

Joint  
Eighteenth International Conference on  
**HIGH PRESSURE SEMICONDUCTOR PHYSICS**  
&  
**Second International Workshop on**  
**HIGH PRESSURE STUDY OF**  
**SUPERCONDUCTORS**



July 23 - 27, 2018  
CosmoCaixa Museum  
Barcelona  
Spain

# Acknowledgements

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**Joint Eighteenth International Conference on  
HIGH PRESSURE SEMICONDUCTOR PHYSICS  
&  
Second International Workshop on  
HIGH PRESSURE STUDY OF SUPERCONDUCTORS**

**About the conference**

The Eighteenth International Conference on High Pressure Semiconductor Physics (HPSP18) is a satellite of the International Conference on the Physics of Semiconductors (ICPS 2018) to be held in Montpellier, France, during the first week of August. The International Workshop on High Pressure Study of Superconductors (WHS2) will merge with HPSP series for the second time in Barcelona, after the success of the first joint meeting in Tokyo in 2016. The aim of HPSP18&WHS2 is to bring together young and experienced researchers from different fields to meet during a single-session conference for the exchange of ideas, dissemination and discussion of their latest results in research areas dealing with the application of high pressure and other forms of stress to study both semiconductors and superconductors. The HPSP18&WHS2 conference will review the latest advances and developments of bulk and nanostructured semiconductor and/or superconductor materials and devices using high pressure techniques, including advances in pressure-induced superconductivity, novel materials, design of high pressure apparatus, and other related topics. Finally, by bringing together scientists in semiconductor and superconductor high pressure physics, we expect to create new synergies, strengthening activities in both research areas.

HPSP is a biennial meeting with a long-standing tradition. The first two meetings took place in Poland (1985) and Montpellier (1986) as a Polish-French Meeting on High Pressure Applications in Semiconductors. The success of these early conferences made it clear that the topic of high-pressure semiconductor physics attracted a great interest. Consequently, in 1988 the series was convened under its present name, being organized as a satellite of the traditional International Conference on the Physics of Semiconductors (ICPS series). HPSP conferences were held in:

- HPSP3, Tomaszów, Poland (1988)
- HPSP4, Porto Carras, Greece (1990)
- HPSP5, Kyoto, Japan (1992)
- HPSP6, Vancouver, Canada (1994)
- HPSP7, Schwäbisch Gmünd, Germany (1996)
- HPSP8, Thessaloniki, Greece (1998)
- HPSP9, Sapporo, Japan (2000)
- HPSP10, Guildford, UK (2002)
- HPSP11, Berkeley, USA (2004)
- HPSP12, Barcelona, Spain (2006)
- HPSP13, Fortaleza, Brazil (2008)
- HPSP14, Changchun, China (2010)
- HPSP15, Montpellier, France (2012)
- HPSP16, Mexico City, Mexico (2014)
- HPSP17&WHS, Tokyo, Japan (2016)
- HPSP18&WHS2, Barcelona, Spain (2018)

## **Scientific Topics**

Submission of original work is solicited covering the following list of scientific topics:

1. Electronic structure
2. Mechanical properties including vibrational, elastic and piezoelectric properties
3. Optical properties
4. Electrical transport phenomena in semiconductors & superconductors
5. Impurity and defect states
6. Structural studies including phase transitions
7. Magnetic diluted semiconductors & spin dependent properties
8. Thermoelectricity and thermal properties
9. Carbon-related semiconductors
10. Low-dimensional, layered & nanostructured materials
11. Superconducting materials & pressure-induced metallization and superconductivity
12. Organic & hybrid materials
13. Strongly correlated electron systems
14. Novel materials, structures and devices
15. New experimental or computational techniques

## **Invited Speakers**

Marvin L. Cohen, Berkeley University, USA

Isaac F. Silvera, Harvard University, USA

Mikhail Eremets, MPI for Chemistry, Mainz, Germany

Eugene Gregoryanz, University of Edinburgh, UK

John S. Tse, University of Saskatchewan, Canada

Paolo Postorino, University of Roma Sapienza, Italy

Bingbing Liu, Jilin University, China

Sofia-Michaela Souliou, ESRF, Grenoble, France

Stanislaw Krukowski, UNIPRESS, Warsaw, Poland

Olivier Pages, Université de Lorraine, France

Sergey Ovsyannikov, University of Bayreuth, Germany

Shanti Deemyad, University of Utah, USA

Kazuyuki Matsubayashi, Tokyo, Japan

Julio Pellicer-Porres, Valencia University, Spain

Manuel Núñez-Regueiro, Institut Neel CNRS, France

Aitor Bergara, Universidad del País Vasco (EHU), Spain

Shinji Watanabe, Kyushu Institute of Technology, Japan

Ingo Loa, University of Edinburgh, UK

Vladimir Solozhenko, CNRS, Paris, France

Agata Kaminska, Institute of Physics, Warsaw, Poland

Miriam Peña-Alvarez, University of Edinburgh, UK

Suchi Guha, University of Missouri, USA

Alfonso San Miguel, University of Lyon, France

Yoshihisa Mori, Okayama University of Science, Japan

Markus R.Wagner, TU Berlin, Germany

## **Venue**

The HPSP18&WHS2 conference will be held at the *CosmoCaixa Museum*, which is the first interactive science museum in Spain. This space, inaugurated for the recreation and dissemination of science, would provide a unique and stimulating environment for all conference participants. The Museum is located approximately 10 km west of the Barcelona-El Prat International Airport and it is about 15 minutes (highly dependent on traffic) drive from downtown Barcelona and/or easily accessible by public transportation such as bus and train (FGC). Barcelona is within one hour drive from well-known tourist attractions such as the Montserrat or seashore cities like Sitges or Tossa de Mar.

More information on the facilities and their location of the CosmoCaixa Museum of Science are available at: <https://obrasociallacaixa.org/en/ciencia/cosmocaixa/el-museo>

## **ADDRESS**

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08022 Barcelona, Spain  
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Fax +34 93 253 74 73  
[icosmocaixa@magmacultura.net](mailto:icosmocaixa@magmacultura.net)*

## **TRANSPORT**

### **Bus**

Lines H4, V13, V15, 22, 73, 75, 60 and 196

### **Generalitat trains (FCG)**

Line L7, CosmoCaixa - Av. Tibidabo station

### **By road**

Exit 6 and 7 of the Ronda de Dalt ring road

### **Parking**

Saba – CosmoCaixa

Timetable: from 7 am to 11 pm

Tel. +34 93 253 74 88

## **CAFETERIA - RESTAURANT**

### **ARCASA – CosmoCaixa**

Gluten-free cooking

Timetable: from 10 am to 8 pm

Tel. +34 93 253 74 51

## **Presentation Formats**

Invited talks: 30 min total (25 min talk + 5 min discussion).

Contributed talks: 15 min total (12 min talk + 3 min discussion).

A computer for projection will be available. Authors are required to bring their presentation on either a memory stick or use their own computer.

Posters: Pin-up boards will be provided to accommodate 120 cm x 90 cm (DIN A0) posters.

## **Publication**

Conference participants are kindly invited to submit original manuscripts for publication in a *Focus Series on High Pressure Semiconductor and Superconductor Physics* in the international journal *Papers in Physics*

<http://www.papersinphysics.org/index.php/papersinphysics/pages/view/highpressuresemiconductor>

After peer-review, accepted manuscripts will be published **open access** as regular articles as part of the Focus Series. In Papers in Physics, authors may ask for Open Review, which means that the reviewers are not anonymous and their names will be stated in the published paper. Moreover, if the editors consider the reports valuable for the readers, the publication of Commentaries from the reviewers are encouraged, with due Replies from authors, if necessary.

Reception of submissions for this focus series of Papers in Physics edited by Andrés Cantarero, Alejandro R. Goñi and J. Sebastián Reparaz is open.

If you wish to submit a manuscript for inclusion in this focus series, you can follow the standard process for regular articles (see authors guidelines:

<http://www.papersinphysics.org/index.php/papersinphysics/about/submissions#authorGuidelines> and indicate you would like the paper to be considered for the "Focus series on High Pressure Semiconductor and Superconductor Physics". The articles will be limited in length to a MAXIMUM of **10** printed pages for **invited** speakers and **5** pages for **contributed** papers.

### **Organizing Committee**

A.R. GOÑI (Chair), Barcelona, Spain

F. RODRÍGUEZ (Co-Chair), Santander, Spain

M.I. ALONSO (Local Arrangements), Barcelona, Spain

A. MORENO (Local Arrangements), Barcelona, Spain

A. FRANCISCO (Local Arrangements), Barcelona, Spain

A. CANTARERO (Publication), Valencia, Spain

J.S. REPARAZ (Publication), Barcelona, Spain

## **HPSP18 & WHS2**

### **Scientific Program**

#### **Monday, July 23**

##### **Registration & Museum Visit (15:00-19:00)**

#### **Tuesday, July 24**

##### **Registration (8:00-9:00)**

##### **Opening & Welcome**

(Àgora hall, CosmoCaixa Museum)

**Tu1.1 (9:00-9:05): Opening (Goñi, Alejandro R.).**

**Tu1.2 (9:05-9:15): Welcome (Director of the Area of Scientific Disclosure and CosmoCaixa: Portabella, Jordi).**

##### **Overview on High Pressure Physics of Semiconductors & Superconductors**

(Àgora hall, CosmoCaixa Museum. Chair: Weinstein, Bernard)

**Tu1.3 (9:15-10:00): Plenary (Cohen, Marvin L.), High Pressure Effects in Semiconductors, Metallization, and Superconductivity.**

##### **Pressure-Induced Metallization and/or Superconductivity-I**

(Àgora hall, CosmoCaixa Museum. Chair: Syassen, Karl)

**Tu1.4 (10:00-10:30): Invited (Silvera, Isaac F.), Two Pathways to Metallic Hydrogen and Deuterium.**

##### **Coffee Break (10:30-11:00)**

**Tu2.1 (11:00-11:30): Invited (Eremets, Mikhail), Molecular semimetallic hydrogen.**

**Tu2.2 (11:30-12:00): Invited (Gregoryanz, Eugene), Raman studies of deuterium and hydrogen high pressures and low temperatures.**

**Tu2.3 (12:00-12:30): Invited (Souliou, Sofia-Michaela), High-Tc cuprates under hydrostatic and uniaxial compression.**

**Tu2.4 (12:30-12:45): Oral (Toulemonde, Pierre), Pressure-Temperature phase diagram of superconducting FeSe single crystals probed by neutron and x-ray diffraction, x ray emission and absorption spectroscopies.**

**Tu2.5 (12:45-13:00): Oral (Medvedev, Sergey), Pressure-induced superconductivity in the pyrite phase of palladium diselenide.**

##### **Lunch (13:00-15:00)**

### **Electronic Structure & Optical Properties**

(Àgora hall, CosmoCaixa Museum. Chair: Cohen, Marvin L.)

**Tu3.1 (15:00-15:15):** Oral (Pravica, Michael), *Fluorine chemistry at extreme conditions: possible synthesis of HgF4.*

**Tu3.2 (15:15-15:30):** Oral (Sun, Baoquan), *Influence of polar pressure transmission medium on the pressure coefficient of excitonic interband transitions in monolayer WSe2.*

**Tu3.3 (15:30-15:45):** Oral (Lesniewski, Tadeusz), *Inducing the luminescence of quenched Ce<sup>3+</sup> centres in gadolinium gallium garnet by high pressure.*

**Tu3.4 (15:45-16:00):** Oral (Mahlik, Sebastian), *Influence of high hydrostatic pressure on intraconfigurational transition in lanthanide ions doped inorganic hosts.*

### **Impurity & Defect States**

(Àgora hall, CosmoCaixa Museum. Chair: Cohen, Marvin L.)

**Tu3.5 (16:00-16:30):** Invited (Kaminska, Agata), *High Pressure Study of the Yellow Luminescence in Be-doped GaN.*

### **Coffee Break (16:30-17:00)**

### **Structural Studies Including Phase Transitions-I**

(Àgora hall, CosmoCaixa Museum. Chair: Eremets, Mikhail)

**Tu4.1 (17:00-17:30)** Invited (Krukowski, Stanislaw), *Electronic aspects of adsorption at semiconductor surfaces: the equilibrium pressure, growth and doping.*

**Tu4.2 (17:30-18:00)** Invited (Tse, John), *Mechanisms for Structural Phase Transformations in High Pressure Solids.*

**Tu4.3 (18:00-18:15)** Oral (Argaman, Uri), *Prediction of the stability of the rhombohedral phase in IV-VI monochalcogenides and its origin.*

**Tu4.4 (18:15-18:30)** Oral (Polian, Alain), *SnI4 and GeI4 under high pressure: a combined X-ray absorption X-ray diffraction study.*

**Tu4.5 (18:30-18:45)** Oral (Shirai, Koun), *Order-Disorder Phase Transition from delta-O to alpha-T boron.*

### **Gathering organized by the Women Under High Pressure Group**

(Àgora hall, CosmoCaixa Museum)

**Tu4.6 (18:45-19:15)** Oral (Peña Álvarez, Miriam & Deemyad, Shanti), *HPSP18&WHS2 Women under High Pressure.*

### **Reception Cocktail (19:30-21:00)**

(Plaça de la Ciència, CosmoCaixa Museum)

**Wednesday, July 25**

**Registration (8:30-9:00)**

### **Organic & Hybrid Materials**

(Àgora hall, CosmoCaixa Museum. Chair: Campoy-Quiles, Mariano)

**We1.1 (9:00-9:30):** Invited (Postorino, Paolo), *Pressure-induced order-disorder transitions in hybrid perovskites.*

**We1.2 (9:30-10:00):** Invited (Guha, Suchi), *Blue-emitting organic semiconductors under pressure: new perspectives on intermolecular order.*

**We1.3 (10:00-10:15):** Oral (Perevedentsev, Aleksandr), *Unravelling the Interplay between Microstructure and Photophysics for Luminescent Magnus' Green Salt Derivatives using Pressure-Dependent Spectroscopy.*

#### Low-Dimensional, Layered & Nanostructured Materials

(Àgora hall, CosmoCaixa Museum. Chair: Alonso, Ma. Isabel/Garriga, Miquel)

**We1.4 (10:15-10:30):** Oral (González, Jesús), *Pressure dependence of multiphonon resonant Raman scattering on 2Hc-MoS<sub>2</sub> microcrystalline samples: the semiconductor to metal electronic phase transition.*

#### Coffee Break (10:30-11:00)

**We2.1 (11:00-11:30):** Invited (San Miguel, Alfonso), *Tuning dimensionality in nanosystems under extreme conditions.*

**We2.2 (11:30-11:45):** Oral (Santoro, Mario), *Synthesis and Raman spectroscopy of a layered SiS<sub>2</sub> phase at high pressures.*

**We2.3 (11:45-12:00):** Oral (Sánchez-Royo, Juan Francisco), *Centrosymmetric MoS<sub>2</sub> under pressure: revealing spin-polarized nature of bulk electronic bands.*

**We2.4 (12:00-12:15):** Oral (Livneh, Tsachi), *High pressure and low temperature Raman scattering in Inorganic Fullerenes of MoS<sub>2</sub>.*

**We2.5 (12:15-12:30):** Oral (Manjón, Francisco Javier), *High-pressure study of high-mobility Bi<sub>2</sub>O<sub>2</sub>Se semiconductor.*

**We2.6(12:30-12:45):** Oral (Forestier, Alexis), *Partial strain transfer between layers in isotopically labeled bilayer graphene under high pressure.*

**We2.7 (12:45-13:00):** Oral (Zhao, Yixuan), *Application of high pressure and high temperature to produce a Bi nanowire/silica nanotube composite for thermoelectric applications.*

#### Lunch (13:00-15:00)

#### Structural Studies Including Phase Transitions-II

(Àgora hall, CosmoCaixa Museum. Chair: Silvera, Isaac F.)

**We3.1 (15:00-15:30):** Invited (Peña-Alvarez, Miriam), *Temperature Dependence of Rotational Modes in Fluid Hydrogen and Deuterium.*

**We3.2 (15:30-15:45):** Oral (Liu, Xiao-Di), *Phase diagram of hydrogen, deuterium and hydrogen-deuterium mixtures at high pressures and low temperatures.*

**We3.3 (15:45-16:00):** Oral (Liarokapis, Efthymios), *Pressure induced lattice anomalies in La<sub>2-x</sub>S<sub>x</sub>CuO<sub>4</sub>.*

**We3.4 (16:00-16:15):** Oral (Andrada-Chacón, Adrián), *Pressure induced phase transition and metallization in 1T-HfSe<sub>2</sub>.*

**We3.5 (16:15-16:30):** Oral (Moreira, Sanclyaton), *Phase Transition in Beta-Carotene Crystal under High Pressure.*

#### Coffee Break (16:30-17:00)

#### Poster Session I – Odd Numbers (17:00-19:00)

(Ambaixades, CosmoCaixa Museum)

**We4.1-P1 (17:00-19:00):** Poster (Dybala, Filip), *Determination of pressure coefficients in MoS<sub>2</sub>, MoSe<sub>2</sub>, WS<sub>2</sub>, and WSe<sub>2</sub> van der Waals crystals by optical studies at room temperature.*

**We4.2-P3 (17:00-19:00):** Poster (Ves, Sotirios), *High pressure response of the Raman modes of Dy<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub>.*

**We4.3-P5 (17:00-19:00):** Poster (Muñoz, Alfonso), *CeScO<sub>3</sub> perovskite under pressure from ab initio simulations.*

**We4.4-P7 (17:00-19:00):** Poster (Pavlov, Sergei), *Stressed THz silicon lasers.*

**We4.5-P9 (17:00-19:00):** Poster (Wang, Yu), *Kinetic boundaries and phase transformations of ice I at high pressure.*

**We4.6-P11 (17:00-19:00):** Poster (Mujica, Andrés), *Study of the evolution of the vibrational and electronic properties of several tin chalcogenides under compression.*

**We4.7-P13 (17:00-19:00):** Poster (Syassen, Karl), *Structural pathways and lattice dynamics of ReO<sub>3</sub> under pressure.*

**We4.8-P15 (17:00-19:00):** Poster (Buga, Sergei), *Advanced Thermoelectrical Bi<sub>2-x</sub>S<sub>b</sub>Te<sub>3-C60</sub> Nanocomposites.*

**We4.9-P17 (17:00-19:00):** Poster (Ovsyannikov, Sergei), *Thermoelectric properties of compressed germanium.*

**We4.10-P19 (17:00-19:00):** Poster (Arvanitidis, John), *Pressure evolution of the samarium valence in Sm<sub>2.75</sub>C<sub>60</sub>.*

**We4.11-P21 (17:00-19:00):** Poster (Han, Bo), *Excitonic properties of hBN/WSe<sub>2</sub> monolayer/hBN van der Waals heterostructures under hydrostatic pressure.*

**We4.12-P23 (17:00-19:00):** Poster (Jin, Meiling), *Superconductivity emerging from a Weyl semimetal NbIrTe<sub>4</sub> under pressure.*

**We4.13-P25 (17:00-19:00):** Poster (Campoy-Quiles, Mariano), *Elucidating the role of planarity and intermolecular distance on the optical properties of conjugated polymers.*

**We4.14-P27 (17:00-19:00):** Poster ([Weinstein, Bernard](#)), *Pressure-optical studies of band gap tuning, Raman phonons, and stability in BaZrS3.*

**We4.15-P29 (17:00-19:00):** Poster ([Uwatoko, Yoshiya](#)), *Development of Two-stage Multianvil Apparatus for High Pressure and Low Temperature Measurements.*

**Thursday, July 26**

**Registration (8:30-9:00)**

**Mechanical Properties, incl. Vibrational, Elastic & Piezoelectric Properties**

(Àgora hall, CosmoCaixa Museum. Chair: [Polian, Alain](#))

**Th1.1 (9:00-9:30):** [Invited \(Pagès, Olivier\)](#), *Pressure-induced phonon freezing in ZnSe-based mixed crystals: phonons, phonon-polaritons and ab initio calculations.*

**Th1.2 (9:30-10:00):** [Invited \(Pellicer-Porres, Julio\)](#), *BiVO<sub>4</sub> polymorphism studied by high pressure-high temperature Raman measurements and ab-initio calculations.*

**Th1.3 (10:00-10:30):** [Invited \(Wagner, Markus R.\)](#), *Strain engineering as a tool to tune the acoustic phonon dynamics of suspended nanostructures.*

**Coffee Break (10:30-11:00)**

**Novel Materials, Structures & Devices**

(Àgora hall, CosmoCaixa Museum. Chair: [Kaminska, Agata](#))

**Th2.1 (11:00-11:30):** [Invited \(Ovsyannikov, Sergei\)](#), *High-pressure high-temperature synthesis and phase transitions in simple oxides.*

**Th2.2 (11:30-12:00):** [Invited \(Liu, Bingbing\)](#), *New ordered Structure of Amorphous Carbon Clusters from Compressing C<sub>8</sub>H<sub>8</sub>/C<sub>60</sub>.*

**Th2.3 (12:00-12:15):** Oral ([Sung, Ha-Jun](#)), *Prediction of a novel superconducting Si allotrope and its high-pressure Na-Si precursor.*

**Th2.4 (12:15-12:30):** Oral ([Montesdeoca, Denise](#)), *Open Circuit Voltage Increase of GaSb/GaAs Quantum Ring Solar Cells under High Hydrostatic Pressure.*

**Th2.5(12:30-12:45):** Oral ([Eales, Timothy](#)), *Evidence for Disorder Induced Band Mixing Effects in Ge<sub>1-x</sub>Sn<sub>x</sub> Alloys using Hydrostatic Pressure.*

**Th2.6 (12:45-13:00):** Oral ([Deng, Zheng](#)), *Pressure effect on diluted magnetic semiconductors with independently controllable charge and spin.*

**Lunch (13:00-15:00)**

**Structural Studies Including Phase Transitions-III**

(Àgora hall, CosmoCaixa Museum. Chair: [Gregoryanz, Eugene](#))

**Th3.1 (15:00-15:30):** Invited (Loa, Ingo), *Complex Alloy Phases in Bismuth Tellurides at High Pressure.*

**Th3.2 (15:30-16:00):** Invited (Deemyad, Shanti), *Unstable, Metastable and Ground State Structures of Lithium.*

**Th3.3 (16:00-16:30):** Invited (Solozhenko, Vladimir), *Equilibrium p-T phase diagram of zinc oxide.*

**Coffee Break (16:30-17:00)**

**Poster Session II – Even Numbers (17:00-19:00)**  
(Ambaixades, CosmoCaixa Museum)

**Th4.1-P2 (17:00-19:00):** Poster (Jara-Martínez, Enrique), *Structural correlations in Cs<sub>2</sub>CuCl<sub>4</sub>: pressure dependence of electronic and vibrational structures.*

**Th4.2-P4 (17:00-19:00):** Poster (Rodríguez-Hernández, Plácida), *High-pressure elastic, vibrational and structural study of monazite-type GdPO<sub>4</sub> from ab initio simulations.*

**Th4.3-P6 (17:00-19:00):** Poster (Porras-Montenegro, Nelson), *Transmittance of 1D superconductor-semiconductor photonic crystal as a function of pressure, temperature, and thickness of the component layers.*

**Th4.4-P8 (17:00-19:00):** Poster (Akahama, Yuichi), *Reentrant structure transition of indium at 130 GPa.*

**Th4.5-P10 (17:00-19:00):** Poster (Freire, Paulo), *High pressure on the orthorhombic phase of nanostructured MoO<sub>3</sub>.*

**Th4.6-P12 (17:00-19:00):** Poster (Syassen, Karl), *Phases of LaTiO<sub>3</sub> under pressure.*

**Th4.7-P14 (17:00-19:00):** Poster (Pravica, Michael), *Synthesis of a novel structure of cesium superoxide via x-rays and high pressure.*

**Th4.8-P16 (17:00-19:00):** Poster (Korobeynikov, Igor), *Thermoelectric properties of TX<sub>3</sub> (M – Ti, Zr, X – S, Se, Te) under high pressure.*

**Th4.9-P18 (17:00-19:00):** Poster (Takarabe, Kenichi), *High Pressure Study of Hall Effect in Thermoelectric Mg<sub>2</sub>Si Semiconductor.*

**Th4.10-P20 (17:00-19:00):** Poster (Bogdanov, Evgeny), *2D Electrons Concentration and Mobility in n-GaAs/AlGaAs:Si under Uniaxial Stress.*

**Th4.11-P22 (17:00-19:00):** Poster (Buga, Sergei), *Metastable Superconductive Phase of Topological Insulator Sb<sub>2</sub>Te<sub>3</sub> Obtained by High-Pressure-High-Temperature Treatment.*

**Th4.12-P24 (17:00-19:00):** Poster (Francisco-López, Adrián), *High pressure study of optical and vibrational properties of methylammonium lead iodide perovskites.*

**Th4.13-P26 (17:00-19:00):** Poster (Yang, Wenge), *Pressure enhanced performance in perovskite photovoltaic materials.*

**Th4.14-P28 (17:00-19:00):** Poster ([Min, Byeong-Hun](#)), Installation of a laser drilling system and diamond anvil cell for transport measurements up to 60 GPa.

**Th4.15-P30 (17:00-19:00):** Poster ([Xiao, Hong](#)), Pressure-tuned superconductivity and normal-state behavior in  $\text{Ba}(\text{Fe}_{0.943}\text{Co}_{0.057})_2\text{As}_2$  near the antiferromagnetic boundary.

**Banquet (20:00-23:00)**

EL PRINCIPAL DEL EIXAMPLE  
C/ Provenza 286, 08008 BARCELONA  
[www.elprincipaleixample.com](http://www.elprincipaleixample.com)

**Friday, July 27**

**Registration (8:30-9:00)**

**Pressure-Induced Metallization and/or Superconductivity-II**

(Àgora hall, CosmoCaixa Museum. Chair: [Deemyad, Shanti](#))

**Fr1.1 (9:30-10:00):** [Invited](#) ([Bergara, Aitor](#)), *Anharmonic effects and optical spectra in superconducting hydrogen.*

**Fr1.2 (10:00-10:15):** [Oral](#) ([Li, Bin](#)), *Superconductivity in Titanium Hydrides at High Pressures.*

**Fr1.3 (10:15-10:30):** [Oral](#) ([Zhu, Jinlong](#)), *Superconductivity emerging from a Weyl semimetal  $\text{NbIrTe}_4$  under pressure.*

**Coffee Break (10:30-11:00)**

**New Experimental or Computational Techniques**

(Àgora hall, CosmoCaixa Museum. Chair: [Reparaz, J. Sebastián](#))

**Fr2.1 (11:00-11:15):** [Oral](#) ([Matsumoto, Ryo](#)), *Diamond Anvil Cell with Boron-doped Metallic Diamond Electrodes for Resistivity Measurement under High Pressure.*

**Fr2.2 (11:15-11:45):** [Invited](#) ([Mori, Yoshihisa](#)), *Development of Thermoelectric Measurement at High-temperature and High-pressure using Six-axis Multi-Anvil Press.*

**Electrical Transport Phenomena in Semiconductors & Superconductors**

(Àgora hall, CosmoCaixa Museum. Chair: [Reparaz, J. Sebastián](#))

**Fr2.3 (11:45-12:00):** [Oral](#) ([Yahniuk, Ivan](#)), *Pressure-driven topological phase transitions in  $\text{HgTe}/(\text{Cd},\text{Hg})\text{Te}$  quantum wells.*

**Fr2.4 (12:00-12:30):** [Invited](#) ([Núñez-Regueiro, Manuel](#)), *The pressure evolution of the basal electrical resistivity of cold pressed single crystal graphite.*

**Strongly Correlated Electron Systems**

(Àgora hall, CosmoCaixa Museum. Chair: [Muñoz, Alfonso](#))

**Fr2.5(12:30-13:00):** [Invited](#) ([Watanabe, Shinji](#)), *Grüneisen Parameter in Quantum Critical Yb-Based Quasicrystal.*

**Lunch (13:00-15:00)**

**Fr3.1(15:00-15:30):** Invited (Matsubayashi, Kazuyuki), *Pressure-induced novel superconductivity and quantum critical phenomena in nonmagnetic systems.*

**Fr3.2 (15:30-15:45):** Oral (Kuwayama, Takanori), *Relationship between superconductivity and magnetism on FeSe<sub>1-x</sub>S<sub>x</sub> (x = 0.12) studied by <sup>77</sup>Se-NMR under pressure.*

**Fr3.3 (15:45-16:00):** Oral (Fujiwara, Naoki), *Quantum Critical behavior of LaFeAsO<sub>1-x</sub>H<sub>x</sub> under pressure.*

**Closing**

**Fr3.4 (16:00-16:15):** Summary (Rodríguez, Fernando).

**Fr3.5 (16:15-16:30):** Closing (Goñi, Alejandro R.).

# High Pressure Effects in Semiconductors, Metallization, and Superconductivity

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The effects of pressure on the metallization of material systems and their possible transition into the superconducting state will be discussed primarily from a theoretical point of view. A classic example is the transformation of semiconducting silicon in the diamond structure at atmospheric pressures to metallic forms at high pressures. It was possible for theory to predict new high pressure metallic silicon structures and their superconducting properties. Other examples of this kind will be described.

In the search for superconductivity at high transition temperatures, much of the focus has been on class 2 superconductors such as the cuprates and iron based systems. Here the effects of pressure (both external and internal) have been important. However, an important obstacle has been that at present there is no consensus on a theory of class 2 superconductors. Hence making reliable predictions is difficult.

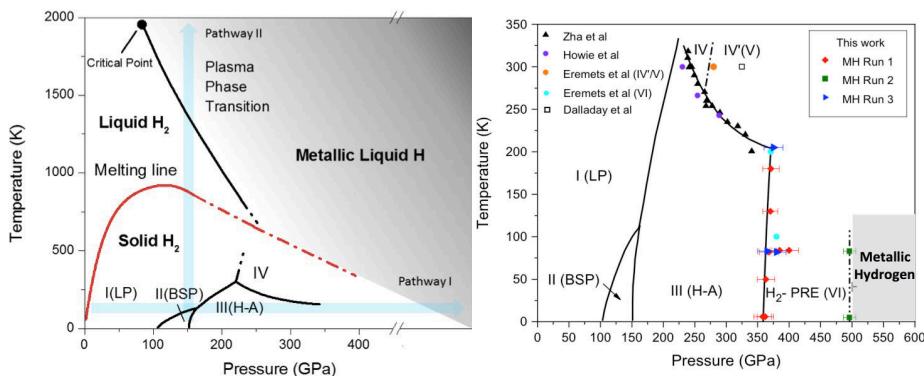
In contrast, class 1 superconductors are understood using the theory of Bardeen, Cooper, and Schrieffer, and both predictions and suggestions for increasing superconducting transition temperatures can be made with some confidence. Some of these theoretical results and proposals will be discussed. Among them is the importance of covalent bonding and structures based on light atoms such as hydrogen and carbon. For the latter, the amorphous-like Q-Carbon material has attracted recent attention because of the observation of superconductivity at 37K and 55K in specific boron doped samples. Some theoretical research will be reported for this system. For hydrogen, theorists have been constrained by an inability to predict reliable high pressure structures. As a result, predictions of the properties of metallization arising from band overlap or partially filled bands has been difficult. The lack of precise structural information for some hydrogen compounds and Q-Carbon are also constraints on theory in this field. Nevertheless, useful calculations have been done, and some of these will be discussed. More importantly, it is hoped that experimental results to be discussed at this conference on metallization of hydrogen and high temperature superconductivity in hydrogen/sulfur systems should help to define the most promising paths for theorists to follow.

## Two Pathways to Metallic Hydrogen and Deuterium

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Hydrogen and its isotopes can be insulators, semiconductors, metals, and possibly superconductors with very high critical temperatures, all depending on the density and the bonding, molecular or atomic. At zero pressure ( $P$ ) and low temperature ( $T$ ) (below 14 K) hydrogen crystallizes as a molecular solid. Wigner and Huntington (WH) studied the dependence of the hydrogen phase diagram on density finding that at a high density or pressure, the molecular bond destabilizes and molecules dissociate to form atomic metallic hydrogen (MH). We have observed this transition at 495 GPa [1], shown in the figure, at liquid helium and liquid nitrogen temperatures. The phase called  $H_2$ -PRE becomes black at high pressure and is semiconducting, before hydrogen metallizes. It was also realized that at a lower, but still high pressure and very high temperatures, there is a temperature driven transition to liquid atomic metallic hydrogen (LMH). This liquid-liquid phase transition is sometimes called the Plasma Phase Transition or the PPT. We have determined the phase line for LMH and liquid atomic deuterium for several values of  $P$  and  $T$ , as well as optical properties and optical conductivity [2, 3]. We observe isotopic differences in the phase lines.



**Figure.** The phase diagram of hydrogen showing the two pathways to MH (left panel, blue arrows). The left panel shows the high temperature pathway to liquid MH; the right shows the low temperature path to the WH phase of MH.

There are several interesting predictions for MH that we are studying: metastability, optical properties in the IR, and the possibility of room temperature superconductivity. MH at low temperatures has probably never before existed in the Universe, thus this is an exciting area of study on a unique material. LMH is the principle component of giant outer planets such as Jupiter and gives rise to its magnetic field via the dynamo. In this talk we shall discuss the techniques and observations that enabled us to make this breakthrough to observe MH that was predicted 83 years ago.

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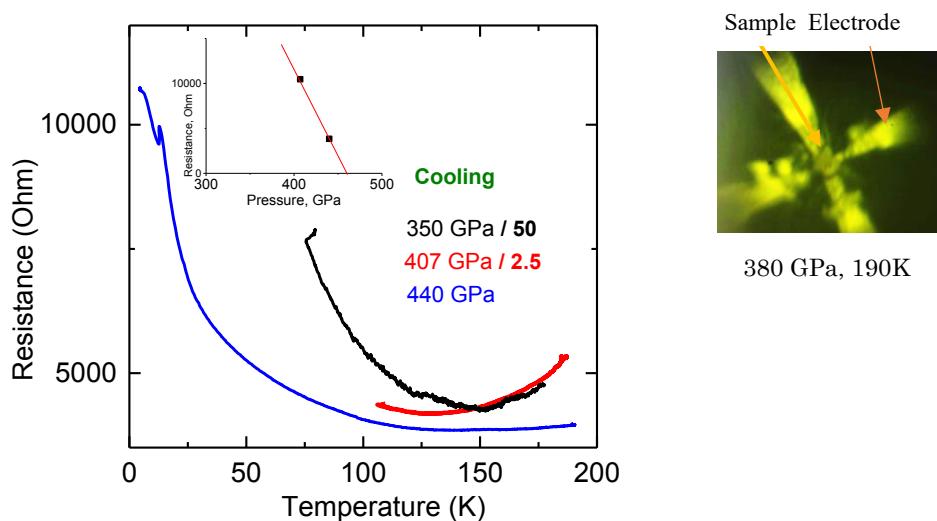
## Molecular semimetallic hydrogen

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Establishing metallic hydrogen is a goal of intensive theoretical and experimental work since 1935 when Wigner and Huntington predicted that insulating molecular hydrogen dissociates and transforms to a metal at high-pressure  $\sim 370\text{-}500$  GPa according to recent calculations. In another scenario, the metallization can be first realized through overlapping of electronic bands in molecular hydrogen in the 250–500 GPa pressure range. The calculations are not accurate enough to predict which option is realized. Our data say that hydrogen transforms to semimetal by closing the indirect band gap in the molecular phase III at pressure  $\sim 360$  GPa [1]. Above this pressure, the metallic behaviour in the electrical conductivity appears, the reflection significantly increases. With pressure, the electrical conductivity strongly increases as measured up to 440 GPa (Fig. 1). The Raman spectra evidence that hydrogen is in the molecular phase III at pressures at least up to  $\sim 420\text{-}440$  GPa. At higher pressures measured up to 480 GPa, both vibron and phonon modes in the Raman signal disappear indicating further transformation to a good molecular metal or to an atomic state.



**Figure 1.** Temperature dependence of resistance of hydrogen at different pressures. The upper curves are scaled (the coefficients are indicated) to allow for a visual comparison with the two other curves on the plot. At low temperature the resistance increases, but the behavior is not that of a semiconductor, as  $R(T)$  can be described with activated behavior, but with an extremely small activation energy of  $\sim 2$  meV. The insert shows an extrapolation of the resistance to higher pressures, which indicates that the state of a good metal can be reached below 500 GPa.

Right. Photograph of the sample of hydrogen (bright spot in the center) together with four attached electrodes at 380 GPa and 190 K. The photo was taken in a reflection illumination

## Raman studies of deuterium and hydrogen at high pressures and low temperatures

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The discovery of phases IV [1,2] and V [3] has recently reignited interest in the studies of the dense hydrogen. As a result of this discovery, the phase diagrams of hydrogen and deuterium above 180 GPa and at 300 K have been extensively studied both experimentally and theoretically. The experimental studies radically expanded both phase diagrams by pushing the achievable  $P$ - $T$  conditions to new limits. Despite the remarkable progress in our understanding of the behavior of both isotopes at very high pressures, there has been no attention given to the  $P$ - $T$  conditions at medium compressions. The behavior of hydrogen at these conditions is important to understand the evolution of the system during its transformation from the weak intermolecular state with strong intra-molecular forces (e.g., phases I, II, and III) to the layered phases (e.g., phases IV and V) with weaker intra-molecular bonding and stronger intermolecular interactions. At the same time, the rich and fascinating physics, which governs the behavior of dense hydrogens can still provide some unexpected and interesting results.

I will revisit  $P$ - $T$  phase diagrams of hydrogen and deuterium and present our resent Raman measurements on both isotopes in a wide pressure and temperature range. I will show how the quantum effects influence the *ortho-para* conversion rates and how rotational motion of the molecules depends on density.

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- [3] Dalladay-Simpson et al. *Nature* (2016)

## High- $T_c$ cuprates under hydrostatic and uniaxial compression

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High pressures are widely used in the study of high-temperature cuprate superconductors offering valuable insights on the superconducting mechanism and leading to record values of their superconducting transition temperature,  $T_c$ . In the well-studied  $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$  family, it has been shown that the effect of hydrostatic pressure application on  $T_c$ , is the net outcome of different, opposite in sign uniaxial pressure derivatives [1,2,3]. Combined hydrostatic and uniaxial pressure studies are required to clarify the role played by the underlying lattice in mediating superconductivity and its interplay with other electronic orders in the cuprates phase diagram.

We have used high resolution inelastic x-ray scattering to investigate the effect of hydrostatic [4] and uniaxial [5] compression on the charge density wave instability which competes with superconductivity in underdoped  $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$ . We will discuss the very different results obtained under hydrostatic and uniaxial compression with respect to the pressure dependence of  $T_c$  and to the pressure-induced modification of the crystal structure, as well as to alternative tuning parameters of the electronic ground state.

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## Pressure – Temperature phase diagram of superconducting FeSe single crystals probed by neutron and x-ray diffraction, x-ray emission and absorption spectroscopies

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In addition to its low pressure nematic state [1,2,3], FeSe shows a pressure-induced antiferromagnetic (AFM) order [4] simultaneously where  $T_c$  increases strongly, from 9K up to 35K at 6-7GPa.

We confirm, thanks to x-ray diffraction under high pressure (HP), that its low temperature orthorhombic distortion is retained in the region of superconductivity and antiferromagnetism coexistence [5]. Moreover, at  $P>7$ GPa, the decrease of  $T_c$  is found concomitant with the formation of a new polymorph, with an orthorhombic Pnma structure, characterized by a 3D network of face sharing FeSe<sub>6</sub> octahedra [6]. This 3D phase coexists with the low pressure 2D form up to the highest pressure studied.

We have also studied the magnetism of FeSe by performing resonant inelastic x-ray scattering (RIXS) at K-edge of iron. The x-ray absorption spectra (XAS) measured at 10K and HP are strongly modified at 7GPa, corresponding to the change from the tetrahedral to the octahedral coordination of Fe in the Pnma structure. More interestingly the x-ray emission spectra (XES) measured at the K  $\beta'$  line shows a significant increase related to the sudden enhancement of the local Fe magnetic moment occurring in the FeSe 3D form [7]. Corroborated by ab-initio simulations, this evidences a low-spin (LP) to a high-spin (HP) transition. Finally, our neutron diffraction experiments under HP-low T have not revealed any detectable long range magnetic order associated to the intermediate pressure-induced AFM phase or to the 3D HP polymorph despite its higher iron magnetic moment.

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- [2] P. Massat, P. Toulemonde, Y. Gallais *et al.*, *PNAS USA* **2016**, 113, 9177.
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## Pressure-induced superconductivity in the pyrite phase of palladium diselenide

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The exploration of the chemical, structural and electronic parameters of a solid which lead to the appearance or the enhancement of superconductivity is an ongoing topic of intensive research. In transition-metal dichalcogenides, a class of compounds known for their unusual electronic properties and rich intercalation chemistry, superconductivity often competes with diverse exotic phases. Here we report the emergence of superconductivity after the pressure-induced transition to the pyrite-type structure. The critical temperature

depends on pressure with a typical dome shape, reaching a maximum value of  $T_c = 13.1$  K at a pressure  $\sim 23$  GPa. This is by far the highest critical temperature of superconductivity reported up to now in the family of transition-metal dichalcogenides.

Our lattice dynamic studies show unambiguously a correlation between critical temperature and the bonding of  $\text{Se}_2$ -dumbbells in the pyrite structure underlining the crucial role of bonding as tuning parameter for superconductivity. Ab initio calculations of the electronic band structure of pyrite  $\text{PdSe}_2$  indicate its topologically nontrivial nature in the form of Dirac crossings and nodal lines in the vicinity of the Fermi level. Nodal lines close to the Fermi level can lead to novel exotic superconducting states.

The significance of the bonds length as a tuning parameter for superconductivity allows to expect even higher  $T_c$  values in other pyrite compounds. The tuning of their crystal and electronic structure can be accomplished by application of pressure or by chemical substitution, eventually stabilizing the superconducting state at ambient pressure. The discovery of topological bands in  $\text{PdSe}_2$  pyrite suggests further studies on other transition-metals compounds in the pyrite structure with respect to topological properties and their relation to superconductivity.

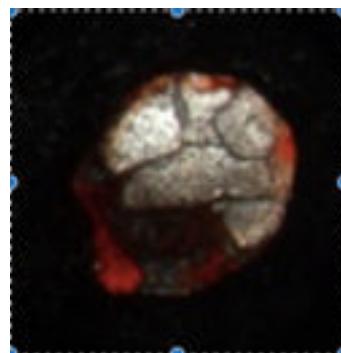
## Fluorine chemistry at extreme conditions: possible synthesis of HgF<sub>4</sub>.

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We sought to confirm a prediction that HgF<sub>4</sub> would form under conditions of an excess of molecular fluorine and high pressure from HgF<sub>2</sub>.<sup>1</sup> Two sets of experiments were performed on HgF<sub>2</sub> and HgF<sub>2</sub> + XeF<sub>2</sub> mixture, respectively, both pressurized inside a symmetric diamond anvil cell. Both samples were separately irradiated at the Advanced Photon Source (APS) with white x-rays. In the mixture sample, molecular fluorine was released upon irradiation via XeF<sub>2</sub> +hv→Xe+F<sub>2</sub> as confirmed by Raman spectroscopy.<sup>2</sup> The sample color turned yellow shortly after irradiation at low pressure and then deep red when pressurized near 40 GPa similarly to the color changes observed when pressurizing solid molecular oxygen. The pure HgF<sub>2</sub> sample, on the other hand, did not decompose with irradiation and remained stable to the highest pressure studied (45 GPa). We observed the formation of solid α-F<sub>2</sub> under pressure (the highest pressure it has ever been observed) via Raman spectroscopy including other dramatic spectral alterations suggesting the formation of at least one more compound within the mixture which we suspect is HgF<sub>4</sub> synthesized via the following proposed reaction: HgF<sub>2</sub>+F<sub>2</sub>→HgF<sub>4</sub>. Far-infrared (IR) experiments were performed at the Canadian Light Source on both samples. As pressure was increased in the mixed and irradiated sample, a broad peak or peaks appeared near 474 cm<sup>-1</sup> above 25 GPa which then disappeared above 33 GPa. The peak or peaks reappeared when the pressure was reduced below 33 GPa and then again disappeared below 25 GPa as the pressure was reduced to ambient. This observed behavior has been predicted previously.<sup>1</sup> This peak was absent in the virgin HgF<sub>2</sub> sample at all investigated pressures. X-ray diffraction and Resonant X-ray emission (L-edge) studies conducted of both samples at the APS Sector 16 ID-B and 16 ID-D beam lines respectively indicated significant alterations in the irradiated mixture sample at various pressures.



**Figure 1:** Molecular fluorine (deep red), probably in the alpha phase, near 40 GPa produced via x-ray irradiation of a mixture of HgF<sub>2</sub> and XeF<sub>2</sub>, as viewed through one diamond pressurizing the sample.

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## Influence of polar pressure transmission medium on the pressure coefficient of excitonic interband transitions in monolayer WSe<sub>2</sub>

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Influence of the pressure transmission medium (PTM) on the excitonic interband transitions in monolayer tungsten diselenide (WSe<sub>2</sub>) has been investigated using photoluminescence (PL) spectra under hydrostatic pressure up to 5 GPa. Three kinds of PTMs, condensed argon (Ar), 1:1 n-pentane and isopentane mixture (PM), and 4:1 methanol and ethanol mixture (MEM, a PTM with polarity), are used. It is found that when either Ar or PM is used as PTM the PL peak of exciton related to the direct K-K interband transition shows a pressure-induced blue-shift at the rates of  $32 \pm 4$  and  $32 \pm 1$  meV/GPa, respectively, while it becomes up to  $50 \pm 9$  meV/GPa when MEM is used as PTM. The indirect A-K interband transition presents almost no shift with increasing pressure up to approximately 5 GPa when Ar and PM are as PTM, while it shows a red-shift at the rate of  $-17 \pm 7$  meV/GPa by using MEM as PTM. The results reveal that the optical interband transitions of monolayer WSe<sub>2</sub> are very sensitive to the polarity of PTM. The anomalous pressure coefficient for polar PTM of MEM is ascribed to the existence of hydrogen-like bonds between hydroxyl in MEM and Se atom under hydrostatic pressure.

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## Inducing the luminescence of quenched Ce<sup>3+</sup> centres in gadolinium gallium garnet by high pressure.

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In this work we present results of spectroscopic measurements (photoluminescence spectra, luminescence decay kinetics) of Gd<sub>3</sub>Al<sub>2</sub>Ga<sub>3</sub>O<sub>12</sub>:Cr<sup>3+</sup> (GAGG:Ce<sup>3+</sup>) and Gd<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub>:Ce<sup>3+</sup> (GGG:Ce<sup>3+</sup>) garnets performed under high pressure up to 30 GPa and across temperatures from cryogenic up to above RT as well as measurements of photocurrent excitation spectra (PCE).

In the Gd<sub>3</sub>(Al,Ga)<sub>5</sub>O<sub>12</sub>:Ce<sup>3+</sup> mixed garnets, the presence and efficiency of the typical Ce<sup>3+</sup> luminescence (related to transitions between the excited states of 5d<sup>1</sup> configuration and states of the ground configuration 4f<sup>1</sup>) strongly depends on the Al/Ga ratio, and gradually deteriorates with increasing gallium content up to a point of total quenching of luminescence in GGG:Ce<sup>3+</sup>. The reason of this effect is a gradual lowering of the energy of the edge of conduction band (CB) with increasing Ga content. This in turn diminishes the energetic distance between the 5d excited states of Ce<sup>3+</sup> and CB leading to gradual increase of the probability of thermally assisted autoionization – transfer of electron from Ce<sup>3+</sup> to the conduction band. This leads to progressively smaller activation energy value for nonradiative quenching of luminescence, down to essentially zero for pure gallium sample – GGG:Ce<sup>3+</sup> where all of the 5d states are virtually degenerated with CB, leading to no observable luminescence regardless of temperature. The existence of autoionization quenching mechanism was verified by photocurrent excitation (PCE) spectroscopy measurements of Gd<sub>3</sub>(Al,Ga)<sub>5</sub>O<sub>12</sub>:Ce<sup>3+</sup>. In the PCE spectra, bands related to optical transitions between 4f and 5d states were detected confirming that excitation of Ce<sup>3+</sup> leads to transfer of electron to the CB.

For the GGG:Ce<sup>3+</sup> sample under the influence of high hydrostatic pressure in the DAC, we have observed that the Ce<sup>3+</sup> luminescence in GGG becomes visible around 2 GPa and increases in intensity as the pressure increases. This result indicated that the edge of the CB shifts towards higher energy with respect to Ce<sup>3+</sup> levels, effectively exposing the initially degenerated excited states of Ce<sup>3+</sup> from the conduction band. In the next step, measurement of luminescence decay kinetics of the GGG:Ce<sup>3+</sup> sample with respect to temperature and pressure were performed by means of time resolved emission spectroscopy. For each investigated pressure, the temperature dependence of luminescence decay time allowed to determine the activation barrier for nonradiative quenching, which is the distance to the edge of the CB. Therefore, pressure dependence of the Ce<sup>3+</sup> - CB energetic distance has been obtained.

From the obtained spectroscopic measurement results under high pressure (PL emission energy, activation energy for autoionization) a detailed discussion of the location of ground and excited states of Ce<sup>3+</sup> with respect to CB, as well as its pressure dependence shall be provided. The combination of experimental data of time resolved emission spectroscopy measurement at high pressure and temperature dependent PCE allowed to present a kinetic model of relaxation of excited Ce<sup>3+</sup> centres in GGG:Ce<sup>3+</sup> and GAGG:Ce<sup>3+</sup> host. The model takes into account both radiative and nonradiative processes, involving deexcitation path related to transitions to impurity trapped exciton (ITE) state as the main luminescence quenching mechanism. The fact that the photoluminescence of GGG:Ce<sup>3+</sup> appeared at elevated pressure, combined with the experimentally obtained pressure dependence of Ce<sup>3+</sup> - CB energetic distance allowed to estimate the energy of the ITE to be ~600 cm<sup>-1</sup>.

## Influence of high hydrostatic pressure on intraconfigurational transition in lanthanide ions doped inorganic hosts

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Inorganic hosts doped with lanthanide ions are known for their use in scintillators, phosphors in fluorescent lamps, white LEDs and glow-in-the-dark materials. Recently, a lot of work has been devoted to verifying the possibility of using such phosphors in the field emission display (FED) technology and the medical phototherapy and photodiagnostics.

Optical transitions occurring between the lanthanide ions localized states, can belong to the  $4f^n$  ( $f-f$  transition) or the  $4f^n$  and  $4f^{n-1}5d$  electronic configurations ( $f-d$  transitions). The  $f-f$  transitions are parity forbidden and result in the narrow excitation and emission bands, since the electrons occupying the  $f$  orbitals are effectively shielded from the environment by the completely filled  $5s^25p^6$  shells. In contrast, the parity allowed  $f-d$  transitions with typical broad bands are strongly affected by the crystalline environment. This type of transition is most common for  $\text{Ce}^{3+}$  and  $\text{Eu}^{2+}$  doped compounds.

The energy of the  $4f^{n-1}5d$  electronic configuration states of lanthanide ions in relation to the energy of free ion is reduced by the depression energy. The depression energy is a sum of the energy of the centroid shift related to the change in ligands polarization accompanying the transition of an electron from  $f$  to  $d$  shell and the energy of the crystal field splitting. In the ligand- field polarization model the depression is proportional to  $R^{-6}$  whereas the energy of the crystal field splitting is proportional to  $R^{-5}$ , where  $R$  is central ion-ligands distance.

Since applying high pressure causes the reduction of bond lengths, and, as a consequence, increase of the crystal field strength and the centroid shift, a strong pressure-induced red shift of the luminescence related to the  $d-f$  transition is expected in the majority of cases. However, in this study we will show the results of high pressure spectroscopic studies of inorganic materials doped with lanthanide ions in which  $d-f$  transitions occur, while the value of redshift of luminescence is negligibly small or even equal to zero.

## High Pressure Study of the Yellow Luminescence in Be-doped GaN

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Before realization of the p-type doping in gallium nitride by using magnesium, beryllium had been taken into account as a natural candidate for such doping. However, so far no one was able to realize p-type conductivity in such way. On the one hand, hybrid density functional calculations [1] have shown that Be is a deeper acceptor (550 meV ionization energy) than Mg (260 meV ionization energy), and that this is the fundamental reason why Be p-type doping is ineffective. On the other hand it has been also suggested that with increasing doping level most of the beryllium is incorporated into the crystal in the interstitial position. In such position beryllium acts as a donor not as an acceptor [2]. Another model proposes that the nitrogen vacancies are responsible for self-compensations mechanism in doped gallium nitride [3].

It is well known that GaN:Be possesses two luminescence bands; one at 3.38 eV and a second near 2.2 eV at an energy that is close to that of the parasitic yellow luminescence often existing in undoped GaN crystals. In order to shed more light on this issue, we performed high hydrostatic pressure studies of bulk, Be-doped gallium nitride crystals using the diamond anvil cell technique. We observed a splitting of the yellow luminescence line under hydrostatic pressure into two components, one which is strongly dependent on applied pressure and another whose pressure dependence is more modest. Together with hybrid functional calculations, we attribute the strongly-varying component to the beryllium-oxygen complex. The second component of the yellow luminescence possesses very similar pressure behavior to the yellow luminescence observed in undoped samples grown by the same method, behavior which we find consistent with the C<sub>N</sub> acceptor. At higher pressure, we observe the vanishing of yellow luminescence and a rapid increase in luminescence intensity of the UV line. We explain this as the pressure-induced transformation of the Be-O complex from a highly localized state with large lattice relaxation to a delocalized state with limited lattice relaxation, also observed in positron annihilation experiment as a function of temperature [4].

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## Electronic aspects of adsorption at semiconductor surfaces: the equilibrium pressure, growth and doping

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It is shown that the adsorption at semiconductor surfaces entail the change of their electronic properties, including the number of states, their energy and occupation. Thus during the process the electron may be shifted between the states, both decreasing or even increasing the energy which contributes to the energy balance, i.e. it affects the adsorption energy. The effect may change the adsorption energy by several electronvolts. The effect persist for the Fermi energy pinned by specific, partially filled surface states. When the electron transfer is not possible, i.e. the surface states are fully empty or fully occupied, that occurs for specific coverage of the surface, the Fermi level is no longer pinned, that entails the sudden change of the adsorption energy. That is associated by the change of the equilibrium pressure over the surfaces by several orders of magnitude. The span is so large that the typical growth proceeds in the situation that the Fermi level is not pinned, it is dependent on the Fermi level in the bulk, i.e. the doping. The presented examples include adsorption of hydrogen, ammonia and nitrogen at GaN(0001) and AlN(0001) metal surfaces. Parallel results were obtained nitrogen terminated GaN(0001) surface. Similar results are shown for Si adsorption at SiC(0001) Si-polar surface. Thus the effect is universal, it occurs for majority of the growth processes. The electronic properties may be easily affected by presence of other species at the surface, affecting the electric charge balance. Thus the effect may explain surfactant influence on the growth and doping of semiconductor crystals and layers.

## Mechanisms for Structural Phase Transformations in High Pressure Solids

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We present a new strategy for the search for the minimum energy pathway for structural transformations in high pressure crystalline solids. The methodology does not require the assumption of *a prior* reaction coordinate. Random pathways were chosen based on the known atomic coordinates of the initial and final structures and improve iteratively using a global optimization scheme based on the particle-swarm optimization procedure [1]. We verified this procedure on several known structural transformations and applied it to explore the transition states of the successive high pressure transformations in Si and the more complex face-center-cubic to cI16 phase transformation of Li at high pressure. Applications on several mineral systems will be illustrated.

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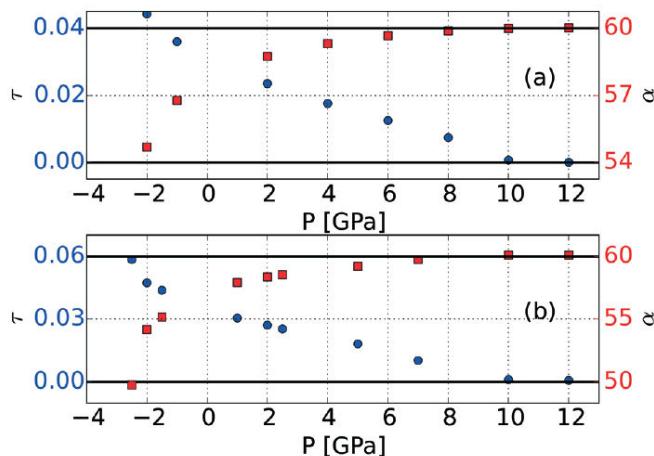
## Prediction of the stability of the rhombohedral phase in IV–VI monochalcogenides and its origin

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The rhombohedral monotellurides, GeTe and SnTe, are non-centrosymmetric materials with ferroelectric behavior and potential applications in thermoelectricity and spintronics. In a previous computational study, it was found that the rhombohedral phase may also be the thermodynamically most stable phase in SnSe and GeSe at low temperatures. In the present study, we explore the mechanical and thermodynamic stability of the rhombohedral phase in these systems and its enhancement as a function of pressure and temperature using density functional theory calculations. Within the region of stability, we examine the structure, bonding and physical properties of the rhombohedral phase. This phase is a distorted rock-salt phase forming a non-spherical lone-pair with an opposite directionality to the chemical bond. The monochalcogenides in this phase exhibit ferroelectric behavior, and we calculate the electric polarization. Finally, the transition from a rhombohedral to rock-salt phase at high pressures is examined and found to be second-order at zero Kelvin.



**Figure** Distortion parameters from the rock-salt phase:  $\tau$  in units of the lattice parameter, displayed as circles, and  $\alpha$  in degrees, displayed as squares. (a) for GeTe and (b) for GeSe.

Uri Argaman, Ran E. Abutbul, Elad Segev and Guy Makov, CrystEngComm, 2017, 19,6107

## SnI<sub>4</sub> and GeI<sub>4</sub> under high pressure: a combined X-ray absorption X-ray diffraction study

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Thanks to the advent of nanopolycrystalline diamonds<sup>[1]</sup> usable as anvils in diamond anvil cells we could measure on the same set-up (SAMBA beamline, Synchrotron SOLEIL) under the same conditions X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) to study the behavior of the molecular semiconductors SnI<sub>4</sub> and GeI<sub>4</sub> at high pressures. Reverse Monte Carlo (RMC)<sup>[2]</sup> and traditional XAS analysis have been applied and XRD data has been used to provide lattice parameters and detect phase transitions.

In these molecular compounds Sn(Ge) is localized at the center of I<sub>4</sub> tetrahedron. Under pressure they exhibit reversible pressure induced amorphization (PIA)<sup>[3,4]</sup>, accompanied by metallization. The mechanism proposed to explain the transformation is a charge transfer from intramolecular bonds (Sn(Ge)-I) to intermolecular bonds (I-I). At ambient pressure these compounds crystallize in a cubic structure with the molecules interacting through Van der Waals forces. At high pressure, charge transfer leads to the creation of Sn(Ge)-I-I-Sn(Ge)-I chains<sup>[5]</sup> and conductivity increases. Such mechanism can effectively explain the amorphization and the metallization, but it has not been fully demonstrated due to the lack of crystallographic information.

In SnI<sub>4</sub>, XRD data indicate a progressive amorphization that takes place above 15 GPa. EXAFS reveals a more complex picture where Sn-I compression is followed by expansion and splitting in two sub shells. RMC XAS fitting was used to analyze the complex coordination scheme around the iodine atoms. From radial distribution functions we observe the approach of I atoms of different SnI<sub>4</sub> tetrahedra and the formation of I-I bonds. Between 10 and 15 GPa a redistribution of the number of intra and inter I-I bonds is observed, until they become equivalent, while Sn-I and I-I distributions remain different even after amorphization.

Our results are in agreement with the model proposed by Pasternak and Taylor<sup>[4]</sup> (creation of chains of linked SnI<sub>4</sub> tetrahedra), and provide a new understanding on this process of amorphization. SnI<sub>4</sub> results will be compared to those recently obtained on the isomorphic GeI<sub>4</sub>.

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## Order-Disorder Phase Transition from $\delta$ -O to $\alpha$ -T boron

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Crystalline boron is the last monatomic system for which the phase diagram is not fully determined yet. Among many allotropes of boron, the tetragonal phase is a particularly confusing phase. Theoretically,  $\alpha$ -T boron with the B composition 52 ( $\alpha$ -T-B<sub>52</sub>) is predicted [1]. Several HPHT syntheses of  $\alpha$ -T-B<sub>52</sub> were reported. Surprisingly, in spite of similar conditions of preparations, all the reported structures are more or less different. A theoretical study by Uemura *et al* has identified the characteristic features of pure  $\alpha$ -T-B<sub>52</sub> [2]. Based on this study, now it is almost certain the existence of  $\alpha$ -T-B<sub>52</sub> at high pressures and high temperatures.

Recently, Ekimov *et al* synthesized hydrogenated  $\alpha$ -T-B<sub>52</sub>H<sub>m</sub> by a thermal decomposition of decaborane by HPHT method, with the initial H content being  $m=7.7$  [3]. Afterwards they annealed the crystals at ambient pressure and observed two phase transitions as  $T$  was raised. At  $T_{a1}=450^\circ\text{C}$ ,  $m$  reduced to 4.7, and at  $T_{a2}=700^\circ\text{C}$  hydrogen was fully released. During the second step, the tetragonal lattice underwent a transition to an orthorhombic lattice (called  $\delta$ -O-B<sub>52</sub>). In this paper, we focus on the transition from  $\alpha$ -T-B<sub>52</sub> to  $\delta$ -O-B<sub>52</sub>. This transition casts a new light on the stability of  $\alpha$ -T-B<sub>52</sub>.

The structure of  $\delta$ -O-B<sub>52</sub> is a slightly distorted variant of  $\alpha$ -T-B<sub>52</sub>: four icosahedra B<sub>12</sub> are almost the same with a small lattice distortion of  $\Delta a/a=1.4\%$ . Our calculation shows the energy gain by transforming to  $\delta$ -O-B<sub>52</sub> is small, 2meV/atom. There is no energy barrier, so that  $\alpha$ -T-B<sub>52</sub> should spontaneously transform to  $\delta$ -O-B<sub>52</sub>. Why were there no experiments reporting this transition?

The clue for answering this question is the interstitial atoms with partial occupancy: especially the half occupied 4c sites. The origin of the orthorhombic distortion occurs only when two atoms at 4c sites are ordered in the zigzag arrangement. These two 4c atoms are randomly distributed in the as-grown crystals of HPHT methods. It turned out that  $\delta$ -O-B<sub>52</sub> is the ordered structure with respect to two 4c atoms and stable at low  $T$ , whereas  $\alpha$ -T-B<sub>52</sub> is a disordered variant of  $\delta$ -O-B<sub>52</sub> and is stable the high  $T$ . Hence the transition can be regarded as the order/disorder transition. Our calculation shows the transition temperature as  $T_{od}=1300\text{K}$ . However, in view of the high temperature of the synthesis, it is difficult for  $\delta$ -O-B<sub>52</sub> to grow. Then, the next question arises is what makes it possible to obtain  $\delta$ -O-B<sub>52</sub> in Ekimov's experiment. Usually, once the high-temperature phase is crystalized, the structure is frozen in, and hence the low-temperature phase never appears. This is the case for all the experiments except Ekimov's one. In Ekimov's case, although the pristine crystals had the T lattice, hydrogen atoms must have special role. The hydrogen-release temperature  $T_{a2}$  is much lower than  $T_{od}$ , so that the strong affinity of causing the O lattice acts on the T lattice. However, there is an energy barrier to prevent two 4c-site atoms from moving. The hydrogen release triggers the movement of B atoms so arranged.

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## Pressure-induced order-disorder transitions in hybrid perovskites

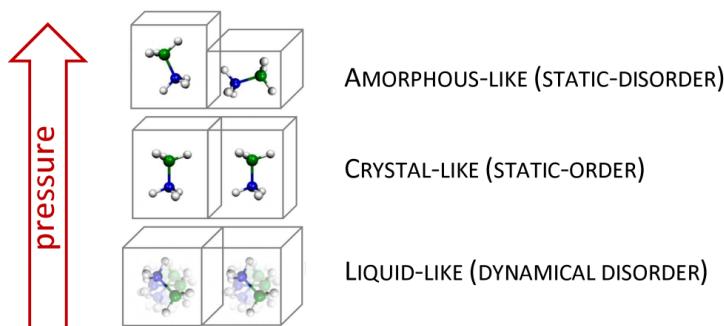
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Currently organometal halide perovskites are among the most promising materials for solar cells technology. Indeed the efficiency of devices based on these materials has been pushed well beyond 20% in a few years as a result of increasing research efforts aimed to optimize properties like long diffusion length, largely tunable bandgap and high absorption coefficients. Nevertheless, high-pressure studies of these hybrid perovskites are scarce despite knowledge of the effects induced by volume compression on the structural and optical properties is crucial to develop a focused strategy for improving performances of known compounds or searching for new materials [1,2]. In particular, it has been recently shown that a long diffusion length, crucial for photovoltaic application, results from polaronic conduction due to a *liquid-like* behavior of the organic cations within the inorganic perovskitic cage [3].

We investigated optical and structural properties of several methylammonium (MA) lead halide perovskites ( $\text{MAPbX}_3$  with  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) under high-pressure [4-5]. These systems show a common behavior on increasing pressure: the organic cations are freely rotating at low pressure, then freeze within a crystal order and, on further increasing pressure, enter in an apparently *amorphous* phase where the organic molecular structure is however preserved (Figure 1). On releasing pressure, the systems show an almost complete reversibility. A comparison of the pressure effects and of the PT phase diagrams obtained in compounds with different halogens, enabled us to identify a common scheme for the observed behavior, where a key role is played by the hydrogen-bond whose strength can be tuned by compressing the perovskitic cage around the organic cation.



**Figure 1:** Pressure evolution of organic cation ordering

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## Blue-emitting organic semiconductors under pressure: new perspectives on intermolecular order

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Molecular-level chain conformations and intermolecular self-organization are essential parameters for controlling transport and optical emission in  $\pi$ -conjugated oligomers/polymers. Fundamentally important are also other levels in the solid state structure - from intramolecular details to the complex polymer hierarchies and macroscopic anisotropy. Hydrostatic pressure is an elegant tool to enhance intermolecular interactions in  $\pi$ -conjugated systems and influence their molecular geometry without any chemical intervention. Over the past decade, high pressure optical spectroscopy using a diamond anvil cell (DAC) has been highlighted in a variety of  $\pi$ -conjugated blue-emitting polymers and molecules. These studies have emphasized the differences in singlet versus triplet excitons [1], changes in backbone conformation deduced from optical measurements [2], and several other attributes of the tuning properties of pressure on conjugated molecules/polymers [3].

Although optical spectroscopic studies of polyfluorenes (PFs) under high pressure have been carried out over the last decade, they lacked concomitant structural information due to the difficulties in X-ray scattering measurements through a DAC for soft materials. In the recent years, we have taken steps in this area with new synchrotron sources and development towards soft materials with changes in experimental designs and data analysis. X-ray data have confirmed the planarization of backbone predicted by optical studies and further provide insights into the intermolecular order as a function of pressure and molecular weight [4,5]. In this presentation, we will highlight our recent work on ethyl-hexyl substituted PF under pressure.

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# Unravelling the Interplay between Microstructure and Photophysics for Luminescent Magnus' Green Salt Derivatives using Pressure-Dependent Spectroscopy

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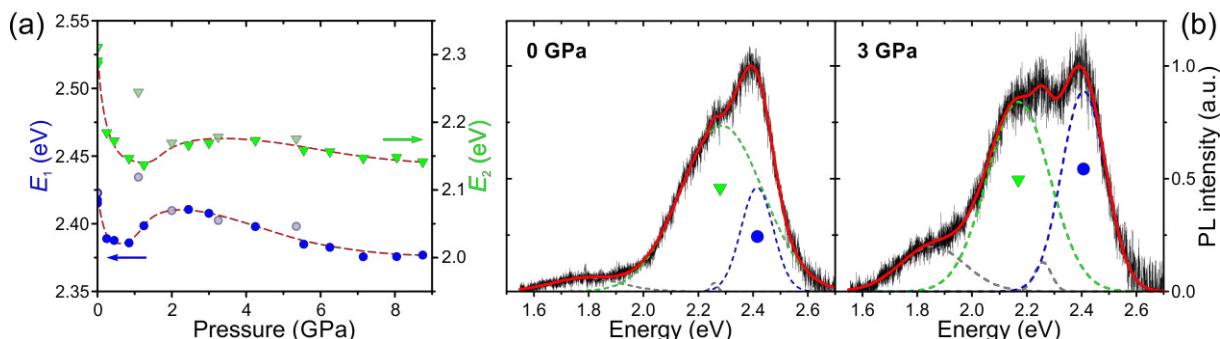
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Semiconducting light-emitting materials based on conjugated (macro-)molecules possess enormous technological potential owing to low-cost large-area solution-based processing and the possibility of tuning the spectral properties by chemical modification. Despite recent progress, several obstacles remain, e.g., the decrease of luminescence efficiency and spectral purity upon degradation under ambient conditions, thus motivating further pursuit of high-performance materials.

Here we report the first instance of synthesis and characterisation of luminescent derivatives of the so-called Magnus' Green salt (MGS) [1] – a quasi-1D semiconductor comprising a linear chain of Pt atoms substituted with organic ligands. The resultant coordination compounds, termed ‘M-cyanoplatinates’, have the general formula  $[\text{Pt}(\text{NH}_2\text{L})_4][\text{Pt}(\text{CN})_4]_n$  where L is an alkyl group. Unlike MGS, M-cyanoplatinates can be solution-processed into thin films. Using ‘matrix-assisted’ assembly we show that their luminescent properties are enabled by the stacking of anion-cation dimers into 1D chains. The luminescence of M-cyanoplatinates is found to be remarkably stable, even following thermal annealing in air at 200 °C. M-cyanoplatinates thus represent a promising new strategy for stable next-generation light-emitting materials.

We also report the use of photoluminescence (PL) and Raman spectroscopy at varying hydrostatic pressures (up to 9 GPa) in order to elucidate the relationship between intra- and inter-chain microstructure of M-cyanoplatinate films and the resulting optical properties. Notably, such analysis allows the spectrally-overlapping, simultaneously-occurring radiative decay processes to be resolved.



**Figure 1:** Pressure dependence of the luminescence properties of  $[\text{Pt}(\text{NH}_2\text{L})_4][\text{Pt}(\text{CN})_4]_n$  where L = 6-methylheptyl. (a) Evolution of peak maxima in the PL spectra. Solid and open symbols correspond to data recorded at increasing and decreasing pressures, respectively. Dashed red lines are a guide to the eye. (b) Representative PL spectra recorded at the indicated pressures. Solid black lines: actual data; dotted lines: Gaussian fitting peaks; solid red lines: sum fits. The spectra are peak-normalised for clarity.

## Pressure dependence of multiphonon resonant Raman scattering on 2H<sub>c</sub>-MoS<sub>2</sub> microcrystalline samples: the semiconductor to metal electronic phase transition

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Two-dimensional atomic crystals, such as graphene, hexagonal boron nitride, and transition metal dichalcogenides (TMDCs), have attracted considerable attention because of their unique electrical, optical, and mechanical properties. The last class of materials is especially interesting for the next generation of electronic and optoelectronic devices because in contrast to graphene, TMDCs are semiconductors with a nonzero bandgap. Among them, molybdenum disulfide, MoS<sub>2</sub>, has been the most intensively studied. 2H<sub>c</sub>-MoS<sub>2</sub> has P<sub>63</sub>/mmc space group symmetry and consists of a hexagonal plane of Mo atoms sandwiched by two hexagonal planes of S atoms. The unit cell contains two alternating layers with an AB stacking along the c axis. In the bulk, it is a semiconductor with a direct (indirect) band gap of 1.96 eV (1.2 eV) at 300K. In this work Raman-scattering spectra of 2H<sub>c</sub>-MoS<sub>2</sub> were measured at room temperature under hydrostatic pressures up to 30 GPa, in diamond anvil cells. In order to get a deeper insight into the lattice dynamics of 2H<sub>c</sub>-MoS<sub>2</sub>, we performed measurements in a backscattering geometry with a resonant ( $E_L = 1.92$  eV) and a non-resonant excitation ( $E_L = 2.54$  eV). From the results we have estimated the pressure dependence of the multiphonon resonant Raman scattering process involving the LA(M) and the TA(M) and/or ZA(M) phonon replicas of vibrational modes from M points of the Brillouin zone. At about 22 GPa we have observed a splitting in the frequencies of the  $E_{1g}$  and  $E'^{1g}$  first order modes and also a small discontinuity in the 2LA(M) mode. In this pressure range simulations predict a structural phase transition, where the original 2H<sub>c</sub> stacking changing to 2H<sub>a</sub> stacking typical of 2H-NbSe<sub>2</sub>, through layer sliding [1]. This first order transition has also been observed by X-ray diffraction and electrical measurements under pressure [2]. From FTIR measurements under pressure we observe the semiconductor to metal electronic phase transition at about 65 GPa. The ab-initio calculations allow us to estimate that the indirect gap becomes zero at pressures of the order of 25 GPa, a value that is lower than that obtained experimentally.

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## Tuning dimensionality in nanosystems under extreme conditions

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Pressure is a three-dimensional concept. When applied to low dimensional systems there is a general trend towards system dimensionality increase. Such evolution can manifest in very different ways involving either bond reconstruction, nanostructure fragmentation or geometrical changes. The prototypical case of nanoscale high pressure dimensional modification is fullerene polymerization under extreme conditions. Here we will concentrate on less obvious mechanisms leading to dimensionality evolution in nanomaterials. We will for this consider the high pressure behavior of fullerites, carbon and h-BN nanotubes and graphene in different environments.

After considering the generalization of the fullerene (0D) polymerization mechanism for dimensionality change in other 1D and 2D systems [1,2], we will review dimensionality modifications in intercalated/filled nanosystems [3-5], 1D to 2D changes due to the geometrical evolution of carbon nanotubes [6-8] and h-BN nanotubes [9] or 2D to 3D changes related to the interaction with the environment of graphene and other 2D-systems [10-12].

Finally, the opportunities offered by dimensionality tuning for the development of pressure mediated nano-engineering will be discussed including the case of nanocomposites [13]

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## Synthesis and Raman spectroscopy of a layered SiS<sub>2</sub> phase at high pressures

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Dichalcogenides are known to exhibit layered solid phases, at ambient and high pressures, where 2D layers of chemically bonded formula units are held together by weak van der Waals forces. These materials are of great interest for solid-state sciences and technology, along with other 2D systems such as graphene and phosphorene. SiS<sub>2</sub> is an archetypal model system of the most fundamental interest within this ensemble. Recently, high pressure (GPa) phases with Si in octahedral coordination by S have been theoretically predicted [1] and also experimentally found to occur in this compound [2]. At variance with stishovite in SiO<sub>2</sub>, which is a 3D network of SiO<sub>6</sub> octahedra, the phases with octahedral coordination in SiS<sub>2</sub> are 2D layered. Very importantly, this type of semiconducting material was theoretically predicted to exhibit continuous bandgap closing with pressure to a poor metallic state at tens of GPa. I will present on the synthesis of layered SiS<sub>2</sub> with octahedral coordination obtained in a diamond anvil cell at 7.5-9 GPa, by laser heating together elemental S and Si at 1300-1700 K [3]. Indeed, Raman spectroscopy up to 64.4 GPa is compatible with continuous bandgap closing in this material with the onset of either weak metallicity or of a narrow bandgap semiconductor state with a large density of defect-induced, intra-gap energy levels, at about 57 GPa. Importantly, our investigation adds up to the fundamental knowledge of layered dichalcogenides.

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## Centrosymmetric MoS<sub>2</sub> under pressure: revealing spin-polarized nature of bulk electronic bands

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By removing interlayer interactions in layered materials, a new class of systems has emerged which are characterized by two-dimensional (2D) electronic systems with rich physical properties that are absent in their bulk counterparts and can be technologically exploited. Among the layered materials studied so far, 2D single layers of transition-metal dichalcogenide (TMD) semiconductors such as MoS<sub>2</sub>, MoSe<sub>2</sub>, WS<sub>2</sub>, and WSe<sub>2</sub> have raised a large interest for ultrathin optoelectronics and photonics due to their direct band gap at the degenerate but not equivalent K and K' points of the 2D Brillouin zone and strong exciton luminescence. However, the fact that makes 2D TMDs unique is the combination of strong spin-orbit interactions, broken inversion symmetry and time-reversal symmetry, which leads to coupled spin-valley physics that opens the door to new valleytronic devices based on 2D TMDs.

Valleytronic functionalities become possible due to the non-centrosymmetric nature of 2D TMDs. Inversion symmetry is restored when they stack together in the most commonly available 2H polytype, however, some recent spin-resolved photoemission results indicate that valence bands at K point in 2H-MoS<sub>2</sub> retain a high spin-polarized character in spite of its centrosymmetric nature [1,2]. In this work we report results on the absorption coefficient measured in 2H-MoS<sub>2</sub> under pressure and band structure calculations performed by density functional theory. By means of this high-pressure strategy, which pursues the enhancement of interlayer interactions, we show that not only valence bands of centrosymmetric MoS<sub>2</sub> at K(K') points point but also the conduction bands at these points, exhibit a large spin-polarization. Moreover, our results indicate that the spin-arrangement of conduction band states of MoS<sub>2</sub> at K-point opposes to that observed in tungsten-based TMDs. We discuss these results and their consequences for the bright/dark nature of excitons and the search of single-photon emitters in 2D TMDs.

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## High pressure and low temperature Raman scattering in Inorganic Fullerenes of MoS<sub>2</sub>

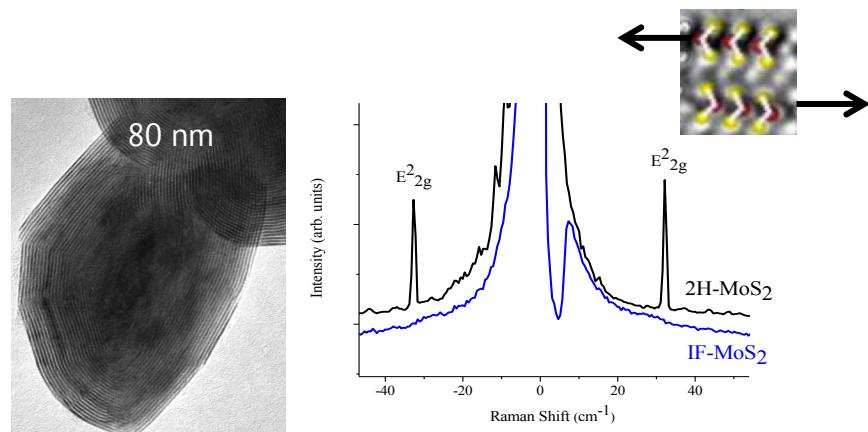
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Resonance Raman scattering has been widely used to study electronic band structures and to investigate the nature of electron-phonon interactions in semiconductors. A key issue in those studies is the role played by intermediate exciton states. We previously [1, 2] demonstrated how Raman scattering of bulk 2H-MoS<sub>2</sub> is resonantly tuned by pressure and temperature - shifting of the excitons energies, towards that of the exciting laser. Here [3] we extend our study to Inorganic Fullerenes (IF) of MoS<sub>2</sub> and find fundamentally different behavior: No resonant Raman for IF-MoS<sub>2</sub> (Fig. 1) for first and second -order Raman transitions.



**Figure 1:** TEM of IF of MoS<sub>2</sub> (left); Shear mode Raman scattering in the bulk and its absence in the IF (right)

Limits on the use of excitons as intermediate state in the scattering process concern, among other aspects, their lifetime. We attribute this different behavior to structural effects that reduce the exciton lifetime: the relative abundance of defects and the random nature of the trigonal prismatic MoS<sub>2</sub> layers [4].

Incommensuration of the layers, which is naturally more pronounced at small particles that are more curved, produces shifts of the layers relative to their adjacent layers and prevents the formation of a pure 2H or 3R symmetry [4]. The random stacking and incommensurate and “interlocked” nature of the IF structure is argued to be the origin of the hindrance of the shear movement (Fig. 1) that we demonstrate in our IF Raman study and the absence of sliding of the layers for 2H<sub>c</sub>-2H<sub>a</sub> transformation, that is known to appear at pressures higher than 16 GPa in the bulk 2H-MoS<sub>2</sub> [1].

We will present the pressure and temperature dependent Raman scattering and compare the resonant response of the IF system to that of the bulk of 2H-MoS<sub>2</sub>. The effect of structural damage and the IF “interlocked” nature on the Raman spectra, will also be discussed.

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## High-pressure study of high-mobility Bi<sub>2</sub>O<sub>2</sub>Se semiconductor

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We report a joint experimental and theoretical study of the structural, vibrational, elastic, optical and electronic properties of the layered high-mobility semiconductor Bi<sub>2</sub>O<sub>2</sub>Se [1] at high pressure by means of X-ray diffraction, Raman scattering and optical absorption measurements combined with *ab initio* theoretical calculations. We report a complete and detail description of its structural, vibrational and optical properties of Bi<sub>2</sub>O<sub>2</sub>Se under compression. The good agreement between experiments and calculations allows providing accurate equation of state, Raman-active mode frequencies and pressure coefficients as well as the optical bandgap of the material. Both Raman-active modes and optical bandgap are described consistently in this material at room pressure for the first time. Bi<sub>2</sub>O<sub>2</sub>Se shows a remarkable structural stability up to 30 GPa, unlike other Sillén-type compounds [2], which undergo a tetragonal to collapsed tetragonal pressure-induced phase transition at relatively low pressures, and unlike their parents Bi<sub>2</sub>O<sub>3</sub> [3,4] and Bi<sub>2</sub>Se<sub>3</sub> [5], which undergo several first- and second-order phase transitions at low pressures. Noteworthy, Bi<sub>2</sub>O<sub>2</sub>Se exhibits considerable electronic changes around 4 GPa, likely related to the progressive shortening and hardening of the long and weak Bi-Se bonds linking the Bi<sub>2</sub>O<sub>2</sub> and Se atomic layers. Our understanding of Bi<sub>2</sub>O<sub>2</sub>Se under compression could help to improve the electronic and thermoelectric properties of compounds based in this interesting compound and help to understand the behavior of other Sillén-type compounds under compression and in general that of layered materials lacking van der Waals forces between their layers.

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## Partial strain transfer between layers in isotopically labeled bilayer graphene under high pressure

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Graphene and other low-dimensional crystals present an intrinsic mechanical strength approaching the theoretical strength predicted by Griffith in 1921 for a defect-free crystal [1]. This brings the possibility for a gigantic tuning of physical properties using mechanical stress.

High pressure techniques allow obtaining large mechanical strains in graphene sheets deposited on substrates. In our experiments, supported graphene is loaded in a pressure transmitting medium (PTM) within a diamond anvil cell (DAC) pressure apparatus. The compressive strain in the graphene sheet arises from the volume reduction of the bulk substrate – which is governed by its equation of state [2]. Recently, it has been shown that this transfer takes place with a certain efficiency depending on the roughness of the substrate, its adhesive character and the rigidity of the 2D system [3-5]. However, the effect of the PTM on the mechanical response of graphene layers under pressure can be large, and it is difficult to dissociate it from the substrate mechanical contribution. In the case of n-layer systems with  $n > 2$ , the higher bending rigidity of the graphene system leads to a loss of conformation and adhesion on the substrate with the consequent reduction of mechanical efficiency transfer [6].

Here we studied turbostratic bi-layer samples under high pressure, which preserves the graphene high mechanical sensitivity to the substrate and the PTM – with a weaker coupling between the two layers compared to the case of a Bernal stacking. The strain in graphene sheets is measured by *in situ* Raman spectroscopy. The sensitive in-plane E2g phonon (G band) energy is used to monitor the lattice distortion. The bottom graphene sheet presents carbon natural isotopic abundance, while the top layer is enriched in <sup>13</sup>C. This setup allows separating the signals of the two graphene sheets: one in contact with the PTM and one in contact with the substrate. Different G band energy shift with pressure are observed for the two layers, which indicates a mechanical decoupling between the two adjacent graphene sheets.

Our results are discussed in terms of the different compressibilities of the various elements of the system (the substrate and the PTM), as well as the adhesion of graphene to these surfaces. We show that graphene presents a very high sensitivity to the nature of the PTM (essentially through its volume-pressure equation of state) and to the phase transitions observed in the PTM with increasing pressure (crystallization, phase transitions).

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## Application of high pressure and high temperature to produce a Bi nanowire/silica nanotube composite for thermoelectric applications

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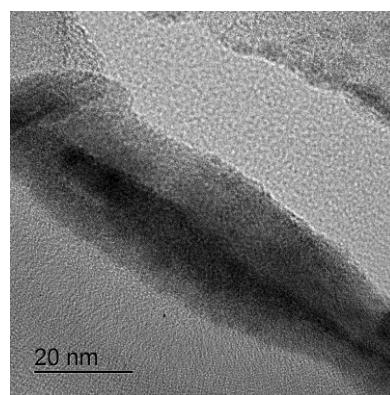
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The performance of a thermoelectric material is determined by dimensionless thermoelectric figure of merit  $ZT=S^2\sigma T/\kappa$ , in which  $S$  is the Seebeck coefficient,  $\sigma$  is the electrical conductivity,  $\kappa$  is the thermal conductivity. Many investigations have demonstrated that low-dimensional thermoelectric materials have higher thermoelectric performances than their bulk form and can be widely used for thermoelectric applications. This is because the modifications of their electronic structure compared to bulk material can enhance  $\sigma$  and  $S$  simultaneously and their lower dimensions will increase the phonon scattering and hence decrease the lattice thermal conductivity. As bismuth is the one of the best thermoelectric materials for Peltier cooling, we hope to improve its properties by designing bismuth nanowires (low-dimensionality) for which large enhancement of the thermoelectric properties have been predicted<sup>1, 2</sup>. Porous materials such as silica nanotubes are ideal for designing a network of nanowires because silica nanotubes present a multiwall nanotube structure with an outer diameter of 30 - 35 nm and inner diameter of 4 - 6 nm. In our study, silica nanotubes were obtained from chrysotile fibers treated with nitric acid. Bi nanowires with exceptional properties can be obtained in nanotubes by inserting liquid Bi at an external pressure larger than the critical pressure related to the surface tension of the metal and the pore diameter by the Laplace equation. A semimetal–semiconductor transition of Bi can be also induced by the quantum confinement of the electron in nanowires with the diameter below 50 nm<sup>1</sup>.

In order to obtain such a nanocomposite, solid bismuth and silica nanotubes were loaded in a resistively heated, diamond anvil cell. The pressure was increased to 0.5 GPa and the bismuth was melted at high temperature, then the liquid Bi was inserted in the nanotubes by increasing the pressure to 2.4 GPa at temperatures around 550 K. Then, these micrometer-sized recovered samples from rhenium gasket were characterized using transmission electron microscopy. The TEM image indicates that the silica nanotubes were filled with 4nm diameter Bi nanowires (figure 1). We will extend our study to measure  $S$ ,  $\sigma$  and  $\kappa$  of this nanocomposite obtained under HP-HT conditions in the near future.



**Figure** TEM image of a Bi nanowire in a silica nanotube obtained under HP-HT conditions

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## Temperature Dependence of Rotational Modes in Fluid Hydrogen and Deuterium

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Since 1906, when Lyman first recorded Hydrogen's spectral signature, the understanding of this fundamental measurement has been key in the early development of quantum mechanics. Additionally, hydrogen is an archetypal system giving insights into more complicated structures of matter, particularly molecules, and therefore experimental endeavors to accurately extend its phase diagram are essential.

In diamond anvil cell the pressure can be measured either optically e.g. ruby fluorescence or by x-ray diffraction [1,2]. However, both methods have serious limitations above 200-250 GPa which could lead to the significant discrepancies between different experiments. Recently, the frequency of hydrogen vibrational mode at 300 K was proposed as the gauge to compare the compression state of hydrogen between different experiments even though the absolute pressure might not be known [3].

On the other hand, temperature metrology is generally based on the response of a thermocouple in the resistive heating or black body radiation emitted by the hot coupler typically used with transparent materials e.g. hydrogen in the laser heating experiments. In the former, the temperature readings depend on the gradient of temperature within the anvil and the distance between the sample and the thermocouple [4,5], while in the latter the temperature of the sample could differ from that of the coupler [6]. An ideal diagnostic tool could be the Raman thermometry, using the spectral response of hydrogen itself as marker.

I will present our Raman experiments on liquid hydrogen and deuterium in a wide temperature range, from 100 K up to 1000 K, employing cryostat and resistive heating technologies. High quality Raman spectra were collected, and temperatures were deduced from the intensities of the rotational modes and compared to those obtained from the thermocouple. I will discuss the advantages, dis-advantages and limitations of this method.

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## Phase diagram of hydrogen, deuterium and hydrogen-deuterium mixtures at high pressures and low temperatures

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The elemental hydrogen under compression has been an alluring topic in the high-pressure sciences for several decades. Despite numerous theoretical and experimental studies recently<sup>1-3</sup>, most of them are focused on the ultrahigh pressure, there are less studies at the area of middle pressures and low temperatures where phase II existed. Phase II is important to understand the dense hydrogen and other isotopes<sup>4-9</sup>, and also there are several outstanding problems remain in this area, such as the structure of phase II, the influence of the isotopic mass difference, quantum motion and para-ortho equilibrium on the transition pressure to phases II and III, etc. In this report, we present in situ high-pressure (0-200 GPa) low-temperature (4-300K) Raman data for both isotopes. The phase transition line between phase I, II and III are revisited. The presence of a novel phase, phase II', which is unique to deuterium and distinct from the known phase II, is demonstrated. Furthermore, we also present in situ high-pressure (0-200 GPa) low-temperature (4-300 K) Raman data of hydrogen-deuterium mixtures, showing totally different behavior in “phase II” from that of pure hydrogen and deuterium. The updated phase diagrams of hydrogen, deuterium and hydrogen-deuterium mixtures demonstrate the difference between the isotopes at low temperatures and moderate pressures, providing new information on the phase diagrams of them.

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## Pressure induced lattice anomalies in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

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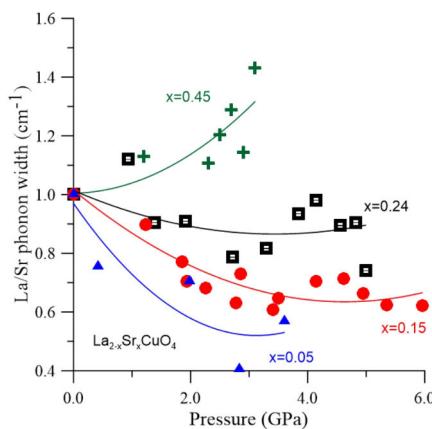
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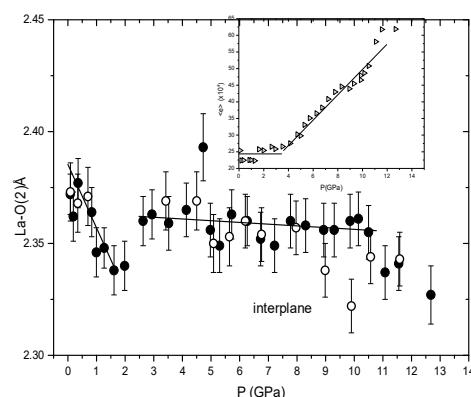
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The effect of hydrostatic pressure on pure and near-optimally doped superconducting  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  compound ( $x=0.0$  and  $0.15$ ) has been measured with synchrotron XRD using two pressure transmitting media (methanol-ethanol and neon) at room temperature (RT) and 20 K. The data from the two media deviate above  $\sim 7$  GPa. For virgin  $\text{La}_2\text{CuO}_4$  there is a clear structural phase transition with hydrostatic pressure and the compound passes from orthorhombic to tetragonal at roughly 3 GPa at RT while this pressure is shifted to a much higher value ( $\approx 10$  GPa) at 20 K. Our hydrostatic pressure room-temperature micro-Raman investigations on polycrystalline and single crystal of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  for various Sr concentrations revealed spectral anomalies that depend on the amount of doping. Figure 1 presents the variation with pressure of the La/Sr phonon width and shows that, contrary to the normal behavior, it decreases with pressure up to  $\sim 3$  GPa for low doping levels before starting increasing at higher pressures. This apparent anomaly seems to depend strongly on the amount of Sr substitution decreasing with  $x$  and disappearing at higher doping levels (Fig.1). Similar results, but to smaller extend, have been observed for the frequency of the La/Sr phonon and the apical oxygen mode. Based on these results we have performed synchrotron powder XRD measurements on the optimally doped  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  using methanol-ethanol as pressure transmitting medium. We have found lattice modifications at about the same pressure ( $\sim 2-3$  GPa) as presented in Figure 2 for the La-O(2) bond length. This lattice anomaly and an unexpected increase of microstrains (Fig.2 inset) seem to be related with the Raman measurements indicating that it is an intrinsic effect. This effect is not related with any lattice disorder but most probably with the charge transfer as indicated by the variation with pressure of the La-O(2) bond length.



**Figure 1** Pressure dependence of the La/Sr phonon width at various doping levels of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ .



**Figure 2** Pressure dependence of La-O(2) bond length and microstrains (inset) for  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ .

## Pressure induced phase transition and metallization in 1T-HfSe<sub>2</sub>

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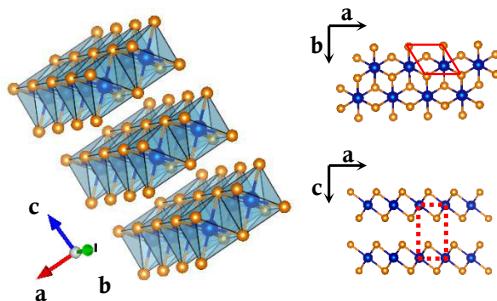
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Transition metal dichalcogenides (TMDs) with MX<sub>2</sub> stoichiometry are layered materials formed by stacking of two dimensional layers, commonly linked through weak Van der Waals interlayer interactions (see Figure 1). Although TMDs have acquired during last years an extremely large attention due to their interesting physical properties and phenomena [1,2], some materials remain still scarcely studied. Currently, we are particularly interested on 1T-HfSe<sub>2</sub>, since, to our knowledge, no high pressure studies have been reported in the literature. Additionally, recent first-principles calculations suggest that HfX<sub>2</sub> materials are small band gap semiconductors with large work functions and reasonable carrier mobility [3].



**Figure 1.** Crystallographic structure of 1T-HfSe<sub>2</sub>

In this study, we address the characterization of the crystallographic and electronic structure of 1T-HfSe<sub>2</sub> under high pressure conditions. For this purpose, we have performed several synchrotron x-ray diffraction experiments (XRD) at high pressure, as well as some other experiments completed in our laboratory involving Raman spectroscopy, optical absorption measurements and DFT calculations.

As the analysis of XRD data reveals, pressure induces a structural phase transition in 1T-HfSe<sub>2</sub> at around 12 GPa, also evidenced by the visible changes in the Raman spectra under pressure. By combining experimental data from XRD experiments and DFT calculations, we have been able to identify the high pressure phase as a baddeleyite structure.

Additionally, optical absorption spectra were acquired at high pressure, allowing us to determine the band gap value and follow its pressure dependence. 1T-HfSe<sub>2</sub> shows an indirect band gap close to 1 eV at ambient conditions, which is gradually reduced by the application of hydrostatic pressure. Metallization of the solid was observed at around 10 GPa. Experimental results obtained from optical absorption was also complemented by using DFT, thus confirming the evolution of the electronic structure.

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## Phase Transition in Beta-Carotene Crystal under High Pressure

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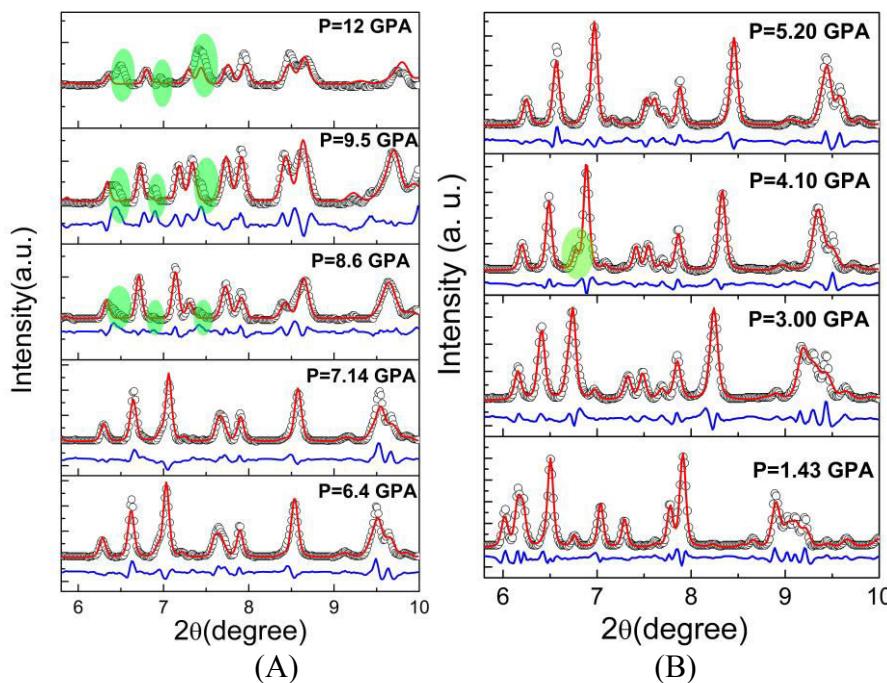
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Recently, beta-carotene crystals have been grown and studied as a function of temperature and hydrostatic pressure. It semiconductor properties has been known since 2006 (Durães, J. A. [1] and Aydin, M, [2].

For this work the crystals were grown at room temperature, by slow evaporation (Properly closed to allow a rate of 1 ml by day) using hexane as an organic solvent and they acquire an average size of the 40  $\mu\text{m}$ . The Raman spectra exhibit, at 219 K (, clear modifications in the spectral range of the lattice and internal vibrational modes (Da Silva, Kleber [3], work published in 2015).

In this work we study the Raman spectra and X Ray as a function of the hydrostatic pressure on the beta-carotene crystal in the range of 0 to 12 GPa. Pressure-dependent Raman Analyses of the results lead us to conclude that there are at least two new pressure-induced phase transitions. One around 4.1 GPa and other one, phase transitions, at 9.5 GPa. The intensities and line widths of the Raman modes as well as the Rietveld refinement of the X-ray spectra are compatible with conformational changes of the beta-carotene molecules.



**Figure:** X ray diffraction with Rietveld refinement. The shadow green shows the phase transitions

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## Determination of pressure coefficients in MoS<sub>2</sub>, MoSe<sub>2</sub>, WS<sub>2</sub>, and WSe<sub>2</sub> van der Waals crystals by optical studies at room temperature.

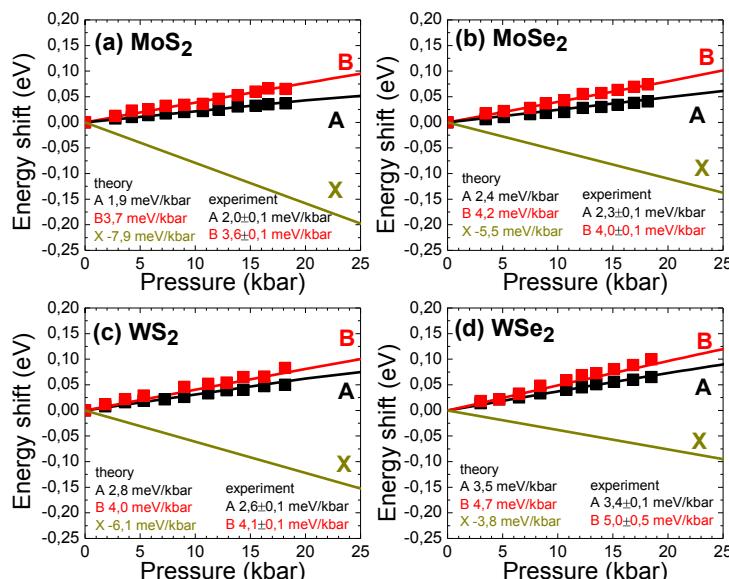
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Two dimensional materials such as van der Waals (vdW) crystals based on transition metal dichalcogenides (TMDs) have attracted broad interest because of their unique mechanical and optical properties [1]. In this work the behavior of optical properties of four vdW crystals (MoS<sub>2</sub>, MoSe<sub>2</sub>, WS<sub>2</sub>, and WSe<sub>2</sub>) has been studied experimentally under high hydrostatic pressure at room temperature and was supported by computational predictions of electronic band structure within the density functional theory (DFT). Comparison of few approaches to DFT study using different functionals is shown and quantitatively analyzed. Energies of optical transitions were determined by photoreflectance (PR) spectroscopy. The pressure induced shift of two direct optical transitions A and B is clearly visible in PR spectra. After fitting of experimental curves with the Aspnes formula [2] pressure coefficients for those transitions have been found to be:  $\alpha_A=2.0\pm0.1$  and  $\alpha_B=3.6\pm0.1$  meV/kbar for MoS<sub>2</sub>,  $\alpha_A=2.3\pm0.1$  and  $\alpha_B=4.0\pm0.1$  meV/kbar for MoSe<sub>2</sub>,  $\alpha_A=2.6\pm0.1$  and  $\alpha_B=4.1\pm0.1$  meV/kbar for WS<sub>2</sub>,  $\alpha_A=3.4\pm0.1$  and  $\alpha_B=5.0\pm0.5$  meV/kbar for WSe<sub>2</sub>. Experimentally obtained data is in excellent agreement with theoretical calculations (see Fig. 1). Further, DFT studies show that all considered materials have negative pressure induced rates of fundamental indirect band gap estimated to be -7.9 meV/kbar for MoS<sub>2</sub>, -5.51 meV/kbar for MoSe<sub>2</sub>, -6.11 meV/kbar for WS<sub>2</sub>, and -3.79 meV/kbar for WSe<sub>2</sub>. That should cause a semiconductor to metal transition at values of pressure calculated to be 140, 180, 190, and 240 kbar for MoS<sub>2</sub>, MoSe<sub>2</sub>, WS<sub>2</sub>, and WSe<sub>2</sub> respectively [3].



**Figure 1:** Energy shift obtained from PR spectra for MoS<sub>2</sub> (a), MoSe<sub>2</sub> (b), WS<sub>2</sub> (c), and WSe<sub>2</sub> (d) van der Waals crystals. Symbols indicate experimental points and solid lines theoretical calculations.

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## High pressure response of the Raman modes of $\text{Dy}_3\text{Ga}_5\text{O}_{12}$

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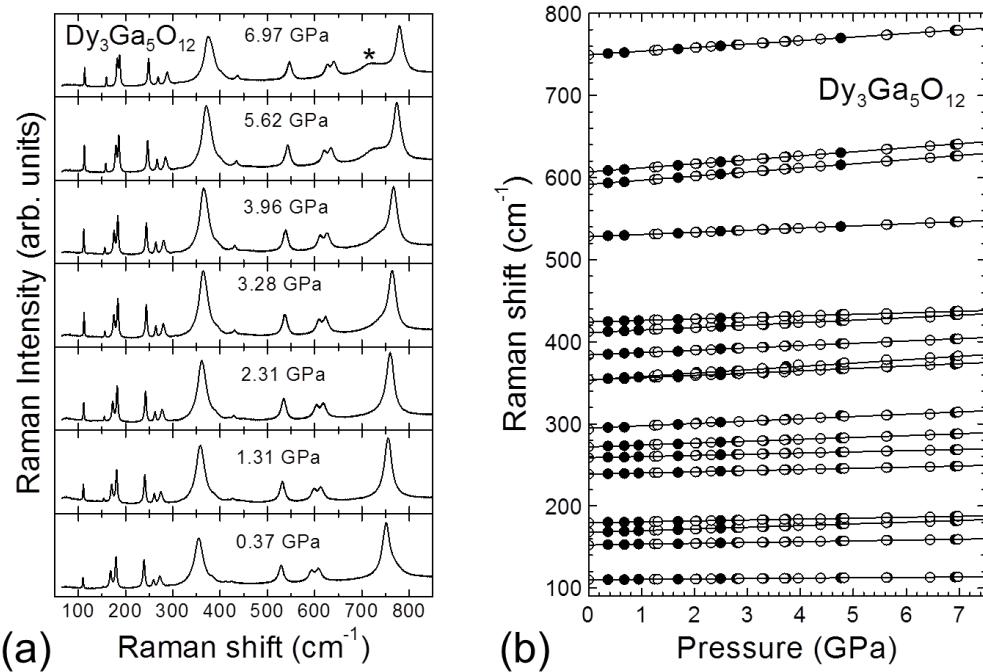
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Rare-earth garnets have attracted the scientific interest due to their exceptional luminescence properties, their high optical transparency and thermal conductivity, as well as their mechanical and chemical stability, finding applications as active elements for near-infrared solid-state lasers, in acousto- and microelectronics, in magnetic memories and optical communications, while they can be also used as optical pressure and temperature sensors for experiments at extreme conditions [1,2].

In this work, we have studied by Raman spectroscopy the pressure response of  $\text{Dy}_3\text{Ga}_5\text{O}_{12}$  crystals, aiming in the elucidation of the individual role played by the different molecular units comprising the garnet structure in the lattice dynamics of this system, as well as in the exploration of its structural stability upon pressure application. More specifically, the pressure dependence of 17 Raman-active modes, out of the 25 predicted by group theory for the garnet bcc structure (space group:  $\text{O}_h^{10}$  [3]) has been followed. With increasing pressure, all Raman peaks shift to higher frequencies, while there is no evidence for any pressure-induced structural phase transition or hysteresis phenomena. The extracted pressure coefficients,  $\Gamma_i = (1/\omega_i)(\partial\omega_i/\partial P)$ , extend over a relatively narrow range ( $4.4\text{--}12.4 \times 10^{-3} \text{ GPa}^{-1}$ ), indicating binding forces of nearly the same nature and order of magnitude and that the binding strength between the various molecular units is comparable.



**Figure** (a) Raman spectra of the  $\text{Dy}_3\text{Ga}_5\text{O}_{12}$  at various pressures. The asterisk marks a parasitic peak of the DAC. (b) Pressure dependence of the Raman frequencies of the  $\text{Dy}_3\text{Ga}_5\text{O}_{12}$ . Open (solid) symbols denote upstroke (downstroke) data, while lines are linear least-square fittings to the data.

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## CeScO<sub>3</sub> perovskite under pressure from *ab initio* simulations.

A. Muñoz\*, and P. Rodríguez-Hernández

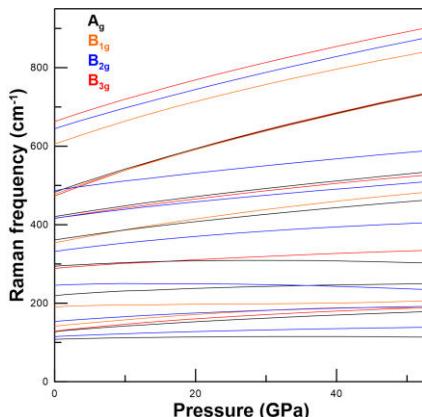
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The ABO<sub>3</sub> perovskite oxides are attracting attention due to their use in electronic devices, and their interesting properties like metal-insulator transitions, magnetic colossal resistance, ferroelectricity, etc. Many minerals of geological interest, related with the lower mantle of Earth, also adopt the perovskite structure. Perovskites compounds have the highest density among fluorides and oxides with ABX<sub>3</sub> formula. Many perovskite-type oxides have studied under high pressure, but few studies focus their attention on rare earth scandates. Recently an experimental synchrotron X-ray powder diffraction work [1] performed in the impact of pressure on the stability of CeScO<sub>3</sub> perovskite-type compound, reports that this compound remains stable until the maximum experimental pressure reached of 40 GPa.

In present work CeScO<sub>3</sub> perovskite-type has been studied under high pressure by *ab initio* simulations in the framework of density functional theory using the pseudopotential method and the Generalized Gradient Approximation (GGA) to describe the exchange correlation energy. Our study focuses on the structural, dynamical and elastic properties of this compound. Results about the structure and its evolution under pressure, the equation of state and the compressibility are presented. The shortening of A-X and B-X bond lengths and the evolution of the polyhedra can explain the behavior of these compound under high pressure. The Raman and Infrared frequencies, and their pressure coefficients are also analyzed. Finally, the study of the elastic constants provides information related with the elastic properties of this compound and its mechanical stability. In our first principles simulations we found that CeScO<sub>3</sub> presents a mechanical instability at about 50 GPa.



**Figure 1:** Pressure dependence of the Raman modes of CeScO<sub>3</sub>

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## Stressed THz silicon lasers

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This study was focused on influence of uniaxial crystal deformation on operation of the THz-range silicon lasers. The silicon crystals doped by hydrogen-like impurity centers can act as laser sources under optical pumping by the mid-infrared emission [1]. The stimulated emission is built at low lattice temperatures due to population inversion formed on excited impurity levels, such populations are controlled by interaction with different phonons of silicon lattice. By application of uniaxial stress to a silicon crystal, particular umklapp-type electron scattering accompanying with intervalley phonons are significantly reduced [2]. This mechanism has the largest influence on the stimulated emission in THz silicon lasers, including complete change of the lasing transitions or significant changes in the lasing thresholds and efficiency [3,4]. Additional advantages come from reduction of internal optical losses caused by elimination of dynamically induced negatively charged donors and their complexes.

Theoretical calculations of nonequilibrium populations on the donor states under uniaxial compression deformation of crystals in the ranges from zero stress up to 3 kbar, mostly in the [100] direction, cover the large spectrum of possible changes in the silicon laser output parameters [5].

Varying the strain may cause not only changes in working transitions of silicon lasers and the associated sharp change in lasing frequency (such as in n-Si:As) but also a more gradual frequency tuning, related to the effect of strain on the spin-orbit splitting of the 1s(T<sub>2</sub>) states (cases of n-Si: Bi and n-Si: Sb). Such stress-dependent lasing operation as well as related changes in the lifetimes of the donor excited states in silicon will be discussed.

This study has been supported by the InTerFEL Russian-German project (BMBF no. 05K2014; Ministry of Education and Science of Russia, agreement no. RFMEFI61614X0008). We acknowledge support by the EC FP7 project CALIPSO (No.312284) for the Transnational access to the European FELs and Synchrotron facilities and the FELIX laboratory staff.

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## Kinetic boundaries and phase transformations of ice I at high pressure

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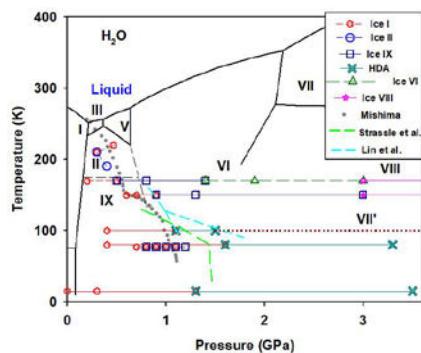
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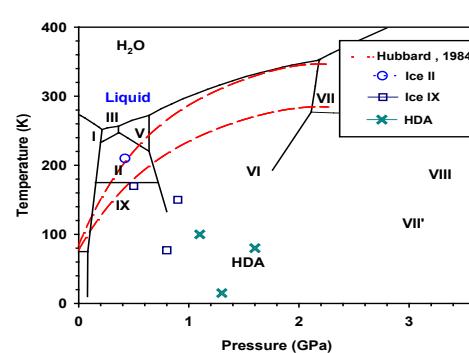
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Raman spectroscopy in DAC have been employed to study phase boundaries and transformation kinetics of H<sub>2</sub>O ice at high pressures up to 16 GPa and temperatures down to 15 K in this work. Ice I formed at nearly isobaric cooling of liquid water transforms on compression to high-density amorphous ice (HDA) at 1.1 – 3 GPa at 15-100 K and then crystallizes in ice VII with the frozen-in disorder (ice VII') which remains stable up to 14.1 GPa at 80 K and 15.9 GPa at 100 K. Unexpectedly, on decompression of ice VII', it transforms to ice VIII in its domain of metastability, and then it relaxes into low-density amorphous ice (LDA) on a subsequent pressure release and warming up. On compression of ice I at 150-170 K, ice IX is crystallized and no HDA ice is found; further compression of ice IX results in the sequential phase transitions to stable ices VI and VIII. Cooling ice I to 210 K at 0.3 GPa transforms it to a stable ice II. Our extensive investigations provide missing previously information on the phase diagram of water, especially on the kinetic paths that result in formation of phases which otherwise are not accessible; these results are keys for understanding the phase relations including the formation of metastable phases. The accurate measurements document can be used for the phase identification in the future research and supply a complementary to the inelastic scattering techniques diagnostics of vibrational properties. Furthermore, the *in situ* Raman investigations of compression kinetics of ices provides an important baseline for understanding of behavior of subducted planetary ices in ice satellites<sup>1-6</sup> suggesting a possible existence of ordered ice IX in addition to the previously proposed ices I, II, III, V, and VII in icy moons.



**Figure 1.** Summary of the present experimental results on cooling.



**Figure 2.** Phase diagram of water ice.

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## Study of the evolution of the vibrational and electronic properties of several tin chalcogenides under compression

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Tin chalcogenide compounds are known to exist under different stoichiometries, depending on tin valence, which exhibit different properties, and are promising materials as intercalation compounds and for optoelectronic applications. As part of a comprehensive study on this class of compounds we present here results for the SnS<sub>2</sub> and SnSe members of the family, including a study of the evolution under pressure of the vibrational properties of their known phases (with a focus on Raman-active modes), phase energetics and stability, and electronic structure. The theoretical study was done within the *ab initio* framework of the density functional theory (DFT), using the projector augmented scheme and a basis of plane waves, with inclusion (for the structural relaxation and total energy calculations of the phases) of van der Waals corrections to the interlayer interactions of the layered structures. We analyse the changes induced by the application of pressure and compare with results from previous studies on this class of compounds. We also investigate the effects of different levels of the theoretical approximations made in the DFT calculations.

## Structural pathways and lattice dynamics of $\text{ReO}_3$ under pressure

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Rhenium trioxide  $\text{ReO}_3$  is a metallic transition metal compound. It crystallizes in a cubic primitive structure (*SG Pm-3m, Z=1*). The structure is analogous to that of cubic perovskites  $\text{ABO}_3$  with the six-coordinated B sites occupied by Re and A sites empty. The cubic phase, consisting of  $\text{ReO}_3$  octahedra linked by corners only, becomes unstable at about 0.5 GPa. Previously reported high pressure phases observed at ‘intermediate’ pressures between 0.5 GPa and about 12 GPa include tetragonal (*P4/mbm, Z=2*), cubic skutterudite (*Im-3, Z=8*), and monoclinic  $\text{MnF}_3$ -type (*C2/c, Z=12*). Upon increasing pressure beyond 12 GPa, a rhombohedral  $\text{VF}_3$ -type structure (*R3c, Z=6*) is adopted. The octahedral coordination of Re is preserved in these high pressure phases which all can be interpreted as superstructures derived from the cubic primitive phase.

The previous observations of the pressure-driven structural behavior of  $\text{ReO}_3$  at intermediate pressures appear to be partly inconsistent concerning the number of high pressure phases and the sequence of phase transitions between 0.5 and 12 GPa. This motivated us to perform high-pressure synchrotron x-ray diffraction and Raman scattering studies of  $\text{ReO}_3$  up to 20 GPa. Furthermore, in order to be able to interpret our experimental observations, we have performed DFT-based calculations of total energies and vibrational mode frequencies as a function of volume reduction. Our results explain the apparent controversy encountered in the literature regarding the pressure-induced structural evolution of  $\text{ReO}_3$ . The structural sequence involves second- and first-order phase transition paths. In particular, as evidenced by the total energy calculations, different second-order transition paths compete which makes the structural evolution of  $\text{ReO}_3$  extremely sensitive to external parameters (e.g. powder versus single crystals). Thus,  $\text{ReO}_3$  is an example where the application of pressure leads to ambivalence in the structural behavior.

## Title of Presentation

### Advanced Thermoelectrical Bi<sub>2-x</sub>Sb<sub>x</sub>Te<sub>3</sub>-C<sub>60</sub> Nanocomposites

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V. Kulbachinskiy<sup>2,3</sup>, V Kytin<sup>3</sup>, and V. Blank<sup>1,2</sup>

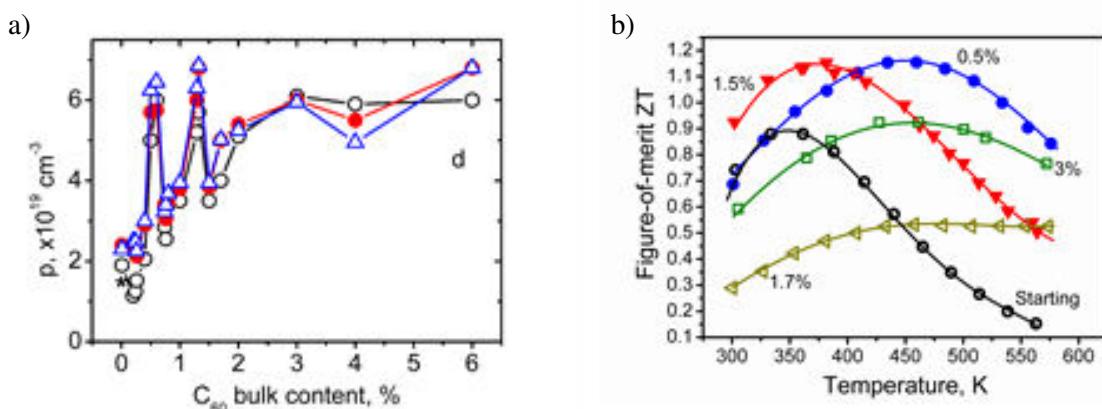
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We produced advanced nanocomposite thermoelectric materials composed from nanocrystallites of Bi<sub>2-x</sub>Sb<sub>x</sub>Te<sub>3</sub> alloys covered by C<sub>60</sub> molecules. The fullerene molecules provide decrease in heat transport and particular charge transfer in the nanocomposite. Bi<sub>2-x</sub>Sb<sub>x</sub>Te<sub>3</sub> nano-powders were mechanically alloyed with C<sub>60</sub> fraction in the range of 0 to 6 vol. % in a planetary mill. After the mill treatment Bi<sub>2-x</sub>Sb<sub>x</sub>Te<sub>3</sub>-C<sub>60</sub> powder was loaded in a piston-cylinder cell in pure Ar atmosphere, compressed at a pressure of 0.5 GPa, and sintered by heating up to 400°C. Sintered samples have been annealed in hydrogen steam at 300°C during 2 hours. The mean crystalline size of nanograins was 30-40 nm after the sintering and the Raman spectra confirmed that C<sub>60</sub> molecules were not transformed into other carbon forms or polymerized. C<sub>60</sub> molecules cover thermoelectric alloy nanograins, thus provide thermal phonons blocking. Besides, molecules act as electron traps, and thus decrease the density of free electrons in n-type semiconductor and generate holes in p-type materials. The density of free charge carriers and their Hall mobility change nonmonotonically with the increase of fullerene content (Fig. 1a).



**Figure 1:** Density of halls in Bi<sub>0.5</sub>Sb<sub>1.5</sub>Te<sub>3</sub>-C<sub>60</sub> nanocomposites at room temperature and 77K as a function of C<sub>60</sub> bulk content (a) and temperature dependencies of the figure of merit ZT of Bi<sub>0.5</sub>Sb<sub>1.5</sub>Te<sub>3</sub>-C<sub>60</sub> nanocomposites with different content of C<sub>60</sub> (b).

The maximum value of thermoelectric figure of merit ZT = 1.15 was obtained in p-type nanocomposite that is 30% higher than in the undoped starting material (Fig. 1b). Here ZT = S<sup>2</sup>σT/k; S is the Seebeck coefficient, σ and k are the electrical and thermal conductivities, T is the temperature.

From Fig. 1 one can clearly see that nonmonotonic dependence of density of halls over C<sub>60</sub> fraction causes substantial variation of ZT number on fullerene content and extends large value of ZT in the range of temperatures 400-500K, that is very important for real application in thermoelectrical devices. In particular, nanocomposites with the "resonant" C<sub>60</sub> fractions of 0.5% and 1.5% have the highest ZT values of 1.15 and broad functional temperature range. The "resonant" values are explained within the model of C<sub>60</sub> electron acceptor properties - electronic traps.

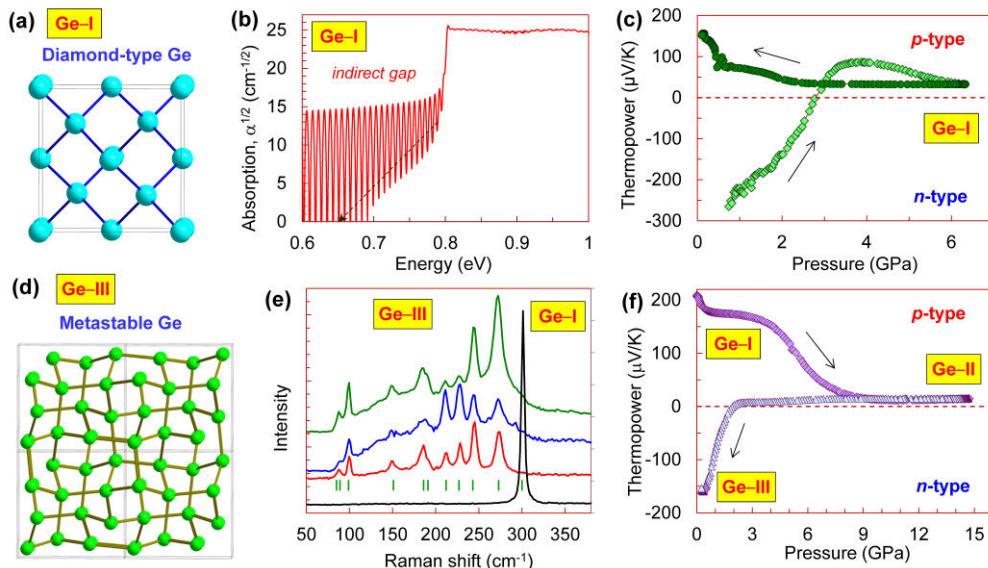
## Thermoelectric properties of compressed germanium

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Controlled tuning the electrical, optical, magnetic, mechanical and other characteristics of the leading semiconducting materials is one of the primary technological challenges. In this work we demonstrated that the electronic transport properties of conventional single-crystalline wafers of germanium may be dramatically tuned by application of moderate pressures. We investigated the thermoelectric power (Seebeck coefficient) of *p*- and *n*-type germanium under high pressure to 20 GPa. We established that an applied pressure of several GPa drastically shifts the electrical conduction to *p*-type [1] (Figure). The *p*-type conduction is conserved across the semiconductor-metal phase transition at near 10 GPa. Upon pressure releasing, germanium transformed to a metastable *st12* phase (Ge-III) with *n*-type semiconducting conductivity (Figure). The semiconductor character of this *st12* phase was recently established in another experimental work [2]. We proposed that the unusual electronic properties of germanium in the original cubic-diamond-structured phase could result from a splitting of the “heavy” and “light” holes bands, and a related charge transfer between them. We suggested new innovative applications of germanium, e.g., in technologies of printing of *n*–*p* and *n*–*p*–*n* junctions by applied stress. Thus, our work has uncovered a new face of germanium as a ‘smart’ material.



**Figure** Crystal structure of cubic-diamond-type Ge-I (a) and metastable tetragonal, Ge-III (d) polymorphs of germanium. (b) Near infrared absorption of Ge-I showing its indirect band gap of about 0.65 eV and a direct one of about 0.8 eV. Pressure dependencies of the thermopower for the Ge-I phase (c) and across the Ge-I  $\rightarrow$  Ge-II  $\rightarrow$  Ge-III transitions (f). (e) Comparative Raman spectra of Ge-I and Ge-III phases; the dashes are wave numbers reported for Ge-III in the literature.

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## Pressure evolution of the samarium valence in $\text{Sm}_{2.75}\text{C}_{60}$

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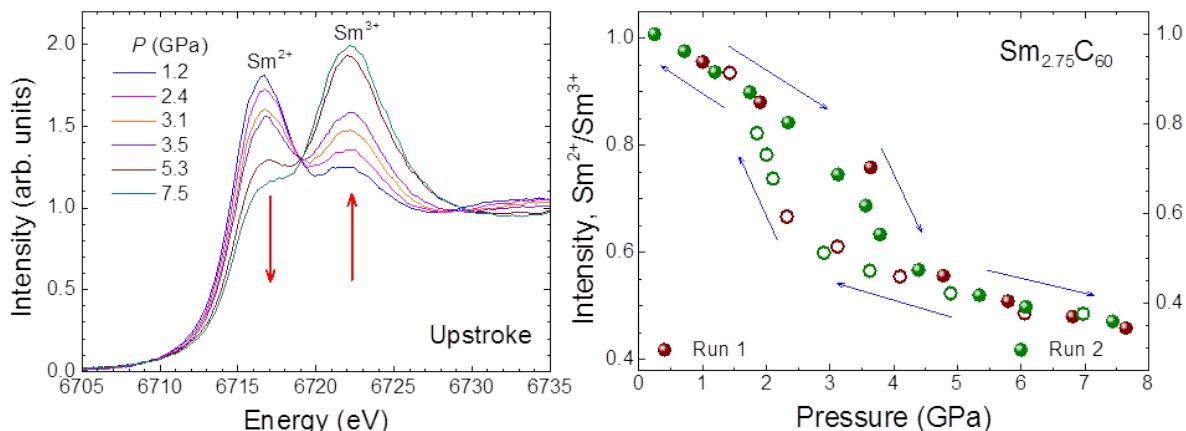
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Rare-earth fullerenes constitute an intriguing class of highly-correlated molecular systems due to the strong coupling between two electronically active sublattices  $\{\pi(\text{C}_{60}) \text{ and } 4f, 5d(\text{rare-earth})\}$ . High-resolution synchrotron X-ray diffraction (XRD) and magnetic susceptibility measurements of the  $\text{Sm}_{2.75}\text{C}_{60}$  fulleride revealed an isosymmetric phase transition and a dramatic isotropic volume increase below 32 K, which was attributed to a Sm valence transition from  $(2+\varepsilon)^+$  to nearly  $2^+$  upon cooling [1]. Moreover, high pressure XRD measurements showed a lattice collapse of the fulleride at  $\sim 4$  GPa, accompanied by a reversible colour change from black to golden [2] -similar to what was earlier observed in intermediate valence Sm monochalcogenides like  $\text{SmS}$  [3]- that was attributed to a rare-earth valence transition from  $(2+\varepsilon)^+$  to  $3^+$ . This scenario was further supported by our high pressure Raman data that are indicative of an insulator-to-metal transition at elevated pressures [4].

In this work, we present our recent X-ray absorption near edge spectroscopy (XANES) measurements on the Sm L<sub>3</sub>-edge, aiming to probe directly the pressure evolution of the Sm valence state in  $\text{Sm}_{2.75}\text{C}_{60}$ . This study confirmed the mixed Sm valence already at normal conditions. The high pressure evolution of the XANES spectra clearly shows a monotonic increase (decrease) of the  $\text{Sm}^{3+}$  ( $\text{Sm}^{2+}$ ) feature that becomes more prominent at  $\sim 4$  GPa, compatible with a pressure-induced change in the average Sm valence (Figure). This could account for the huge lattice collapse and the insulator-to-metal transition observed in the  $\text{Sm}_{2.75}\text{C}_{60}$  fulleride upon pressure application.



**Figure** (Left) High pressure XANES spectra of  $\text{Sm}_{2.75}\text{C}_{60}$  at the Sm L<sub>3</sub>-edge recorded upon pressure increase. (Right) Pressure dependence of the intensity ratio of the  $\text{Sm}^{2+}$  and  $\text{Sm}^{3+}$  peaks. Closed (open) symbols correspond to pressure increase (decrease).

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## Excitonic properties of hBN/WSe<sub>2</sub> monolayer/hBN van der Waals heterostructures under hydrostatic pressure

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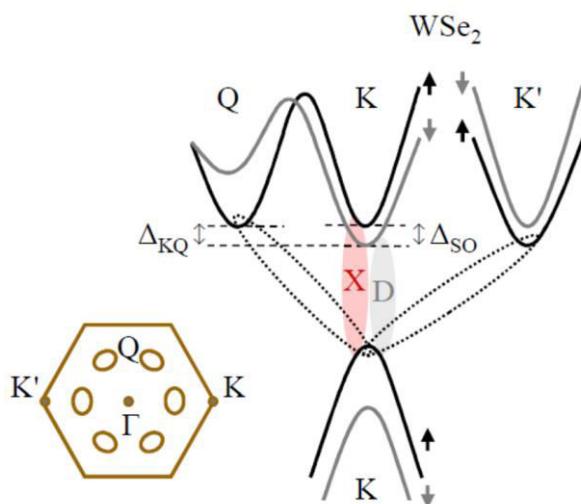
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Transition metal dichalcogenide (TMDC) monolayers have emerged as exciting 2D materials as they present strong light-matter interaction governed by robust excitons and interesting spin/valley selective optical selection rules. Momentum forbidden excitons (i.e. indirect excitons) have been proposed to play a strong role in the optical properties of WSe<sub>2</sub> monolayers [1]. Yet, their optical signature has never been evidenced clearly.

In this work, we study the optical properties of WSe<sub>2</sub> monolayers by photoluminescence (PL) and photoluminescence excitation (PLE) as a function of hydrostatic pressure and discuss the effects of pressure on intrinsic excitonic properties and the possible occurrence of a direct-to-indirect crossover. For comparison we also study the pressure dependence of the optical properties of WSe<sub>2</sub> monolayers encapsulated into hexagonal boron nitride (hBN) layers. The atomically flat and charge free surface of hBN is known to considerably reduce the inhomogeneous linewidth of the low temperature optical transitions [2] and to reduce the exciton binding energy due to change of dielectric environment. Applying pressure may favor the coupling between WSe<sub>2</sub> and hBN due to the reduced interlayer distance.



**Figure 1:** Sketch of the band structure of single-layer WSe<sub>2</sub> showing direct K-K excitons and indirect Q-K excitons.

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# Superconductivity emerging from a Weyl semimetal NbIrTe<sub>4</sub> under pressure

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The topological properties have received strong interest both theoretically and experimentally in recent years. Insulators can be classified into conventional insulators and topological insulators with protection by time-reversal symmetry. By analogy from insulator to metal, semimetals are divided into trivial and nontrivial semimetals topologically in electronic structure, with the latter including Weyl, Dirac, and node-line semimetals.

Weyl semimetals are semimetals or metals whose quasiparticle excitation is the Weyl fermion. Remarkably, Weyl fermions are robust while carrying currents, giving rise to exceptionally high mobility [1]. It was predicted that an inversion-breaking single crystal NbIrTe<sub>4</sub> is a Weyl semimetal candidate [2].

In this study, we obtained measurements based on the resistivity, synchrotron X-ray diffraction, using the Weyl semimetal NbIrTe<sub>4</sub> at high pressures. Our experiments indicated that NbIrTe<sub>4</sub> exhibited a pressure-induced superconductivity at 1.6GPa with transition temperature ( $T_c^{onset}$ ) ~2.2K. The superconducting transition temperature increased to a maximum ~5.1 K with pressures up to 15.8GPa. The possible topological superconductivity emerges in the Weyl semimetal phase could provide abundant evidence for understanding the fundamental mechanism and potential pathway for functional device design from the practical aspect.

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- [2]. Li, Lei, et al. "Ternary Weyl semimetal NbIrTe<sub>4</sub> proposed from first-principles calculation." *Physical Review B* 96.2 (2017): 024106.

# Elucidating the role of planarity and intermolecular distance on the optical properties of conjugated polymers

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Semiconducting polymers continue to attract great attention as possible cost-effective and easy to process candidates for optoelectronic devices. These traits are related to their solution processability. Films so produced can exhibit a large variety of microstructures, which ultimately define the optical and electrical properties of these systems. There are, in fact, many open questions remaining regarding how different structural changes influence the optical properties of these polymers. In order to disentangle the contributions of different effects, such as planarity, interchain interactions and the dielectric constant, we have investigated thin polymer films under high hydrostatic pressure. This allowed us to gradually change the intermolecular distance without chemically altering the molecules, and therefore could be the basis for a clean and deeper understanding that could potentially result in new design rules for improved properties.

We have chosen poly(9,9-dioctylfluorene) (PFO) and poly(3-hexylthiophene) (P3HT), as model polymers for organic light-emitting diodes and organic solar cells, respectively. We have measured their room temperature absorption, photoluminescence (PL) spectra and refractive index up to 8 GPa. The recorded differences in bathochromic shifts with pressure are employed to estimate the relative strengths of the aforementioned mechanisms. For PFO, we estimate that out of the 270 meV red shift, ca 50% corresponds to interchain interactions. Contrary to expectations, this contribution is about three times larger than the one stemming from an increased planarization of the molecules under pressure. Regarding the dielectric function of the polymers, we have found a very modest increase under high pressure. Interestingly, the increase in film density appears to be strongly compensated by a decrease in oscillator strength. Finally, this knowledge helps us to understand the effect of pressure on the charge transfer (CT) state formed in mixtures of P3HT donor and solution derivative fullerene PCBM as acceptor. Indeed, we have found a strong red shift in the CT emission.

# Pressure-optical studies of band gap tuning, Raman phonons, and stability in BaZrS<sub>3</sub>

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The results of comprehensive optical experiments investigating the effects of applied hydrostatic pressure on the novel material BaZrS<sub>3</sub> are discussed. The direct absorption edge, and allowed and forbidden Raman scattering, are measured to 8.9 GPa at room and cryogenic temperatures for the distorted perovskite *Pnma* phase of BaZrS<sub>3</sub>. The maximum pressure in our experiments is sufficient to also probe the stability of this as-grown BaZrS<sub>3</sub> phase for compressions achieved at 1 *atm* in more dense alloys, such as BaZr<sub>1-x</sub>Ti<sub>x</sub>S<sub>3</sub>, now being considered for photovoltaics. High pressure optical absorption measurements find that the BaZrS<sub>3</sub> band gap (1.74 eV at 1 *atm*) shifts to lower energy with pressure at a rate of  $\sim -0.015$  eV/GPa. This shift due to compression drives the band gap toward values more favorable for solar absorption, and combined with the negative chemical shift of the gap produced by Ti alloying, offers a path toward improved photovoltaic efficiency in structurally stable BaZr<sub>1-x</sub>Ti<sub>x</sub>S<sub>3</sub> alloys.[1][2] The Raman results at 1 *atm* allow us to assign 21 of the 24 Raman active phonons to observed spectral peaks at frequencies in agreement with ab-initio theoretical calculations. The observed and theoretical intensities also agree, except for a peak at 392 cm<sup>-1</sup>. Employing resonance Raman spectroscopy, we show that the anomalous strength of this peak arises from forbidden scattering due to the Frohlich interaction. All the Raman peaks shift to higher frequency with increasing pressure. The shifts are nearly linear over the full pressure range studied, and there are no discontinuities that might signal a structural transformation. The observed mode Gruneisen parameters  $-d\ln\nu/d\ln V$  fall in the range 0.7 – 1.7, and their values for the different peaks correspond reasonably with the findings of the ab-initio calculations. The effects of pressure on the phonon frequencies in BaZrS<sub>3</sub> reflect a stable quasiharmonic solid. Our results indicate that the distorted perovskite *Pnma* phase of this material is stable to at least 8.9 GPa, providing prospects for advanced photovoltaic (and other) applications *via* band gap engineering in alloys of BaZrS<sub>3</sub> with appropriate transition metals.

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# Development of Two-stage Multianvil Apparatus for High Pressure and Low Temperature Measurements

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Various high-pressure devices have been developed for in-situ physical property measurements at low temperatures. Much effort in this direction has been devoted to increase the highest achievable pressure and to improve the pressure hydrostaticity. These two factors are particularly important in exploring pressure-induced emergent quantum phenomena in strongly correlated materials with multiple competing interactions. The level of hydrostaticity depends on the compression geometry in addition to pressure transmitting medium. In comparison with opposed anvil type apparatus, multianvil-type apparatus can maintain better pressure homogeneity even if the pressure transmitting medium becomes solidified at low temperature and/or high pressure.[1] The single-stage cubic type device developed in ISSP [2] is one typical multianvil apparatus that can generate hydrostatic pressures above 10 GPa. The design of miniature “palm”-type cubic anvil cell also enabled integration with <sup>3</sup>He or dilution refrigerator so as to reach temperatures as low as 10mK.[3,4] These developments of cubic-type apparatus are essential for us to discover novel quantum phenomena [5] and new superconducting materials [6] in the past few years.

To further push the highest achievable hydrostatic pressure to over 20 GPa, we adopted the Kawai-type design and recently developed a two-stage multianvil apparatus for low-temperature measurements. The second stage consists of eight tungsten-carbide cubes with truncation edge length of 3.0 mm. The octahedron gasket with integrated fin made of Ceramacast 584 (Aremco Products, Inc.) was fabricated by ourselves according to Ref. [7]. The sample assembly with the sample hanging in a Teflon capsule (I.D. 1.5mm, O.D. 2 mm) filled with Daphne 7373 is similar with the setup in cubic anvil cell.[2] We have performed the pressure calibration at room temperature by detecting the phase transitions of Bi, Sn, Pb, ZnS, GaAs and GaP in electrical resistivity measured with a standard four-wire method. Figure 1 displays the resistivity as a function of loading force for Bi, Pb, and GaAs at room temperature. The characteristic phase transitions of Bi at 2.55, 2.7 and 7.7 GPa are clearly observed at loading force of 11.11, 12.66, and 35.63 tons, respectively. We successfully observed the metallization of GaAs at 18 GPa under a loading force of ~ 120 tons and expected to exceed 20 GPa under 150 tons. In the presentation, I will also show the result of low-temperature measurements.

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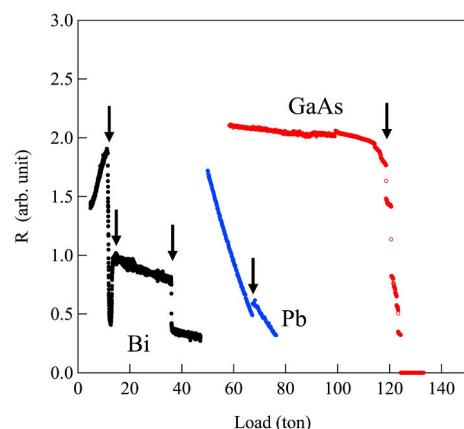


Fig.1 Resistivity of Bi, Pb, and GaAs as a function of loading force. The arrows indicate the structure phase transitions or insulator-metal transition.

# Pressure-induced phonon freezing in ZnSe-based mixed crystals: phonons, phonon-polaritons and *ab initio* calculations

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At the emergence of the science of materials at the beginning of the XXth century, W. Pauli recommends that physicists should focus on simple systems in which models can be developed at the ultimate scale of the atom themselves. Twenty years later Bell Labs achieve the synthesis of Ge with 10N purity (99.9999999 %) corresponding to a single atom species on a regular lattice, moreover a cubic one. Clearly, with semiconductors like Ge and Si, physicists dispose of geometrical-like objects that can be tested experimentally and confronted with atomistic models. Same situation with the next arriving binary compounds derived from Ge and Si ten years later, such as GaAs or ZnSe, in which cations and anions alternate on the same lattice. Problems arise in the mid-sixties with the emergence of the related mixed crystals. A unique A↔B atom substitution on the regular lattice – giving rise to the most simple ‘complex system’ one can imagine thus a benchmark one for the study of disorder – generates not only a chemical disorder but also a distortion of the lattice (as needed to accommodate the contrast in the bond length/stiffness of the constituting species). The order is lost! The crucial issue then is to access the nature of the A↔B atom substitution, as to whether this is ideally random or due to local clustering/anticlustering for some reason.

To tackle this issue experimentally one needs a local probe, such as the bond force constant that is conveniently addressed at the laboratory scale by using optical vibrational spectroscopies, such as Raman scattering or far-infrared absorption. In the past decade we could achieve a unified understanding of the Raman/infrared spectra of the basic mixed crystals derived from Si and Ge within our so-called percolation scheme [1]. This distinguishes between the like bonds of a given species at the mesoscopic scale, *i.e.* depending on whether they are connected (and vibrate in their own environment) or isolated (and vibrate in the foreign environment of the other species), leading to a generic 1-bond→2-vibration pattern. As such the percolation scheme materializes a natural ability behind vibrational spectroscopies to elucidate the nature of the A↔B atom substitution in a mixed crystal, on a quantitative basis.

In this communication we explore another potential application behind the percolation scheme, *i.e.* as to whether it can provide any insight at the unusual mesoscopic scale regarding the lattice dynamics of a mixed crystal at the approach of its pressure-induced structural transition. The pressure-dependence of the 1-bond→2-mode percolation doublet of various ZnSe-based mixed crystals is studied experimentally with this end in view using high-pressure backward and near-forward Raman scattering by phonons and phonon-polaritons [2], respectively. The discussion of the experimental data is supported by *ab initio* phonon calculations done on prototypal percolation-type impurity motifs [2].

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## BiVO<sub>4</sub> polymorphism studied by high pressure-high temperature Raman measurements and ab-initio calculations.

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The photocatalytic activity of BiVO<sub>4</sub> strongly depends on the crystalline phase and sample form, being nanoparticles of particular interest. The thermodynamically stable polymorph of BiVO<sub>4</sub> at ambient conditions is a monoclinic distortion of a scheelite-type phase (SCH), named fergusonite (F). F and SCH are related by a ferroelastic instability. BiVO<sub>4</sub> can also be prepared with a zircon (Z) structure. The high pressure (HP)-high temperature (HT) F-SCH phase boundary has been studied by XRD [1]. The pressure and temperature coefficients of the optical A<sub>g</sub> soft mode (63 cm<sup>-1</sup>) have been also determined [2-3].

We report here HP-HT Raman experiments performed on F-BiVO<sub>4</sub> powder and single crystal samples. We also present results from nano powders of Z-BiVO<sub>4</sub>. We complement previous Raman experiments discussing the behavior of the whole set of Raman active modes as well as extending the pressure range and introducing simultaneous HP-HT conditions. The HP behavior of Z-BiVO<sub>4</sub> will be discussed for the first time.

HP was generated using a diamond-anvil cell (DAC). HT was achieved by external heating of the DAC. The pressure transmitting medium was either Ne or a 16:3:1 methanol–ethanol–water mixture. Pressure was determined using the ruby or SrB<sub>4</sub>O<sub>7</sub>:Sm<sup>2+</sup> luminescence. Temperature was measured with a K-type thermocouple. The 632.8 nm line of a He-Ne laser was used to excite Raman spectra, which were collected in the backscattering geometry.

We performed calculations of the total energy within the framework of the density functional theory and the projector-augmented wave method, as implemented in the Vienna *ab initio* simulations package (VASP). The exchange-correlation energy was described with the HSE06 hybrid functional. Lattice-dynamics calculations were also performed to study the pressure dependence of zone center modes. We obtained the frequency, pressure coefficient and symmetry of each mode. In addition, we calculated the full phonon dispersion curves at selected pressures.

The temperature and pressure behavior of the F lattice modes reflects the distortions associated to the ferroelastic instability. The *ab initio* calculations show a complete softening of the acoustic branch. The linear coefficients of the Z phase are in sharp contrast with the behavior observed in the F phase. The F to SCH second order phase transition occurs at 1.4 GPa (ambient temperature) and 510 K (ambient pressure). The Z to SCH, irreversible, first order phase transition is observed from 660 to 760 K (ambient pressure) and from 3.3 to 4.3 GPa (ambient temperature). We found evidences of additional structural changes around 18 GPa, which in the downstroke were found to be not completely reversible.

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## Strain engineering as a tool to tune the acoustic phonon dynamics of suspended nanostructures

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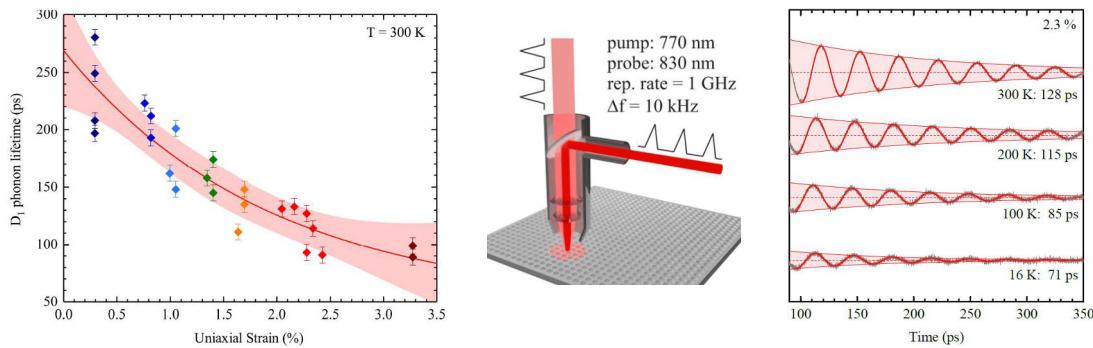
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**Figure 1:** Acoustic phonon lifetimes of the first order symmetric phonon mode in suspended Ge nanobridges as function of uniaxial strain (left), schematic illustration of measurement concept for determination of acoustic phonon lifetimes by time-domain femtosecond pump-probe reflectivity measurements (center), temperature dependent time resolved phonon dynamics in a Ge nanobridge with a uniaxial strain of 2.3%.

The capability to tune the acoustic phonon dynamics in technologically relevant group IV nanostructures provides a promising prospect to control the propagation of acoustic and thermal phonons with great implications on nanoscale hypersound and thermal transport. Despite their fundamental importance, accurate measurements of acoustic phonon lifetimes are challenging and their values are still unknown for most materials. Even in the case of the extensively studied group IV semiconductors, measurements of phonon lifetimes are scarce and the impact of strain engineering is barely understood.

In this work, we address the influence of tensile stain on the thermo-mechanical properties of suspended Ge nano-bridges with thicknesses below 100 nm. It is shown that the acoustic phonon lifetimes can be tuned both by strain engineering of the suspended structures and strain modification by temperature variation in addition to a strong dependence on the thickness of the suspended structures [1]. The combination of temperature dependent micro-Raman and time-domain femtosecond pump-probe reflectivity measurements allows for a complete decoupling of the effects of temperature, geometry, and strain on the acoustic phonon dynamics [2, 3].

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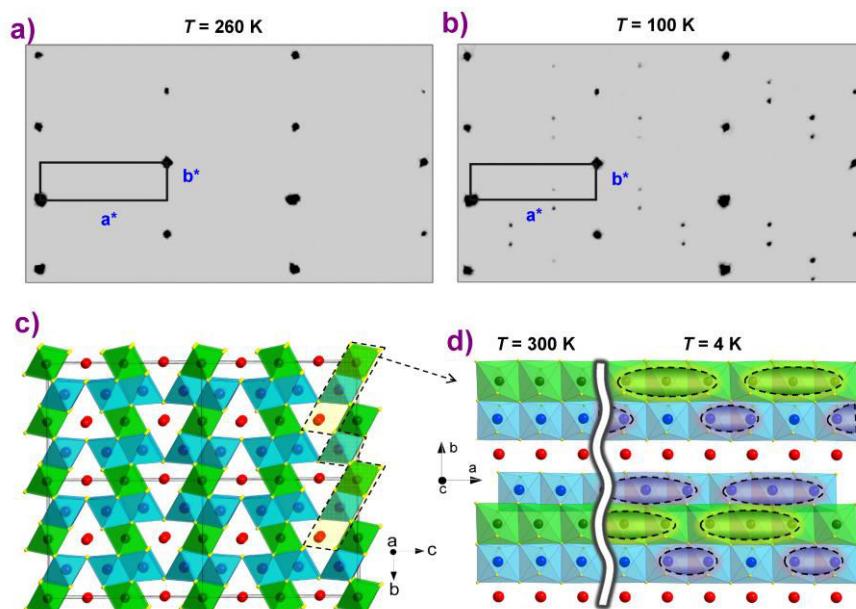
## High pressure high temperature synthesis and phase transitions in simple oxides

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In this presentation, I will present recent results on phase transformations in simple transition metal oxides at high-pressure high-temperatures (HP-HT) conditions. A number of HP-HT polymorphs, was fund to be recoverable at ambient conditions. This circumstance enables more comprehensive investigations of their physical properties and indicates an industrial potential of these new polymorphs. I will review recent results for titanium, manganese and other oxides with the focus on their relevance for the semiconductor physics and industry. I will also present results for new polymorphs of iron oxides composed of with mixed-valent iron cations. These iron oxides demonstrate charge-ordering-driven “metal-semiconductor”-type phase transitions at low temperatures (Figure 1) [1], and external stimuli, like applied high pressure can remarkably affect these charge-ordering transitions and physical properties of iron oxides.



**Figure** (a, b) Examples of reciprocal lattices of X-ray diffraction intensities of Fe<sub>4</sub>O<sub>5</sub> at 260 K and 100 K. a\* and b\* are the axes of reciprocal lattices. (c) Crystal structure projected down the a-axis at room temperature. (d) Crystal structure projected down the c-axis at room and low temperatures. The low-temperature structure demonstrates the preference to dimeric or trimeric ordering in different Fe chains.

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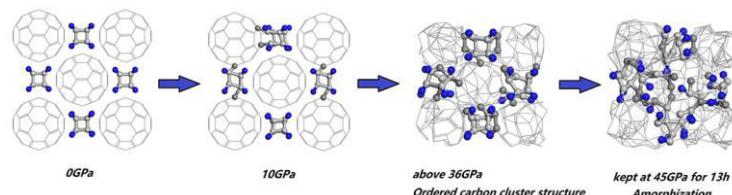
## New ordered Structure of Amorphous Carbon Clusters from Compressing C<sub>8</sub>H<sub>8</sub>/C<sub>60</sub>

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Traditional solids can be categorized by their structures into crystalline, quasi-crystalline and amorphous, based on the degree of static translational order. Carbon, as one of the most versatile elements, has the ability to form various allotropes. From the oldest diamond, graphite, to recently discovered fullerene, nanotube, graphene, etc, all these well-known carbon allotropes belong to either crystalline or amorphous materials and greatly contribute to the development of material science and the technical applications in various fields. It is generally acknowledged that designing and searching for new carbon allotrope has been the focus in material science because of the scientific importance. Recently, long range ordered structures constructed with amorphous building blocks (in this case collapsed fullerene clusters), named “OACC”, have been obtained in compressing solvated fullerene crystals containing aromatic solvents. As a new category of solids, the discovery of such materials expands our structure categorization of solids, as well as open a new door for designing novel materials, for which developing new strategy for material design and tuning the corresponding microstructures for desirable properties are fundamentally important. In this work we report a new amorphous carbon clusters constructed ordered materials by compressing C<sub>60</sub>/C<sub>8</sub>H<sub>8</sub>(cubane) co-crystal, which is induced by the reactions between the stiff fullerene and the high energetic cubane.

The C<sub>60</sub>/C<sub>8</sub>H<sub>8</sub> co-crystal is an interesting rotor-stator compound. The stiff, football like C<sub>60</sub> molecules rotate freely in the lattice, acting as “rotors”, while the static cubane with dice like carbon cage occupies the octahedral voids among C<sub>60</sub> in the lattice and act as a bearing (stator) between the rotating C<sub>60</sub> molecules. Upon compression, the C<sub>8</sub>H<sub>8</sub> play significant role in stabilizing the boundary interactions of the highly compressed or collapsed C<sub>60</sub> clusters which preserve their long range ordered arrangement up to 45 GPa, while as duration time increases at high pressure, the gradual random bonding between C<sub>8</sub>H<sub>8</sub> and carbon clusters under pressure due to “energy release” of highly compressed cubane, leads to the loss of ability of C<sub>8</sub>H<sub>8</sub> in stabilizing the carbon cluster arrangement, and thus a transition from short range disorder to long range disorder (amorphization) in the formed material. The spontaneous bonding reconstruction most likely results in a 3D network in the material, which can create ring crack indentations on diamond anvils. Such material might be potentially superhard and is promising for practical applications. Our work thus indicates that new strategy for new material design can be possibly developed by tailoring the boundary interactions of amorphous building blocks by using high energetic molecules.



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## Prediction of a novel superconducting Si allotrope and its high-pressure Na-Si precursor

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Diamond Si (*d*-Si), which is the thermodynamic ground state at ambient conditions, is a semiconductor with an indirect band gap that is the basis of modern semiconductor technology. In addition, Si exists in various metastable forms such as amorphous Si, polycrystalline Si, Si nanowires, and Si clathrates. Under compression, *d*-Si transforms to the  $\beta$ -Sn and subsequently to simple hexagonal (*sh*) phase. Although the  $\beta$ -Sn and *sh* phases are superconducting, they do not maintain their crystal structures upon pressure release. Another route for synthesizing other Si allotropes is to use appropriate chemical precursors that can be produced using high-pressure techniques and may maintain their stability at ambient conditions. Examples are  $\text{Na}_8\text{Si}_{46}$  (type-I),  $\text{Na}_{24}\text{Si}_{136}$  (type-II), and  $\text{NaSi}_6$  compounds, which lead to  $Pm\bar{3}n$ - $\text{Si}_{46}$ ,  $Fd\bar{3}m$ - $\text{Si}_{136}$ , and  $Cmcm$ - $\text{Si}_6$  clathrates by Na degassing process followed by pressure release.

In this work, we report the prediction of two novel superconducting Si allotropes,  $P6/m$ - $\text{Si}_6$  and its chemical precursor  $P6/m$ - $\text{NaSi}_6$  [1]. We explored new Na-Si clathrates at high pressure using a crystal structure search method, in which the conformational space annealing algorithm for global optimization is combined with first-principles electronic structure calculations [2]. We propose that the  $P6/m$ - $\text{NaSi}_6$  clathrate can be synthesized above 12.4 GPa by comparing its enthalpy with those of other known Na-Si clathrates. We suggest that  $P6/m$ - $\text{Si}_6$  can be obtained by removing Na from the  $P6/m$ - $\text{NaSi}_6$  precursor. The  $P6/m$ - $\text{Si}_6$  allotrope is almost identical to the *sh* structure except for open channels along the *c*-axis. Through phonon spectra calculations and molecular dynamics simulations, we confirmed that both the  $P6/m$ - $\text{Si}_6$  and  $P6/m$ - $\text{NaSi}_6$  clathrates are stable and superconducting at zero pressure, with the critical temperatures of about 12 and 13 K, respectively. Our prediction of novel Si clathrates will stimulate experimentalist to synthesize new exotic Si allotropes useful for Si-based devices.

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## Open Circuit Voltage Increase of GaSb/GaAs Quantum Ring Solar Cells under High Hydrostatic Pressure

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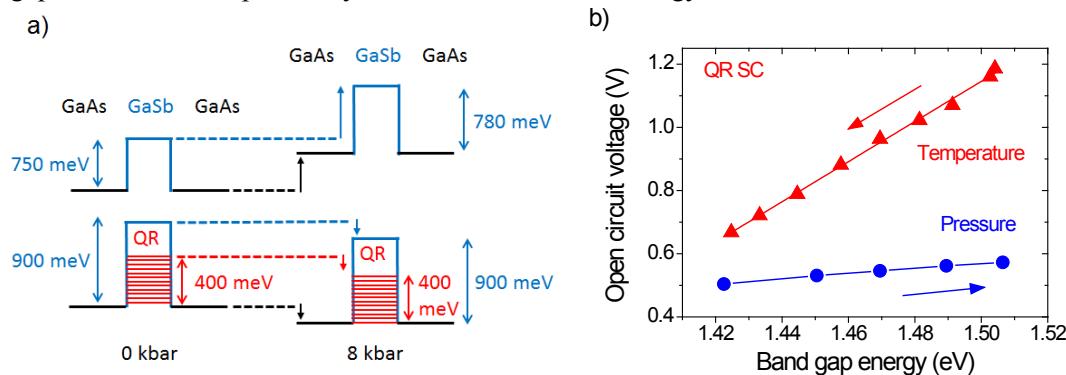
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Intermediate band solar cells (IBSC) have the potential to achieve high power conversion efficiency under solar concentration and have continued to attract valuable research interest [1,2]. The intermediate step in the band gap can increase the photocurrent without degrading output voltage, leading to higher efficiency than in the host material. However, experimentally it is still a challenge to probe the intermediate band concept. In this respect GaSb/GaAs quantum ring cells (QRSC) have been reported, where the type II band alignment provides longer carrier lifetime enhancing the extracted photocurrent compared to the type I InAs/GaAs system [3,4]. The reduction in open-circuit voltage, however, is larger in such structures due to non-radiative recombination *via* the highly localised QR hole states [3].

Here we report on intermediate band GaAs solar cells containing GaSb quantum rings (QR) under hydrostatic pressure using He gas as a pressure medium at room temperature, where by applying 8 kbar the band gap of the solar cell increases by 85 meV. Band offsets and QR confinement energy under 0 and 8 kbar applied pressure are shown in fig. 1(a). This increase in the host material gap reduces the non-radiative recombination, thereby enhancing the open-circuit voltage in QRSC by 15%, as shown in fig. 1(b) (blue circles). We observed that temperature is more efficient in recovering the open-circuit voltage since the intrinsic carrier concentration decreases abruptly – see fig 1(b). Consequently, hydrostatic pressure is a powerful technique that allows study of the role of the bandgap of the host independently of the carrier thermal energy distribution in solar cell devices.



**Figure 1** (a) 300 K energy band diagram for GaSb/GaAs QRSC under 0 and 8 kbar applied hydrostatic pressure. (b) Open-circuit voltage *versus* energy gap as the temperature decreases from 310 to 90 K (red triangles) and applied pressure increases (blue circles). Linear fits to the experimental data points are shown as solid lines.

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## Evidence for Disorder Induced Band Mixing Effects in Ge<sub>1-x</sub>Sn<sub>x</sub> Alloys using Hydrostatic Pressure

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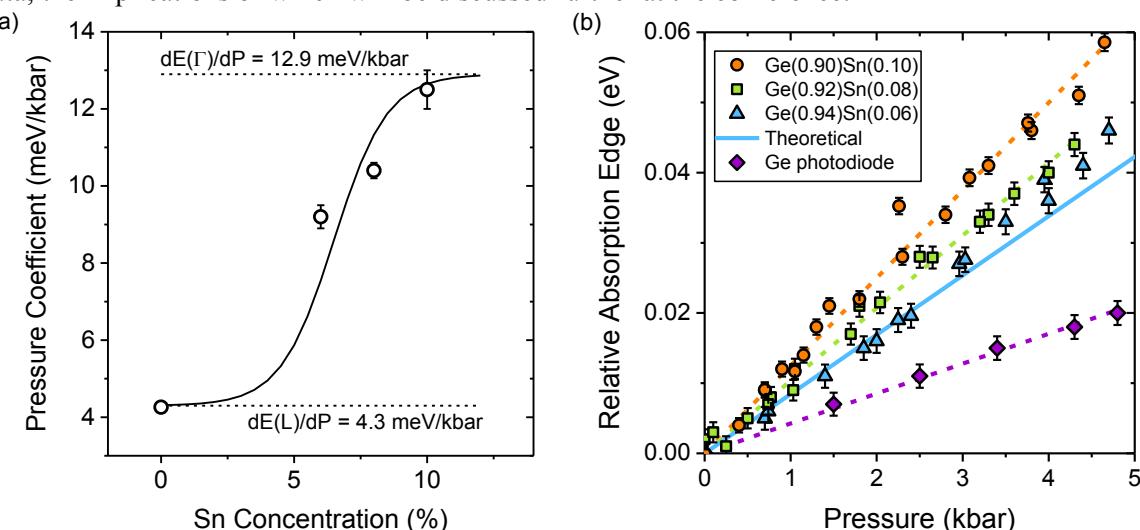
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Although Ge is fundamentally an indirect bandgap semiconductor, introducing  $\alpha$ -Sn into the Ge lattice lowers the energy of the direct  $\Gamma$  valley relative to the conduction band minima at L. Band engineering of GeSn through strain and alloy composition can also significantly enhance carrier mobilities and tunnelling rates, establishing GeSn as a promising material system for future MOSFET and tunnelling-FET (TFET) devices. Most significantly a fundamentally direct bandgap group IV material has the potential to realise a CMOS compatible light source monolithically integrated onto Si 1. The present understanding of the bandgap evolution of GeSn alloys is that there is a sharp transition from in GeSn from an indirect to direct band, with increasing Sn concentration. Using hydrostatic pressure we report on the bandgap character of GeSn samples with Sn concentrations at 6%, 8% and 10% [2]. The bandgap character is determined from measurements of the pressure coefficient of the effective band edge. The pressure coefficients of the relative band edge for the three Sn concentrations is displayed in the left panel below. In contrast to the prevailing view in the literature, we do not observe a sharp transition from an indirect to direct bandgap behaviour. Instead, the pressure coefficient of the band edge, or bandgap character, changes smoothly with Sn concentration. This behaviour can be understood as band mixing effects between the  $\Gamma$ - and L- conduction band states. In order to investigate the compositional dependence of these band mixing effects, the pressure dependence of the conduction band states are modelled using HSE-DFT. The theoretical variation of the band gap for a Ge0.94Sn0.06 supercell is plotted in the right panel, showing good agreement with the experimental data; the implications of which will be discussed further at the conference.



**Figure a)** pressure coefficient of the absorption edge as a function of %Sn. **b)** relative change in the absorption edge for 6, 8 and 10% Sn concentrations as a function of pressure.

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## Pressure effect on diluted magnetic semiconductors with independently controllable charge and spin

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We report our recent work on II-II-V type  $(\text{Ba},\text{K})(\text{Zn},\text{Mn})_2\text{As}_2$ , a new diluted magnetic semiconductor (DMS) which is doped with charge and spin independently. The Curie temperature ( $T_c$ ) of  $(\text{Ba},\text{K})(\text{Zn},\text{Mn})_2\text{As}_2$  (230K) is a reliable record of charge mediated ferromagnetism among all the DMS. To reach higher  $T_c$ , high pressure is used as a promising technique. With the diamond anvil cell (DAC) to generate high-pressure, high resolution synchrotron spectroscopies (diffraction, emission, absorption and dichroism) are utilized to detect evolution of crystal structure and the electronic states with pressure. We reveal that distortion of  $[\text{MnAs}_4]$  tetrahedra and reduction of interlayer As-As distance induced by pressure are intimately connected to electronic structure, especially the p-d hybridization, which is a key factor to affect ferromagnetism. These results provide valuable information to understand the relationship between fine crystal structure and ferromagnetism in DMS, implying higher  $T_c$  can be reached by optimizing crucial features via applying pressure.

Acknowledgement: We would like to thank Professors Ho-Kwang Mao, Daniel Haskel and Wenge Yang for collaboration.

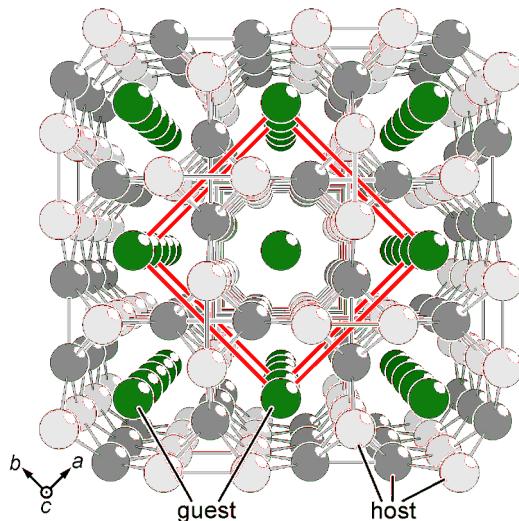
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## Complex Alloy Phases in Bismuth Tellurides at High Pressure

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Bismuth tellurides (with compositions  $\text{Bi}_m\text{Te}_n$ ) are a class of intermetallic compounds exhibiting intriguing physical phenomena including superconductivity, thermoelectricity, electronic-topological transitions and topological insulation. Despite extensive measurements of their physical properties at high pressure, the understanding of the crystal structures of various Bi-Te high-pressure phases has remained fragmentary. Using systematic high-pressure synchrotron x-ray diffraction experiments, it was shown that the materials across the series transform from ordered intermetallic compounds at low pressure to substitutional alloys at high pressure and, surprisingly, that gentle annealing at only 100°C induces partial ordering that creates unusual semi-ordered alloys [1]. Using density-functional calculations, the driving forces for these unusual transitions are identified and electronic properties of the high-pressure alloys predicted. Before transforming to the body-centred-cubic alloys, some bismuth tellurides adopt complex host-guest crystal structures, very similar to those observed previously in the pure elements Ba and Bi (and others) at high pressure, as shown in Fig. 1. Compared to the elemental host-guest phases, atomic order represents an additional degree of freedom in the compound/alloy phases, which will be discussed here.



**Figure 1:** Ba-IV and Bi-III type host-guest crystal structure.

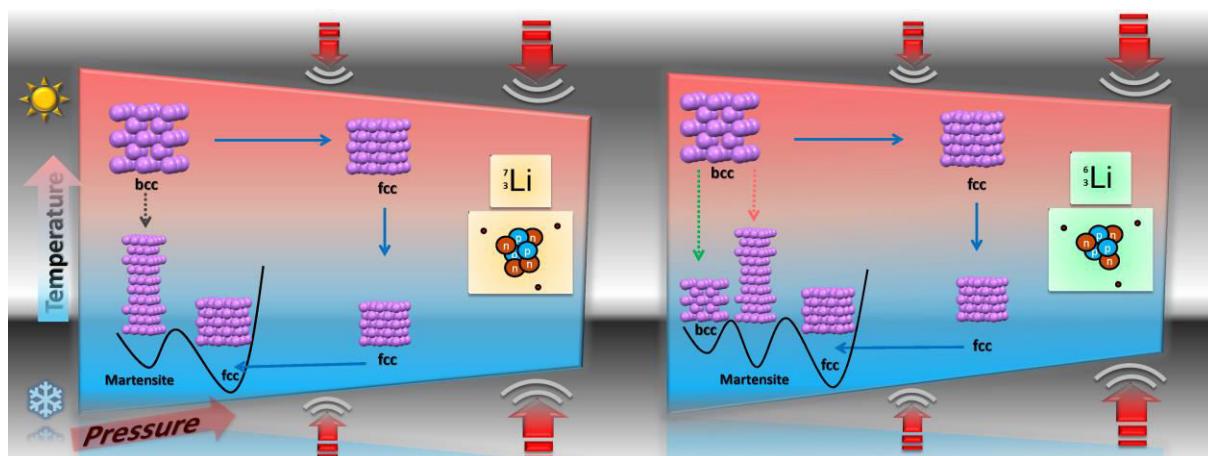
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# Unstable, Metastable and Ground State Structures of Lithium

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Even at zero temperature lattice of lithium remains far from static. In periodic table lithium is the first element immediately after helium and the lightest metal. While fascinating quantum nature of condensed helium is suppressed at high densities, because of the presence of long range interactions in metallic systems, lithium is expected to adapt more quantum solid behavior under compression. Physics of dense lithium offers a rich playground to look for new emergent quantum phenomena in condensed matter. In this talk I will discuss the physics of ultra-light materials under extreme pressures and will present some of our studies on quantum contributions to the structural phase transitions of lithium at low temperature, the structure of its low temperature structure and will present our results on the resolving the long lasting mystery of lithium ground state<sup>1,2</sup>.



Metastability and quantum effects in ground states structures of lithium isotopes (image credit: W.Z Cai).

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## Equilibrium $p$ - $T$ phase diagram of zinc oxide

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Solid-state phase transitions and melting of wurtzite ( $w$ -ZnO) and rock salt ( $rs$ -ZnO) polymorphs of zinc oxide have been studied at pressures up to 8 GPa and temperatures up to 2500 K using *in situ* synchrotron X-ray diffraction and quenching experiments.

Due to the existence of a strong kinetic barrier, at room temperature the  $w$ -ZnO  $\rightarrow$   $rs$ -ZnO phase transition shows a substantial (up to 9 GPa) hysteresis. The hysteresis loop narrows with the temperature increase, and at  $\sim$ 1000 K the branches of direct and reverse transitions merge at pressure of about 5.8 GPa, that can be considered as the equilibrium transition pressure, which is in good agreement with the experimental value of standard enthalpy of the  $rs$ -ZnO  $\rightarrow$   $w$ -ZnO transition [1].

The equilibrium  $p$ - $T$  phase diagram of zinc oxide has been constructed based on experimental data and thermodynamic analysis. Calculations of phase equilibria have been performed using models of phenomenological thermodynamics with interaction parameters derived from our experimental data on ZnO melting at high pressures and high temperatures. The proposed phase diagram represents only thermodynamic equilibria between crystalline phases and liquid, not influenced by kinetic phenomena, and explains all thermodynamic aspects of ZnO polymorphism.

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## Structural correlations in $\text{Cs}_2\text{CuCl}_4$ : pressure dependence of electronic and vibrational structures.

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$\text{Cs}_2\text{CuCl}_4$  is a wide-gap Charge-Transfer (CT) semiconductor exhibits a puzzling optical behaviour under pressure associated with the  $\text{Cu}^{2+}$  absorption and its structural changes [1]. Both  $\text{Cl}^- \rightarrow \text{Cu}^{2+}$  CT and  $d-d$  absorption bands undergo unusual pressure shifts and intensity changes showing abrupt jumps about 4 GPa. The yellow-orange blue colour exhibited by this crystal at ambient conditions and below 4 GPa is mainly defined by the tail of the CT band at about 450 nm [2]. The  $\text{CuCl}_4^{2-}$  tetrahedra, which are flattened by the Jahn-Teller (JT) effect, are isolated from each other in the orthorhombic lattice (*Pnma*). Their  $d-d$  bands do not affect the color as they are split by the JT distortion and appear in the near-infrared range at 1110 and 1820 nm [2]. The isolated character of  $\text{CuCl}_4^{2-}$  in this crystal is clearly revealed by Raman spectroscopy through the internal distorted ( $\text{C}_{2v}$ ) tetrahedron modes at  $\Gamma$ , which constitutes an efficient probe for local and crystal structures. The variation of the crystal structure under pressure had been investigated by x-ray diffraction in the 0–4 GPa range [3]. No evidence of structural transformation was detected in this pressure range. However,  $\text{Cs}_2\text{CuCl}_4$  undergoes a structural phase transition, which could not be identified by x-ray diffraction [3], yielding a deep color change from orange to black [4].

In this work, we present an optical absorption and Raman spectroscopy under pressure in the 0 – 20 GPa range. We aim establishing correlations between crystal structure and electronic and vibrational properties with focus on JT effects, and exploring the high-pressure structure associated with the abrupt optical changes (electronic structure) transforming the crystal color from range to black. Pioneering studies [1,4] evidenced a profound change of the electronic spectra about 4 GPa but no precise indication on either the vibrational or the crystal structure was given. We show that the intense piezochromism at 4 GPa is associated with a structural phase transition from independent  $\text{CuCl}_4^{2-}$  flattened tetrahedra to a phase bearing more interconnected, increased coordination number  $\text{Cu}^{2+}$ .

A detailed analysis on the variations of crystal, vibrational and electronic structures in the *Pnma* phase together with a discussion on the high-pressure phase will be given at the Conference. The results will be compared with those reported in the isostructural non-JT compound  $\text{Cs}_2\text{CoCl}_4$  [5].

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## High-pressure elastic, vibrational and structural study of monazite-type $\text{GdPO}_4$ from ab initio simulations.

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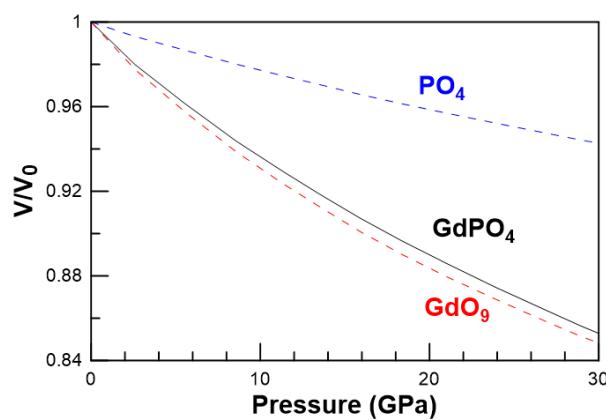
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The  $\text{APO}_4$  orthophosphates compounds ( $A=$  trivalent material) are analogous materials to orthoarsenates, orthovanadates, and orthosilicates. They are basically formed by  $\text{AO}_8$  or  $\text{AO}_9$  polyhedral and  $\text{PO}_4$  tetrahedra. The size of the ionic radio of the  $A$  cation defines the two different structures where this family compounds crystallizes.  $\text{APO}_4$  compounds with the ionic radio lower than Gd crystallize in the tetragonal zircon structure ( $I4_1/\text{amd}$ , space group 141 with  $Z=4$ ). The rest of orthophosphates crystallize in a monoclinic lower symmetry phase, monazite structure ( $P2_1/n$ , space group 14 with  $Z=4$ ). Monazite structure is isostructural to cerium phosphate mineral (monazite). The structure can be viewed as being composed by alternating edge-sharing  $\text{AO}_9$  polyhedra, with a structural distortion derived from a rotation of the  $\text{PO}_4$  tetrahedra and a lateral shift of the (100) planes that reduces symmetry from tetragonal to monoclinic.

In this work  $\text{GdPO}_4$  monazite-type has been studied under high pressure by first principles calculations in the framework of density functional theory. The work focuses on the analysis of the structural, dynamical and elastic properties of this material. Results about the structure and its evolution under pressure, the equation of state and the compressibility are reported. The evolution of the Raman and Infrared frequencies, and their pressure coefficients are also presented. Finally, the study of the elastic constants allows to provide information related with the elastic properties of this compound and their mechanical stability.



**Figure 1:** Relative variation with pressure of the unit-cell and polyhedral volumes for  $\text{GdPO}_4$ .

## Th4.3-P6

Transmittance of 1D superconductor-semiconductor photonic crystal as a function of pressure, temperature, and thickness of the component layers.

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Using the transfer matrix method, we study the transmittance of 1D photonic crystals made of alternated layers of a semiconductor (GaAs) and a high-T<sub>c</sub> superconductor ( $HgBa_2Ca_2Cu_3O_{8+\delta}$ ) under the effects of temperature, applied hydrostatic pressure, and thickness of the layers. The frequency-dependent dispersion formula according to the two-fluid model was adopted to describe the optical response of the superconducting system. We found that increasing the superconductor (semiconductor) layer thickness results in a shift to higher (lower) values of the transmittance cutoff frequency. Additionally, this cutoff frequency is shifted to lower values with the temperature. Also, we found that the width of the photonic bandgaps is modified with the applied pressure. The most notorious result is observed near the 17 THz region, where a new gap appears with the increase in pressure.

## Reentrant structure transition of indium at 130 GPa

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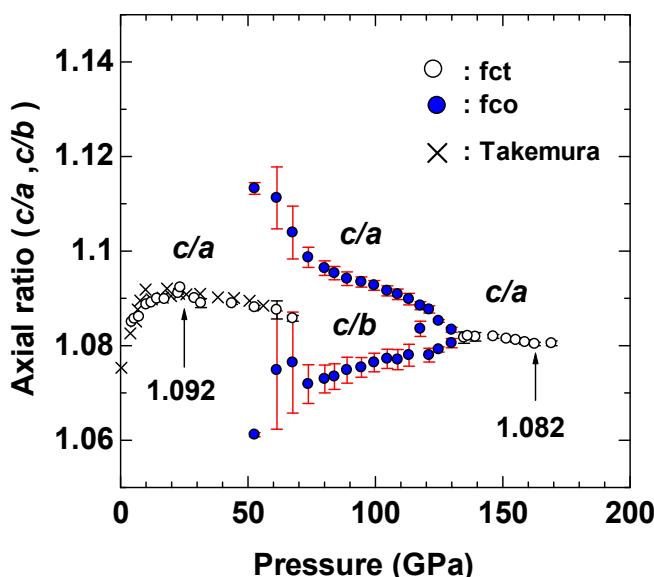
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Elemental material indium (In) is a rare metal with extremely low shear modulus and shows superconductivity at low temperature of 3.4 K. It has a base-centered tetragonal (bct) structure at ambient condition. The structure corresponds to a face-centered tetragonal (fct) and is derived from a face-centered cubic (fcc) by a tetragonal distortion; the  $c/a$  ratio of lattice constants is slightly larger than 1.0. Since aluminum (Al) of the same group in the periodic table has a simple fcc structure, the origin of the unusual structure of In has been attracted attention of many scientists.

Focusing on the high-pressure stability of this unique structure, high-pressure x-ray diffraction studies of In have been conducted at pressure up to 90 GPa and a structure transition to an orthorhombic phase (fco) has found at around 60 GPa. [1,2] After that, the stability of the fco phase has been verified by *ab initio* theoretical calculations. [3-5] Recent theoretical study has proposed a five-stage structural phase transition at pressure up to 1000 GPa: fct( $c/a > 1$ ) -fco-fct( $c/a < 1$ )-fco-fct( $c/a > 1$ ) -fcc.[6] However, 100 GPa range experimental studies of In remain quite difficult because of its extremely low shear modulus. The proposed phase transitions have not been verified yet.

In this paper, we report the extension of the structural study of In at pressure up to 170 GPa using synchrotron powder x-ray diffraction experiments and confirm an fco-fct phase transition at 130 GPa. The reentrant structure transition is of second order like and the  $c/a$  ratio of the fct high pressure phase is larger than 1.0. The observed structure transition is different from the theoretical prediction. [6] The pressure dependence of the axial ratio of each phase is shown in Figure 1.



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**Figure 1.** The pressure dependence of the axial ratio of each phase.

## High pressure on the orthorhombic phase of nanostructured MoO<sub>3</sub>

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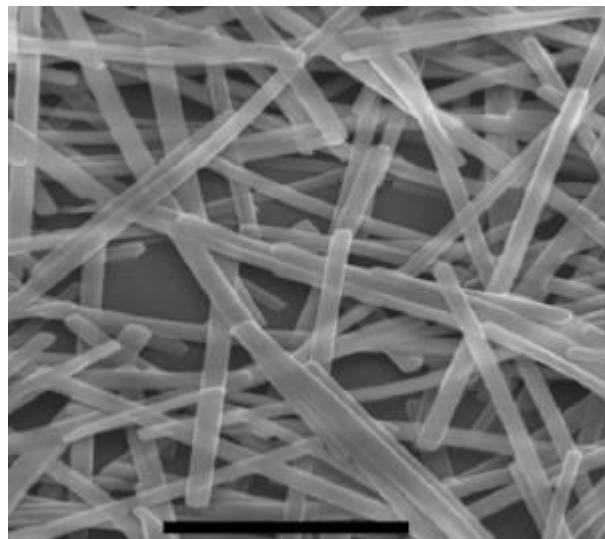
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Molybdenum oxide presents several structural polymorphs, being an interesting model to investigate how nanostructured materials behave in comparison with the bulk counterpart. The orthorhombic phase of MoO<sub>3</sub> (called  $\alpha$ -MoO<sub>3</sub>-form), is thermodynamically stable. It has a lamellar structure formed by asymmetrical MoO<sub>6</sub> octahedra connected through corner-linking along [100] and edge-sharing along [001]. Among several possible forms of the orthorhombic MoO<sub>3</sub>, we have investigated the crystal in the nanoribbons morphology (see Figure).

In a previous work, authors [1] showed that nanoribbons  $\alpha$ -MoO<sub>3</sub> exhibit distinct Raman bands behavior upon temperature variation when compared with the bulk crystal. Also, it is known that several materials present different behavior between the nanostructure and the bulk counterpart under high pressure conditions. Using a diamond anvil cell we have investigated in the present work the vibrational behavior of the material under pressures through Raman spectroscopy up to 21 GPa. We have observed that the nanoribbons undergo a phase transition from the orthorhombic  $\alpha$ -MoO<sub>3</sub> phase (space group *Pbnm*) to the monoclinic phase MoO<sub>3</sub>-II (space group *P2<sub>1</sub>/m*) at 5 GPa. This is an impressive result because the bulk monoclinic phase undergoes the same phase transition only at 12 GPa [2]. Additionally, changes observed in the Raman spectra suggest a collapse of the nanoribbons morphology during the phase transition. Finally, scanning electron microscopy (SEM) images showed that the morphology of the samples is modified during the compression experiment: it goes from the nanoribbons to spherical particles after compression, as indicated by *ex-situ* images.



**Figure** SEM image of  $\alpha$ -MoO<sub>3</sub> as synthesized.

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## Phases of LaTiO<sub>3</sub> under pressure

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The family of Ti-based RTiO<sub>3</sub> compounds, where R stands for a rare-earth ion, crystallize in the GdFeO<sub>3</sub>-type perovskite structure (SG *Pnma*,  $Z=4$ ) at ambient conditions [1]. They all have a single electron in the  $t_{2g}$  orbitals of the Ti 3d shell ( $Ti^{3+}$ ) and are all Mott insulators [2,3]. Upon decreasing the ionic radius in the rare-earth series from La to Y, the structural distortions increase and, consequently, the one-electron bandwidth gets smaller [2,3]. LaTiO<sub>3</sub> exhibits the smallest structural distortions among the series and, concomitantly, has the smallest optical band gap ( $E_g \sim 0.1$  eV [1]). The latter implies that LaTiO<sub>3</sub> is on the verge of an insulator-to-metal transition. Indeed, previous high-pressure mid-infrared reflectivity investigations [4] detected the onset of an insulator-to-metal transition above 10 GPa.

The pressure-induced metallization motivated us to perform high-pressure x-ray diffraction (XRD) and Raman studies on LaTiO<sub>3</sub> in order to detect the response of the structure and the lattice dynamics. From our XRD study, we observe an *isostructural* transition taking place at  $\sim 10$  GPa which coincides with the metallization of the compound. Upon further compression, the orthorhombic *Pnma* phase transforms into a tetragonal *I4/mcm* structure above 30 GPa. High-pressure Raman studies at ambient and low temperatures are consistent with the XRD results. We have observed an unusual enhancement of the Raman intensity upon entering the metallic state; a possible explanation of this peculiar behavior in terms of electronic correlations is offered.

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## Synthesis of a novel structure of cesium superoxide via x-rays and high pressure.

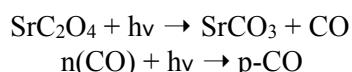
E. Evlyukhin<sup>1</sup>, E. Kim<sup>1</sup>, D. Goldberger<sup>1</sup>, P. Ciflugu<sup>1</sup>, P. Weck<sup>2</sup>, M. Pravica<sup>1\*</sup>

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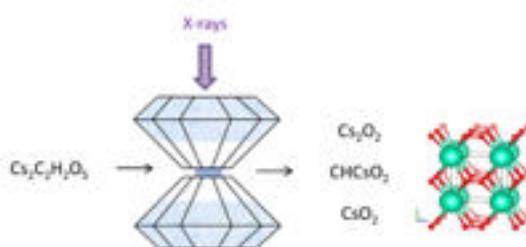
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Recently, we have created a novel compound (doped polymeric carbon monoxide) by irradiating strontium oxalate with synchrotron hard x-rays via the following suspected chemical reactions at ambient and high pressure [1]:



We sought to investigate catatonic dependence of this x-ray photochemical reaction by irradiating cesium oxalate monohydrate ( $\text{Cs}_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$ ) in a diamond anvil cell (DAC) at ambient and high pressure ( $\leq 0.5$  GPa). When irradiated with X-rays of energies near the K-edge of cesium ( $\sim 36$  keV) [2] at high pressure, the material transformed into a number of products including cesium superoxide ( $\text{CsO}_2$ ) as evidenced with Raman spectroscopy and x-ray diffraction. The diffraction pattern observed from  $\text{CsO}_2$  exhibits a new type of crystal structure which previously has not been reported to the best of our knowledge. According to first principle calculations the observed crystal structure is a new type of bcc structure. Additionally, based on cascades of ultrafast electronic relaxation steps triggered by the absorption of X-ray photons, we propose a model explaining the X-ray induced damage of multitype bounded matter. This discovery may enable a means for novel chemical and structural synthesis harnessing highly energetic, highly penetrating, and highly focusable hard x-rays in combination with high pressure.



**Figure 1:** (Left): Schematic of the experiment. (Right): Theoretically-predicted crystal structure of  $\text{CsO}_2$  computed from the observed diffraction pattern produced after irradiating  $\text{Cs}_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$  in a DAC. The green and red spheres represent Cs and O atoms, respectively.

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## Thermoelectric properties of $\text{TX}_3$ ( $\text{M} = \text{Ti}, \text{Zr}$ , $\text{X} = \text{S}, \text{Se}, \text{Te}$ ) under high pressure

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A number of recent works demonstrate an enormous technological potential of 2D trichalcogenides of the transition metals,  $\text{TX}_3$  ( $\text{T} = \text{Ti}, \text{Zr}, \text{Hf}, \text{Nb}$ , or  $\text{Ta}$ , and  $\text{X} = \text{S}, \text{Se}$  or  $\text{Te}$ ), e.g., for nano-electronics, optoelectronics, flexible electronics, third-generation solar photovoltaic applications, and novel nanophotonic devices [1-2]. For these and other reasons, this class of functional 2D materials is promising for industry.

In this work we experimentally investigated an effect of applied high pressure on variations of the thermoelectric and electrical properties of single-crystalline 2D titanium and zirconium trichalcogenides ( $\text{TiS}_3$ ,  $\text{ZrS}_3$ ,  $\text{ZrSe}_3$  and  $\text{ZrTe}_3$ ) at the range of pressure up to 10 GPa. Single-crystalline samples of all these 2D materials were grown by a direct reaction of a cation wire and a corresponding chalcogen. High pressure experiments were carried out with automated setup with anvil-type high-pressure cell of a toroidal type in which both hard-alloy anvils had semispherical cavities [3]. We followed pressure evolution of the Seebeck coefficient and electrical resistance for these four compounds at room temperature. We observed a number of crossovers in their pressure behavior and addressed them to band structure reconstruction. Our study shows that some of these compounds, if they are appropriately strained or alloyed, may be promising for thermoelectricity. We propose a number of potential industrial applications of the new effects we found in these 2D materials.

The research was carried out within the state assignment of FASO of Russia (theme “Electron” No. AAAA-A18-118020190098-5).

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## High Pressure Study of Hall Effect in Thermoelectric Mg<sub>2</sub>Si Semiconductor

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Mg<sub>2</sub>Si is an indirect-bandgap semiconductor with the energy gap of 0.64 eV at room temperature[1] and the higher electron doping to about 10<sup>20</sup> cm<sup>-3</sup> is achieved with various dopants[2, 3] and the sintering of the Mg<sub>2</sub>Si powder is also possible[4]. Higher doping and easy sintering are important for making the thermoelectric device. The first generation Mg<sub>2</sub>Si thermoelectric device expected to convert high-temperature heat energy at about 500 °C to electric energy is currently developing for the field test[5]. To improve further electronic transport and thermoelectric power factor and to understand phonon transport to decrease lattice thermal conductivity work together in making better thermoelectric Mg<sub>2</sub>Si [2, 5, 6]. For the next generation Mg<sub>2</sub>Si thermoelectric device the higher conductivity more than 1 mΩ<sup>-1</sup>·cm<sup>-1</sup> is expected to reach the better thermoelectric power factor exceeding 10 mW/K<sup>2</sup>m. In the last few years the several high-pressure studies for the thermoelectric doped Mg<sub>2</sub>Si semiconductor have been published on the Seebeck effect decreasing with increasing pressure[7], the neutron bombardment effect colliding with Mg atom[8], the mid-infrared optical property showing the light effective masses from 0.255m<sub>e</sub> to 0.361m<sub>e</sub>[9], and the phase transformation occurring at about 10 GPa from the ambient anti-fluorite phase (*Fm-3m*) to the anti-cotunnite phase (*Pnma*)[10]. We have studied for the first time the Hall effect in sintered thermoelectric *n*-type Al-doped Mg<sub>2</sub>Si to elucidate the carrier transport mechanism up to the pressure of 2.5 GPa and in the range of temperature from 10 K to 300 K. The conclusion which we have obtained is that the scattering of electron of thermoelectric sintered *n*-type Al-doped Mg<sub>2</sub>Si is primarily the impurity scattering and the intervalley scattering but the grain boundary scattering is not important.

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## 2D Electrons Concentration and Mobility in n-GaAs/AlGaAs:Si under Uniaxial Stress

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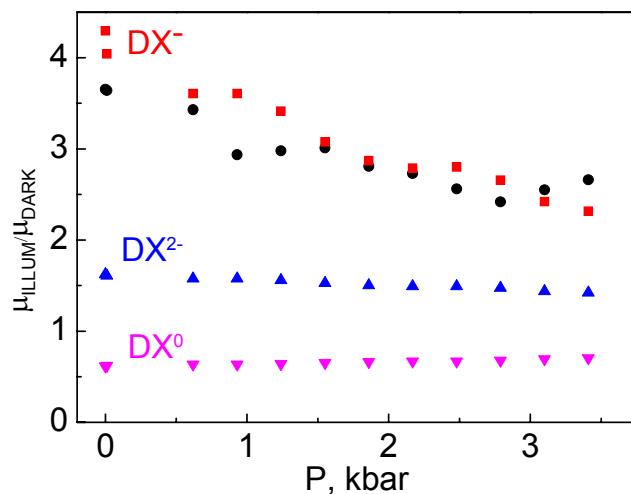
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High quality  $n$ -GaAs/Al<sub>0.29</sub>Ga<sub>0.71</sub>As:Si single heterostructures, grown by MBE epitaxy on (001) GaAs substrate and characterized (at temperature  $T = 4.2$  K in the dark) by initial electron concentration  $n = 2 \cdot 10^{11} \text{ cm}^{-2}$  and mobility  $\mu_{\text{dark}} = 2.2 \cdot 10^5 \text{ cm}^2/\text{V}\cdot\text{s}$ , were investigated under external uniaxial compression up to  $P = 3.5$  kbar along [110] direction in the dark and after illumination.

Illumination by infrared diode ( $h\nu = 1.32 \text{ eV} < E_g = 1.67 \text{ eV}$  – energy gap in Al<sub>0.29</sub>Ga<sub>0.71</sub>As at the temperature of the experiment  $T = 1.7$  K) leads, after the diode switching, to the persistent photoconductivity (PPC) with 2D electron concentration and mobility in the quantum well (QW) increased in 2.5 and 4 times correspondingly. Qualitatively, this result implies light excitation of deep DX centers, connected with Si dopant and responsible for the persistent photoconductivity, that is accompanied with decrease of scattering centers after the spacer.

Under compression, we observed decrease of 2D electrons mobility and concentration in PPC state. They are controlled by arising piezoelectric field, that at  $P \sim 3$  kbar is already comparable with electric field at the heterointerface and directed in our case from the heterointerface to the substrate [1]. Taking into account that at  $T = 1.7$  K the main scattering mechanism in a QW is ionized impurity scattering due to remote donors [2] and taking into consideration some geometry characteristics of the investigated heterostructures, we can quantitatively calculate the ratio  $\mu_{\text{illum}}/\mu_{\text{dark}}$  on the base of the observed concentration behavior (see Fig.1). We assume that electrons, leaving the QW in arising piezoelectric field, tunnel back to DX centers.



**Figure 1:** Experimental (circles) and calculated for a number of models pressure dependence of  $\mu_{\text{illum}}/\mu_{\text{dark}}$  ratio.

The represented on the Figure 1 results of calculations are performed for the 3 models of DX center ground state: (1)  $\text{DX}^-$  - negative and gives away one electron under illumination, (2)  $\text{DX}^{2-}$  - negative and gives away two electrons, (3)  $\text{DX}^0$  – neutral. Good agreement with the experimental results let us conclude that the ground  $\text{DX}^-$  state is realized in the investigated heterostructures and under illumination:  $\text{DX}^- + h\nu \rightarrow \text{DX}^0 + e^-$ .

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## Metastable Superconductive Phase of Topological Insulator Sb<sub>2</sub>Te<sub>3</sub> Obtained by High-Pressure-High-Temperature Treatment

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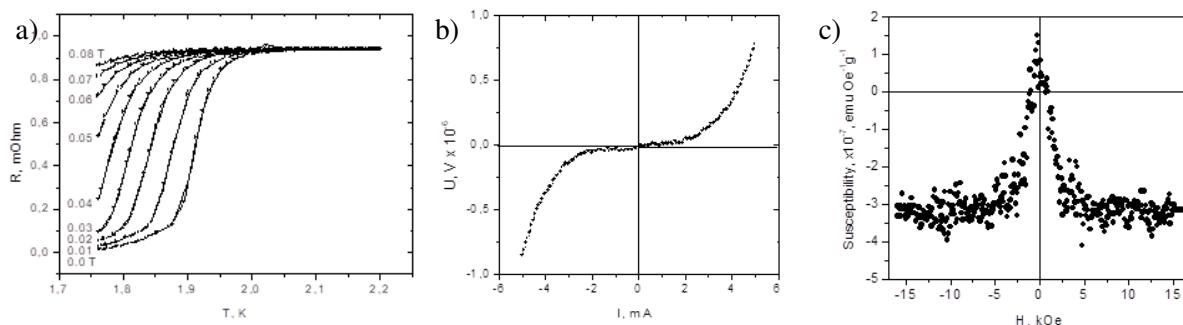
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Extensive high-pressure studies revealed phase transitions of topological isolators like Sb<sub>2</sub>Te<sub>3</sub>, Bi<sub>2</sub>Te<sub>3</sub> and Bi<sub>2</sub>Se<sub>3</sub> into new structures which possess superconductivity at low temperature and high pressure [1-3]. Superconducting topological insulators attract much attention due to unusual quantum states – Majorana fermions, appropriate to non-abelian quantum computing. However, structures of superconducting high-pressure phases investigated earlier were ordinary, not topological insulator. In our study we employed the method of high-pressure-high-temperature (HPHT) treatment at P = 4 GPa, T=873K to synthesize new metastable phase of Sb<sub>2</sub>Te<sub>3</sub> which is superconductive with T<sub>Conset</sub> = 2.0 K at normal pressure (Fig. 1a) and displaying the particular topological insulator properties. Its crystal structure is monoclinic (*C2/m*) with the cell dimensions: *a*=15.644(80) Å, *b*=4.282(8) Å, *c*=9.382(20) Å, β=89.70(5)°. In the temperature range of 50 - 3 K the electrical conductivity decreases as a square root function of temperature that is typical to degenerate semiconductors due to quantum corrections to electron-electron interaction and proper to 2D superconductors. The low critical current value of about 2 mA in the metastable m-Sb<sub>2</sub>Te<sub>3</sub> phase (Fig.1 b) and an absence of the detectable heat capacity effect at the superconducting transition also indicate a low-dimensional character of the superconductivity which may refer to the surface of the crystal grains. The zero-field magnetic susceptibility cusp (Fig. 1c) and linear positive magnetoresistance indicate the topological insulator state. Thus metastable phase of Sb<sub>2</sub>Te<sub>3</sub> topological insulator obtained by high-pressure-high-temperature treatment possesses surface superconductivity and may be interesting for Majorana fermions search.



**Figure 1.** Magnetic field effect on superconductivity transition temperature in m-Sb<sub>2</sub>Te<sub>3</sub> phase (a). Current-voltage characteristic at T = 1.76 K (b) Magnetic susceptibility vs magnetic field at room temperature (c).

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# High pressure study of optical and vibrational properties of methylammonium lead iodide perovskites

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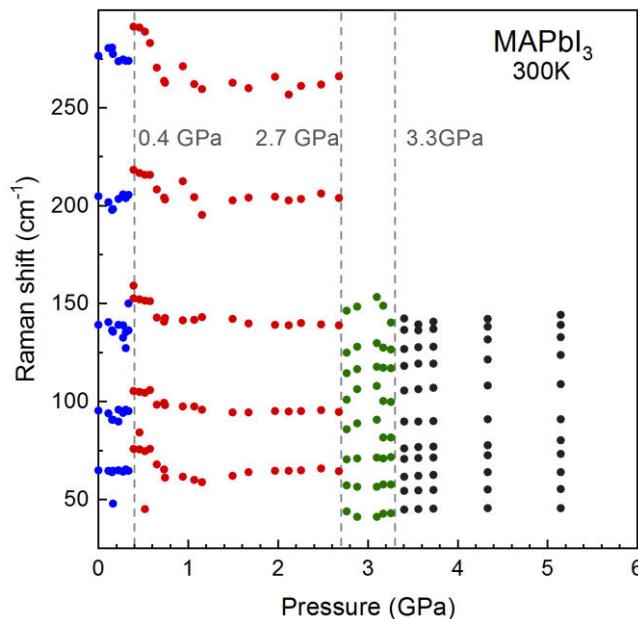
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The structural phase behavior of high quality single crystals of methylammonium lead iodide ( $\text{CH}_3\text{NH}_3\text{PbI}_3$  or  $\text{MAPbI}_3$ ) was revisited by combining Raman scattering and photoluminescence (PL) measurements under high hydrostatic pressure up to ca. 10 GPa. Both PL and Raman spectra show simultaneous changes in their profiles that indicate the occurrence of three phase transitions subsequently at around 0.4 GPa, 2.7 GPa and 3.3 GPa. At the second phase transition, the Raman spectra exhibit a pronounced reduction in linewidth of the phonon modes of the inorganic cage, similar to the changes observed at the tetragonal-to-orthorhombic phase transition occurring at around 160 K but ambient pressure [1]. This behavior is interpreted as evidence for the locking of the organic cations in the cage voids above 2.7 GPa, due to the reduced volume and symmetry of the unit cell. At the third phase transition, reported here for the first time, the PL is greatly affected, whereas the Raman experiences only subtle changes related to a splitting of some of the peaks. This behavior may indicate a change mostly in the electronic structure with little effect on the crystal structure. Strikingly, no amorphization of the sample was observed up to the highest pressure which reached close to 10 GPa, in frank discrepancy with most of the high-pressure (x-ray) data of the literature [2], which established an onset of 3 GPa for the set in of an amorphous phase in  $\text{MAPI}_3$ .



**Fig. 1:** Raman mode frequencies of the inorganic cage phonons of  $\text{MAPI}_3$  as a function of pressure. Pressures at which a phase transition occurs are indicated by vertical dashed lines.

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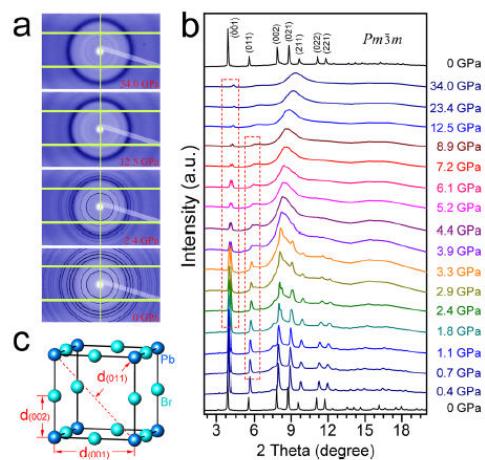
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## Pressure enhanced performance in perovskite photovoltaic materials

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Hydrostatic pressure provides a very efficient route to tune the materials properties, and has been widely used for new materials synthesis and enhancing their performance. The recent fast development on the organic-inorganic hybrid perovskites (ABX<sub>3</sub>) attracted great interest on the advanced photovoltaic and optoelectronic applications. Here we demonstrate the pressure effect to the halide perovskite family with their structural evolution, band gap engineering, light induced photocurrent enhancement, and structure stability under pressure cycling. Combining the available x-ray, transport and optical probing tools with pressure treatment, we can tune the band-gap towards the Shockley-Queisser limit, double the carrier lifetime, improve the photocurrent at high pressure and quenched samples. In this talk, we will compare the pressure effect on the performance with different organic ions A, lead and non-lead B ions, and different halide choice in X. The comprehensive results can improve our understand on the fundamental mechanism of the crystalline structure, electronic structure, physical and chemical properties, and develop a routine pass-way for advanced materials synthesis with tailored properties.



**Figure** The structure evolution of MAPbBr<sub>3</sub> under high pressure.

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- [3] X. Lu et al., Adv. Mater. 28, 8663 (2016)
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## Installation of a laser drilling system and diamond anvil cell for transport measurements up to 60 GPa

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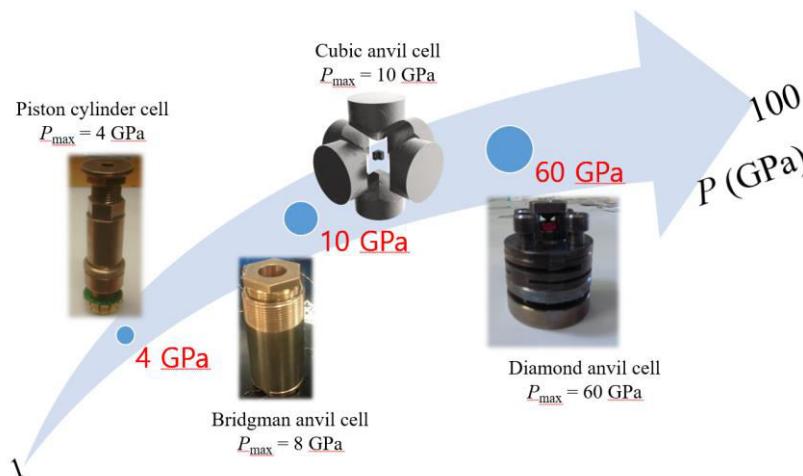
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Various novel physical phenomena have been discovered under high pressure [1]. High pressure has become important tuning parameter in condensed matter physics up to date. We have built various pressure tools from 0.2 to 60 GPa for measuring the transport properties under high pressure. We made the piston cylinder cell under 3 GPa, which can be used in QD-PPMS. It has been already used in our laboratory, I modified it to use higher pressure up to 4 GPa. Secondly, I have built the Bridgman anvil cell which can be used from 2 to 8 GPa. In case of Bridgman cell we can not measure the resistivity under 2 GPa. We have had a need for higher pressure experiment than 8 GPa for a long time. Now we build the diamond anvil cell. We set up the laser drilling system for making the hole of gasket which is most difficult part to build the DAC. Now we succeed it and can be made the size of hole about 50 micro-meter. Especially we use the cubic Boron Nitride(c-BN) which is the thicker than metal gasket of sample space [2]. It is only possible by laser drilling system. The various pressure tools are prepared in our laboratory; we can investigate the physical properties under multiple pressure.



**Figure.** The spectrum of pressure tools from 1 to 60 GPa.

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## Pressure-tuned superconductivity and normal-state behavior in $\text{Ba}(\text{Fe}_{0.943}\text{Co}_{0.057})_2\text{As}_2$ near the antiferromagnetic boundary

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Superconductivity in iron pnictides is unconventional and pairing may be mediated by magnetic fluctuations in the Fe sublattice. Pressure is a clean method to explore superconductivity in iron based superconductors by tuning the ground state continuously without introducing disorder. Here we present a systematic high pressure transport study in  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$  single crystals with  $x = 0.057$ , which is near the antiferromagnetic instability. Resistivity  $\rho = \rho_0 + AT^n$  was studied under applied pressure up to 7.90 GPa. The parameter  $n$  approaches a minimum value of  $n \approx 1$  at a critical pressure  $P_c = 3.65$  GPa. Near  $P_c$ , the superconducting transition temperature  $T_c$  reaches a maximum value of 25.8 K. In addition, the superconducting diamagnetism at 2 K shows a sudden change around the same critical pressure. These results may be associated with a possible quantum critical point hidden inside the superconducting dome, near optimum  $T_c$ .

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## Anharmonic effects and optical spectra in superconducting hydrogen

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### Abstract:

The recent measurement of a superconducting critical temperature ( $T_c$ ) of 203 K in the sulfur hydrogen system is a major breakthrough in the field of superconductivity. This measurement offers new hopes to find sooner than later room-temperature superconductivity in other hydrogen-rich compounds or hydrogen itself. Actually, many theoretical calculations have predicted astonishingly high  $T_c$  values for hydrogen at megabar pressures. However, considering that anharmonicity has shown to decrease  $T_c$  in several hydrides, one might expect anharmonicity might strongly impact superconductivity in hydrogen too. We present first-principles calculations of metallic atomic hydrogen in the 400-600 GPa pressure range in a tetragonal structure with space group  $I4_1/amd$ , which is predicted to be its first atomic phase, and characterize anharmonic phonon frequencies within the stochastic self-consistent harmonic approximation (SSCHA) and the associated modification on its predicted superconducting transition temperature [1]. Additionally, we will also present the full optical spectra of atomic hydrogen in this phase, which can help to experimentally characterize the metallic and superconducting transitions [2].

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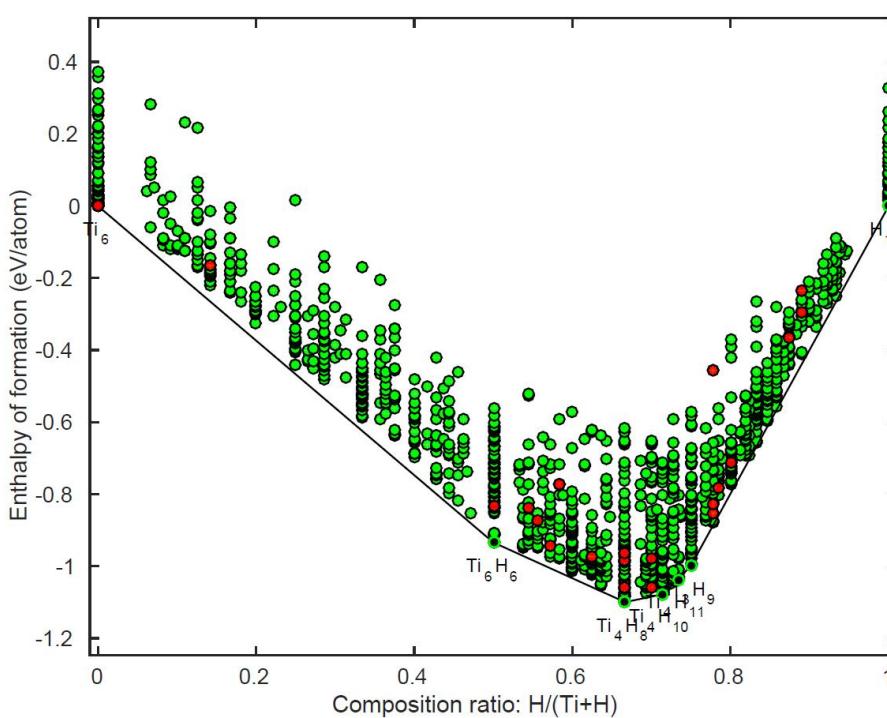
## Superconductivity in Titanium Hydrides at High Pressures

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Discovery of high-temperature superconductivity in sulfur hydrides at megabar pressures breaks the traditional belief for conventional superconductors. Exploration of superconductivity in phonon-mediated hydrides compounds has activated great interests in the research field of high-temperature superconductivity. Dense hydrides are expected to show very unusual physical properties, such as metallic conductivity and high-temperature superconductivity. We use first-principles calculations to study structural, vibrational, and superconducting properties of titanium hydrides at high pressures. A series of H-rich structures have been explored. We report its high-pressure novel structural phases accompanied by electronic calculations and electron-phonon couplings. Our simulations established the high temperature superconductive nature of titanium hydrides and provided useful route for experimental verification.



**Figure.** Convex hull diagram of Ti-H system at 100 GPa. Ti<sub>6</sub>H<sub>6</sub>, Ti<sub>4</sub>H<sub>8</sub>, Ti<sub>4</sub>H<sub>10</sub>, Ti<sub>4</sub>H<sub>11</sub> and Ti<sub>3</sub>H<sub>9</sub> are stable compositions.

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# Superconductivity emerging from a Weyl semimetal NbIrTe<sub>4</sub> under pressure

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The topological properties have received strong interest both theoretically and experimentally in recent years. Insulators can be classified into conventional insulators and topological insulators with protection by time-reversal symmetry. By analogy from insulator to metal, semimetals are divided into trivial and nontrivial semimetals topologically in electronic structure, with the latter including Weyl, Dirac, and node-line semimetals.

Weyl semimetals are semimetals or metals whose quasiparticle excitation is the Weyl fermion. Remarkably, Weyl fermions are robust while carrying currents, giving rise to exceptionally high mobility [1]. It was predicted that an inversion-breaking single crystal NbIrTe<sub>4</sub> is a Weyl semimetal candidate [2].

In this study, we obtained measurements based on the resistivity, synchrotron X-ray diffraction, using the Weyl semimetal NbIrTe<sub>4</sub> at high pressures. Our experiments indicated that NbIrTe<sub>4</sub> exhibited a pressure-induced superconductivity at 1.6GPa with transition temperature ( $T_c^{onset}$ ) ~2.2K. The superconducting transition temperature increased to a maximum ~5.1 K with pressures up to 15.8GPa. The possible topological superconductivity emerges in the Weyl semimetal phase could provide abundant evidence for understanding the fundamental mechanism and potential pathway for functional device design from the practical aspect.

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## Diamond Anvil Cell with Boron-doped Metallic Diamond Electrodes for Resistivity Measurement under High Pressure

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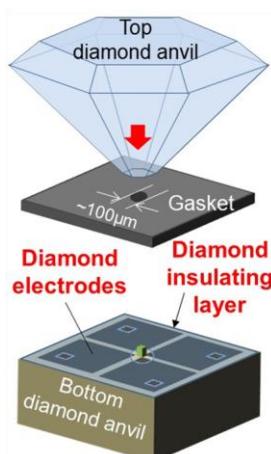
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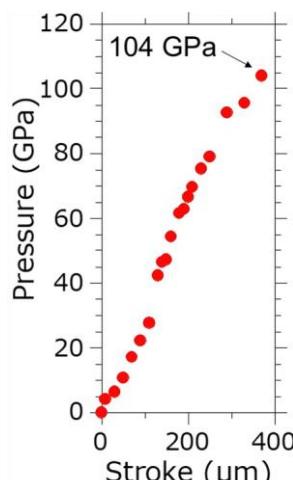
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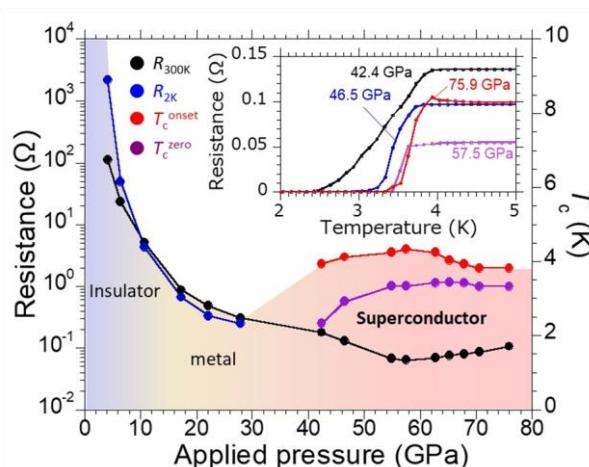
High pressure is a promising tool to obtain new functional materials which cannot appear under ambient pressure. For example, the discovery with great surprise of high temperature superconductivity in  $H_3S$  at  $\sim 200$  K was recently reported under 150 GPa [1]. Diamond anvil cell (DAC) is most useful apparatus to generate high pressures, however, a resistivity measurement using DAC is quite difficult because it requires tiny and hard electrodes. Moreover, an insulating layer should be inserted between the electrodes and a metal gasket to separate each other, which is also broken by applying pressure. In this study, we focused on the boron-doped metallic diamond and undoped diamond as a very hard electrode [2,3] and an insulating layer [4], respectively, as shown in Fig. 1. The maximum pressure of the developed DAC was confirmed up to 104 GPa (Fig. 2). The resistivity measurements of carrier-doped  $SnSe_{0.99}S_{0.01}$  single crystals have been demonstrated using the developed device under various pressures. As shown in Fig. 3, we clearly observed the insulator-metal-superconductor transition with the increase of pressure up to 75 GPa, using the developed DAC.



**Figure 1 :**  
Configuration of DAC



**Figure 2 :** Pressure generation



**Figure 3 :** Pressure phase diagram of  $SnSe_{0.99}S_{0.01}$   
Inset shows the  $R-T$  near the superconducting transition

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## Development of Thermoelectric Measurement at High-temperature and High-pressure using Six-axis Multi-Anvil Press

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The research of the thermoelectric material, which can change the heat energy into the electric energy, has been actively studied as one of the methods to aim at the low carbon society. Especially, magnesium silicide ( $Mg_2Si$ ) is a promising thermoelectric semiconductor because the raw materials of it have a large deposit and a harmless to the human body. We have performed the high-pressure synthesis by means of a piston cylinder method to synthesize to the high purity  $Mg_2Si$  with the stoichiometric composition of Mg:Si=2:1, because the high-pressure technique can control not only the evaporation of Mg but also the reaction temperature of  $Mg_2Si$  [1]. In the thermoelectric measurement of the compound, the thermoelectric performance never improved dramatically. However, Morozova et al. reported that the Power factor of Al-doped  $Mg_2Si$  at 2 GPa increased by 10 times of the ambient pressure [2]. In order to understand the behavior under high-pressure, it is necessary to develop the measurement technique of the Seebeck coefficient and the electric resistance under high-pressure and high-temperature.

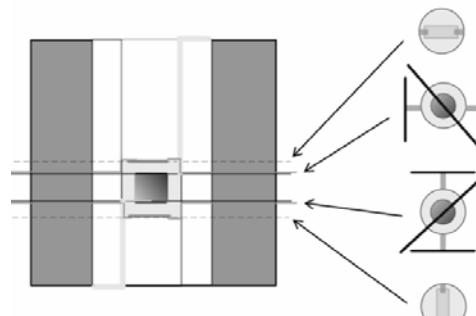
In this paper, we developed the thermoelectric measurement system at high-temperature and high-pressure using six-axis multi-anvil press.

The pressure was generated by the six-axis multi-anvil press, which was installed in the Institute for Planetary Materials, Okayama University. High-pressure cell consists of a pyrophyllite body as a pressure medium, zirconia tube as heat insulator, two graphite disks as heaters, 4-leads for the measurements and powder supply, two thermocouples to measure the both side temperature of sample, as shown Fig. 1. The sample was placed in the offset-position, and the size was 2.25 mm in height and 3.0 mm in diameter. The temperature was controlled, individually to generate the temperature gradient in the sample. The pressure experiment was carried out from 1.0 GPa to 2.5 GPa. The temperature condition was from 573 K to 773 K with 50 K intervals and the temperature difference for the temperature gradient was from minus 20 K to plus 20 K.

The results of Seebeck coefficient were reproducibility obtained by the several cycle measurements within the difference of  $20 \mu V/K$ . The Seebeck coefficient increased because the carrier increased with increasing temperature. The value of Seebeck coefficient under pressure became smaller than that at ambient pressure, and the temperature, which the value of Seebeck coefficient was maximum, shifted to higher temperature. It is considered that the mobility of carrier decreased under pressure. The pressure dependence of the Seebeck coefficient increased with increasing pressure, because the band-gap of the semiconductor narrowed under pressure.

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**Fig.1** Schematic image of high-pressure cell for the measurement.

## Pressure-driven topological phase transitions in HgTe/(Cd,Hg)Te quantum wells

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Recently a new class of matter, topological insulators (TI), was predicted and experimentally observed in HgTe/(Cd,Hg)Te quantum wells (QWs) with inverted band structures [1,2]. In these systems bulk states coexist with gapless surface/edge states protected by time reversal symmetry.

By changing the QW width, HgTe/(Cd,Hg)Te system can be tuned from the trivial band insulator (BI) phase into the topological insulator phase [1]. As shown in Ref. 3, such a phase transition can also be driven by using a hydrostatic pressure or temperature (see Figure 1).

In this work, we report on experimental and theoretical investigations of pressure-driven phase transitions in HgTe/(Cd,Hg)Te quantum wells forming two-dimensional topological insulator (2DTI). We observe that nonlocal resistance (a fingerprint of charge transport via edge states) survives up to a certain critical magnetic field  $B_c$ . With increasing hydrostatic pressure,  $B_c$  decreases and eventually vanishes at some critical pressure  $P_c$ . Our results are interpreted in terms of the pressure-induced transition from 2DTI phase to normal band insulator phase. The determined pressure dependence of  $B_c$  shows good agreement with results of theoretical pressure dependent band structure computations within the eight-band  $\mathbf{k} \cdot \mathbf{p}$  model [3].

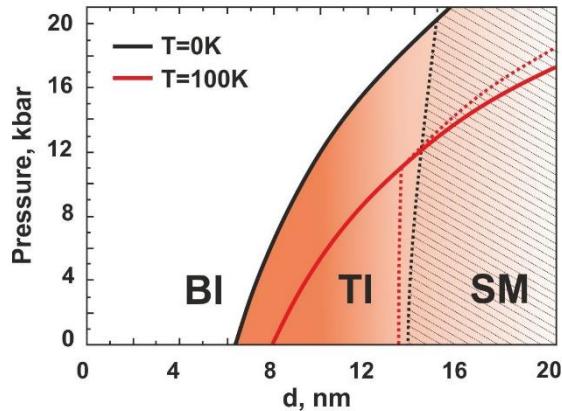


Figure 1: Pressure phase diagram for (001) HgTe/Cd<sub>0.7</sub>Hg<sub>0.3</sub>Te QWs, grown on a CdTe buffer [3,4]

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## The pressure evolution of the basal electrical resistivity of cold pressed single crystal graphite

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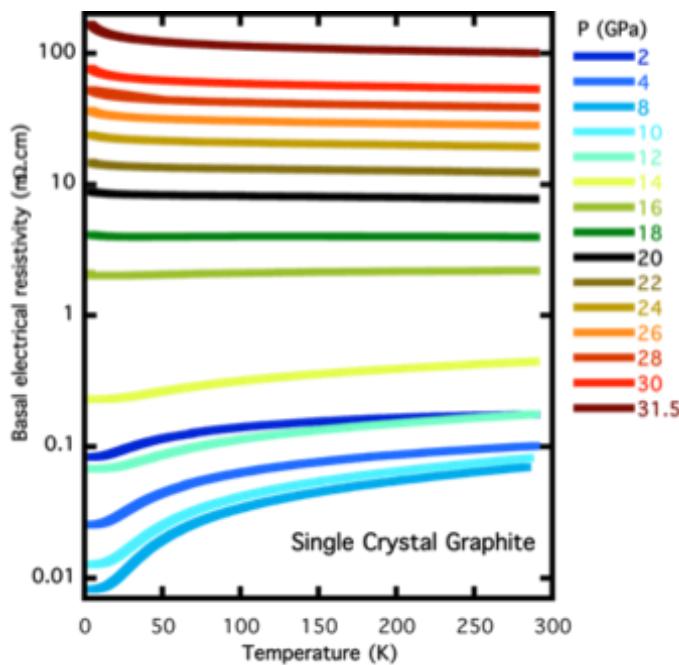
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We perform an extensive study of the basal electrical resistivity of single crystalline natural graphite as a function of temperature between 4 and 300K and as a function of pressure, applied at ambient temperature, up to 30GPa. We observe the transition to the cold compressed graphite phase. We describe the evolution of the low temperature scattering in the metallic state at low pressures, comparing it to DFT calculations. We follow the evolution of the resistivity of the sample at high pressures as it is transiting towards the high reassure structure and conclude that it is due to tunneling between graphitic regions separated by insulating sp<sup>3</sup> regions.



**Figure1** Electrical resistivity of a natural graphite single crystal as a function of temperature for different pressures. As a function of pressure we observe first an increase of metallicity and then a gradual increase of the resistivity with a passage to an activated behavior..

## Grüneisen Parameter in Quantum Critical Yb-Based Quasicrystal

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Unconventional quantum criticality discovered in heavy-electron quasicrystal (QC)  $\text{Yb}_{15}\text{Al}_{34}\text{Au}_{51}$  has attracted great interest [1]. The criticality is common to those observed in periodic crystals  $\beta\text{-YbAlB}_4$  [2] and  $\alpha\text{-YbAl}_{1-x}\text{Fe}_x\text{B}_4$  ( $x=0.014$ ) [3], which is well explained by the theory of critical Yb-valence fluctuations (CVF) [4]. The QC  $\text{Yb}_{15}\text{Al}_{34}\text{Au}_{51}$  exhibits the robust criticality under pressure and a new type of scaling called  $T/B$  scaling, which are also explained by the theory of the CVF [5,6].

Recently, *not* diverging Grüneisen parameter  $\Gamma$  toward the lowest temperature  $T=70$  mK has been observed in the QC  $\text{Yb}_{15}\text{Al}_{34}\text{Au}_{51}$ [7]. Surprisingly, its absolute value  $|\Gamma|$  at  $T=70$  mK is smaller than that in the 1/1 approximant crystal (AC)  $\text{Yb}_{14}\text{Al}_{35}\text{Au}_{51}$ , which shows the Fermi-liquid behavior. This poses a serious challenge to the conventional understanding that  $|\Gamma|$  diverges at *any* quantum critical point (QCP) [8].

To clarify the mechanism, first we construct the complete framework for calculating the specific heat  $C$ , the thermal-expansion coefficient  $\alpha$ , and the Grüneisen parameter  $\Gamma$  near the magnetic QCP on the basis of the theory of spin fluctuations [9]. Then, we apply this formalism to the case of the CVF near the QCP of the valence transition. We show that the measured behaviors of  $C$ ,  $\alpha$ , and  $\Gamma$  in the QC  $\text{Yb}_{15}\text{Al}_{34}\text{Au}_{51}$  are naturally explained, which are consistent with the robust criticality under pressure [10]. The difference in  $\Gamma$  at the lowest temperature between the QC and AC is shown to reflect the difference in the pressure derivative of characteristic energy scales between the CVF and the Kondo temperature.

In the presentation, we discuss these newly clarified aspects of the quantum critical phenomena in strongly-correlated electron systems. If time permits, we also discuss the recently-measured lattice-constant dependence of the Yb valence in the QC  $\text{Yb}_{15}(\text{Al}, \text{Ga})_{34}(\text{Au}, \text{Cu})_{51}$  [11], which reveals that  $\text{Yb}_{15}\text{Al}_{34}\text{Au}_{51}$  is located at just the point where the Yb valence starts to change sharply as a function of the lattice constant [12].

This presentation is based on the work done in collaboration with K. Miyake.

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## Pressure-induced novel superconductivity and quantum critical phenomena in nonmagnetic systems

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Understanding the mechanism of superconductivity and a strange metallic behaviour near a quantum critical point (QCP) is a focus of intense research efforts in condensed matter physics. In particular, the unconventional criticality, which cannot be explained by the spin fluctuation theory, has been experimentally reported and evokes the involvement of other fluctuations associated with such as charge and orbital instability. However, the complex coupling to magnetic degrees of freedom prevents the investigation of the role of other degrees of freedoms. In this talk, we present our recent high-pressure studies on nonmagnetic quadrupolar system PrTi<sub>2</sub>Al<sub>20</sub> [1] and possible excitonic insulator Ta<sub>2</sub>NiSe<sub>5</sub> [2], providing new insights into the unconventional quantum critical behavior and the emergence of superconductivity possibly associated with such as an orbital and excitonic instability [3,4]. These works have been done in collaboration with A. Sakai, S. Nakatsuji, N. Katayama, A. Nakano, H. Sawa, T. Kaneko, T. Toriyama, T. Konishi, Y. Ohta, Y. Ikemoto, T. Moriwaki, H. Okamura, T. Mizokawa, M. Nohara, K. Kitagawa, H. Takagi and Y. Uwatoko.

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## Relationship between superconductivity and magnetism on $\text{FeSe}_{1-x}\text{S}_x$ ( $x = 0.12$ ) studied by $^{77}\text{Se}$ -NMR under pressure

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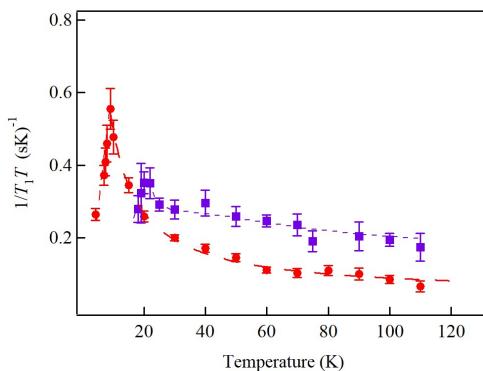
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Recently, the relationship among superconductivity, nematicity, and magnetism has been paid much attention in iron-based systems. S-doped FeSe offers an attractive stage in investigating the relationship. FeSe has a unique  $T$ - $P$  phase diagram: following a nematic phase at high temperatures, a superconducting (SC) phase manifests below 9 K without magnetism. The nematic phase disappears under pressures above 2 GPa, and instead an antiferromagnetic (AF) phase manifests [1]. In S-doped FeSe, the nematic phase and the AF phases are separated by the SC phase in the  $T$ - $P$  phase diagram [2], which allows one to investigate the effect of nematicity and magnetism on superconductivity separately.

We investigated the relationship between magnetic fluctuations and superconductivity via  $^{77}\text{Se}$  NMR for 12%-S doped FeSe, where  $T_c$  reaches 26 K at 3.0 GPa. Figure shows the relaxation rate divided by temperature ( $1/T_1T$ ). At 0.1 MPa, clear Curie-Weiss behavior was observed in  $1/T_1T$ , and the peak corresponds to  $T_c$ . In general, magnetic fluctuations are enhanced near the AF phase boundary, and thus the Curie-Weiss behavior would be enhanced at 3.0 GPa. However, the Curie-Weiss behavior is hardly enhanced despite that  $T_c$  is enhanced at 3.0 GPa. A possibility to understand this anomalous result is that the SC state would be different between low and high pressure regimes. To confirm this assumption, the measurements at intermediate pressures between 0.1 MPa and 3.0 GPa are needed. In the conference, we will show the data measured at 1.0 and 2.0 GPa, and discuss the relationship between superconductivity and magnetism.



**Figure** Relaxation rate divided by temperature ( $1/T_1T$ ) measured at  $^{77}\text{Se}$  sites under a magnetic field of 60 kOe. The peaks at 9 K and 22 K correspond to  $T_c$  at ambient and 3.0 GPa, respectively.

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# Quantum Critical behavior of $\text{LaFeAsO}_{1-x}\text{H}_x$ under pressure

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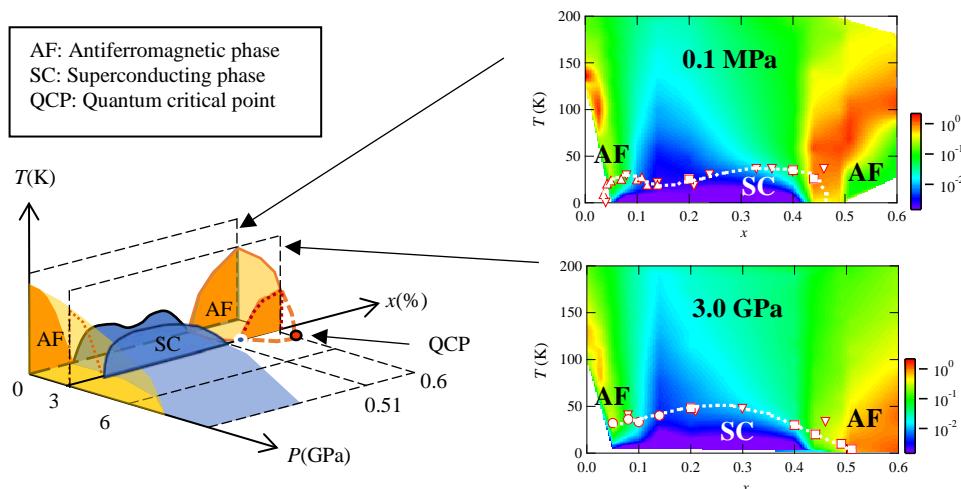
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Hydrogen-doped LaFeAsO is a prototypical iron-based superconductor. However, its phase diagram is quite unique unlike the conventional one: the SC phase is sandwiched between two antiferromagnetic (AF) phases appearing in lightly ( $x \leq 0.05$ ) and heavily ( $x \geq 0.49$ ) H-doped regimes [1, 2]. Figure 1 shows a schematic phase diagram and color plots of magnetic fluctuations determined from the relaxation rate of  $^{75}\text{As}$  divided by temperature ( $1/T_1T$ ). The AF phase ( $x \geq 0.49$ ) is strongly suppressed by applying a pressure of 3.0 GPa. A pressure-induced phase transition from the AF to SC phases occurs at  $x \sim 0.5$ . A "bare" AF quantum critical point (QCP) manifests at  $x \sim 0.55$  [3] and is located away from the optimal doping level ( $x \sim 0.2$ ) [4]. For  $x = 0.6$ ,  $1/T_1T$  exhibits a peak at  $T_N$  followed by Curie-Weiss behavior with decreasing temperature. The result suggests that the gapped excitation originating from the AF state and the gapless excitation characteristic to the QCP coexist. We applied further pressure for  $x = 0.6$  to investigate whether a pressure-induced AF QCP manifests. We found that the peak of  $1/T_1T$  remains up to 3.7 GPa, and it completely disappears at 4.0 GPa, implying that the pressure-induced QCP is located at around 4.0 GPa.

At the conference, we will compare two QCPs appearing by H doping and pressure application in relationship with the superconductivity.



**Figure 1.** Schematic phase diagram of  $\text{LaFeAsO}_{1-x}\text{H}_x$  and color plots of spin fluctuations measured from  $1/T_1T$  at  $^{75}\text{As}$ . Squares show the superconducting transition temperatures ( $T_c$ ) determined from the NMR measurements, and triangles and circles are  $T_c$ s determined from the resistivity measurements.

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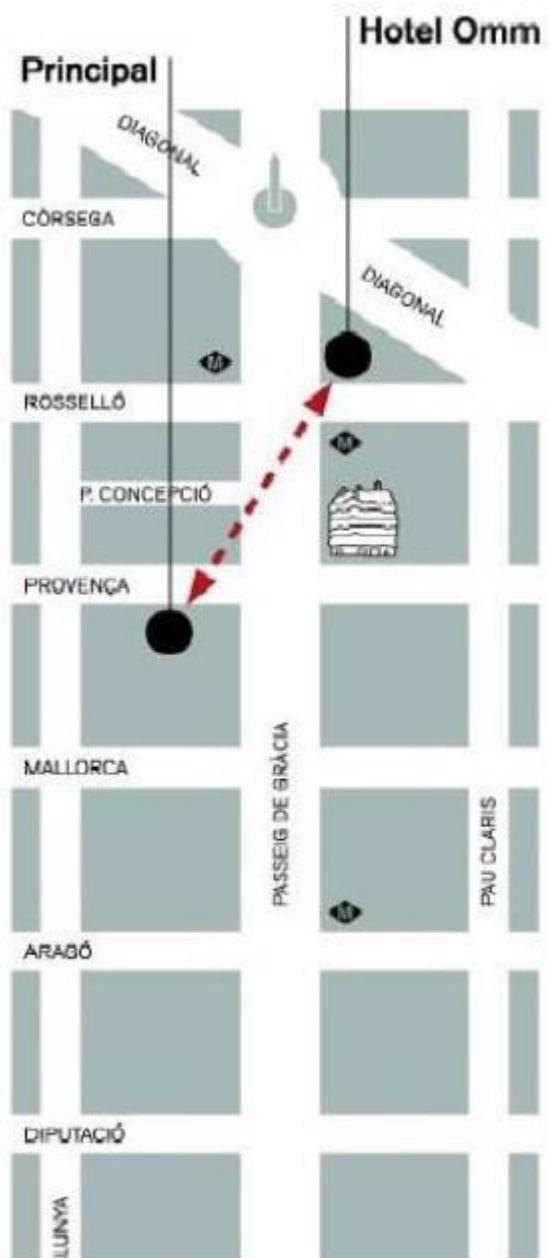
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## **Further information**

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