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NSC KIPT NAS of Ukraine, Kharkiv (3)

IMP NAS of Ukraine, Kyiv (1)

Controlling the material properties under extreme conditions and in the vicinity of phase transitions

CYCLE OF WORKS FOR THE STATE PRIZE OF UKRAINE IN SCIENCE AND TECHNOLOGY IN 2020

APPLIED BY THE ACADEMIC COUNCIL OF
IVAN FRANKO NATIONAL UNIVERSITY OF LVIV
January 29, 2020

PUBLICATIONS

Overall **185** publications:

- **11** monographs;
- **2** review articles,
- **164** journal articles with impact factor
- 2 popular-science articles.

Citations/h-index:

- ✓ Web of Science – 2026/23,
- ✓ Scopus – 2130/23,
- ✓ Google Scholar – 2966/27
- ✓ Defended dissertations on the research topic:

6 Doctor of Sciences and **23** Ph.D.

PARTICIPANTS FROM LVIV

- Plevachuk Yuriy, born in 1958, doctor of physical and mathematical sciences, senior researcher, head of Research and Development department of Ivan Franko National University of Lviv
- Sklyarchuk Vasyl, born in 1959, doctor of physical and mathematical sciences, senior researcher of Ivan Franko National University of Lviv
- Bryk Taras, born in 1963, doctor of physical and mathematical sciences, Research Deputy Director of the Institute for Condensed Matter Physics
- Kozlovskii Mykhailo, born in 1952, doctor of physical and mathematical sciences, professor of the Institute for Condensed Matter Physics

PARTICIPANTS FROM NSC "KIPT" (KHARKIV)

- Peletminskii Oleksandr, born in 1975, Ph.D. in phys. and math. sci., senior researcher, senior staff scientist
- Slyusarenko Yurii, born in 1957, Dr.Sci. in phys. and math. sci., professor, Academician of NASU, head of department
- Sotnikov Andrii, born in 1983, Ph.D. in phys. and math. sci., senior researcher, senior staff scientist

PARTICIPANT FROM IMP (KYIV)

- Rud Oleksandr, born in 1958, Dr.Sci. in phys. and math. sci., professor, head of department in IMP NAS of Ukraine

Controlling the material properties under extreme conditions and in the vicinity of phase transitions

- The aim of the work is to describe and analyze the phase states, which arise in materials under extreme conditions and demonstrate new and unusual properties in order to obtain new knowledge about materials and their possible application in qualitatively new technologies of the future.
- The work cycle covers an intercompatible study of different types of phase transitions in complex physical systems, in wide ranges of control parameters such as temperature, pressure and external field.

The novelty and reliability of the results are based on the complex nature of the research, which combines the three main methods of knowledge of physical phenomena: :

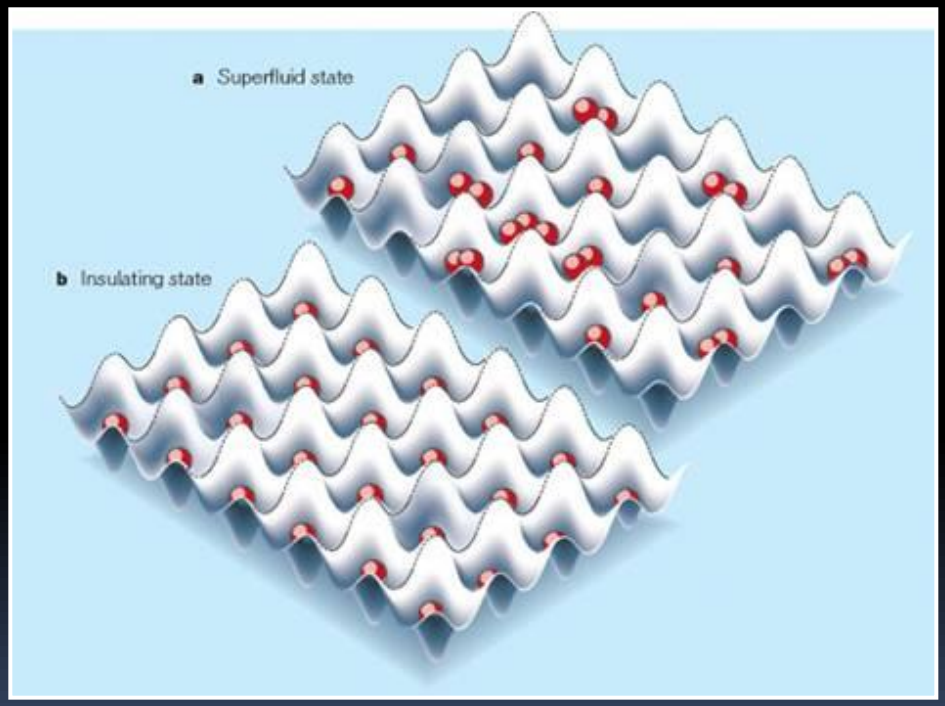
- microscopic theories,
- techniques of first-principle computer modeling,
- precision experimental research in extreme thermodynamic conditions in domestic and foreign laboratories.

Controlling the material properties under extreme conditions and in the vicinity of phase transitions

- The methods of research proposed and implemented by the authors allowed to combine a number of important results both fundamental and applied in the field of research objects such as magnetic systems, including high-density systems, composed of alkali metal atoms in a wide range of temperature and pressure changes (from ultra-cold vapor to metals) and under the influence of an external electromagnetic field, systems based on tellurium and selenium at different temperatures and concentrations.
- The research opens the prospects for using the obtained results in metallurgy, instrumentation and engineering, space technology, for development of a number of new composite materials of special purpose: anti-friction wear-resistant, electrical, magnetic; with the development of atomic lasers, supersensitive optical switches, devices for focusing and energy storage in solar panels in dark weather, and also for controlling the group speed of the light in a Bose condensate by means of an external magnetic field.

Theory of spatially-periodic states in Bose-Einstein condensate (BEC)

- ✓ Periodic phases in BEC are obtained and investigated (analog of the superfluid crystal)



- A.S. Peletminskii, S.V. Peletminskii, and Yu.V. Slyusarenko, Laser Phys., 2002, Vol. 12, No.1 p. 162-185.
- A.S. Peletminskii, S.V. Peletminskii, and Yu.V. Slyusarenko, Theor. Math. Phys., 2000, Vol. 125, No.1, p. 1431-1452; doi: 10.1007/BF02551046.

Ultaslow-light phenomenon

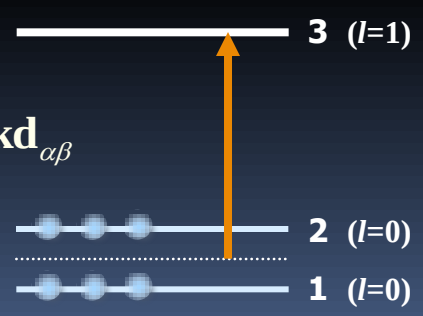
$$\epsilon^{-1}(\mathbf{k},\omega) = 1 + \frac{g}{2\pi^2 k^2} \sum_{\alpha\beta} \left|\sigma_{\alpha\beta}(\mathbf{k})\right|^2 \frac{n_\alpha - n_\beta}{\omega - \Delta\varepsilon_{\beta\alpha} + i\gamma_{\beta\alpha}}$$

$$v_g = \frac{c}{n + \omega \cdot \partial n / \partial \omega}$$

$$n \approx \sqrt{\epsilon}$$

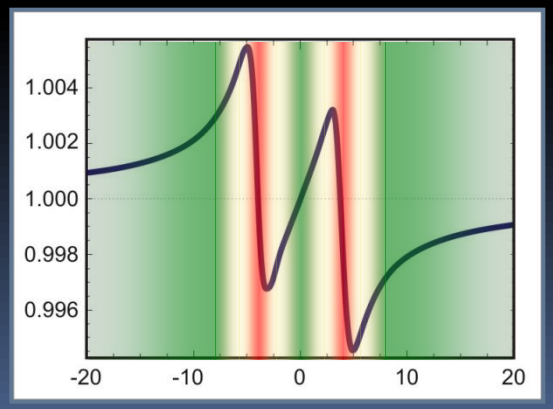
The optical pulses can be slowed in the regions of high transparency and strong dispersion (close to resonances) down to $v_g \sim 300$ m/s

3-level system

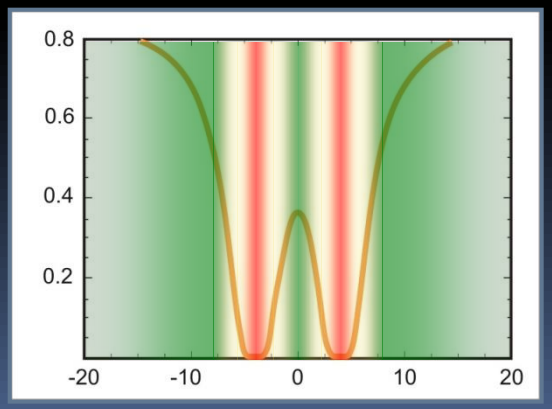


$$\sigma_{\alpha\beta}(\mathbf{k}) \approx i\mathbf{k}\mathbf{d}_{\alpha\beta}$$

Refractive index

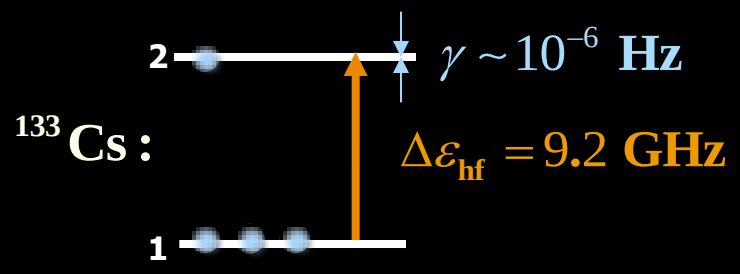


Transmitted light



- Yu. Slyusarenko and A. Sotnikov. Physical Review A **78**, 053622 (2008)

Slowing of microwave radiation

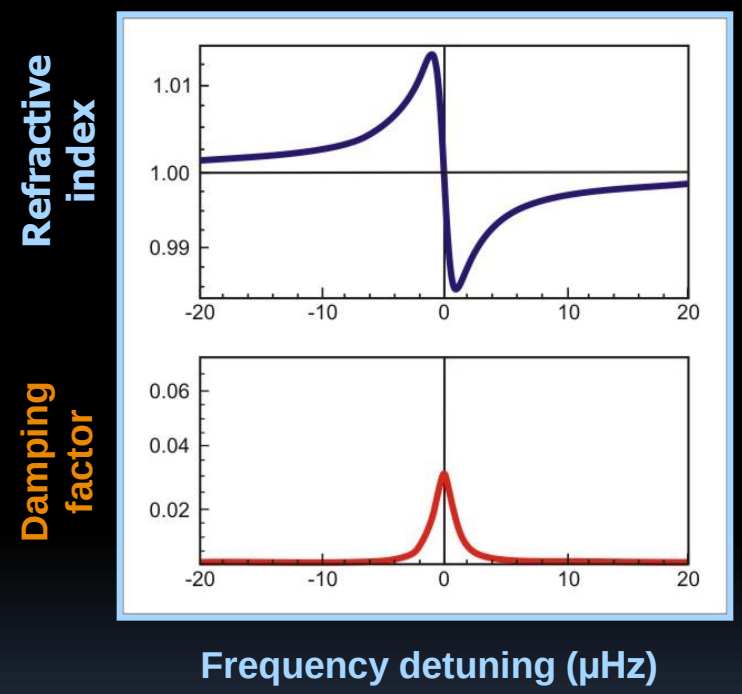


$$10^{-3}\ \text{cm}^{-3} << |n_1 - n_2| << 10^{16}\ \text{cm}^{-3}$$

Cesium atoms in the BEC state with the density $n_1 = 1.3 \cdot 10^{13}\ \text{см}^{-3}$

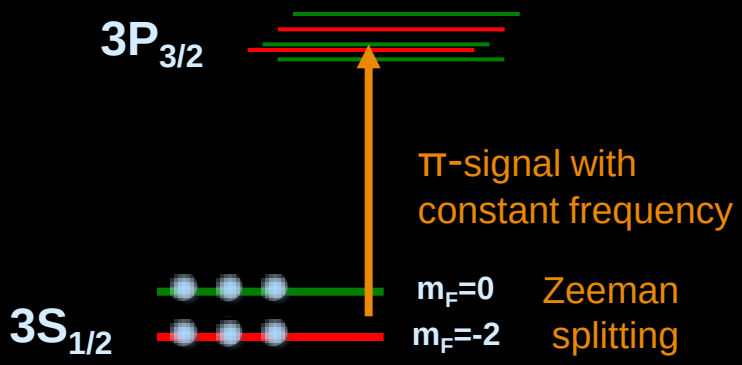
Group velocity of the pulses:

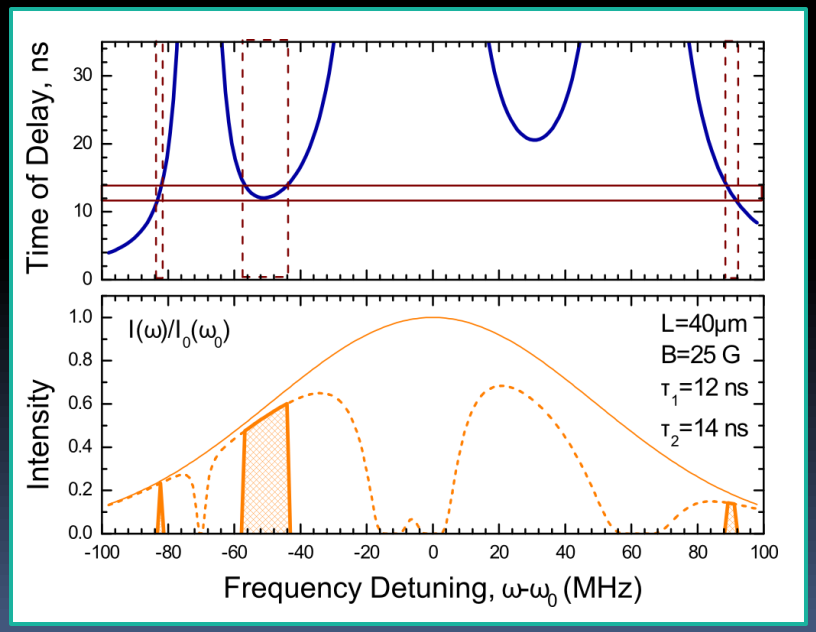
$$v_g \approx 0,06\ \text{cm/s}$$

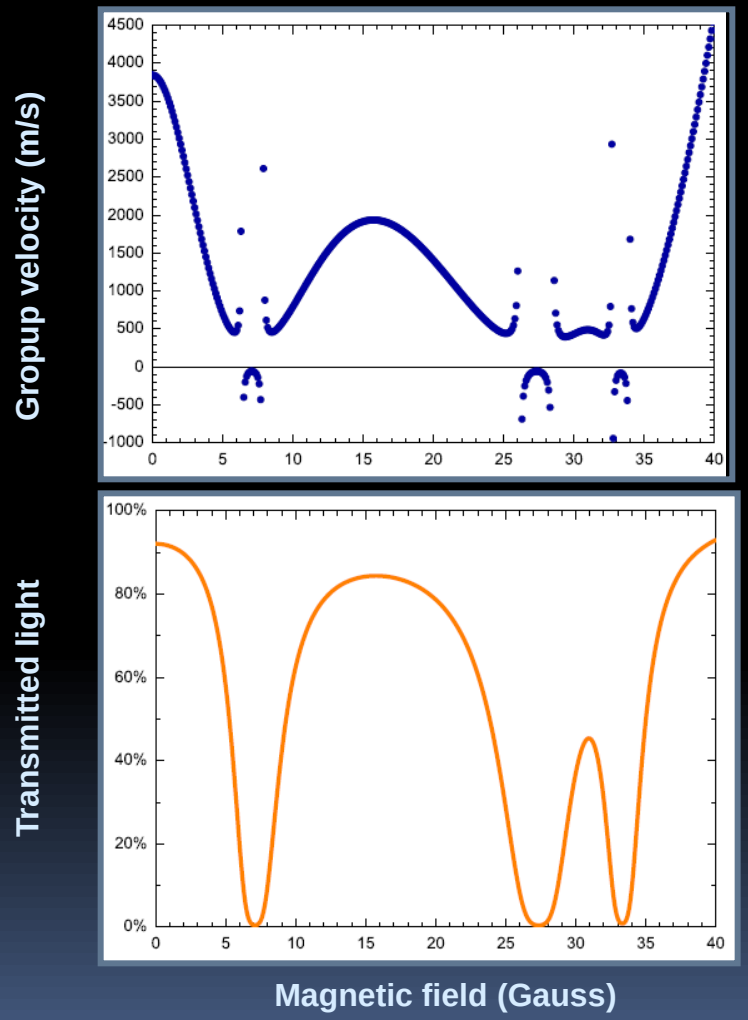


- **Yu.V. Slyusarenko, A.G. Sotnikov.**
  Journal of Low Temperature Physics 2008, V.150, N.3/4

Controlling of the light velocity by an external magnetic field and filtering of pulses

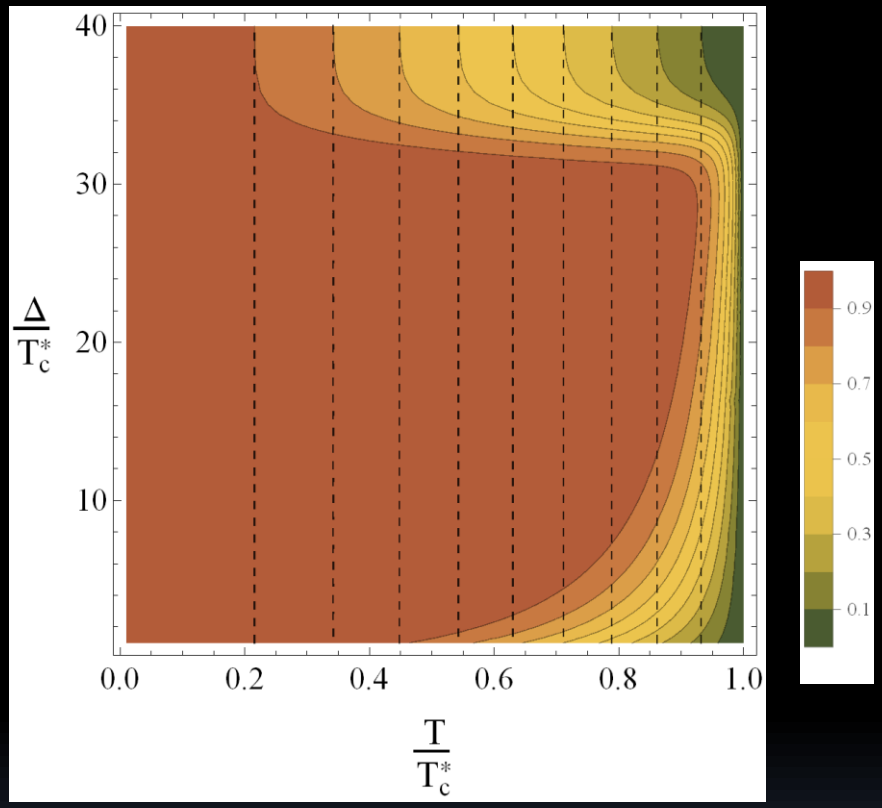






- Yu. Slyusarenko and A. Sotnikov. Phys. Lett. A, 2009, Vol. 373, p. 1392-1395.
- Yu.V. Slyusarenko, A.G. Sotnikov, Low Temperature Physics, 2010, V.36 p.671

BEC of photons and their fraction in the condensate



$$n_{ph}^{0}\ T \approx n_{ph}\left\{1-\left(\frac{T}{T_c^*}\right)^{3/2}\exp\left[-\Delta\left(\frac{1}{T}-\frac{1}{T_c^*}\right)\right]\right\}$$

Density of the atomic BEC

$$n_{\alpha_1}^{0}\ T \approx n\left\{1-\left(\frac{T}{T_c}\right)^{3/2}\right\},$$

$$T_c^* \approx T_c$$

“Avalanche”-condensation regime

- Yu. Slyusarenko, A. Kruchkov, Phys. Rev. A, 2013, Vol.88, No.5, 013615.
- N.P. Boychenko, Yu.V. Slyusarenko, Cond. Matter Phys., 2015, Vol. 18, 43002.

“Stopped light”

$$v_g \equiv \left(\frac{d\omega(k)}{dk} \right)_{k=0} = 0$$

Due to “avalanche” condensation of almost all photons below critical temperature, and because the group velocity is zero for condensed photons, this regime can be viewed as “the stopped light”.

In addition, the regimes of inverse occupation of atomic levels by the temperature lowering (without employing artificial electromagnetically-induced transparency) are suggested.

Atomic and photonic BEC for the everyday human needs

Slowing of electromagnetic pulses

Pulse is not distorted

(the intensity is reduced only)

- Nonlinear optics: creation of extremely sensitive optical switches (due to low laser power)
- Data storage (?)
- Sensitive detectors of magnetic fields (group velocity strongly depends on the atomic spectrum)
- Quantum information devices (?)
- Filters for electromagnetic pulses

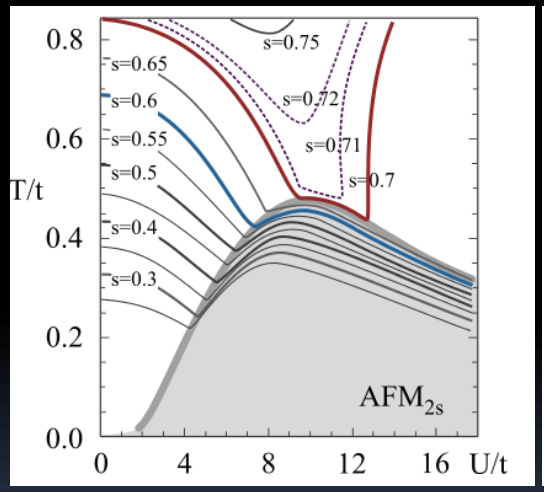
Stopping of electromagnetic pulses

- Creation of new laser sources
- Focusing and accumulating of the solar energy in cloudy weather

Quantum magnetism of three-component fermionic mixtures in optical lattices

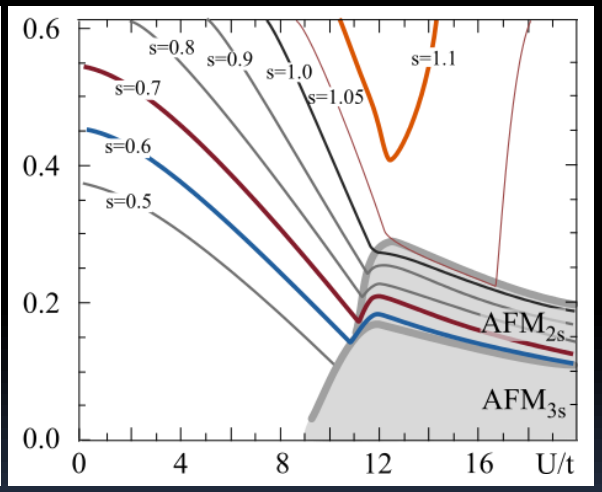
- ✓ The finite-temperature phase diagram is obtained for the first time;
- ✓ Thermodynamic properties of phases and transitions are comprehensively investigated;
- ✓ Crucial advantages of these mixtures for approaching magnetic ordering are pointed out (higher entropy).

Two-component mixture



Magnetism is beyond the reach at S>0.7Nk$_B$ (experimental situation)

Three-component mixture



Magnetism is within the reach at S>0.7Nk$_B$ (experimental situation)

Experimental realization of samples

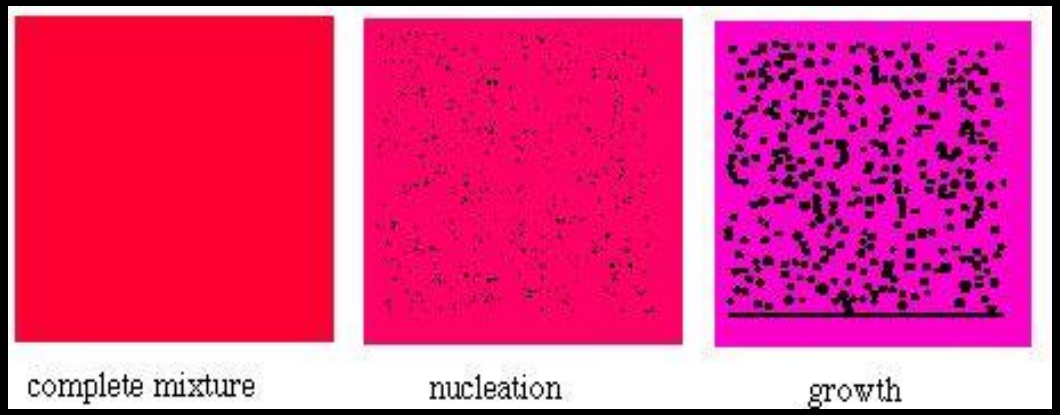
Application as universal quantum simulators

High-Tc super-conductivity

- ➢ A. Sotnikov, Physical Review A **92**, 023633 (2015).

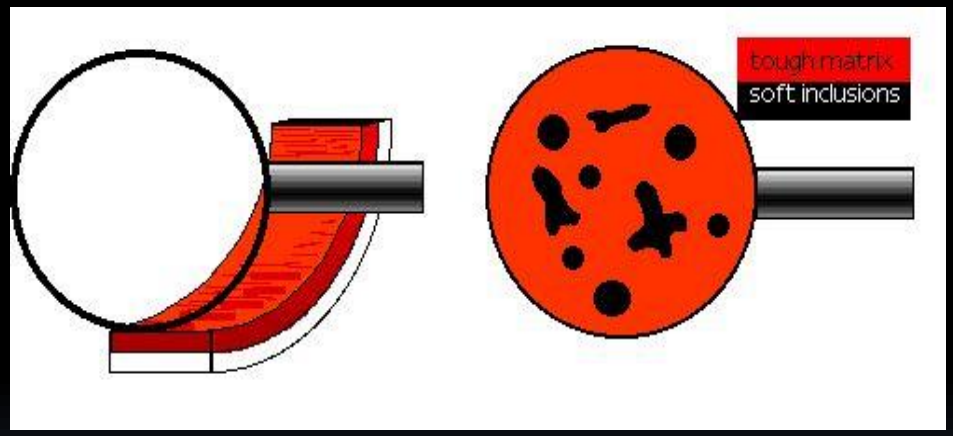
The monothectic systems studied are promising materials for finely dispersed mixtures

- **Self-lubricated bearings in car engines (Cu-Sn-Pb, Al-Pb, Al-Bi, Al-Si-Pb, Al-Si-Bi)**
- **Composite superconductors (Cu-V)**
- **Granular GMR (Cu-Co)**
- **Smelting of Ag (Ag-Pb-Zn)**
- **Electrical contacts and switches (Ni-Ag)**



Production problems:

- **Rapid phase separation prevents the production of finely dispersed mixtures with the prospect of practical application**
- **High temperatures**



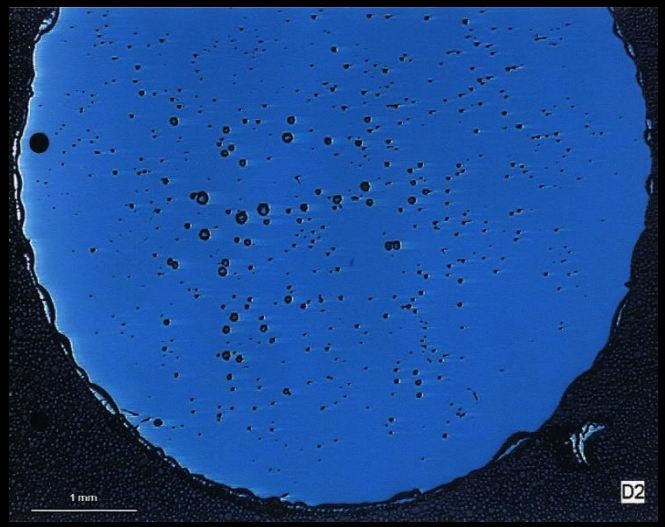
Causes of rapid phase separation:

- **gravity-dependent sedimentation**
- **Marangoni convection etc.**

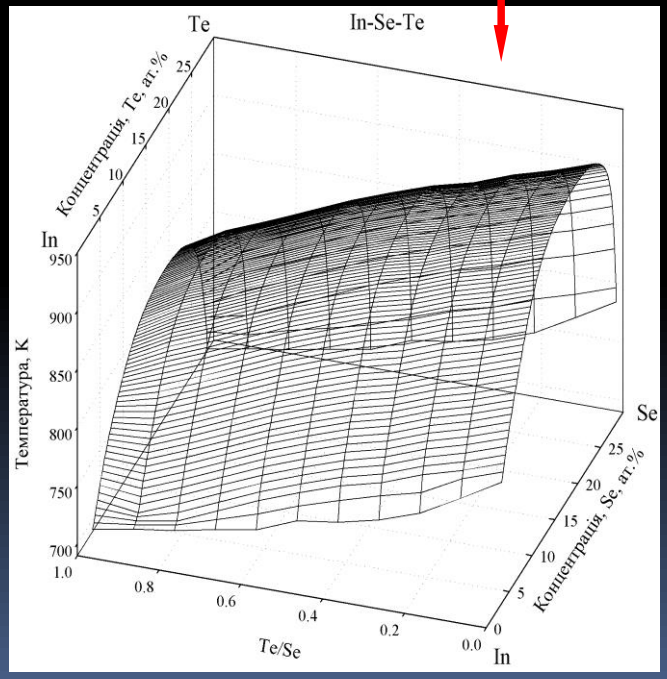
Important information about the effect of thermocapillary convection on the process of phase separation in metal melts under microgravity conditions, was obtained. The formation of the dispersed melt structure was studied and the density of the droplet flow of one of the phases was calculated along the other matrix, and also the temperature and temperature dependences of this process were investigated.

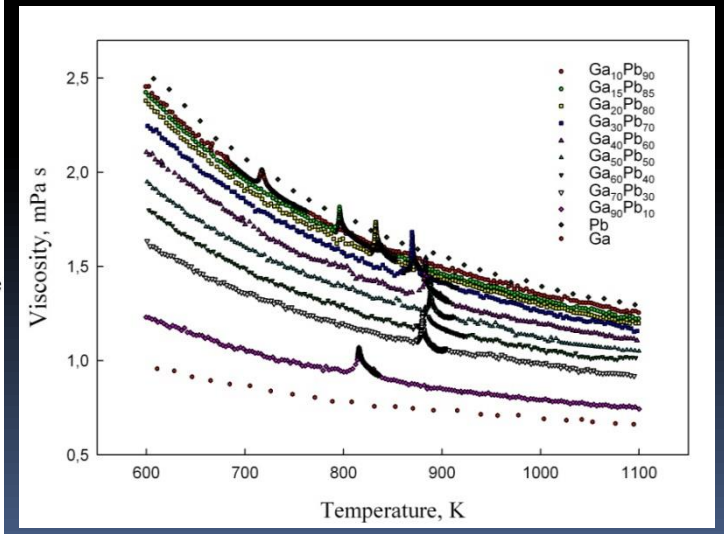
Investigation of critical phenomena in monotectic systems in laboratory conditions and in space

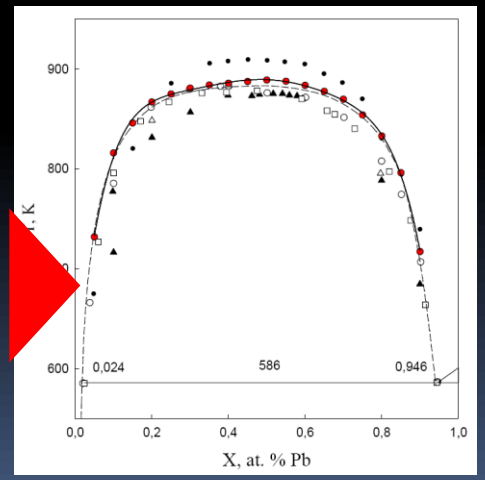
Marangoni convection
Critical parameters
Nucleation



Determination of separation surfaces in liquid-liquid phases







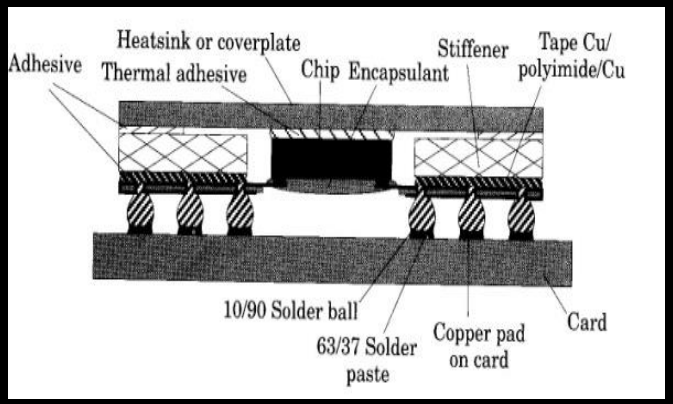
Determination of binodal lines, based on the electrical conductivity and viscosity data

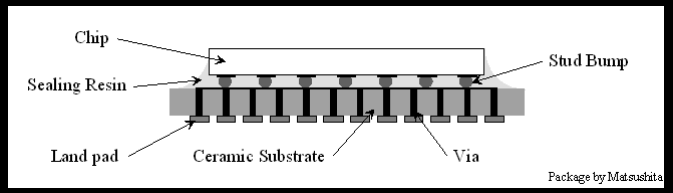
New materials for lead-free solders

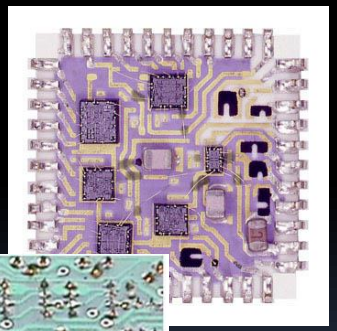
- **The Association Agreement between Ukraine and the EU allows the transition to economic integration, which involves transition to European standards.**

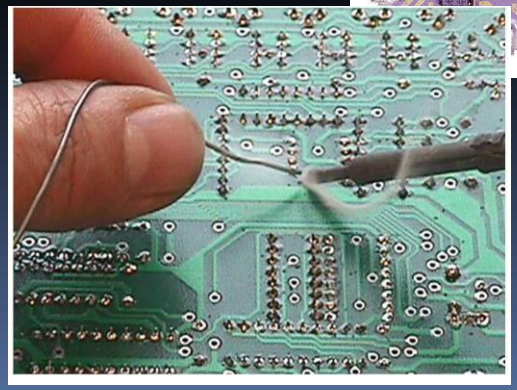
- This means that according to the EU and EU Directives (WEEE "Waste Electrical and Electronic Equipment" and 2002/95 / EC "Restriction of the Use of Some Hazardous Substances (RoHS) in Electrical and Electronic Equipment"), the use of lead-free solders instead of traditional Sn-Pb will be mandatory.

- **In this regard, the deployment of domestic production of lead-free solders can be more cost-effective than importing foreign analogues.**

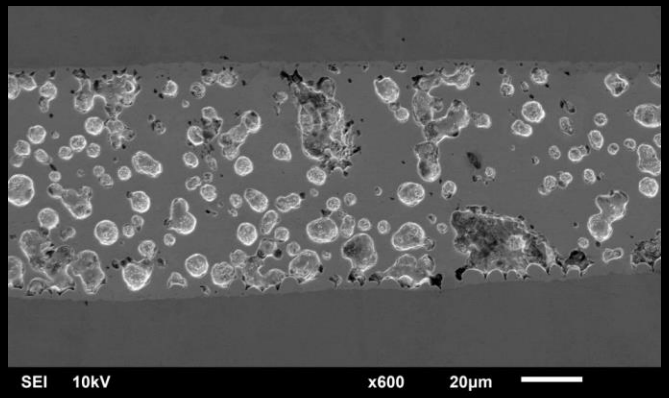








Modification of structurally sensitive properties of materials for production of new lead-free solders by nanoparticles

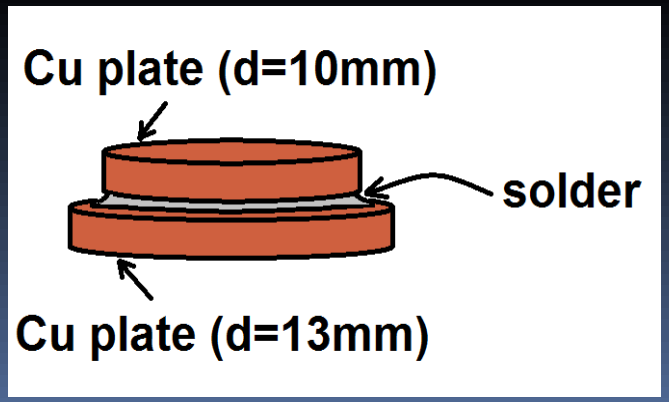


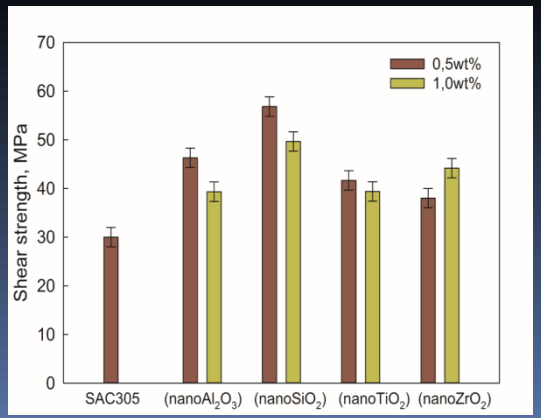
Microstructure (SEM) of soldered joints of SAC305 alloy with admixtures of Al_2O_3 nanoparticles

The purpose: **The methods and technological processes for the implementation of nanoparticles in materials for new lead-free solders based on Sn are proposed. The nanoparticles stabilize the structure of the solder, which undergoes during the crystallization significant modifications under external influences (electric and magnetic fields, temperature gradients, cooling velocities, vibrations), prevent the formation of frictional fissures and the spread of contacts, reduce graininess, and improve wetting of the surface.**

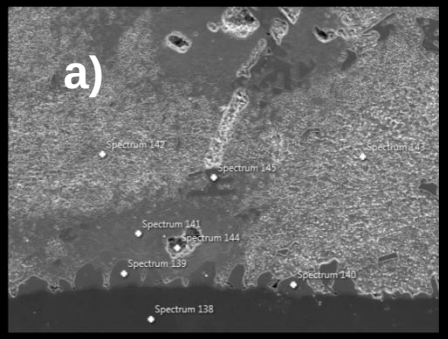
Innovative aspect. **The technology of obtaining materials for solders in the form of thin foil or ribbon of thickness 20-30 μm by the method of fast quenching is used. The shape of these tapes is convenient for soldering wide sections with precisely defined sizes, which is used for soldered joints of large surfaces**

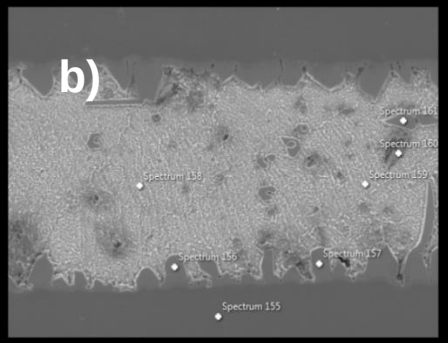
.

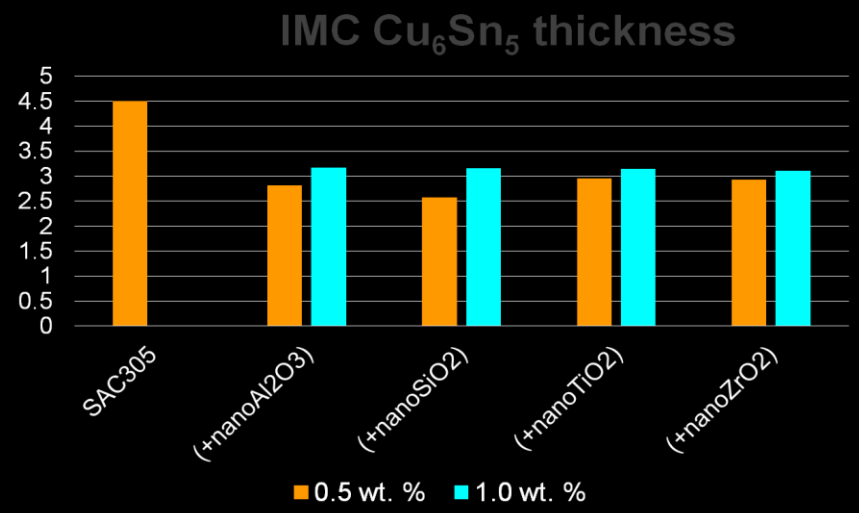




Morphology and growth of the interphase layer of IMCS on solder / Cu border



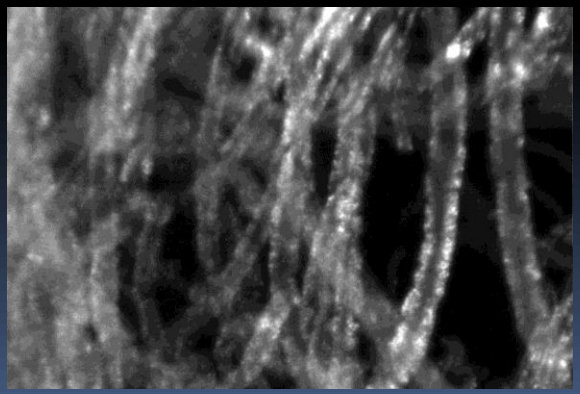




Reduction of intermetallic layers

SEM images (a) SAC387
(b) (SAC387)99.9(nanoCo)0.1

Influence of carbon nanotubes on the physical properties of lead-free solders



carbon nanotubes coated with Au

Addition of carbon nanotubes in certain proportions:

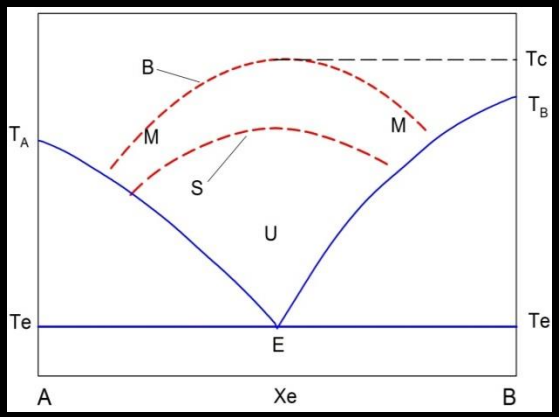
- **Improves mechanical properties (strength, shear resistance, plasticity)**
- **Improves solder solubility of the surface**
- **Does not affect the electrical characteristics**
- **Prevents the formation of intermetallics**

Lead-free soldered nanoparticles are the key to miniaturizing the contacts in electronic devices

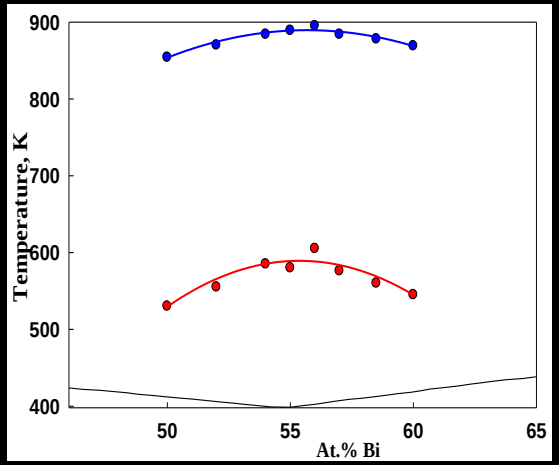
Model of microsegregation

The metastable non-equilibrium quasieutectic structure in the melt

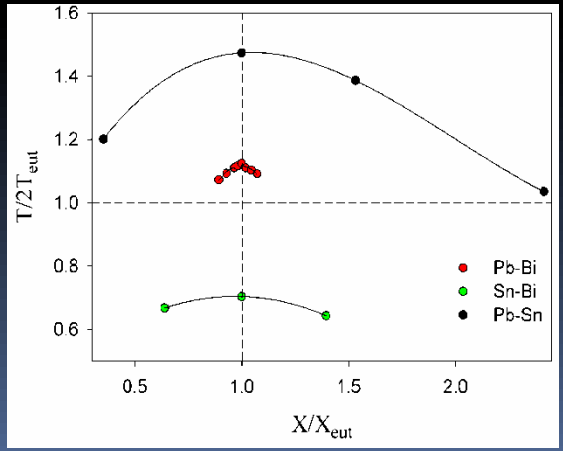
Areas with different thermodynamic stability, which, like in monotectics, are separated by spinodal and binodal lines, and are abnormal concentration fluctuations.



The similarity of systems with monotechics and eutectics with respect to the mechanism of phase decay and crystallization is proved: the systems are not solutions, but the two-phase systems of high dispersion



In monotectic systems, temperature-time regimes regulate the size of particles of one phase in another, which leads to macroscopic separation.



In eutectic systems, as a special case of systems with limited solubility of components, the size of parts of one of the phases, varying in temperature changes, do not reach such sizes as in monotectics, and sedimentation stability persists to the temperature of the beginning of solidification.

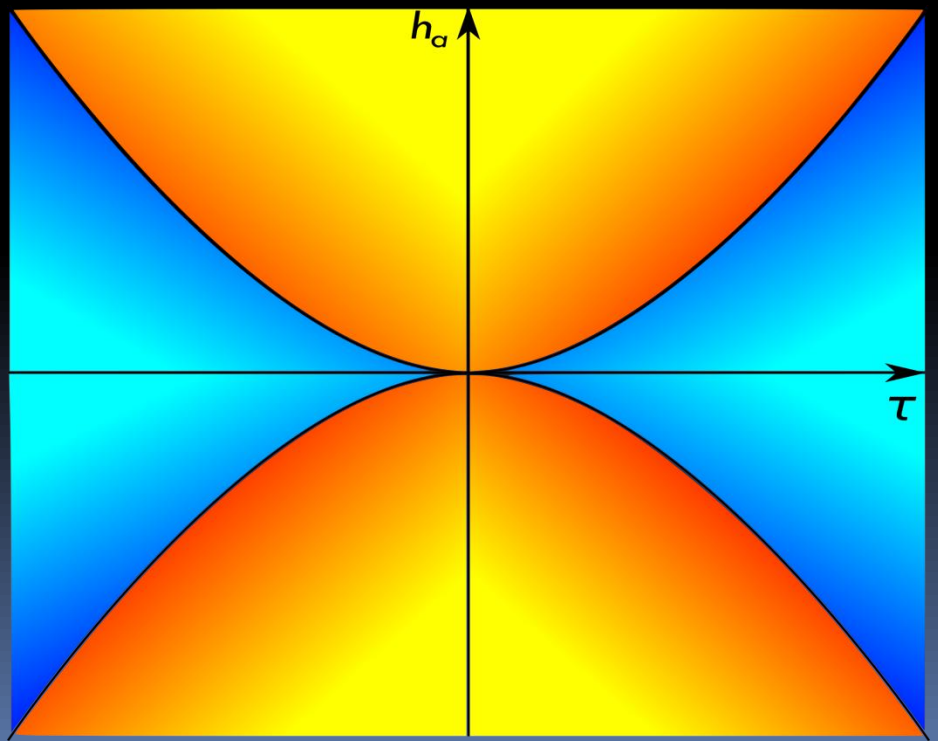
Free energy of the Ising model in the outer field

$$F = F_a + F_s + F_h$$

$$F_a = -kTN\left(\ln chh - F_{02}h^2 + \gamma_0 + \gamma_1\tau + \gamma_2\tau^2\right)$$

$$F_s = -kTN\gamma_s\left(h_a^2 + h_c^2\right)^{\frac{d}{d+2}}$$

$$F_h = -kTN\left[e_0 h_a\left(h_a^2 + h_c^2\right)^{\frac{1}{2(d+2)}} - e_2\left(h_a^2 + h_c^2\right)^{\frac{d}{d+2}}\right]$$



The marginal value of the field

Kozlovskii M.P. Phase Transition (2007).

$$h_c = \tau_a^{\,p_0};\ p_0 = \ln E_1 / \ln E_2 = \delta\beta$$

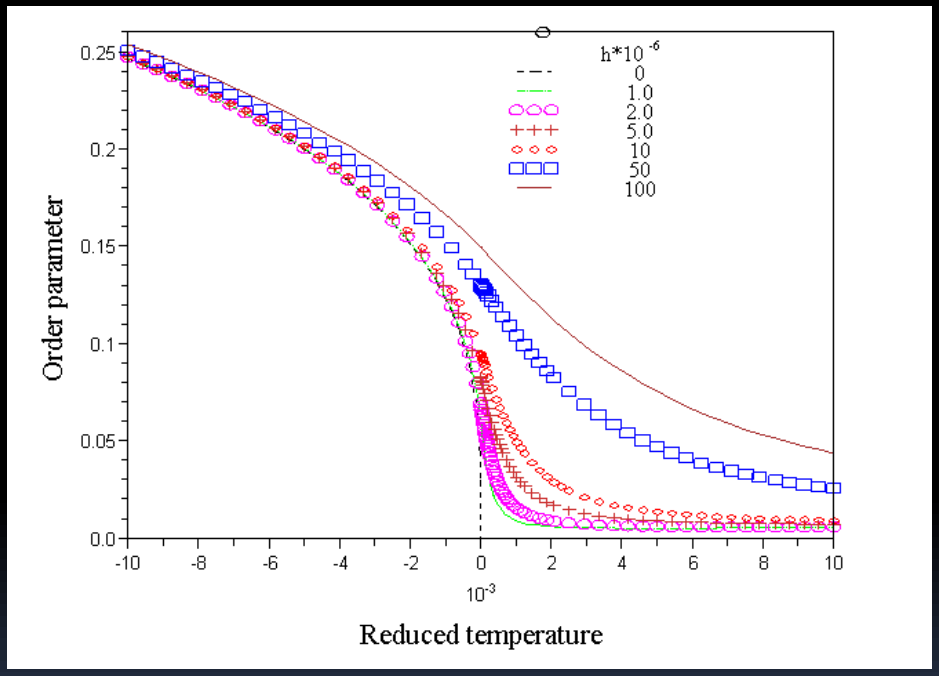
$$\tau_a = \tau\frac{c_{1k}}{f_0};\ \tau = \left(T - T_c\right)/T_c$$

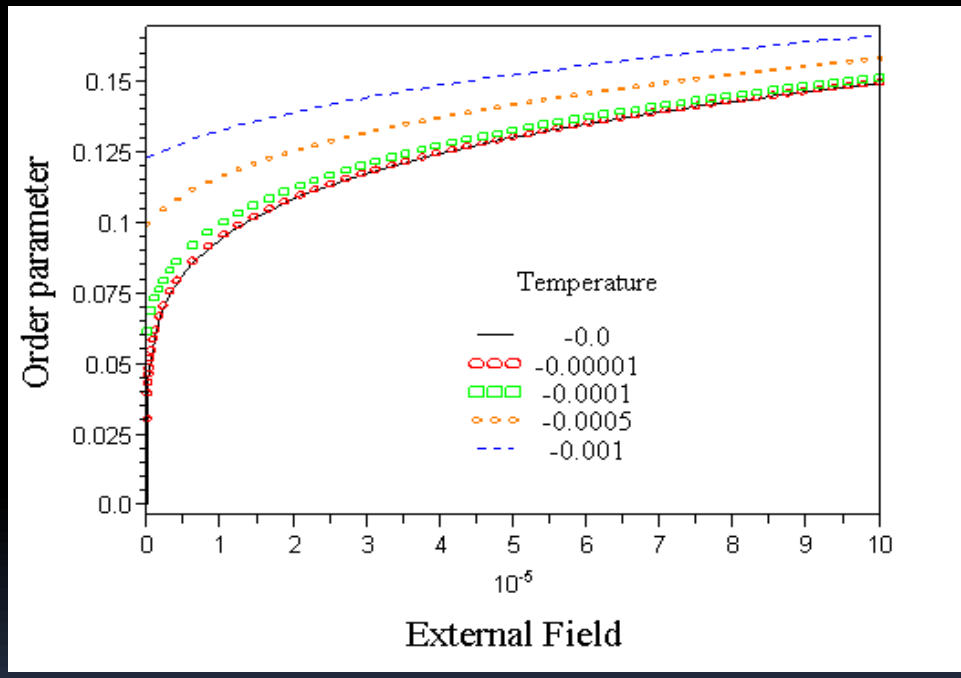
Temperature and field behavior of the order parameter

$$M = -\frac{1}{N}\left(\frac{dF}{d\mathcal{H}}\right)_T = \sigma_{00}(h_a + h_c)^{\frac{1}{\delta}}$$

- crossover form of state equation

In extreme cases

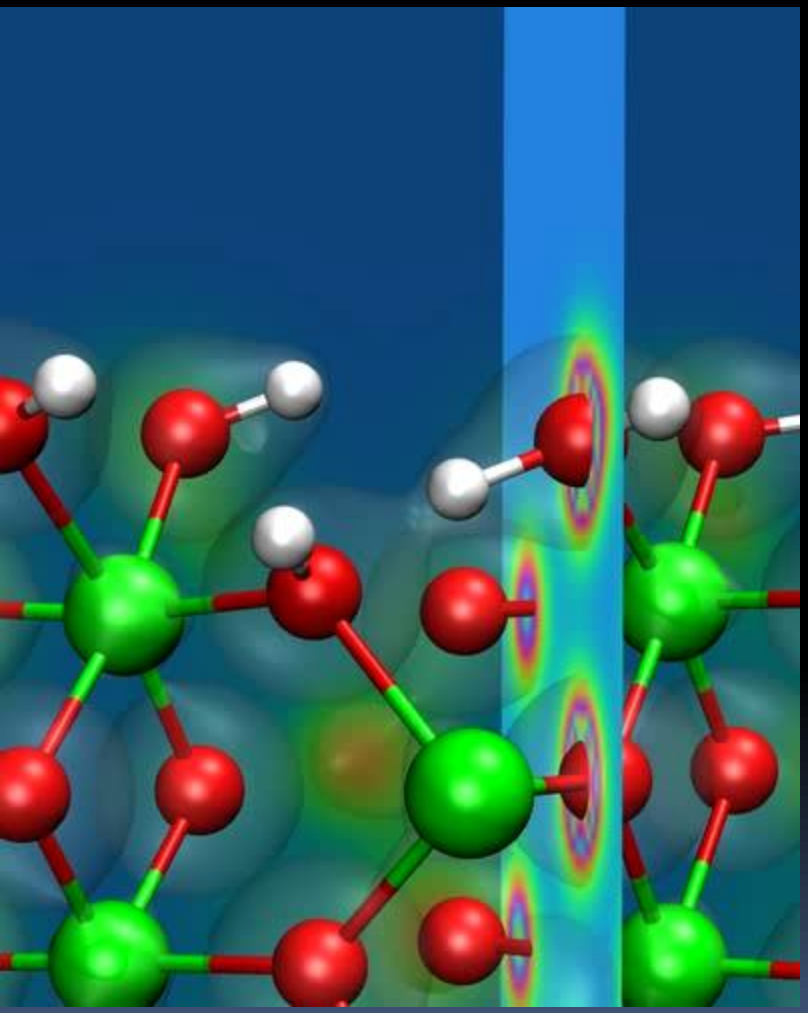




The order parameter of the system as a function of temperature (left) at different values of the field, and as a function of the field (right) for some temperature values

M.Kozlovskii, R.Romanik, JML, 2012

Ab initio моделювання конденсованих систем в екстремальних умовах



- Класичні рівняння руху для N іонів

$$m_i \vec{R}_i(t) = \vec{F}_i(t)$$

реальна маса іонів

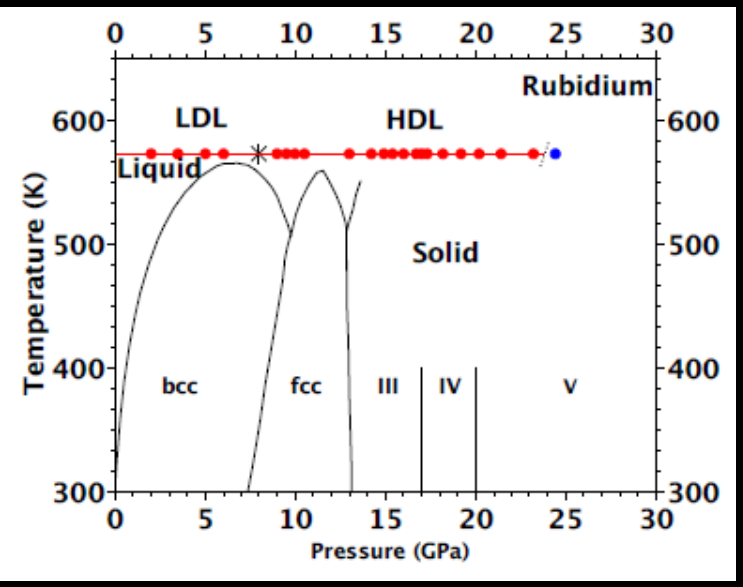
Сили Геллмана-Фейнмана, що діють на іони

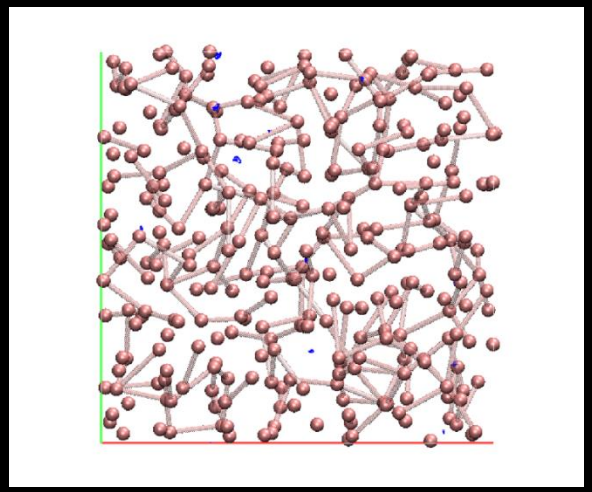
- На кожному часовому кроці розраховується Nz/2 власних функцій гамільтоніану Кона-Шема

$$H = -\frac{\nabla^2}{2} + W(\vec{r},\vec{r}\,') + \int d\vec{r}\,' \frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} + \mu_{xc}(\vec{r},\vec{r}\,')$$

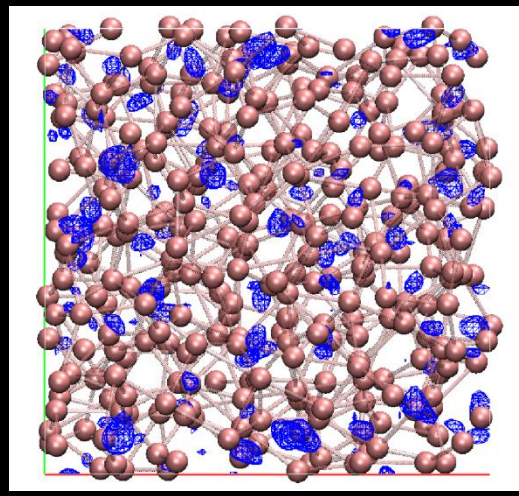
Обмінно-кореляційні ефекти при високих тисках повинні враховувати градієнтні поправки (GGA) : BLYP, PBE, PW91, ……

Розплав Rb: встановлено існування структурного перетворення при P~12 GPa





ELF, 1.2 GPa

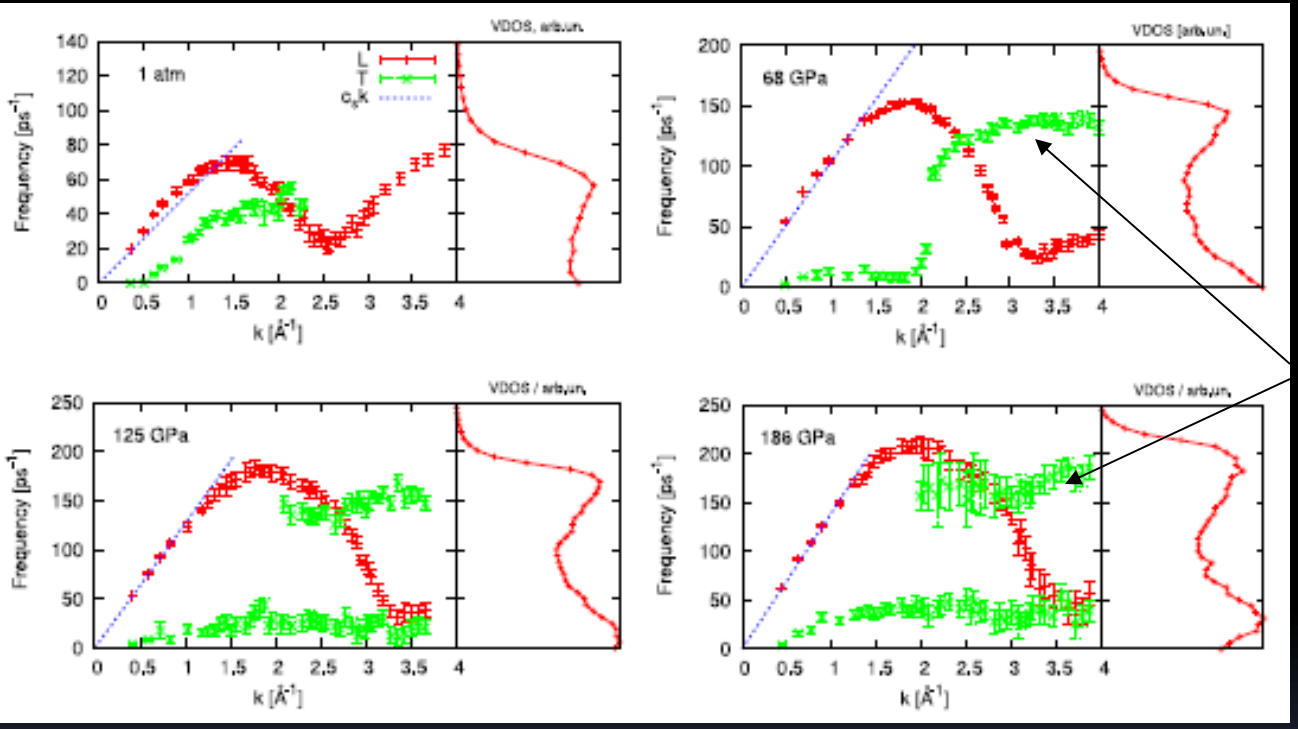


ELF, 27.4 GPa

Існування структурного переходу в розплаві Rb при тисках ~ 12 GPa встановлено з немонотонної поведінки структурних характеристик (парні функції розподілу та структурні фактори) та динамічних величин: дифузії та швидкості поширення звуку. Встановлено появу областей локалізації електронів (electron localization functions - ELF) при високих тисках в розплаві Rb (сині області між іонними остовами).

T.Bryk, S. DePanfilis, F.A.Gorelli, E.Gregoryanz, M.Krisch, G.Ruocco, M.Santoro, T.Scopigno, A.P.Seitsonen. Phys. Rev. Lett. V. 111, 077801 (2013)

Поява екзотичних поперечних мод в розплаві Li при високих тисках

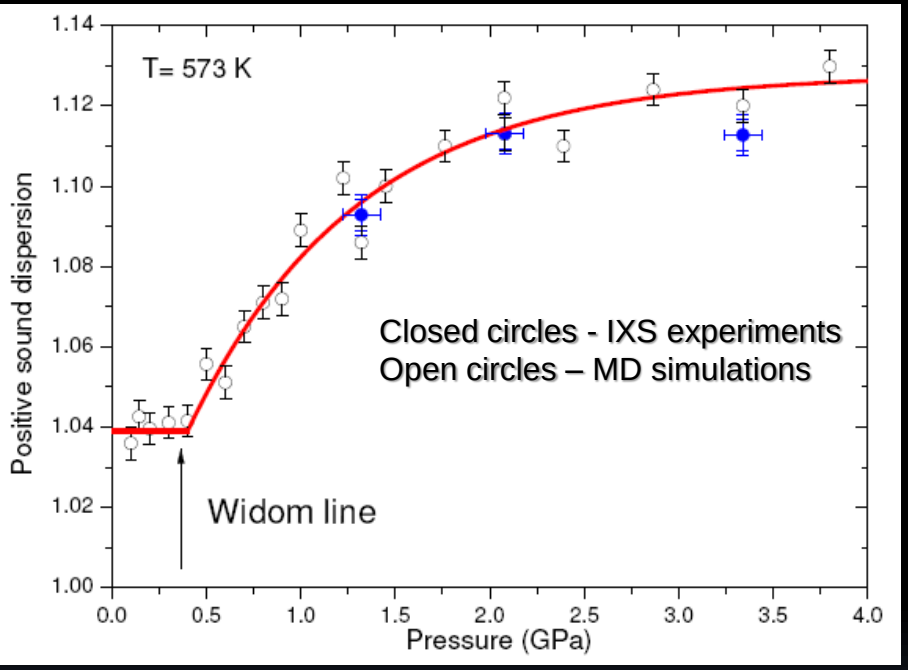


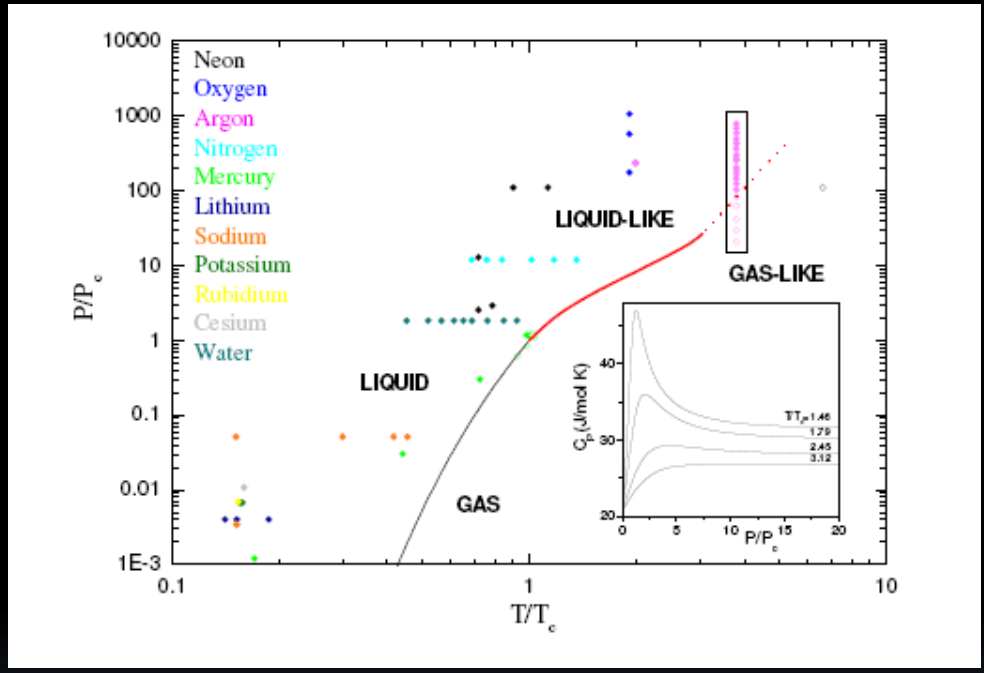
При прикладанні тиску спостерігається ще одна, високочастотна гілка поперечних збуджень, яка існує лише в другій псевдо-зоні Брілюена.

T.Bryk, G.Ruocco, T.Scopigno, A.P.Seitsonen. J. Chem. Phys. V. 143, 104502 (2015)

Існування таких незвичних поперечних мод при високих тисках було підтверджено кількома групами для розплавів Na, Zn, Tl, Fe

Позитивна дисперсія звукових збуджень як критерій поділу надкритичних флюїдів на рідинний та газовий типи





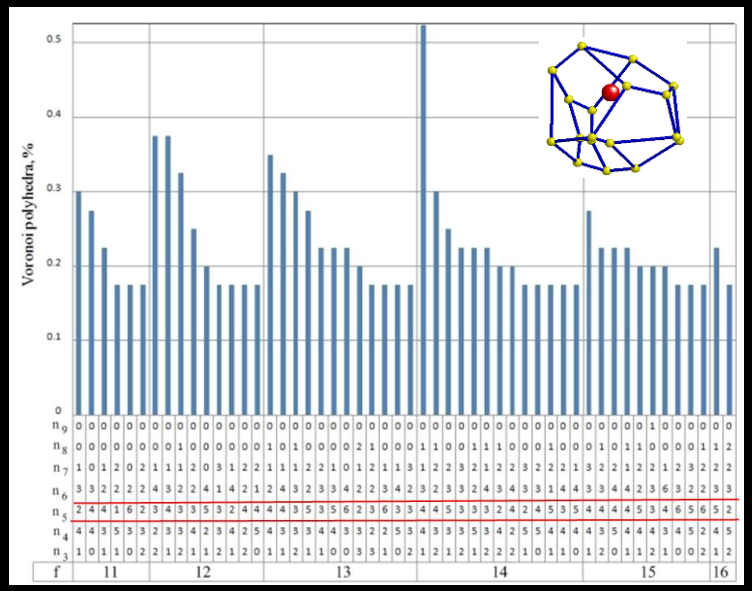
Експерименти по непружному розсіюванні рентгенівських променів та МД моделювання для надкритичного аргону встановили зникнення позитивної дисперсії звукових збуджень в окол лінії Відома.

G.G.Simeoni, T.Bryk, F.A.Gorelli, M.Krisch, G.Ruocco, M.Santoro, T.Scopigno. Nature Phys.V.6, 503 (2010)

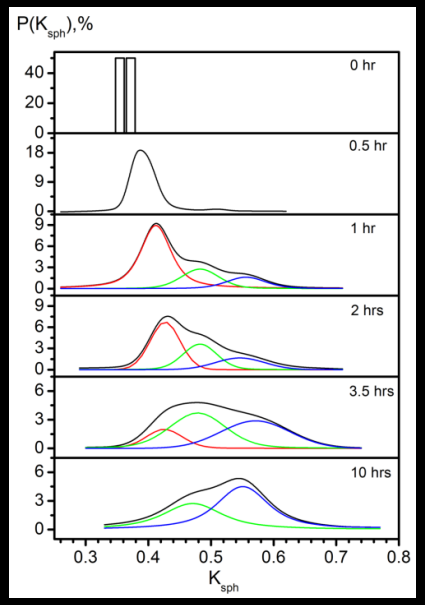
Теорія позитивної дисперсії акустичних збуджень пояснила її залежність від тиску

T.Bryk, I.Mryglod, T.Scopigno, G.Ruocco, F.Gorelli, M.Santoro. J.Chem.Phys. V.133, 024502 (2010)

Evolution of topological characteristics of the local atomic arrangements in the carbon structure at the quasi-continuous transition from crystalline to amorphous state in the course of graphite ball milling

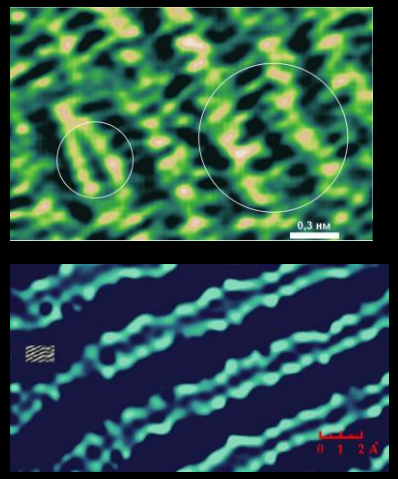


Polyhedral analysis of amorphous carbon synthesized by 10 hrs graphite ball milling (BM); on the insert - typical Voronoi polyhedron (PV)



Distribution of PV sphericity coefficient in BM graphite P(Ksph) (Ksph= $36\pi V^2/S^3$, where V and S are volume and area of PV) (diamond - 0.46; random point system - 0.57)

New local hetero-allotropic structures of carbon



Locally inhomogeneous structure of amorphous carbon (10 hrs BM graphite) (top), and segment of two-layer bi-graphite (bottom)

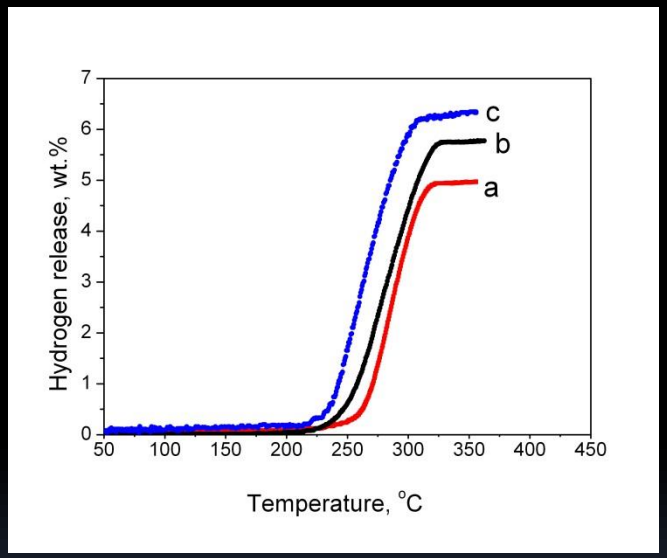
It is proposed to use the peak value of the distribution P (Ksph) as a parameter of the topological short range atomic order in disordered and amorphous materials

A.D. Rud, I.M. Kiryan. J Non Cryst Sol. 386 (2013), 1-7.

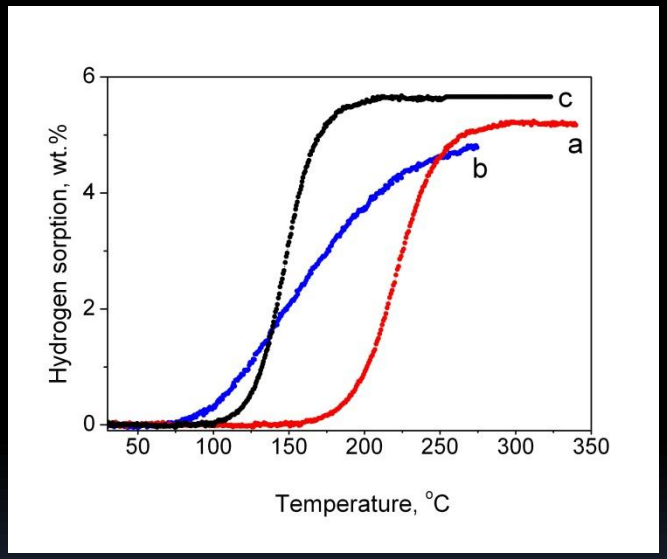
Alexander D. Rud et al. Materials Today: Proceedings, 5 (2018), 26089–26095.

Mg-based hydrogen storage materials

New hydrogen sorption materials have been developed on the basis of magnesium nanocomposites produced by ball milling of Mg with the addition of various allotropes of carbon or MAX-phase Ti_3AlC_2 for the solid state hydrogen storage for using in environmentally-friendly hydrogen economy, which satisfy the DOE requirements - not less than 5% wt. of deposit H_2, sorption temperature up to 150 ºC, ability to reversible sorption-desorption cycles



Hydrogen thermal desorption by the Mg - 7 wt. % Ti_3AlC_2 composite after:
(a) - ball milling in hydrogen,
(b) - the 3rd cycle of hydrogen sorption-desorption,
(c) - the 6th cycle of hydrogen sorption-desorption



Hydrogen sorption by samples:
(a) - Mg;
(b) - Mg - 5 wt. % Ti_3AlC_2;
(c) - Mg - 7 wt. % Ti_3AlC_2

A.D. Rud, A.M. Lakhnik. Int Journal Hydrogen Energy, 2012, 37 (5), 4179-4187.

A.D. Rud, A.M. Lakhnik, V.G. Ivanchenko, et al. Int J Hydrogen Energy, 2008, 33 (4), 1310-1316.