

# Structural assignments of NMR chemical shifts in $\text{Ge}_x\text{Se}_{\{1-x\}}$ glasses through first principles calculations for $\text{GeSe}_2$ , $\text{Ge}_4\text{Se}_9$ , and $\text{GeSe}$ crystals

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Results published: M. Kibalchenko, J. R. Yates, C. Massobrio, A. Pasquarello, Structural assignments of NMR chemical shifts in  $\text{Ge}_x\text{Se}_{\{1-x\}}$  glasses through first principles calculations for  $\text{GeSe}_2$ ,  $\text{Ge}_4\text{Se}_9$ , and  $\text{GeSe}$  crystals. *Phys. Rev. B* 82 (2010) 020202

# Introduction: $\text{Ge}_x\text{Se}_{\{1-x\}}$ glasses

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- sensitive to the absorption of electromagnetic radiation<sup>1</sup>
- applications in passive and active optics<sup>2</sup>

<sup>1</sup> A. Zakery and S. R. Elliott, J. Non-Cryst. Solids 330, 1 (2003)

<sup>2</sup> K. Shimakawa, A. Kolobov, and S. R. Elliott, Adv. Phys. 44, 475 (1995)

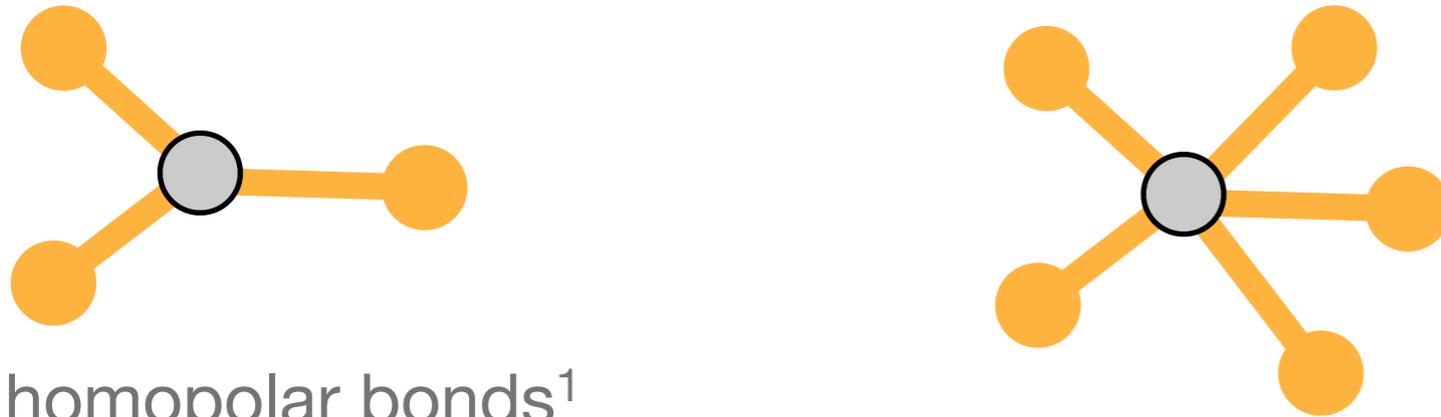
# Introduction: $\text{Ge}_x\text{Se}_{1-x}$ glasses

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- corner-sharing and edge-sharing tetrahedral arrangements<sup>1</sup>



- under-coordinated and over-coordinated atoms<sup>2</sup>



- homopolar bonds<sup>1</sup>



<sup>1</sup> I. Petri, P. S. Salmon, and H. E. Fischer, Phys. Rev. Lett. 84, 2413 (2000)

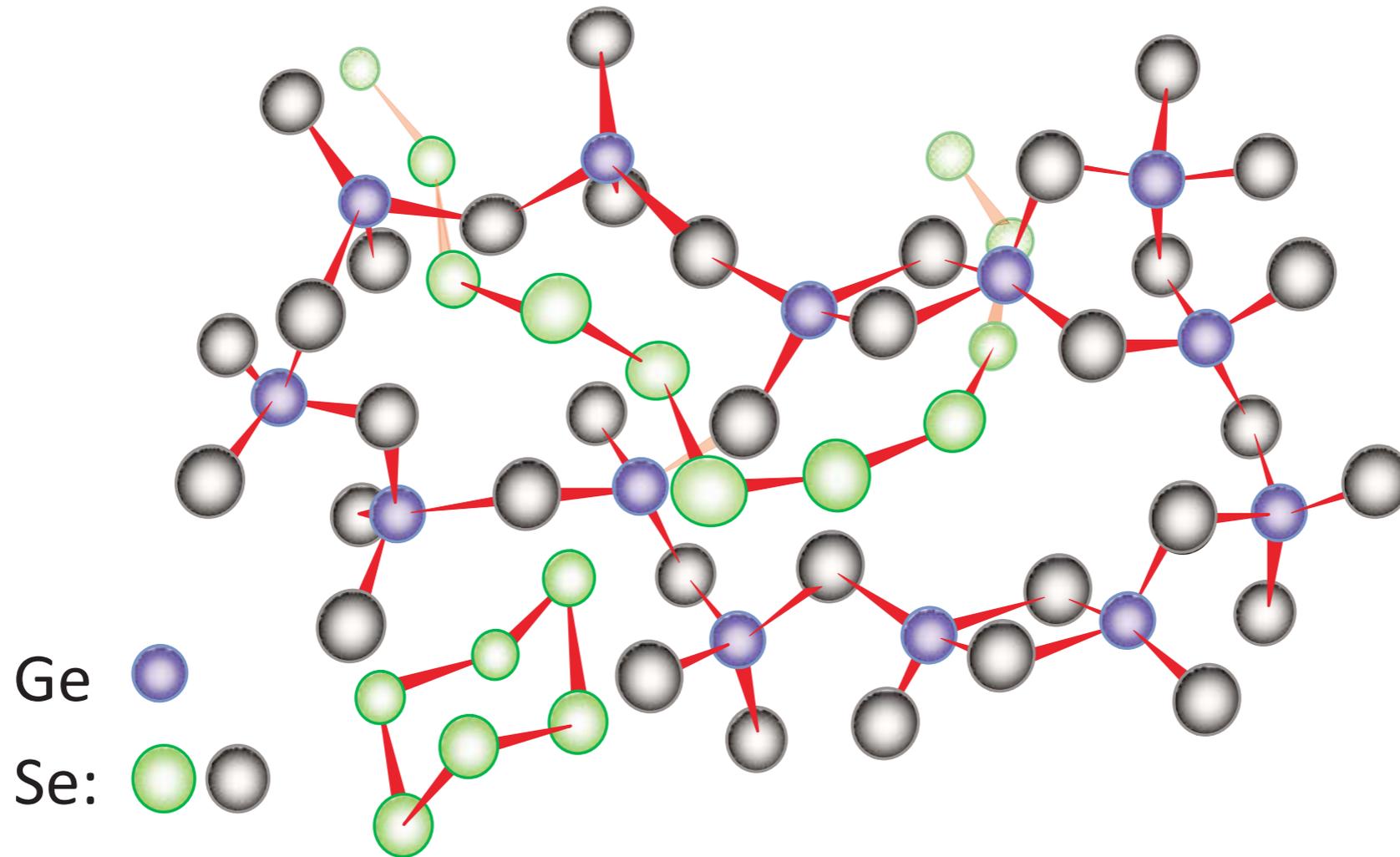
<sup>2</sup> C. Massobrio, M. Celino, P. S. Salmon, R. A. Martin, M. Micoulaut, and A. Pasquarello, Phys. Rev. B 79, 174201 (2009)

C. Massobrio and A. Pasquarello, Phys. Rev. B 77, 144207 (2008)

# Introduction: $\text{Ge}_x\text{Se}_{1-x}$ glasses

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1. bimodal phase: Se-Se-Se bonds and Ge-Se-Ge bonds only<sup>1</sup>
2. fully bonded with intermediate configurations<sup>2</sup>

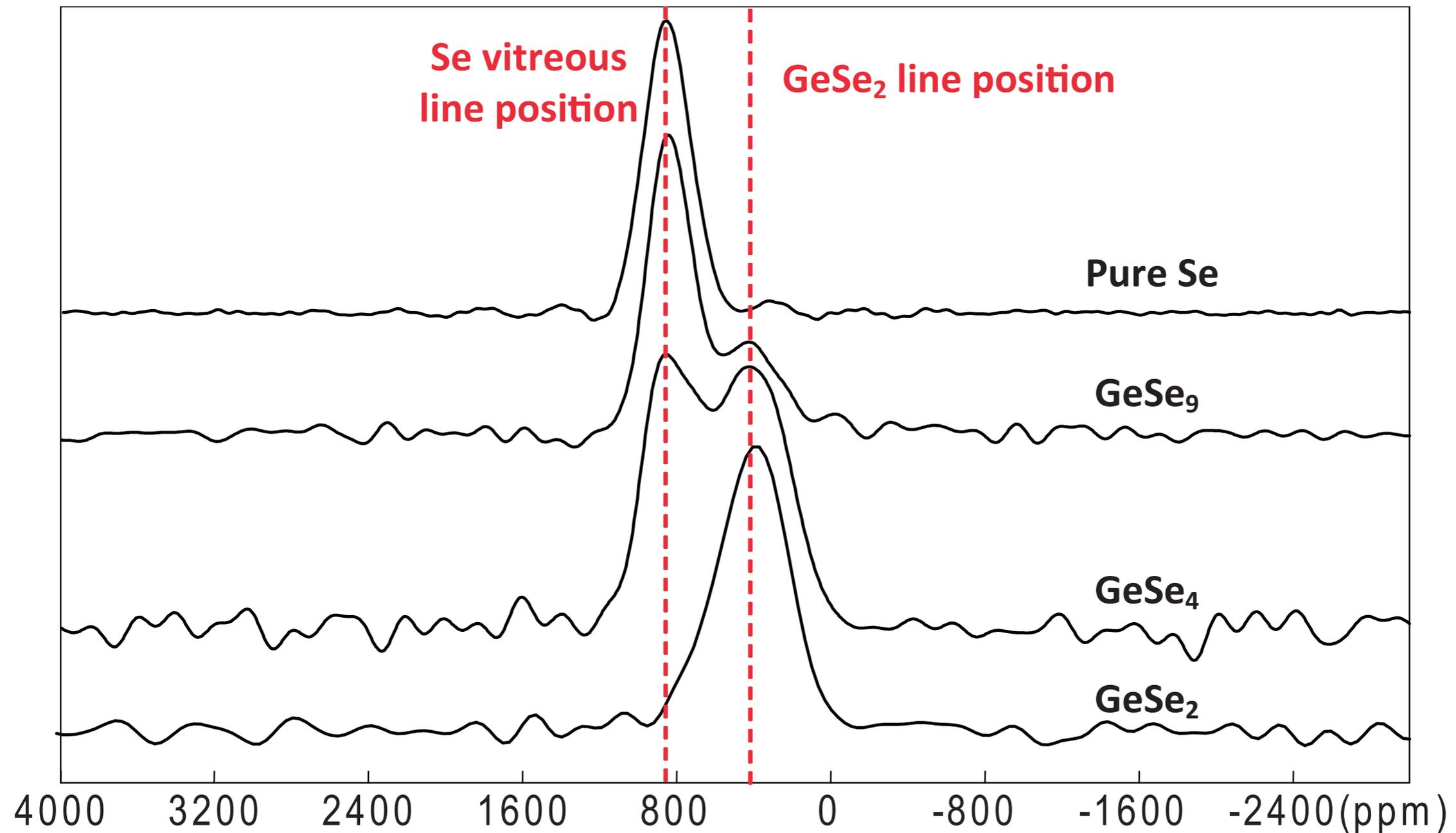


<sup>1</sup> P. Lucas ..., and B. Bureau, Phys. Rev. B 80, 214114 (2009)

<sup>2</sup> E. L. Gjersing, S. Sen, and B. G. Aitken, J. Phys. Chem. C 114, 8601 (2010)

# Introduction: $\text{Ge}_x\text{Se}_{1-x}$ glasses

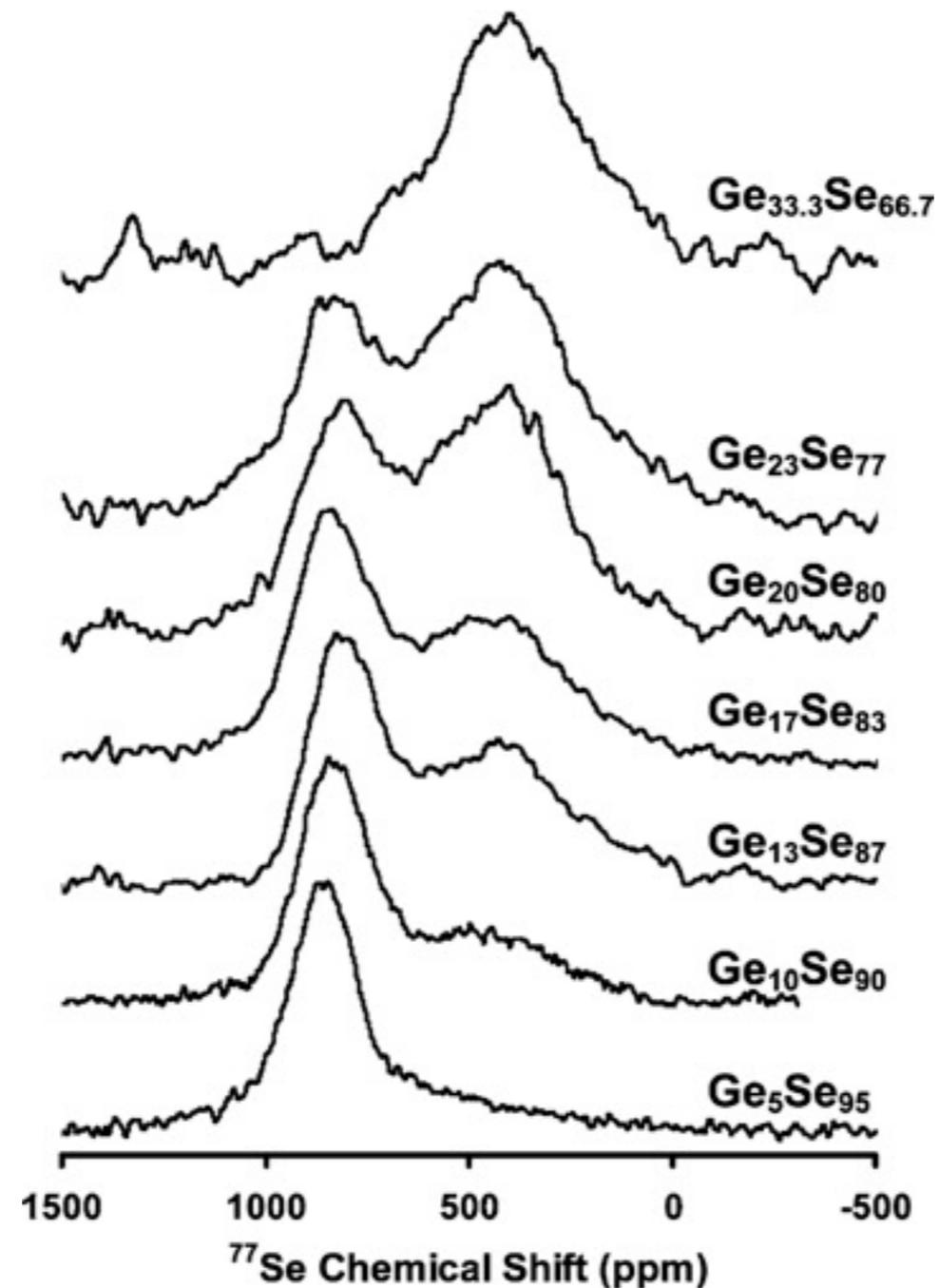
experimental spectra used to justify bimodal phase: Se-Se-Se bonds and Ge-Se-Ge bonds only<sup>1</sup>



<sup>1</sup> P. Lucas ..., and B. Bureau, Phys. Rev. B 80, 214114 (2009)

# Introduction: $\text{Ge}_x\text{Se}_{1-x}$ glasses

experimental spectra used to justify fully bonded model with intermediate configurations<sup>2</sup>



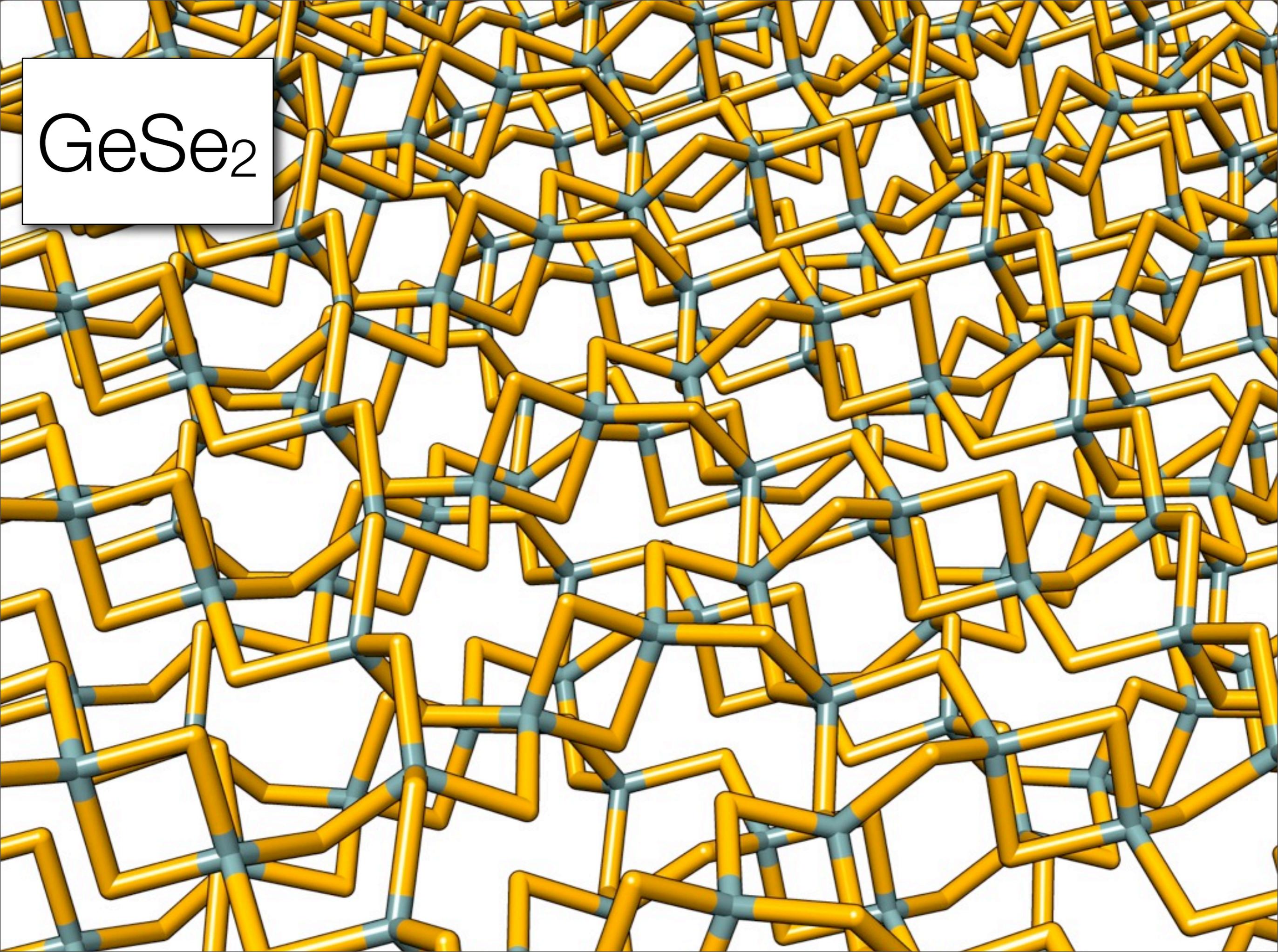
<sup>2</sup> E. L. Gjersing, S. Sen, and B. G. Aitken, J. Phys. Chem. C 114, 8601 (2010)

# Aim

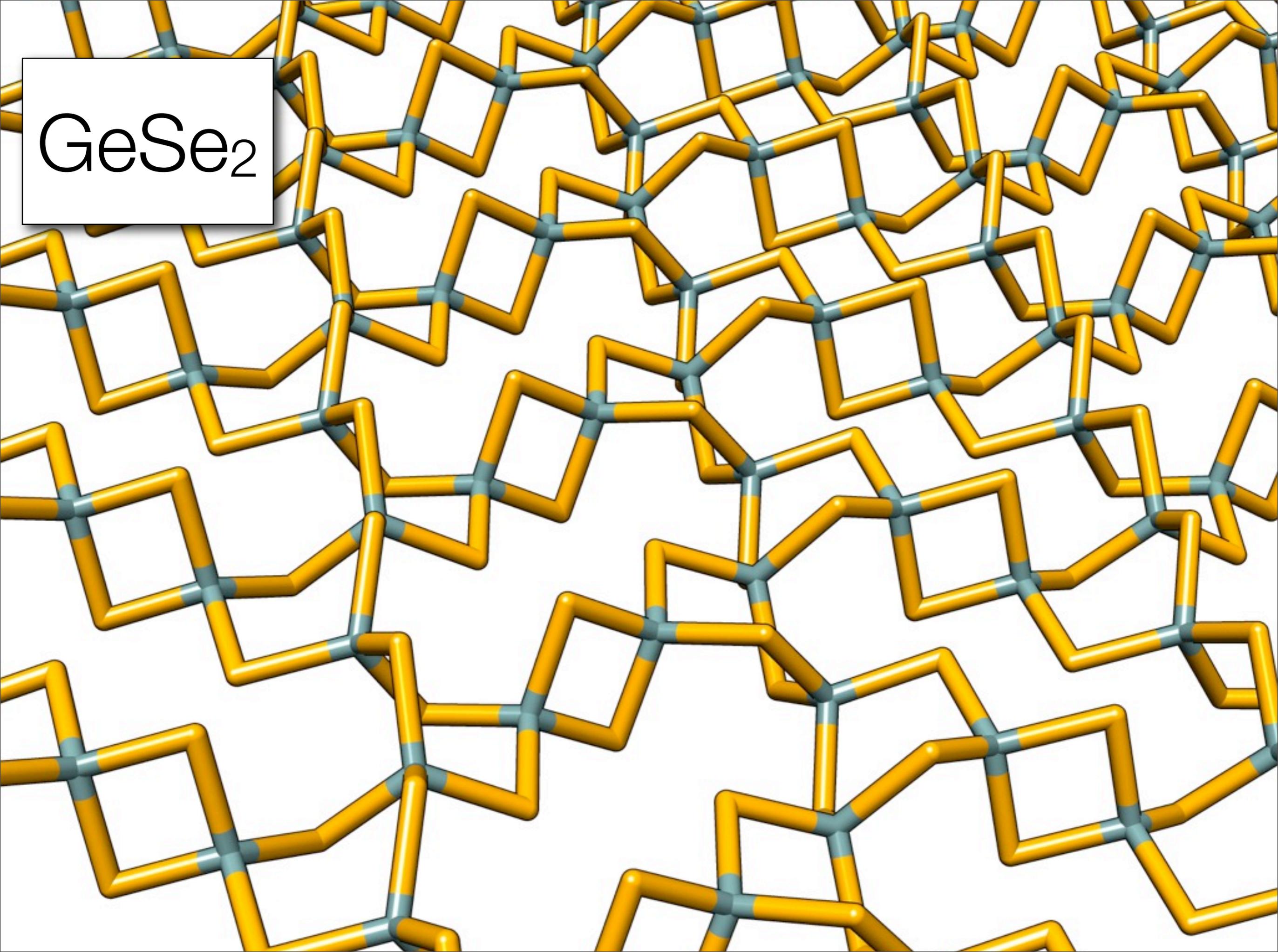
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To provide structural assignments for the experimentally measured NMR spectra

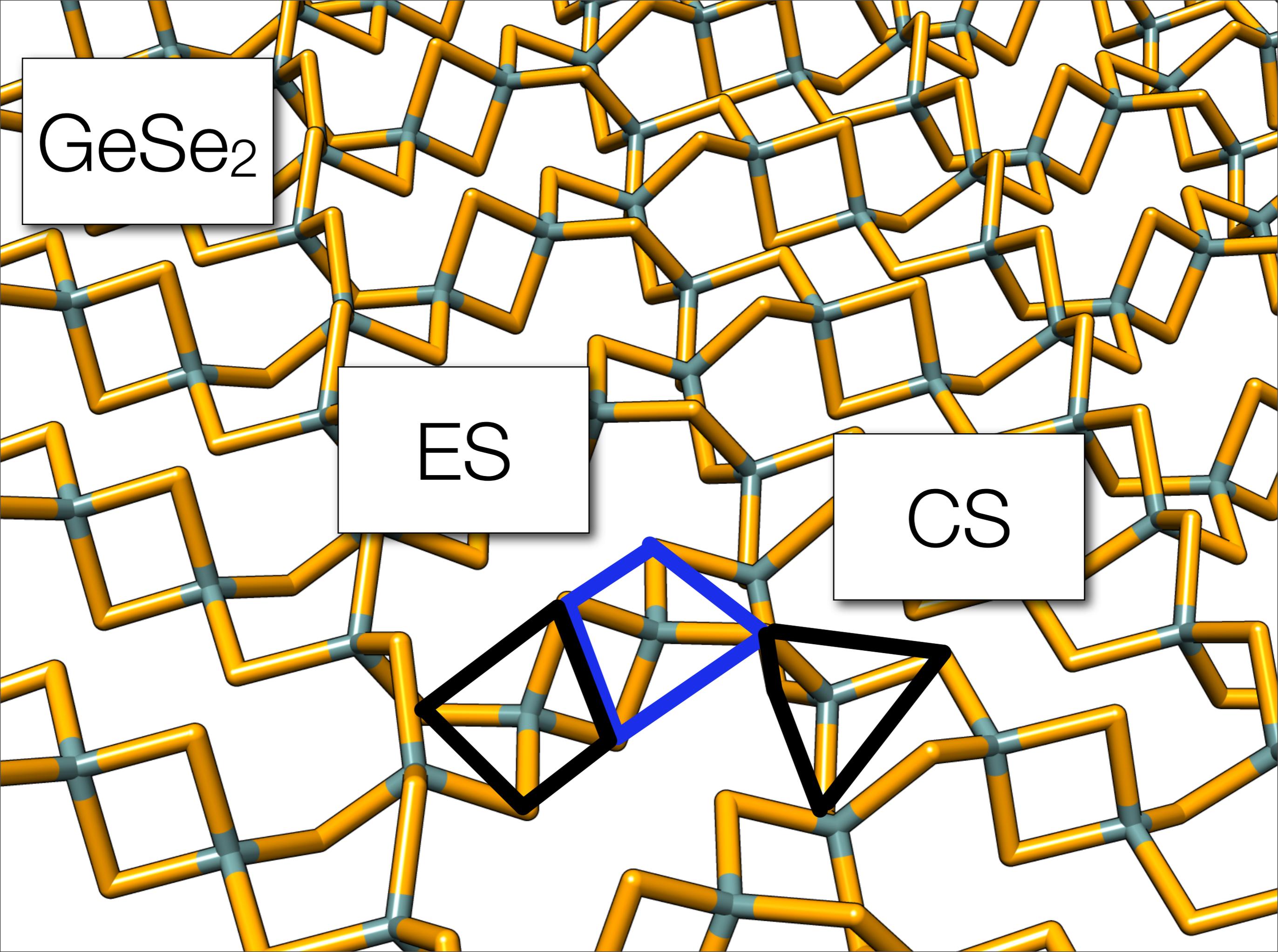
GeSe<sub>2</sub>



GeSe<sub>2</sub>

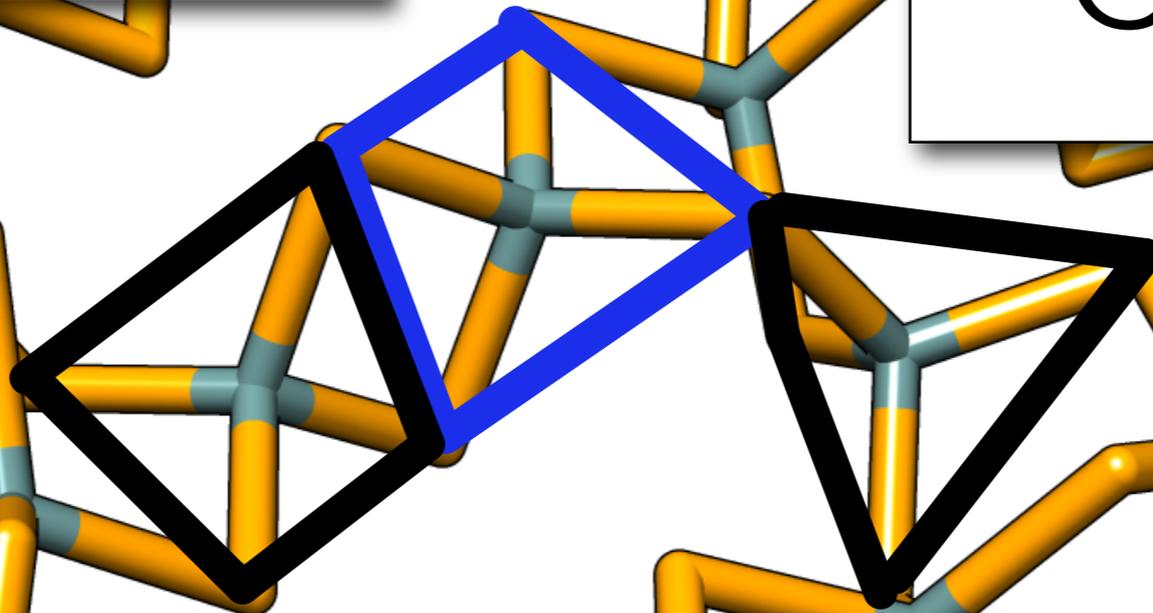


$\text{GeSe}_2$

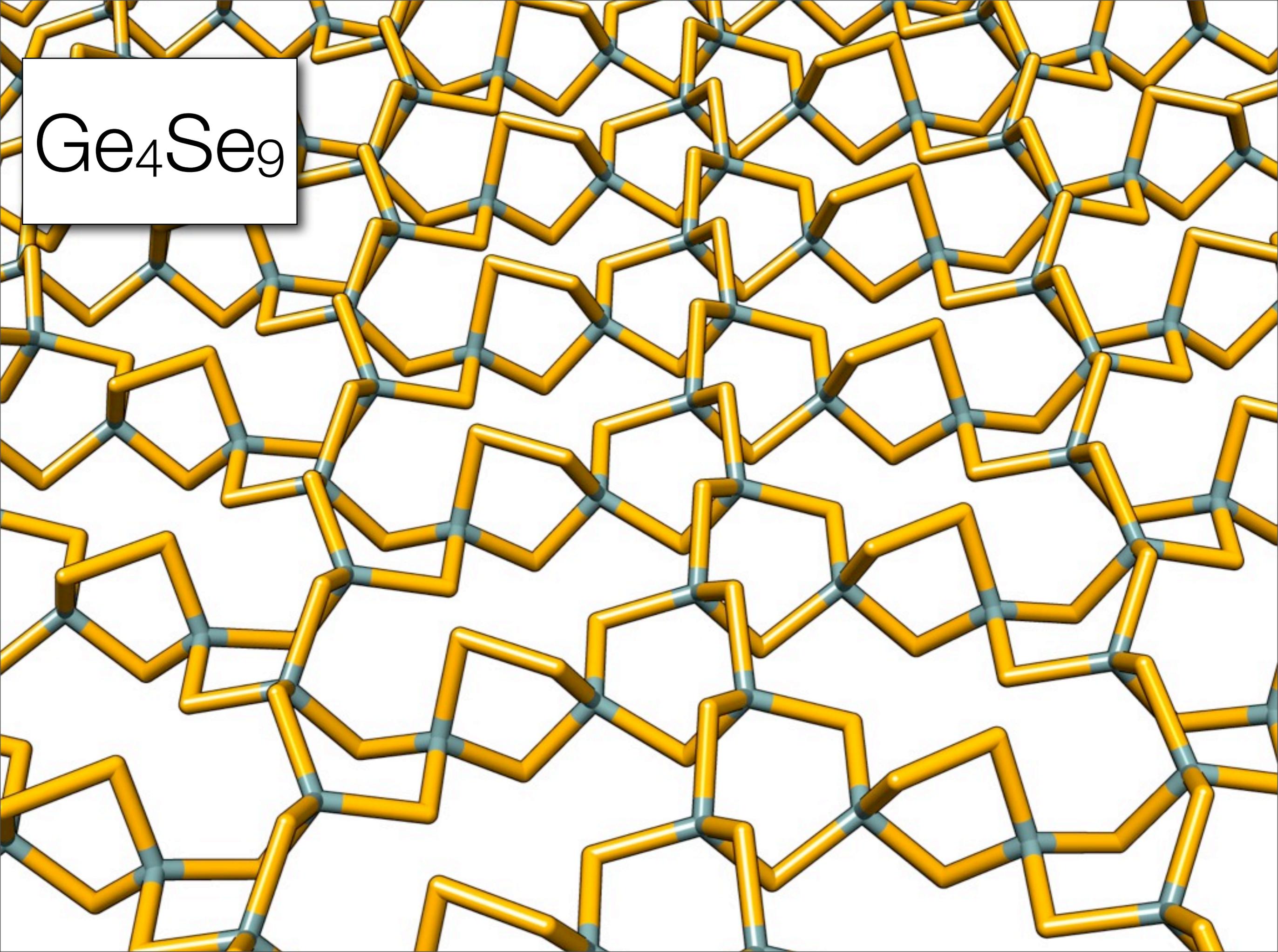
A ball-and-stick model of the GeSe2 crystal structure. The structure consists of a network of interconnected rings. The rings are primarily six-membered and eight-membered. The atoms are represented by orange spheres (Se) and grey spheres (Ge). The bonds are shown as orange and grey sticks. The overall structure is a complex, interconnected network of rings.

ES

CS



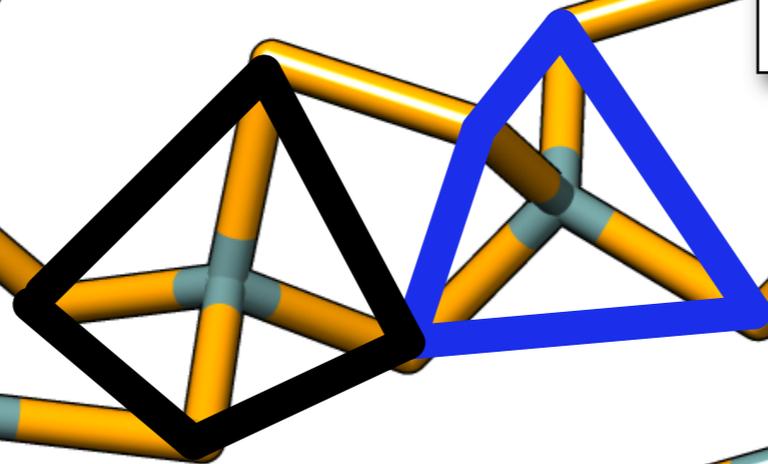
$\text{Ge}_4\text{Se}_9$



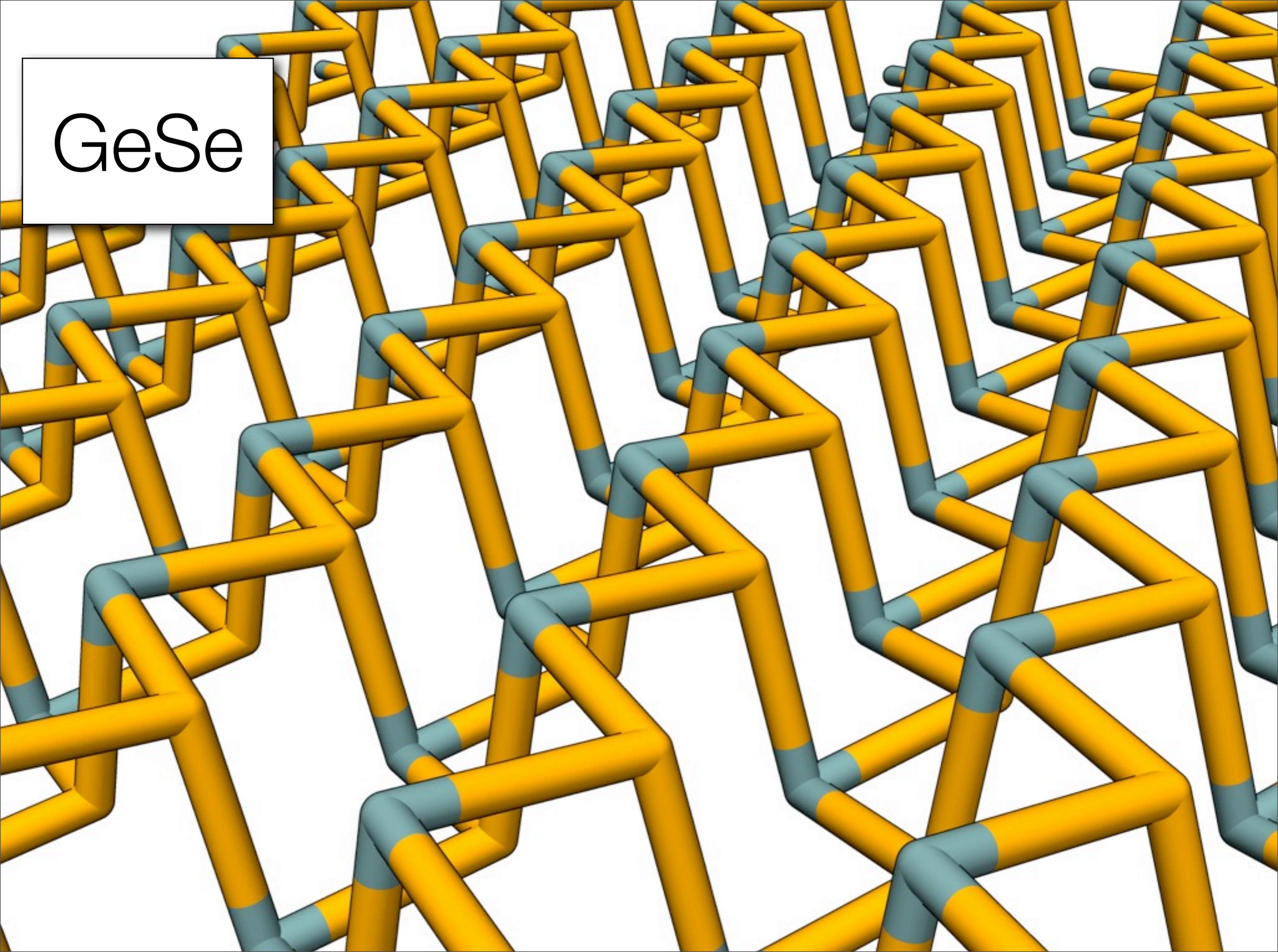
$\text{Ge}_4\text{Se}_9$

Se-Se-Ge

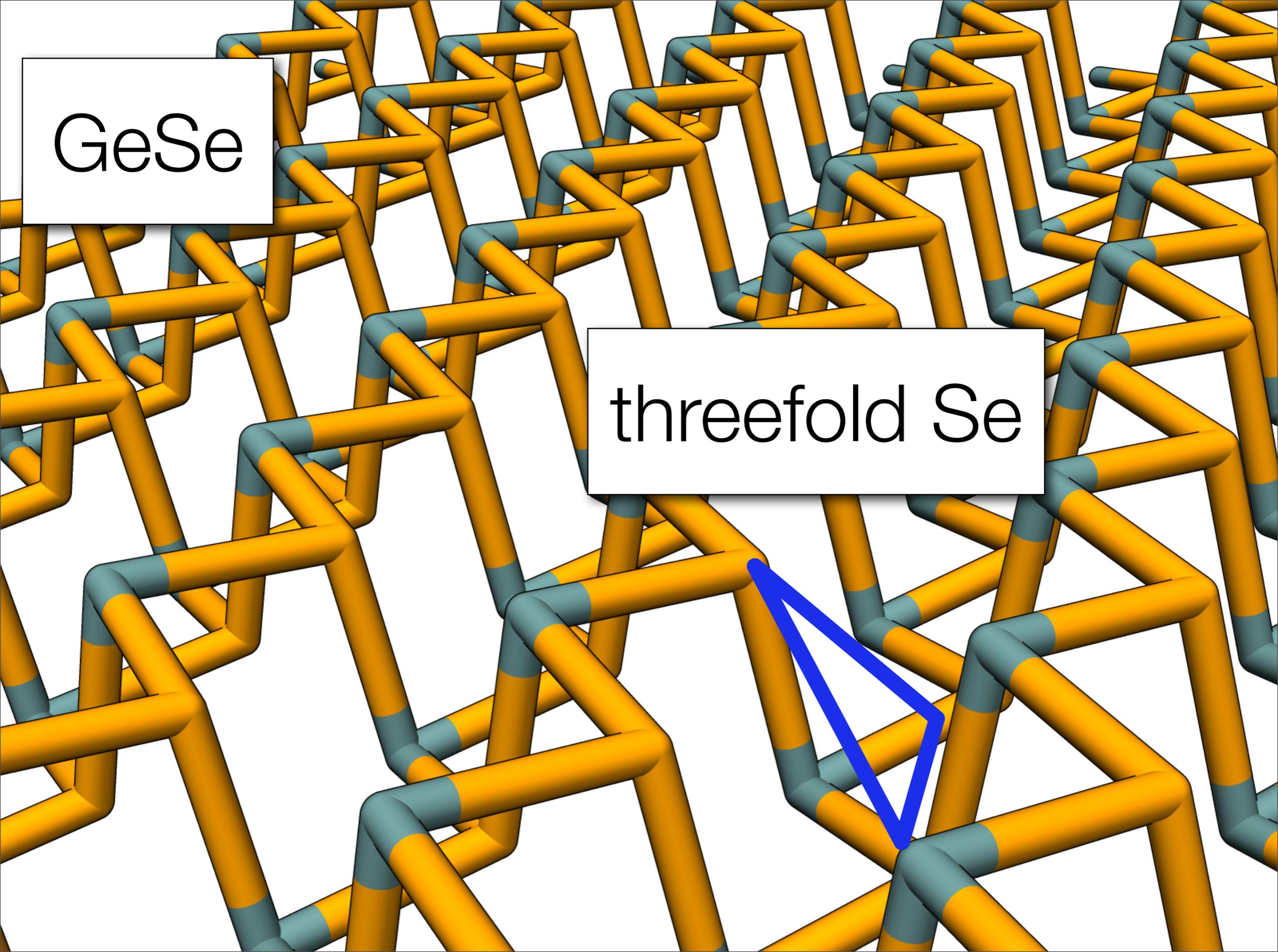
CS



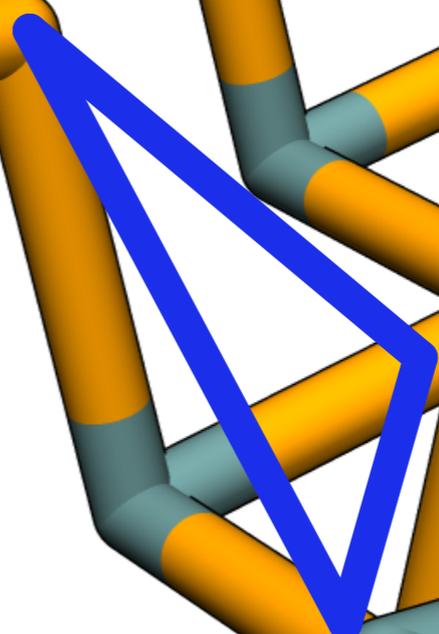
GeSe



GeSe

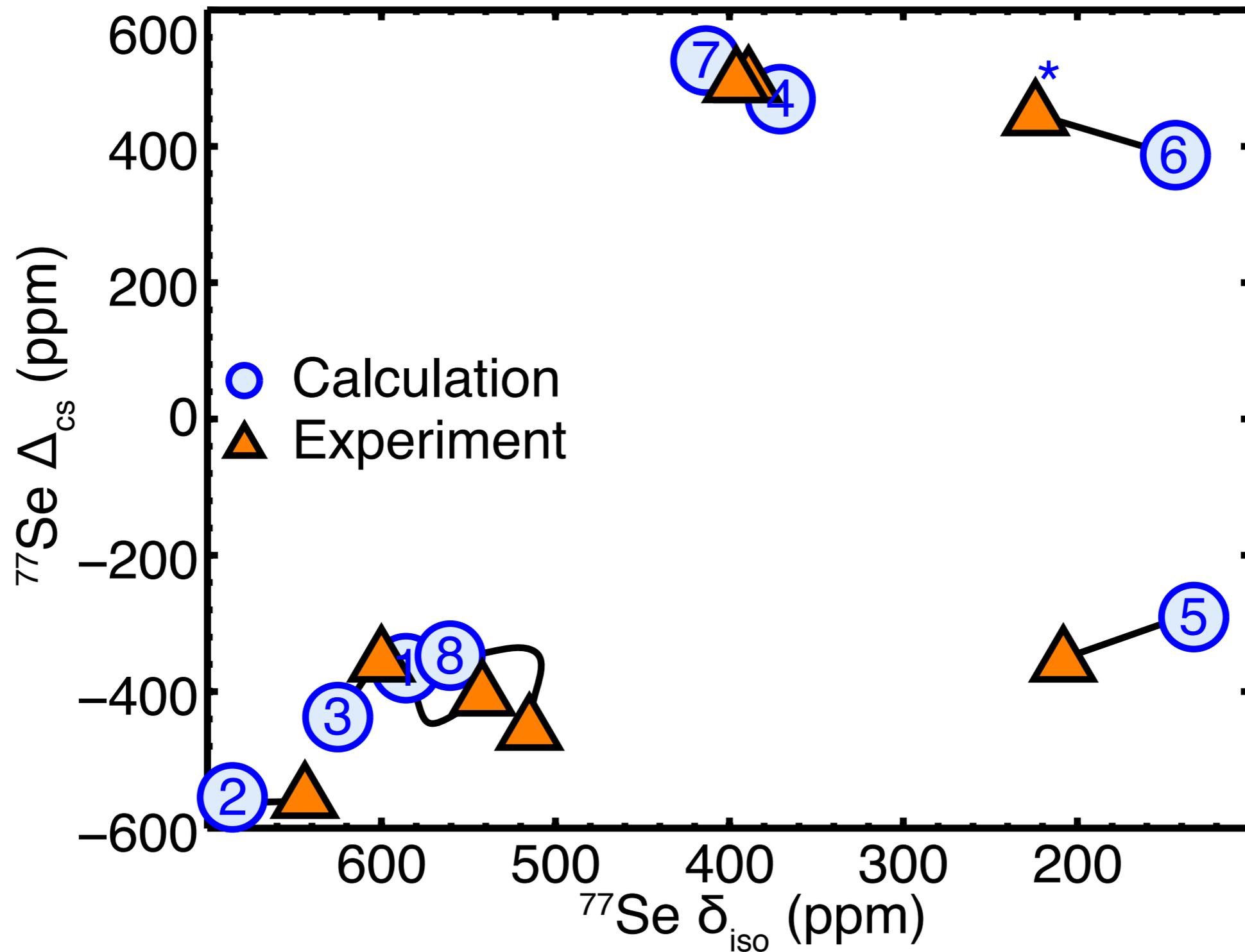
A 3D ball-and-stick model of the GeSe crystal structure. The structure consists of a network of interconnected chains. The chains are primarily composed of yellow spheres (representing Ge atoms) and blue spheres (representing Se atoms). The Se atoms are arranged in a zigzag pattern, forming a threefold coordination environment. The Ge atoms are coordinated to the Se atoms, creating a complex, layered structure. The overall appearance is that of a dense, interconnected network of atoms.

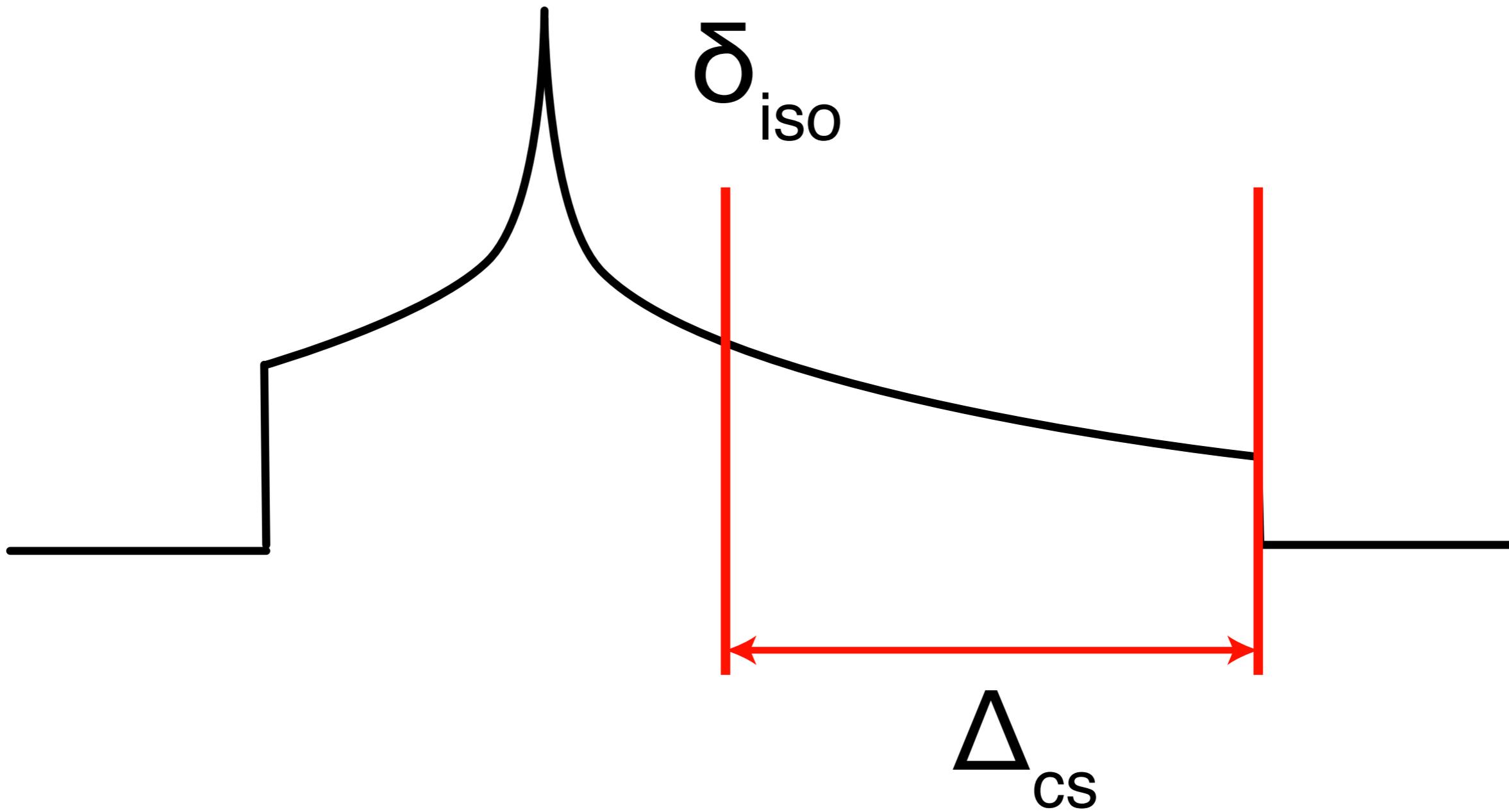
threefold Se

A blue triangle is drawn on the model, highlighting a specific site where a Se atom is coordinated to three Ge atoms. This site is labeled as a "threefold Se" site. The triangle is formed by three blue lines connecting the vertices of the Se-Ge-Ge-Ge tetrahedron.

# Establishing reliability of calculation

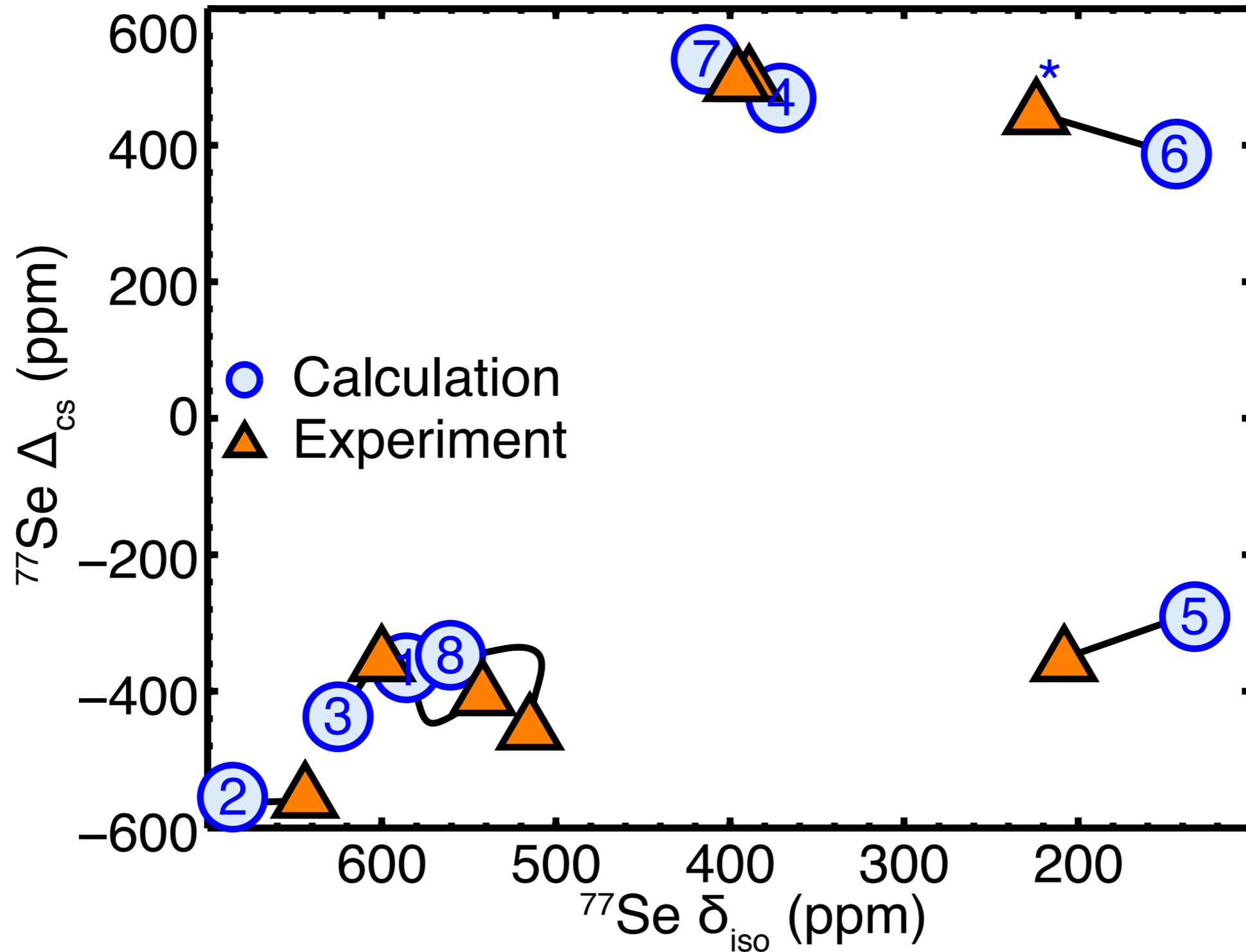
GeSe<sub>2</sub>



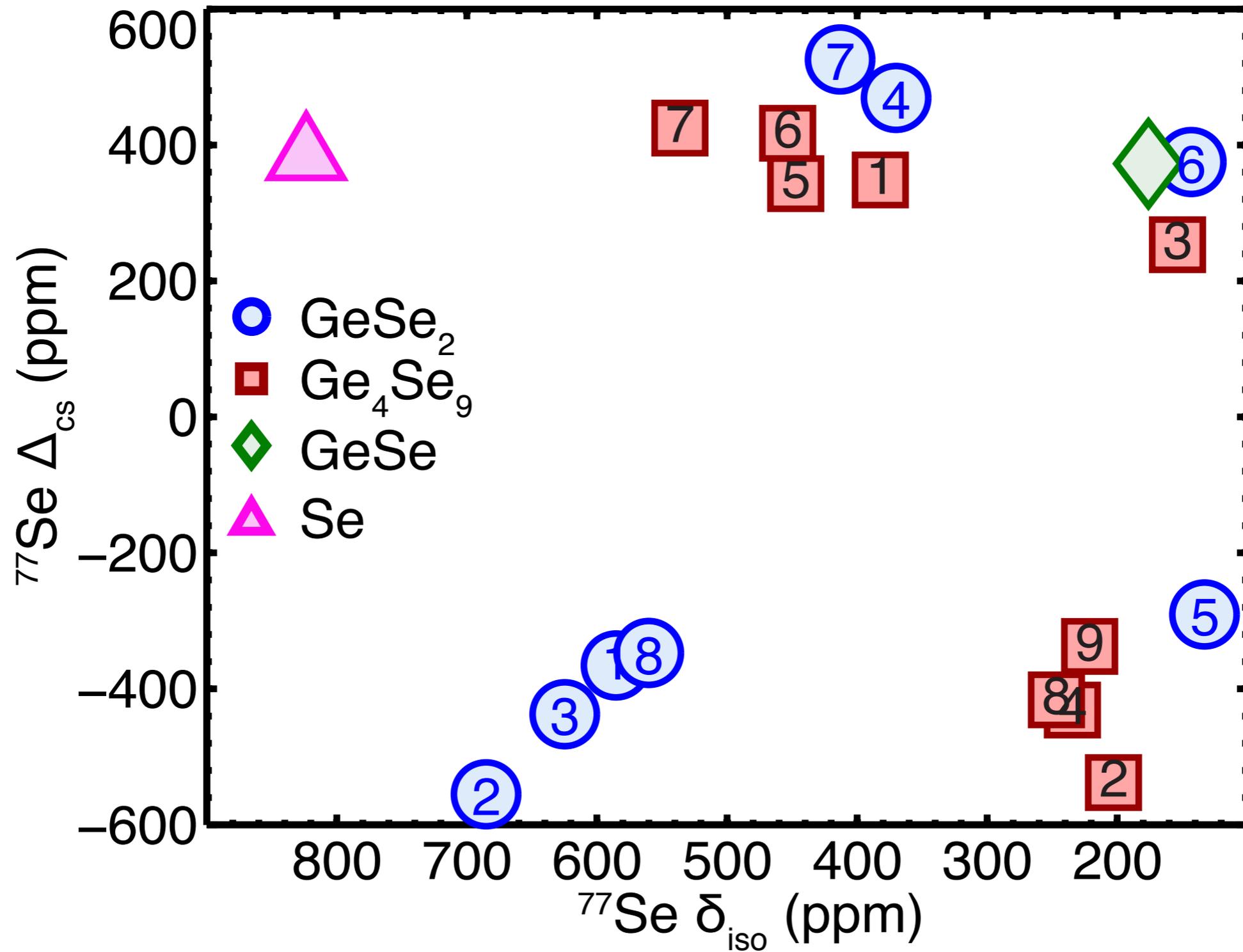


# Establishing reliability of calculation

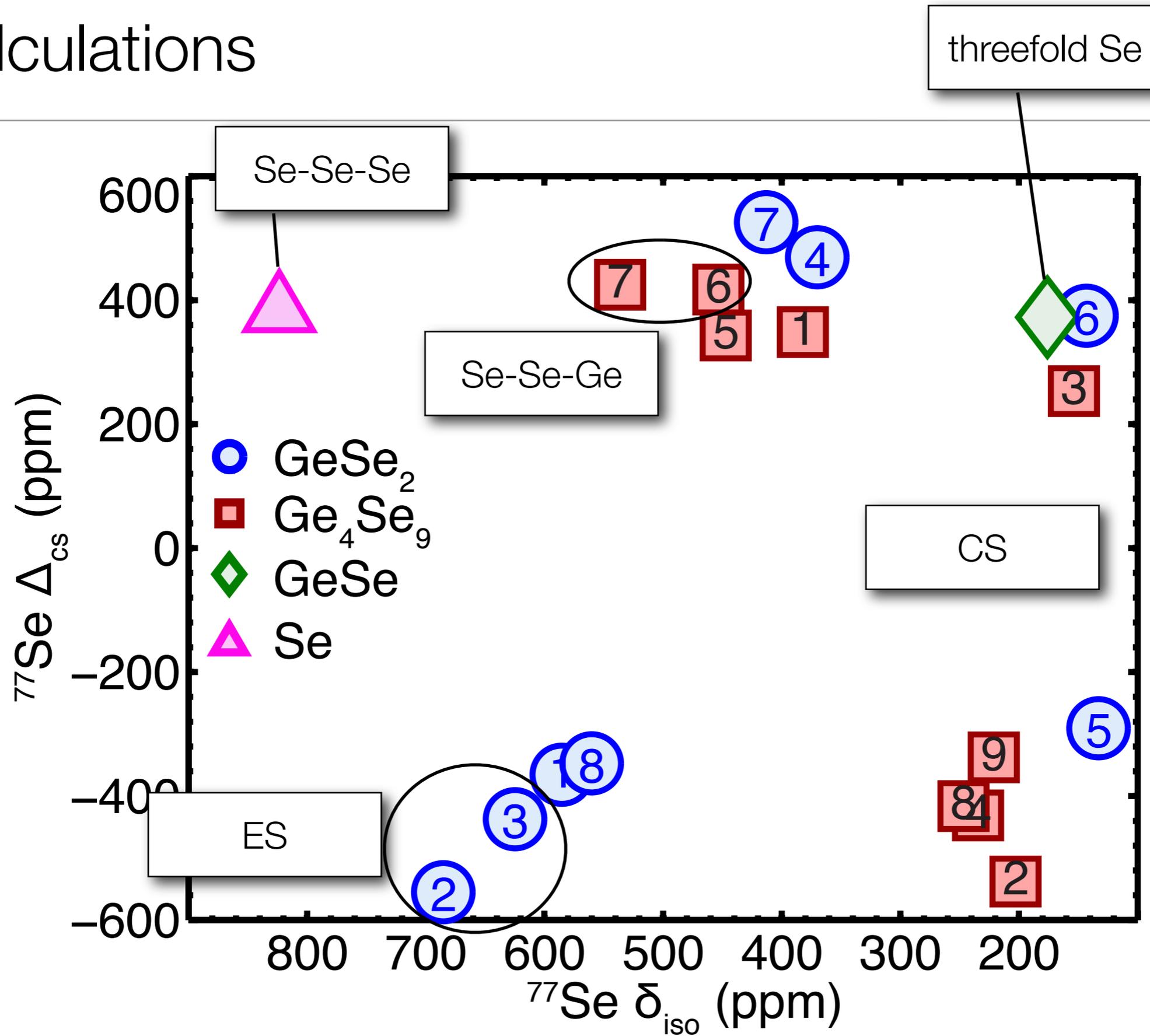
GeSe<sub>2</sub>

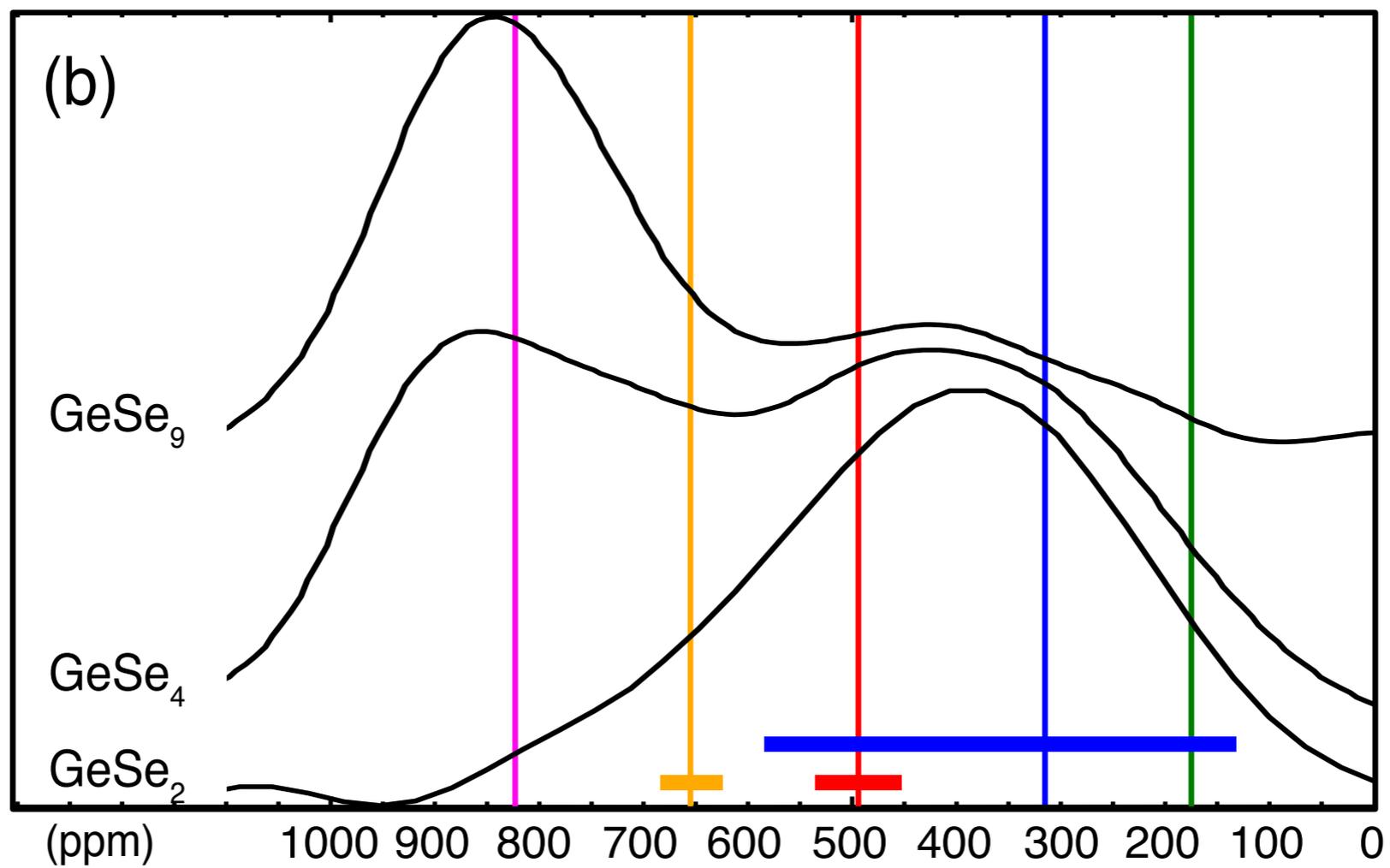
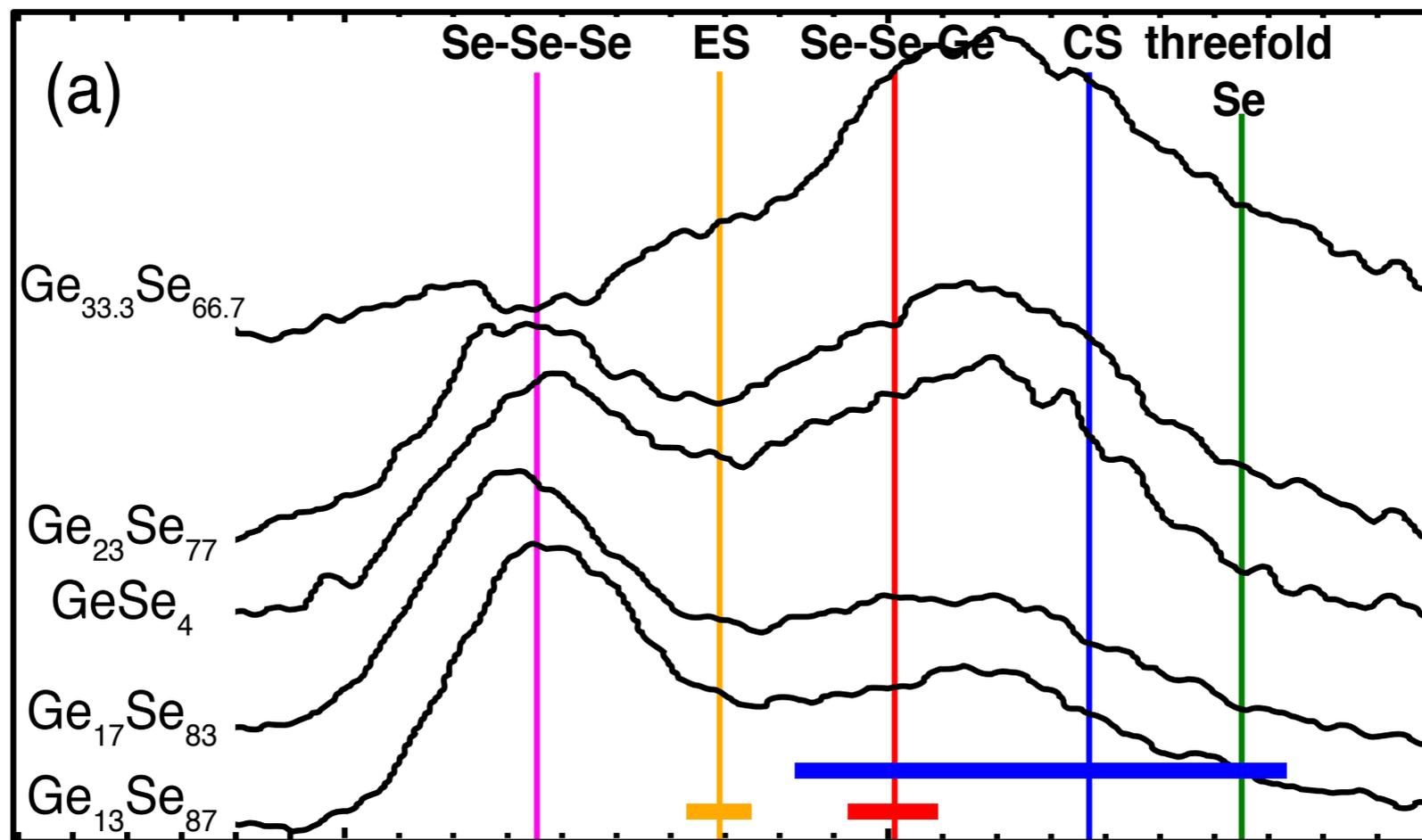


# Calculations



# Calculations





# Conclusion

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- one of the experimentally observed peak results from overlapping contributions from various bonding configurations
- our interpretation is consistent with the occurrence of Ge-Se-Se linkages
- bimodal description is not necessary

# Acknowledgements

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- Mike Payne
- Jonathan R. Yates  
University of Oxford
- Carlo Massobrio  
Institut de Physique et de Chimie des Matériaux de Strasbourg, France
- Alfredo Pasquarello  
EPFL, Switzerland

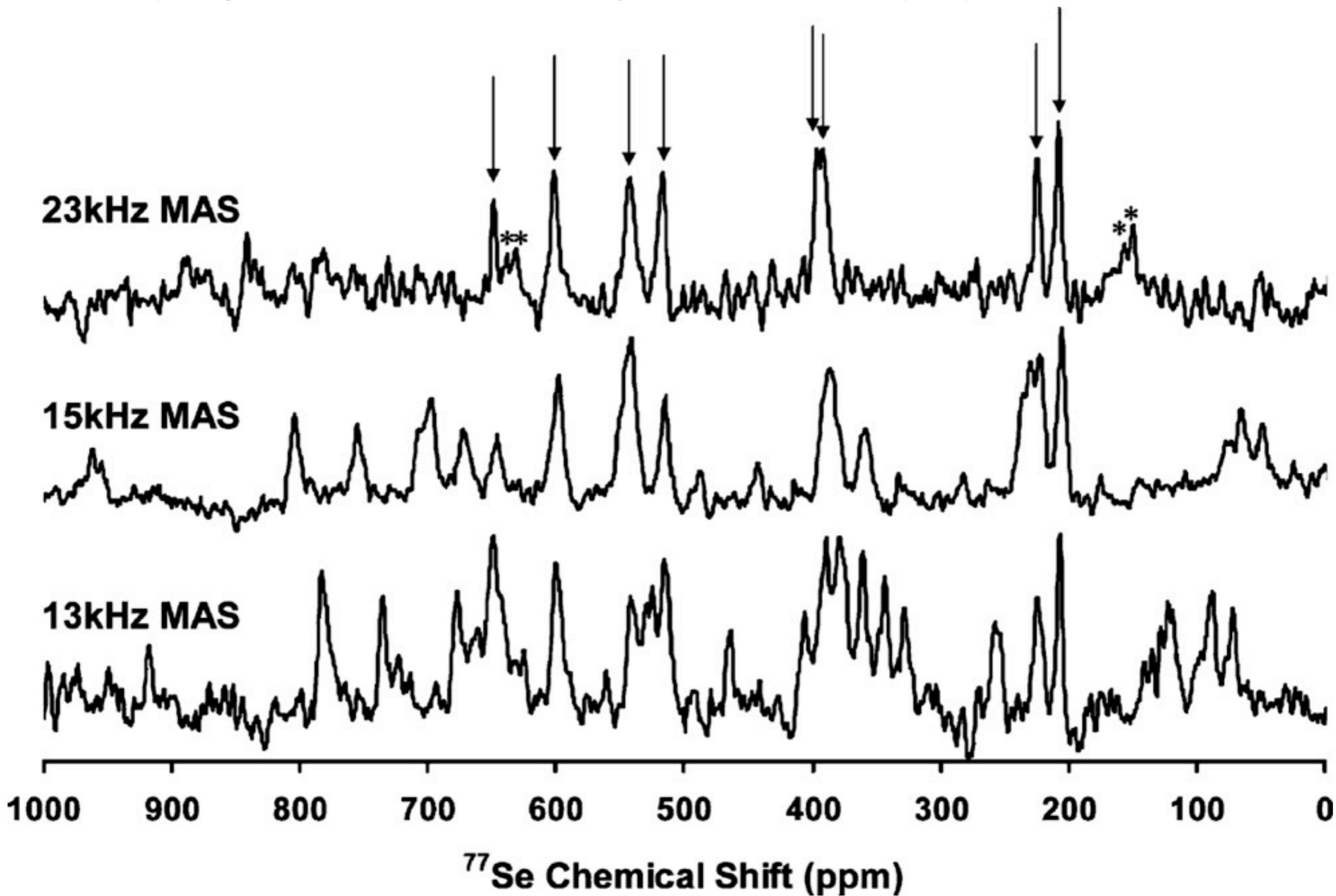
**TCM**

**EPSRC**

Thank you for listening

back up slides

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<sup>2</sup> E. L. Gjersing, S. Sen, and B. G. Aitken, J. Phys. Chem. C 114, 8601 (2010)

