“First principles investigation of chemical disorder in v-$GeSe_2$”

Luigi Giacomazzi

CNR-INFM/Democritos National Simulation Center and
The Abdus Salam International Centre for Theoretical Physics (ICTP)
(Trieste, Italy)

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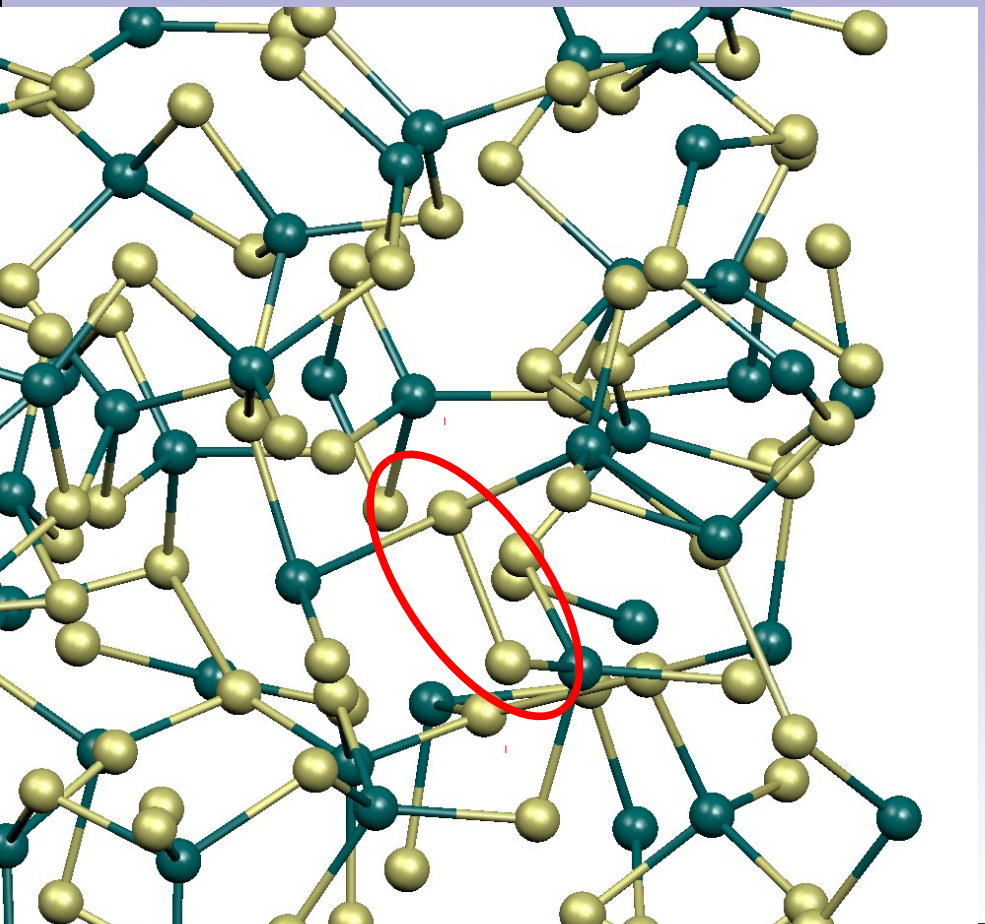
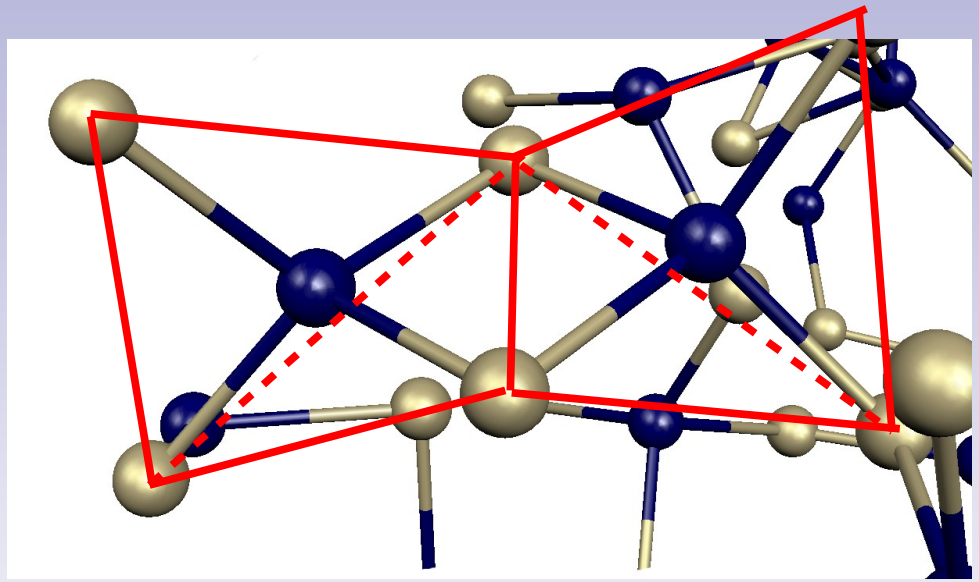
Introduction

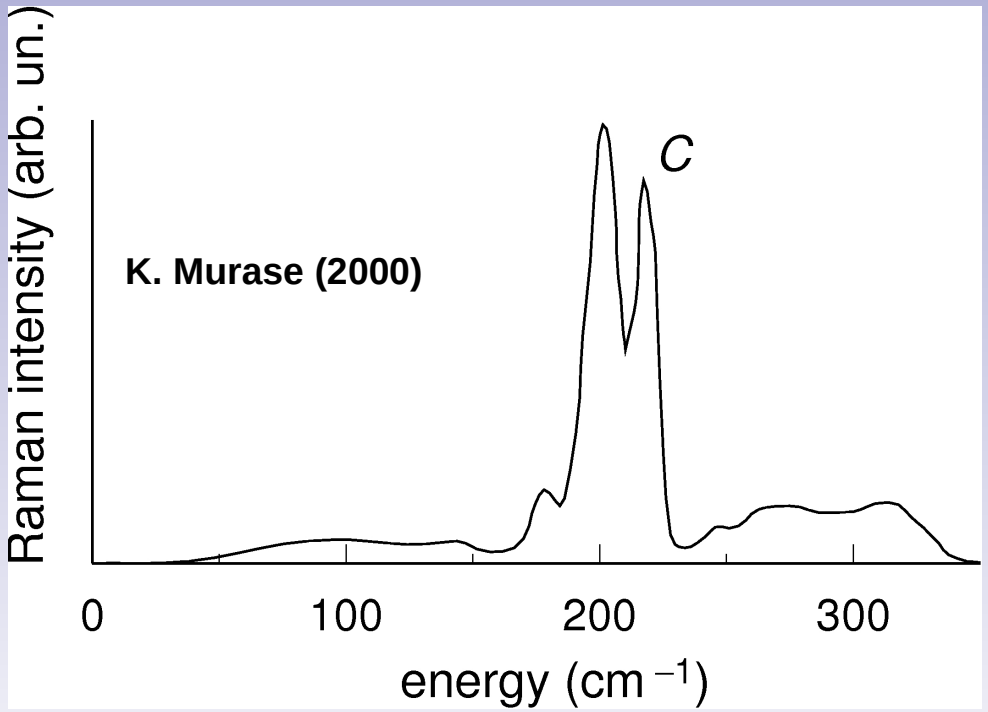
- *v*-$GeSe_2$ is a prototypical chalcogenide glass.
- Structural differences with respect to chemically ordered *v*-GeO_2 or *v*-SiO_2:
  - Edge-sharing tetrahedra
  - Homopolar bonds Se-Se and Ge-Ge
  - Over- and under-coordinated atoms.

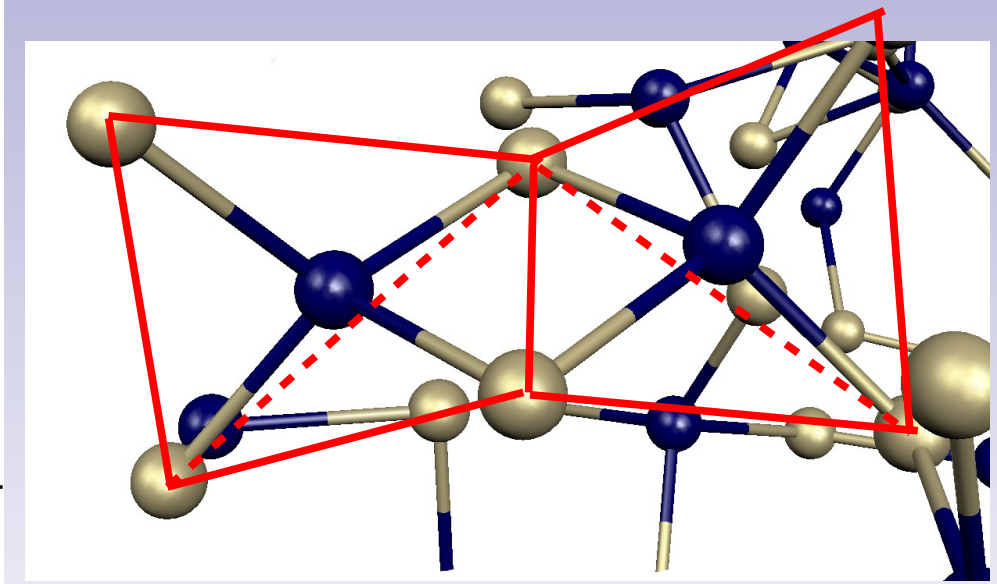




Introduction

Edge-sharing tetrahedra are supposed to originate the *C* line of the Raman spectrum





Questions

- What can we say about chemical order in v-GeSe2 by using first-principles methods ?

- How good are standard DFT functionals for calculating electronic structure properties e.g the dielectric constant ?

Outline

- Models generated by using Perdew-Wang (PW) GGA functional: struct. properties, vibrational spectra, dielect const...
- Models generated by using Becke-Lee-Yang-Parr (BLYP). Comparison with PW.
- NMR results
- Conclusions

L. Giacomazzi, C. Massobrio and A. Pasquarello, J. Phys. Cond. Matter **23**, 295401 (2011)
L. Giacomazzi, C. Massobrio and A. Pasquarello, Phys. Rev. B **75**, 174207 (2007)
M. Kibalchencko et al J. Phys. Chem. (2011).

PW models of *v*-$GeSe_2$

Model I and II:

- Quenching from the melt by classical molecular dynamics
- Classical potentials:

P. Vashishta, R.K. Kalia, G.A. Antonio, and I. Ebbsjö, PRL **62** (1989)

Damped *ab-initio* dynamics in order to further relax the atomic positions.

Quantum-espresso package [www.quantum-espresso.org]

Model III:

- Quenching from the melt by *ab-initio* molecular dynamics
- Damped *ab-initio* dynamics in order to further relax the atomic positions.

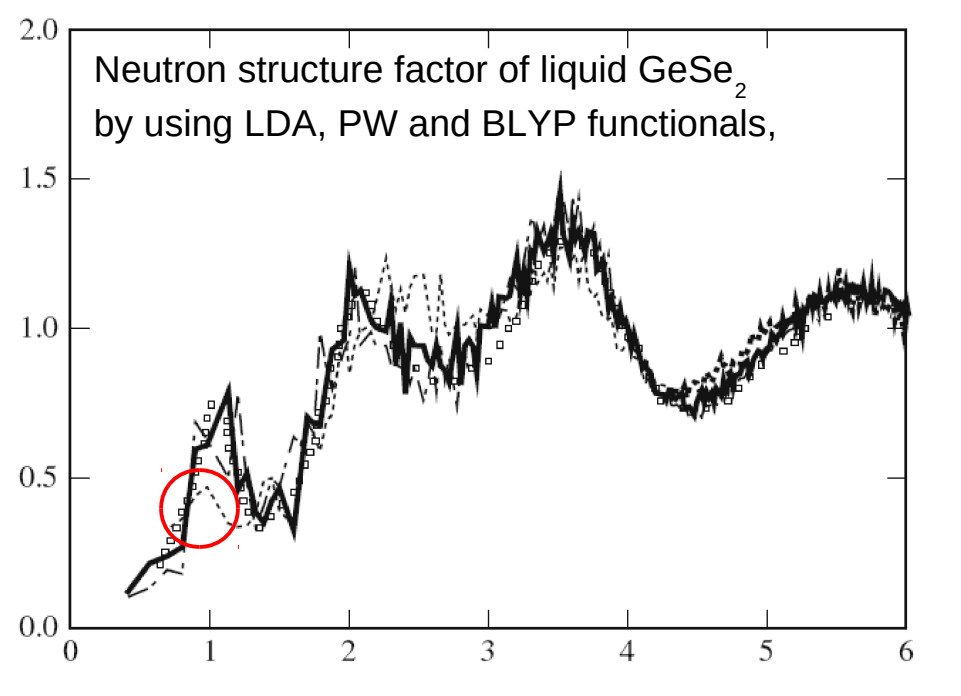
L. Giacomazzi, C. Massobrio and A. Pasquarello, J. Phys. Cond. Matter **23**, 295401 (2011)
L. Giacomazzi, C. Massobrio and A. Pasquarello, Phys. Rev. B **75**, 174207 (2007)

DFT functionals

- Electronic structure is treated within **GGA** (**PW** or **BLYP**) to DFT**.**

Core-valence interactions are described through a norm-conserving pseudo-potentials for Se and Ge.

- **LDA** does not give reliable structures:



Massobrio, *Atomic-Scale Modeling of Nanosystems and Nanostructured Materials* (2010)

PW models of *v*-$GeSe_2$

Two contending conceptions of the structure:

- **Strong chemical order:** Models I and II.
  The structure is mainly given by regular tetrahedra.
  [Vashishta, Kalia, Antonio, and Ebbsjö, Phys. Rev. Lett. 62 (1989)]

- **Weak chemical order:** Model III.
  The structure features a rich variety of nearest neighbor motifs, as found in first-principles MD of liquid $GeSe_2$.
  [Massobrio, Pasquarello, and Car, PRL 80, 2324 (1998)]

Structural properties of PW Models of *v*-$GeSe_2$

Table 4.2: Composition of first-neighbor shells of Ge and Se atoms expressed as a percentage in our models of *v*-$GeSe_2$. For each composition, the coordination is indicated by ℓ. For Ge-Se and Se-Se bonds, we used cutoff radii of 3.0 and 2.7 Å, respectively. Ge-Ge bonds do not occur in our models. We also quantify the amount of homopolar bonds and of edge-sharing tetrahedra (ES-T) in terms of percentages of the involved atoms.

	Composition	ℓ	Model I	Model II	Model III	Expt.
Ge						
	Se_3	3	5	7	20	
	Se_4	**4**	**95**	**93**	**78**	
	Se_5	5	–	–	2	
Se						
	Ge	1	1	–	1	
	SeGe	2	3	8	20	
	Ge_2	**2**	**92**	**86**	**55**	
	Se_2	2	–	–	4	
	$SeGe_2$	3	2	–	–	
	Se_2Ge	3	–	1	–	
	Ge_3	3	2	5	20	
Se-Se			**5**	**9**	**24**	**20**
Ge-Ge			–	–	–	25
ES-T			**33**	**15**	**55**	**34**

Strong chem. order

Experimental data: **I. Petri et al. (2000).**

Structural properties of PW Models of *v*-$GeSe_2$

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Weak chem. order

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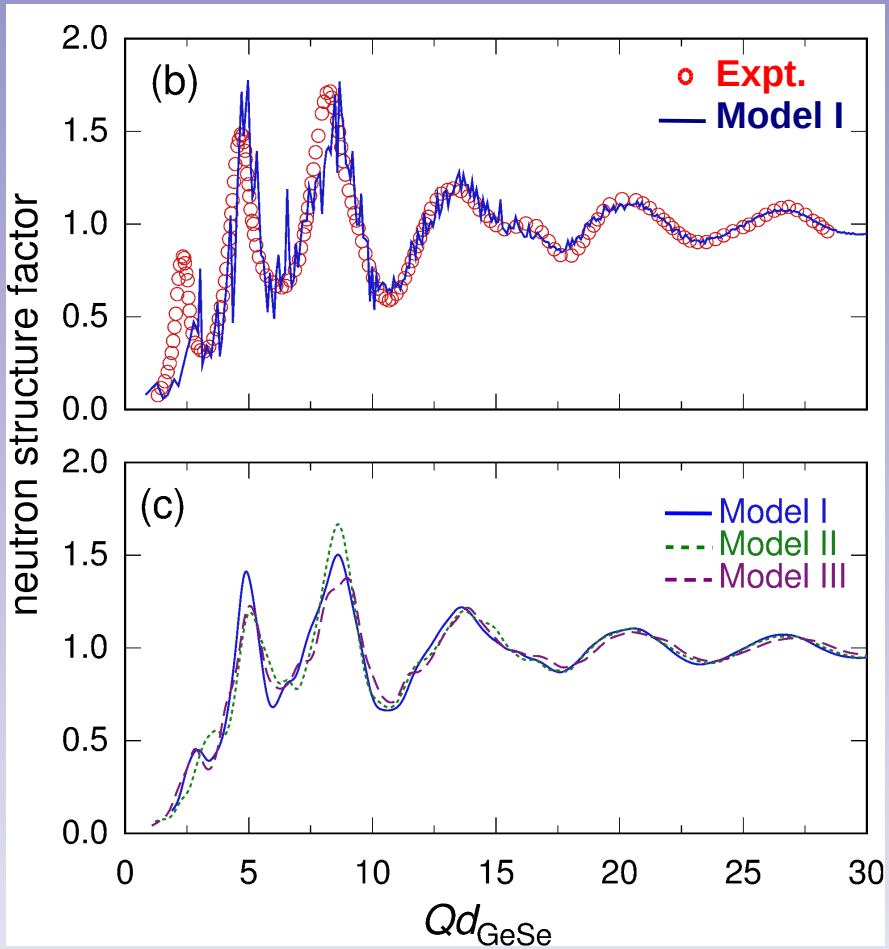
Structural properties of PW Models of *v*-$GeSe_2$

	N	∠ Ge-Se-Ge	∠ Se-Ge-Se	d_{GeSe} (Å)
Strong chem. order				
Model I	180	100.6° (12.1°)	109.1° (9.5°)	2.42 (0.05)
Model II	120	107.8° (12.7°)	108.6° (12.0°)	2.44 (0.07)
Weak chem. order				
Model III	120	100.7° (16.2°)	106.8° (11.3°)	2.47 (0.13)
Expt.				2.36

- d_{GeSe} is remarkably longer than expt. for all the PW models

Neutron structure factors



Expt. S. Susman et al. JNCS 125, 168 (1990)

PW models: electronic properties of *v*-$GeSe_2$

- Finite electric field scheme for calc ε_∞ and also for accessing the infrared and Raman spectra [P. Umari and A. Pasquarello PRL 89, 157602 (2002)].

	Model I	Model II	Model III	Expt.
ε_∞	7.2	7.65	7.3	5.5
B. Gap (eV)	0.50	0.62	0.81	2.2

- ε_∞ is for all the models about 30% larger than the expt. value

Vibrational density of states of *v*-$GeSe_2$

i) Diagonalize the dynamical matrix

ii) Calculate the vibrational density of states (*v*-DOS):

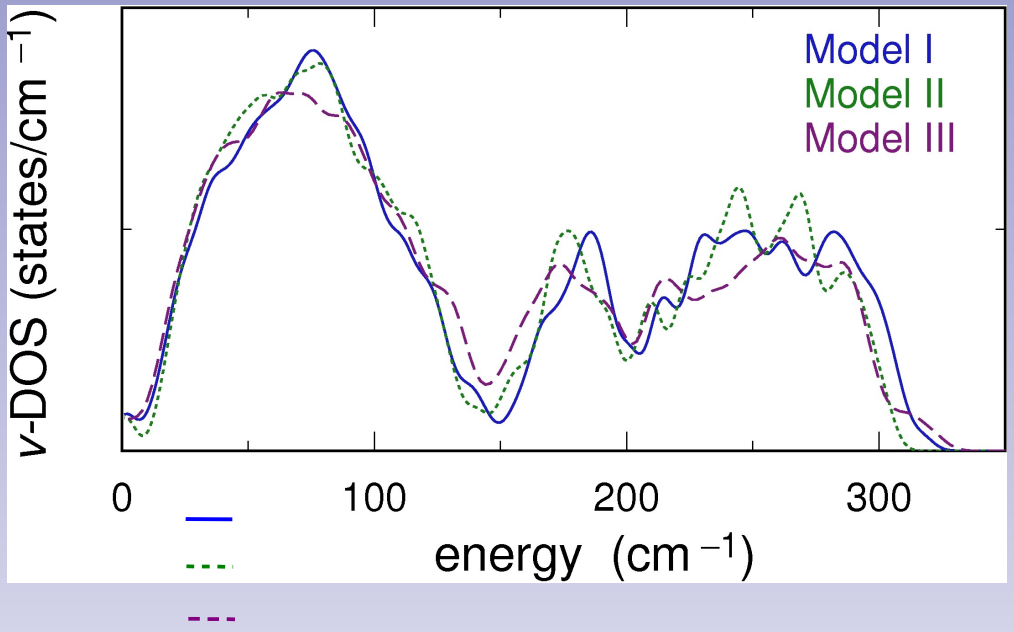
$$\rho(\omega)=\frac{1}{3N}\sum_n \delta(\omega_n-\omega)$$

iii) Calculate general spectra S (infrared,....)

$$S(\omega)=C(\omega)\cdot\rho(\omega)$$

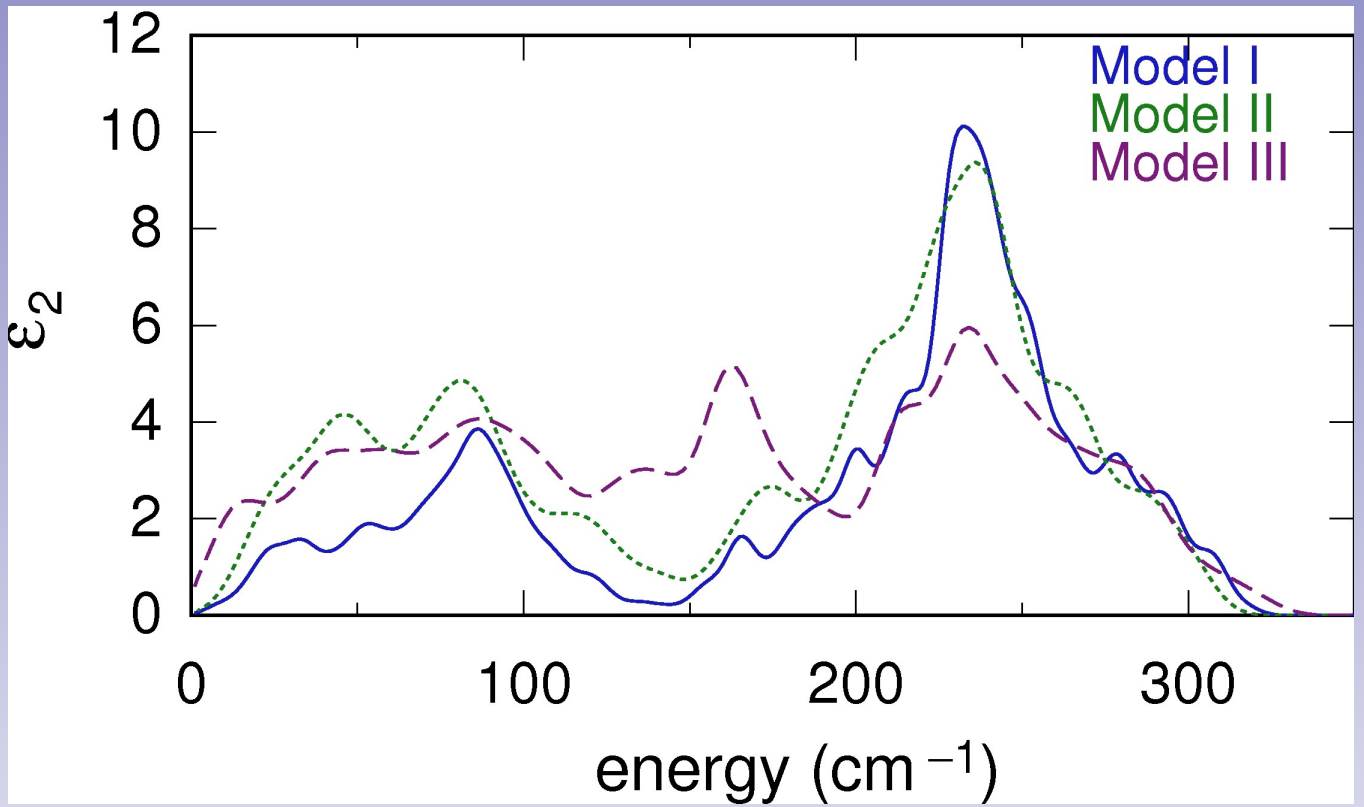
[Shuker and Gammon PRL(1970)]

iv) Compare with experimental data



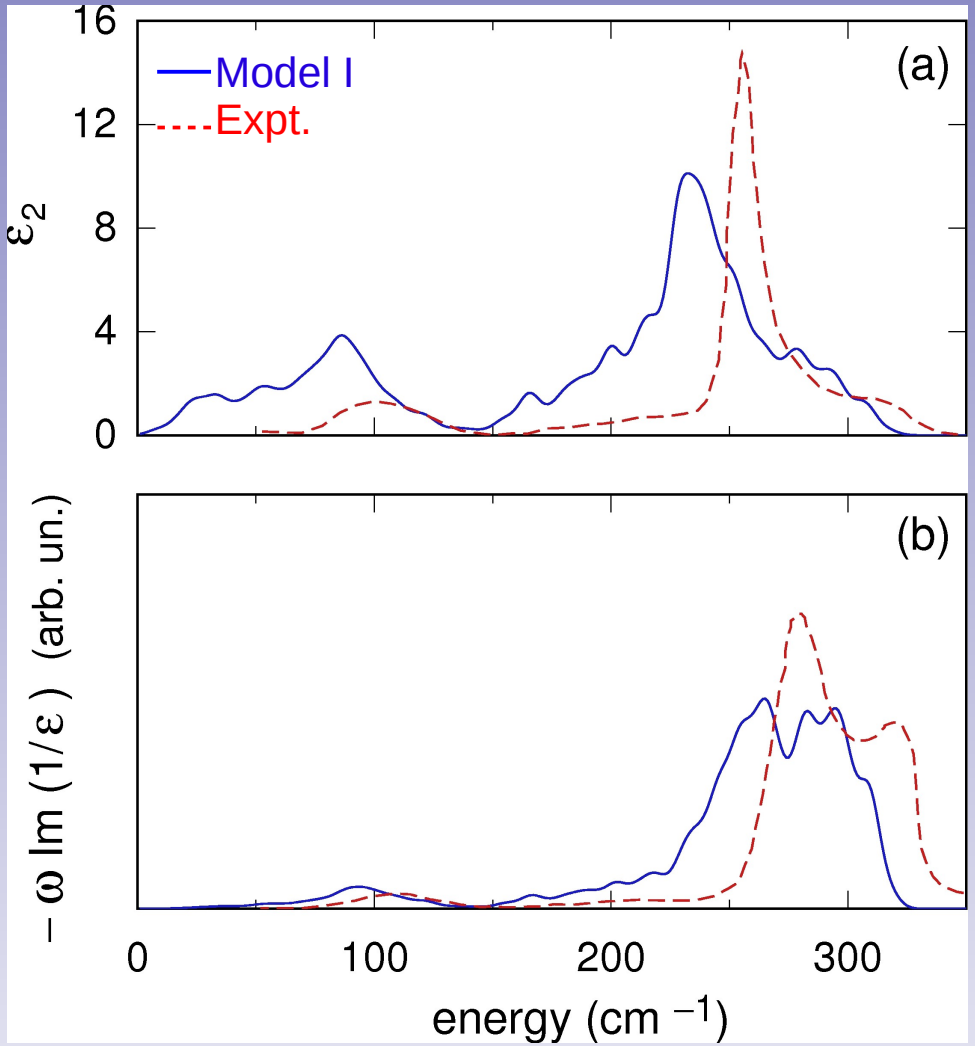
• No significant differences among the model structures are observed for the v-DOS

PW Models: Infrared spectrum of *v*-$GeSe_2$



- Significant differences among the model structures are observed for the imaginary part of the dielectric function.

Infrared spectra of *v*-$GeSe_2$



- Finite electric field scheme for accessing the infrared and Raman spectra [P. Umari and A. Pasquarello PRL 89, 157602 (2002)].
- Experimental data:
  K. Murase in *Insulating and semiconducting glasses* Vol 17, ed. by P. Boolchand (WSP, Singapore, 2000), pp. 415-463.

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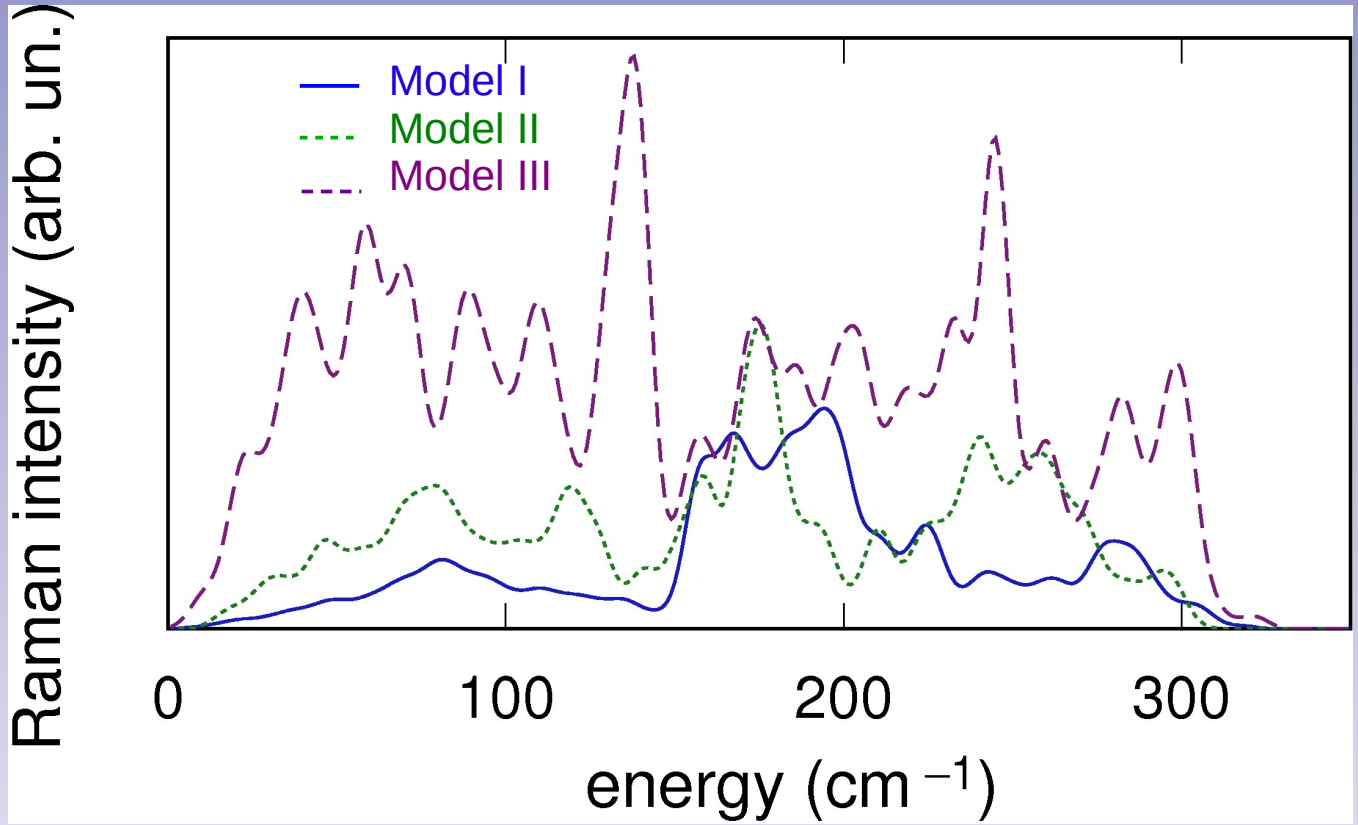
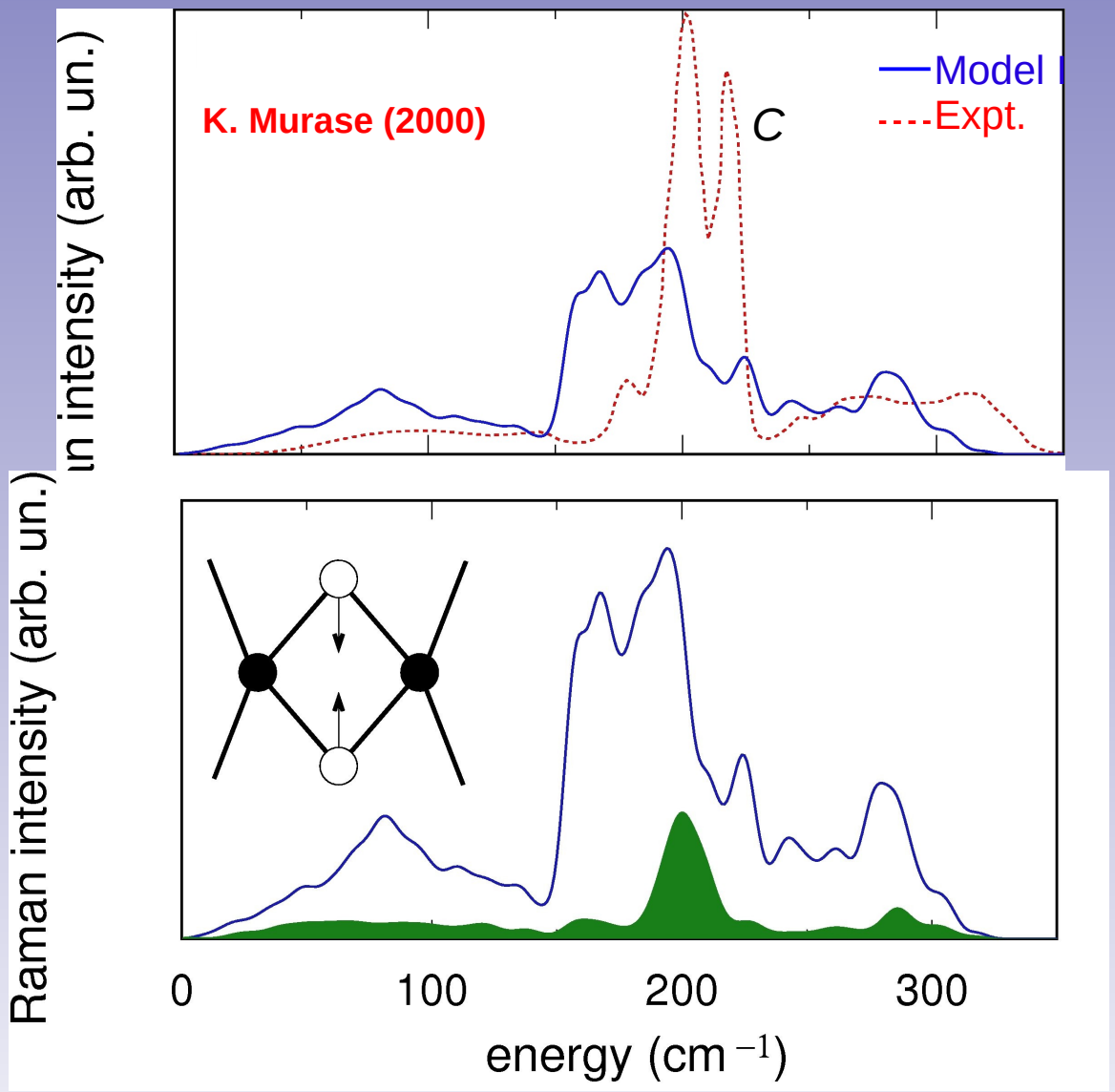
Raman spectra of *v*-$GeSe_2$



- Significant differences among the model structures are observed for the Raman spectra.

Raman spectra of *v*-$GeSe_2$



•Projection onto Se breathing motions in four-atom rings supports the ***assignment of the companion line to Se in ES tetrahedra***.

PW Models: conclusions (I)

- Diffraction probes and neutron vibrational density of states are *not sufficiently selective* to discriminate among models.
- *Significant* differences are observed for the infrared and Raman Spectra.
- The comparison with experiments finally favors a structural model of *v*-$GeSe_2$ with *strong* chemical order.

but...

- The high freq dielectric const is largely *overestimated*
- Mean bond length is also *overestimated*

...and if we choose BLYP functional ?

BLYP Models

We consider two models:

I) C-BLYP is obtained from PW Model I (C-PW) by a first-principle relaxing of the atomic positions with BLYP.

II) FP-BLYP is obtained by quench-from-the-melt and damped dynamics relaxation of the atomic positions *fully first-principles.* The fully first-principles PW Model III is named (FP-PW)

BLYP Models: structural properties

Model	C-PW	C-BLYP	FP-PW	FP-BLYP
Ge-Se (Å)	2.42 (0.05)	2.37 (0.06)	2.47 (0.13)	2.40 (0.14)

- BLYP gives Ge-Se bond length in better agreement with the experimental one ~2.36 Å

BLYP Models: structural properties

First-neighbor coordination shells of Ge and Se

	ℓ	C-PW	C-BLYP	FP-PW	FP-BLYP
Ge					
Se_3	3	5	5	20	15
Se_4	4	95	95	78	83
Se_5	5	—	—	2	2
Se					
Ge	1	1	1	1	—
SeGe	2	3	3	20	12
Ge_2	2	92	92	55	68
Se_2	2	—	—	4	5
$SeGe_2$	3	2	2	—	—
Ge_3	3	2	2	20	14
Ge_4	4	—	—	—	1

• FP-BLYP shows a degree of chemical disorder comparable to FP-PW (“weak chem. order”)

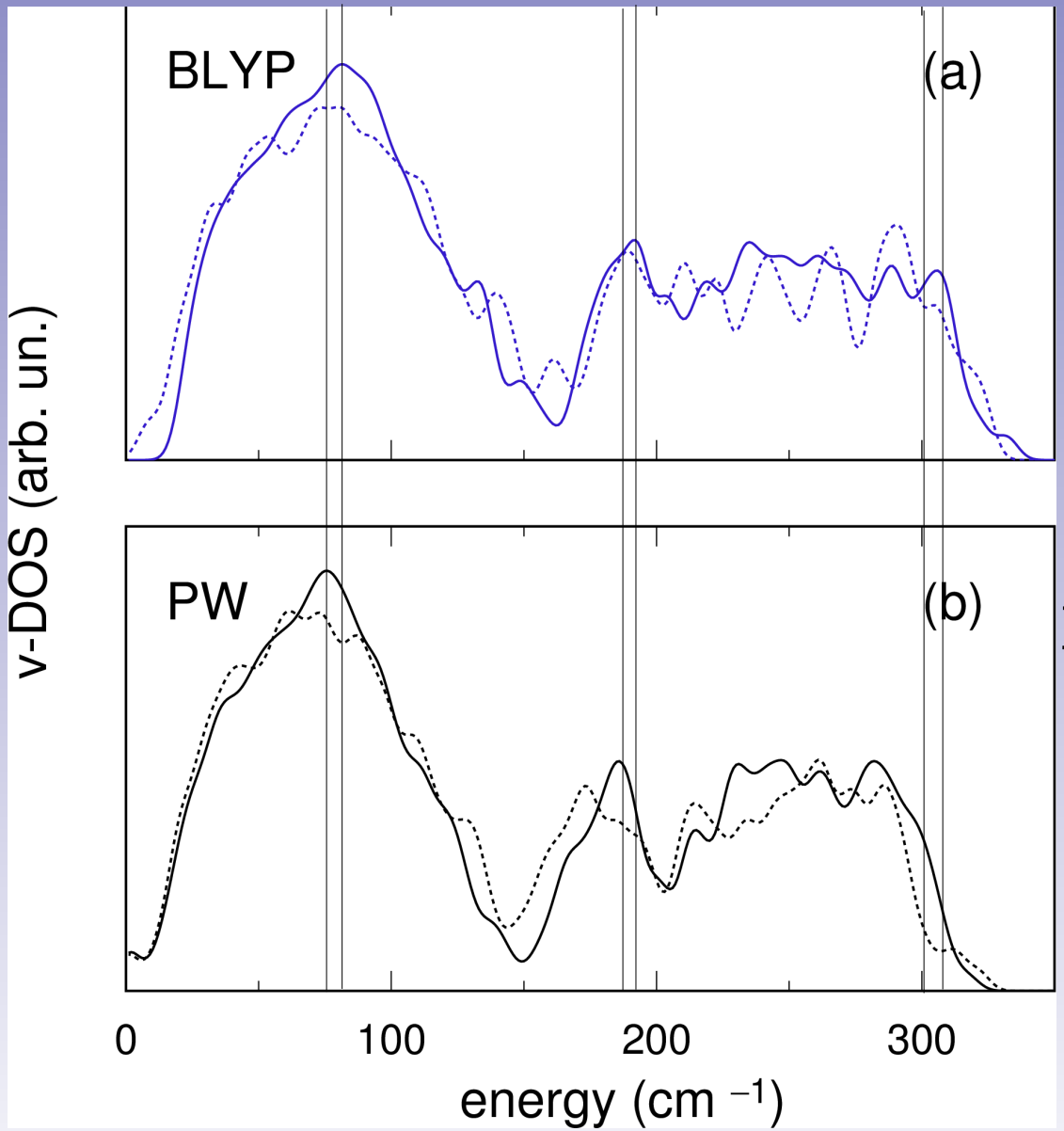
BLYP Models: electronic properties

- Finite electric field scheme for calc ε_∞ and also for accessing the infrared and Raman spectra [P. Umari and A. Pasquarello PRL 89, 157602 (2002)].

	C-PW	C-BLYP	FP-PW	FP-BLYP	Expt.
ε_∞	7.2	6.2	7.3	6.1	5.5
B. Gap (eV)	0.50	0.43	0.81	1.1	2.2

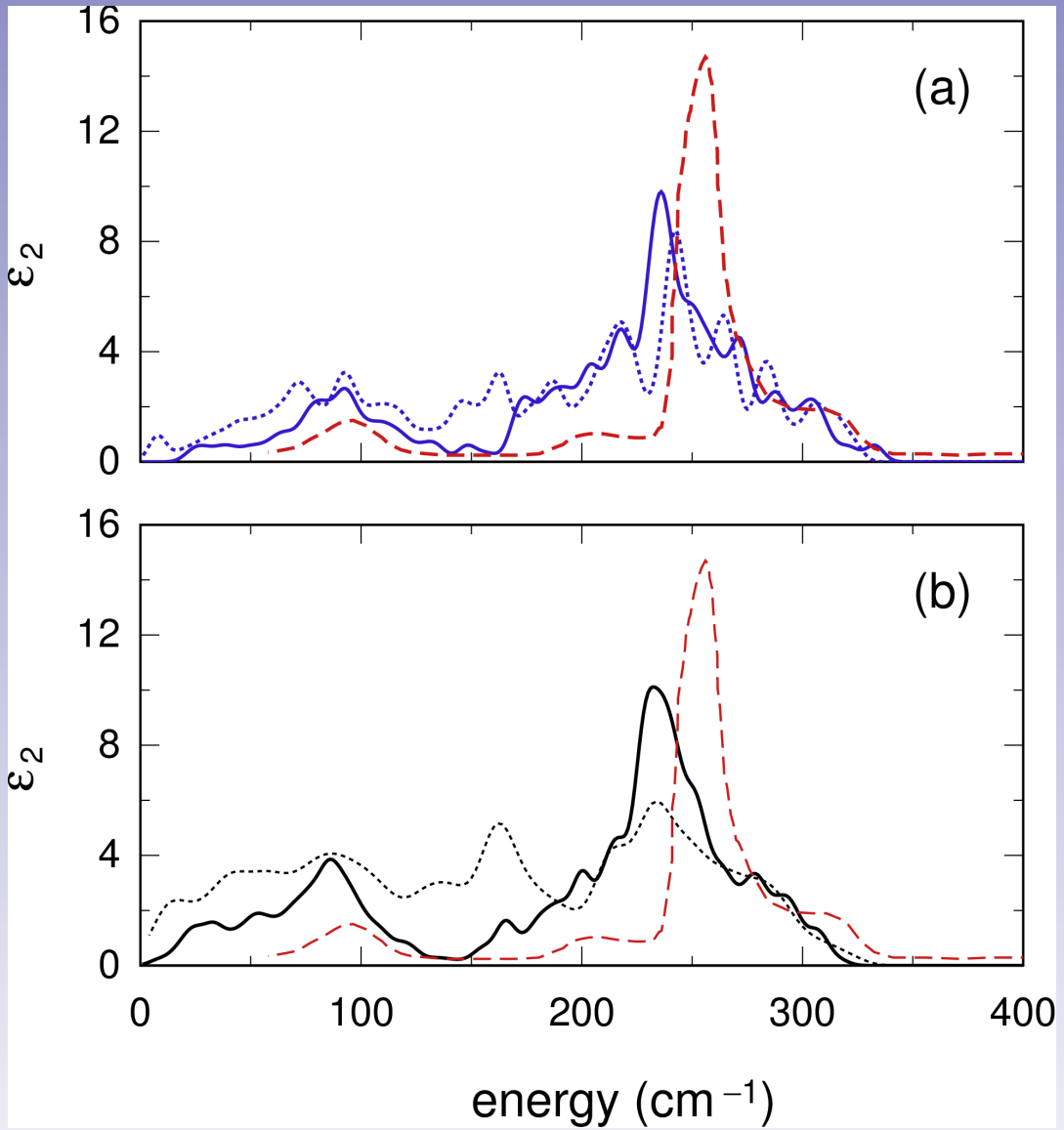
- BLYP ε_∞ is for all the models only about 10% larger than the expt. value

PW vs BLYP v-DOS of *v*-$GeSe_2$



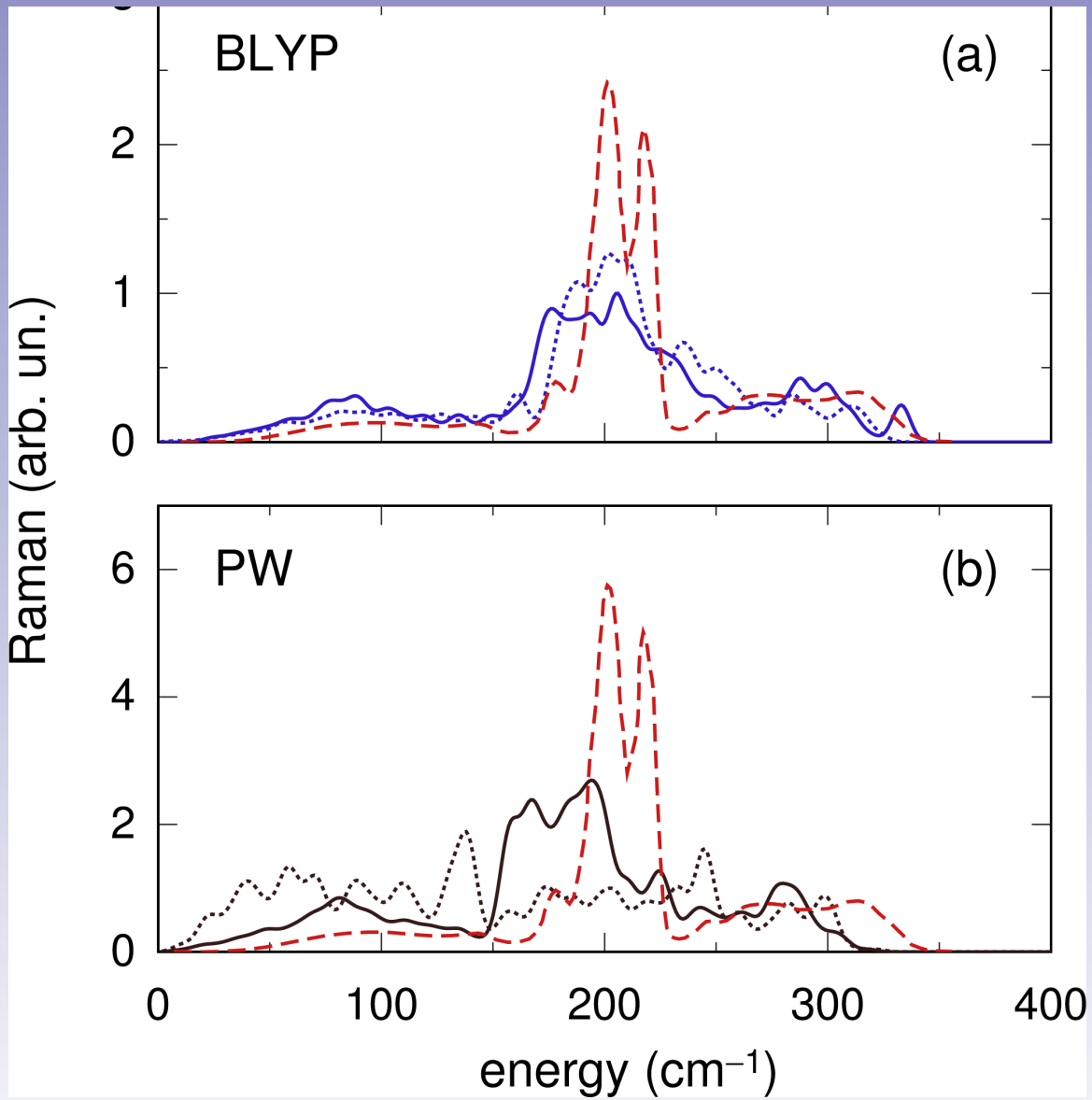
• BLYP shifts the frequencies of a few % wrt PW and improves comparison with vibrational spectroscopy experiments.

PW vs BLYP infrared spectra of *v*-$GeSe_2$



Experimental data taken from:
K. Murase in *Insulating and semiconducting glasses* Vol 17, ed. by P. Boolchand (WSP, Singapore, 2000), pp. 415-463.

PW vs BLYP Raman spectra of *v*-$GeSe_2$



FP-BLYP
C-BLYP
Expt.

FP-PW
C-PW
Expt.

Experimental data taken from:
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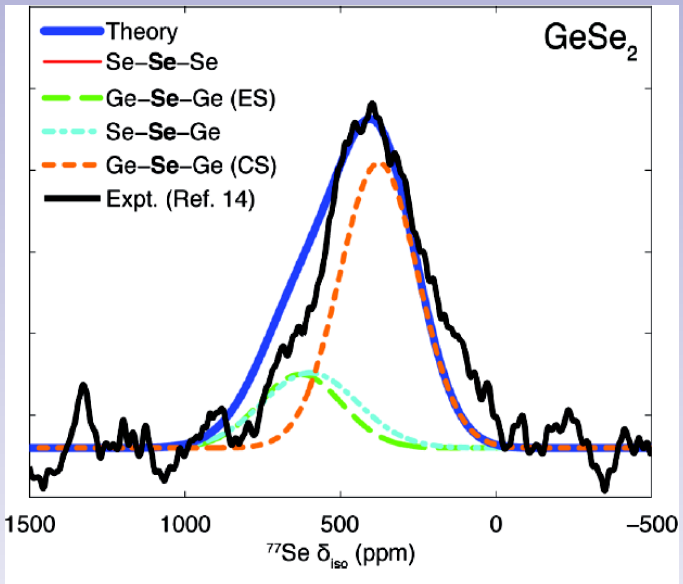
First-principles NMR calculations

- Perdew-Burke-Ernzerhof (PBE) functional
- In $GeSe_2$ about 20% of the Se atoms belong to Se-**Se**-Ge units
- High fraction of Se belongs to corner-sharing and edge-sharing arrangements as inferred from neutron scattering data (80% Se) of Petri et al PRL (2000).

config.	δ_{iso}	σ	$GeSe_2$
Se–**Se**–Se	828	141	0%
Ge–**Se**–Ge (ES)	628	132	17%
Se–**Se**–Ge	597	152	20%
Ge–**Se**–Ge (CS)	376	126	63%



M. Kibalchencko et al J. Phys. Chem. (2011).

Conclusions

- **FP-BLYP** models featuring up to 80% of Ge regular tetrahedra may give reasonably good Raman spectrum → *No reason to pretend 95% of regular tetrahedra*: v-$GeSe_2$ structure may still be *compatible* with a rather "weak chemical order".

- **FP-BLYP** shows dielectric constant and band gap are closer to expt. than **FP-PW**. → **BLYP** gives better description of the electronic structure than PW.

- **BLYP** vibrational properties of v-$GeSe_2$ are improved compared to PW ones as already seen for the structure [Micoulaut et al PRB (2009)]

- **FP** analysis of **NMR** chemical shifts supports the picture of v-$GeSe_2$ as a quite ordered network with 80% of Se belonging to regular CS and ES tetrahedra.

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Thank you
for your attention