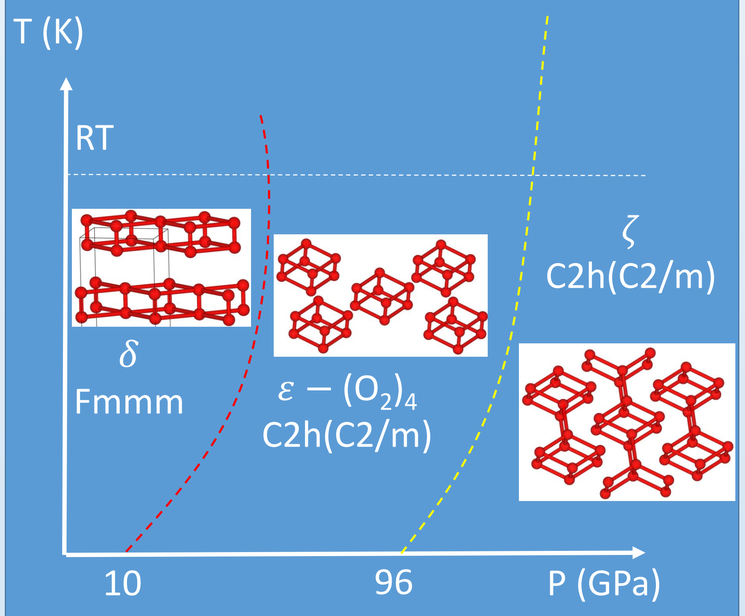
The Hubbard- and van der Waals-corrections on the DFT calculations of the epsilon-zeta transition in the solid oxygen

Le The Anh
Quemix Inc.

INTRODUCTION 1

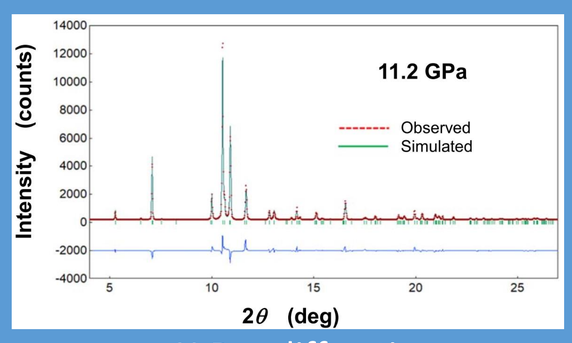
High-pressure physics and strongly-correlated materials



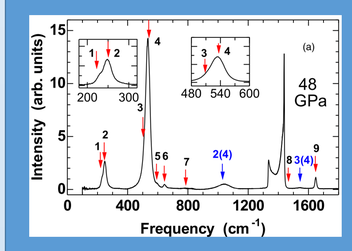
Simplified phase diagram of solid oxygen

INTRODUCTION 2

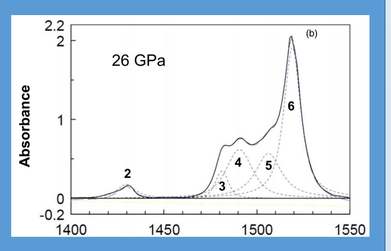
Experimental methods to explore the structures



X-Ray diffraction



Raman



IR absorption

Yuichi Akahama *et al* 2019 *Jpn. J. Appl. Phys.* **58** 095502

INTRODUCTION 3

Theoretical physics of many-body systems

1. Hartree-Fock

$$E_x^{HF} \cong -\frac{1}{2}\iint d^3r_1 d^3r_2 \frac{\phi^*_{n,k}(r_1)\phi^*_{m,q}(r_2)\phi_{n,k}(r_2)\phi_{m,q}(r_1)}{|r_1 - r_2|}$$

2. Hubbard V

$$E = E_{\mathrm{DFT}} + \frac{1}{2}\sum_{I,\sigma} U^I \,\mathrm{Tr}\left[(\mathbf{1} - \mathbf{n}^{I\sigma})\,\mathbf{n}^{I\sigma}\right] - \frac{1}{2}\sum_{I,J,\sigma} V^{IJ}\,\mathrm{Tr}\left[\mathbf{n}^{IJ\sigma}\mathbf{n}^{JI\sigma}\right]$$

3. van-der-Waals

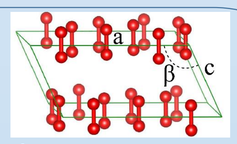
Semi-empirical

$$E_{XC}^{vdW} = E_X^{GGA} + E_C^{disp}$$
$$E_C^{disp} = C_6\frac{1}{|\boldsymbol{R_A} - \boldsymbol{R_B}|^6} + C_8\frac{1}{|\boldsymbol{R_A} - \boldsymbol{R_B}|^8} + \cdots$$

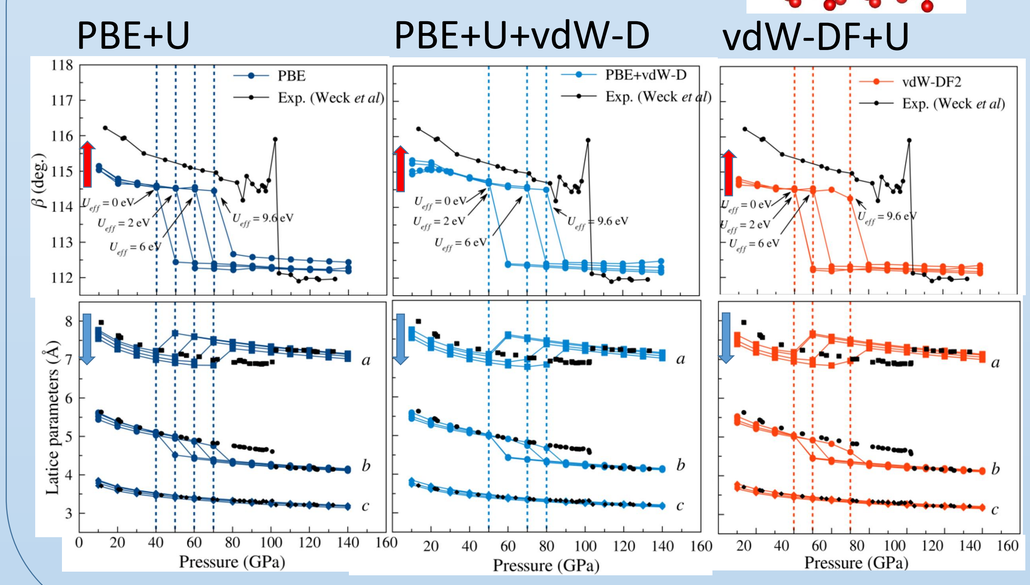
Fully ab-initio

$$E_c^{\mathrm{nl}}[n] = \frac{1}{2}\int \mathrm{d}^3\mathbf{r}\int \mathrm{d}^3\mathbf{r}'\, n(\mathbf{r})\phi[n](\mathbf{r},\mathbf{r}')n(\mathbf{r}')$$

+U *vs* +U+vdW: Structure



PBE+U | PBE+U+vdW-D | vdW-DF+U



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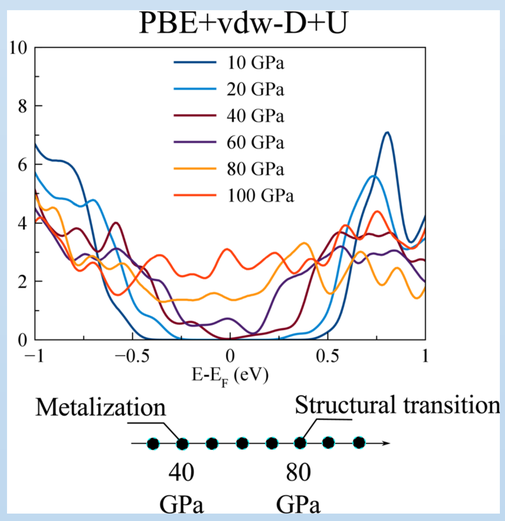
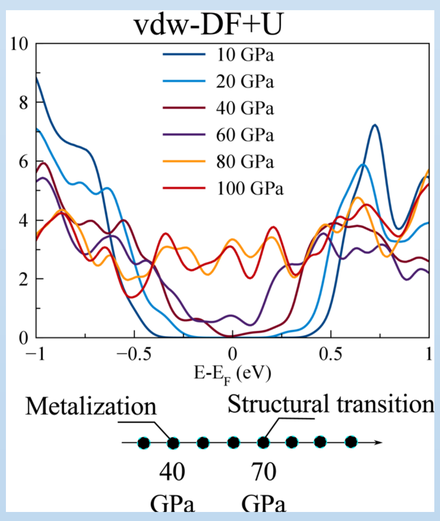
Metallization *vs* Structural transition





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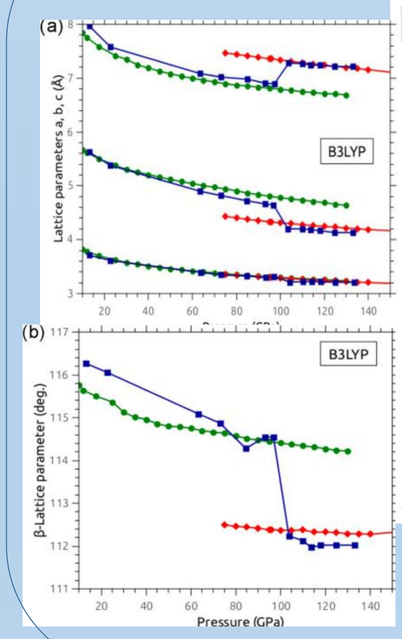
Hartree-Fock physics



	pressure (GPa)	% of HF exchange
HF	no transition up to 160	100
LDA	25, no phase coexistence	
GGA		
BLYP	30, no phase coexistence	
SOGGAXC	25, phase coexistence 25–35	
PBE	30, phase coexistence 30–45 (50)[a]	
B88PW91	30, phase coexistence 30–50	
Meta-GGA		
M06-L	10, phase coexistence 10–25	
Hybrid		
M06	80, phase coexistence 80–120	27
PBE0	85, phase coexistence 85–155	25
B3PW91	75, phase coexistence 75–145	20
B3LYP	75, phase coexistence 75–135	20
Experiment[b]	95, phase coexistence 95–110	

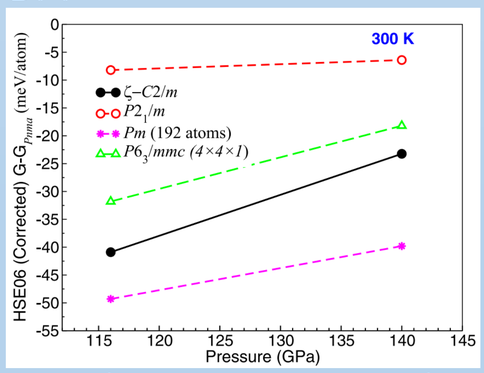
[a]From ref 13 with the PW basis set. [b]Exp. from ref 7.

B3LYP also predicted the co-existence of the epsilon and zeta phases.

J. Chem. Theory Comput. 2015, **11, 3**, 1195–1205

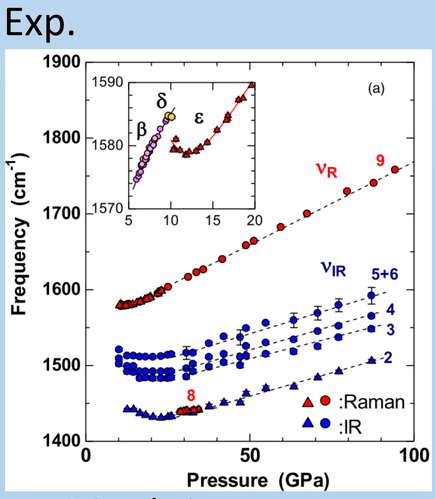
Un-solved problems

DFT



Zeta phase: Pm symmetry has lower enthalpy than C2/m

Exp.



- C2h(C2/m): 12 Raman + 9 IR
- D2h: 9 Raman + 6 IR

PRB 2024 **110**, 064106

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Summary

- High pressure phases of solid oxygen are complex.
- It requires both correct short-range and long-range treatments on the equal footing.

Summary

- Possible long-range treatments are:
  - Hartree-Fock exchange
  - Inter-site Hubbard +V
  - van-der-Waals
- Within the two-body correlation approximation.