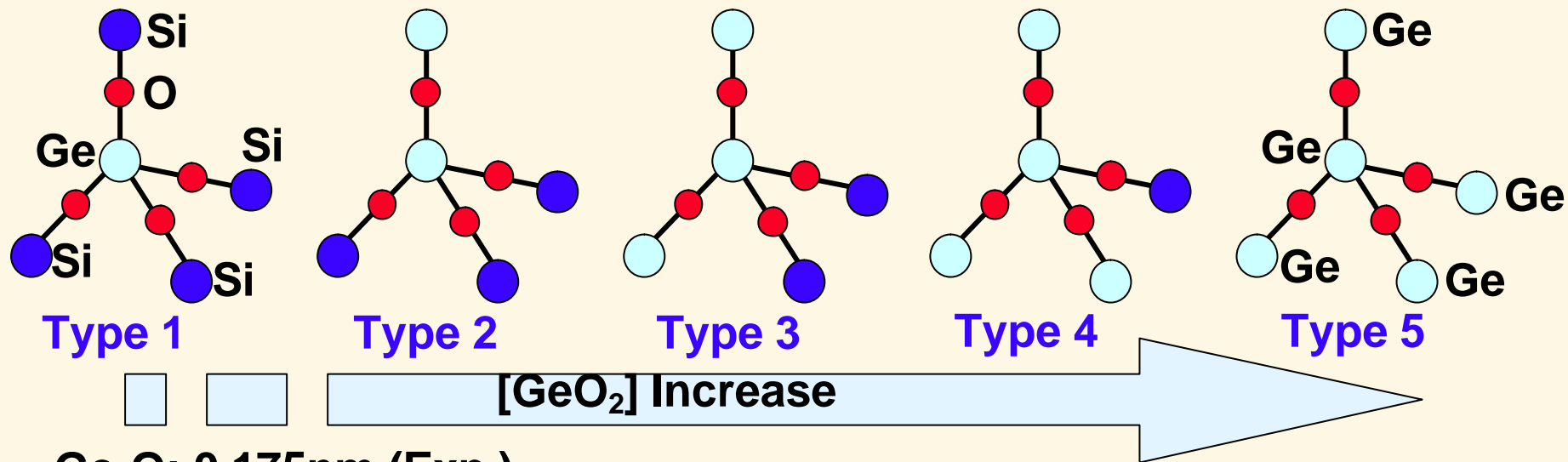
(Calculated Energy is normalized with GeO₂ peak energy)

1. GeO₂ Clustering
2. Structure Deformation
3. 2nd Nearest-neighbor Vacancy

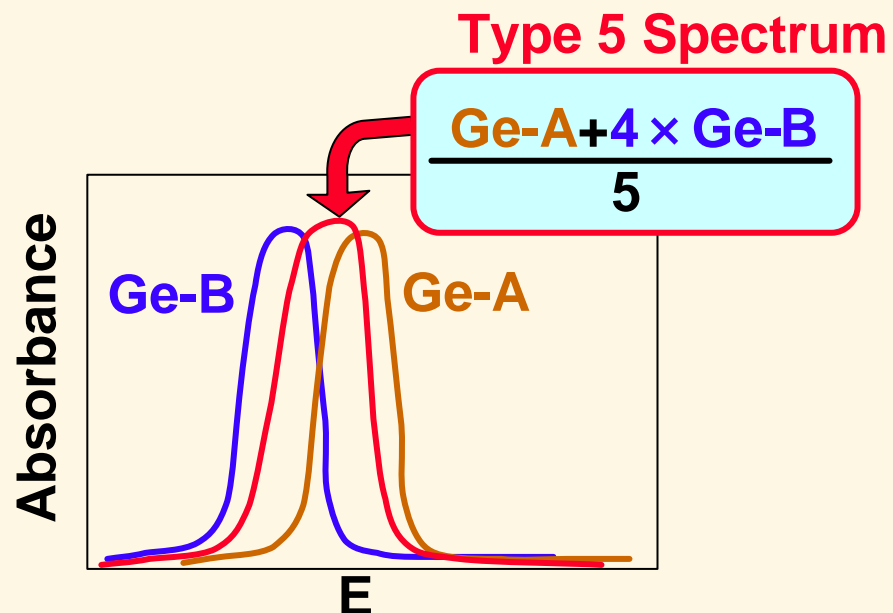
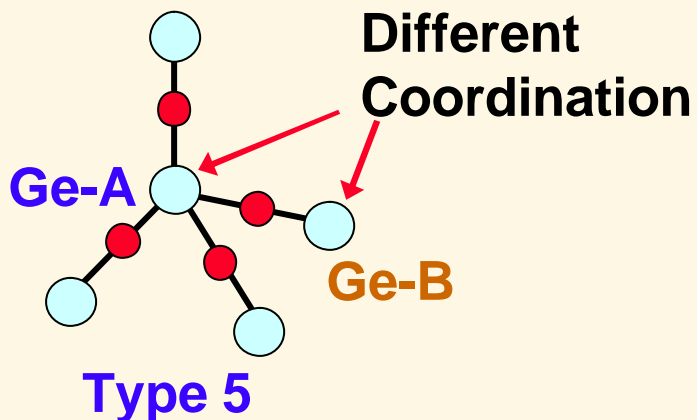
Calculated Model

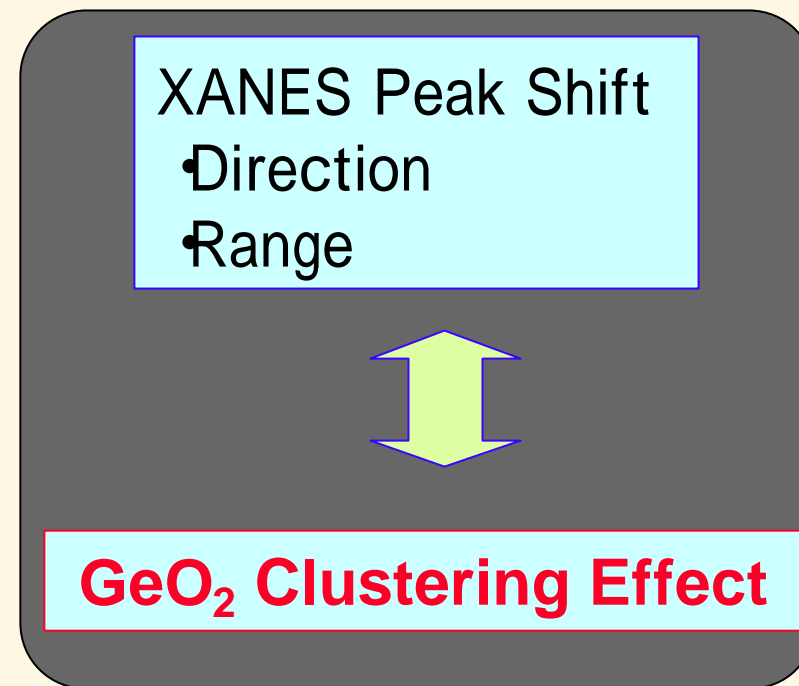
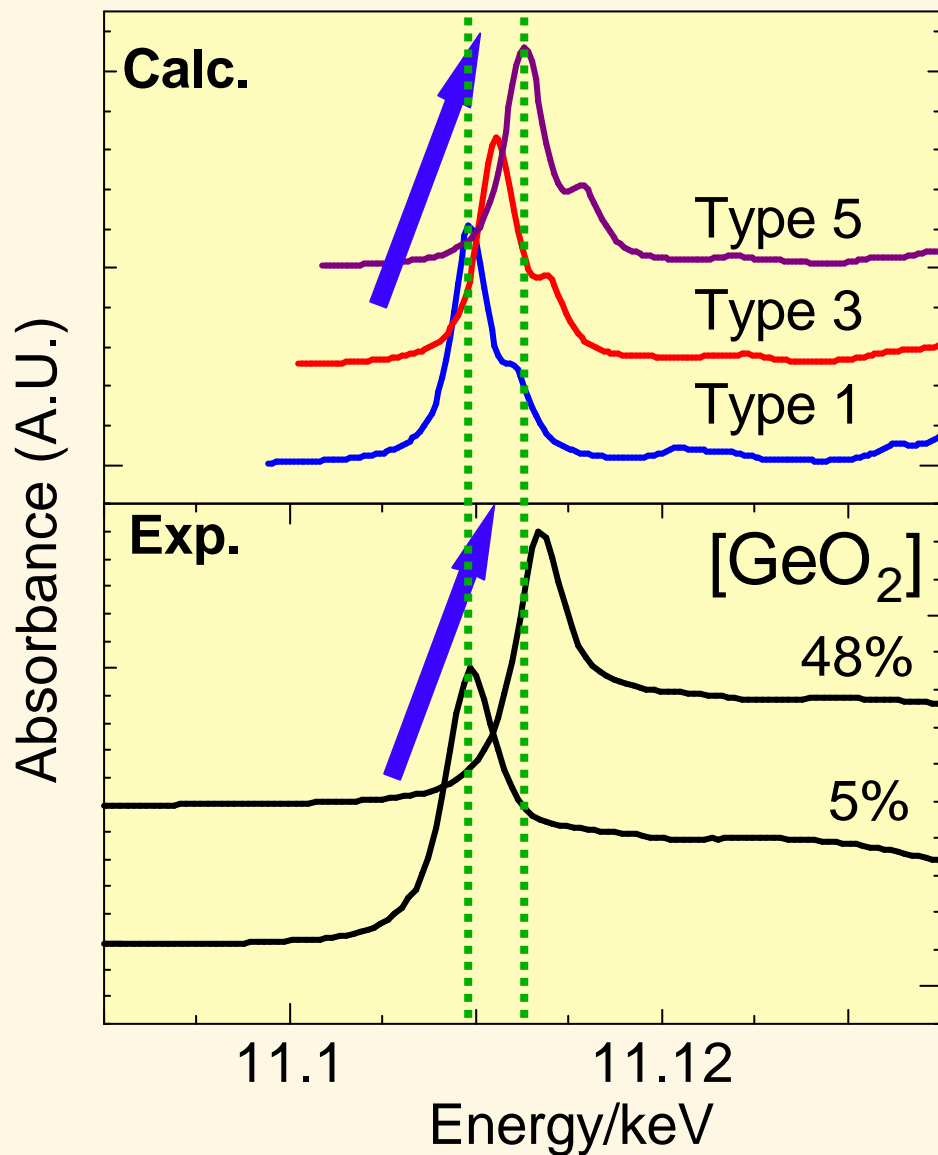


Source 1. GeO₂ Clustering

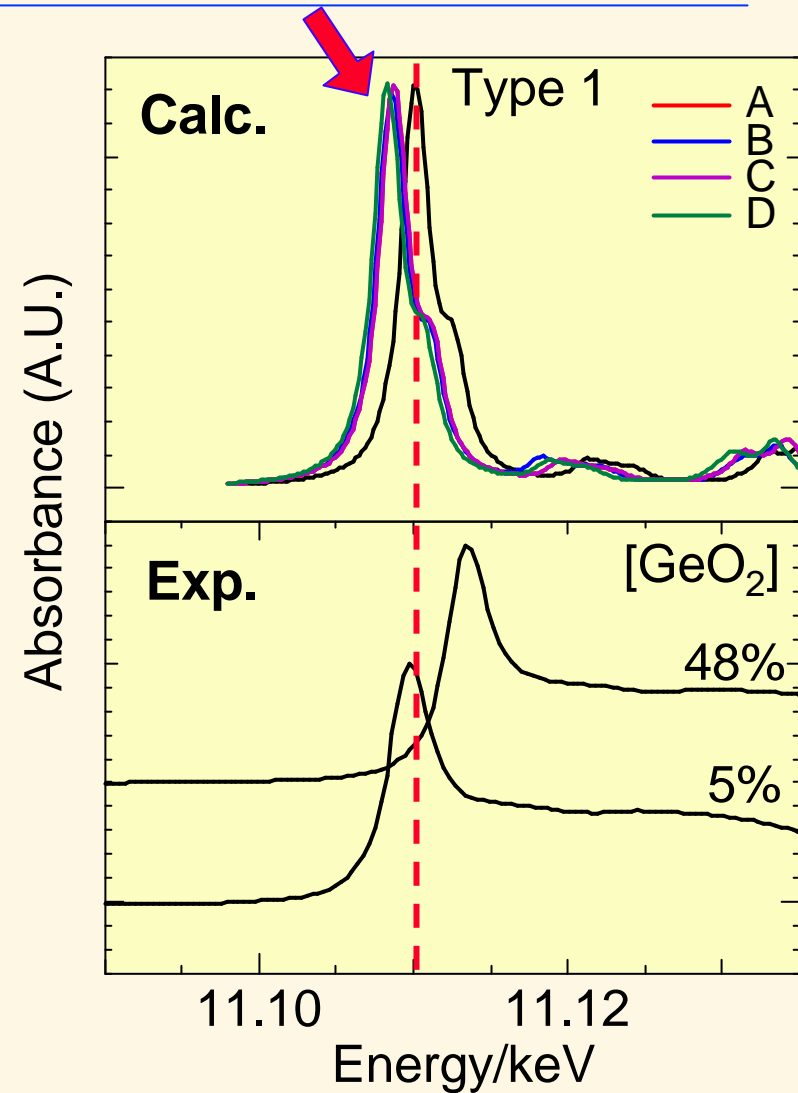
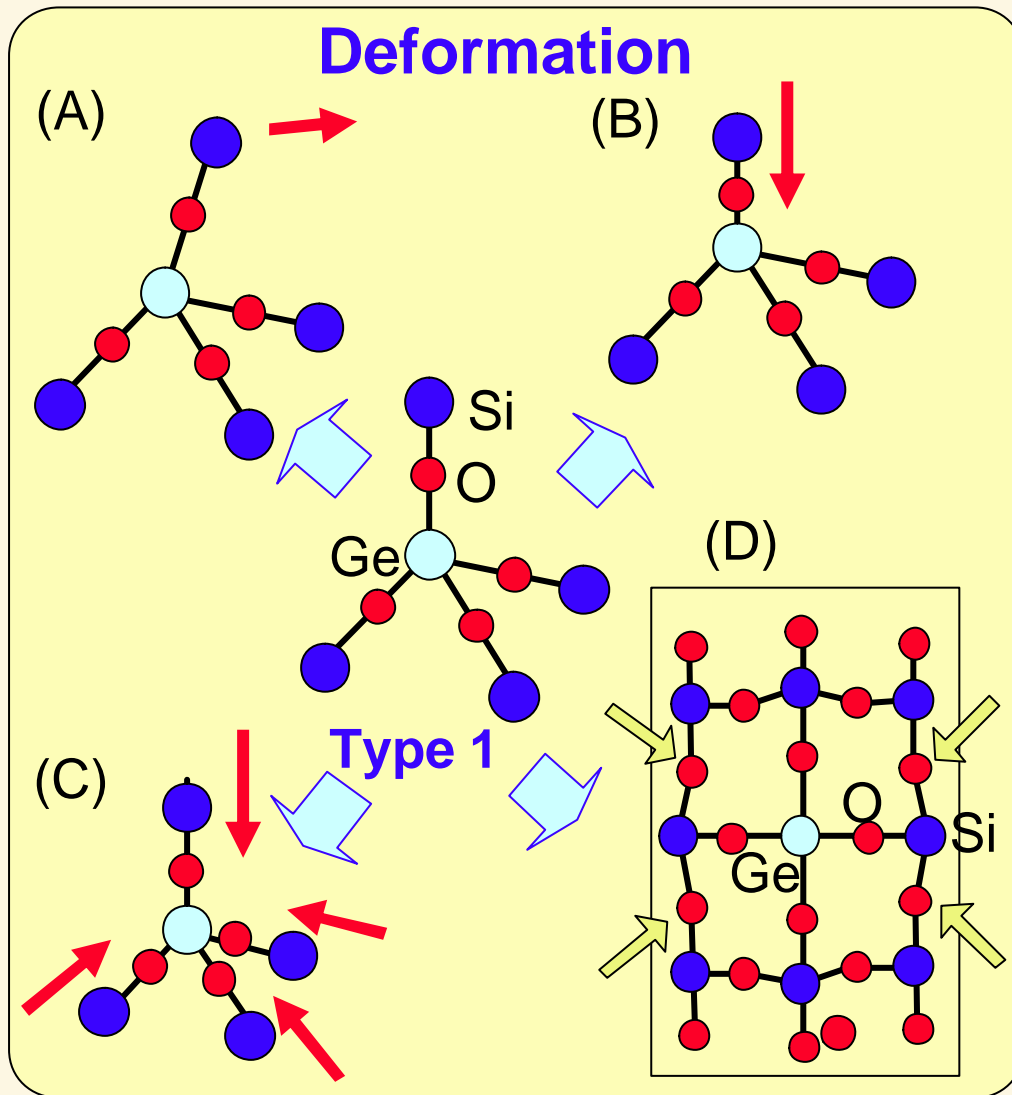


Ge-O: 0.175nm (Exp.)
Si-O : 0.175nm

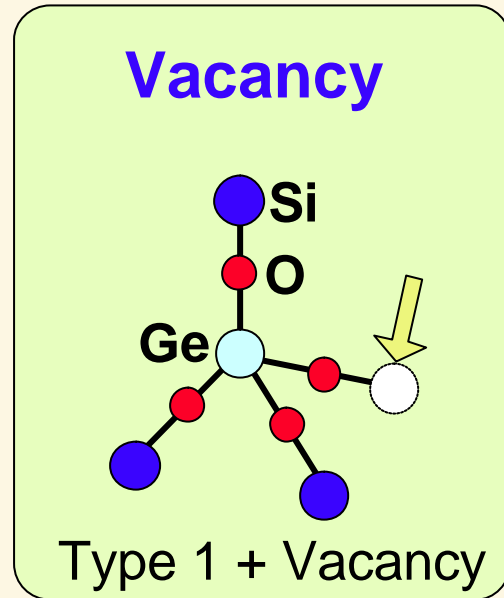




(Calculated Spectrum are normalized with Ge(1) peak energy and 5GeO₂-SiO₂)



Effect of Deformation is Small

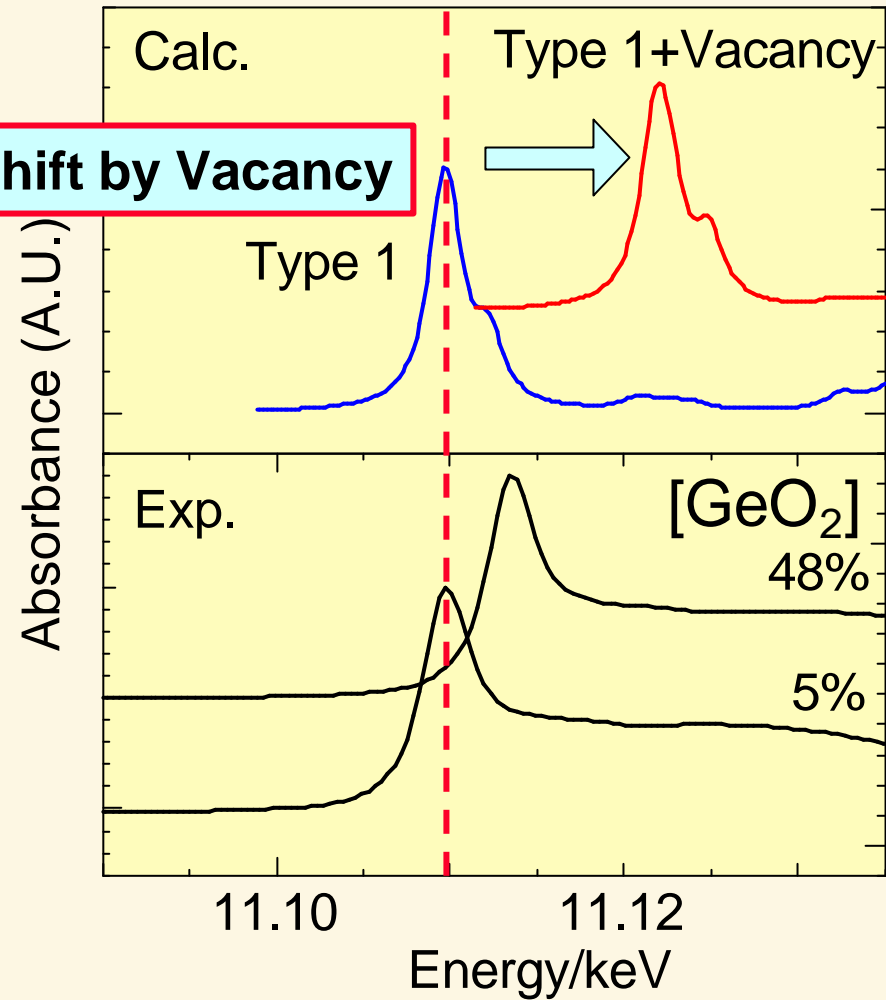


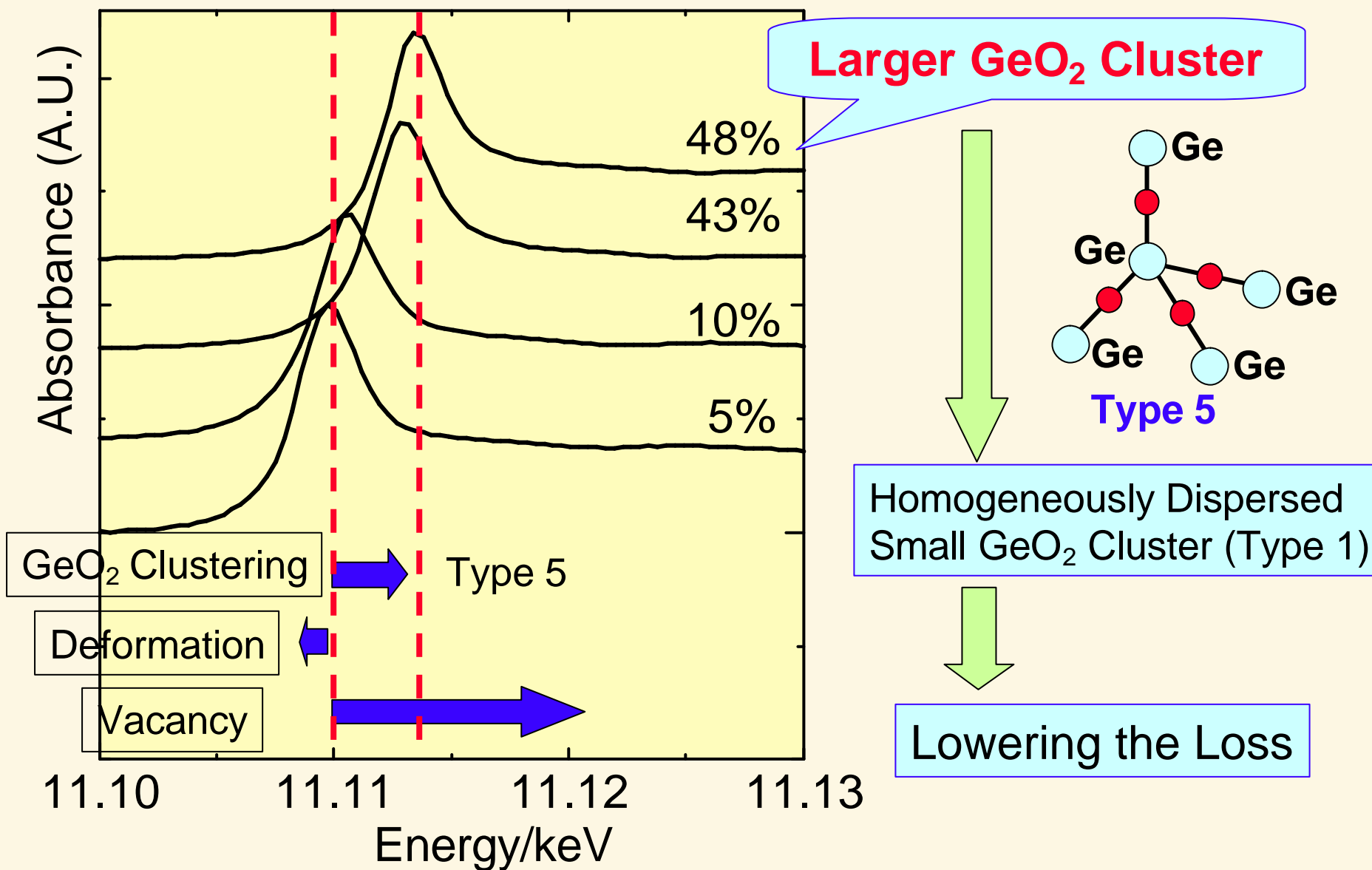
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Large Shift

[Vacancy] is very low
Replaced by Impurity Atom

Peak Shift by Vacancy





Summary

The method for local structural analysis of Ge in GeO₂/SiO₂ glass was developed; XAFS measurements and simulation.

- XANES energy shifts were explained by the GeO₂ clustering effects with DV-X_α simulation.
- High GeO₂ doped SiO₂ glass may have large GeO₂ cluster.

Future Prospect

- XAFS measurements in optical fiber shape specimen to evaluate the relation of its character.
- Local structural analysis of other elements in SiO₂ optical fiber glasses.