First Principles NMR study for Ge-O-Ge angle in vitreous GeO_2

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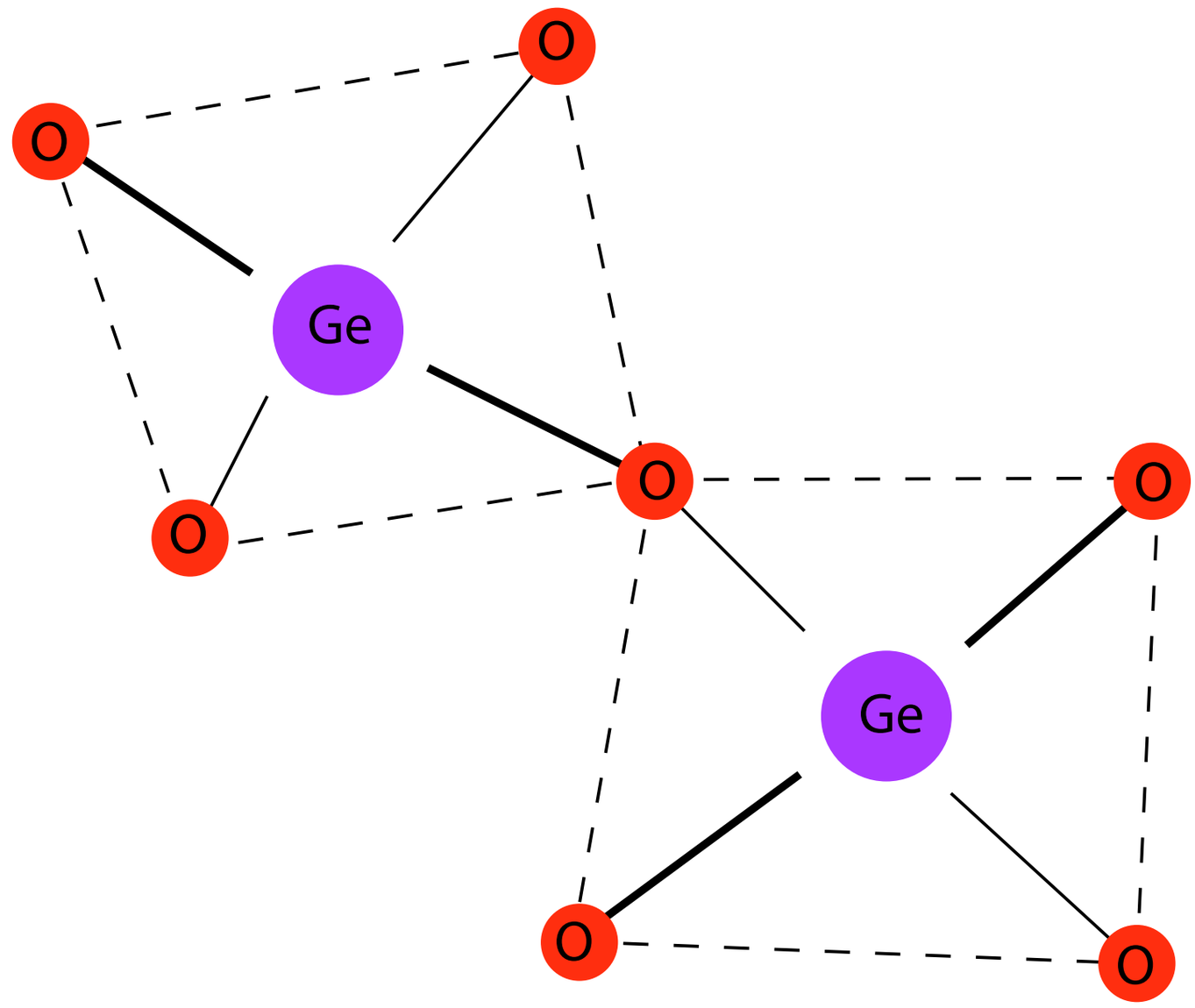
Introduction

- Optics
- Microelectronics
- Radioactive waste storage

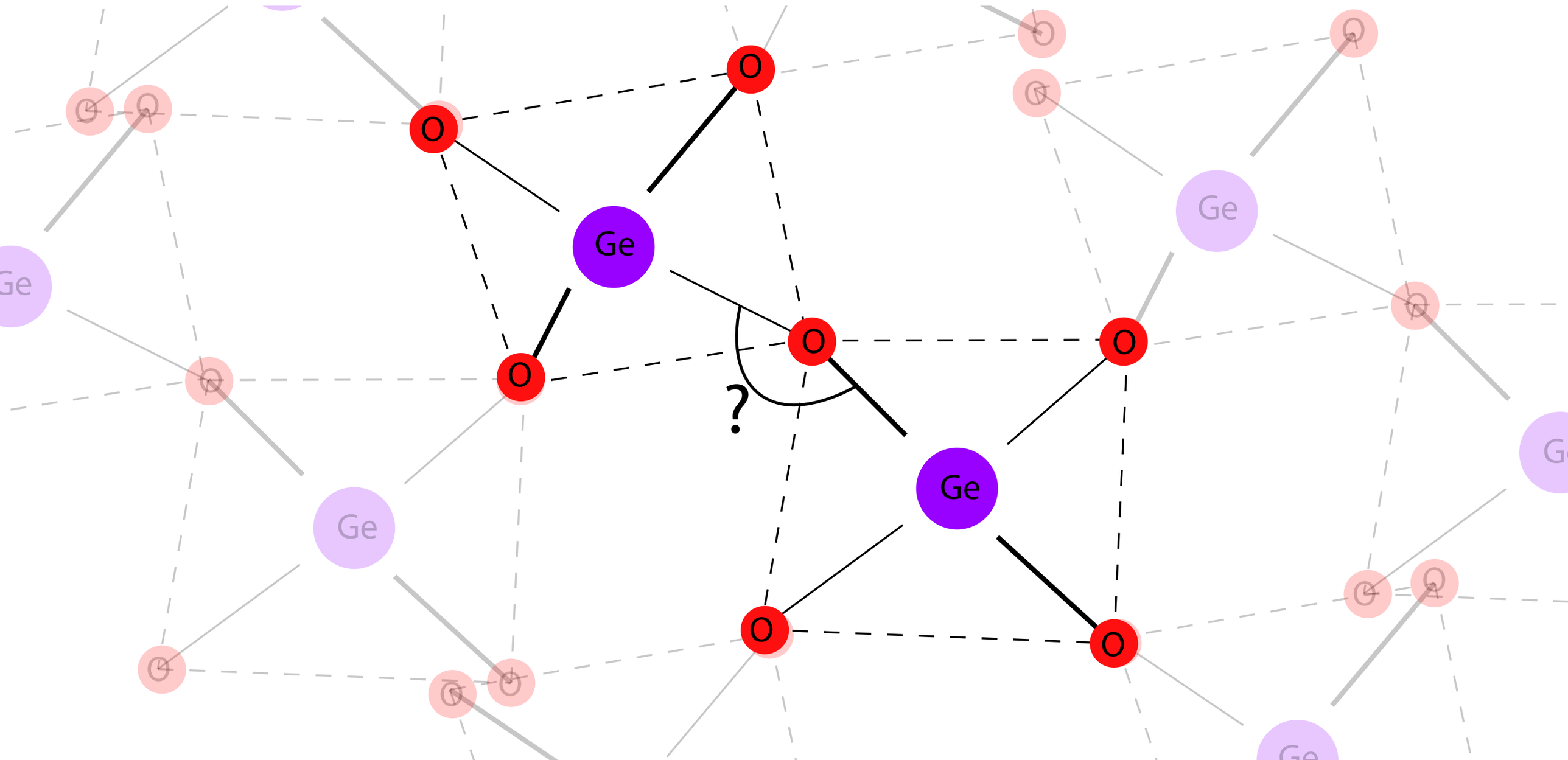
Introduction

- Short range order is well characterised using diffraction probes



Introduction

- Medium range order? - difficult for diffraction probes
- Described by distribution of Ge - O - Ge angles



Introduction

- Solid State NMR experiment is sensitive to medium range length scales
- We need to establish correlation between measured NMR parameters and structure

Calculation

- Preparing models of vitreous GeO_2:

- subject to periodic boundary conditions
- cubic simulation cells
- experimental density

1. classical molecular dynamics starting with SiO_2
2. rescaling of simulation cell by Ge-O / Si-O bond length ratio
3. damped first principles molecular dynamics

Models of vitreous GeO_2

	Size (atoms)	Ge-O-Ge
Model A	168	135.0º (10.6º)
Model B	36	130.2º (10.9º)

- models showed good agreement with available experimental data for
- diffraction structure factors
- vibrational spectra

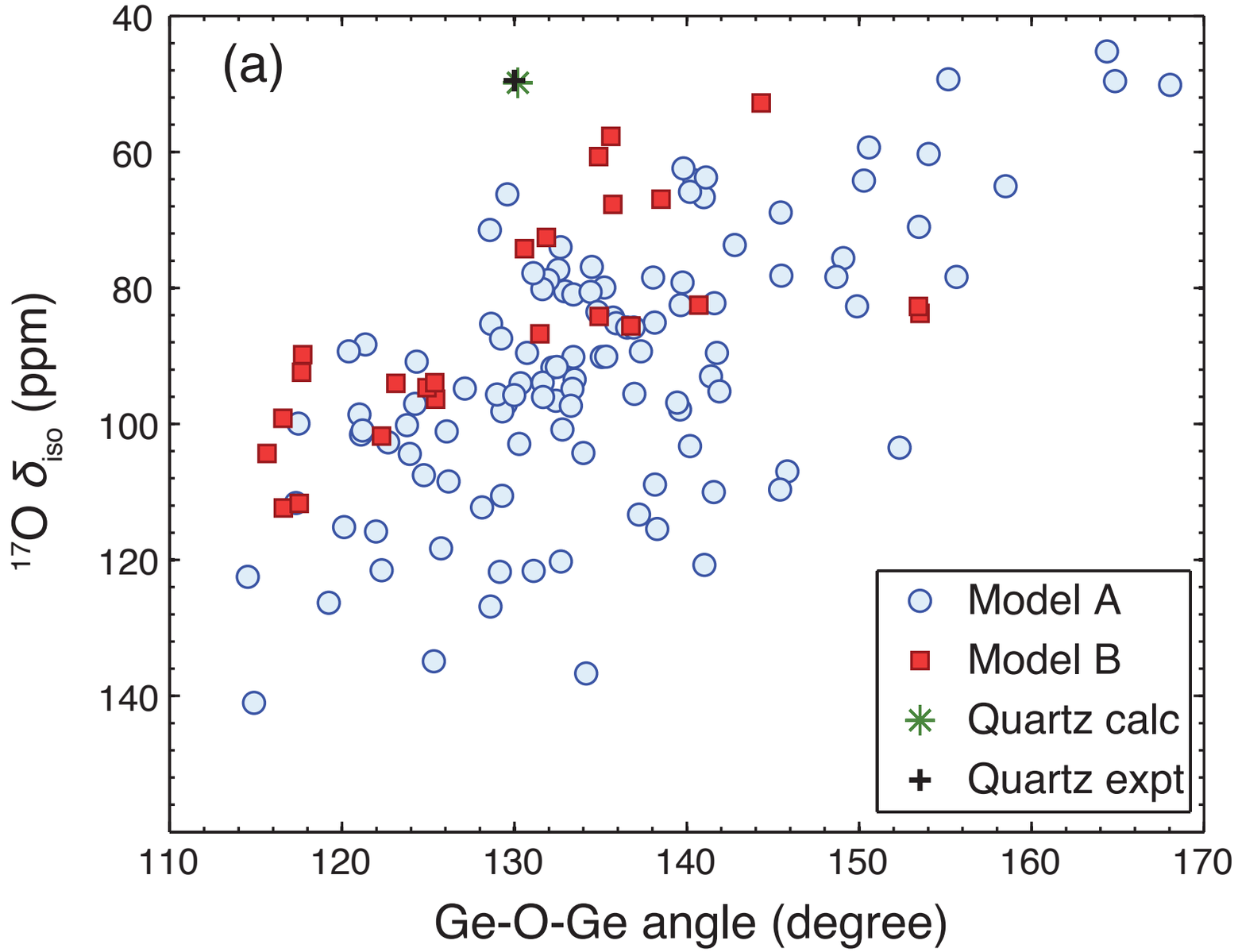
NMR Calculations

- GIPAW in CASTEP
- ultrasoft pseudopotentials
- PBE exchange-correlation functional
- cut off energy of 500 eV
- Brillouin zone sampled using a MP grid with a maximum spacing of 0.055 A^{-1}
- Accuracy: 2 ppm for ^{17}O and ^{73}Ge shieldings and within 0.1 Mhz for ^{17}O and ^{73}Ge quadrupole coupling constants

NMR parameters of interest

- isotropic shifts
    - measures chemical shielding effect due to induced electric currents
- quadrupole coupling constants C_Q
- electric-field-gradient asymmetry parameter η
    - measure electronic density around the nucleus

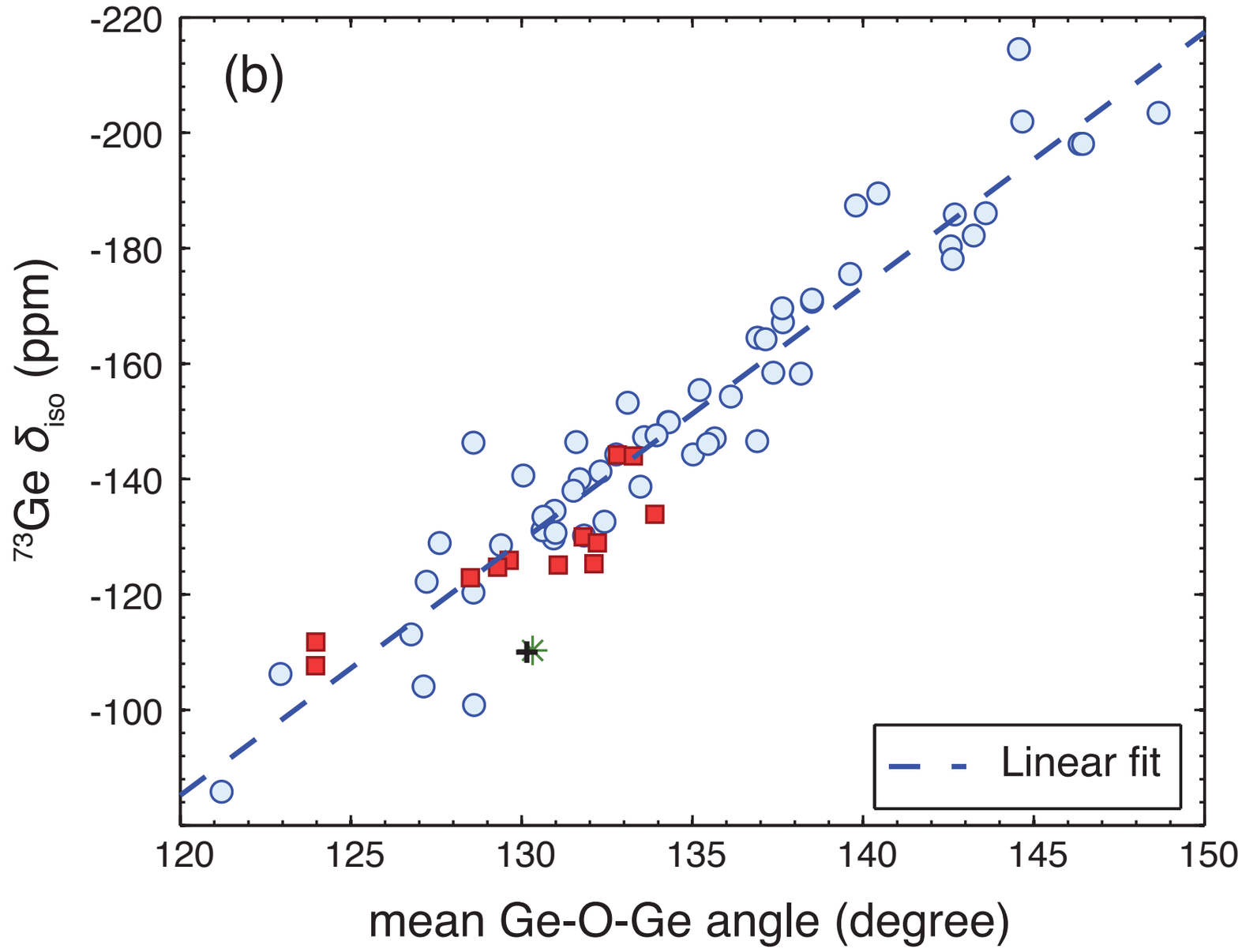
Correlations with Ge-O-Ge angle



general trend can be observed

^{17}O isotropic shift

Correlations with Ge-O-Ge mean angle



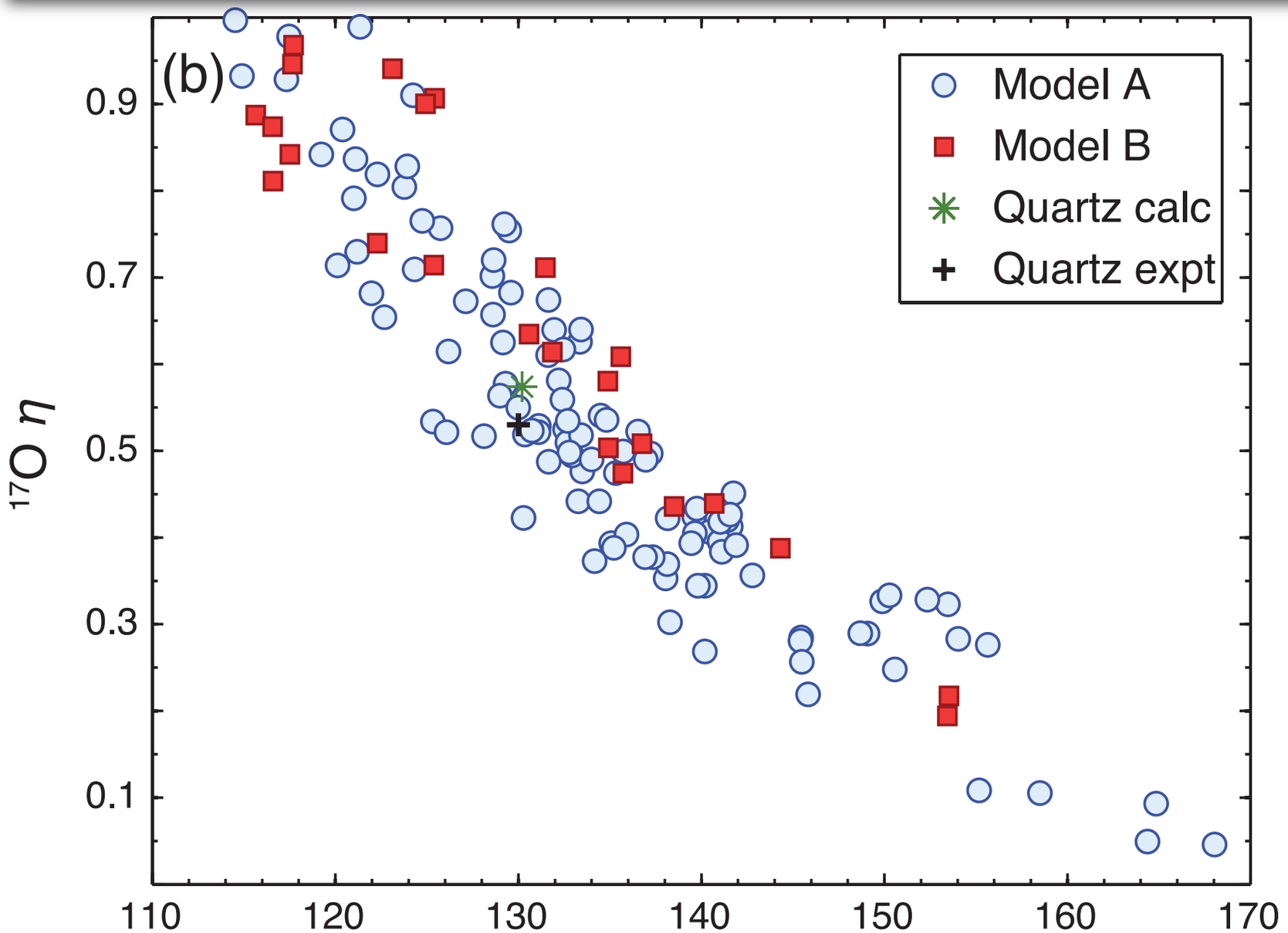
clear correlation can be observed

^{73}Ge isotropic shift

Correlations for ^{73}Ge EFG parameters

no obvious structural correlation found

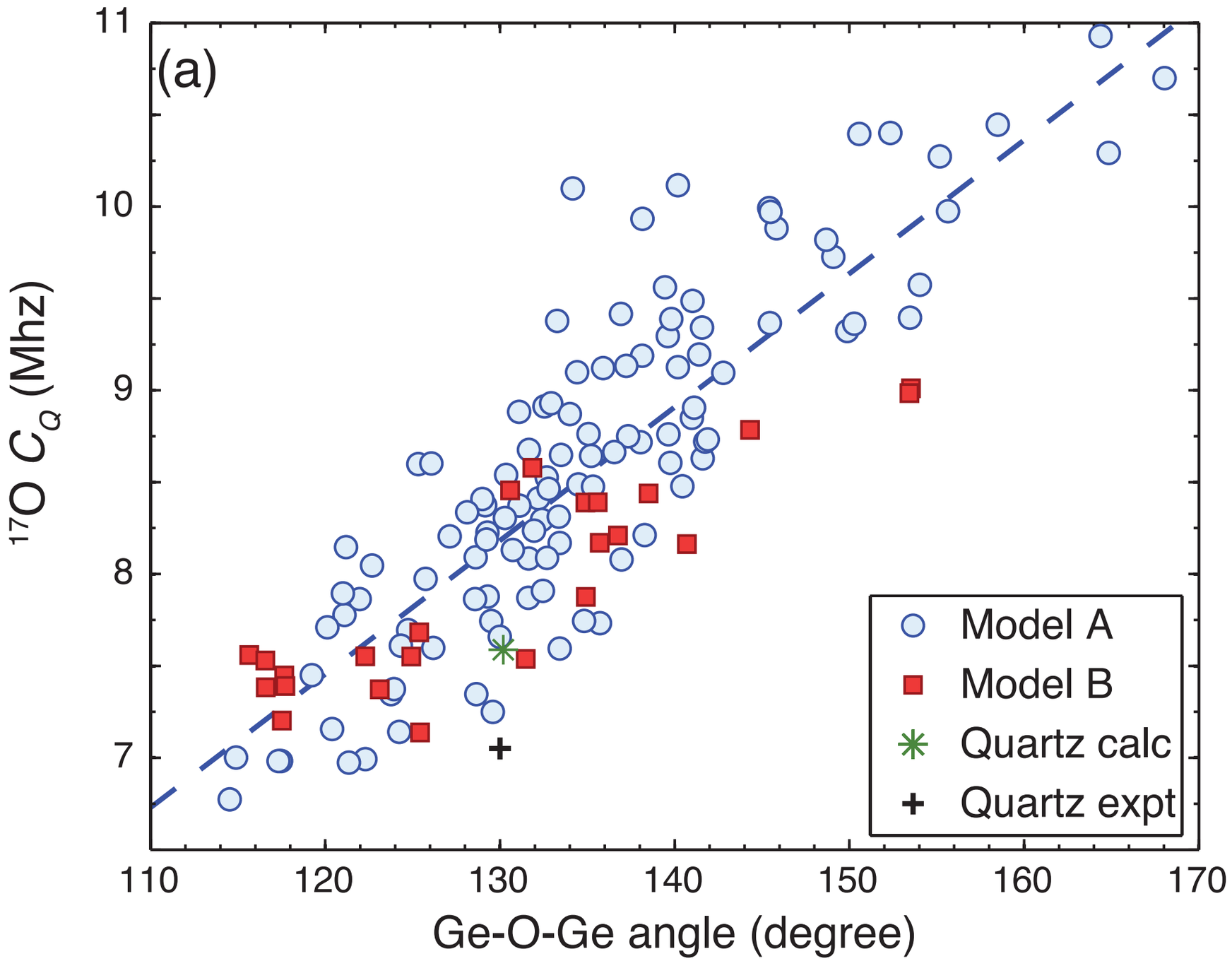
Correlations with Ge-O-Ge angle



clear trend can be observed

^{17}O asymmetry EFG

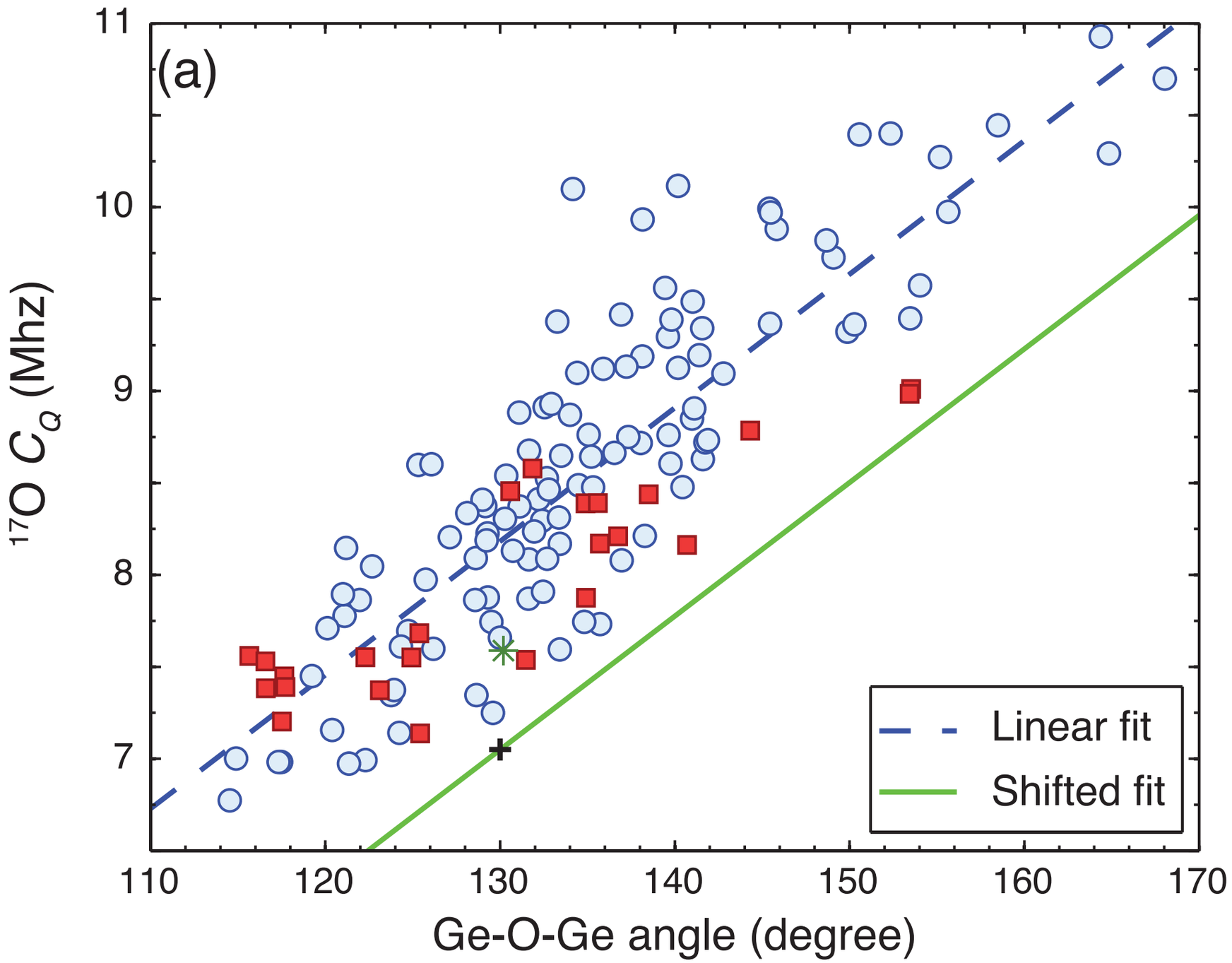
Correlations with Ge-O-Ge angle



clear trend can be observed

^{17}O quadrupole coupling constant

Correlations with Ge-O-Ge angle



can use shifted fit to extract structural data

^{17}O quadrupole coupling constant

So what is the mean Ge-O-Ge angle?

	^{17}O Cq (Mhz)	Ge-O-Ge
Du and Stebbins, 2006	7.4	135°
Hussin, Dupree, Holland, 1999	7.1	131°

- and we showed that typical Ge-O-Ge angles in vitreous GeO_2 lie between 124° and 139°

Conclusion

- 2 vitreous GeO_2 models
- CASTEP NMR calculations
- experimental Cq measurements
- mean Ge-O-Ge angle of 135°

Acknowledgements

- Jonathan Yates
- Alfredo Pasquarello
- Mike Payne

TCM

EPSRC

Thank you for listening

back up slides

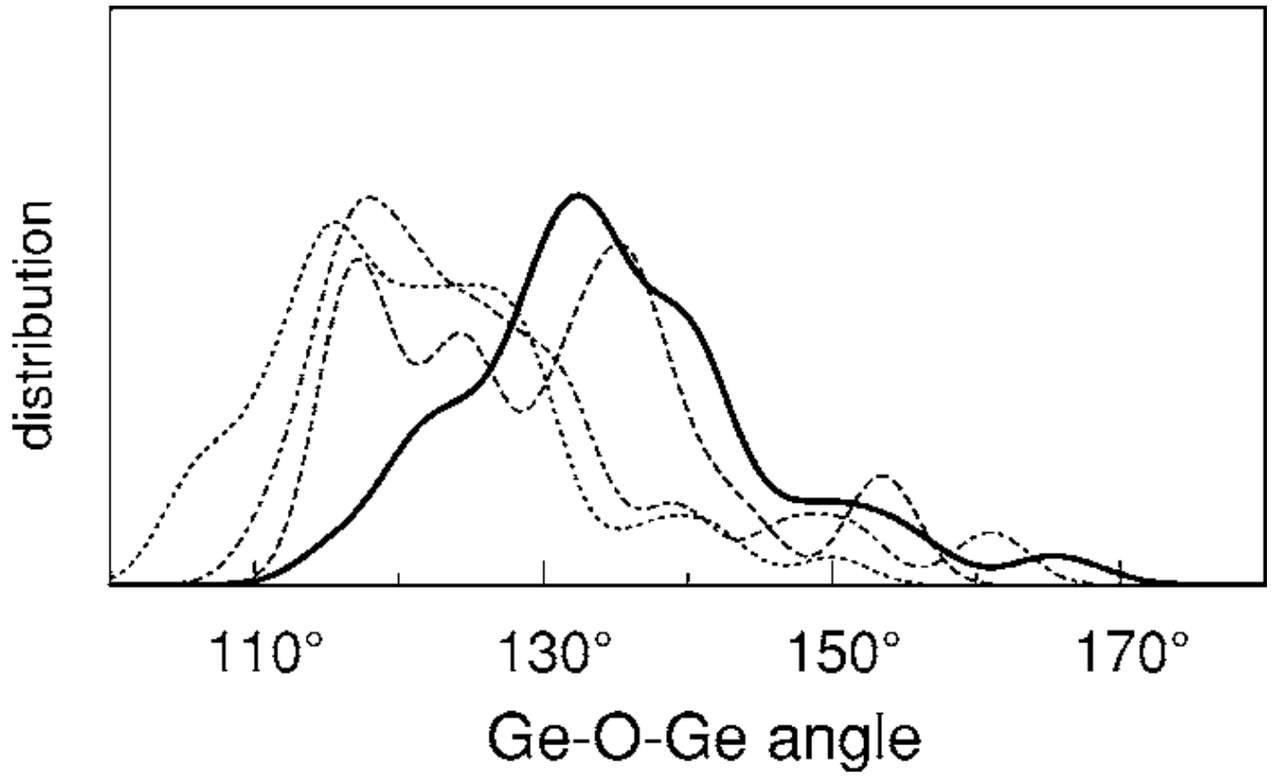


FIG. 4. Distribution of the Ge-O-Ge intertetrahedral angle for our four models of v-GeO_2: model I solid , model II dot-dashed , model III dotted , and model IV dashed . A Gaussian broadening of 2.5° is used.

Giacomazzi L, Umari P and Pasquarello A 2006 Phys. Rev. B 74 155208