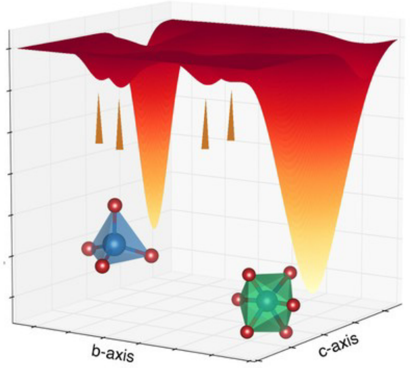
Silica: Multiple Phases, other than a glassy structure

采用同步辐射 X 射线衍射测量和理论建模，发现了科学家们一直努力寻找的 SiO_2 体系中遗失的一环 - 四个五配位的新的二氧化硅相，在相变路径上不同的亚稳定态包含了从四配位、五配位到六配位三种不同的硅氧结构体系，同时也验证了非加热压缩技术可以有效捕捉到相变的中间态，用以揭示硅材料真正的相变机制。

Silicon dioxide, commonly called silica, is one of the most-abundant natural compounds and a major component of the Earth's crust and mantle. It is well-known even to non-scientists in its quartz crystalline form, which is a major component of sand in many places. It is used in the manufacture of microchips, cement, glass, and even some toothpaste. Silica's various high-pressure forms make it an often-used study subject for scientists interested in the transition between different chemical phases under extreme conditions, such as those mimicking the deep Earth.



Caption: Free-energy profile showing the transition pathway from coesite to the high pressure post-stishovite. Orange arrows indicate intermediate states.

The first-discovered high-pressure, high-temperature denser form, or phase, of silica is called coesite, which, like quartz, consists of building blocks of silicon atoms surrounded by four oxygen atoms. Under greater pressures and temperatures, it transforms into an even denser form called stishovite, with silicon atoms surrounded by six oxygen atoms. The transition between these phases was crucial for learning about the pressure gradient of the deep Earth and the four-to-six configuration shift has been of great interest to geoscientists. Experiments have revealed even higher-pressure phases of silica beyond these two, sometimes called post-stishovite. The team, including the Geophysical Laboratory's Qingyang Hu, Jinfu Shu, Yue Meng, Wenge Yang, and Ho-Kwang, "Dave" Mao, demonstrated that under a range from 257,000 to 523,000 times normal atmospheric pressure (26 to 53 gigapascals), a single crystal of coesite transforms into four new, co-existing crystalline phases before finally recombining into a single phase that is denser than stishovite, sometimes called post-stishovite, which is the team's fifth newly discovered phase. This transition takes place at room temperature, rather than the extreme temperatures found deep in the earth. Scientists previously thought that this intermediate was amorphous, meaning that it lacked the long-range order of a crystalline structure[1]. This new study uses superior x-ray analytical probes to show otherwise—they are four, distinct, well-crystalized phases of silica without amorphization. Advanced theoretical calculations performed by the team provided detailed explanations of the transition paths from coesite to the four crystalline phases to post-stishovite[2].

Ref :
1,Hu, Q.Y., et al.Polymorphic phase transition mechanism of compressed coesite,Nat. Commun.6, 6630 (2015).
2.Hemley R. J., Jephcaot A. P., Mao H-K., Ming L. C. and Manghnani M. H. Pressure-induced amorphization of crystalline silica.Nature334, 52-54 (1988)

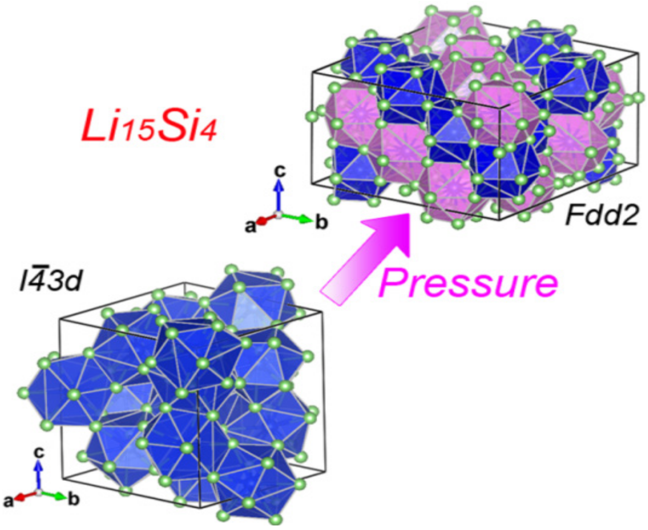
A promising novel phase for silicon anode lithium−ion battery

在高压下合成了一种 $Li_{15}Si_4$ 的新相（β-$Li_{15}Si_4$），与常压结构相比，新相中原子排列更密集，具有更好的力学性能。这种新相的发现为克服锂离子电池硅负极材料易发生破坏的问题提供了一种新的思路。

Silicon is widely regarded as one of the most promising anode materials for next-generation lithium-ion batteries. However, the lithiation of silicon will induce large volume changes and ultra-high stress, which eventually causes mechanical failure of the material. This hinders the application of silicon anodes. Pressure was found to be a unique method which could change the properties and structure of the Li–Si system.

Combining in-situ synchrotron x-ray diffraction, and Raman spectroscopy measurements at high pressure conditions together with ab initio evolutionary metadynamics calculations, Zeng and co-workers investigated the structure and properties change of $Li_{15}Si_4$, which is the only crystalline phase from silicon anode lithium-ion batteries. They discovered a novel phase (β-$Li_{15}Si_4$, space group: Fdd2) when $Li_{15}Si_4$ (α-$Li_{15}Si_4$, space group: I43d) was compressed to above 7 GPa. Moreover, this beta-$Li_{15}Si_4$ phase could be quenched to ambient pressure. Theoretical modeling shows beta-$Li_{15}Si_4$ has higher elastic modulus, packing density while lower volume expansion (~25%) compared with alpha-$Li_{15}Si_4$ during lithiation. These show that beta-$Li_{15}Si_4$ have superior resistance to deformation and fracture under stress. This means that the mechanical weakness of the anode material could be effectively improved.

The results in this work not only bring a new member to the important Li-Si system, but also provide a new perspective on how to overcome the long-standing challenge of the mechanical failure in silicon anode lithium-ion batteries by the atomic level structure design for the first time.



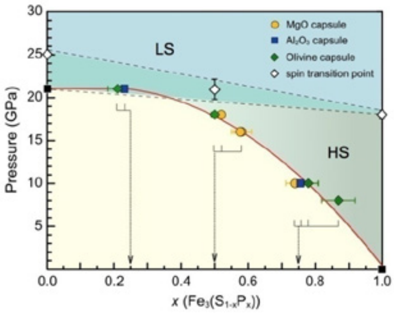
Caption: The atomic structure of alpha-$Li_{15}Si_4$ (lower left) and beta-$Li_{15}Si_4$ (upper right). Each silicon atom is surrounded by lithium atoms (green spheres) with the coordination number of 12 (shown in blue polyhedra) or 13 (shown in pink polyhedra).

Ref：
Zhidan Zeng,* Qingfeng Zeng, Nian Liu, Artem R. Oganov, Qiaoshi Zeng, Yi Cui, and Wendy L. Mao*,A novel phase of $Li_{15}Si_4$ synthesized under pressure,Adv. Energy Mater., 5, 1500214 (2015).

Phase stabilities and spin transitions of $Fe_3(S_{1-x}P_x)$ at high pressure and its implications in meteorites

在不同温压条件下 $Fe_3(S,P)$ 固溶体的相图以及 S、P 的成分随压力的变化。$Fe_3(S,P)$ 固体溶液中 S 的溶解度随压力的增加而增加 ,$Fe_3(S,P)$ 固溶体中 S 的含量随压力的变化也使其成为一种潜在的标型矿物，对于研究陨石及地幔捕捞体所经历的温压路径有一定的指示作用。

Iron phosphides can be crystallized to single phase alloyed with one or several metallic elements or combined with other non-metallic elements to form much more complex minerals. Some iron meteorites groups (IIAB, IIIAB, IVA, and IVB) are believed to have evolved in the Fe-Ni-S-P system. In Elga meteorite with IIE type, Fe_3P and Fe-Ni-P-S alloy forms rims and spheres around silicate inclusions, with S and P nearly evenly distributed. Such feature can be important clues of dynamic pressure process the host meteorite has experienced. Besides, sulfur and phosphorus have also been considered as potential "light elements" that present in planetary cores. Therefore, measurements of the physical properties of the Fe-P-S phases at high pressure will provide constraints on core properties.



Caption: The maximum solubility of S in $Fe_3(S_{1-x}P_x)$ solid solution at about 1173 - 1200 K as a function of pressure. Dotted arrows indicate the S/P ratios of the starting compositions. The area between the dashed lines illustrates the uncertainty of the spin transition.

we synthesized high-quality $Fe_3(S_{1-x}P_x)$ high-pressure phases in the multi-anvil press at 1200 K, 8-21 GPa and investigated the phase stability of $Fe_3(S,P)$ solid solutions. The physical properties of $Fe_3(S_{0.5}P_{0.5})$ were further studied in the diamond-anvil cell by synchrotron X-ray diffraction and emission spectroscopy. The solubility of S in the $Fe_3(S,P)$ solid solution increases with increasing pressure. The minimum pressure to synthesize the pure Fe_3S and $Fe_3(S_{0.13}P_{0.87})$ is about 21 and 8 GPa, respectively. The observed discontinuity in unit-cell parameters at about 18 GPa is caused by the high-spin to low-spin transition of iron, supported by X-ray emission spectroscopy data. Spin transition will lead to a shrink of iron radii in the compound, which is in favor of S to substitute into the structure. The sulfur solubility in $Fe_3(S,P)$ solid solutions could be an excellent pressure indicator if such solid solutions are found in nature.

The mantle makes up nearly three-quarters of Earth's volume and through convection connects the deep interior with the surface. Redox state is important because it affects mineral assemblages, element mobility and the style of degassing, and all are intimately linked to the evolution of the primitive atmosphere since the planet's formation. However, the redox state of the deep Earth is not well constrained and its effect on mantle dynamics is unknown.

In this study, we compressed two enstatite chondritic lower mantle model samples with identical bulk compositions but formed under different oxygen fugacities (fO_2) up to ~90 GPa and 2400 K, and observed that Al_2O_3 forms a phase separate from the dominant bridgmanite (Bm) phase in the more reduced composition, in contrast to a more Al-rich, Bm-dominated assemblage in the more oxidized starting composition. As a result, the reduced material forms an assemblage that is ~1-1.5% denser than the oxidized material. Geodynamic simulations indicate that the 1-1.5% density difference would cause more rapid ascent of oxidized material, and faster descent of denser reduced material into thermochemical piles at the core-mantle boundary (CMB). The model leads to heterogeneous redox conditions in the Earth's interior, which has profound implications for interpreting large low-shear velocity provinces (LLSVPs) in the lower mantle as well as the rise of oxygen in the Earth's early atmosphere.

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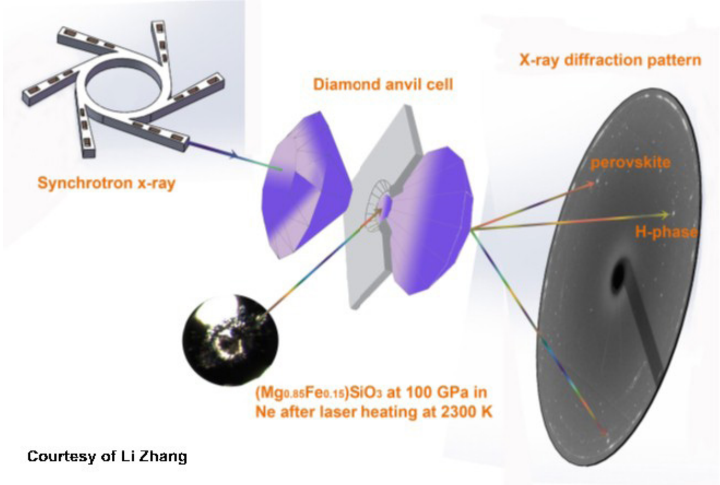
Osadchii, E.G., Novikov, G.V., and Baryshnikova, G.V. (1981) The Elga meteorite: Silicate inclusions and shock metamorphism. Lunar and Planetary Science Conference, 12, 1049–1068.

A new phase in the deep lower mantle?

通过对不同含铁钙钛矿在下地幔条件下的系统性研究，在多次重复性实验中取得突破性发现：含铁的硅酸盐钙钛矿在下地幔深部所对应的温度、压力条件下会分解为两个相，即无铁的钙钛矿和六方结构相，这一新相的发现使人们不得不对过去 30 年对地球下地幔矿物组成的已有认知重新进行思考，并且 H 相的发现意味着下地幔或许有更多未知的新相期待被挖掘。



Courtesy of Li Zhang

Caption: Synchrotron x-ray probes minerals in the deep mantle: Fe-bearing perovskite disproportionates to a nearly Fe-free $MgSiO_3$ perovskite phase and an Fe-rich phase with a hexagonal structure (H-phase).

The Earth's lower mantle comprises >55% by volume of our planet, extends from 670 to 2900 kilometers in depth. The mantle gets hotter and the materials are squeezed to higher pressures with increasing depth. The pressure and temperature ranges from 237,000 times atmospheric pressure (24 gigapascals) and ~1600 Kevin at the top of the lower mantle and reach 1.3 million times atmospheric pressure (136 gigapascals) and ~2500 K above the core-mantle boundary.We actually don't have any direct access to this depth. Instead, we have two ways to examine the lower mantle: experiments that artificially squeezing minerals to high pressure and simultaneously heating to high temperature to see what they turn into; seismic waves that pass through the Earth, slowing down and speeding up depending on composition and temperature that they interact.

High pressure-temperature experiments in the past suggested that the predominant phase was $(Mg,Fe)SiO_3$with nominally 10 mol% Fe in the orthorhombic perovskite structure until the $(Mg,Fe)SiO_3$pv transforms to the post-perovskite structure near the D" layer of the lower mantle. Using laser-heated diamond anvil cells, at pressures of 95 to 101 gigapascals and temperatures of 2200 to approximately 2400 Kelvin, the researchers found that such iron-bearing perovskite disassociates into two phases, one an iron-depleted perovskite and a new mineral that is iron-rich and hexagonal in structure, called the H-phase. This discovery fundamentally changes our knowledge of the mineralogical constitution of the lower mantle.

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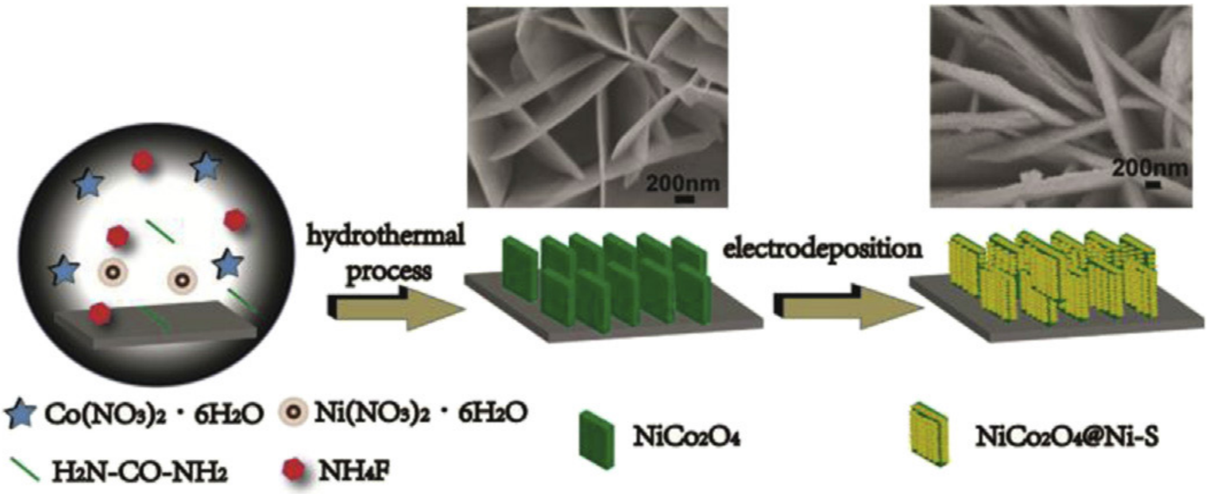
Hierarchical $NiCo_2O_4$@nickel−sulfide nanoplate arrays for high performance Supercapacitors

通过硫化镍电沉积和水热合成两步工艺结合，在 Ni-S 上生成了一种新的核壳分层功能材料 $NiCo_2O_4$@Ni-S 纳米板阵列。这种阵列表现出高比电容和循环稳定性，在电流密度 8mA/cm^2 时，比电容 1.8F/cm^2；在电流密度 8mA/cm2 时，比电容 1.15F/cm^2。



Caption: Schematic illustration of the two-step synthesis of hierarchical NiCo2O4@NieS core-shell nanoplate arrays for supercapacitors.

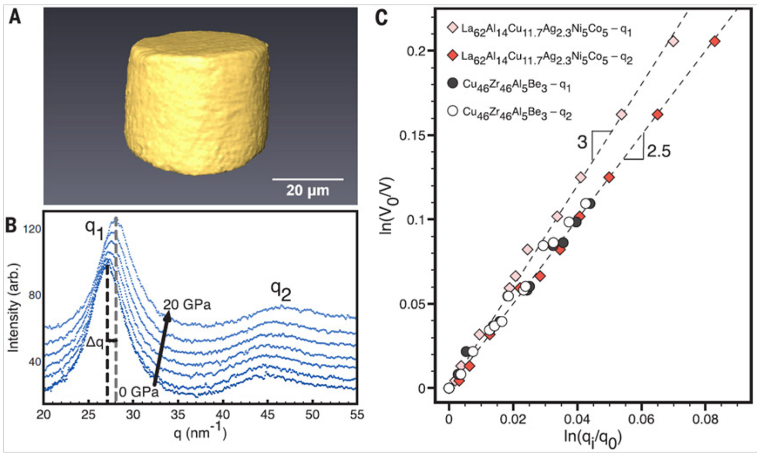
The environmental issues have pushed human being to find novel energy sources instead of fossil fuels to meet the increasing demands of energy consumptions. Currently, it is deeply urgent to develop reliable green energy storage technologies to achieve a secured and reliable energy supply. The high power performance of supercapacitors has made them important complement power sources of batteries to meet the increasing demands of energy storage and conversion. In the two categories of supercapacitors (electrochemical double layer capacitor - EDLC and pseudocapacitor) with different charge storage mechanisms, the EDLC with traditional carbon materials has very limited specific energy. Researchers are trying to develop pseudocapacitive materials based on faradaic reactions with the specific capacitance an order of magnitude higher than that of carbon. To this end, metal oxides have been extensively studied as pseudocapacitor electrode materials, and it has been shown that the architecture design is very important to improve their supercapacitor performance. In particular, 3D array electrodes have drawn much attention because of their facile preparation and excellent performance.

Recently, the HPSTAR group in Changchun produced a new hierarchical core-shell functional-material through a two-step process combining hydrothermal synthesis and electrodeposition of nickel sulfide (Ni-S) on $NiCo_2O_4$ ($NiCo_2O_4$@Ni-S) nanoplate arrays. Weak crystalline Ni-S nanosheets have been uniformly coated on the $NiCo_2O_4$ nanoplate array obtained by hydrothermal growth. Such $NiCo_2O_4$@NieS arrays can deliver high specific capacitances of 1.85 F cm^{-2} and 1.15 F cm^{-2} at current rates of 8 mA cm^{-2} and 40 mA cm^{-2}, respectively, and also exhibit good cycling stability. The good stability of $NiCo_2O_4$ arrays, the good contact between nickel sulfides and $NiCo_2O_4$ arrays, and the pores present within nickel sulfides are responsible for the excellent electrochemical performances of such $NiCo_2O_4$@Ni-S hierarchical core-shell nanoplate arrays. Capacitance fading of the $NiCo_2O_4$@Ni-S arrays, on the other hand, is attributed to the surface coarsening of the Ni-S nanosheets. The present study can be extended to fabricate other oxides/sulfides core/shell arrays (for example, $NiCo_2O_4$@CoS2, NiO@Ni_3S_2, etc.) as electrode materials for electrochemical energy storage applications.

Ref.:
Q. Chu, W. Wang , X. Wang, B. Yang , X. Liu, J. Chen, Hierarchical $NiCo_2O_4$@nickel−sulfide nanoplate arrays for high performance supercapacitors, Journal of Power Sources. 276, 19−25 (2015)

Metallic glass: homogenous in appearance, fractal at heart

发现了一个特定的分形模型 - 过滤群的堆积，给出了金属玻璃的压缩实验中观测的 2.5 次幂关系的完美解释，此研究给出了金属玻璃从微观到宏观尺度上的原子结构一致性的描述。



Caption: (A) Three-dimensional reconstructed sample volumes from in-situ high pressure transmission x-ray microscopy data at ~ 0 GPa. (B) in-situ high pressure x-ray diffraction data with increasing pressure from ~ 0 GPa to 20 GPa. (C) Volume scaling with scattering vectors q_1 and q_2 for $Cu_{46}Zr_{46}A_{15}Be_3$ and $La_{62}A_{114}Cu_{11.7}Ag_{2.3}Ni_5Co_5$ metallic glasses.

In general, the melt of any substance can be frozen into a disordered solid called glass if cooled rapidly enough. Metallic glass was born in 1960s by melt quenching, which retains the non-directional metallic bonding compared to the conventional crystalline metals but lack regular atomic packingand the associated typical defects, such as dislocations and grain boundaries. Metallic glasses thus display many unique properties combining extremely high strength, high hardness, good wear resistance, high corrosion resistance and etc. They have attracted substantial research efforts for decades, which aimed to probe the structure, properties and the underpinning factors controlling glass formation. However, the understanding about the atomic structure of metallic glass is still limited to very local length scale. How the local clusters extend to efficiently fill up the three dimensional space without crystalline symmetry yet remains elusive.

Recent high pressure study on metallic glasses by Dr. Qiaoshi Zeng et al., revealed a non-cubic 2.5 power law scaling of the sample volume with respect to the first diffraction peak position [Zeng et al. PRL 112,185502(2014)]. The universality of the 2.5 power law in the structure-properties relationship of metallic glasses strongly suggests a common fractal feature of their structure. However, it is well known that the fractal structure usually involves macroscopic voids and pores as the length scale becomes large which is therefore thought to be unlikely to describe the densely packed structure of metallic glasses.

Following the discovery of 2.5 power law, the team continually found a specific class of fractal, the continum percolation cluster with the fractal dimension of ~ 2.52 for metallic glasses in the present work. This model avoids introducing macroscopic voids and pores by limiting the fractal structure within a finite correlation length. On the length scale above this correlation length, the system is homogeneous. That means there is a power law exponent crossover from 2.5 to 3 when the length scale increases across the correlation length. The researchers utilized in-situ high pressure x-ray diffraction,tomography measurements as well as molecular dynamics simulations on several different metallic glass materials, repeatedly confirmed the existence of this crossover and the continuum percolation cluster model for metallic glasses.

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D.Z. Chen, C.Y. Shi, Q. An, Q.S. Zeng, W.L. Mao, W.A. Goddard, III, J.R. Greer, Fractal atomic-level percolation in metallic glasses, Science, 349 1306 (2015).

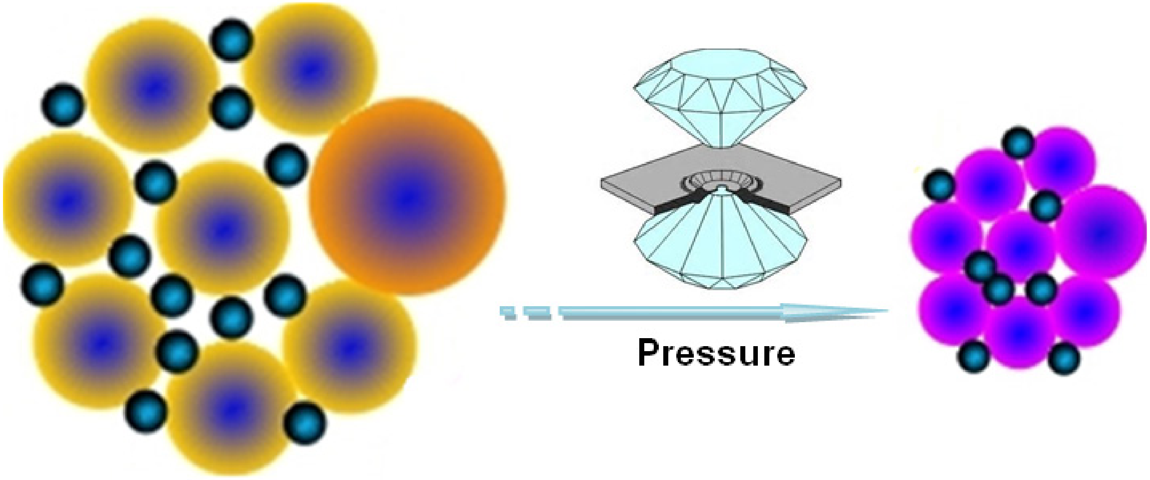
Q.S. Zeng,* Yu Lin, Yijin Liu, Zhidan Zeng, Crystal Y. Shi, Bo Zhang, Hongbo Lou, Stanislav V. Sinogeikin, Yoshio Kono, Curtis Kenney-Benson, Changyong Park, Wenge Yang, Weihua Wang, Hongwei Sheng, Ho-kwang Mao, Wendy L. Mao, General 2.5 Power Law of Metallic Glasses, PNAS, 113, 1714 (2016).

Pressure induced seemed phase transition in metallic glass along with abnormal thermal expansions

在液氦和甲乙醇等传压介质的静水压条件下（直至约 5 万个大气压），研究了三元 Ce 基金属玻璃结构随压力变化的行为，发现该金属玻璃在室温条件下从低密度非晶态到中等密度非晶态再到高密度非晶态的多形态转变现象。

Metallic glasses (MGs) are new comers to the glass family. They are different from the traditional network forming glasses due to metallic bonds in their structure. Besides the disorder structure can actually improve some properties of metallic glasses. Metallic glasses can therefore combine the advantages and avoid many of the problems of normal metals and glasses, having superior strength and durability, which makes metallic glasses has wide commercial applications for decades. It's well known that polymorphism is very common phenomena in metal, or alloy. Even amorphous ice, silica, and silicon were reported to exhibit "polyamorphism" in the glassy state. These lead researchers also try to find "polyamorphsim" in metallic glasses since 2007.

High pressure is an extremely powerful tool for exploring new structure or properties of materials. Using diamond anvil cell, a research team including Dawei Fan from HPSTAR investigated the structural evolution in a Ce-based metallic glass ($Ce_{65}Co_{25}Al_{10}$) with pressure at room temperature (RT) and near the glass transition temperature by synchrotron X-ray diffraction. The Ce-based MG shows low-medium-high densification processes with pressure at both temperatures. A relatively abrupt and discontinuous change in volume happened on the sample around ~50, 000 times atmospheric pressure (5 gigapascals) at 390 Kelvin. This was obvious attributed to "a possible weak first-order phase transition." Furthermore, an abnormal negative thermal expansion shows on Ce-based MG from 0.6 to 9gigapascals. "It is pressure which play the dominate role on the polyamorphic transformations and the abnormal thermal expansion," explained by the authors.

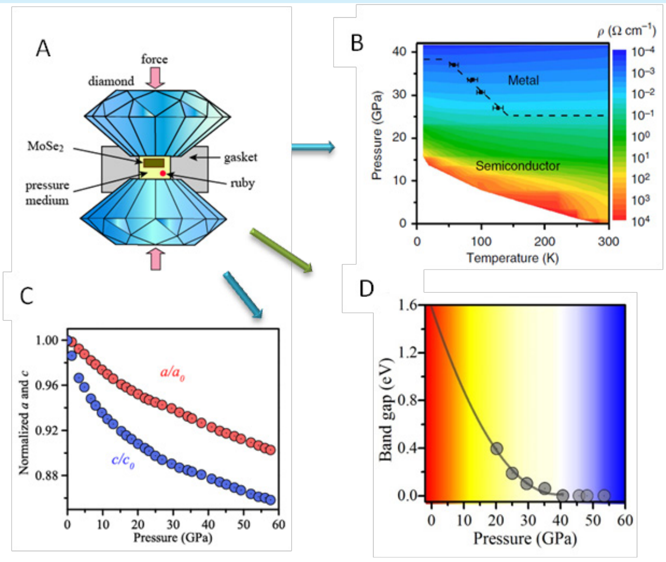


Caption: Pressure leads to densified process in Ce-based metallic glass.

Ref:
Q. Luo, G. Garbarino, B. Sun, D. Fan, Y. Zhang, Z.Wang, Y. Sun, J.Jiao, X. Li, P. Li, N. Mattern, J. Eckert, and J. Shen, Hierarchical densification and negative thermal expansion in Ce−based metallic glass under high pressure, Nat. Commun. 6, 5703 (2015)

Pressure induced metallization without structural transition in layered $MoSe_2$

通过高压原位同步辐射衍射技术、红外光谱、拉曼光谱、电阻测量及第一性原理计算多方位研究了压力对层状二硒化钼 $MoSe_2$ 的晶体及电子结构的影响。多种实验测试表明 $MoSe_2$ 在高压下并未发生类似于 MoS_2 的结构相变，却伴随有金属化的转变。



Caption: (A) Schematic of the high pressure DAC set up; (B) Temperature-pressure-resistivity contour map; (C) Normalized cell parameters a/a_0 and c/c0 versus pressure; (D) Evolution of band gap under pressure.

Transition metal dichalcogenides (TMDs) have attracted intense scientific and engineering interest since the discovering of graphene in 2004. In the past decade, people mainly use three experimental methods: applying electrical field, utilizing quantum confinement with samples thinning down into monolayers, or employing stress or strain to vary the electronic structure of TMDs. In recent years, pressure is found to be a powerful tool for tuning mechanical and optical properties in TMDs, eg. MoS_2.

At ambient conditions, MoS_2 and $MoSe_2$ are iso-structural in crystal structures and have highly similar electronic structures, so it's nature to assume asimilar structure transition would also occur in $MoSe_2$ just like that happened in MoS_2. However, in this new study, both high-pressure x-ray diffraction data and Raman spectroscopy indicated no crystal structure change on $MoSe_2$ up to some 600, 000 atmospheric pressure (60 gigapasals). To explore the observed stability of $MoSe_2$, the team carry out ab-initio simulation, find that the energy barrier for layer sliding in $MoSe_2$ is much higher than that in MoS_2, and the high-pressure phase of $MoSe_2$ bear higher energies than the initial structures, which possibly make the crystal-structure transition unfavorable. Additionally, somewhat more surprising is the metallization of $MoSe_2$ at about 400, 000 times Earth's atmosphere (40 GPa) from high-pressure IR spectroscopy and temperature-dependent resistivity measurements. These results demonstrate that pressure doesn't result in crystal structure change but the electronic structure transition, which is rarely seen in TMDs.

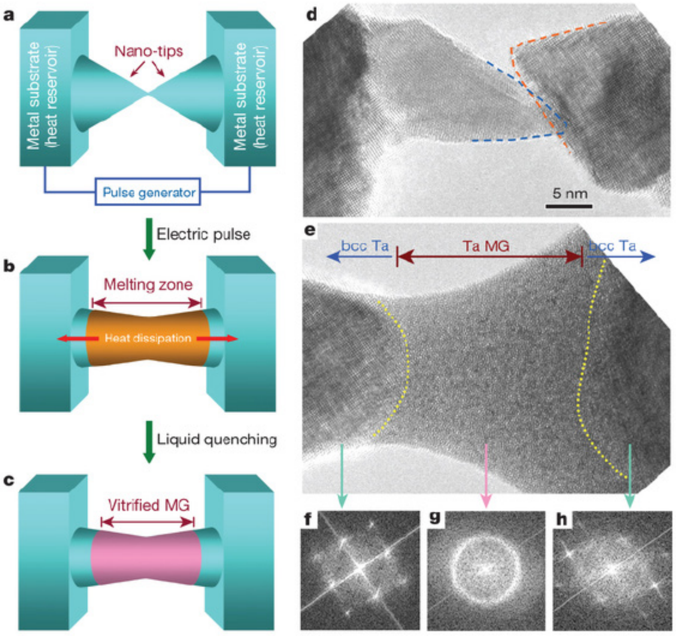
Through high-pressure IR spectroscopy, electrical resistivity measurement combined with ab-initio calculations, the team find that the band-gap of $MoSe_2$ (in the range of visible to IR region) as well as its electronic structure both exhibit strong dependence on pressure.

Ref.:

Z. Zhao, H. Zhang, H. Yuan, S. Wang, Y. Lin, Q. Zeng, G. Xu, Z. Liu, G. K. Solanki, K. D. Patel, Y. Cui, H. Y. Hwang, and W. L. Mao, Pressure induced metallization with absence of structural transition in layered molybdenum diselenide, Nat. Commun. 6, 7312 (2015).

Creating metallic glass from pure metallic liquids with unprecedentedly high quenching rate.

单质金属玻璃需要冷却速率极快实验上很难实现。通过设计纳米加热系统，通过脉冲电流局部熔化金属（形成小体积的金属液），然后迅速向周围基体散热冷却，形成小体积的单质金属玻璃样品，用于研究其结构和性质。



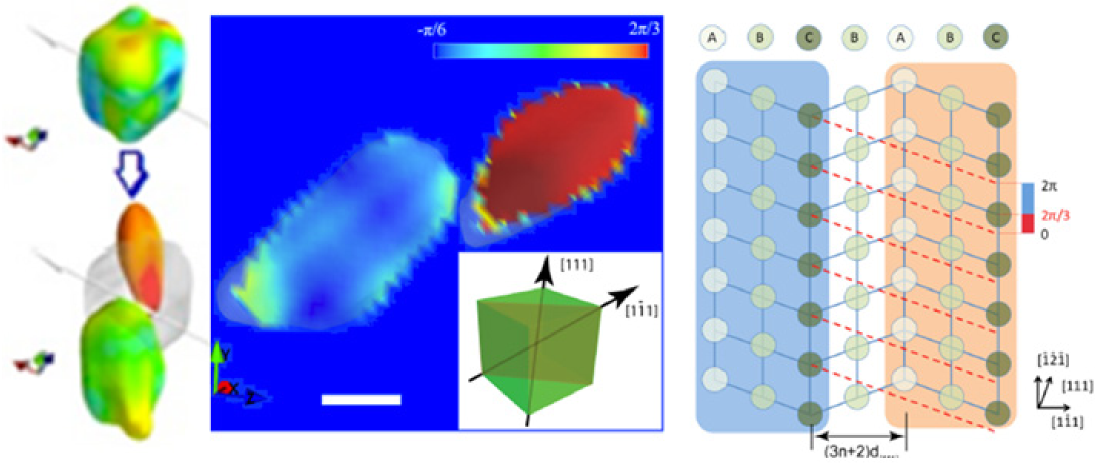
Caption: A method proposed to make monatomic metallic glass by ultrafast rapid quenching.

In this work, PI Sheng at HPSTAR, in collaboration with Scott Mao from the University of Pittsburg, successfully prepared monatomic metallic glass for the first time. If the cooling rate is sufficiently fast, it is thought that any metallic liquid can be frozen into a glassy state, which can in turn yield a solid metal with unusual and potentially useful mechanical properties. In practice, such glass formation is mainly limited to metals composed of two or more elements: the cooling rates required to produce a monatomic metallic glass are usually too high to be achieved experimentally. In this work, we proposed a way around this experimental difficulty by developing a nanoscale heating system in which a pulsed electrical current can locally melt the metal (briefly forming a small volume of metallic liquid), which then rapidly loses its heat into the surrounding solid bulk and leaves behind a sample of monatomic metallic glass amenable for study of its structure and properties.

Ref.:
L. Zhong, J. Wang, H. Sheng, Z. Zhang, and S. X. Mao, Formation of monatomic metallic glasses through ultrafast liquid quenching, Nature 512, 177 (2014).

Deformation twinning in silver nanocrystal

在应力大约 2 GPa 的条件下，对单个银纳米管的扭曲进行了一系列成像，发现了一个银纳米晶体在塑性形变过程中发生了分裂，此分裂现象与常见的形变孪晶一致。有助于理解纳米晶粒的形变机理，提供更多的表征工具来帮助优化纳米材料的性能。



Caption: Lattice distortion and deformation twinning in silver nanocrystal at ～ 2 GPa.

Previous study by Dr. Wenge Yang et al., using Bragg CDI technique, visualized the strain andmorphology evolutions in a 400 nm sized gold under various high-pressure conditions (Nature Communications 4, 1680, 2013); This study, for the first time, combined CDI with high-pressure technique.

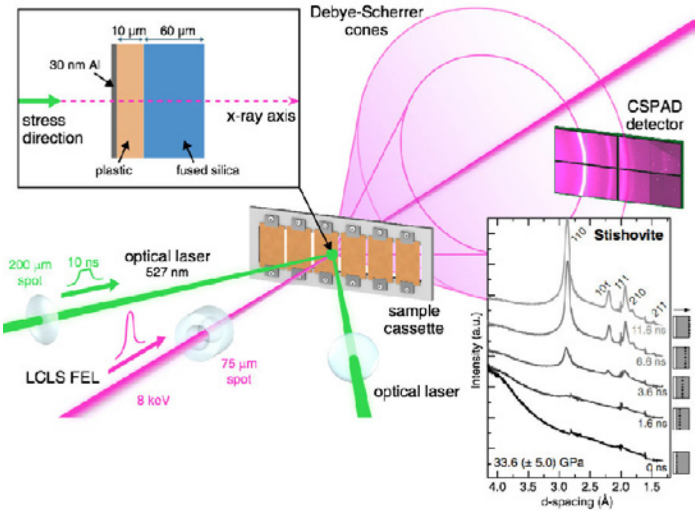
Following the high-pressure CDI measurement on nano-gold, Yang et al., applied the same techniques to single crystal silver nanocube to in-situ track the strain evolution and deformation process in the nanocrystals again. The high-special resolution of CDI enables the scientists to image the shape and lattice distortion inside nanocrystals in real conditions, and in real time. Diamond-anvil cell technique was applied to achieve the external shear stress for nanocube-silver. At shear stress of some 2 GPa, a serials of distortions are imaged in silver nanocube. Moreover,a split of a single silver nanocrystal was observed during the plastic deformation at the same conditions, which is identified to be deformation twinning.

This study represents another step forward followed by the breakthrough of high-pressure structure study in nanocrystals. “These mean that the CDI method would be a unique in situ approach to study a nanocrystal’s response to external stress, said Dr. Yang, “it will facilitate the understanding and interoperation of the deformation mechanism of nanocrystals and thus provide characterization tool to boost the rational design and tuning properties of nanomaterials”.

Ref.:
X. Huang, W. Yang, R. Harder, Y. Sun, M. Lu, Y. S. Chu, I. K. Robinson, and H. K. Mao, Deformation Twinning of a Silver Nanocrystal under High Pressure, Nano Lett. 15, 7644 (2015).

Watching laser-shocked stishovite grow from amorphous silica in nanoseconds

对非晶二氧化硅在原位冲击压缩下非晶二氧化硅的x光衍射测量，从非晶二氧化硅到斯石英相变仅经历几个纳秒，首次观察到冲击引起非晶体到晶体成核及生长过程。



Caption: Experimental configuration of the XFEL probe and optical laser driver. The lattice response of the sample was captured in a Debye-Scherrer geometry. Inset: example of XRD resulting from azimuthal integration of CSPAD data for a suite of time delays under shock compression. A schematic of the target is shown on the right side for each time delay (white: plastic; grey: fused silica). A dashed line indicates the approximate location of the shock front; arrow is the shock-propagation direction.

The high-pressure behavior of silica has been of long-standing scientific interest owing to its fundamental and technological importance and geophysical significance. The phase transition from crystalline quartz or amorphous silica to stishovite is one of the most studied high pressure transitions in materials science.

In the present work, the researchers utilized the intense, ultrashort pulses from a fourth generation synchrotron source, the X-ray free-electron laser (XFEL) at LCLS, to capture the evolution of the transition in shock-compressed fused silica. Using LCLS, the researchers in situ observed the formation and growth of stishovite from shock-compressed amorphous silica over the course of several nanoseconds. Above 180,000 atmospheric pressure (18 gigapasals), the nucleation of stishovite completed in less than 2 nanoseconds.

Though the process from a disordered to ordered material was expected to be slow, the researchers found that the grains grew rapidly, and the growth trend supports a coalescence mode rather than a diffusion-based mechanism.

This first demonstration of shock induced crystallization of an amorphous material via femtosecond diffraction will lead to a greater understanding of a number of important problems in shock physics, and their relation to geophysics. However, “our findings are only a starting place for exploring novel physics and new materials,” said Wendy Mao, one of the principal investigators on this project.

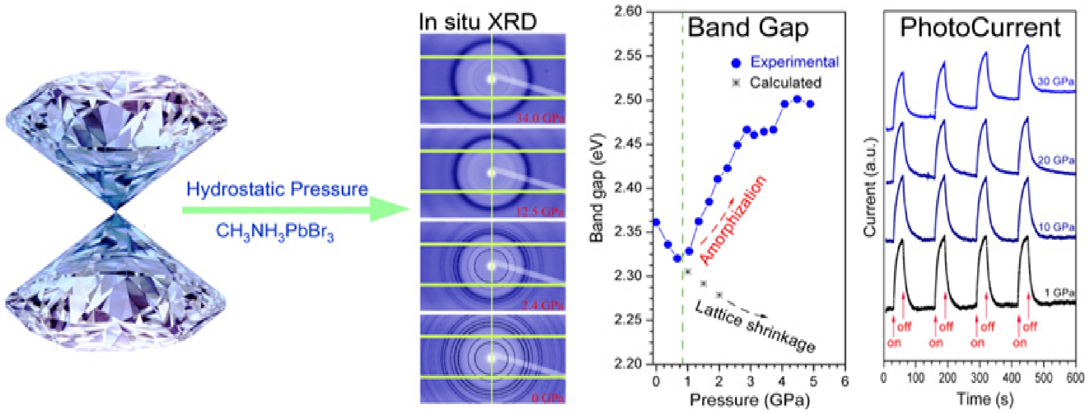
“We expect many more exciting discoveries as we explore shocked-induced phase-transition using XFELs,” said Wenge Yang, “which make it possible to capture detailed information during phase transitions on an ultrafast timescale.”

Ref.:

A. E. Gleason, C. A. Bolme, H. J. Lee, B. Nagler, E. Galtier, D. Milathianaki, J. Hawreliak, R. G. Kraus, J. H. Eggert, D. E. Fratanduono, G. W. Collins, R. Sandberg, W. Yang, and W. L. Mao, Ultrafast visualization of crystallization and grain growth in shock-compressed SiO2, Nat. Commun. 6, 8191 (2015).

Anomalous Photovoltaic Response in $CH_3NH_3PbBr_3$

采用高压原位技术研究了 $CH_3NH_3PbBr_3$- 有机钙钛矿高压下的光电性能，发现 $CH_3NH_3PbBr_3$ 在高压下表现出异常的光电性能，并伴随晶体结构的变化。高压技术在材料设计及调制方面有着巨大的潜力，对非晶有机金属盐类的研究将极大的推进钙钛矿光敏太阳能电池发展。



Caption: Pressure effect on the structure, band gap and photocurrent of $CH_3NH_3PbBr_3$.

Solar energy is the largest noncarbon-based energy source. As opposed to more conventional resources such as coal and fossil fuels, solar energy can serve as a means to solving the serious issue of global warming that has arisen from the evolution of CO_2. The use of solar cells is an effective method of converting solar energy into electric energy, and it represents a very interesting research challenge. A new breed of materials for solar cells with long-term durable solid-state perovskites burst into the limelight in 2012, which are cheap, easy to make, and already capable of converting ~20% of the energy in sunlight to electricity by today. Solution-processable organic-inorganic hybrid perovskites—such as $CH_3NH_3PbX_3$($X = Cl, Br, I$)—have attracted growing attention as light-harvesting materials for mesoscopic solar cells due to their unique optical properties, excitonic properties, and electrical conductivity. The superb photovoltaic performances of the perovskite solar-cell materials are attributed to the combination of useful properties, such as excellent charge-carrier mobility from inorganic metal-halide octahedral building blocks and their plastic mechanical properties introduced by the organic parts.

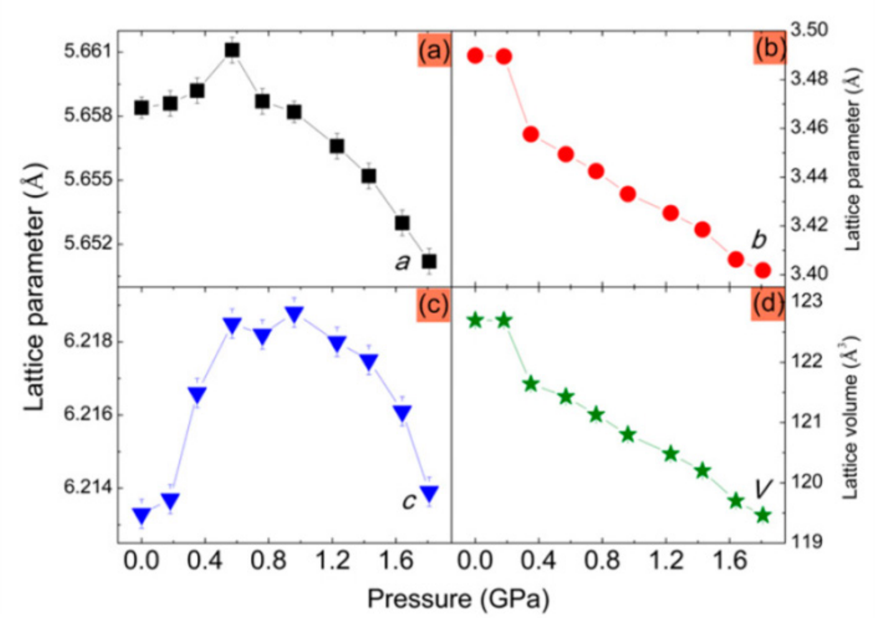
By a serials of measurements including in-situ high pressure X-ray diffraction, photoluminescence, electrical resistance, photocurrent measurements combined with theoretical simulations, the team systematically studied the pressure effect on the crystal structure and photovoltaic performance of organolead bromide perovskite $CH_3NH_3PbBr_3$ ($MAPbBr_3$). Two phase transformations followed by a reversible amorphization were observed during compression and decompression at room temperature. Band-gap evolution of $MAPbBr_3$ derived from photoluminescence measurement shows anomalous behavior with red-shift followed by blue-shift which is due to the competition between compression effect andpressure-induced amorphization. Despite the highly increased electrical resistance under high pressure, the material maintains its semiconductor characteristics and considerable response to the visible light irradiation.

Based on the experimental results and theoretical calculations, the researchers concluded that high pressure was also a powerful technique for material design towards novel functionalities. The future exploration considering amorphous organometal salts with comparable or even better performance than their crystalline form may greatly drive the development of perovskite-sensitized solar cells.

Ref:
J. Am. Chem. Soc.(DOI:10.1021/jacs.5b06346).

Anomalous compression in CrAs

观察到了一种压力导致的等结构相变并展示出奇异的各向异性，这种晶体结构变化与砷化铬的超导具有密切的关联，该研究结果为高压下晶体结构以及与之相关的电子关联提供了新的维度，为砷化铬的超导研究提供了重要的指导。



Caption: Anomalous varing of unit cell parameters a, b,c, and volume of CrAs at high pressures.

Superconductivity has been observed in a majority of 3d transition-metal compounds, except for the Cr- and Mn-based compounds. However, a recent discovery shows superconductivity in CrAs under external pressures (Wei Wu, et al. Nat. Commun. 5, 5508, 2014), which remains metallic state even down to 350 mK. This result again demonstrates that external pressure is an effective and unique approach to tune crystal as well electronic structure of materials.

At ambient conditions, CrAs possess aparamagnetic metallic and the electrons are in itinerant status. It has been shown to exhibit a transition from the antiferromagnetic state to a (low Tc) superconducting state under high pressures and the antiferromagnetic state coexisted with superconducting state between 0.3 ~ 0.8 GPa. The superconductivity appears when the itinerant state occurred around ~ 2 K. The applied pressure shortens the atomic distance and consequently resulted in the expansion of energy band and Fermi surface crossing, thus caused the enhancement of itinerancy.

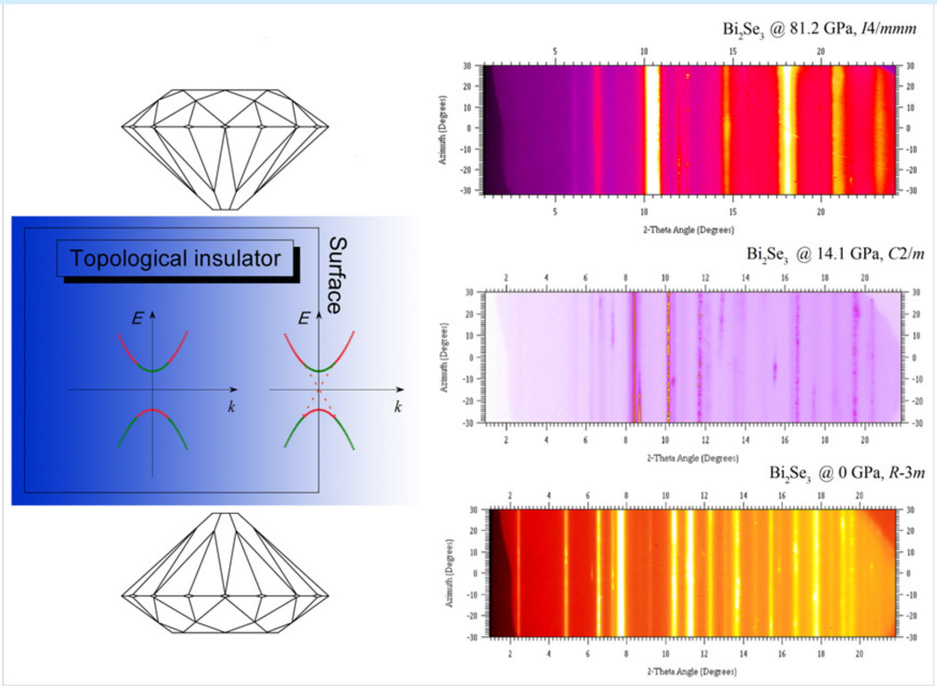
Diamond-anvil-cell is utilized to achieve the high-pressure conditions in this study. Through a detailed analysis of pressure-dependent (up to 1.8 GPa) synchrotron x-ray diffraction data measured of CrAs, the researchers found (111) peak shows an abrupt change during ~0.18 - 0.35 GPa. Additionally, b axis expands first and then shrinks with pressure increasing. This structure evolution was attributed to an isostructural phase transition. This agrees with the pressures, at which CrAs turned to be superconductor. Furthermore, they used theoretical simulations to find possible reason for the connection between the anomalous compression behavior and superconducting in CrAs at the same pressure conditions.

Ref.:

Z. Yu, W. Wu, Q. Hu, J. Zhao, C. Li, K. Yang, J. Cheng, J. Luo, L.Wang, and H. K. Mao, Anomalous anisotropic compression behavior of superconducting CrAs under high pressure, Proc. Natl. Acad. Sci. USA 112, 14766).

Different structure evolution in Bi_2Se_3

拓扑绝缘体 Bi_2Se_3 中发现了两个压力导致的晶体结构相变，该压力导致的晶体结构相变与等结构化合物 Bi_2Te_3 和 Sb_2Te_3 不同，Bi 和 Se 原子半径的巨大差异可以从一个侧面解释为什么 Bi_2Se_3 表现出与 Bi_2Te_3 and Sb_2Te_3 不同的晶体结构演化行为。



Caption: Structural evolution in Bi_2Se_3 under high pressure.

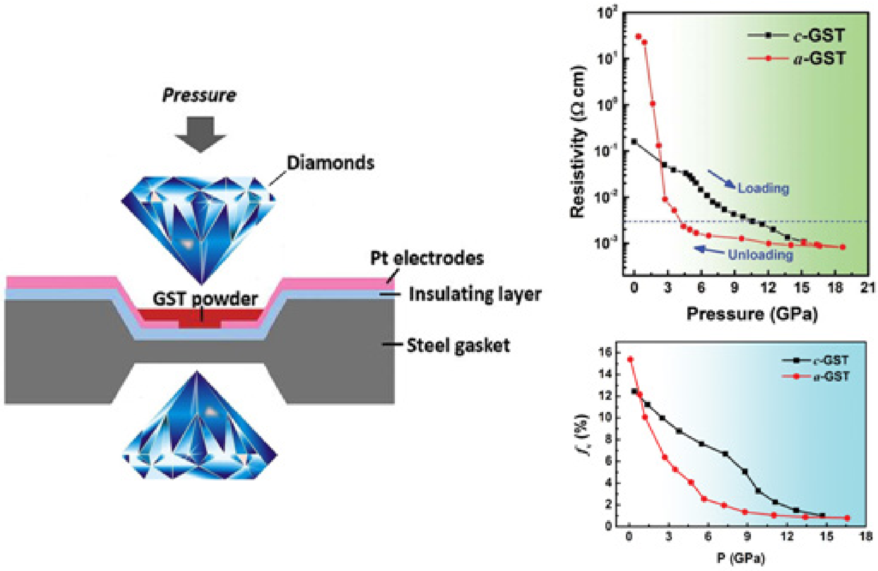
The crisis of energy prompts researchers to explore green/sustainable energy. Thermoelectric materials (such as $Bi_2Te_3$and Bi_2Se_3), as the typical sustainable energy materials used in thermoelectric systems for cooling or heating could also be applied to regenerate electricity from waste heat at electric power plants. While topological insulators (TIs) are electronic materials that have a bulk band gap like ordinary insulators, but feature conducting states on their surface, which are one of the most exciting topics in condensed-matter physics, with a wide range of potential practical applications. Topological insulators (TIs) found in the thermoelectric materials such as Bi_2Te_3, Sb_2Te_3, and Bi_2Se_3 hit the physics spotlight as another exciting newcomer, which act like insulators on the interior, while conduct on the surface.

For isostructural materials, it's nature to assume a similar/same structure transition pathway under the same conditions. Still, different crystal structure or electronic structure transitions are detected in some isostructural materials. The team led by Dr. Wang, utilized diamond-anvil cell technology, x-ray diffraction, Raman spectroscopy combined with theoretical simulations to track the structure evolution in Bi_2Se_3, one of the important TIs. At ambient conditions, Bi_2Se_3 isostructural to Bi_2Te_3 and Sb_2Te_3. The researchers found that the TI in question, Bi_2Se_3 displays a progressive structural evolution compared with Bi_2Te_3 and Sb_2Te_3. It transferred from an ambient rhombohedra structure to a monoclinic phase and eventually to a body-centered tetragonal phase instead of the recently reported disordered body-centered cubic (BCC) phase. “This remarkable difference in atomic radii of Bi and Se in Bi_2Se_3 may explain why Bi_2Se_3 shows different structural behavior from the isocompounds Bi_2Te_3 and Sb_2Te_3” , said Dr. Zhenghai Yu, whose research mainly focus on gaining better understanding of the nature of phase transition in functional mateirals.

Ref.:
Z. Yu, L. Wang, Q. Hu, J. Zhao, S. Yan, K. Yang, S. Sinogeikin, G. Gu, and H. K. Mao,Structural phase transitionsin Bi2Se3 under high pressure, Sci. Rep. 5, 15939 (2015).

Reversed resistivity change in GST

典型的相变材料 GST（$GeSb_2Te_4$）在高压下的电阻率变化研究，观测到了压力导致的电阻率显著变化，奇异的电阻率反转源于压力导致的原子重新排列。而非晶状态的 GST 的空位比例在高压下发生了巨大的变化，佩尔斯型扭曲被大大降低，平均的键长基本保持不变。这些效应最终导致材料从半导体转变为金属相，将有可能为相变器件的设计提供重要的理论指导。



Caption:Experimental setup for high-pressure resistivity measurement (left); Resitivity(right up) as well as fraction vacancies (right down) varying with pressure in GST.

Utlizing diamond-anvil-cell technology combined with theoretical simulations, new research co-authored by Dr. Zhenhai Yu and Dr. Lin Wang from HPSTAR studied the high-pressure electrical property of $GeSb_2Te_4$, a typical phase-change material, observed a pressure-induced reverse of resistivity contrast.

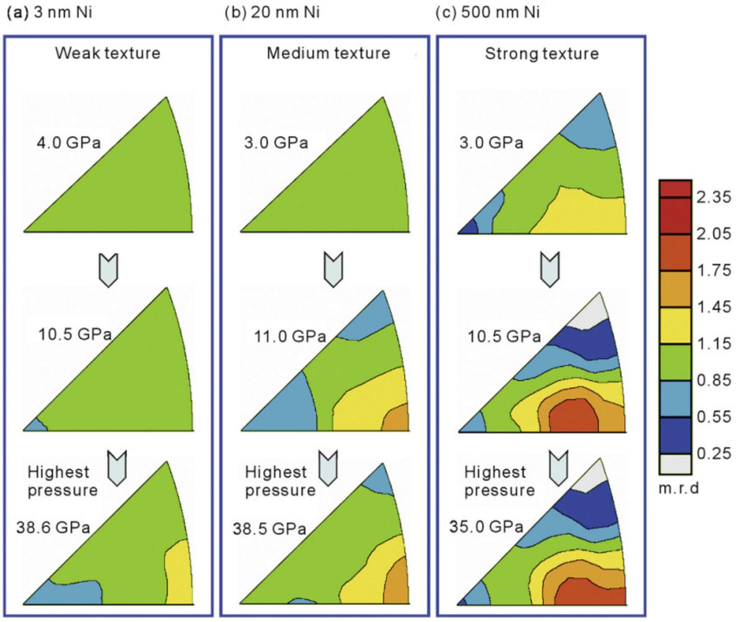
This anomalous resistivity-reversal originates from the atomic rearrangement during phase transition under high pressure, which is also confirmed by molecular dynamic simulations. At pressure below 7 GPa, only relatively small changes happened in the band structure. In contrast, in amorphous GST, the fraction of voids changes drastically with pressure and the Peierls-like distortion is largely reduced, yet the average bond length remains almost constant. These effects eventually turn the semiconducting glass into a metallic phase.

“This work reveals distinct behaviors of amorphous and crystalline phase-change materials under stress, shedding light on the mechanisms of electronic transport in different phases, and thus may have important implications on the design of phase-change memory devices”, said Dr. Zhenhai Yu.

Ref.:
M. Xu , Z. Yu , L. Wang , R. Mazzarello , and M. Wuttig, Reversing the Resistivity Contrast in the Phase-Change Memory Material $GeSb_2Te_4$ Using High Pressure, Adv. Electron. Mater. 1, 1500240 (2015).

Detecting Grain Rotation at the Nanoscale

借助地球物理领域的实验方法-径向衍射技术，成功探测到在相同下，几个纳米级金属镍相对更大尺寸的晶体转动越活跃。在同一压力下，相同晶粒尺寸的铂的形变强度随混合镍晶粒尺寸(从~500nm至3nm)的减小而有规律地变弱。此发现表明，晶粒越小的纳米晶体转动更为活跃。这为探索仅有几纳米尺度上的材料变形机理提供了一种新的手段。



Caption:The inverse pole figures of nickel with different particle size

Controlling the texture of materials is a crucial element in improving the strength and in extending the lifetime of materials. Plastic deformation of coarse grained (> 100 nm) metals has been well-described as a process in which the application of shear stress causes crystallites to rotate within the lattice structure until they achieve a preferred texture. It has proven challenging to determine if the same process occurs in nanomaterials due to the challenges associated with observing the rotation of ultrafine crystals. As reported in the March 4 issue of PNAS [PNAS 111 3350 (2014)], an international team of scientists from six different institutions have now succeeded in observing nanoscale plastic deformation by collecting x-ray diffraction (XRD) on polycrystalline metal samples under high pressure in a radial diamond anvil cell (rDAC). For the series of experiments, the samples consisted of spherical platinum particles (∼1 μm) within a medium of spherical nickel particles (500 nm, 20 nm, or 3 nm). According to Bin Chen, lead author and director of the Shanghai Laboratory of HPSTAR (Center for High Pressure and Technology Advanced Research), “We chose platinum and nickel, because both have fcc structures, and both are relatively easy for performing texture analysis. We also had several sizes of nickel to work with.” Much to the surprise of the research team, the texture strength of platinum dropped significantly as the particle size of the nickel media was reduced, even though the same sized platinum particles were used throughout the experiments.

Refs:

B. Chen, K. Lutker, J. Lei, J. Yan,, S. Yang, and H. K. Mao, Detecting grain rotation at the nanoscale, Proc. Natl. Acad. Sci. USA 111, 3350 (2014).

H. K. Mao, B. Chen, J. Chen, K. Li, J. F. Lin, W. Yang, H. Zheng, Recent Advances in High−Pressure Science and Technology, Matter and Radiation at Extremes. (2016).

Losses in Ferroelectric Materials

通过对铁电材料中能量损耗的全面综述，包括相关机理、表征方法和大量铁电材料已发表数据的系统整理。基于以上信息的整理和分析，提出了一个普适的理论模型描述弹性、介电、压电和机械损耗的内在联系，总结分析了研究和控制铁电材料能量损耗存在的挑战。

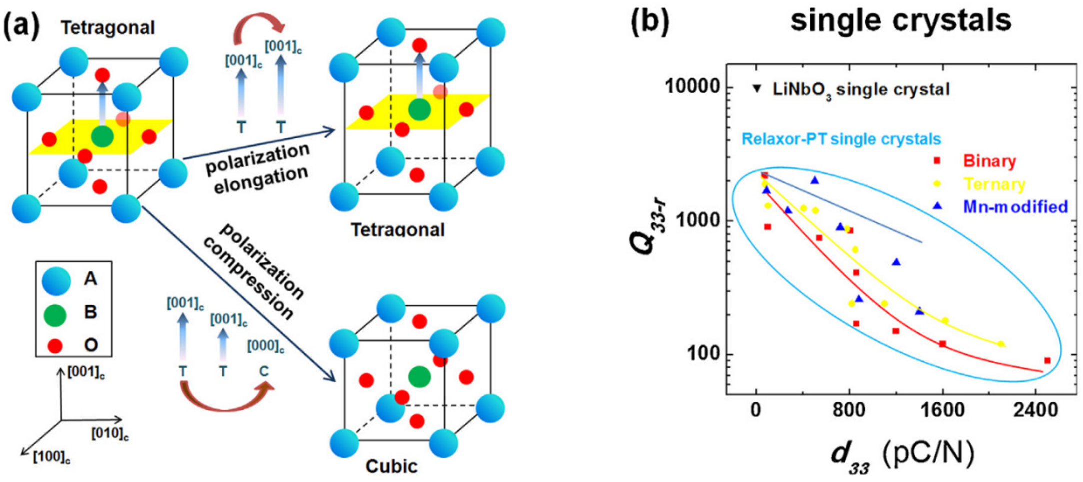
Energy loss (or energy dissipation) is one of most critical issues in ferroelectric materials for engineering applications. This loss including elastic, piezoelectric and dielectric, associated with elasticity, dielectric relaxation and piezoelectric hysteresis in ferroelectrics, have brought many controversies/confusions in the past several decades.

Ferroelectric materials are materials possessing a natural charge polarization that can be reversed by an external electric field, known as the switching process. Over 250 compounds have been found to display such characteristics since the discovering of ferroelectricity in Rochelle salt in 1920. Leadtitanate, $PbTiO_3$, and related compounds are most focused systems.

Ferroelectric draws its name by analogy with ferromagnetism, which describes permanent magnetic materials based on iron that are found in nature. Ferroelectric materials have been widely used as resonators, actuator, transducers, transformers, sensors, non-volatile FeRAM, capacitors, etc. But they've faced one major obstacle—Energy loss (or energy dissipation), which is one of the most key problems in ferroelectrics for high power devices, such as therapeutic ultrasonic transducers, large displacement actuators, SONAR projectors, and high frequency medical imaging transducers. Energy loss may cause significant heat generation in electromechanical devices under strong field driving condition, leading to device failure, especially in high-power transducers and ultrasonic motors.

For decades, scientists have made impressive progresses to reduce energy losses in ferroelectrics using kinds of methods. Several possible mechanisms have been proposed, with many open questions still remaining. Dr. Gang liu, provided a comprehensive review on the energy losses in ferroelectrics by comparing related intrinsic and extrinsic mechanisms, characterization techniques on serials offerroelectric materials, mainly on relaxor-$PbTiO_3$, to provide a deep understanding of correlative reasons involved.

According to the relationship between the mechanical quality factor and measured quality factors, easy polarization variations and domain wall motions related to the intrinsic and extrinsic contributions, are supposed to be responsible for the enhanced functional properties and decreased quality factors in ferroelectric single crystals, explained in the work.



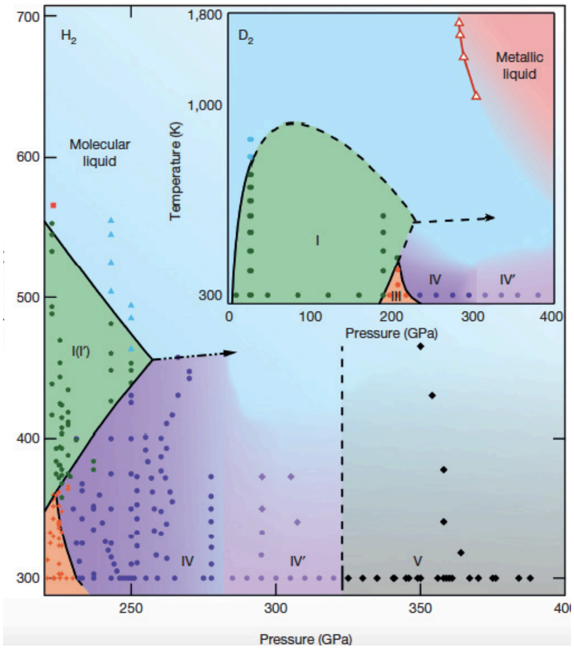
Caption: (a)Schematic polarization elongation and polarization compression in a perovskite unit cell ABO3 with rhombohedral (R) phase, whereby the polarizations are represented by arrows. (b)The relationship between electromechanical quality factor Q and longitudinal piezoelectric constant d33 for various ferroelectrics single crystals

Ref:

G. Liu, S. Zhang, W. Jiang , and W. Cao, Losses in ferroelectric materials, Mater. Sci. Eng., R 89, 1(2015)

Elusive Hot Hydrogen Leads to More Pressing Questions

在 245 GPa （245 万大气压），570 K，通过拉曼光谱的变化发现了氢的新的分子相。此相有可能是人们一直寻找的熔融态氢。如果此分子氢是熔融态的，将打破高压下熔化的新的低温记录。这一新相的发现也是对多年来人们对氢研究的极大推进。



Caption: Phase diagram of hydrogen. The inset shows the P-T paths taken during temperature cycles. The properties of the newly discovered molecular phase, and the question of what happens in the region at higher pressures and temperatures (shown as shaded area), represent exciting areas for future research. Some possible extensions of the phase boundaries are shown by dashed arrows.

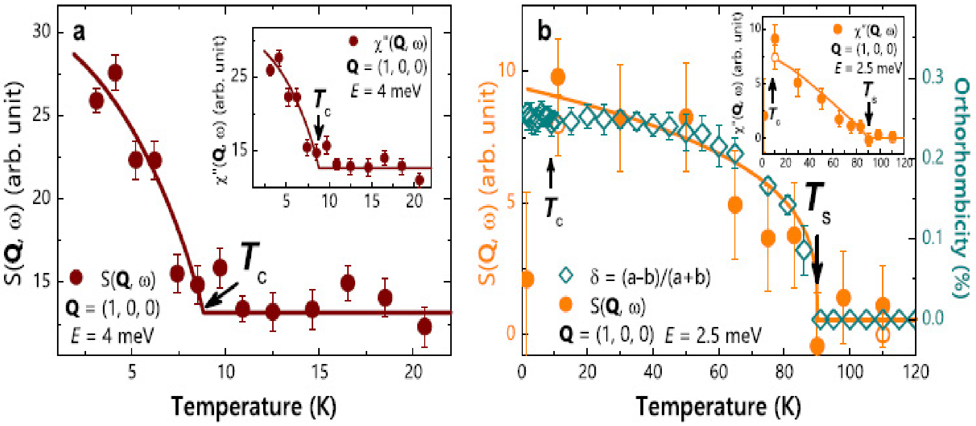
Recent technological advances have enabled studies of hydrogen under extreme compression and variable temperature, leading to the discovery of no fewer than five solid phases. With its strong quantum effect and extremely high compressibility, the rich physics of hydrogen suggests that other unusual phenomena may occur. A missing piece of the puzzle, however, has been what happens at very high pressure and moderate temperature. This is the key region near the boundary between the fluid and solid state, where new phases and interesting properties are expected, and it has been inaccessible in dynamic studies because of rapid temperature rises during compression. Howie and co-workers have met this challenge by improving the resistively heated diamond-anvil cell technique and hydrogen-containment method, enabling them to reach 570K at 245GPa in pure hydrogen. In this region, they observed a striking change in the optical Raman vibrational spectra, indicating the discovery of a new molecular phase. If this phase is indeed the long sought-after molten hydrogen, as interpreted by the authors, this will be the coldest melt for all known materials above 200GPa. To put this in context, compression usually causes a liquid to freeze into a solid; in very rare cases, such as ice and water, compression causes a solid to melt. Hydrogen would set a record high pressure and record low temperature for pressure-induced melting.

This discovery of a new hydrogen phase represents a significant step forward. It is likely to stimulate the development of key experimental tools and techniques to answer the number of questions its observation raises. For example, is the new phase indeed a liquid? Or is it one of the exotic solids predicted by theory, such as the alternating layers of H_2 and graphene-like $3H_2$ rings? Is the melt conductive? Extension of experimental probes into this region, such as infrared spectroscopy, electrical conductivity measurements and X-ray diffraction, in addition to Raman spectroscopy, will be necessary for providing definitive answers to some of these questions.

Ref:
Howie, R.T.;Dalladay-Simpson, P.; Gregoryanz, E. "Raman Spectroscopy of Hot Hydrogen above 200 GPa" Nature Materials, 14, 495-499 (2015).

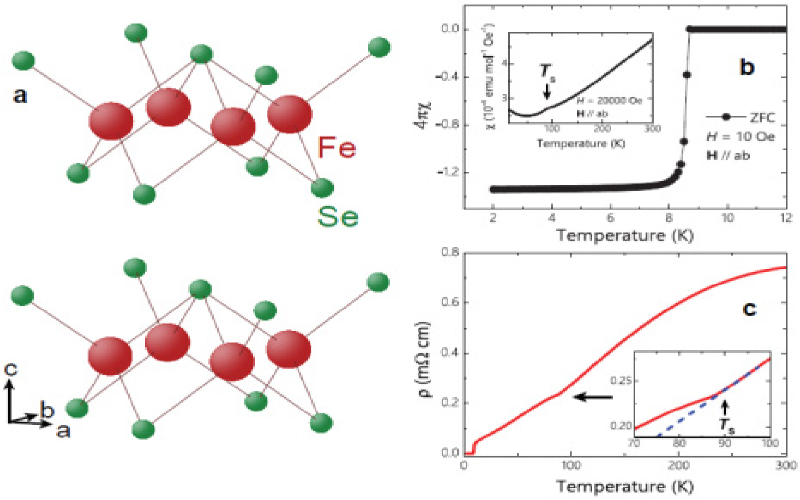
Nematicity and its relation to the superconductivity in 11 systems

铁硒超导体具有复杂，多能隙的特征。另外，利用中子散射技术发现铁硒（FeSe）超导体中存在很强的条纹反铁磁涨落，并发现该涨落和超导电性、向列相 (nematic phase) 的产生有紧密联系，该研究还确定了铁硒超导体的配对波函数存在符号改变 (sign-reversed)。超导能隙宽度在费米面附近不闭合对理解超导机理至关重要。



As for the Cooper pairing mechanism, either spin or orbital degrees of freedom are considered responsible for the orthorhombic phase transition in the parent or lightly doped iron arsenides, which usually precedes the onset of static AFM order, leading to the formation of the so-called spin-nematic state in the narrow temperature region between the two transitions

In the joint project with Fudan university, we have studied the FeSe which exhibits a nematic (orthorhombic) phase transition at Ts = 90 K without antiferromagnetic ordering by neutron scattering, finding substantial stripe spin fluctuations coupled with the nematicity that are enhanced abruptly on cooling through Ts. A sharp spin resonance develops in the superconducting state, whose energy (4 meV) is consistent with an electron–boson coupling mode revealed by scanning tunnelling spectroscopy. The magnetic spectral weight in FeSe is found to be comparable to that of the iron arsenides. Our results support recent theoretical proposals that both nematicity and superconductivity are driven by spin fluctuation.

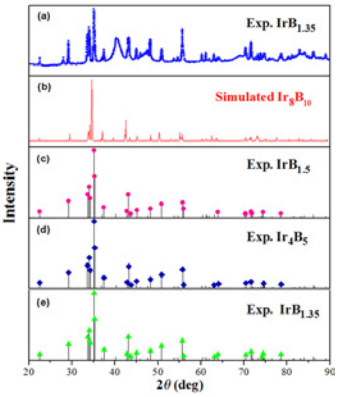


Ref:
Q. Wang, Y. Shen, B. Pan, Y. Hao, M. Ma, F. Zhou, P. Steens, K. Schmalzl, T. R. Forrest, M. Abdel-Hafiez, X. J. Chen, D. A. Chareev, A. N. Vasiliev, P. Bourges, Y. Sidis, H. Cao and J. Zhao, Strong interplay between stripe spin fluctuations, nematicity and superconductivity in FeSe, Nat. Mater. 15, 159–163 (2015).

Structures and stability of novel transition−metal (M = Co, Rh, and Ir) borides are revealed

在高温高压下合成了过渡金属硼化物 CoBx，采用粒子群优化算法结合密度泛函优化搜索结构，系统研究了 9 族金属富硼化物的结构，解决了第一个过渡金属硼化物 Ir-B 的组分和结构存在的长期争议，预测了各种不同组分硼化物的结构、力学性能和电学性能。

Transition-metal borides have attracted considerable investigations in recent years for their outstanding properties and growing applications in industry. A unique electrondeficient bonding environment, as seen in many materials containing boron, enables a rich diversity of stoichiometries and structures of borides. In transition-metal borides, boron can form different polyhedral structures, ranging from symmetric clusters to extended networks, and exhibit fascinating properties, such as superconductivity, superhardness, and topological properties.



Caption:
Simulated XRD pattern of the predicted $IrB_{1.25}$ phase (b) compared to experimentally measured pattern along with the previous suggested stoichiometries. Experimental data in (a), (c), (d), and (e) were reported in previous references.

Binary borides containing group 9 metals (Co, Rh, and Ir) have been extensively studied as catalysts and resistant coatings. The boron-rich borides of this group are relatively less explored; up to now, there have only been two known phases. The first phase was an Ir-B compound synthesized in 1962 with an unidentified crystal structure. The composition of this compound was initially suggested as $IrB_{1.5}$, but other studies indicated that $IrB_{1.35}$ or $IrB_{1.25}$ were both possible. In 2009, the same Ir-B compound was successfully fabricated in thin films that exhibited outstanding superhard behaviors. The structure and stoichiometry of this Ir-B compound has not been solved, which partially motivated the present paper. In 2014, the second member to this family, $CoB_{3.2}$ (Co_5B_{16}), was successfully synthesized under high-pressure high-temperature conditions. In our results, we performed a theoretical investigation of group 9 metal borides, with the emphasis on the boron-rich side. The structure searches were carried out using the particle swarm optimization (PSO) algorithm combined with density functional optimizations. We have addressed the long-standing question on the composition and structure of the first Ir-B compound; We propose this compound to have a novel $IrB_{1.25}$ stoichiometry and a monoclinic Cm structure. The Cm structure is thermodynamically stable, and its interplanar spacing corresponds very well to the measured diffraction patterns. In addition, the present paper discusses a series of new crystalline MBx phases (M= Co, Rh, and Ir; x = 1.5, 2, 3, 4, and 6) that are stable at ambient or high pressures or both. Predicted borides of different stoichiometries exhibit a variety of boron networks, ranging from zigzag chains in M_2B_3, regular rhomboids in MB_2, triangles in MB_3 and $MB_{3.2}$, to distorted rhomboids in MB_4. By changing the chemical compositions, one is able to manipulate the bonding pattern of the boron framework that dictates the mechanic and electronic properties of the system. The results are published in Phys. Rev. B 92, 174106 (2015).

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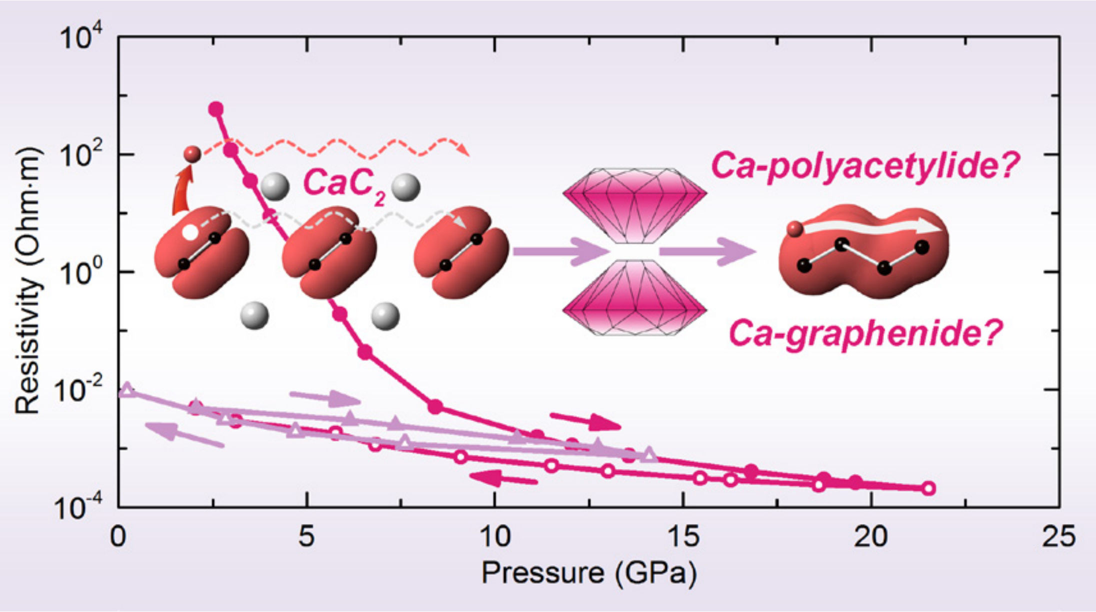
Structural variety beyond appearance: high−pressure phases of CrB_4 in comparison with FeB4,Yunkun Zhang, Lailei Wu,* Biao Wan, Yan Zhao, Rui Gao, Zhiping Li, Jingwu Zhang,* Huiyang Gou,* Ho−kwang Mao, Physical Chemistry Chemical Physics 18 (4), 2361−2368 (2016)

Structures and stability of novel transition−metal (M= Co, Rh, and Ir) borides, Yachun Wang, Lailei Wu, Yangzheng Lin, Qingyang Hu, Zhiping Li, Hanyu Liu, Yunkun Zhang, Huiyang Gou,* Yansun Yao,* Jingwu Zhang, Faming Gao and Ho−kwang Mao, Physical Review B 92 (17), 174106(2015)

Pressure induced polymerization of acetylide anions in CaC_2 and 10^7 folds enhancement of electrical conductivity

将通常用于环境分析的气相色谱质谱联用仪首次应用于分离和确认高压实验回收产物的结构和组分。结合拉曼光谱分析和原子对分布函数分析，确认了高压下 CaC2 聚合物，以及产物聚乙炔和苯的结构。

The composition and structure of the product recovered from high pressure is the key to understand the reaction mechanism. However, the molecules are usually amorphous under high pressure which brings a lot of problems to characterization. In 2015, Gas Chromatography-Mass spectrometer (GC-Ms), which is normally used in the environmental analysis, was first employed in our group, to separate and confirm the composition and structure of the product recovered from high pressure. This method is very sensitive and the product recovered from the diamond anvil cell can be analyzed very well. By performing the GC-Ms combing with the Raman spectra and the atomic pair distribution function (PDF), the polymerization of CaC_2 under high pressure was confirmed and the products with polyacetylene and benzene structure was figured out. Previously, the theoretical calculation shows the CaC_2 can be polymerized into 1D chain, ribbon and 2D graphite sheet at high pressure and the superconductivity is expected. However, these new polymorphs were not obtained experimentally, and even the polymerization of the C_{22}- is not evidenced. Our result is the first solid experimental evidences of the polymerized C_{22}- under high pressure. More investigations using GC-Ms are undergoing.



Refs:

Kuo Li*, Haiyan Zheng*, Takanori Hattori, Asami Sano Furukawa, Christopher A. Tulk, Jamie Molaison, Mikhail Feygenson, Ilia N. Ivanov, Wenge Yang, Ho-kwang Mao. Synthesis, Structure and Pressure Induced Polymerization of $Li_3Fe(CN)_6$ Accompanied with Enhanced Conductivity. Inorg. Chem., 2015, 54, 1276–11282.

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New form of silicon as the next generation energy platform

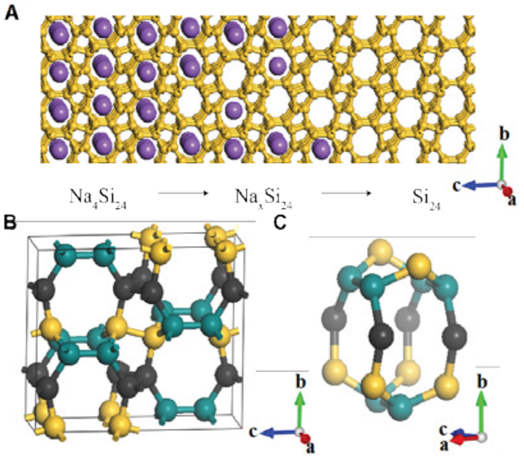
在高压下钠硅化合物研究，发现一个新的高压形态，即 Na_4Si_{24}，在 9 GPa 时稳定，卸载至常压后可回收。一个新的同素异形体硅（Si_{24}）从 Na_4Si_{24} 合成，Si_{24} 的多孔构型将可用于气体过滤或捕捉。

Silicon is the mainstay of contemporary semiconductor science and technology and it is also a key element in Geoscience. The most abundant and stabilized form at ambient conditions is a diamond structured one (d-Si). d-Si has been extensively studied and it possesses an indirect band gap with 1.1 eV while the direct band gap is estimated to be ~ 3.2 eV which is out of visible light energy range. Due to the indirect bandgap nature and a large direct bandgap, it is regarded that the current form of silicon reached its fundamental limit and would be inefficient for future energy platform [1,2].

While people try to find an alternative solution of the next generation energy platform from other materials such as graphene or other two dimensional materials, it seems the answer still remained in silicon [3]. However, during half a century, there has been no progress to find another form of silicon, in spite of huge experimental and theoretical works. In recent our high-pressure study on sodium silicon compounds, we observed a new high-pressure form, namely Na_4Si_{24}, which stabilized at 9 GPa and interestingly it is recoverable to ambient conditions [4]. Na_4Si_{24} consists of completely sp3 bonded silicon atoms and weakly bonded one-dimensional sodium atom arrays. Thus, we could easily evaporate sodium atoms by heating the sample, and silicon keeps the frame-structure.

A new allotrope of silicon (Si_{24}) was successfully synthesized from a high-pressure precursor Na_4Si_{24} [5]. Si_{24} possesses a quasi-direct bandgap of 1.3 eV, which is predicted to be the optimal bandgap for photovoltaic materials. Furthermore, its interesting porous geometryopens up other possible applications for gas filtering or capturing (for example sea water desalination).

Computational part of this work was conducted by Dr. Duck Young Kim and experimental part was done by Strobel group at Geophysical Laboratory.



Caption:
Crystal structure of Si_{24}: A. a schemetic view of sodium evaporation process from Na_4Si_{24} (left) to Si_{24} (right). B. a unitcell of Si_{24} with three different crystallographic positions with different colors. C. a porous cage of Si_{24} framework.

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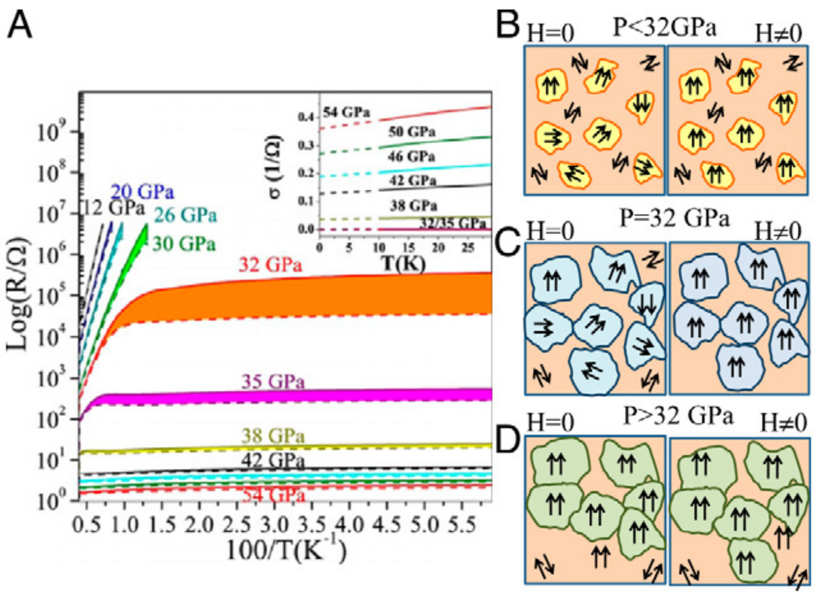
CMR induced in pure lanthanum manganite

发现纯 $LaMnO_3$ 样品在大约 32GPa 压力下，分裂成两种不同的相，金属及非金属相，巨磁阻现象出现在两相竞争最激烈时。对巨磁阻效应的内在机理仍然存在争议，而超巨磁阻效应之前只发现在掺杂的磁性样品中，这是首次在纯磁性材料中发现了超巨磁阻效应。

Manganite compounds, such as $LaMnO_3$ studied by the research team, are particularly promising when it comes to colossal magnetoresistance, because the change from insulator to metal is several orders of magnitude stronger than in other types of compounds. But controlling and the intrinsic mechanism underlying the CMR has remained largely elusive. It was only found before in chemically doped manganite samples, but not in a pure one until this study.

High pressure transport measurements were performed in a pure compound, $LaMnO_3$ with varying temperature and magnetic field. Around 320, 000 atmospheric pressure (32 gigapasals), $LaMnO_3$ separates into two distinct phases, one metallic and one non-metallic. Interestingly, the chemical structure of the non-metallic phase is distorted, while the metallic phase is not. The insulator-to-metal transition occurs when the metallic phase exceeds the non-metallic one by a certain threshold confirmed by theoretical predictions. But the existence of a period when the two phases are mixed together is the crucial ingredient for inducing colossal magnetoresistance. The CMR occurs when the competition between the two phases is at its maximum. The physical separation of the two phases and the interplay between the deformed structure and the non-deformed structures is the key to driving the colossal magnetoresistance.



Caption: (A) Temperature dependence of the resistance Log10(R/Ω)between 12 and 54 GPa. Solid lines are the data collected at 0 T, and dashed lines are the data collected at 8 T. (Inset) Temperature dependence of electrical conductivity: the dashed lines indicate the 0 K extrapolation. (B‐D) Schematic sketches of the PS state over the three different pressure regimes. (B)P<32 GPa: the volume fraction of the FM region is too small and LMO is an insulator. (C) P =32 GPa: LMO is at the percolation threshold and applied magnetic field induces a spin-polarized metallic conduction and CMR. (D)P>32 GPa: the extended, connected FM phase is finally established

Ref:

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