Magnetism and phase transitions in compressed Oxygen

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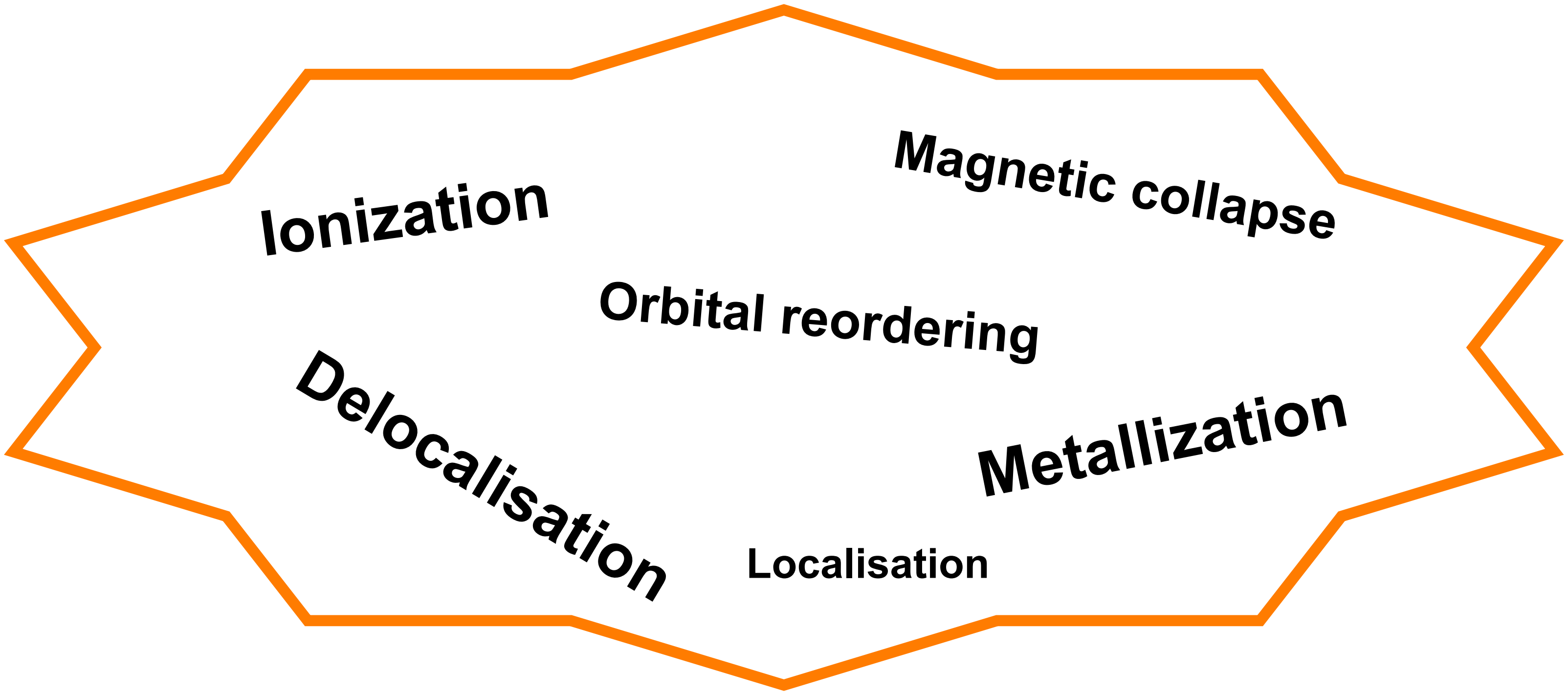
The Abdus Salam
International Centre
for Theoretical Physics

Pressure as a knob to tune electronic states

Pressure range in the universe:
10^{-17} atm (intergalactic voids)
10^{34} atm (center of neutron stars)

P = 1 Mbar => PΔV = 1-10 eV

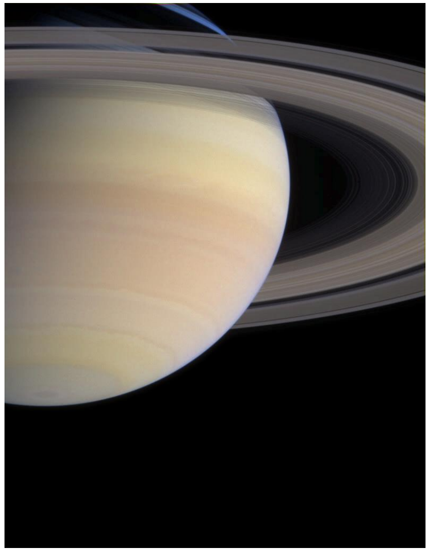


Molecular systems at extreme conditions
Pressure as a knob

Physics

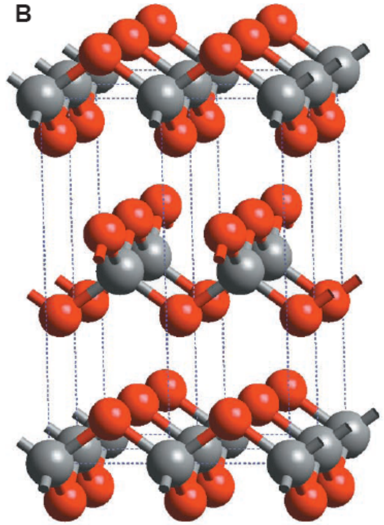
Hydrogen: a quantum solid at high pressure?

Planetary science



Insulator-metal transitions and magnetic fields

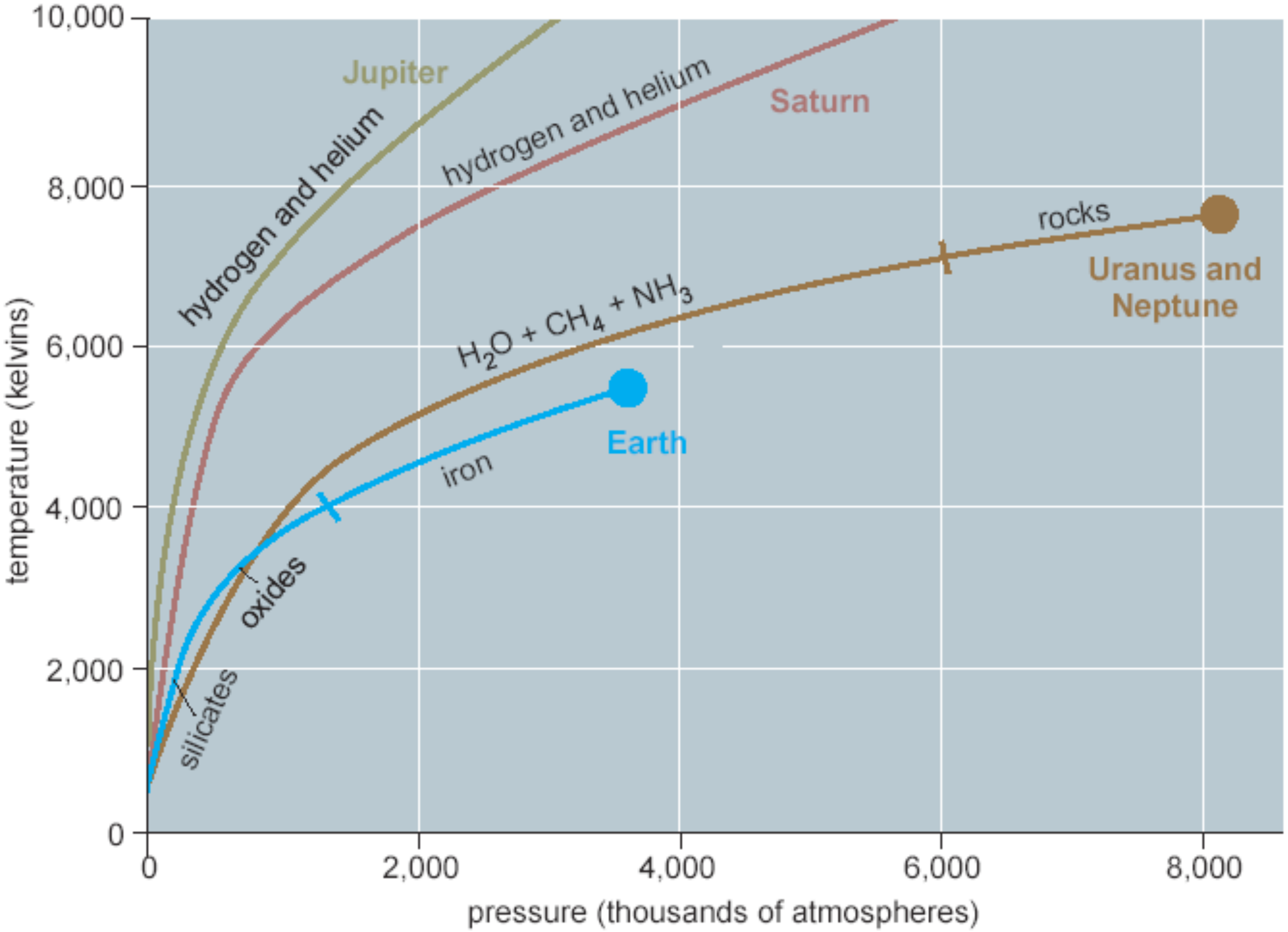
Chemistry/ Materials



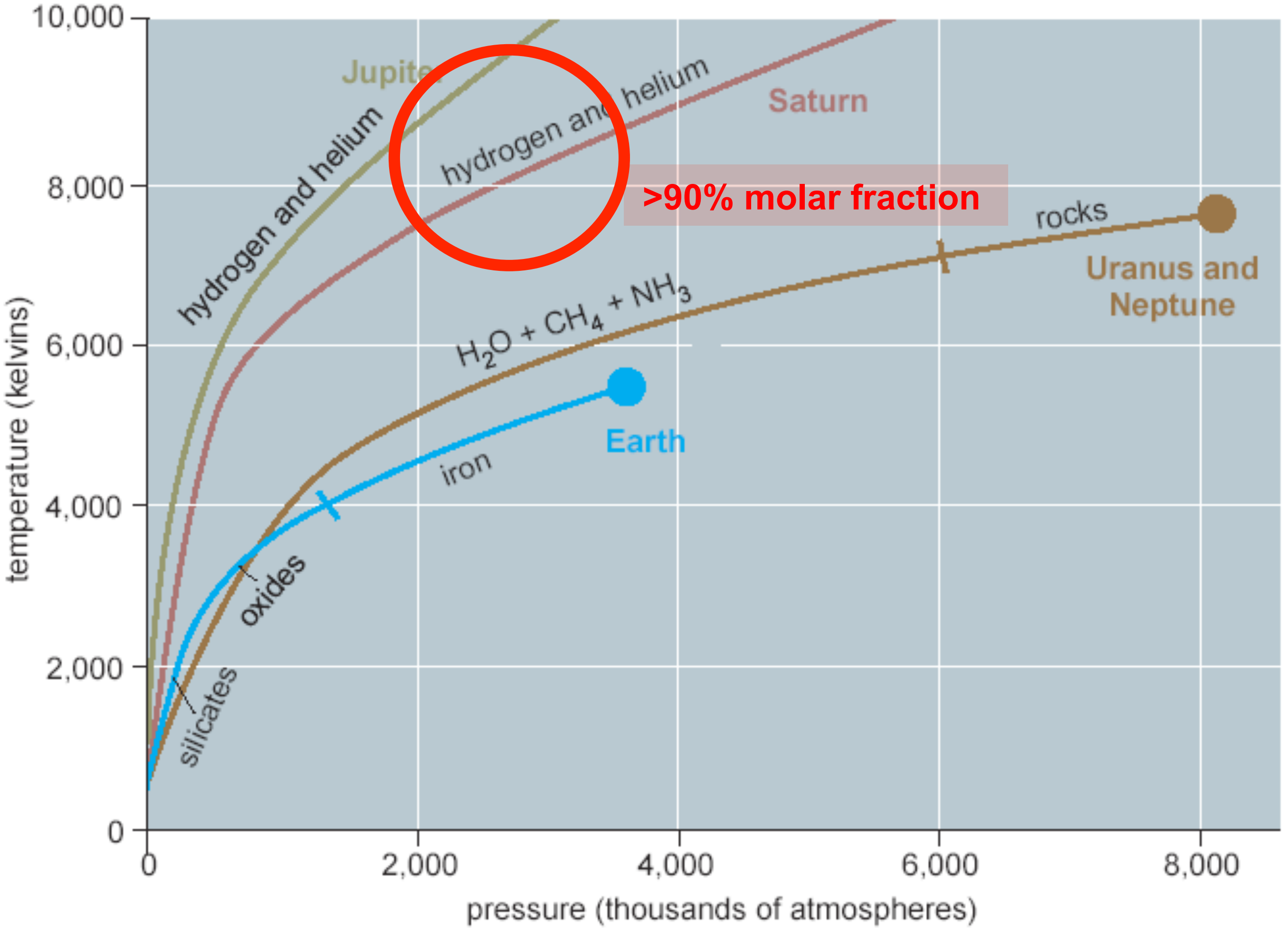
Synthesis of new compounds (CO_2)

P-T conditions inside planets

S. Scandolo and R. Jeanloz, American Scientist 2003



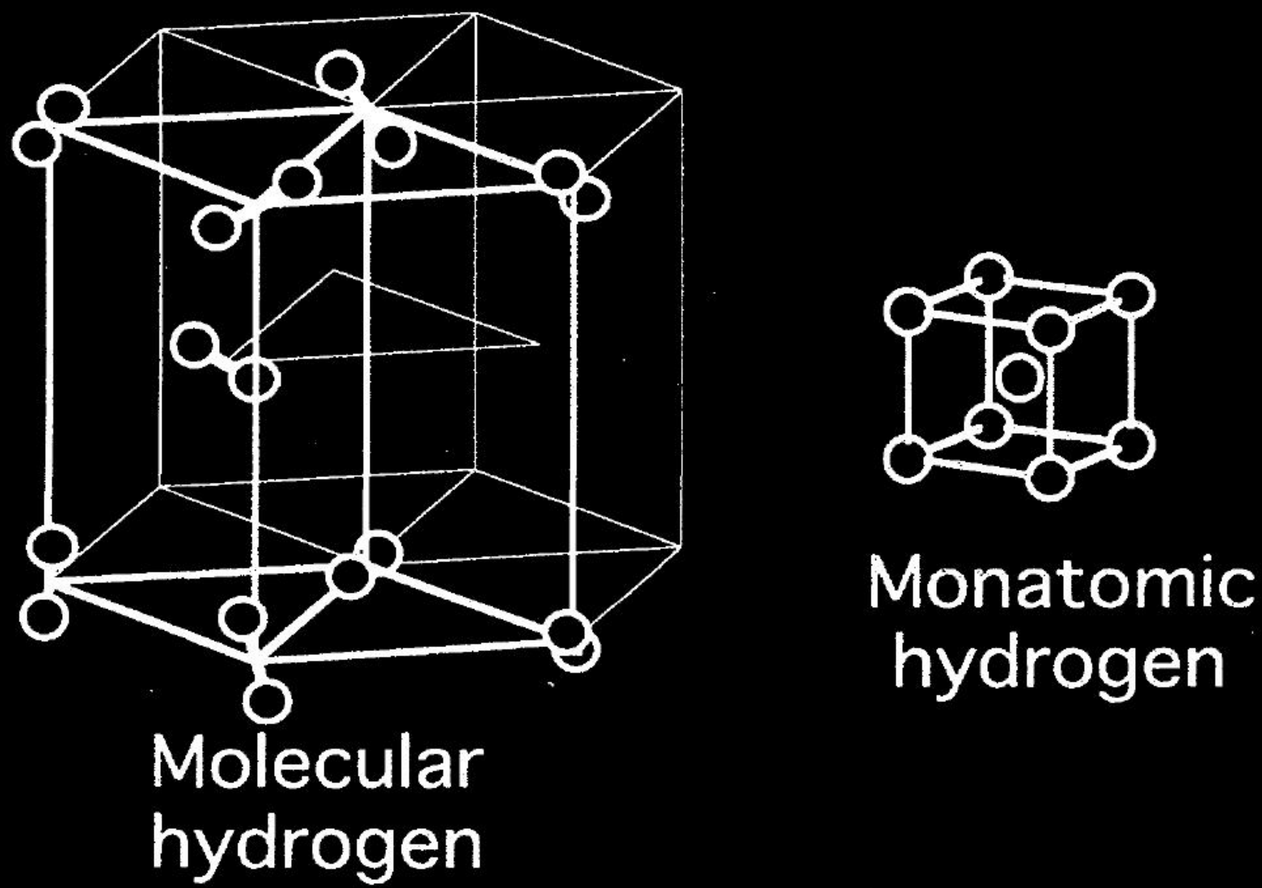
Hydrogen at extreme P-T



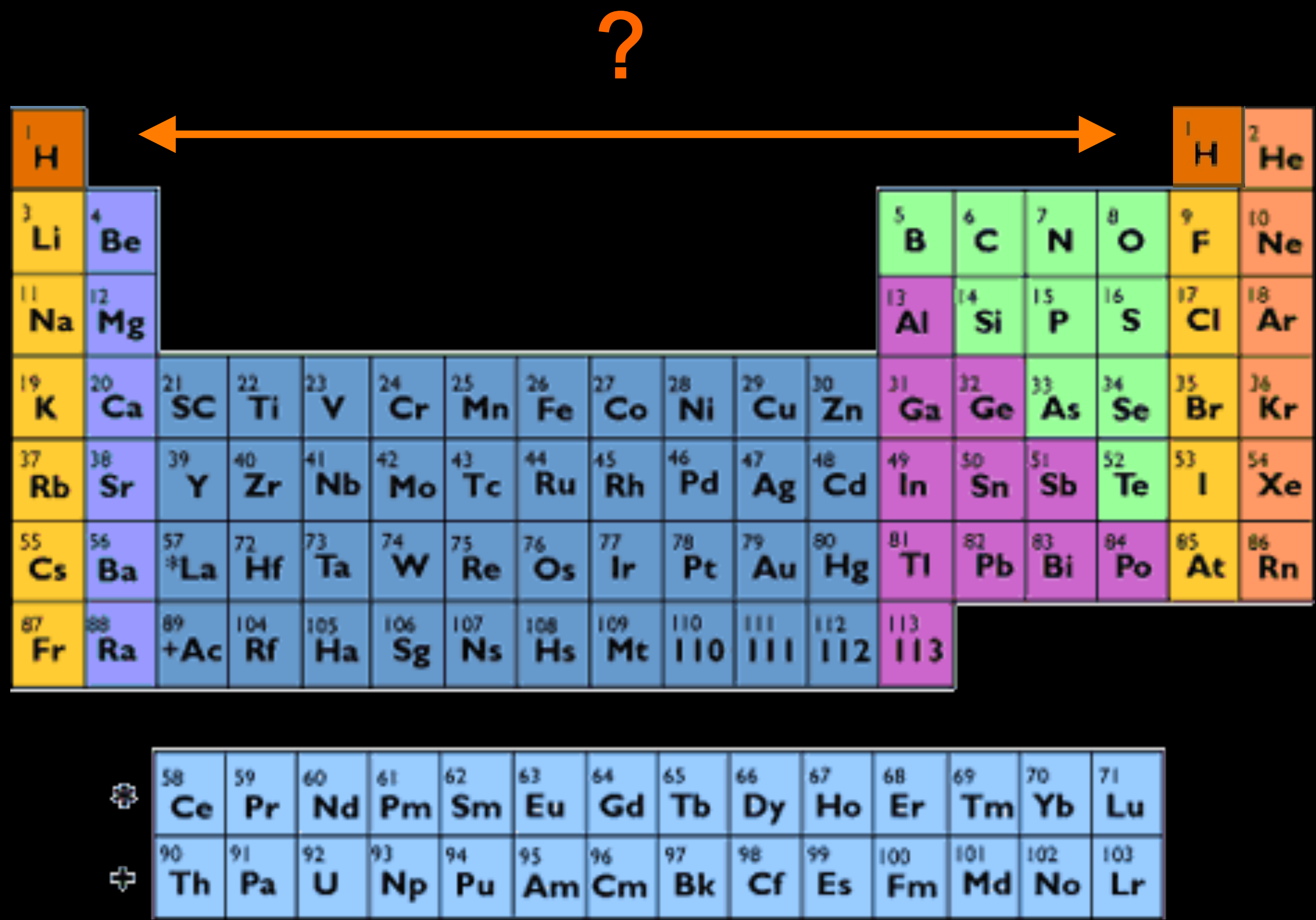
E. Wigner and H.B. Huntington

"On the possibility of a metallic modification of hydrogen"

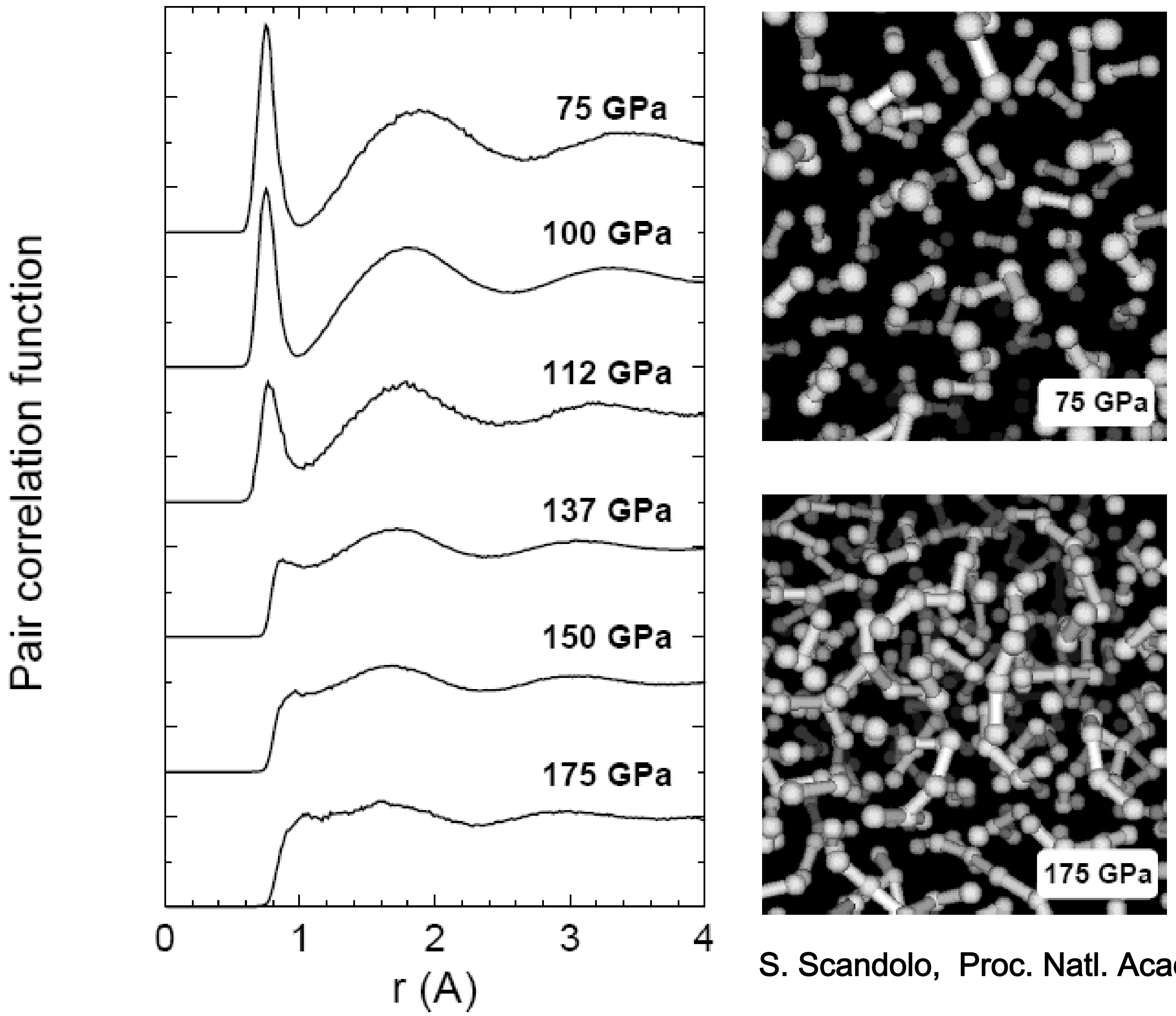
J. Chem. Phys. 3, 764 (1935)



Hemley and Mao, Rev Mod Phys


?
1 H
1 H
2 He
3 Li 4 Be
5 B 6 C 7 N 8 O 9 F 10 Ne
11 Na 12 Mg
13 Al 14 Si 15 P 16 S 17 Cl 18 Ar
19 K 20 Ca 21 SC 22 Ti 23 V 24 Cr 25 Mn 26 Fe 27 Co 28 Ni 29 Cu 30 Zn 31 Ga 32 Ge 33 As 34 Se 35 Br 36 Kr
37 Rb 38 Sr 39 Y 40 Zr 41 Nb 42 Mo 43 Tc 44 Ru 45 Rh 46 Pd 47 Ag 48 Cd 49 In 50 Sn 51 Sb 52 Te 53 I 54 Xe
55 Cs 56 Ba 57 *La 72 Hf 73 Ta 74 W 75 Re 76 Os 77 Ir 78 Pt 79 Au 80 Hg 81 Tl 82 Pb 83 Bi 84 Po 85 At 86 Rn
87 Fr 88 Ra 89 +Ac 104 Rf 105 Ha 106 Sg 107 Ns 108 Hs 109 Mt 110 110 111 111 112 112 113 113
* 58 Ce 59 Pr 60 Nd 61 Pm 62 Sm 63 Eu 64 Gd 65 Tb 66 Dy 67 Ho 68 Er 69 Tm 70 Yb 71 Lu
+ 90 Th 91 Pa 92 U 93 Np 94 Pu 95 Am 96 Cm 97 Bk 98 Cf 99 Es 100 Fm 101 Md 102 No 103 Lr

Molecular to non-molecular sharp transition



S. Scandolo, Proc. Natl. Acad. Sci. USA, 2003

Evidence of a liquid–liquid phase transition in hot dense hydrogen

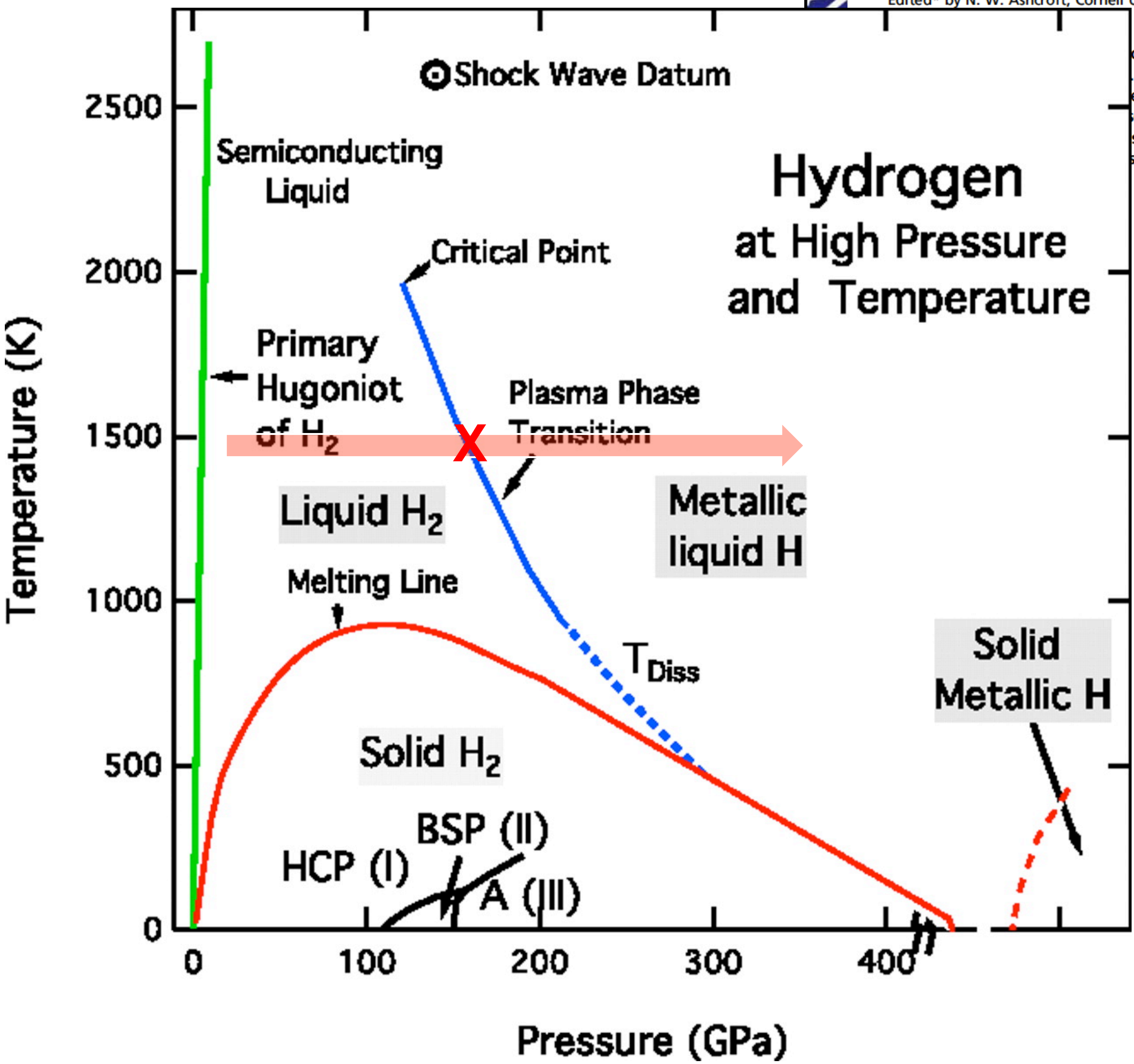
Vasily Dzyabura, Mohamed Zaghoo, and Isaac F. Silvera[1]

Lyman Laboratory of Physics, Harvard University, Cambridge, MA 02138

Edited* by N. W. Ashcroft, Cornell University, Ithaca, NY, and approved April 3, 2013 (received for review January 15, 2013)

hydrogen at static pressures in the
ch for the plasma phase transition to
. We heat our samples substantially
erve a plateau in a temperature vs.
e increases with power. This anom-
s correlated with theoretical predic-
sition.

(18), and later confirmed by Subraman
sufficiently high to confirm the extrapo
Scandolo (20) and others (14, 21–2
the higher temperature region above
found the PPT line. This line is not o
ducting liquid atomic metallic hydrog
dissociation from molecular to atomi
some differences in the calculations by



Dzyabura et al, PNAS 2013

Magnetism in compressed Oxygen
Prediction of a new magnetic phase

The Oxygen molecule has a peculiar (**S=1**) magnetic state

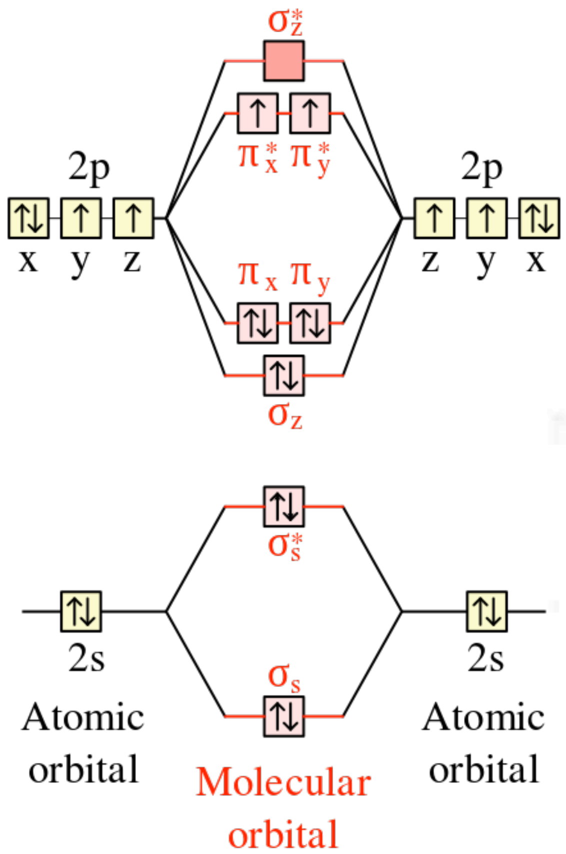
Pressure is known to eventually lead to the **collapse** of magnetism

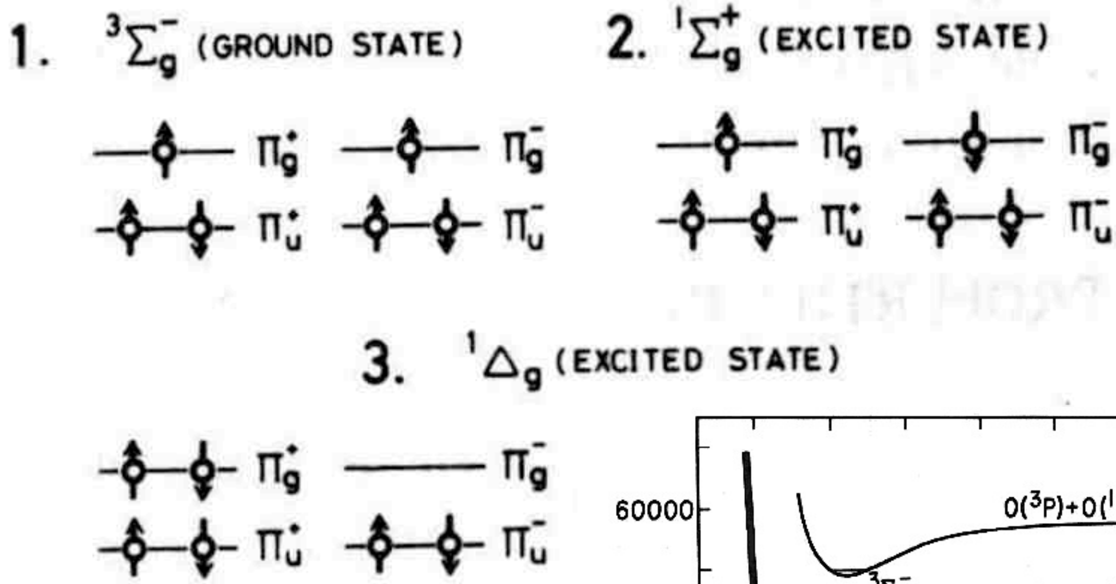
Interplay between pressure-induced **structural** and **magnetic** changes

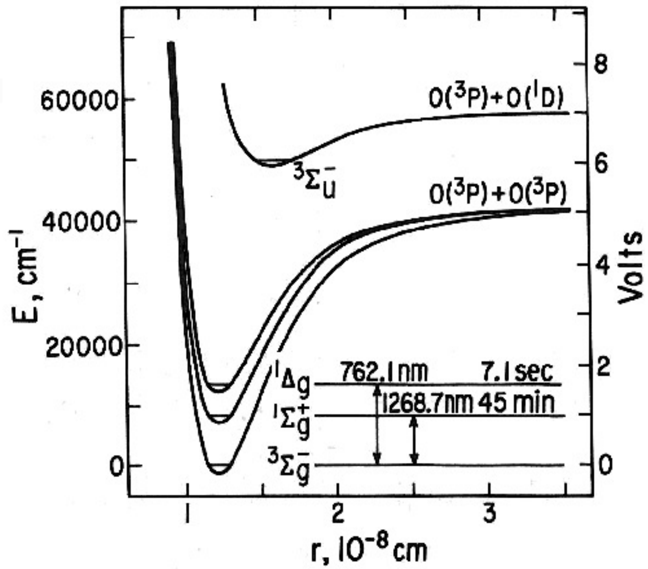
Y. Crespo M. Fabrizio E. Tosatti



Molecular oxygen
Electronic structure

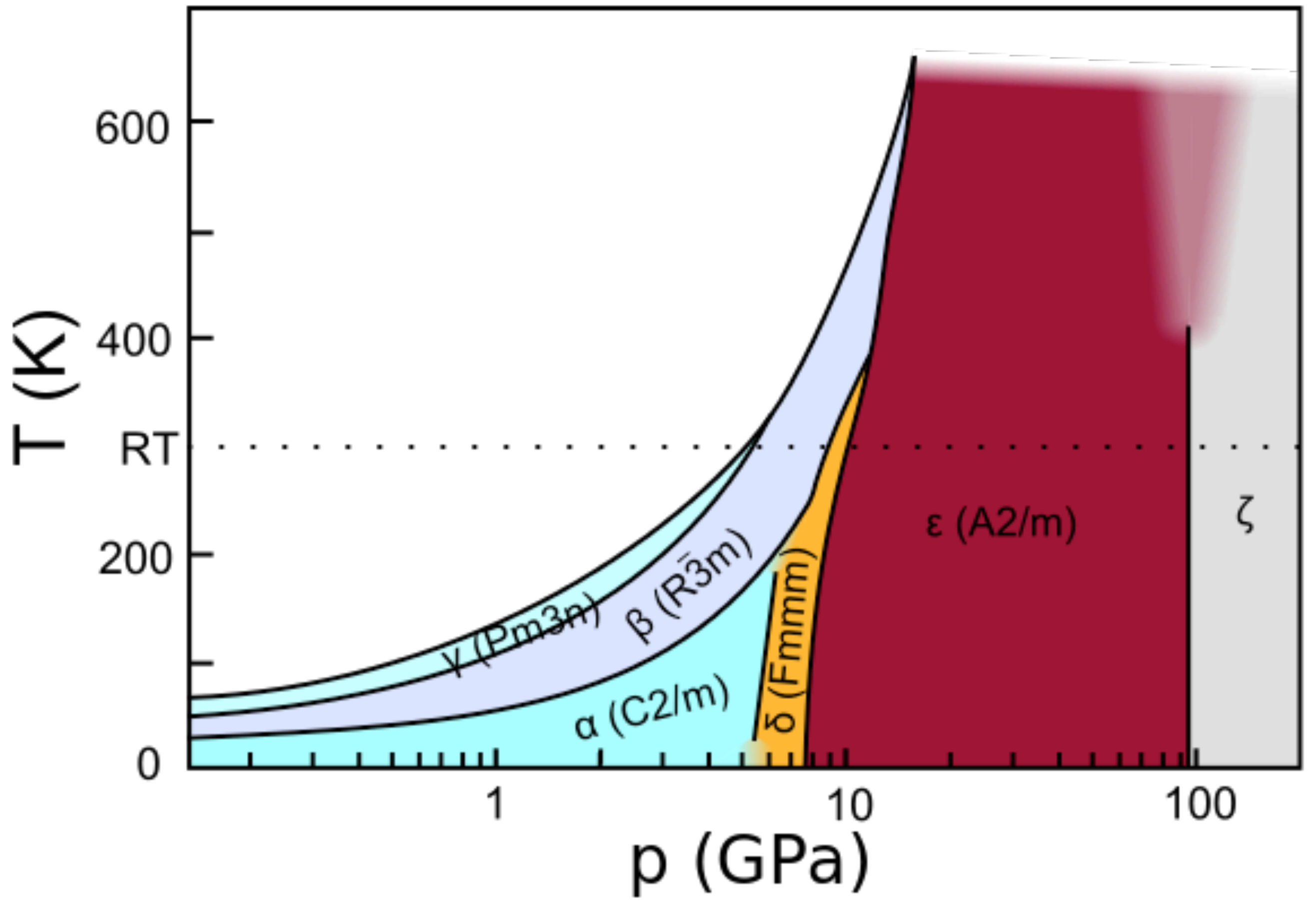






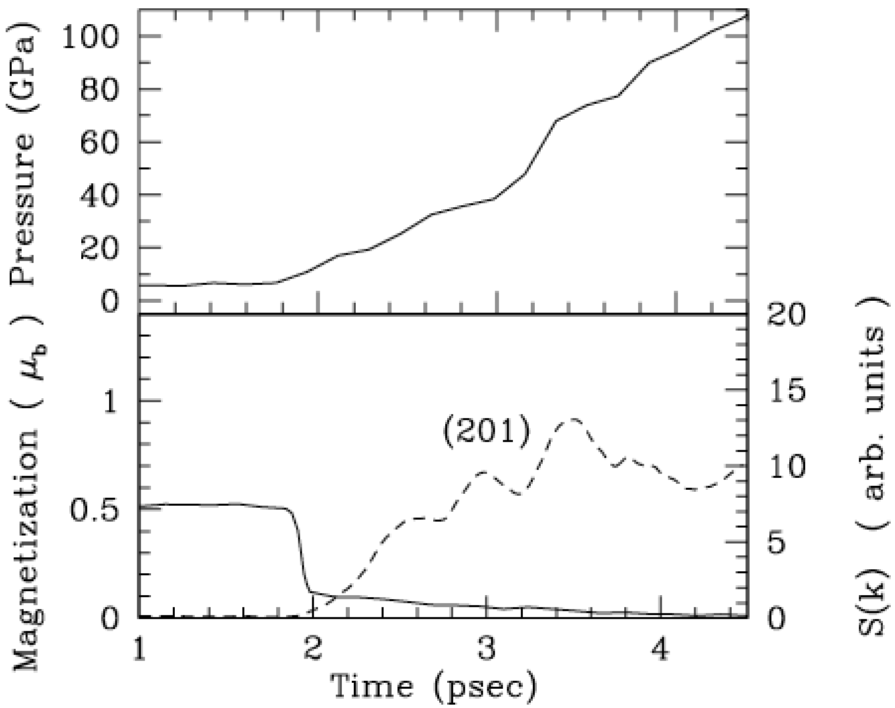
Oxygen phase diagram
Where does magnetism disappear?

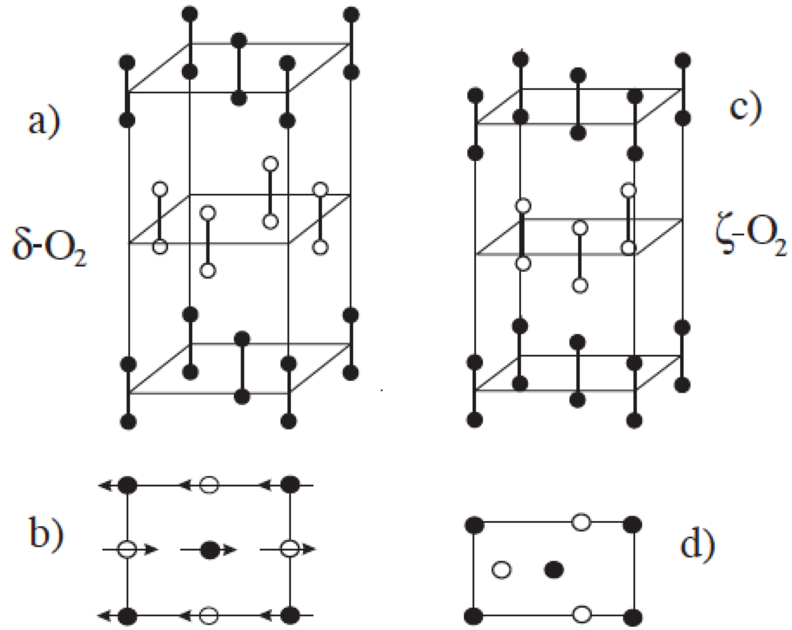
Yu.A. Freiman and H.J. Jodl, Physics Reports **401**, 1-228 (2004)



Magnetic collapse in Oxygen
DFT molecular dynamics

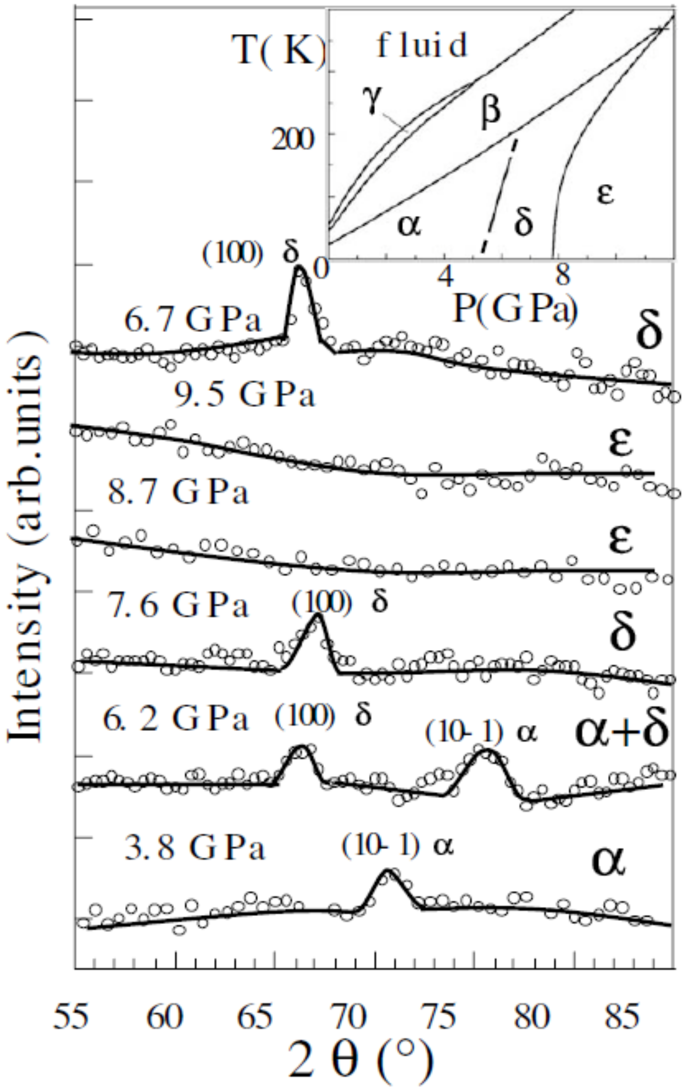
S. Serra et al, Phys. Rev. Lett. **80** , 5160 (1998)





Neutron Diffraction Exps

Goncharenko, Phys. Rev. Lett, **94** 205701, (2005)



Disappearance of the antiferromagnetic long range correlations at δ-ε transition.

Magnetic collapse

However:

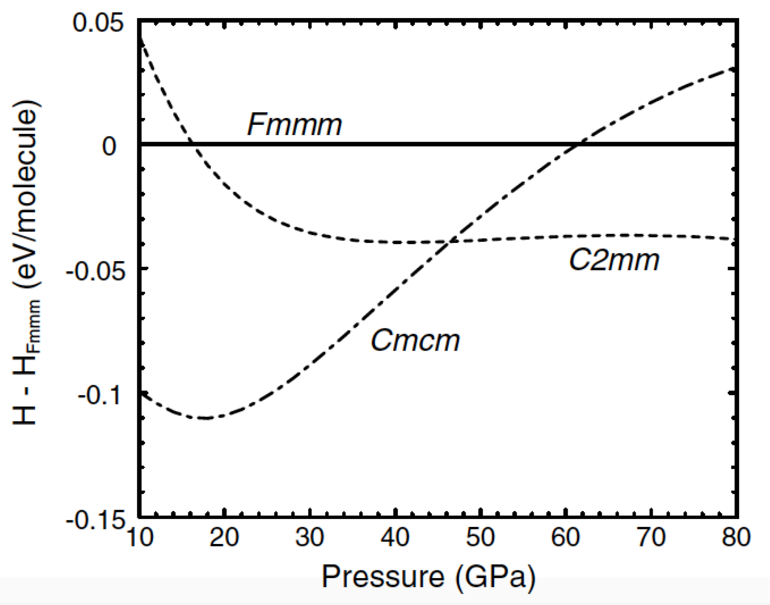
+ No local information (spin state of molecule)
+ Other types of long-range order?
+ Spin disorder?

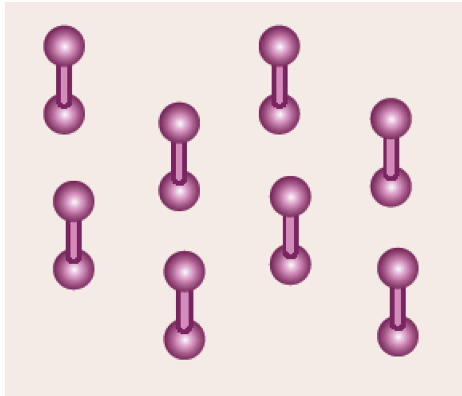
More DFT
Nonmagnetic O_2 structures

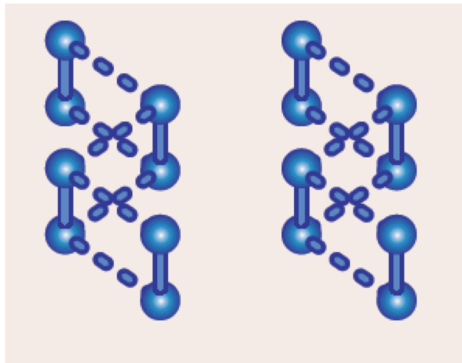
VOLUME 88, NUMBER 20 PHYSICAL REVIEW LETTERS 20 MAY 2002

Low-Energy Linear Structures in Dense Oxygen: Implications for the ϵ Phase

J. B. Neaton[1] and N. W. Ashcroft[2,3]
[1]*Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854-8019*
[2]*Laboratory of Atomic and Solid State Physics and Cornell Center for Materials Research, Cornell University, Ithaca, New York 14853-2501*
[3]*Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge, CB3-0HE, United Kingdom*
(Received 25 January 2002; published 3 May 2002)







ε-O_2: the structure!
molecular clusters 4 x O_2

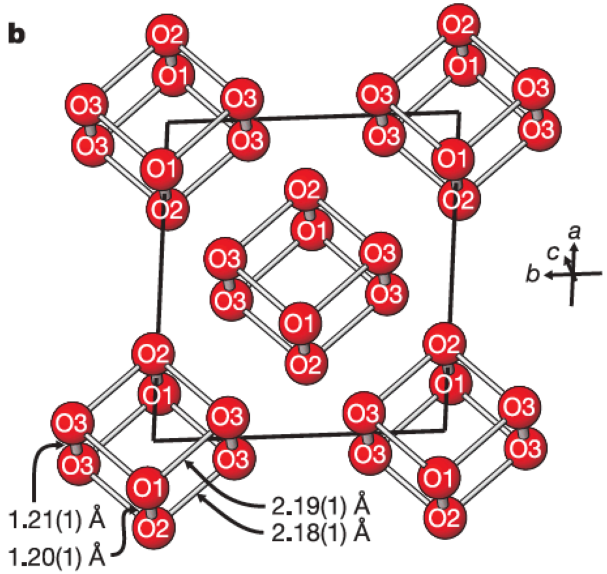
Vol 443|14 September 2006|doi:10.1038/nature05174 nature

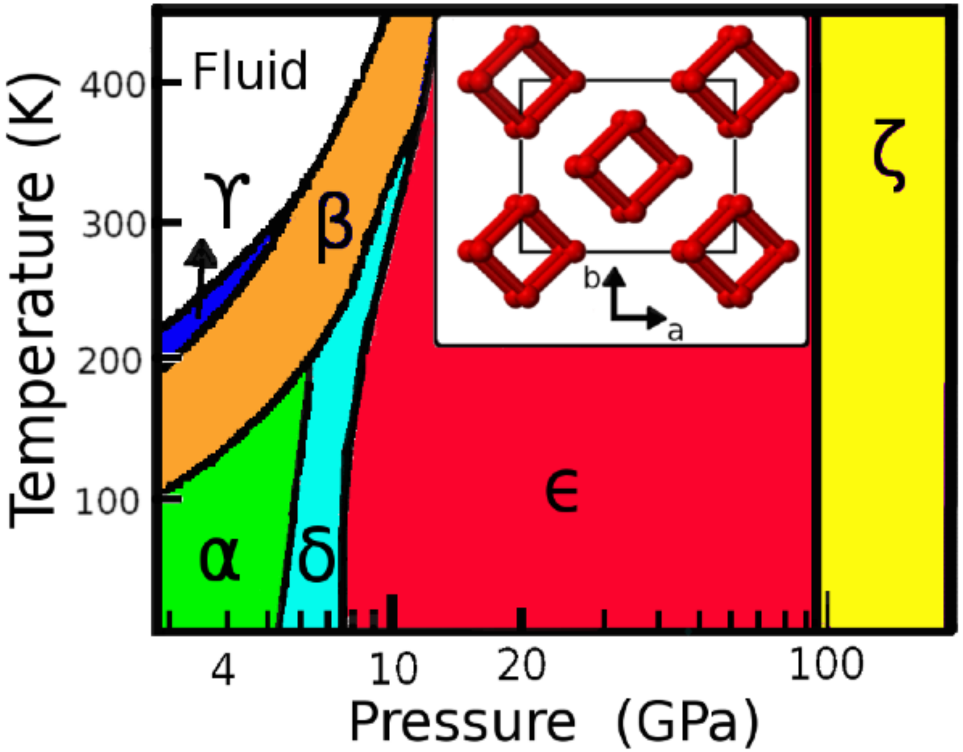
LETTERS

L. Lundegaard et al, Nature 2006

Observation of an O_8 molecular lattice in the ε phase of solid oxygen

Lars F. Lundegaard[1], Gunnar Weck[2], Malcolm I. McMahon[1], Serge Desgreniers[3] & Paul Loubeyre[2]





More DFT
Failure to reproduce correct structure

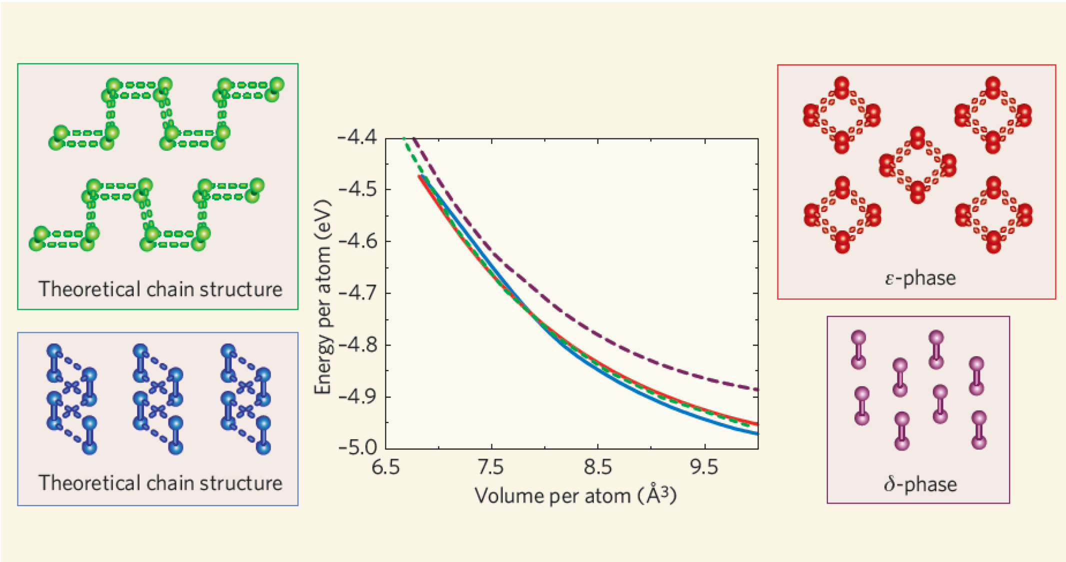
NATURE|Vol 443|14 September 2006

CRYSTALLOGRAPHY

Solid oxygen takes shape

Burkhard Militzer and Russell J. Hemley

Oxygen crystallizes into a sequence of structures, starting as an insulator at low pressure and becoming a superconductor at high pressure. The elusive structure of an intermediate phase has now been determined.

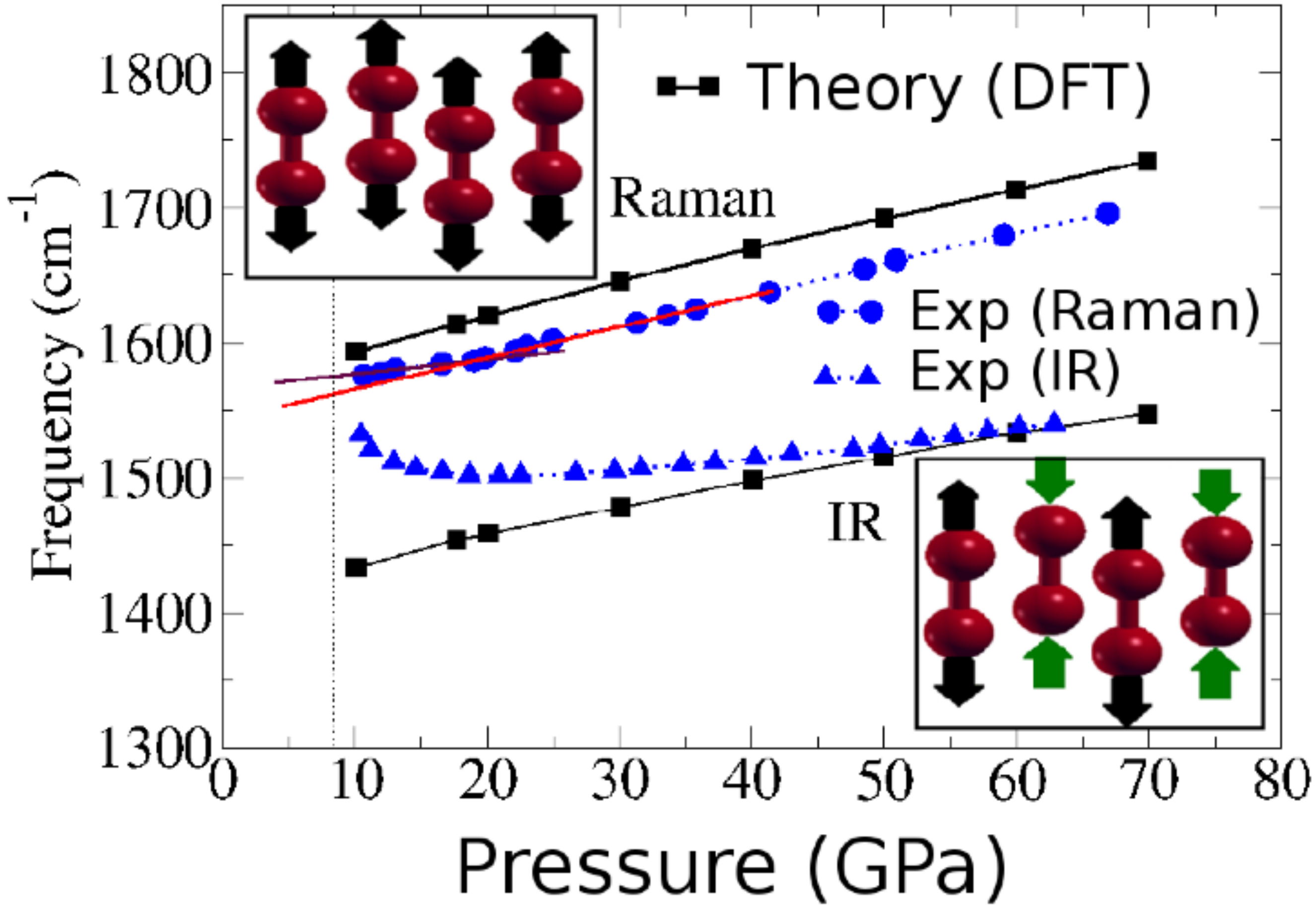


"…However, [DFT] calculations fail to show that the $(O_2)_4$ structure has the lowest energy, which is probably why previous theoretical attempts to predict the correct structure for epsilon-oxygen were unsuccessful."

!!!!

More problems

Vibrational frequencies



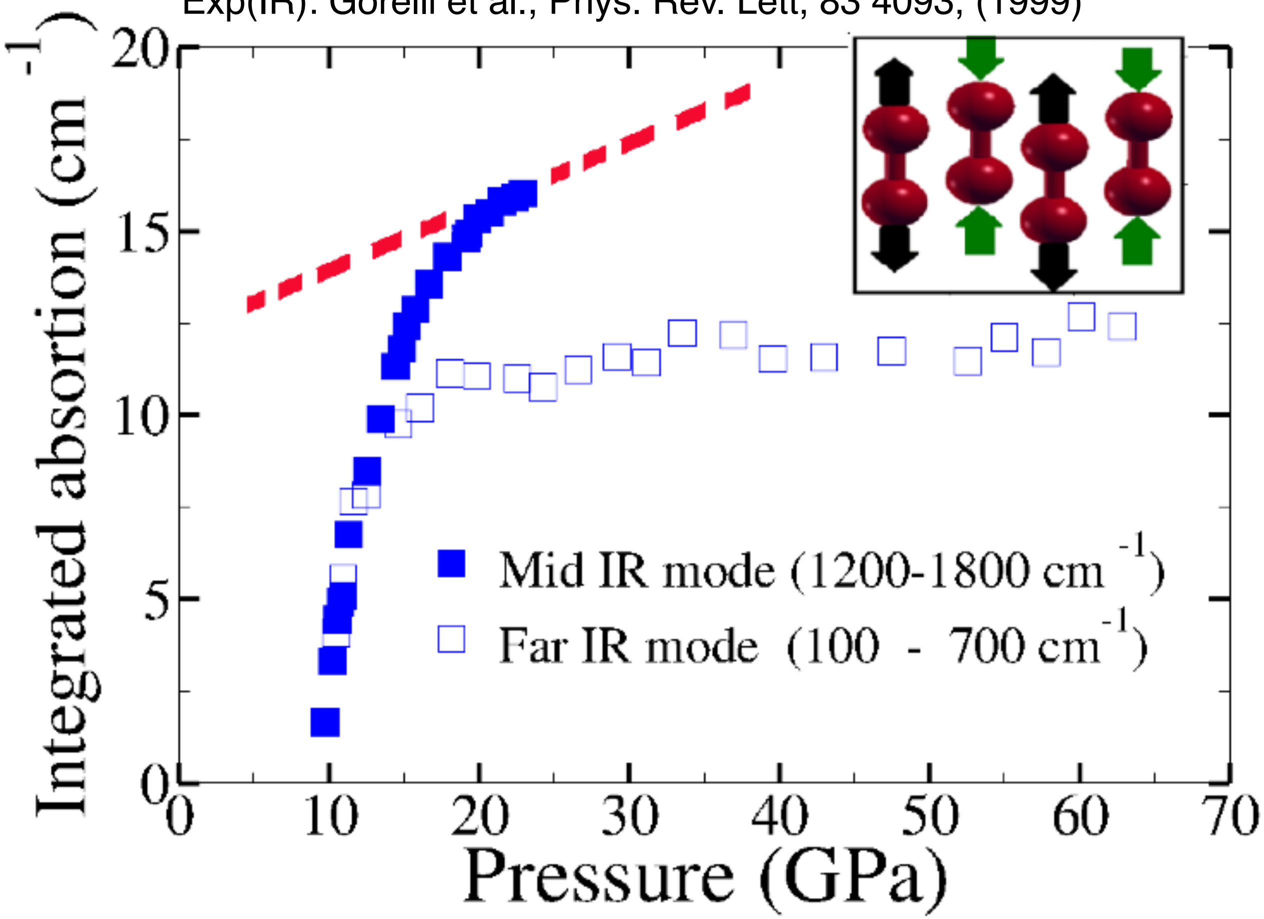
Theory:
Pham et al. Solid State Commun, 149 160, (2009)

Exp(Raman):
Akahama et al., Phys. Rev. B, 54 R15602, (1996),

Exp(IR):
Gorelli et al., Phys. Rev. Lett, 83 4093, (1999)

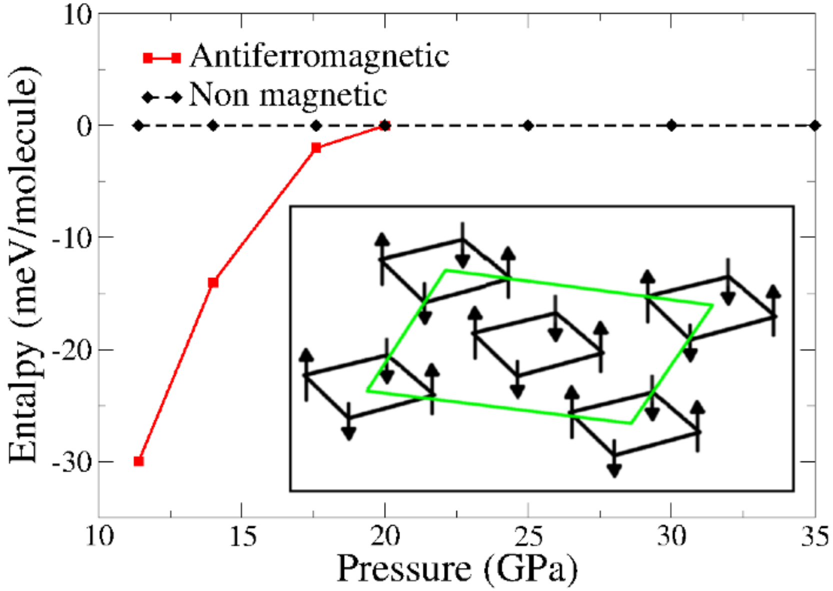
More problems (2)
Infrared activity

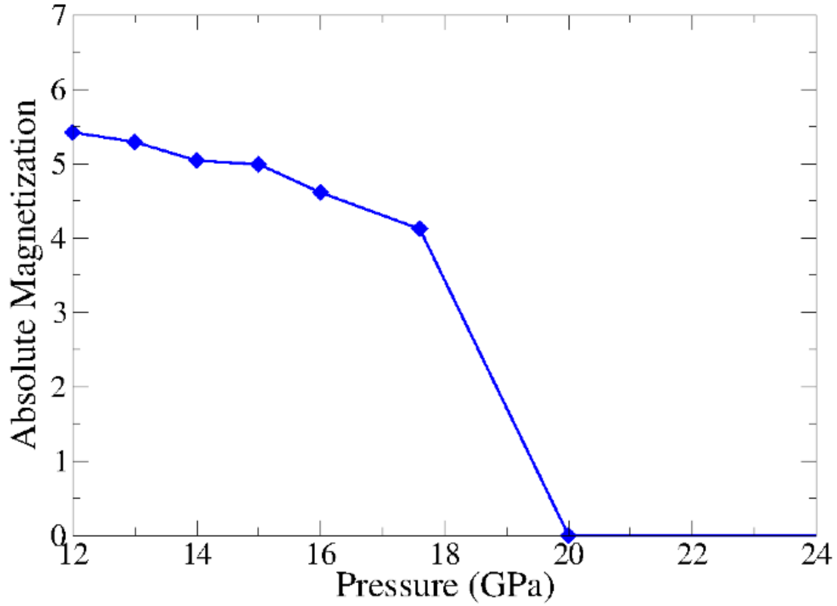
Exp(IR): Gorelli et al., Phys. Rev. Lett, 83 4093, (1999)



GGA+U
ε-O_2 still magnetic!

Y. Crespo, M. Fabrizio, S. Scandolo, E. Tosatti
PNAS **111**, 10427 (2014)

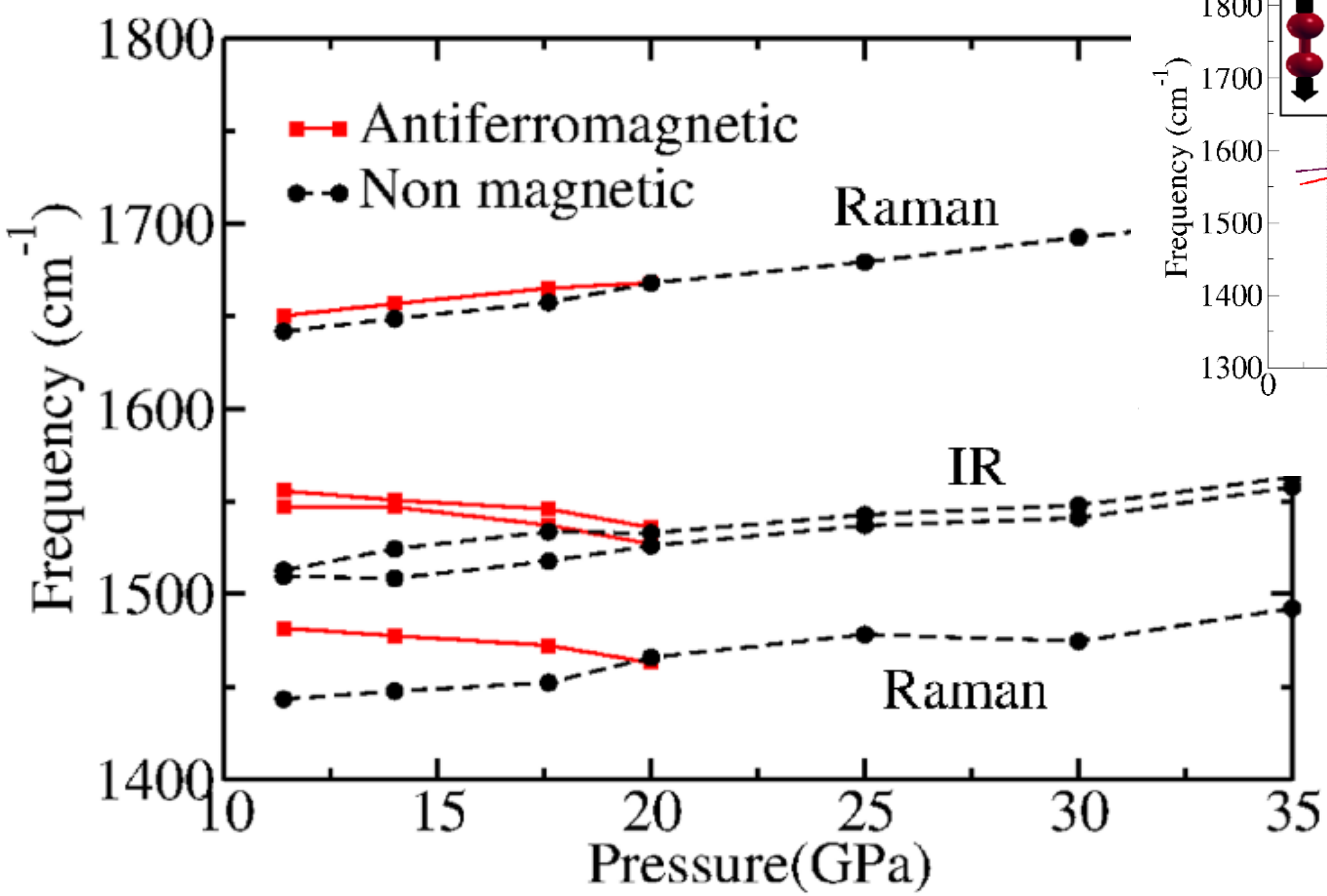


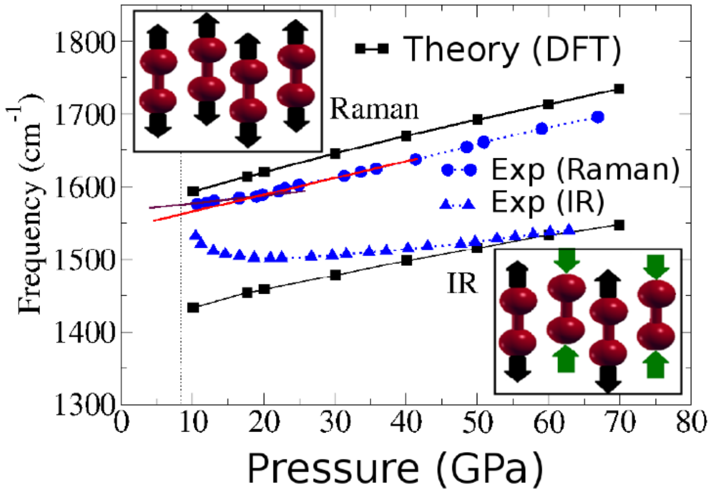


GGA+U: finds antiferromagnetic S=1 ground state of ε-phase between 8-20 GPa, non-magnetic state above 20 GPa!

Magnetism in ε-O_2
Vibrational frequencies

Y. Crespo, M. Fabrizio, S. Scandolo, E. Tosatti
PNAS **111**, 10427 (2014)

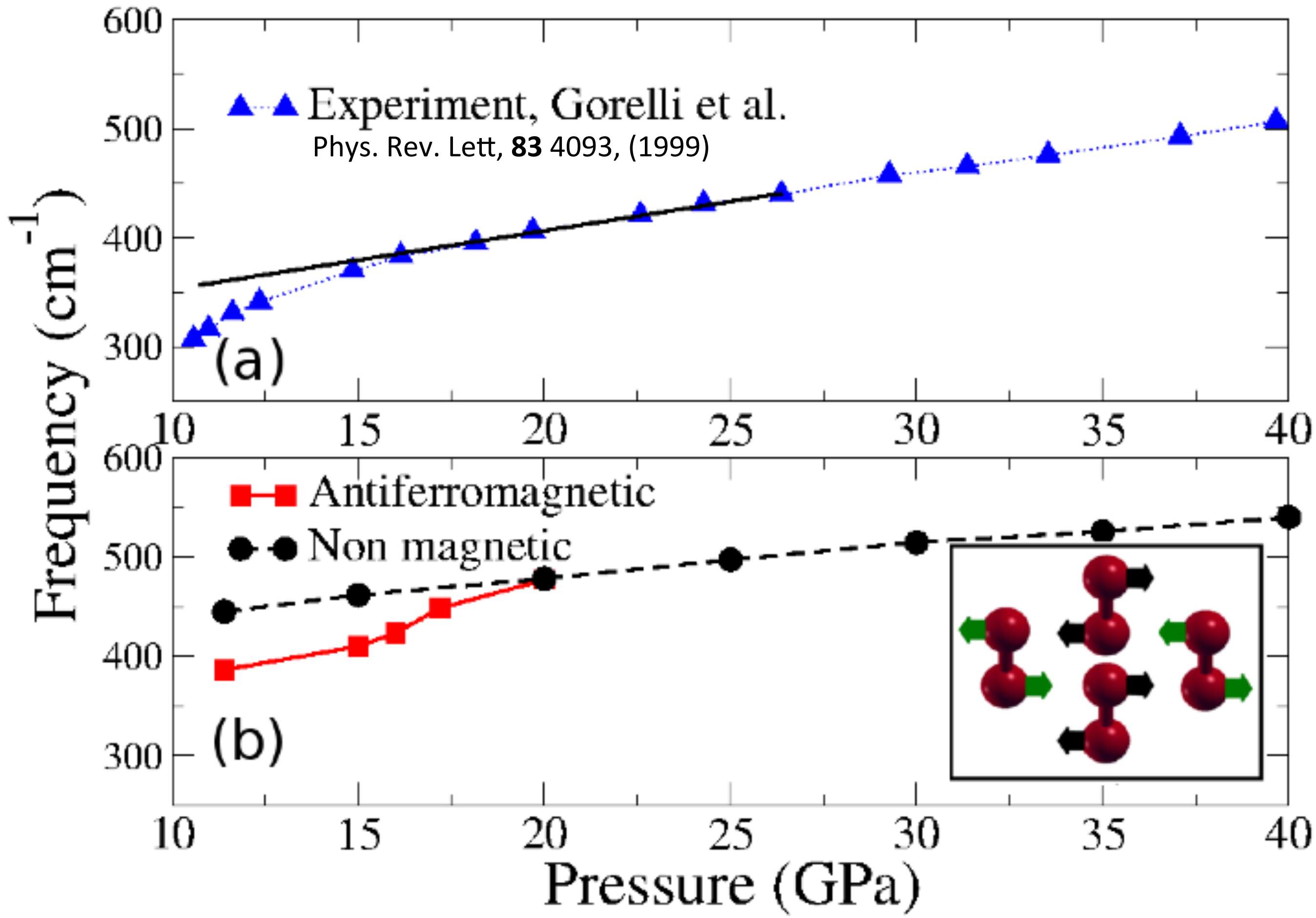




Anomalous pressure dependence of vibrational frequencies due to magnetic transition

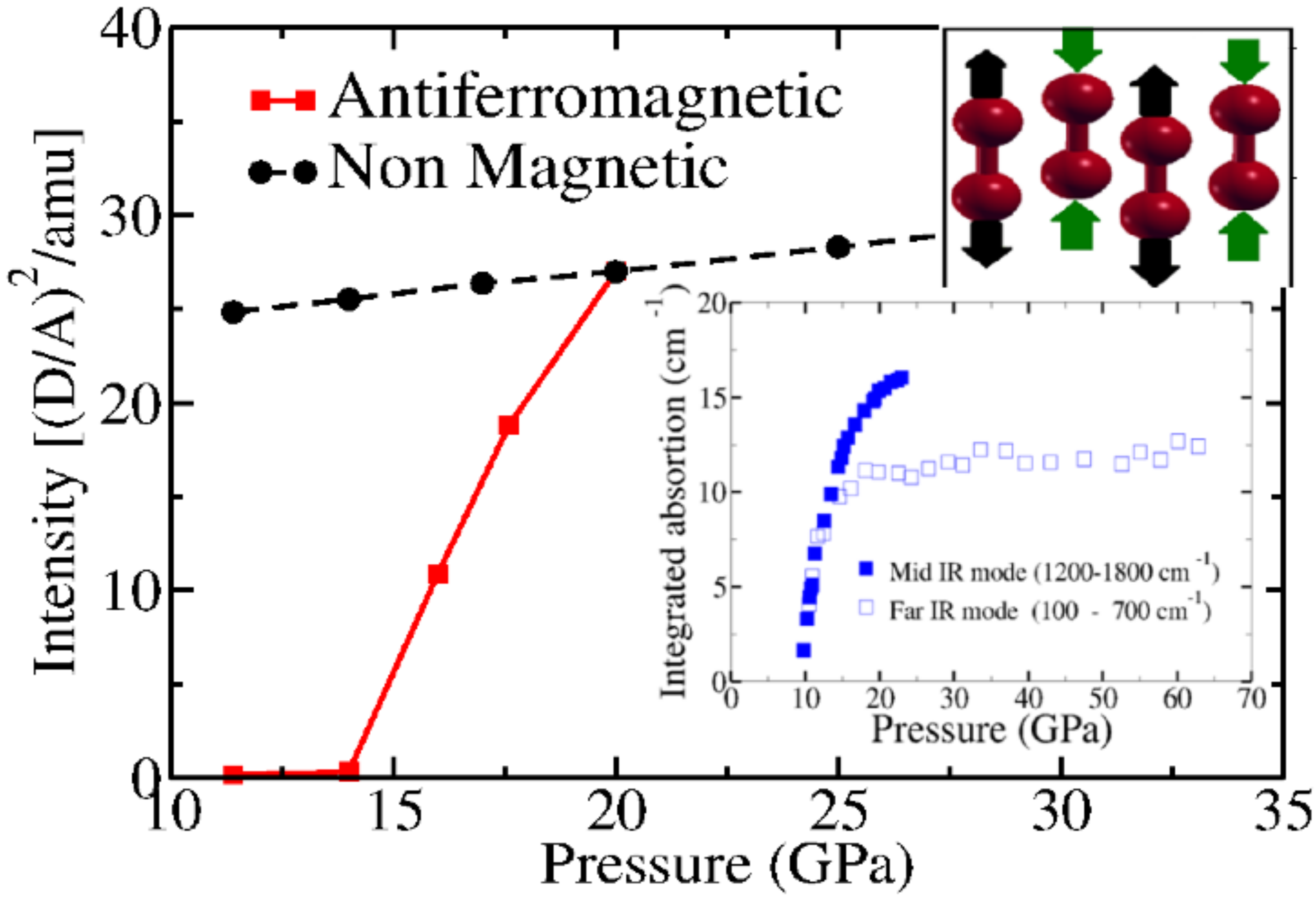
Magnetism in ε-O_2
Bending frequencies

Y. Crespo, M. Fabrizio, S. Scandolo, E. Tosatti
PNAS **111**, 10427 (2014)



Magnetism in ε-O_2
Infrared activity

Y. Crespo, M. Fabrizio, S. Scandolo, E. Tosatti
PNAS **111**, 10427 (2014)



Magnetism in ε-O_2
Infrared activity

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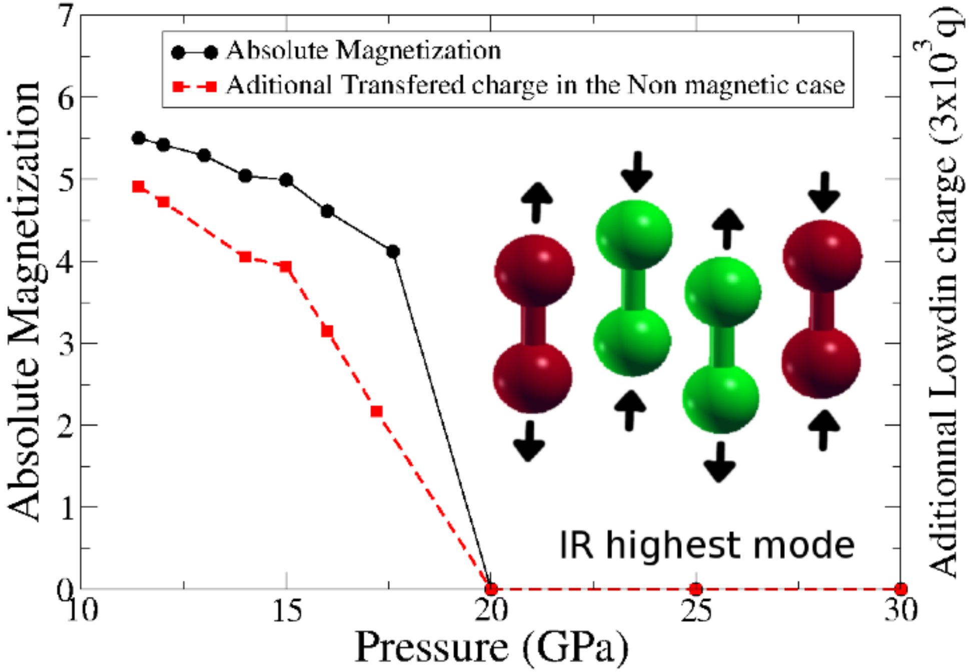
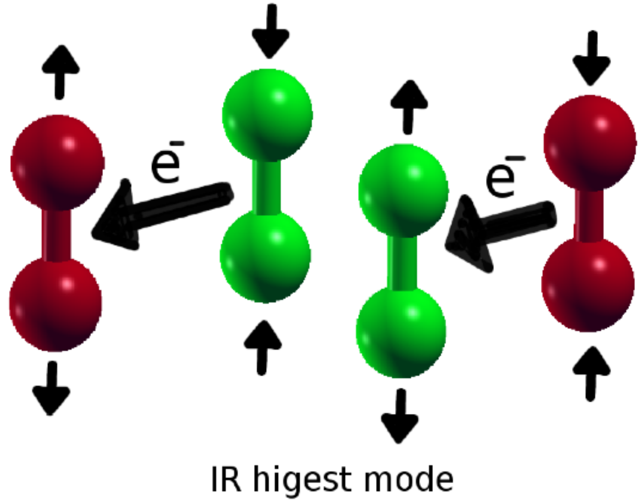
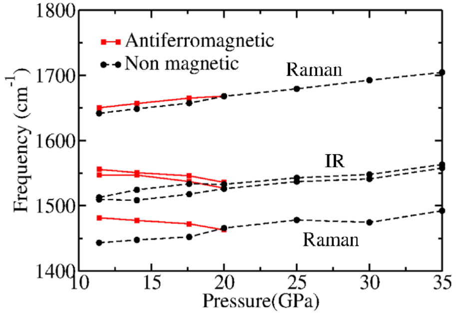
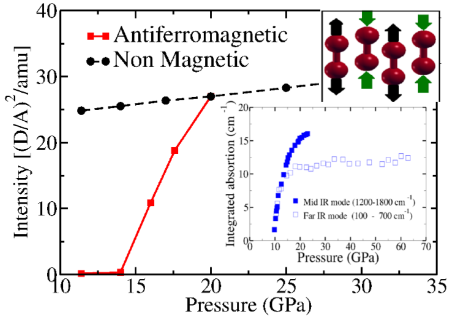
PNAS **111**, 10427 (2014)



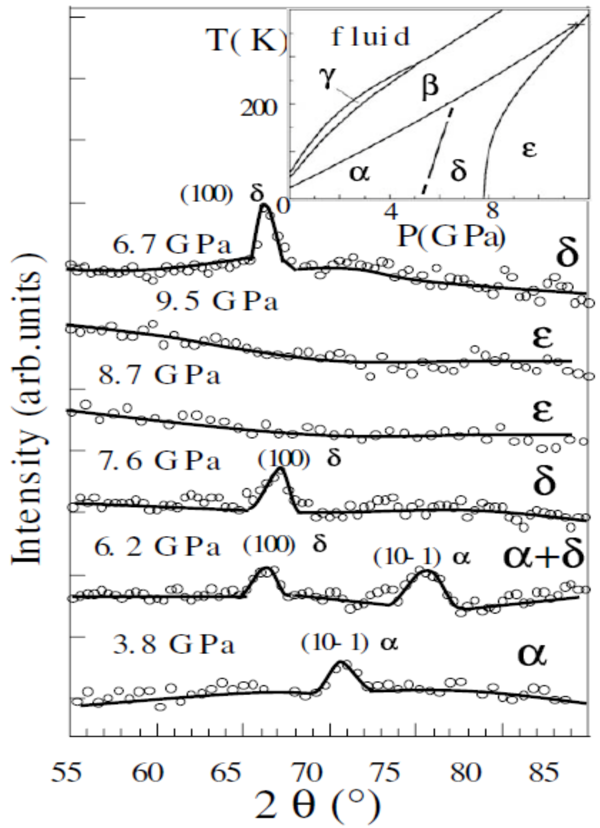


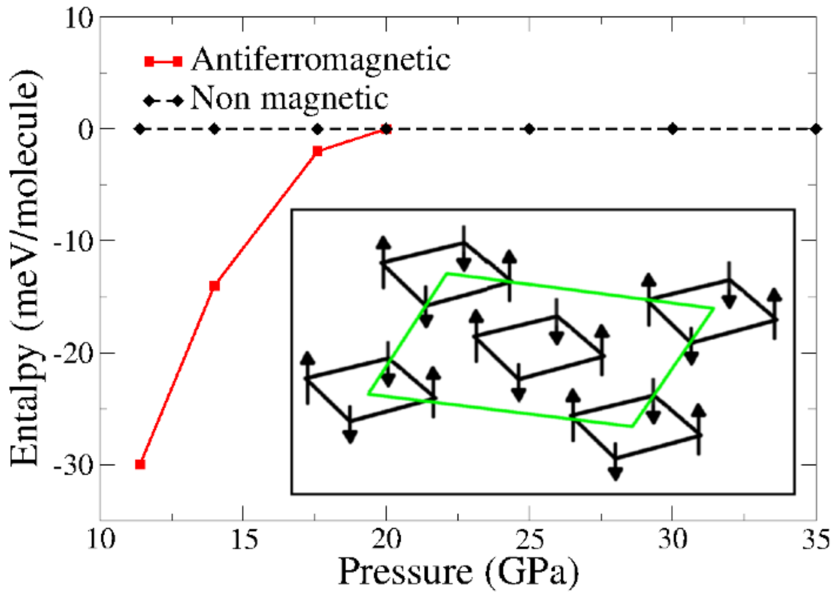




Magnetism in ε-O_2
Long range order?

Y. Crespo, M. Fabrizio, S. Scandolo, E. Tosatti
PNAS **111**, 10427 (2014)





Problem:
DFT antiferromagnetic state is not consistent with absence of long-range order in neutron diffraction experiments

Magnetism in ε-O_2
A collective S=1 singlet phase?

Two competing ground states:

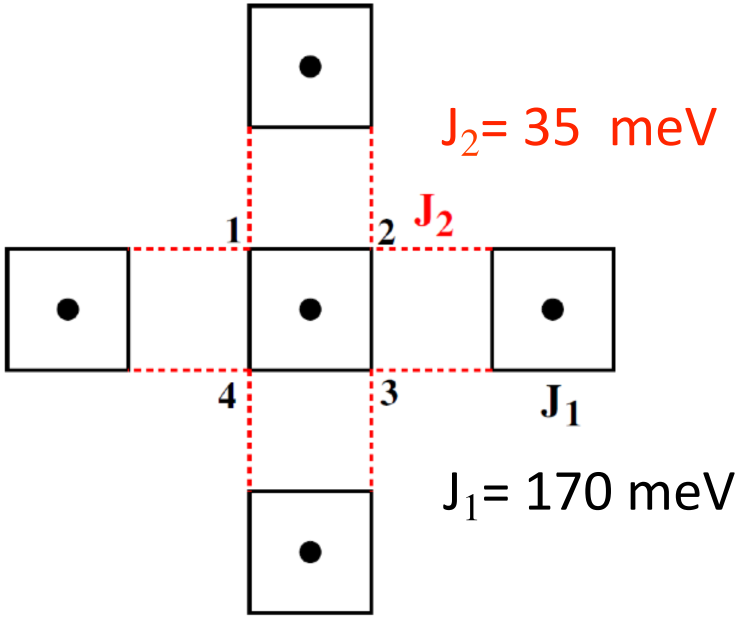
1. Antiferromagnetic Néel 'classical" configuration (DFT result)

   $E(AF) = -J_1-J_2 \sim -0.2$ eV

2. Nonmagnetic "singlet" as collection of independent $(O_2)_4$ singlet ground states

   $E(singlet) = -3/2\ J_1 \sim -0.25$ eV

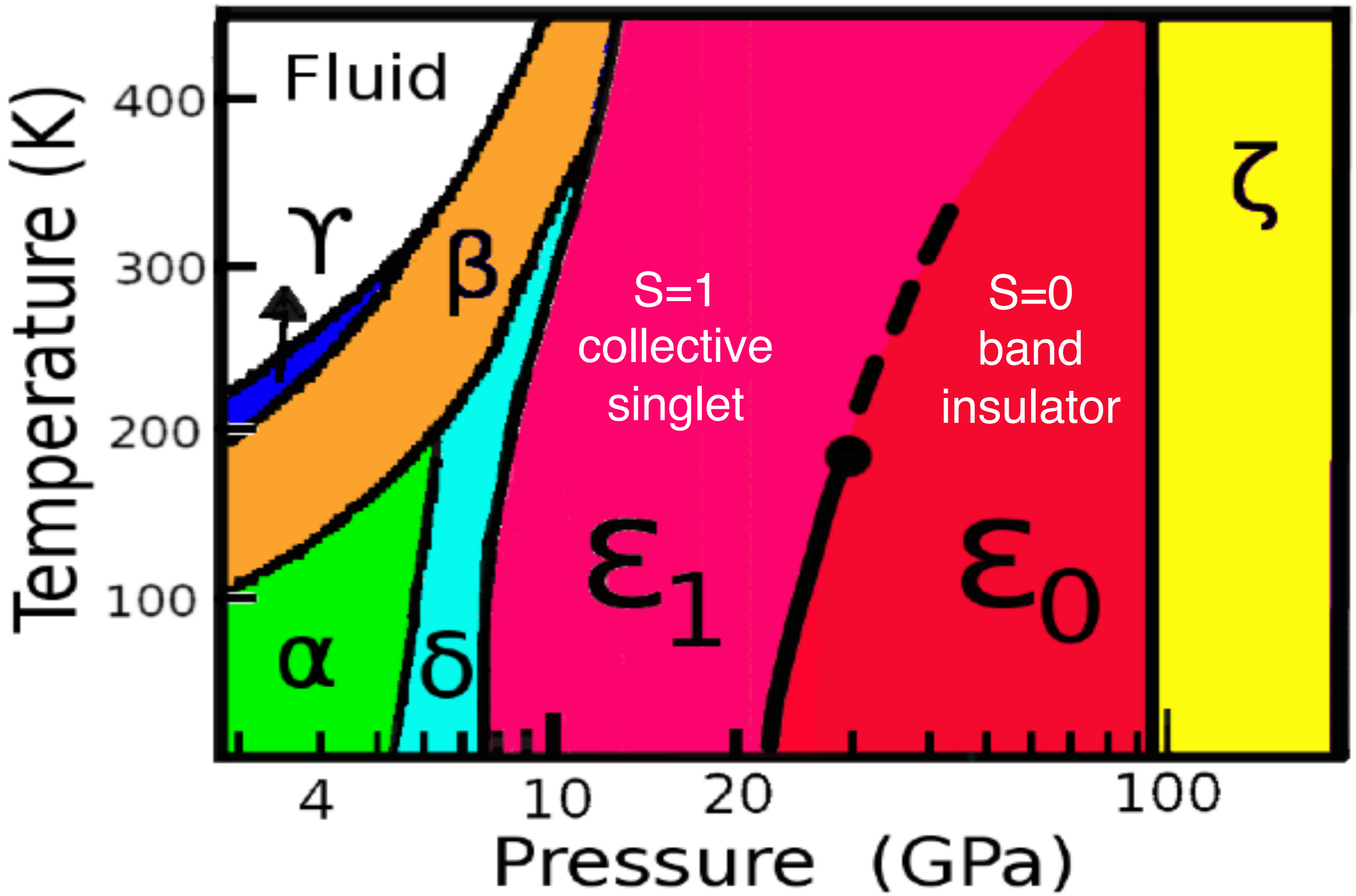
   + quantum fluctuations
   => Spin liquid ?!



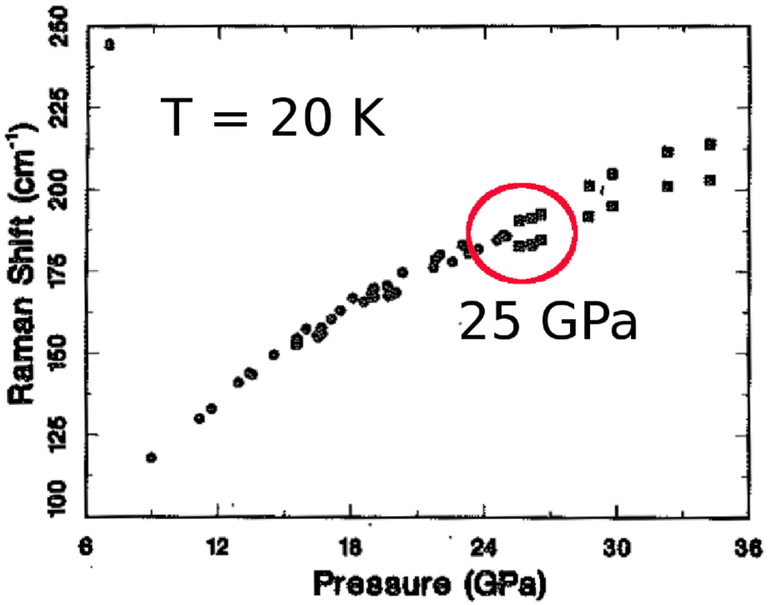
→ Consistent with absence of long-range order in neutron diffraction experiments

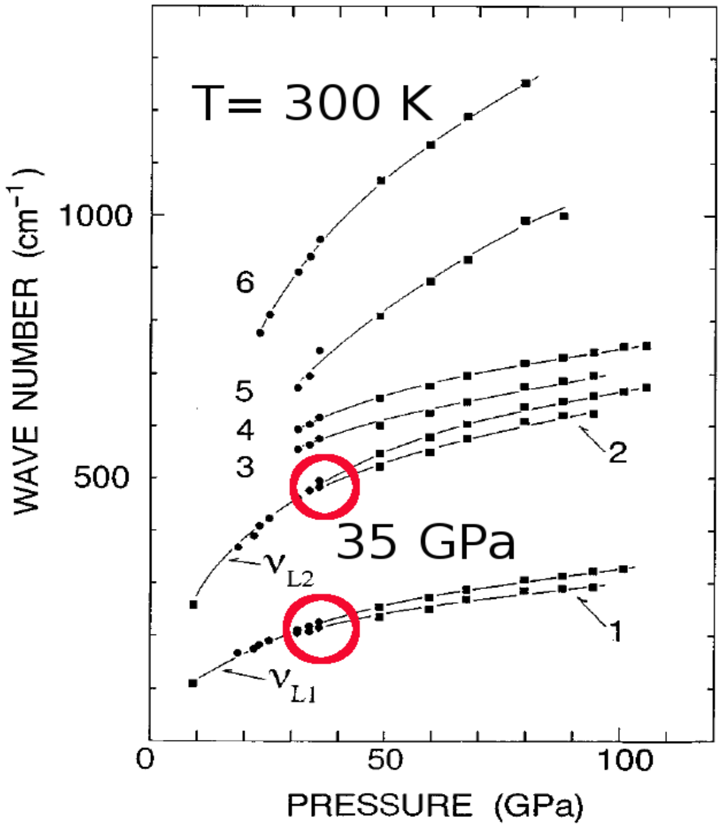
Proposed Oxygen phase diagram

Two "epsilon" phases



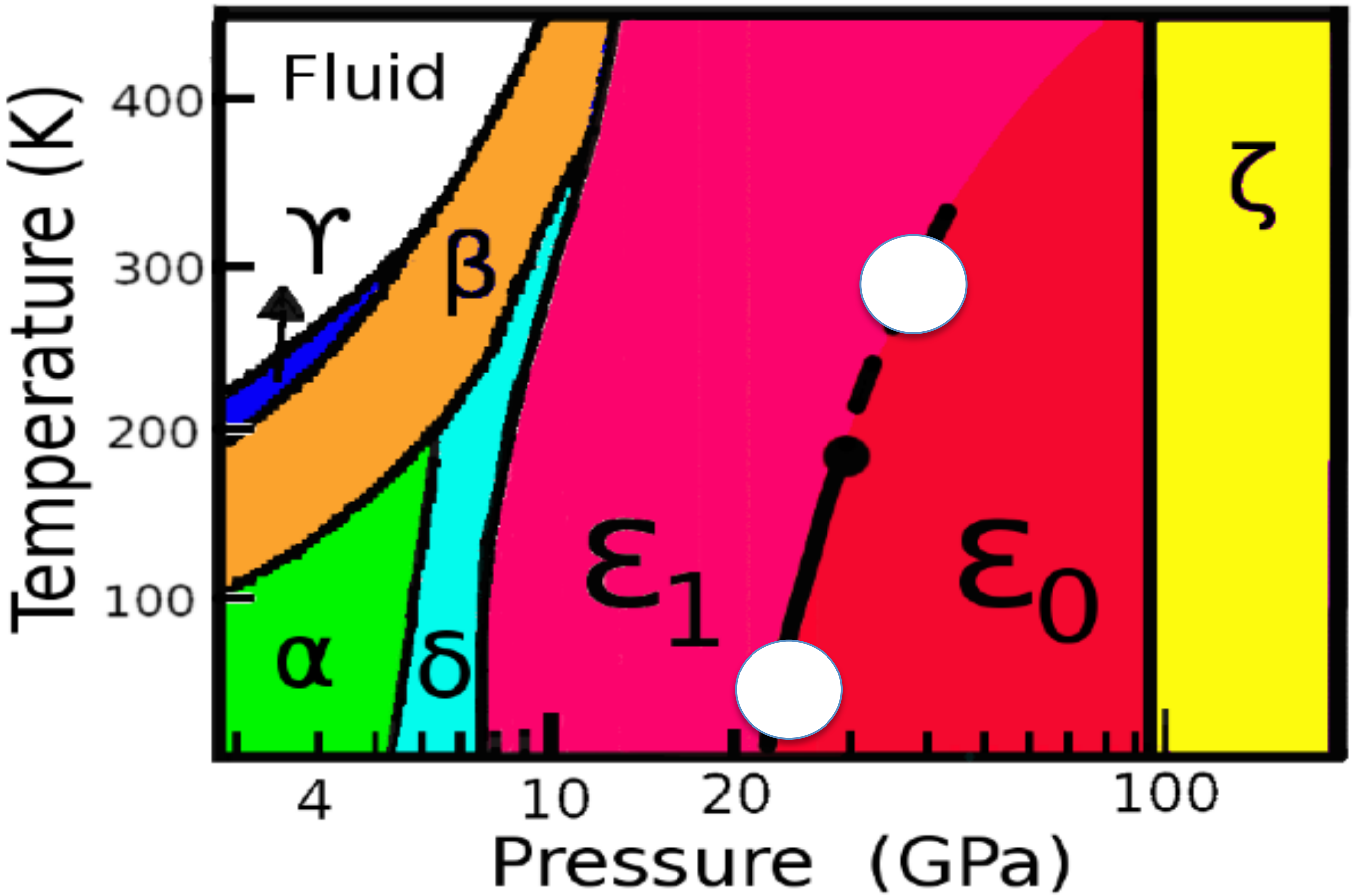
Proposed Oxygen phase diagram
A critical point?





Evidence from vibrational spectroscopy:
+ 1st order transition at low T (25 GPa)
+ smooth crossover at room T (35 GPa)

Conclusion


Fluid
γ
β
α
δ
ε1
ε0
ζ
400
300
200
100
Temperature (K)
4
10
20
100
Pressure (GPa)