

### Институт физики высоких давлений РАН

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# Современное состояние физики высоких давлений



Райвола, Март 2010

Физика высоких давлений - область физики, изучающая свойства вещества при высоких давлениях. Почему это - важно? ~ 90% вещества Вселенной, сосредоточенное в громадных самогравитирующих телах, находится при давлении, превышающим 10 кбар.

## Содержание:

- •Определения
- •История
- •Давление в Природе
- •Техника высоких давлений
- •Шкала высоких давлений

•Фазовые диаграммы и эволюция вещества при высоких давлениях

- •Уравнения состояния и фазовые переходы
- •Некоторые результаты

•Институт физики высоких давлений РАН

Физика высоких давлениий как наука сформировалась в начале прошлого века в результате создания и развития адекватных методов исследования.

Экспериментальная физика высоких давлений оперирует с давлениями, варьирующими от одной до нескольких миллионов атмосфер (1 атмосфера = ~ 0.98 бар; 1 бар = 106 дин / cm2 = 10 Паскаль (Па)).

Диапазон изменения давлений в природе столь велик, что вряд ли сможет быть воспроизведен в лаборатории в обозримое время.

Тем не менее, необходимо отметить, что развитие экспериментальной техники позволяет уже сейчас моделировать условия, существующие в центре Земли



Percy Williams Bridgman 1882-1961

Перси Вильям Бриджмен, гарвардский профессор и нобелевский лауреат, сыграл главную роль в развитии экспериментальной техники высоких давлений и формировании физики высоких давлений как науки.

Основные направления исследований: • Физика конденсированного состояния вещества • Создание новых материалов • Строение Земли и планет

История развития физики высоких давлений не столь богата выдающимися открытиями в отличие, например, от случая физики низких температур.

Физика высоких давлений знаменита своими применениями, которые столь многочисленны и разнообразны, что делает невозможным даже их краткое упоминание. В этой связи <u>физика высоких</u> <u>давлений</u> может быть охарактеризована как скромная «рабочая лошадь» физики конденсированного состояния.

Формула Нобелевской премии Перси В. Бриджмена (1946): "for the invention of an apparatus to produce extremely high pressures and for the discoveries he made therewith in the field of high pressure physics"

## Важные даты

- •1762 1764 Джон Кантон (сжимаемость жидкостей)
- •1820 Якоб Перкинс (давление выше 2000 атм.)
- •1861 Томас Эндрюс (открытие критических явлений)
- •1893 1903 Густав Тамман (плавление, фазовые переходы)
- •1906 Первая статья П. В. Бриджмена
- •1931 публикация книги P.W. Bridgman
  - "The Physics of High Pressure"
- •1955 Первые синтетические алмазы (Дженерал Электрик)
- •1961 Плотный кремнезем (ИФВД)
- •1968 Стабильность металлического водорода

### ( Нил Ашкрофт)

- •1972 Изобретение рубинового манометра (НБС)
- •1977 Давление > 1.7 Мбар(Дэйв Мао и Питер Белл)

### **Pressure units and definitions**

 $1Pa (1N / m^2) = 10 dyn / cm^2 = 10^{-5} bar = 1.02 \cdot 10^{-5} kgf / cm^2$ 

 $P = \frac{F}{S}$ 



volume, V

 $\sigma$ 

 $\Phi(r)$ 

 ${\cal E}$ 

 $P = -\left(\frac{\partial F}{\partial V}\right)_{T}$   $\int p \partial V$   $\int p \partial V / F_{o}$  **Natural units of pressure Pressure = Energy / Volume**  $p_{o} = \varepsilon / \sigma^{3} - \text{molecular unit of pressure}$ 

 $T, l, \varepsilon, \sigma$  – characteristic quantities

 $p_o(He) \approx 84$  bar

 $p_o(Xe) \approx 450$  bar

Atomic unit:

 $e^2/a_o^4 \approx 3.10^2$  Mbar

 $e^2/a_o = 2Ry \approx 27.2 \ eV$  $a_o = \hbar^2/me^2$ (Bohr radius)

<u> ДА ВЛЕНИЕ В ПРИРОДЕ</u>		
	<mark>Давление</mark>	Плотность
	Мбар	<mark>г/ст<sup>3</sup></mark>
Земля (центр)	<b>4</b>	~ <mark>10-20</mark>
Солнце	<b>10</b> <sup>5</sup>	10 <sup>2</sup>
(центр)		
Белые	<b>10</b> <sup>10</sup>	<b>10</b> <sup>6</sup>
карлики		
<mark>Нейтронные</mark>	<b>10<sup>22</sup></b>	<b>10<sup>14</sup></b>
звезды		

## **Evolution of matter at cold compression**



## Melting at extreme conditions



Jones, Ceperley, Phys.Rev.Lett., 76,4572, 1996 -

 $P \propto T^{1+3/n}$ 

 $\Gamma = Z^2 e^2 / r_s kT \approx 150$  $\lambda_T \propto T^{(2-n)} / 2n \qquad T_m \propto V^{-n/3}$  $\lambda_T = \hbar / (mkT)^{1/2}$ 









### "Lentil" or Recessed anvils

(Ivanov, Slesarev, Vereschagin, 1959)



**Toroid** (Khvostancev, Novikov, Vereschagin, 1969) -











### **Diamond Anvils**



## Sulfur (1), Iodine (2) and Mercury Iodide (3) in diamond anvils



## CsJ + Xe in diamond anyils







1 A







Pressure measurements and High Pressure Scale •Primary and secondary gauges •Pros and pressure calibration •Ruby scale •Diamond scale •Pressure medium and pressure calibration



## **MgO High-Pressure Scale**

### (Zha, Mao, Hemley, 2000)







Aidun et al. Phys. Rev.B, 29, 2611, 1984

Zisman et al. 1984





### **Solid – solid critical point in Ce** (Ponyatovsky, 1958)











#### NO. 4471 July 9, 1955

NATURE

to the pressure. The main factor which limits the maximum pressures that can be reached within vessels is the strength of materials. The strongest steels in the most favourable form and size (piano wire, for example) have ultimate tensile strengths of the order of 14,000--21,000 kgm./cm.\*. Sintered carbides, such as 'Carbolov', have compressive strengths of the order of 50,000 kgm./cm.2 or more. The pressure required for reasonably rapid synthesis of diamond was chought by our group to be above the compressive strength of 'Carbolov' in the range 50,000-100,000 kgm./em.ª.

Merely making the walls thicker on a pressure vessel contributes very little to its pressure-holding ability after a certain wall thickness is reached. By using multiple support bands on the cylinder part (a technique used years ago in making large gun barrels), and special scaling gasket devices between



53

(a)

Fig. 3. Man-made diamonds. (a) 1-mm. diamond shown with phonograph needle. (b) 0.2-0.5-mm, octahedra





Fig. 4. X-ray diffraction patterns of man-made and natural diamond (powder camera photograph)

#### **Errors in diamond synthesis**

SIR - In 1955, some of us announced the first reproducible synthesis of diamond<sup>1</sup>. details of which were subsequently published2. These results marked the beginning of the present synthetic-diamond industry. But from the outset there were doubts in our team as to whether the first diamond grown by our technique (which we will call the run 151 diamond) was truly synthetic at all, or whether it was instead just a fragment of a natural diamond seed that got into the experiment inadvertently. We have now reanalysed the run 151 diamond using modern spectroscopic techniques and have found that it is indeed a small piece of a natural type Ia diamond.



Infrared absorption spectra of: a, run 151 diamond; b, a type la natural diamond with 'B'-form nitrogen; c, a typical synthesized diamond (type lb).

In the early 1950s four of us (H. P. B., F. P. B., H. M. S. and R. H. W.), together with H. T. Hall, developed an approach to diamond synthesis at high pressures and temperatures. The pressure scale used in our experiments was Bridgman's 'resistance-jump' scale, which was suspected to be in error in absolute terms above 30 kbar or so. The proximity of our experimental conditions to the calculated graphite-diamond phase boundary was therefore uncertain

The run 151 diamond appeared in an experiment using apparatus made of hard steel. According to the Bridgman 'resistance' scale, the pressure in this run was about 53 kbar, within the diamond stability field3. But later developments revealed that the true pressure could not have been much above 42 kbar, which is insufficient to stabilize diamond.

To investigate the true nature of the run 151 diamond, we recently removed it from the GE archives, cleaned it with acids and rinsed it with water. An infrared absorption spectrum was measured using an IR PLAN microscope attached to a Nicolet 740 FTIR spectrometer. The portion of this spectrum shown in the figure resembles that of a natural nitrogen-containing type Ia diamond<sup>4</sup>. In particular, there are coincidences of the absorption bands at about 1,365 cm<sup>-1</sup> (related to nitrogen platelets), 1.330 cm<sup>-1</sup> (a Raman frequency, rendered infrared-active by defects and impurities), 1,280 cm<sup>-1</sup> (from nitrogen in the 'A' aggregate form) and 1,175 cm<sup>-1</sup> (from nitrogen in the 'B' aggregate form). We also show the spectrum of a typical nitrogen-containing synthetic type Ib diamond, which has characteristic bands at 1.130 and 1.343 cm<sup>-1</sup> (ref. 5); neither of these bands is seen in the run 151 diamond. We conclude that the run 151 diamond is a small piece of a natural type Ia diamond.

How the natural diamond got into the run 151 experiment is not clear, although it came to light only a week later, when the iron pellet from the run was being polished for metallographic examination. After we found this diamond and took it to be synthetic, Hall used a similar synthetic system of iron/iron sulphide/graphite in his 'belt' apparatus, which used a carbide piston and cylinder to achieve high

#### **Galaxies and magnetic fields**

spiral galaxies constitute one of the most important facts suggesting the existence of large amounts of so-called dark matter in the Universe. However, if the galactic gas could be held in equilibrium by forces other than gravity alone, then an important argument for excess galactic mass would be weakened. Battaner et al.1 suggest that stresses from an azimuthal magnetic field at the peripheries of a galactic disk can provide the confining stress needed. Here we reconsider the large, isolated, astrophysical systems is question of magnetic-field and gas equilibgravity. rium, and point out that the simple success of the one-dimensional Battaner et al. model depends on their incomplete treatment of the three-dimensional equilibrium. Application of the well-known virial theorem shows that the addition of magnetic field to their system would require more dark matter to maintain equilibrium, not less.

The pertinent steady-state virial theorem is2

2 
$$(T + T_i) + M + \int_{V_i} d^3 \mathbf{r} x_i F_i = S$$
 (1)

where  $T = \int_{v} d^{3}r \rho v^{2}/2$  is the sum of directed kinetic energies;  $T_t = \int_v d^3 \mathbf{r} \rho \langle u^2 \rangle /$ 2 is the sum of thermal or random kinetic energies;  $M = \int d^3 r B^2 / 8\pi$  is the total magnetic field energy, and  $F_i$  is the force of gravity.  $S = \int_{S} dS_k x_i \{-p\delta_{ik} + M_{ik}\}$  is the surface stress integral, with p the particle But, from the more general virial rela-

pressures6. This led to further successful runs and ultimately to the development of the process for synthesizing diamonds at high pressures and temperatures from graphite reacted with molten group VIII metals and alloys, which we described fully in 1959<sup>2</sup> (after a US Department of Defense secrecy order had been lifted). Our mistake was therefore clearly a most serendipitous one, as it provided the impetus to experiment with that system at higher pressures, leading quickly to the "right" and "reproducible" results. H. P. Bovenkerk

F. P. Bundy

R. M. Chrenko

P.J. Codella

H. M. Strong

#### R. H. Wentorf Jr

GE Corporate Research and Development, Schenectady. New York 12301, USA

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Applying equation (1) to the specific situation addressed by Battaner et al., we first consider the case in which magnetic field stresses can be neglected  $(M \approx 0)$ . Focusing only on the super-keplerian gas - treating it as an isolated system immersed in external gravity --- it is clear that virial equilibrium requires a dynamical balance between the expansive tendency of the gas motions and the confining influence of gravity acting on that gas. The need for dark matter is already encapsulated in this analysis.

Now, with everything else unchanged, assume that the gas is magnetized. According to Battaner et al., assuming a special field configuration, the magnetic stresses should take up some of the expansive tendency of the gas motion, so that the strength of gravity needed diminishes.

### **Diamond: stability, elastic properties**











### ALBERT FRANCIS BIRCH 1903-1992

JOURNAL OF GEOPHYSICAL RESEARCH

VOLUME 57, No. 2

#### JUNE, 1952

#### ELASTICITY AND CONSTITUTION OF THE EARTH'S INTERIOR\*

#### By FRANCIS BIRCH

Harvard University, Cambridge, Massachusetts

(Received January 18, 1952)

#### ABSTRACT

The observed variation of the seismic velocities with depth, below the crust, is examined with reference to the variation to be expected in a homogeneous medium. A general equation is derived for the variation of the quantity,  $\phi = V_P^2 - 4/3 V_S^2$ , in a homogeneous gravitating layer with an arbitrary gradient of temperature. The parameters of this equation are then discussed in terms of the experimental and theoretical relations for solids. The principal parameter is  $(\partial K_T / \partial P)_T$ , the rate of change of isothermal incompressibility with pressure, which can be found for large compressions from Bridgman's measurements. Comparison of observed and expected rates of variation of  $\phi$  throughout the Earth's interior leads to conclusions regarding homogeneity and, with a larger uncertainty, to estimates of temperature.









## Dense silica























**CO**<sub>2</sub>



SiO<sub>2</sub>



TiO<sub>2</sub>







### Quartz-like CO<sub>2</sub> (Iota, Yoo, Cynn, 1999)



## Эволюция кристаллической структуры SiO<sub>2</sub> при высоком давлении


#### Фазовый переход в перовските $MgSiO_3$ при P $\approx 100$ ГПа



The unit cell structures of MgSiO<sub>3</sub>. a) Perovskite; b) postperovskite.





## **Iron EOS** (Dubrovinsky, Saxena et al., 2000)









Hydrogen, 342 GPa, Narayana et al., 1998



Loubeyre et al. Nature,416,613,2002





### Goncharov et al., 2003



H<sub>2</sub> - melting curve

Temperature dependence of the H<sub>2</sub> vibron frequency at high pressure

## Полимеризованный азот









# **Semiconducting Nitrogen**

(Eremetz et al., 2001)



#### **Ordinary Ice (Ice I)**

#### Ice VII, 2GPa

## **Transformations in Ice**

#### (after Hemley and Ashcroft, 1998)





#### Ice X, 60 GPa

Ice X

## **Pairing in dense lithium**

Neaton & Ashcroft, 1999



## New high –pressure phases of lithium Hanfland, Syassen, Christensen, Novikov, 2000







# Sodium (Na)

(Neaton, Ashcroft, 2000)

# Rubidium (Rb)-

(Schwartz, Crzechnik, Syassen, Loa, Hanfland, 1999)







### Фазовая диаграмма Na



Разнообразие кристаллических структур Na при высоких давлениях



oP8

b

в

cl16







## Прозрачный натрий







124 GPa

120 GPa





# **Graphite at High Pressure**





# Raman spectra of graphite single crystal



Light can be seen through graphite single crystal at pressure ~ 20 GPa

#### Structures of graphite and amorphous carbon

Goncharov, Makarenko, Stishov, 1989

QuickTime<sup>™</sup> and a YUV420 codec decompressor are needed to see this picture.

## van der Waals compounds



He(N<sub>2</sub>)<sub>11</sub>,  $P \sim 8.9$  GPa (Vos et al., 1992)







## **Phase transition in Liquid Selenium (!?)**

Brazhkin, Popova, Voloshin, 1989, Endo et al., 1987



## Phase transition in liquid carbon





Glosli, Ree, 1998

**First-Principle Calculations of the carbon compression isotherm at 6000 K (Wu, Glosli, Galli, and Ree, 2002)** 









## **Xe metallization**

(Eremetz et al., 2000)











Pressure (GPa)



# Superconductivity of lithium, (Shimizu et al, 2002)





### Superconductivity in lithium (Deemyad & Schilling, 2003)





### Superconductivity in Boron-doped Diamond (HPPI & LANL, 2003)







## Classical and quantum phase transitions (Coleman, 2001)



Hertz theory (Hertz, 1976)

Space and time electronelectron correlations in magnetic metals

Si et al. results for  $CeCu_6$  (2001)



UGe<sub>2</sub> (Saxena, 2000)



#### **Inelastic neutron scattering in Fe**





Klotz, Braden, 2000

#### **Raman Scattering in Fe**



Merkel, Goncharov et al. 2000


## **Nuclear Inelastic Resonant X-ray Scattering in Fe**



Mao, Xu, Struzhkin, 2001



## Институт физики высоких давлений РАН им. Л.Ф. Верещагина

## (<u>основан в 1958)</u>





