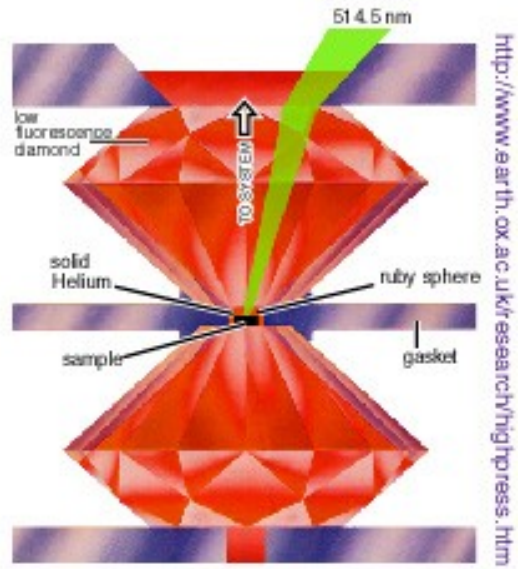
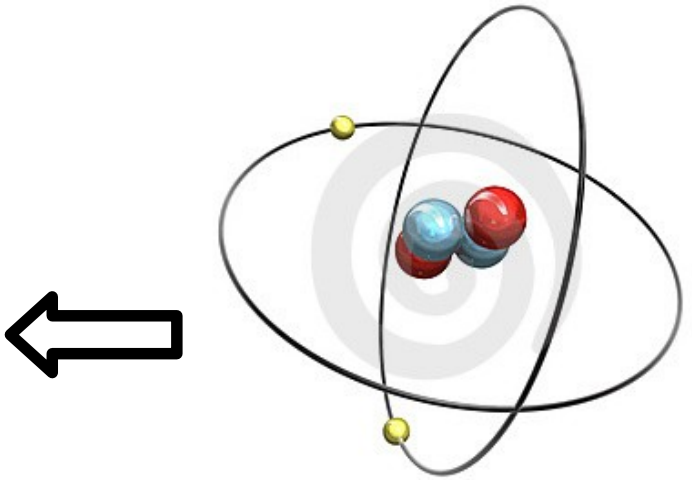
THEORETICAL STUDY OF RARE GASES (RG) AND RG-X (X=He,H_2) MIXTURES UNDER PRESSURE



The Diamond-Anvil Cell (DAC). Raman spectra are excited with 514.5 nm laser light in 135° scattering configuration.



Claudio Cazorla

University College London, UK

Department of Earth Sciences

RGs and mixtures : Outline

1. Interest and Properties

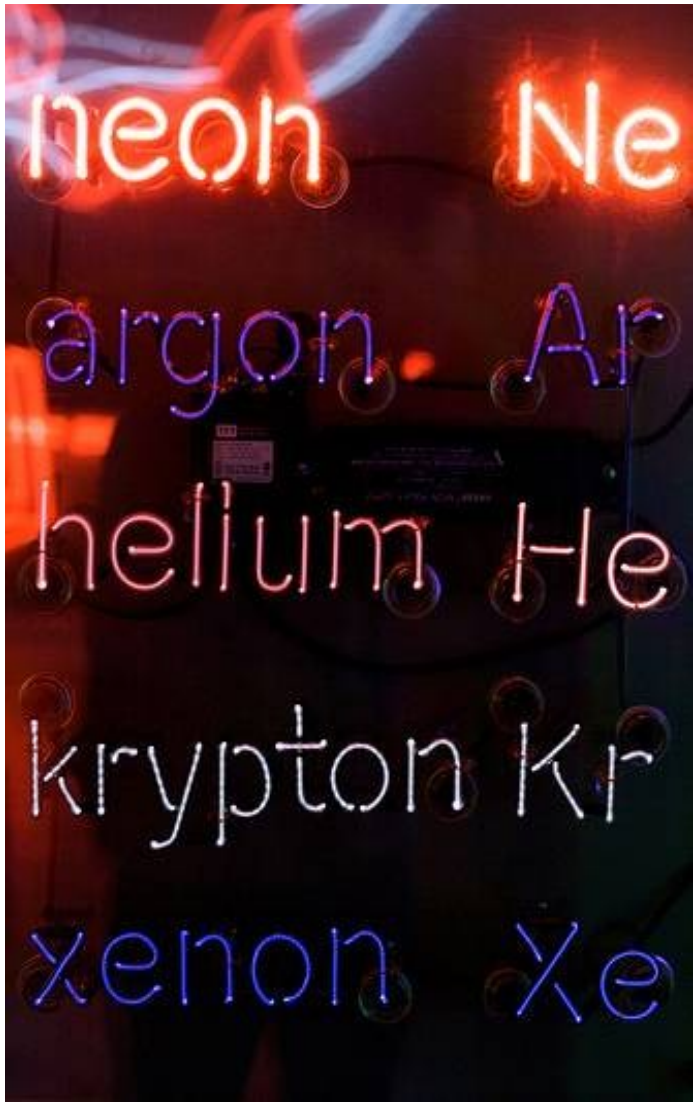
2. Theoretical Methods: brief description

3. ^{4}He up to 60 GPa

4. RG$(He)_2$ mixtures under pressure

5. Ar$(H_2)_2$ compound under pressure

RGs and mixtures : Interest



*** ~25 % of the elements in our galaxy are RGs**

- discharge lamps
- air/sea navigation lights

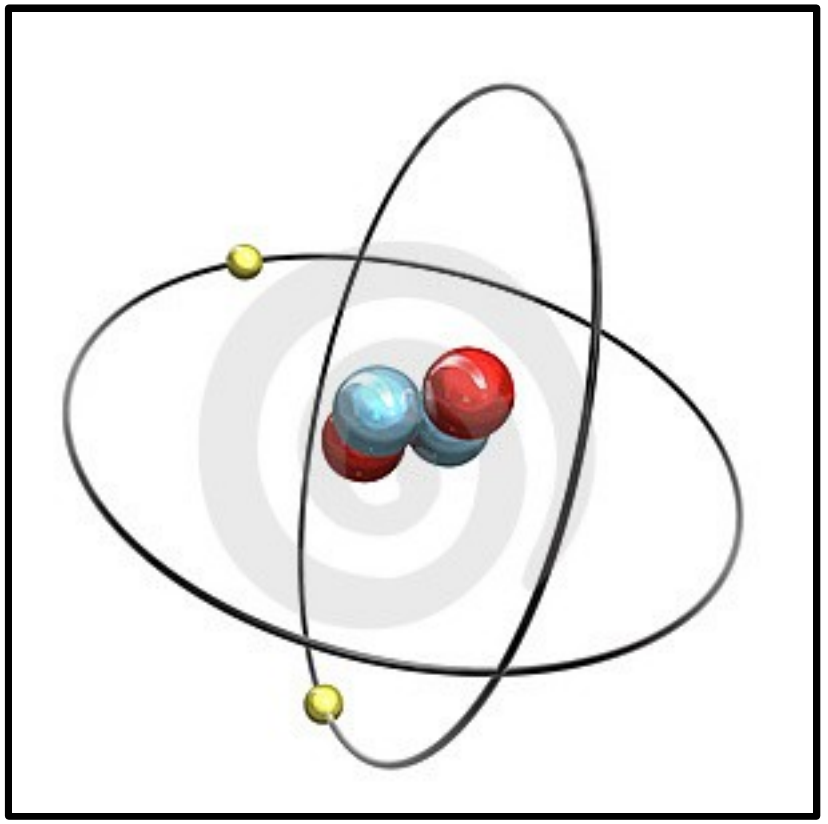
- electric bulbs

- gas-cooled atomic reactors
- research experiments
- He-O to treat asthma

- luminous tubes
- industrial processes

- bubble chamber for quarks detection

RGs and mixtures : Properties

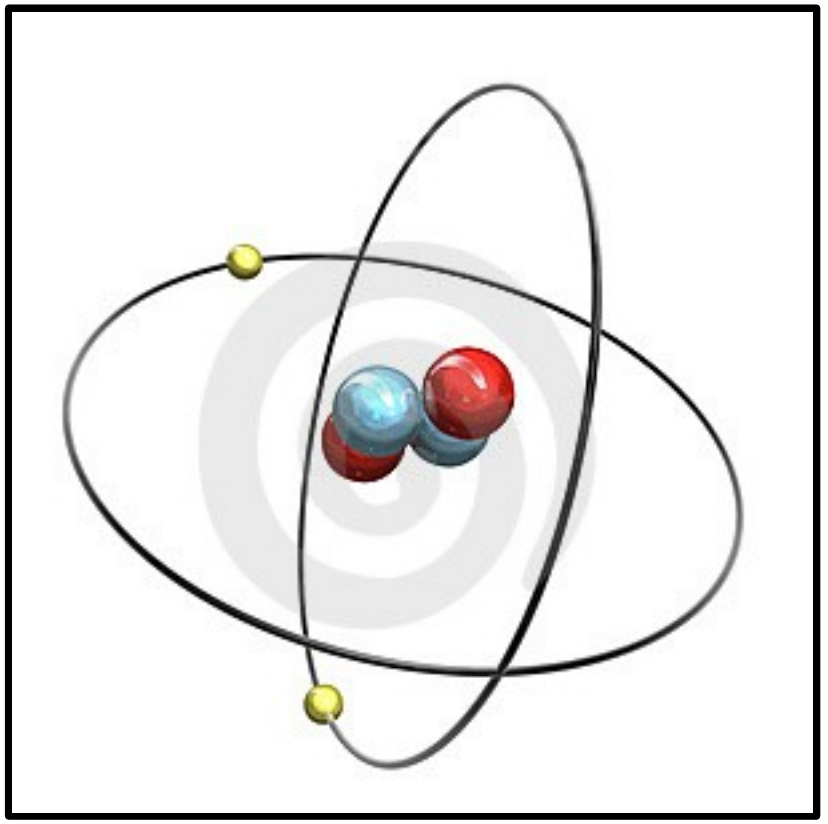


At normal conditions RGs...

- monoatomic gases
- closed-shell electronic structure
- lack of chemical reactivity
- light RGs are very compressible
- are insulators
- interatomic interactions are weak

...seem simple systems

RGs and mixtures : Properties

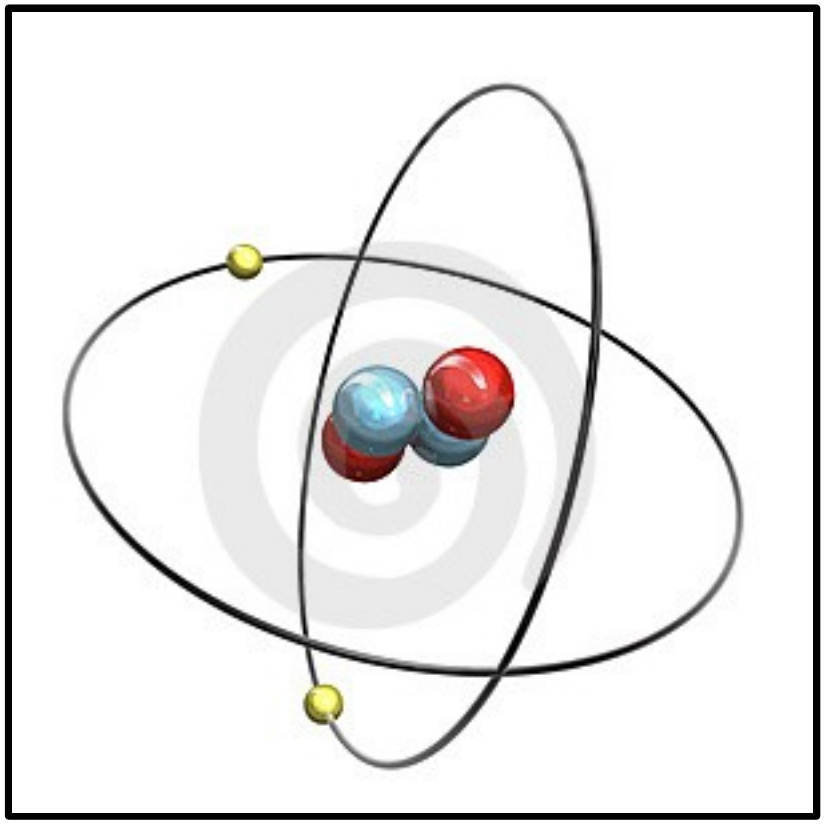


But at ultralow temperature RGs...

- at T=0 ^{4}He is a liquid
- liquid ^{4}He is superfluid
- BEC is observed
- solid ^{4}He (probably) is supersolid
- are anharmonic

...quantum effects become macroscopic!

RGs and mixtures : Properties



and at ultrahigh pressure RGs...

- may turn reactive
- continue being compressible
- crystallize in complex structures
- can conduct electricity

...undergo dramatic phase transitions!

RGs and mixtures: Methods

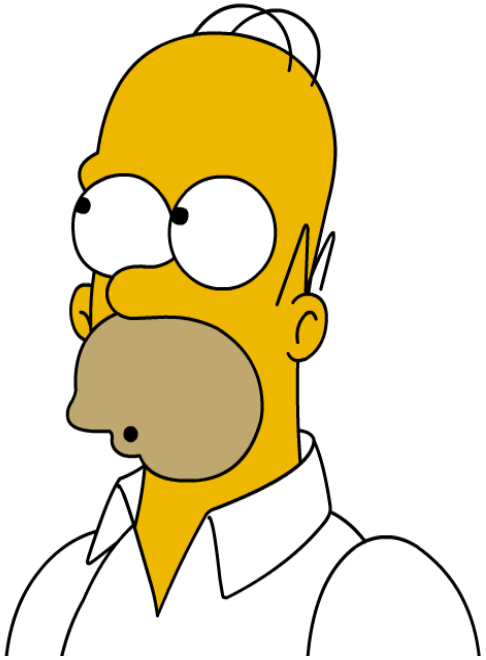
At normal P-T conditions, RG's can be simulated with reliability using **semi-empirical radial pair potentials** (SPP) and **classical molecular dynamics** (MD)

$$V_{LJ}(R) = 4\epsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right]$$

$$\vec{F} = m\vec{a}$$

$$Z(V,T) = \frac{1}{N!\,\Lambda^{3N}} \int e^{-\beta U(\vec{R})}\, d\vec{R}$$

RGs and mixtures: Methods



But at low T and P...

- **Zero-point motion** (ZP)
- statistical **quantum effects** (BEC, superfluidity,...)
- large **anharmonicity**
- **Van der Waals forces** are very important

MD is no longer valid, quantum approaches are required...
Diffusion Monte Carlo (DMC)
Path Integral Monte Carlo (PIMC)

RGs and mixtures: Methods

And at high P and T...

- **Zero-point motion** (ZP) still important
- **anharmonicity** still present
- changes in **electronic structure**
- **Van der Waals forces** still important

SPP no longer valid, electronic structure methods required ...
Density Functional Theory (DFT)
Quasi-harmonic approximation (QH)

RGs and mixtures: Methods

Diffusion Monte Carlo

$$\frac{\partial \Psi}{\partial t} = -i\left(\hat{H} - E_0\right)\Psi \qquad \hat{H} = \hat{T} + \hat{V}$$

$$\Psi(t) = \mathrm{e}^{-i\left(\hat{H} - E_0\right)t}\,\Psi(0)$$

Time-dependent Schrödinger equation

RGs and mixtures: Methods

Diffusion Monte Carlo

$$\Psi(0) = \sum c_n \phi_n \qquad H\phi_n = \epsilon_n \phi_n$$

$$\Psi(t) = \sum \mathrm{e}^{-i(\epsilon_n - E_0)t} c_n \phi_n$$

DMC "trick" $\quad it \rightarrow \tau$

RGs and mixtures: Methods

Diffusion Monte Carlo

$$\Psi(\tau) = \sum e^{-(\epsilon_n - E_0)\tau} c_n \phi_n$$

$$\lim_{\tau \to \infty} \Psi(\tau) \to c_0 \phi_0$$

DMC is an exact Ground-State Method

RGs and mixtures: Methods

Diffusion Monte Carlo

$$G(\vec{R}_1 \rightarrow \vec{R}_2, \tau) = \langle \vec{R}_1 | e^{-(\hat{H} - E_0)\tau} | \vec{R}_2 \rangle$$

$$G(\vec{R}_1 \rightarrow \vec{R}_2, \Delta\tau) \approx \int \langle \vec{R}_1 | e^{-\hat{T}\frac{\Delta\tau}{2}} | \vec{R}_3 \rangle \langle \vec{R}_3 | e^{-\hat{V}\Delta\tau} | \vec{R}_4 \rangle \langle \vec{R}_4 | e^{-\hat{T}\frac{\Delta\tau}{2}} | \vec{R}_2 \rangle d\vec{R}_3 d\vec{R}_4$$

Green's function short imaginary time approximation

RGs and mixtures: Methods

Density Functional Theory

$$E[n(r)] = \hat{T}_{ee} + \hat{V}_{Ie} + \hat{V}_{ee} + \hat{V}_{xc} + \hat{V}_{II}$$

$$V_{Ie}[n(r)] = -\sum_I Z_I \int \frac{n(\vec{r})}{|\vec{R}_I - \vec{r}|} d\vec{r}$$

$$V_{ee}[n(r)] = \frac{1}{2} \iint \frac{n(\vec{r}) n(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} d\vec{r}\, d\vec{r}\,'$$

$$V_{xc}[n(r)] = \int n(\vec{r}) U_{xc}[n(\vec{r})] d\vec{r}$$

RGs and mixtures: Methods

Density Functional Theory

$$E[n(r)] = \hat{T}_{ee} + \hat{V}_{Ie} + \hat{V}_{ee} + \hat{V}_{xc} + \hat{V}_{II}$$

$$n(r) = \sum_i c_i \psi_i^2(r)$$

$$min\ E[n(r)] = E[n_0(r)] = E_0$$

Kohn-Sham equations are solved self-iteratively until the minimum of the energy functional is reached

RGs and mixtures: ^{4}He

Low P approach = DMC with SPP
- ZP 
- Band structure 

High P approach = DFT (LDA/GGA)
- ZP 
- Band structure 

Mixed DMC and DFT approach in order to treat ions and electrons quantum mechanically

C. Cazorla and J. Boronat, J. Phys.:Cond. Matt. ***20****, 015223 (2008)*

RGs and mixtures: ^{4}He

$$E_0(V) = E_{DMC}^{Aziz\,II}(V) + \Delta E^{el}(\vec{R})$$

$$\Delta E^{el}(\vec{R}) = E[n(\vec{R})] - V^{AzizII}(\vec{R})$$

Electronic correlations are included via a 2nd order perturbation correction while ions are treated QM

C. Cazorla and J. Boronat, J. Phys.:Cond. Matt. ***20****, 015223 (2008)*

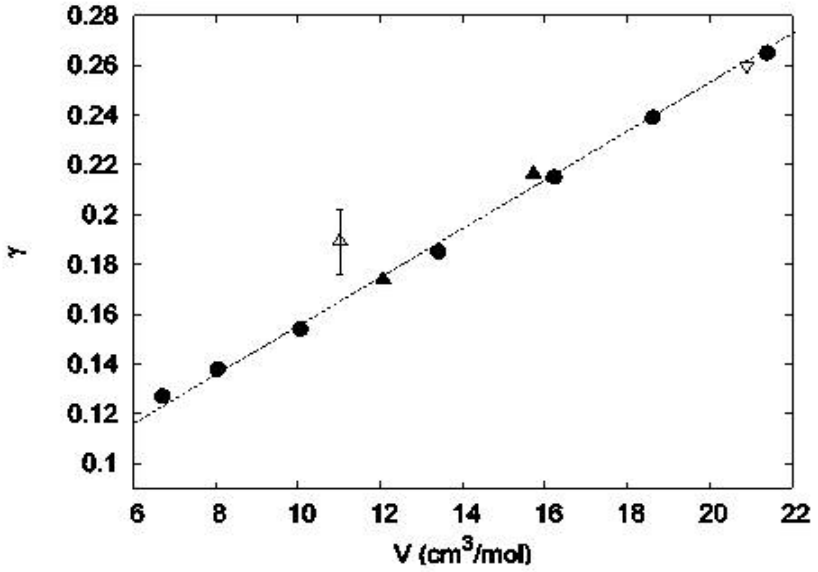
RGs and mixtures: ^{4}He

Table 1. Total, kinetic and potential energies per particle of solid ^{4}He including STC (E_{DMC}, E_k and E_p, respectively) as computed with DMC and the HFD–B(HE) Aziz potential. Figures within parentheses account for the statistical errors.

V (cm^3 mol^{-1})	E_{DMC}/N (K)	E_k/N (K)	E_p/N (K)
22.60	−6.51(2)	21.36(6)	−27.87(6)
20.95	−6.22(2)	24.20(6)	−30.42(6)
19.34	−5.50(2)	27.63(6)	−33.13(6)
17.96	−4.32(2)	32.01(6)	−36.33(6)
16.76	−2.50(2)	35.24(6)	−37.74(6)
15.24	1.63(2)	42.63(6)	−41.00(6)
14.37	5.25(3)	47.09(8)	−41.84(7)
13.41	11.11(5)	53.66(9)	−42.55(8)
10.06	68.80(5)	89.90(9)	−21.10(8)
8.04	192.45(5)	133.00(9)	59.45(8)

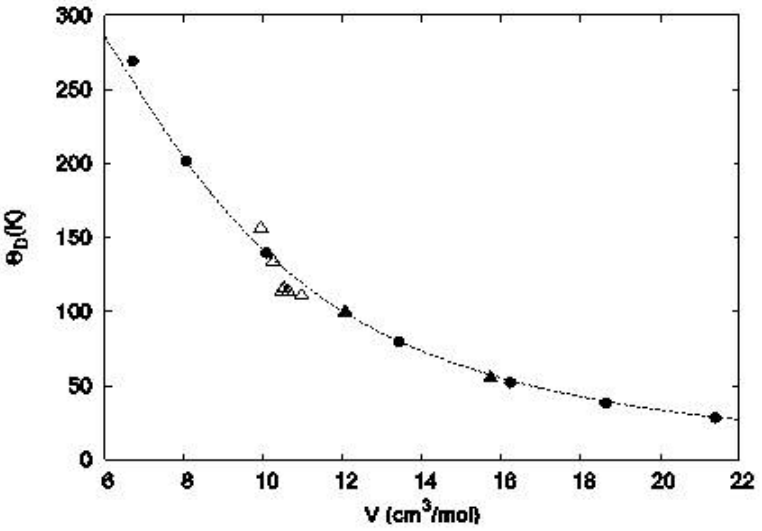
C. Cazorla and J. Boronat, J. Phys.:Cond. Matt. ***20****, 015223 (2008)*

RGs and mixtures: ^{4}He



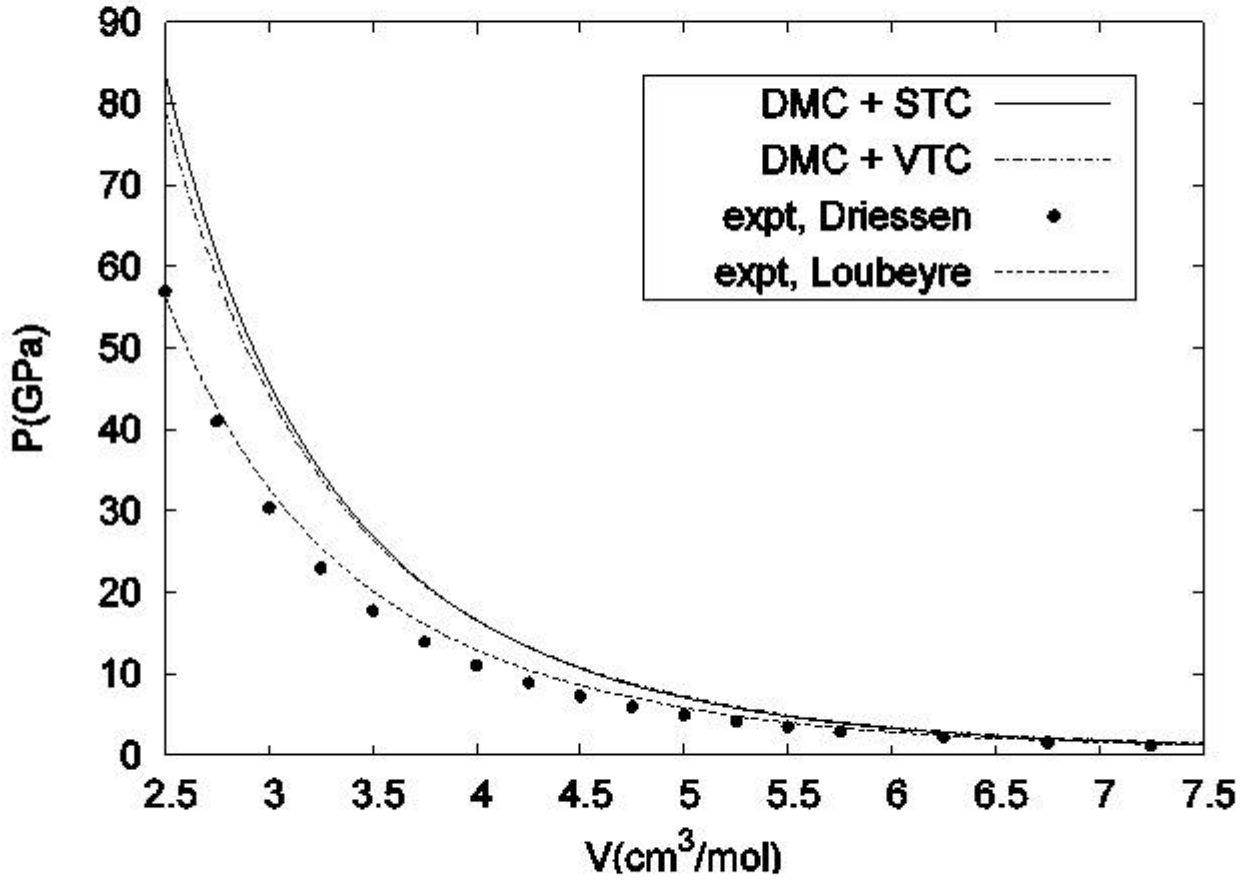
$$\gamma = \frac{\langle u^2 \rangle^{1/2}}{a}$$

$$\Theta_D = \frac{\hbar \omega_D}{k_B}$$



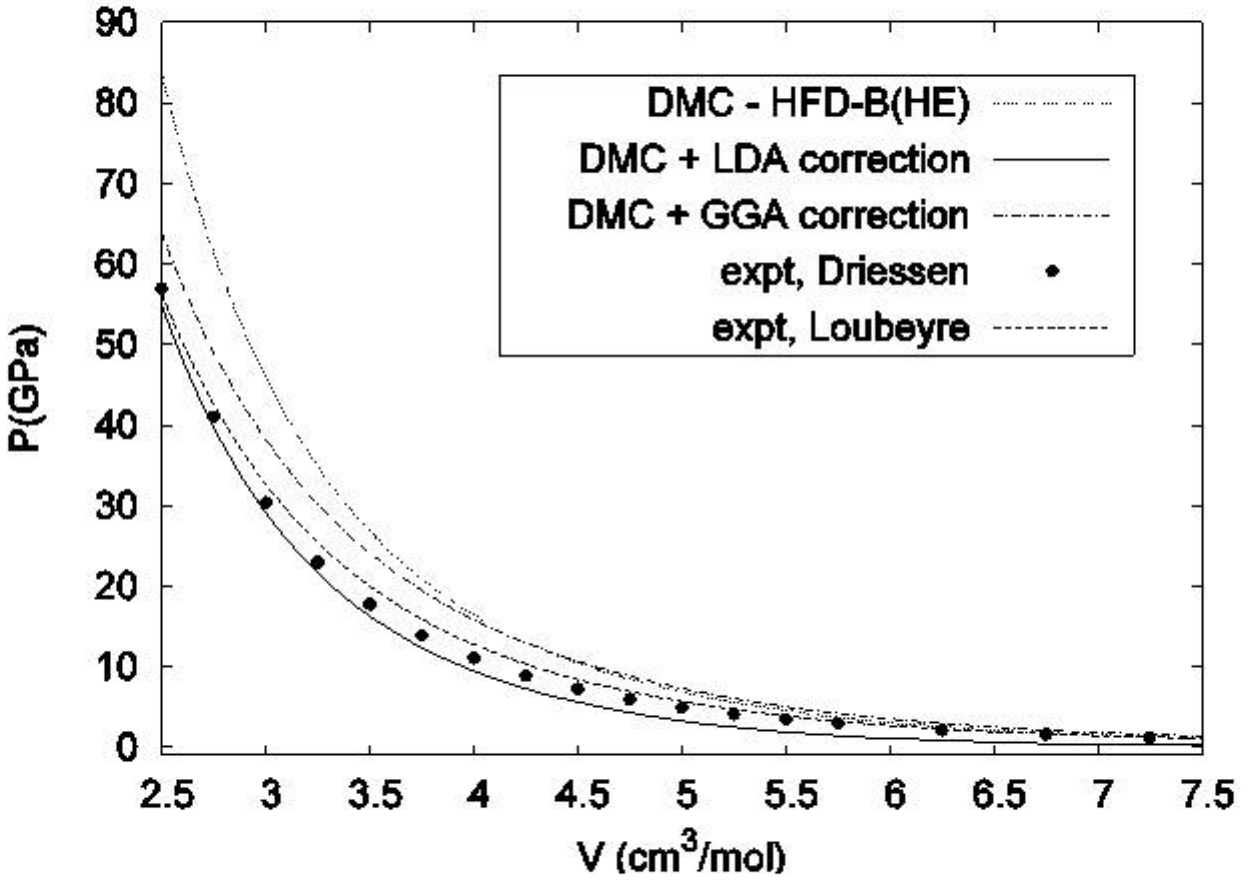
C. Cazorla and J. Boronat, J. Phys.:Cond. Matt. ***20****, 015223 (2008)*

RGs and mixtures: ^{4}He



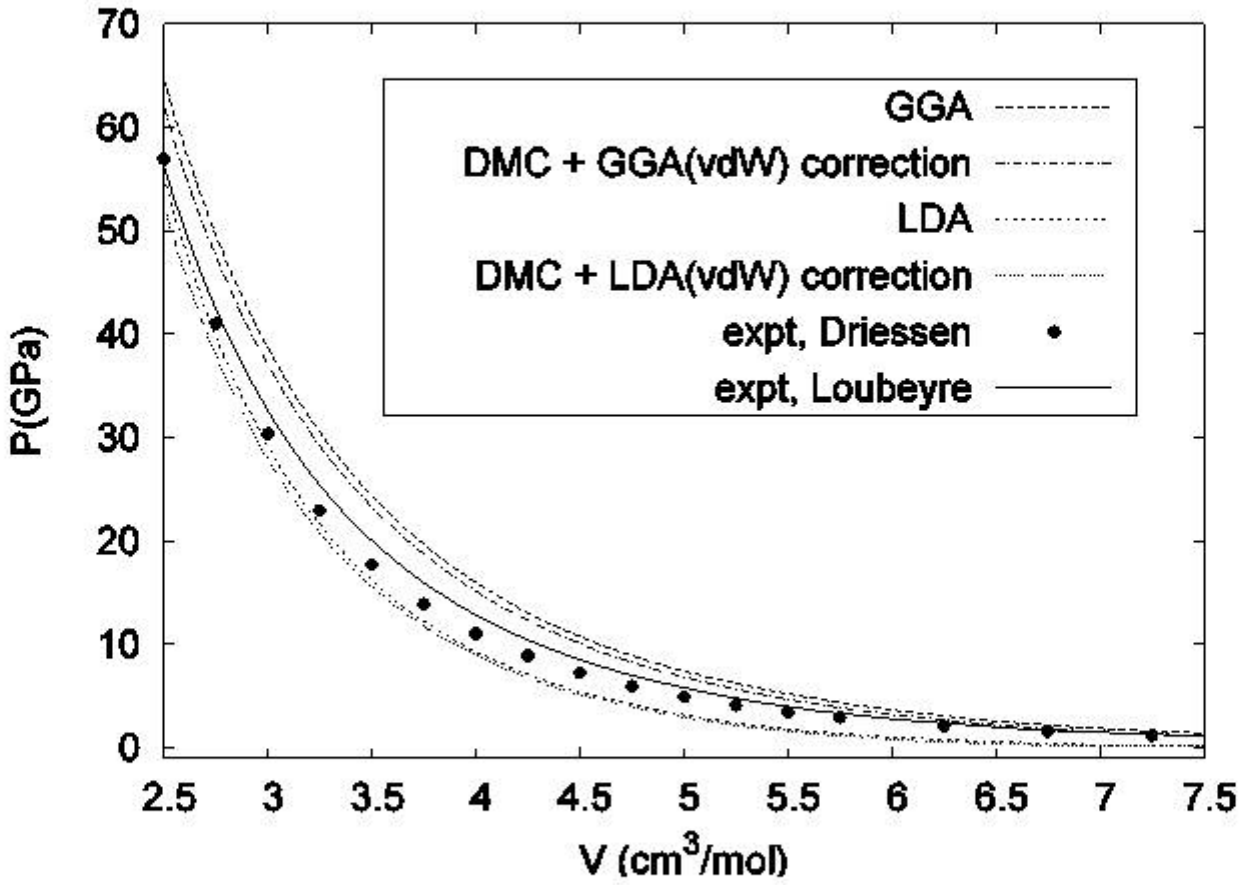
C. Cazorla and J. Boronat, J. Phys.:Cond. Matt. ***20****, 015223 (2008)*

RGs and mixtures: ^{4}He



C. Cazorla and J. Boronat, J. Phys.:Cond. Matt. ***20****, 015223 (2008)*

RGs and mixtures: ^{4}He



C. Cazorla and J. Boronat, J. Phys.:Cond. Matt. ***20****, 015223 (2008)*

RGs and mixtures: ^{4}He

Table 2. Calculated DMC energies and corrections $\langle \Delta E \rangle_{\mathrm{DMC}}$ per particle for solid ^{4}He at some selected volumes. Within the parentheses are the statistical uncertainties, which in the case of the corrections correspond to $\sqrt{\langle \delta \Delta E^2 \rangle}_{\mathrm{DMC}}/N$ (we note that (98) $\equiv \pm 0.98$ and (5) $\equiv \pm 0.05$).

V ($\mathrm{cm^3\ mol^{-1}}$)	E_{DMC}/N (K)	$\langle \Delta E \rangle^{\mathrm{LDA}}_{\mathrm{DMC}}/N$ (K)	$\langle \Delta E \rangle^{\mathrm{GGA}}_{\mathrm{DMC}}/N$ (K)
10.06	68.80(5)	0.00(75)	0.00(14)
6.70	404.55(5)	−352.55(88)	72.06(33)
5.03	1163.54(8)	−813.08(55)	200.43(39)
4.02	2444.11(12)	−1407.99(50)	232.38(35)
3.35	4294.67(15)	−2165.61(61)	43.53(50)
2.87	6728.33(38)	−3113.77(67)	−389.66(51)
2.51	9742.06(49)	−4263.34(98)	−1055.16(98)

C. Cazorla and J. Boronat, J. Phys.:Cond. Matt. ***20****, 015223 (2008)*

RGs and mixtures: ^{4}He

Table 3. Parameters of the fits performed with relation (14) for the resulting EOSs. The headers on this first row correspond to experimental values of reference [2], DMC calculations with pair potential HFD–B(HE), DMC calculations with many-body corrections as obtained with LDA, GGA, LDA plus vdW interaction and GGA plus vdW interaction, respectively. P_{max} is the value of the pressure obtained at the smallest studied volume 2.5 $cm^3\ mol^{-1}$.

	Expt	DMC	LDA	GGA	LDA (v dW)	GGA (v dW)
V_0 ($cm^3\ mol^{-1}$)	13.72	20.16	7.77	12.93	7.06	11.35
B_0 (GPa)	0.225	0.018	1.884	0.510	3.072	0.901
B_0'	7.35	9.85	6.66	6.53	6.19	6.13
P_{max} (GPa)	56.94	83.60	54.83	63.79	52.42	62.00

C. Cazorla and J. Boronat, J. Phys.:Cond. Matt. ***20****, 015223 (2008)*

RGs and mixtures: $Ne(He)_2$

VOLUME 70, NUMBER 2 PHYSICAL REVIEW LETTERS 11 JANUARY 1993

High Pressure Measurements of the He-Ne Binary Phase Diagram at 296 K: Evidence for the Stability of a Stoichiometric $Ne(He)_2$ Solid

Paul Loubeyre, Michel Jean-Louis, and René LeToullec
Laboratoire de Physique de Milieux Condensés, Université Paris 6, Boite 77, 4 place Jussieu, 75252 Paris, France

Lydie Charon-Gérard
Commissariat à l'Energie Atomique, BP n°7, 77181 Courtry, France
(Received 2 November 1992)

The binary phase diagram of He-Ne mixtures has been measured at 296 K in a diamond anvil cell. It is of the eutectic type with no fluid-fluid separation of phases. A homogeneous solid mixture is shown to be stable for a mole fraction of He equal to $\frac{2}{3}$. Single-crystal synchrotron x-ray measurements indicate that this solid is ordered with 12 atoms in the unit cell. Gibbs free energy calculations support the attribution to the $MgZn_2$ type structure. It is the first Laves phase observed in a van der Waals molecular compound.

C. Cazorla, D. Errandonea and E. Sola, Phys. Rev. B ***80****, 064105 (2009)*

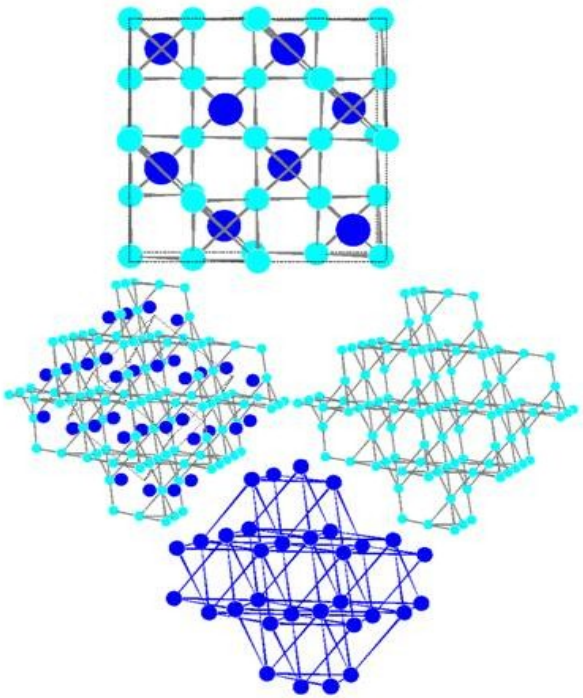
RGs and mixtures: $Ne(He)_2$

RG-He mixtures are **interesting** compounds for:

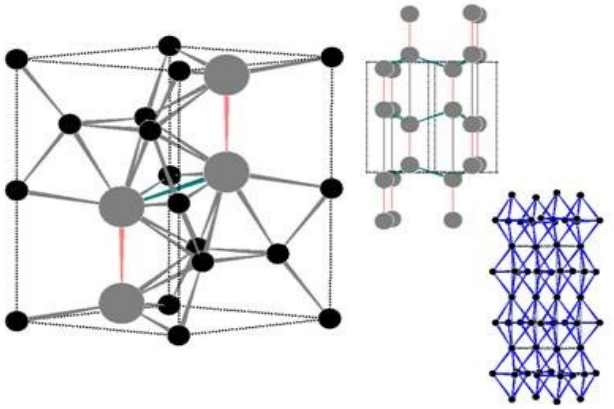
- astrophysics
- science and technology
- crystallography (Laves structures)
- pressure induced electronic phase transitions
- theory challenge

C. Cazorla, D. Errandonea and E. Sola, Phys. Rev. B ***80****, 064105 (2009)*

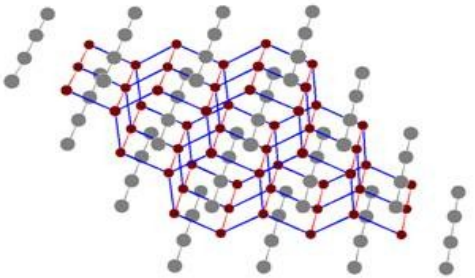
RGs and mixtures: $Ne(He)_2$



$MgCu_2$



$MgZn_2$



AlB_2

C. Cazorla, D. Errandonea and E. Sola, Phys. Rev. B ***80****, 064105 (2009)*

RGs and mixtures: $Ne(He)_2$

Methodology:

* DFT (LDA & GGA)

* Quasi-Harmonic Approximation (QH)

$$F_{\text{harm}}(V,T) = \frac{1}{N_{\mathbf{q}}} k_B T \sum_{\mathbf{q},s} \ln\left\{ 2 \sinh\left[\frac{\hbar \omega_{\mathbf{q}s}(V,T)}{2 k_B T} \right] \right\}$$

Approach reliable at intermediate and high P (vdW issue)

C. Cazorla, D. Errandonea and E. Sola, Phys. Rev. B ***80****, 064105 (2009)*

RGs and mixtures: $Ne(He)_2$

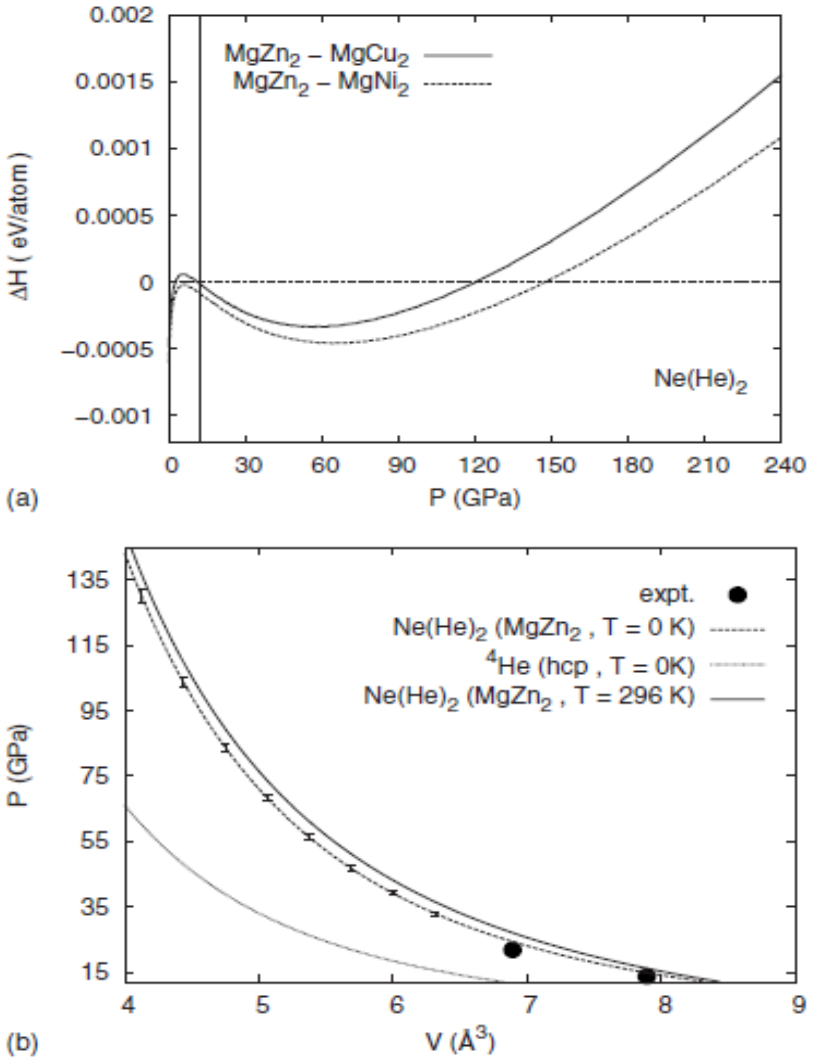


FIG. 3. Top: enthalpy energy difference, ΔH, between the $MgZn_2$, $MgCu_2$, and $MgNi_2$ Laves phases of $Ne(He)_2$ at zero temperature and as a function of pressure. The vertical solid line at 12 GPa separates the low pressure from the intermediate and high-pressure regimes. Uncertainties associated to ΔH amount to 0.1 meV/atom. Bottom: equation of state of $Ne(He)_2$ in the $MgZn_2$ phase structure calculated at $T=0$ and 296 K (uncertainties associated to the zero-temperature case are represented with vertical dashed lines). Experimental data and previous zero-temperature calculations of solid ^4He in the hcp crystal phase are shown for comparison.

$Ne(He)_2$ is a good hydrostatic PTM

RGs and mixtures: $Ne(He)_2$

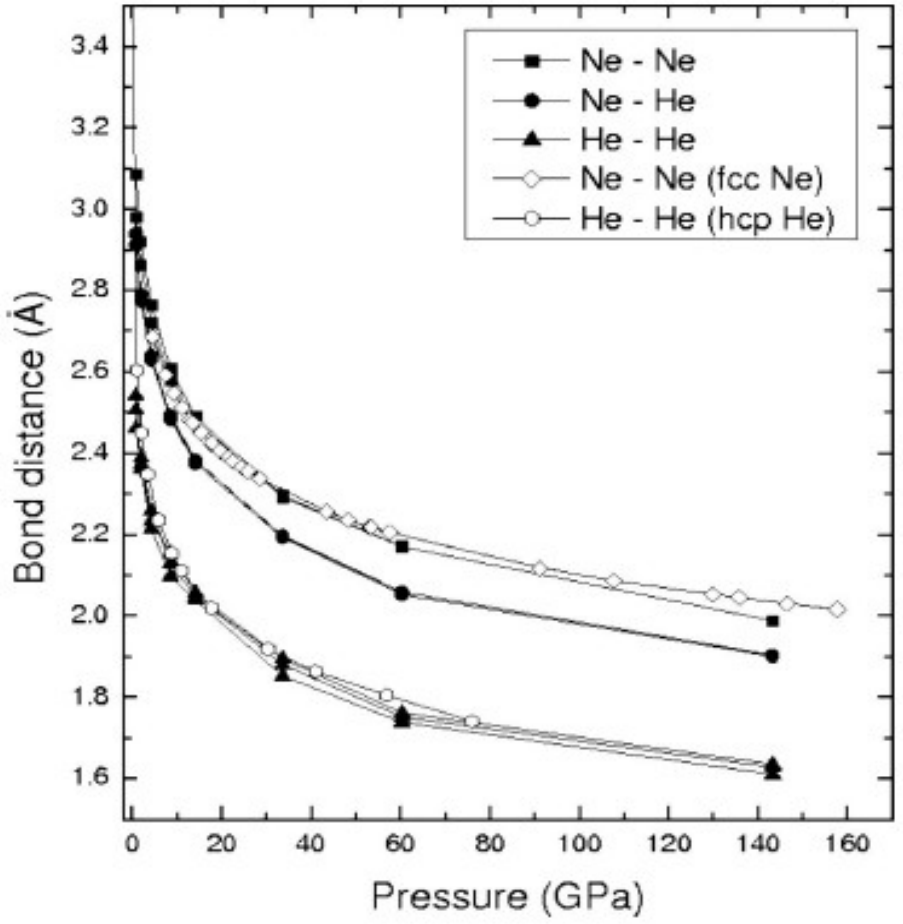


FIG. 4. Pressure-induced variation of atomic He-He, He-Ne, and Ne-Ne bond distances in the $Ne(He)_2$ crystal ($MgZn_2$ structure). Evolution of atomic bond distances in pure ^4He and Ne bulk systems are shown for comparison.

He-He and Ne-Ne sublattices seem not to interact with each other

RGs and mixtures: $Ne(He)_2$

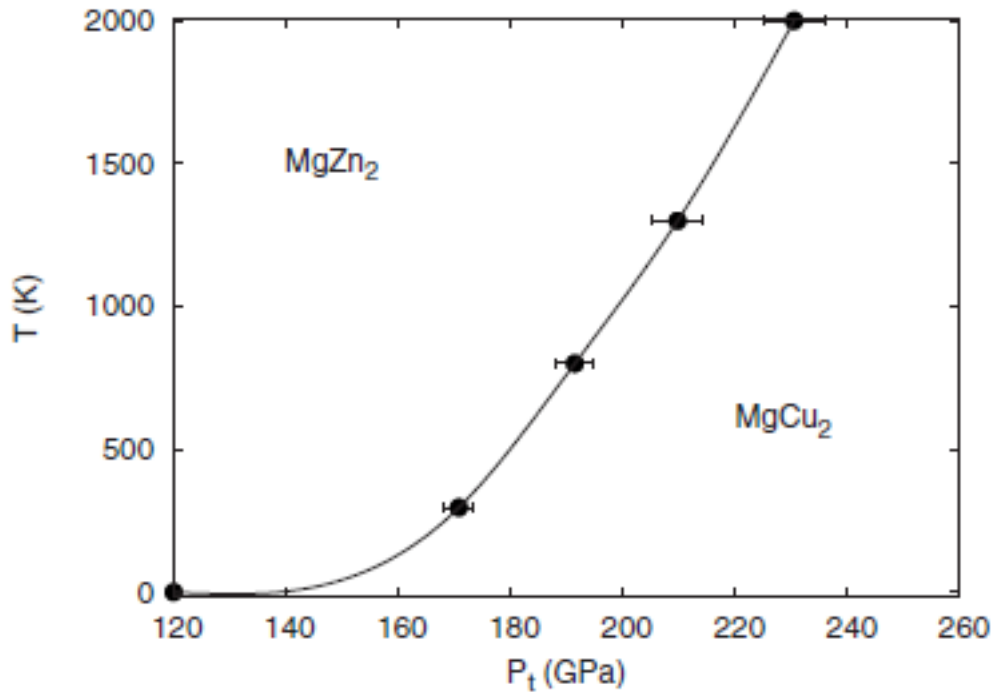


FIG. 5. Calculated $MgZn_2 \rightarrow MgCu_2$ phase boundary in $Ne(He)_2$ as a function of temperature. The solid line is a guide for the eye which connects the points of the solid-solid phase boundary explicitly calculated (solid circles). Uncertainties associated to our calculations are shown in the plot with horizontal solid lines.

C. Cazorla, D. Errandonea and E. Sola, Phys. Rev. B ***80****, 064105 (2009)*

RGs and mixtures: $Ne(He)_2$

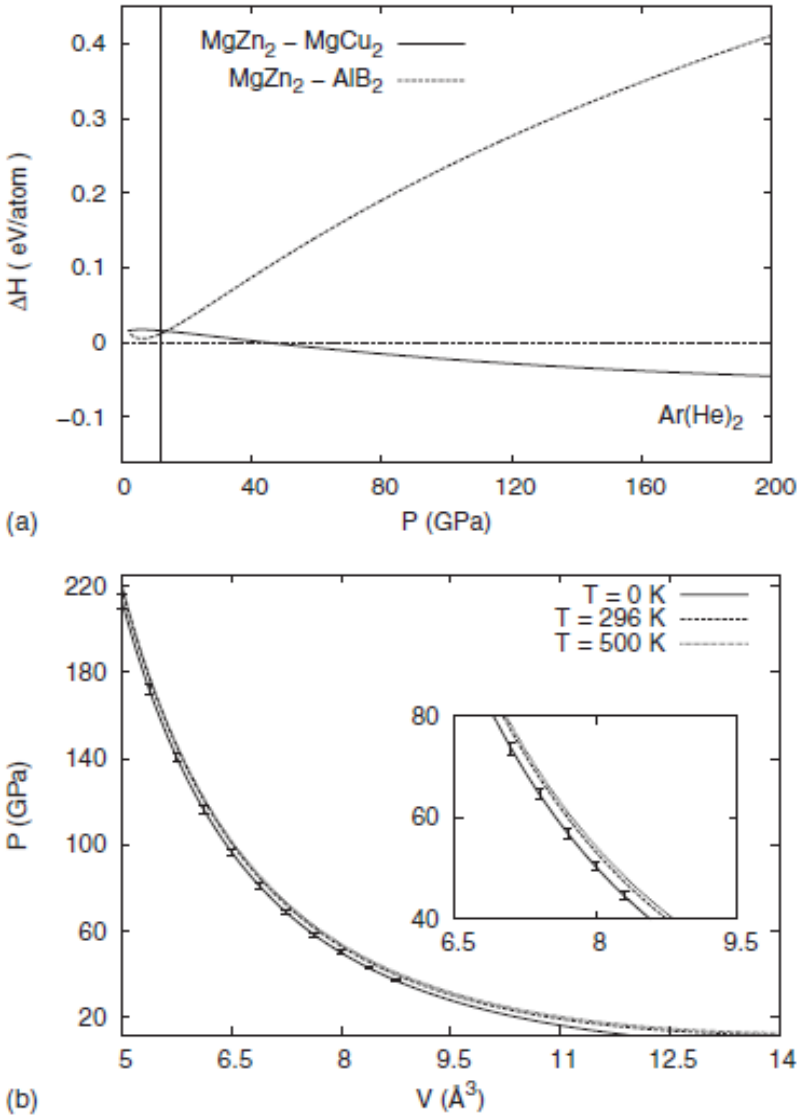


FIG. 8. Top: enthalpy difference between the $MgZn_2$-, $MgCu_2$-, and AlB_2-type phase structures of $Ar(He)_2$ under pressure and at zero temperature. The vertical solid line at 12 GPa separates the low pressure from the intermediate- and high-pressure regimes. Uncertainties associated to ΔH amount to 0.1 meV/atom. Bottom: equation of state of $Ar(He)_2$ in the AlB_2-type phase structure calculated at different temperatures. Uncertainties associated to the zero-temperature case are represented with solid vertical lines.

$Ar(He)_2$ compound

RGs and mixtures: $Ne(He)_2$

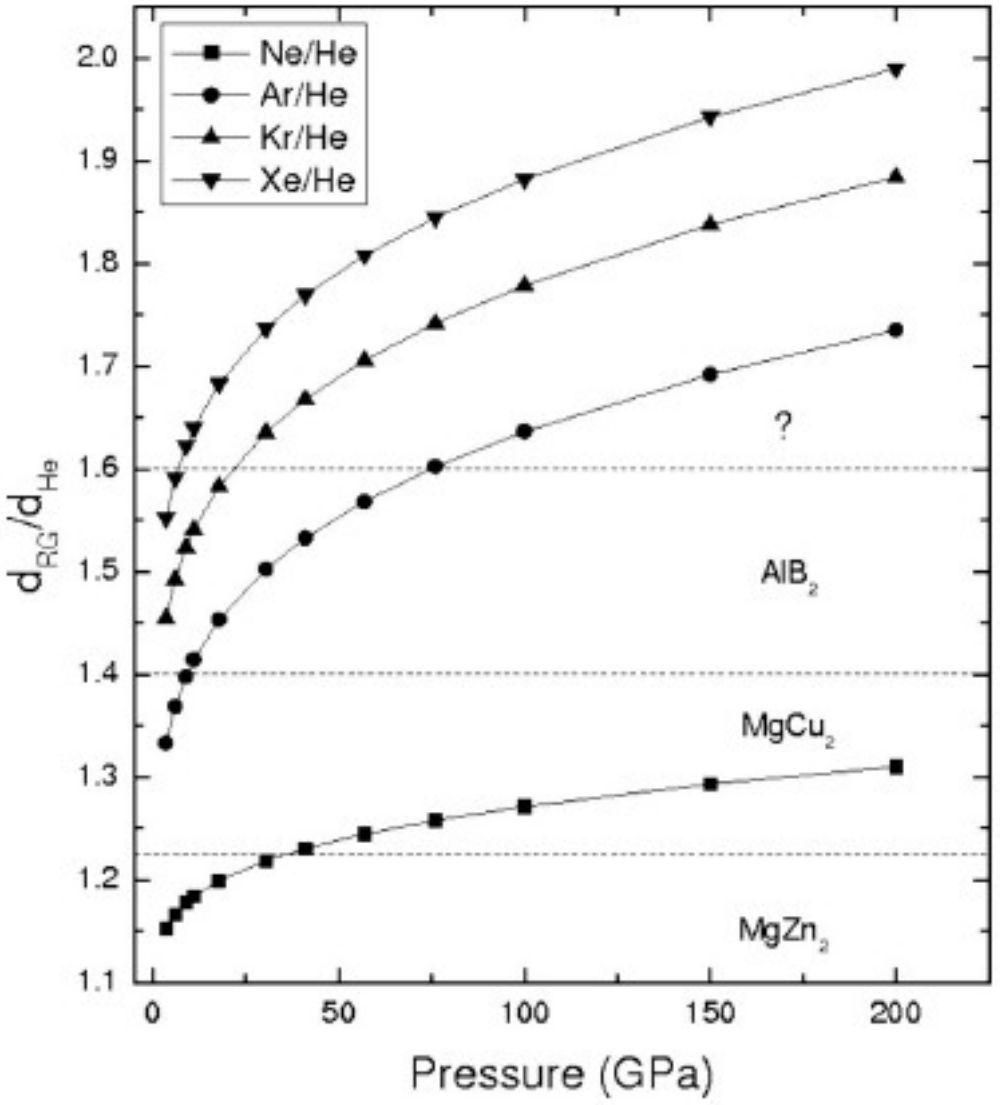


FIG. 11. Zero-temperature qualitative high-P phase diagram of binary RG-He alloys under pressure based on structural data and bond-distance ratio arguments.

Geometry and space-filling arguments seem reliable for predicting properties of RGs mixtures under pressure

RGs and mixtures: $Ne(He)_2$

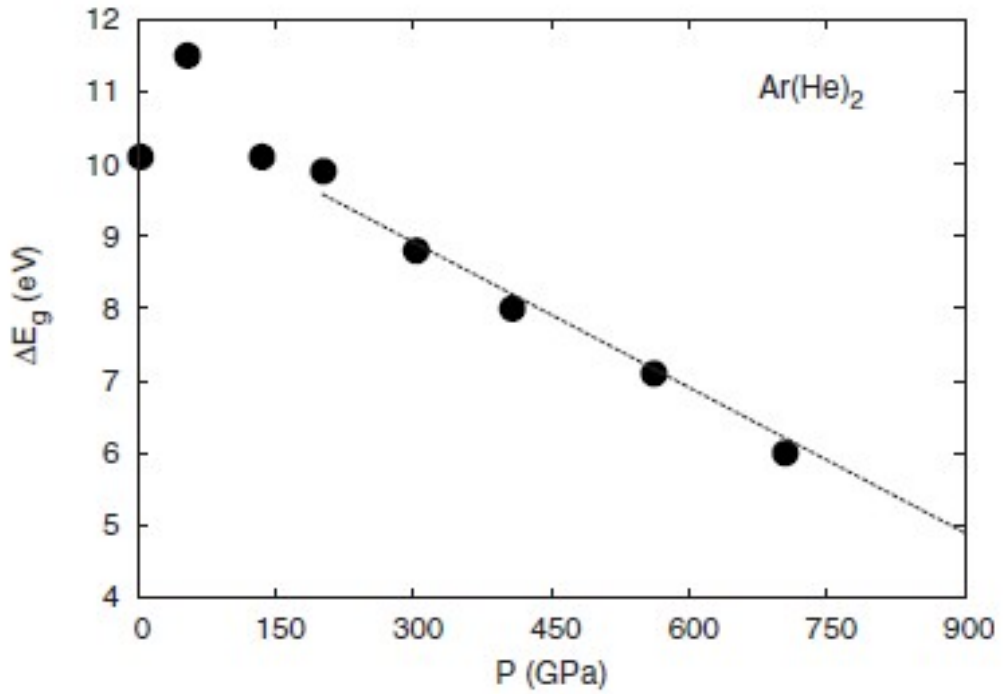


FIG. 13. Evolution of the electronic-band gap of $Ar(He)_2$ in the AlB_2-type phase structure with pressure. The metallization pressure of helium in such compound is estimated to be of order $P_{metal} \sim 1630$ GPa.

Chemical precompression of ^4He by other RGs appears to reduce its corresponding metallization pressure

C. Cazorla, D. Errandonea and E. Sola, Phys. Rev. B ***80****, 064105 (2009)*

RGs and mixtures: $Ne(He)_2$

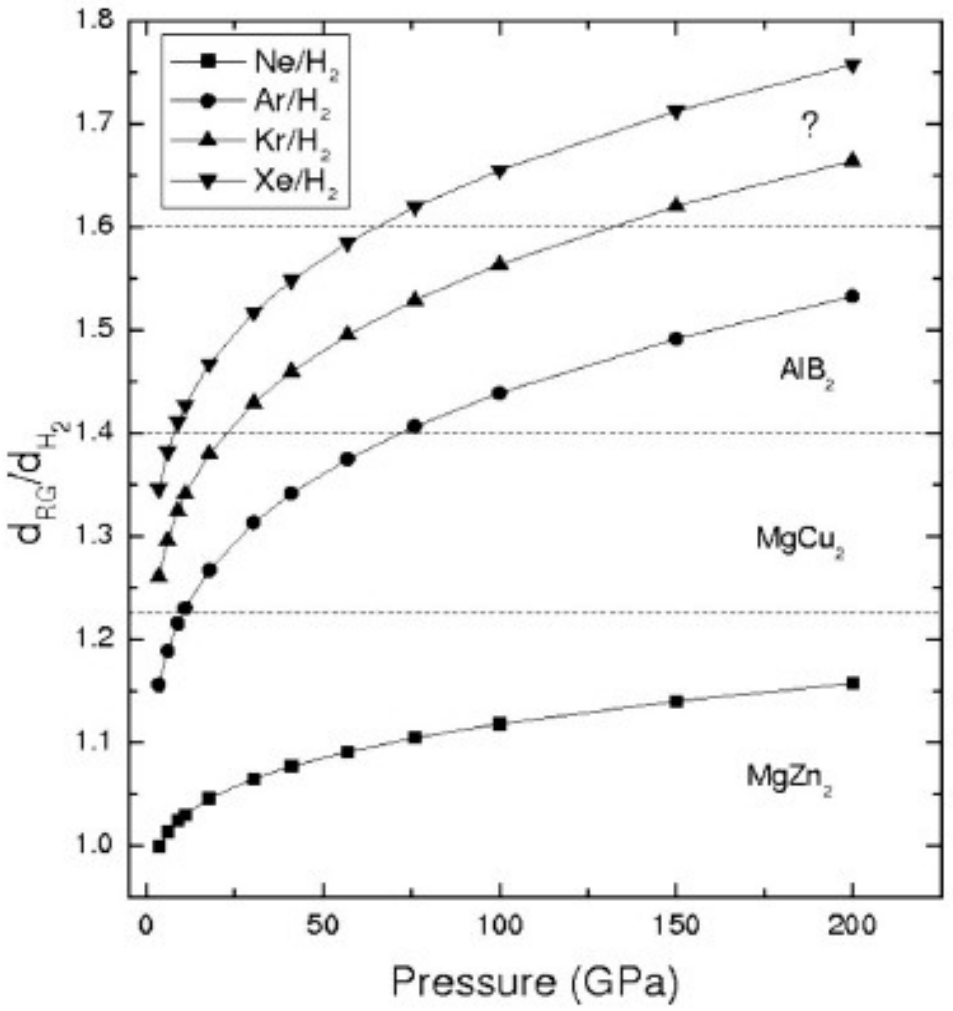


FIG. 14. Zero-temperature qualitative high-P phase diagram of binary RG-H_2 alloys under pressure based on existing experimental data and atomic size-ratio arguments.

Do the same arguments apply to $RG(H_2)_2$ mixtures?

RGs and mixtures: $Ar(H_2)_2$

VOLUME 72, NUMBER 9 PHYSICAL REVIEW LETTERS 28 FEBRUARY 1994

Compression of $Ar(H_2)_2$ up to 175 GPa: A New Path for the Dissociation of Molecular Hydrogen?

Paul Loubeyre, René Letoullec, and Jean-Pierre Pinceaux
Physique des Milieux Condensés, Université Paris 6, boite 77, 4 place Jussieu 75252 Paris, France
(Received 2 November 1992; revised manuscript received 1 June 1993)

Optical observations, Raman scattering, and single-crystal synchrotron x-ray measurements demonstrate the stability of a new stoichiometric compound, $Ar(H_2)_2$. This is a Laves phase with a hexagonal structure isomorphous to $MgZn_2$. A first order phase transition, which is associated with the sudden disappearance of the vibron and a visual increase absorbance of the sample, was observed around 175 GPa in three different experiments, two on $Ar(H_2)_2$ and one on $Ar(D_2)_2$. Optical absorption measurements up to 200 GPa in $Ar(D_2)_2$ have revealed the onset of a possible Drude type metallic behavior above the transition.

C. Cazorla and D. Errandonea, to be published (2009)

RGs and mixtures: $Ar(H_2)_2$

Methodology:

* DFT (LDA & GGA)

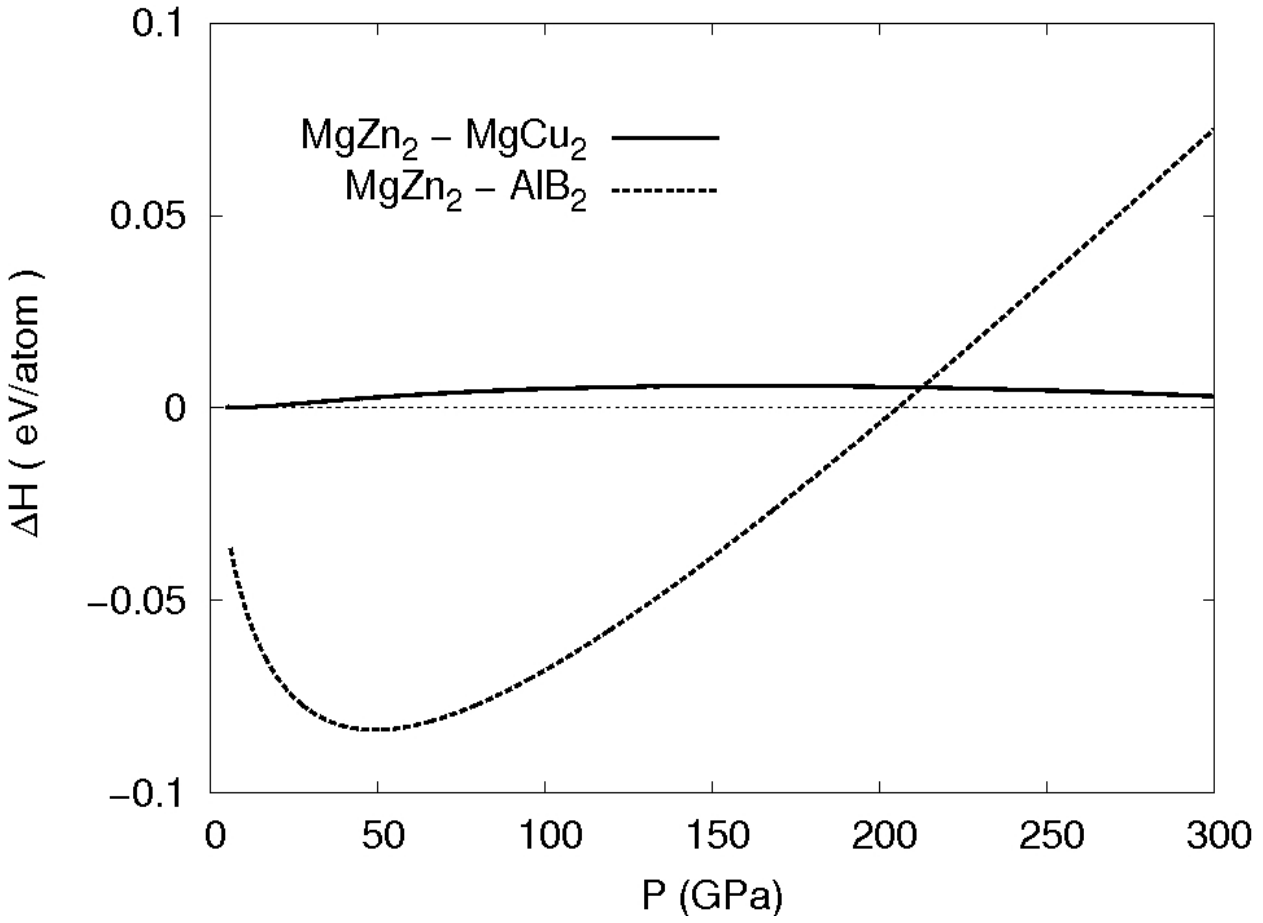
* Quasi-Harmonic Approximation (QH)

$$F_{\mathrm{harm}}(V,T) = \frac{1}{N_{\mathbf{q}}} k_B T \sum_{\mathbf{q},s} \ln\left\{ 2 \sinh\left[\frac{\hbar \omega_{\mathbf{q}s}(V,T)}{2 k_B T} \right] \right\}$$

* *Ab initio* molecular dynamics simulations (AIMD)

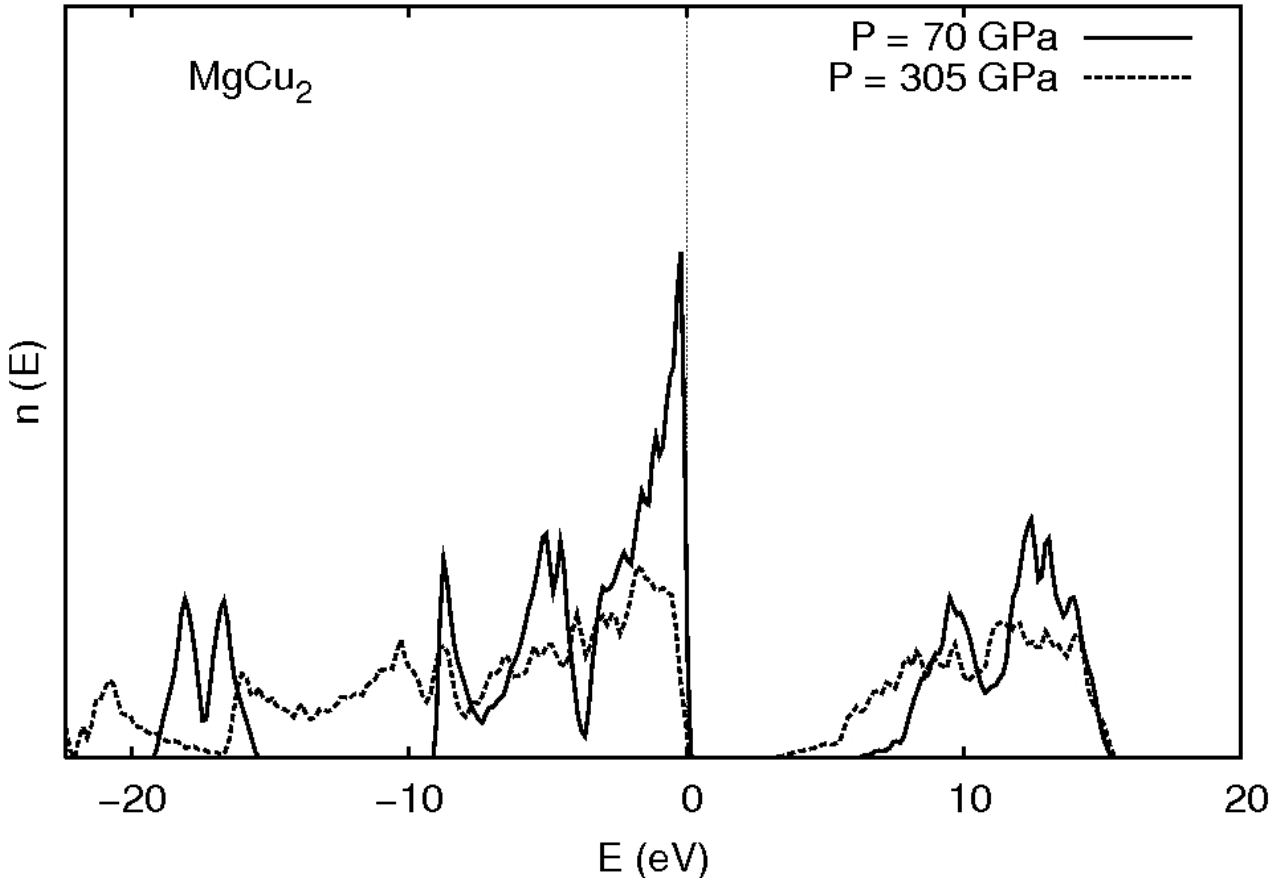
C. Cazorla and D. Errandonea, to be published (2009)

RGs and mixtures: $Ar(H_2)_2$



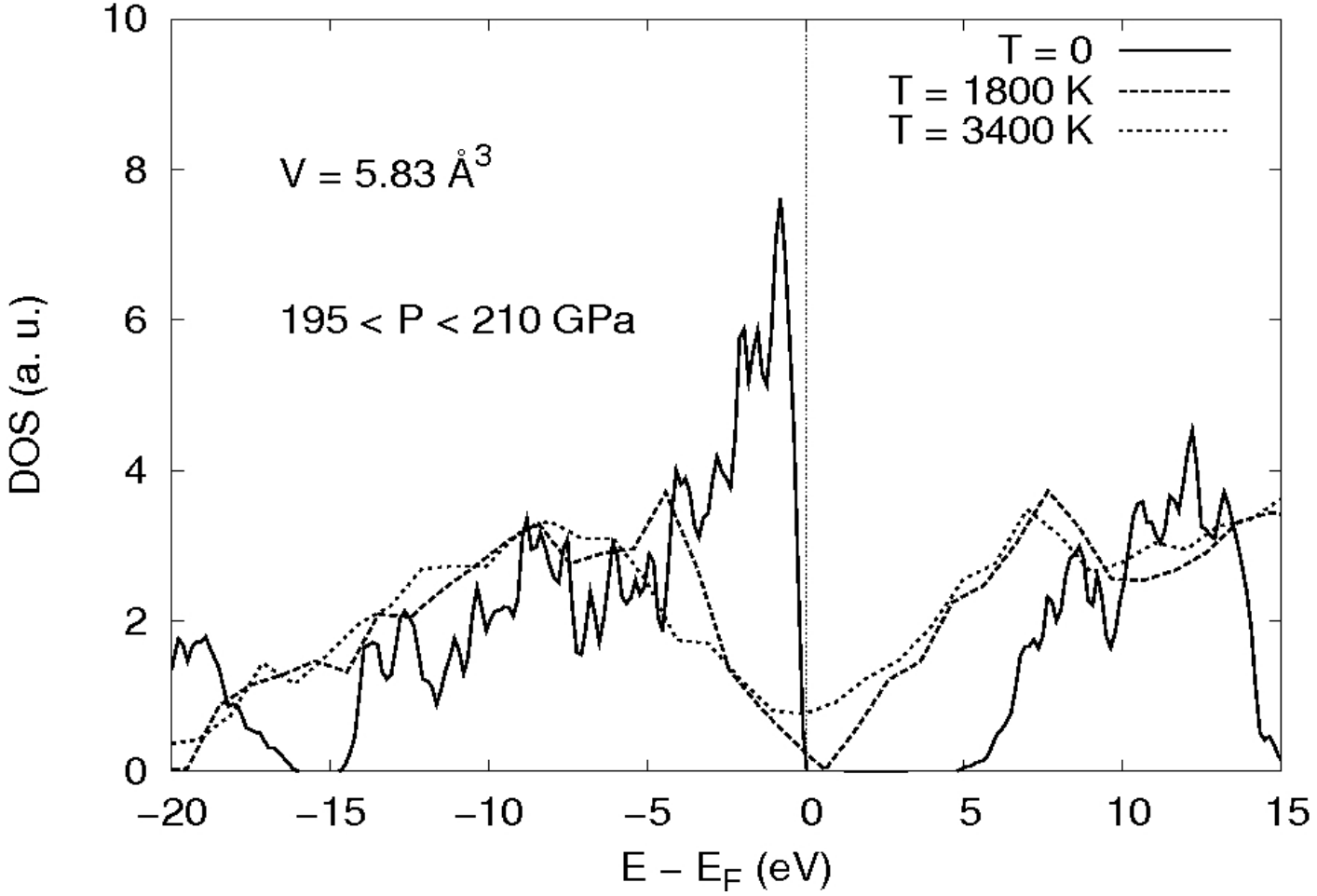
The $MgCu_2$ Laves structure is energetically competitive

RGs and mixtures: $Ar(H_2)_2$



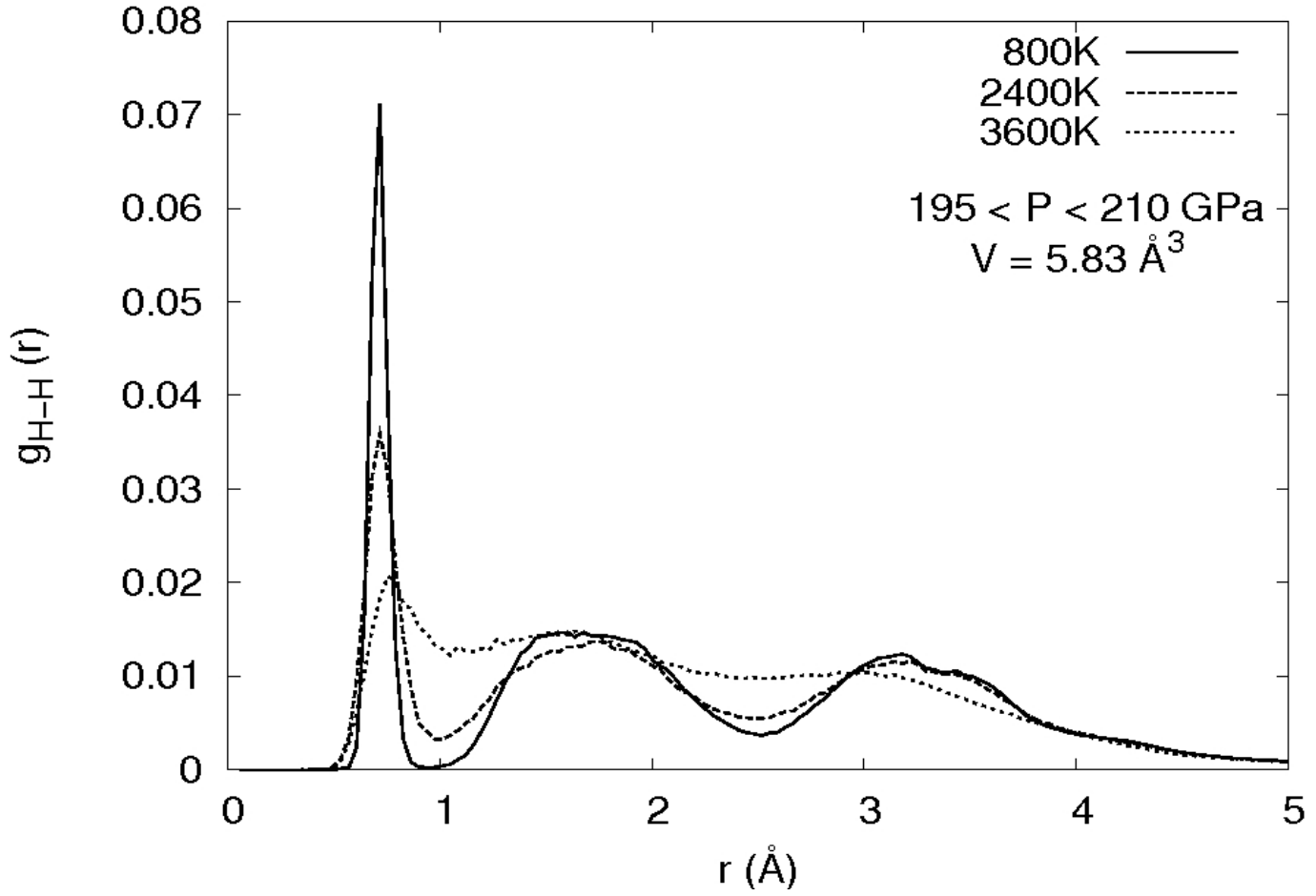
Chemically induced metallization of H_2 not below P~400 GPa

RGs and mixtures: $Ar(H_2)_2$



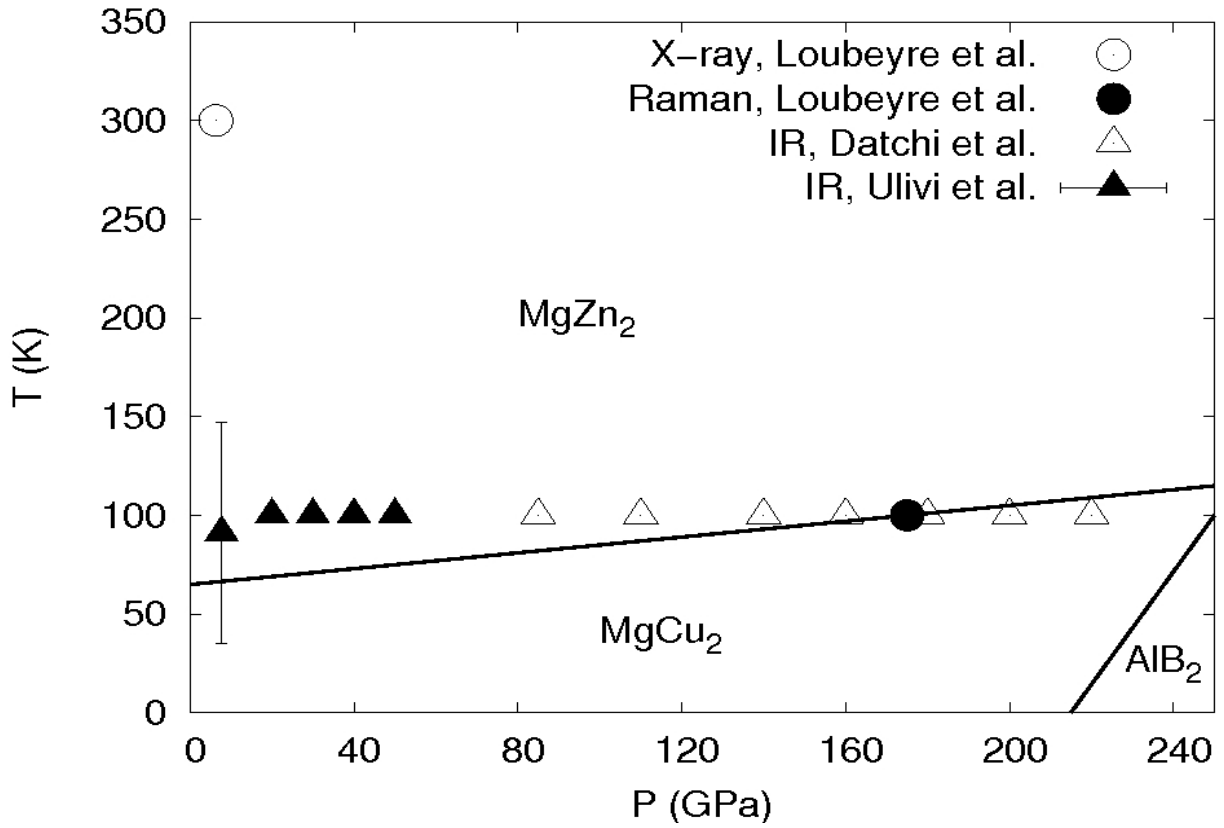
H_2 metallization might be induced by disorder and high T

RGs and mixtures: $Ar(H_2)_2$



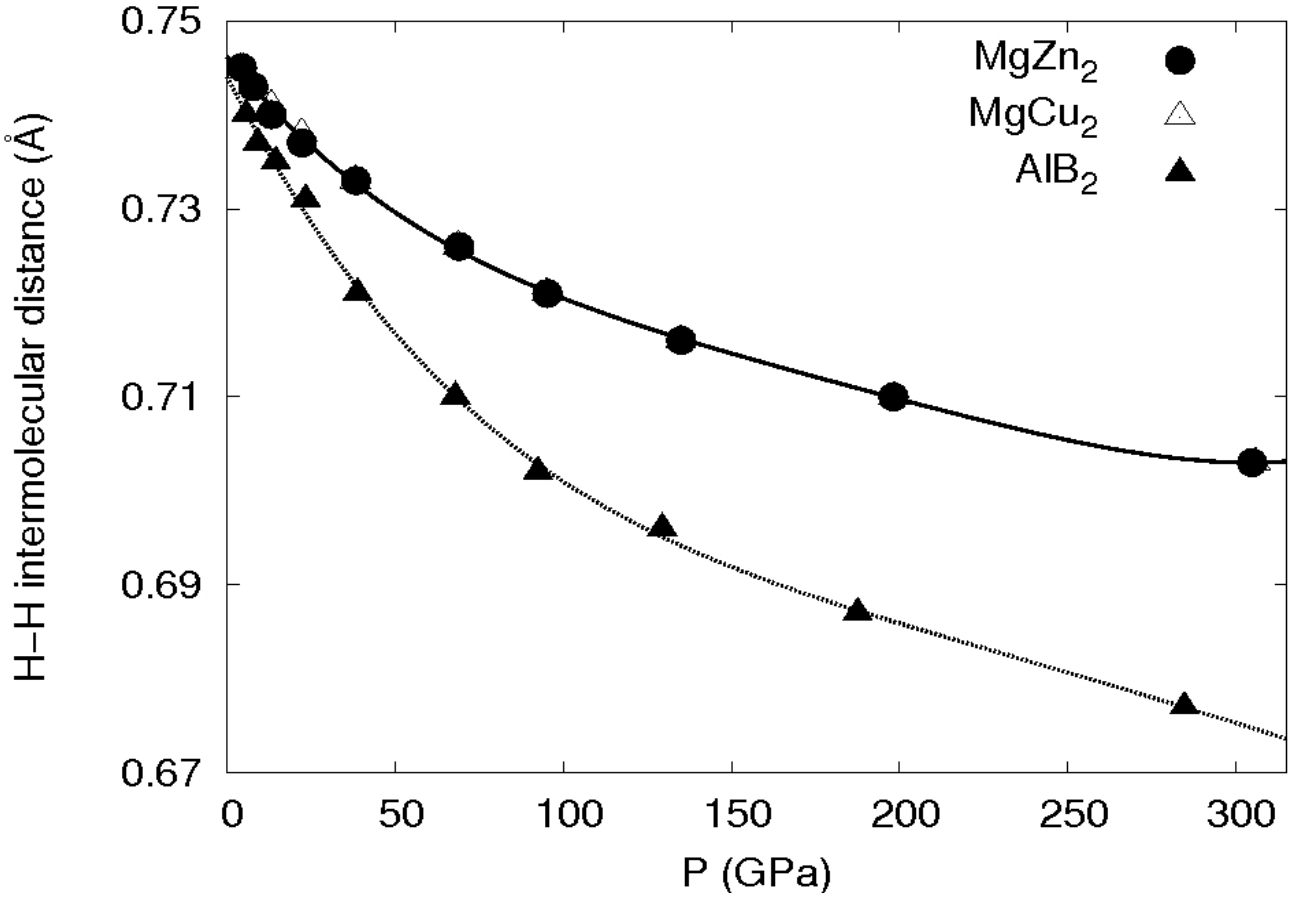
H_2 metallization might be induced by disorder and high T

RGs and mixtures: $Ar(H_2)_2$



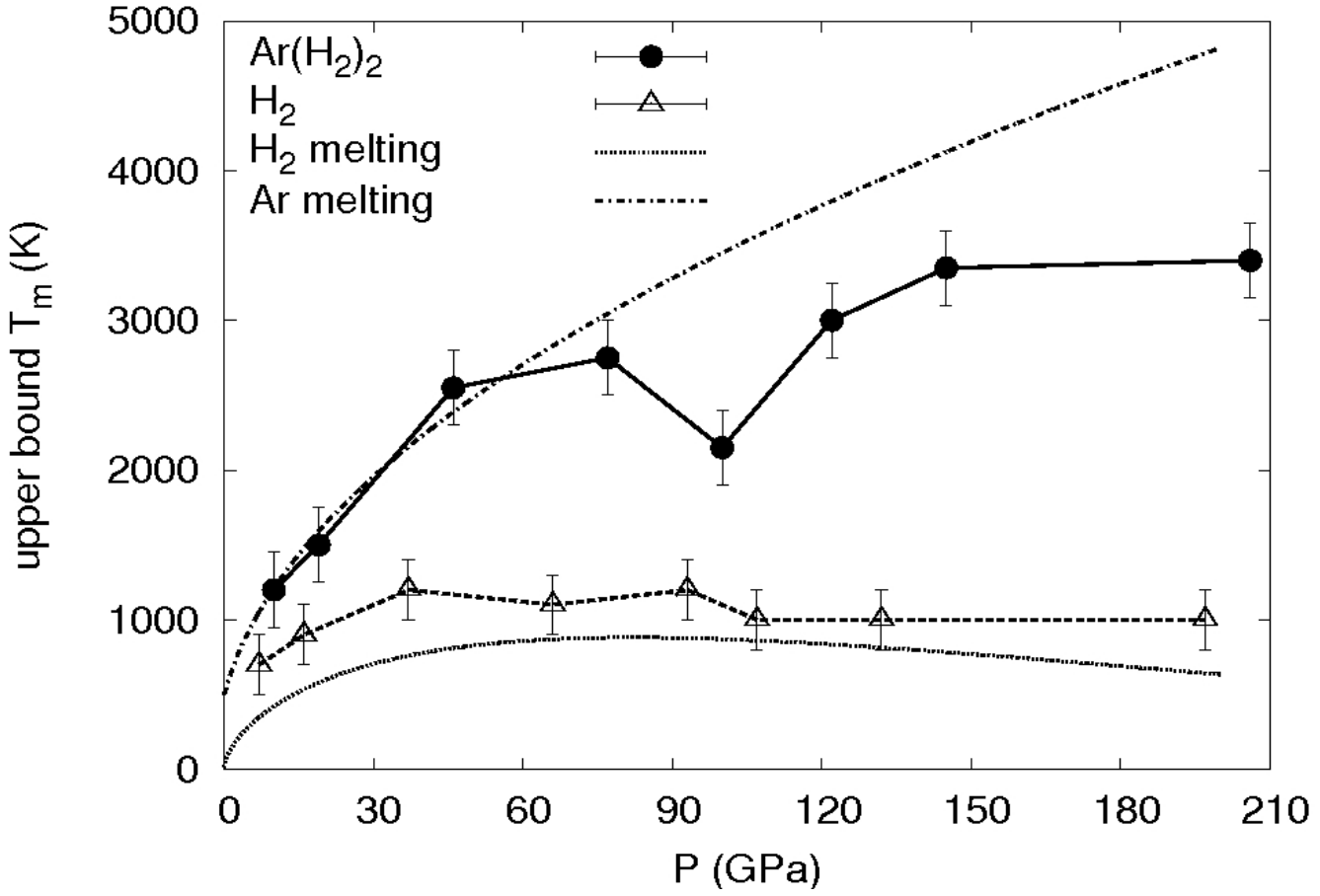
Experimental controversy could be resolved by $MgZn_2 \rightarrow MgCu_2$

RGs and mixtures: $Ar(H_2)_2$



Vibron frequencies in the $MgZn_2$ and $MgCu_2$ phases are similar

RGs and mixtures: $Ar(H_2)_2$



A novel melting behaviour for A(heavy)-B(light) compounds?

RGs and mixtures : Conclusions

* RGs and mixtures are not as simple systems as naively thought once temperature is lowered and/or pressure applied, theoretical treatment is challenging!

* Mixtures of RGs are interesting systems from a crystallographic and materials physics points of view

* Mixtures of RGs with H_2 are interesting systems for astronomy, crystallography and materials physics areas

* By studying the $Ar(H_2)_2$ system probably we have unravelled a new type of melting behaviour under P that can be present in other A(heavy)-B(light) compounds

Acknowledgements

Politechnical University of Catalonia (UPC -Spain-):

- Jordi Boronat
- Joaquim Casulleras
- Gregory Astrakharchick

University College London (UCL -United Kingdom-):

- Mike J Gillan
- Dario Alfe
- Ester Sola

University of Valencia (UV -Spain-):

- Daniel Errandonea