21st USPEX workshop: 17-21 November 2022, Isfahan.

https://qsm.iut.ac.ir/workshop-iut-uspex

The workshop is supported by Skoltech (Moscow) and ICTP (Trieste)



Quantum Simulations of Materia Isfahan University of Technolog

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Modern trends in Computational Materials Discovery

17 - 21 November 2022



Invited Speakers

Registration Program







The workshop is supported by Russian Science Foundation grant No. 19072-30043 "Computational materials discovery laboratory"

The USPEX (Universal Structure Prediction: Evolutionary Xtallography) project



•The most popular code for computational materials design in the world (>8500 users from 83 countries).

- •Effort of >100 man-years.
- >1000 publications, 5 patents.
- •Universal:

-prediction of stable structure AND composition, 3D, 2D, 1D, 0D – systems. -optimization of physical properties,

-prediction of phase transition mechanisms

Basic Facts on USPEX

- The most popular structure prediction code in the world (>7000 users).
- The largest and the most versatile code in this field. Many capabilities are unique.
- The fastest and the most reliable structure prediction code today.
- THE CODE IS FREE, but you have to agree to certain conditions of fair use (register now!).
- Every year ~2 USPEX workshops.
- USPEX mailing list (join it!). USPEX Forum (use it!).
- USPEX Facebook page (join it!).
- USPEX QQ group (group number 326701679 join it!)
- ~10 visiting scholars every year in the Oganov laboratory.
- Support for citizen science: <u>http://uspex-at-home.ru</u>

Features of the USPEX code:

Algorithm:

- Evolutionary optimization (USPEX algrorithm). Options to use random sampling, minima-hopping-like, particle-swarm optimization, metadynamics.
- Initialization using fully random, symmetric random structures, topological random, or user-fed structures.
- Fingerprint niching technique, local order parameter (ARO&Valle, 2009).

Types of runs:

- Global optimization of either the energy or properties (density, hardness, band gap, etc.)
- Pareto optimization of several properties simultaneously.
- Fixed-cell or variable-cell, fixed-composition or variable-composition runs are possible.
- For molecular crystals, can operate with ready-made molecules.
- Low-dimensional systems.
- Harvesting metastable states is possible.
- Phase transition pathways.

Software aspects:

- Interfaced with VASP, SIESTA, CP2k, QuantumEspresso, DMACRYS, GULP, ATK,...
- Excellent scaling on up to 10³⁻⁴ cores.

Analysis:

- Automatic detection of space groups.
- Benefits from powerful analysis and visualization code STM4. **Distribution:**
- USPEX code is freely available at: http://uspex-team.org
- Distributed with a ~100-page manual and ~30 examples.

Statistics

- >8500 users from 83 countries.
- 1607 USA
- >>662 China
- 206 Russia
- 202 India
- 101 Japan
- 96 France
- 97 U.K.
- 82 Germany
- 65 S. Korea
- 50 Italy

Funding of USPEX





ИСКОЙ ФЕДЕРАЦИ ФЕДЕРАЛЬНОЕ АГЕНТСТВО ПО НАУКЕ И ИННОВАЦИЯМ





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National Science Foundation WHERE DISCOVERIES BEGIN



NSFC National Natural Science Foundation of China

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祖國書業



The State University of New York

Industrial partners: Intel, Samsung, Toyota, Fujitsu, APC. ٠

People behind USPEX

Main contributors:

Artem R. Oganov Zahed Allahyari Pavel Bushlanov Andriy Lyakhov Colin Glass Sergey Lepeshkin Guangrui Qian Salah-Eddine Boulfelfel Vladan Stevanovic Artem Samtsevich Harold Stokes Evgeny Tikhonov Maxim Rakitin Vladislav Blatov Ivan Kruglov Xiao Dong

Computational Materials Discovery with the USPEX code





Skolkovo Institute of Science and Technology, Russia

Moscow Institute of Steel and Alloys, Moscow, Russia

Institute of Geochemistry and Analytical Chemistry, Moscow, Russia

Crystal structure determines physical properties. Crystal structure determination was a major breakthrough.



The Nobel Prize in Physics 1914

"for his discovery of the diffraction of X-rays by crystals"



Max von Laue



"for their services in the analysis of crystal structure by means of Xravs"



Sir William Henry Bragg

(from http://nobelprize.org)





"for their outstanding achievements in the development of direct methods for the determination of crystal structures"



Herbert A. Hauptman



Jerome Karle







William Lawrence Bragg

Zincblende ZnS.

One of the first solved structures (1912-1913)



X-ray diffraction: window into the structure of matter



Determination of the structure of DNA (Watson, Crick, 1953)

Some of Nobel prizes based on X-ray diffraction

Nobel Prizes for X-ray Crystallography [edit]

Year [hide] \$	Laureate +	Prize ¢	Rationale +
1914	Max von Laue	Physics	"For his discovery of the diffraction of X-rays by crystals", ^[118] an important step in the development of X-ray spectroscopy.
1915	William Henry Bragg	Physics	"For their services in the analysis of crystal structure by means of X-rays", ^[119]
1915	William Lawrence Bragg	Physics	"For their services in the analysis of crystal structure by means of X-rays" [110]
1962	Max F. Perutz	Chemistry	"for their studies of the structures of globular proteins"
1962	John C. Kendrew	Chemistry	"for their studies of the structures of globular proteins" ^[120]
1962	James Dewey Watson	Medicine	"For their discoveries concerning the molecular structure of nucleic acids and its significance for information transfer in living material ⁽¹²¹⁾
1962	Francis Harry Compton Crick	Medicine	"For their discoveries concerning the molecular structure of nucleic acids and its significance for information transfer in living material ⁽¹²¹⁾
1962	Maurice Hugh Frederick Wilkins	Medicine	"For their discoveries concerning the molecular structure of nucleic acids and its significance for information transfer in living materian ⁽¹²¹⁾
1964	Dorothy Hodgkin	Chemistry	"For her determinations by X-ray techniques of the structures of important biochemical substances"[122]
1972	Stanford Moore	Chemistry	"For their contribution to the understanding of the connection between chemical structure and catalytic activity of the active centre of the ribonuclease molecule" (123)
1972	William H. Stein	Chemistry	"For their contribution to the understanding of the connection between chemical structure and catalytic activity of the active centre of the ribonuclease molecule"[12]
1976	William N. Lipscomb	Chemistry	"For his studies on the structure of boranes illuminating problems of chemical bonding" ⁽¹²⁴⁾
1985	Jerome Karle	Chemistry	"For their outstanding achievements in developing direct methods for the determination of crystal structures" ⁽¹²⁸⁾
1985	Herbert A. Hauptman	Chemistry	"For their outstanding achievements in developing direct methods for the determination of crystal structures ⁽¹²⁸⁾
1988	Johann Deisenhofer	Chemistry	"For their determination of the three-dimensional structure of a photosynthetic reaction centre ^{d[120]}
1988	Hartmut Michel	Chemistry	"For their determination of the three-dimensional structure of a photosynthetic reaction centrev ⁽¹²⁶⁾
1988	Robert Huber	Chemistry	"For their determination of the three-dimensional structure of a photosynthetic reaction centrev ⁽¹²⁶⁾
1997	John E. Walker	Chemistry	"For their elucidation of the enzymatic mechanism underlying the synthesis of adenosine triphosphate (ATP) ^{el127}
2003	Roderick MacKinnon	Chemistry	"For discoveries concerning channels in cell membranes [] for structural and mechanistic studies of ion channels" ^[128]
2003	Peter Agre	Chemistry	"For discoveries concerning channels in cell membranes [] for the discovery of water channels ^{4128]}
2006	Roger D. Kornberg	Chemistry	"For his studies of the molecular basis of eukaryotic transcription ⁴⁽²⁹⁾
2009	Ada E. Yonath	Chemistry	"For studies of the structure and function of the ribosome" ⁽¹³⁰⁾
2009	Thomas A. Steitz	Chemistry	"For studies of the structure and function of the ribosome" ⁽¹³⁰⁾
2009	Venkatraman Ramakrishnan	Chemistry	"For studies of the structure and function of the ribosome" ⁽¹³⁰⁾
2012	Brian Kobilka	Chemistry	"For studies of G-protein-coupled receptors" ^[131]

Briefly About Crystal Structure Prediction

Faraday Discussions

Cite this: Faraday Discuss., 2018, 211, 643



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PAPER

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Crystal structure prediction: reflections on present status and challenges

Artem R. Oganov Dabc Received 30th August 2018, Accepted 30th August 2018

Faraday Discussions (2018)

	REVIEWS
tructure predictio liscovery	n drives materials
tem R. Oganovo 133*, Chris J. Pickardo	55*, Qiang Zhu ⁴ and Richard J. Needs?
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Nature Reviews Materials (2019)





Acc. Chem. Res. 1994, 27, 309-314

Are Crystal Structures Predictable?

Angelo Gavezzotti*



"No": by just writing down this concise statement, in what would be the first one-word paper in the chemical literature, one could safely summarize the present state of affairs





USPEX (Universal Structure Predictor: Evolutionary Xtallography)

- Combination of evolutionary algorithm and quantummechanical calculations.
- >8500 users.
- Solves "formidable" problem of crystal structure prediction.



Energy landscape of Au₈Pd₄



uspex-team.org

Contraction of the second seco

RESEARCH NEWS Crystal structure prediction – evolutionary or revolutionary crystallography?

S. L. Chaplot and K. R. Rao

plot and K. R. Rao CURRENT SCIENCE, VOL. 91, NO. 11, 10 DECEMBER 2006

- Early article about our work

Samrath Lal Chaplot

Quantum-mechanical calculations (using density functional theory

 $\left(-\frac{\nabla_{2}}{2}+v_{e-n}[\rho(\mathbf{r})]+v_{H}[\rho(\mathbf{r})]+v_{xc}[\rho(\mathbf{r})]\right)\phi_{i}(\mathbf{r})=\varepsilon_{i}\phi_{i}(\mathbf{r})$



W. Kohn Nobel Prize in Chemistry 1998



E. Schroedinger Nobel Prize in Physics 1933

Global optimisation methods: Kangaroo's climb to Mt. Everest



Evolutionary Algorithms are like taking a whole plane load of kangaroo's and letting them reproduce freely (not pictured).....

Global optimisation methods: Kangaroo's climb to Mt. Everest













Without any empirical information, method reliably predicts materials



Carbon at 100 GPa – diamond structure is stable

USPEX (Universal Structure Predictor: Evolutionary Xtallography)

- (Random) initial population
- Evaluate structures by relaxed (free) energy
- Select lowest-energy structures as parents for new generation
- Standard variation operators:











(3) Permutation

+(4) Transmutation, +(5) Rotational mutation, +(6) Soft-mode mutation, +...

Why does USPEX work so well? A few tips and tricks



I. Reduction of dimensionality through unbiased symmetric initialization.

formal dimensionality of full energy landscape: d = 3N + 3intrinsic dimensionality of reduced landscape: $d^* = 3N + 3 - \kappa$ number of distinct structures: $C^* \sim \exp(\beta d^*)$ $d^* = 10.9 (d = 39)$ for Au₈Pd₄ $d^* = 11.6 (d = 99)$ for Mg₁₆O₁₆ $d^* = 32.5 (d = 39)$ for Mg₄N₄H₄



II. Reduction of effective dimensionality of problem by structure relaxation (also

reduces "noise" and transforms energy landscape to a convenient shape).

III. Variation operators are defined in subspaces of reduced dimensionality and involve cooperative transformations.

Symmetric initialization

Crystals: 230 space groups Nanoparticles: point groups



Enables moderately efficient random sampling as one of possible USPEX regimes

Zhu, Oganov, et al, Acta. Cryst. B, 68, 215-226 (2012)

New methodological development: topological structure generator (Bushlanov, Blatov, Oganov, 2019)



Example of KN_3 : (a) topological structure, (c) random symmetric structure, (c) energy distribution of topological (TR) and random symmetric structures

Statistics (100 runs) of USPEX performance on MgAl₂O₄ (28 atoms/cell) at 100 GPa

	Original	On-the-fly adaptation	On-the-fly adaptation AND topology
<no. of="" structures=""></no.>	1307	1069	368
Success rate	100%	100%	100%

Predicting new crystal structures without empirical information



New superhard structure of boron (Oganov et al., *Nature*, 2009)



High-pressure transparent allotrope of sodium (Ma, Eremets, Oganov, *Nature*, 2009)



α-boron $E^{DFT} = -6.706 \text{ eV/atom}$ Atoms: 12, Space group: R-3m, Core-hours: 10³ AL-MTP vs. $3 \cdot 10^3 \text{ DFT}$ $|E^{DFT} - E^{MTP}| = 28.6 \text{ meV/atom}$



β-boron approximant $E^{\text{DFT}} = -6.704 \text{ eV/atom},$ Atoms: 106, Space group: *P*1, Core-hours: 7·10³ AL-MTP vs. 6.6·10⁷ DFT $|E^{\text{DFT}} - E^{\text{MTP}}| = 10.1 \text{ meV/atom}$









γ-boron $E^{\text{DFT}} = -6.678 \text{ eV/atom}$ Atoms: 28, Space group: <u>Pnnm</u>, Core-hours: 2·10³ AL-MTP vs. 2.5·10⁴ DFT $|E^{\text{DFT}} - E^{\text{MTP}}| = 58.1 \text{ meV/atom}$

E^{DFT} = –6.667 eV/atom, Atoms: 54, Space group: *Im*-3, Core-hours: 3·10³ AL-MTP vs. 3.5·10⁵ DFT |E^{DFT} – E^{MTP}| = 7.3 meV/atom

$$\begin{split} E^{\text{DFT}} &= -6.667 \text{ eV/atom}, \\ \text{Atoms: 52,} \\ \text{Space group: } P\text{-}42m, \\ \text{Core-hours: } 3\text{-}10^3 \text{ AL-MTP vs. } 3.2 \text{\cdot}10^5 \text{ DFT} \\ |E^{\text{DFT}} - E^{\text{MTP}}| &= 37.3 \text{ meV/atom} \end{split}$$

$$\begin{split} E^{\text{DFT}} &= -6.665 \text{ eV/atom}, \\ \text{Atoms: 26,} \\ \text{Space group: } \underline{Cccm}, \\ \text{Core-hours: } 2\cdot 10^3 \text{ AL-MTP vs. } 2.1\cdot 10^4 \text{ DFT} \\ |E^{\text{DFT}} - E^{\text{MTP}}| &= 13.6 \text{ meV/atom} \end{split}$$

Handling complexity with machine learning: boron allotropes

(E.Podryabinkin, E. Tikhonov, A. Shapeev, A.R. Oganov, PRB, 2019)

- ML potential with active learning (Shapeev, 2018). 800 parameters.
- MAE = 11 meV/atom.
- Reproduced α -, β -, γ -, T52 phases of boron.
- Predicted low-energy metastable cubic cl54 phase.
- Speedup by >100 times.

Cases of record complexity: -Li₁₅Si₄ with 152 atoms/cell -disordered β-boron with 106 atoms/cell

Li-Si



Structural transformation of Li₁₅Si₄ at 7 GPa. New phase has more attractive properties for use in Li-batteries. [Zeng & Oganov, *Adv. Energy Mat.*, 2015]



Crystal structure of β-boron at ambient conditions. [Podryabinkin, Shapeev & Oganov, *Phys. Rev. B*, 2019]

USPEX can handle molecular crystals: solved γ-resorcinol



Prediction of new polymers for flexible capacitors

(Zhu, Sharma, Oganov: J.Chem.Phys. 2014, Nature Commun. 2014)



Protein structure can also be predicted by USPEX [Rachitsky, Kruglov, Finkelstein, Oganov, submitted]



* Number of amino acid residues

Comparing USPEX predictions with experimental protein structures [Rachitsky, Kruglov, Finkelstein, Oganov, submitted]



Structure prediction at finite temperatures [Kruglov & Oganov, submitted]



Within structure search need to:

Take a reference potential – e.g., MLIP.
Relax structures with *NPT*-MD.
Compute free energy with the reference potential:

$$G = PV + F = PV + F_0 + \int_0^1 (U(\lambda) - U_0) d\lambda$$

4/ Compute *ab initio* free energy using thermodynamic perturbation theory: $F_{AL} \simeq F + \langle U_{AL} - U \rangle - \frac{1}{2} \langle [U_{AL} - U]^2 \rangle$

$$_{AI} \simeq F + \langle U_{AI} - U \rangle - \frac{1}{2k_b T} \langle [U_{AI} - U]^2 \rangle$$

Figure S4. P-T phase diagram of Al. Black solid lines correspond to phase transition boundarie calculated in this work with T-USPEX. Black stars, triangles and circles – experimental dat from Ref. Blue line is from Ref. ³⁷, orange dotted line – from Ref. ³⁹. Letters "f", "h" and "b correspond to the most stable phases (from T-USPEX) at given P-T conditions. Black diamond show calculated transition points between different phases.

Prediction of stable structure for a given chemical composition is possible.

Now, let's predict the chemical composition!

To predict thermodynamic stability, we must use the Maxwell construction (the convex hull)

Thermodynamic stability in variable-composition systems



Stable structure must be below all the possible decomposition lines !!
Predictive power of modern methods:



Na₃Cl, Na₂Cl, Na₃Cl₂, NaCl, NaCl₃, NaCl₇ are stable under pressure [Zhang, Oganov, et al. *Science*, 2013].



Chemical anomalies:

- -Divalent CI in Na₂CI!
- -Coexistence of metallic and ionic blocks in Na₃Cl!
- -Positively charged Cl in NaCl₇!



NaCl₃: atomic and electronic structure, and experimental XRD pattern

[Zhang, Oganov, et al., *Science* (2013)] [Saleh & Oganov, *PCCP* (2015)]

Highest-Tc superconductivity: new record, 203 K (Duan et al., Sci. Rep. 4, 6968 (2014))

H-S



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Pressure-induced metallization of dense $(H_2S)_2H_2$ with high- T_c superconductivity

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SUBJECT AREAS: THEORY AND COMPUTATION CONDENSED-MATTER PHYSICS

OPEN

Defang Duan^{1,2}, Yunxian Liu¹, Fubo Tian¹, Da Li¹, Xiaoli Huang¹, Zhonglong Zhao¹, Hongyu Yu¹, Bingbing Liu¹, Wenjing Tian² & Tian Cui¹

Received 7 July 2014 Accepted 29 September 2014 Published 10 November 2014 Correspondence and requests for materials

should be addressed to

T.C. (cuitian@jlu.edu.

¹State Key Laboratory of Superhard Materials, College of physics, Jilin University, Changchun, 130012, P. R. China, ²State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun, 130012, P. R. China.

The high pressure structures, metallization, and superconductivity of recently synthesized H2-containing compounds (H2S)2H2 are elucidated by ab initio calculations. The ordered crystal structure with P1 symmetry is determined, supported by the good agreement between theoretical and experimental X-ray diffraction data, equation of states, and Raman spectra. The Cccm structure is favorable with partial hydrogen bond symmetrization above 37 GPa. Upon further compression, H2 molecules disappear and two intriguing metallic structures with R3m and Im-3m symmetries are reconstructive above 111 and 180 GPa, respectively. The predicted metallization pressure is 111 GPa, which is approximately one-third of the currently suggested metallization pressure of bulk molecular hydrogen. Application of the Allen-Dynes-modified McMillan equation for the Im-3 m structure yields high T, values of 191 K to 204 K at 200 GPa, which is among the highest values reported for H2-rich van der Waals compounds and MH3 type hydride thus far.

SCIENTIFIC REPORTS | 4:6968 | DOI: 10.1038/srep06968

Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system

A. P. Drozdov, M. I. Eremets, I. A. Troyan, V. Ksenofontov & S. I. Shylin

Nature (2015) | doi:10.1038/nature14964 Received 25 June 2015 | Accepted 22 July 2015 | Published online 17 August 2015

A superconductor is a material that can conduct electricity without resistance below a superconducting transition temperature, T_c . The highest T_c that has been achieved to date is in the copper oxide system¹: 133 kelvin at ambient pressure² and 164 kelvin at high pressures³. As the nature of superconductivity in these materials is still not fully understood (they are not conventional superconductors), the prospects for achieving still higher transition temperatures by this route are not clear. In contrast, the Bardeen-Cooper-Schrieffer theory of conventional superconductivity gives a guide for achieving high T_c with no theoretical upper bound—all that is needed is a favourable combination of high-frequency phonons, strong electron-phonon coupling, and a high density of states⁴. These conditions can in principle be fulfilled for metallic hydrogen and covalent compounds dominated by hydrogen^{5, 6}, as hydrogen atoms provide the necessary highfrequency phonon modes as well as the strong electron-phonon coupling. Numerous calculations support this idea and have predicted transition temperatures in the range 50-235 kelvin for many hydrides⁷, but only a moderate T_c of 17 kelvin has been observed experimentally⁸. Here we investigate sulfur hydride9, where a T c of 80 kelvin has been predicted 10. We find that this system transforms to a metal at a pressure of approximately 90 gigapascals. On cooling, we see signatures of superconductivity: a sharp drop of the resistivity to zero and a decrease of the transition temperature with magnetic field, with magnetic susceptibility measurements confirming a T_c of 203 kelvin. Moreover, a pronounced isotope shift of T_c in sulfur deuteride is suggestive of an electron– phonon mechanism of superconductivity that is consistent with the Bardeen-Cooper-Schrieffer scenario. We argue that the phase responsible for high- T_c superconductivity in this system is likely to be H₃S, formed from H₂S by decomposition under pressure. These findings raise hope for the prospects for achieving room-temperature superconductivity in other hydrogen-based materials.

Old record Tc=135 K (Schilling, 1993) is broken: theorists (T. Cui, 2014) predicted new compound H_3S with Tc~200 K.

1

Confirmed by A. Drozdov et al. (Nature 525, 73 (2015)).

Superconductivity is linked with Mendeleev's Table

[Semenok & Oganov, JPCL, 2018; Curr. Opinion Solid St. Mater. Sci., 2020]



Distribution of Tc for hydrides







 $C_{a}H_{6}$ ($T_{c} = 220-235 \text{ K}$)

LaH₁₀ ($T_c = 274 - 286 \text{ K}$) AcH₁₀ ($T_c = 226 - 251 \text{ K}$) YH₁₀ ($T_c = 305 - 326 \text{ K}$) ThH₁₀ ($T_c = 220 - 241 \text{ K}$)

 AcH_{16} ($T_c = 221 - 241 K$)

Thorium decahydride ThH₁₀ ($T_C = 159-161$ K) [Semenok, Troyan, Oganov, Materials Today 2020]

Predicted by us in 2018, synthesized by us in 2019 at 174 GPa!

Theory at 174 GPa gives Tc=167-183 K. Experiment: Tc = 161 K.



Yttrium hydride YH₆ ($T_C = 224$ K, $B_C = 116-158$ T) [Semenok, Troyan, Oganov, *Advanced Materials*, 2021]



Current record: LaH_{10} (Tc = 250 K at 170 GPa)



At higher chemical complexity, we may get higher Tc

Element	$T_{ m c}({ m K})$	Element	$T_{\rm c}({ m K})$	Element	$T_{\rm c}({ m K})$
Al	1.19	Nb	9.2	Tc	7.8
Be	0.026	Np	0.075	\mathbf{Th}	1.37
Cd	0.55	Os	0.65	Ti	0.39
Ga	1.09	Pa	1.3	Tl	2.39
Hf	0.13	Pb	7.2	U	0.2
Hg	4.15	Re	1.7	V	5.3
In	3.40	Rh	0.0003	W	0.012
Ir	0.14	Ru	0.5	Zn	0.9
La	4.8	Sn	3.75	Zr	0.55
Mo	0.92	Ta	4.39		
Compound	$T_{ m c}$ (K)	Compound	$T_{\rm c}({ m K})$	Compound	$T_{\rm c}({ m K})$
Nb ₃ Sn	18.1	MgB_2	39	UPt ₃	0.5
Nb ₃ Ge	23.2	$PbMo_6S_8$	15	UPd_2Al_3	2
Cs_3C_{60}	19	YPd_2B_2C	23	(TMTSF) ₂ ClO ₄	1.2
Cs_3C_{60}	40	$\mathrm{HoNi_2B_2C}$	7.5	$(\mathrm{ET})_{2}\mathrm{Cu}[\mathrm{Ni}(\mathrm{CN})_{2}]\mathrm{Br}$	11.5
High- $T_{\rm c}$ superconductor		$T_{\rm c}({ m K})$	High- $T_{\rm c}$ superconductor		$T_{\rm c}({ m K})$
La1.83Sr0.17CuO4		38	$Tl_2Ba_2Ca_2Cu_3O_{10+x}$		125
YBa ₂ Cu ₃ C) _{6+x}	93	$HgBa2Ca_2Cu_30_{8+x}$		135
$Bi_2Sr_2Ca_2Cu_3O_{10+x}$ 107			$Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_30_{8.33}$		134

...and the record is broken again, reaching roomtemperature superconductivity in an unknown S-C-H compound (Tc = 288 K at 267 GPa)

Room-temperature superconductivity in a carbonaceous sulfur hydride

Elliot Snider, Nathan Dasenbrock-Gammon, Raymond McBride, Mathew Debessai, Hiranya Vindana, Kevin Vencatasamy, Keith V. Lawler, Ashkan Salamat & Ranga P. Dias 🖂

Nature 586, 373–377(2020) Cite this article

One of the long-standing challenges in experimental physics is the observation of roomtemperature superconductivity^{1,2}. Recently, high-temperature conventional superconductivity in hydrogen-rich materials has been reported in several systems under high pressure^{3,4,5}. An important discovery leading to room-temperature superconductivity is the pressure-driven disproportionation of hydrogen sulfide (H_2S) to H_3S , with a confirmed transition temperature of 203 kelvin at 155 gigapascals^{3,6}. Both H₂S and CH₄ readily mix with hydrogen to form guest-host structures at lower pressures⁷, and are of comparable size at 4 gigapascals. By introducing methane at low pressures into the $H_2S + H_2$ precursor mixture for H₃S, molecular exchange is allowed within a large assemblage of van der Waals solids that are hydrogen-rich with H₂ inclusions; these guest-host structures become the building blocks of superconducting compounds at extreme conditions. Here we report superconductivity in a photochemically transformed carbonaceous sulfur hydride system, starting from elemental precursors, with a maximum superconducting transition temperature of 287.7 ± 1.2 kelvin (about 15 degrees Celsius) achieved at 267 ± 10 gigapascals. The superconducting state is observed over a broad pressure range in the diamond anvil cell, from 140 to 275 gigapascals, with a sharp upturn in transition temperature above 220 gigapascals. Superconductivity is established by the observation of zero resistance, a magnetic susceptibility of up to 190 gigapascals, and reduction of the transition temperature under an external magnetic field of up to 9 tesla, with an upper critical magnetic field of about 62 tesla according to the Ginzburg-Landau model at zero temperature. The light, quantum nature of hydrogen limits the structural and stoichiometric determination of the system by X-ray scattering techniques, but Raman spectroscopy is used to probe the chemical and structural transformations before metallization. The introduction of chemical tuning within our ternary system could enable the preservation of the properties of room-temperature superconductivity at lower pressures.

...but that report was incorrect

Article Published: 14 October 2020

RETRACTED ARTICLE: Room-temperature superconductivity in a carbonaceous sulfur hydride

Elliot Snider, Nathan Dasenbrock-Gammon, Raymond McBride, Mathew Debessai, Hiranya Vindana, Kevin

Vencatasamy, Keith V. Lawler, Ashkan Salamat & Ranga P. Dias

<u>Nature</u> **586**, 373–377 (2020) <u>Cite this article</u>

105k Accesses | 363 Citations | 2937 Altmetric | Metrics

Inis article was <u>retracted</u> on 26 September 2022

15 February 2022 Editor's Note: The editors of Nature have been alerted to concerns regarding the manner in which the data in this paper have been processed and interpreted. Nature is working with the authors to investigate these concerns and establish what (if any) impact they will have on the paper's results and conclusions. In the meantime, readers are advised to use caution when using results reported therein.

30 August 2021 Editor's Note: The editors of Nature have been alerted to undeclared access
 restrictions relating to the data behind this paper. We are working with the authors to correct the data availability statement.

Matters Arising to this article was published on 25 August 2021

A <u>Publisher Correction</u> to this article was published on 20 November 2020

• This article has been <u>updated</u>

Predicting Stable Nanoclusters

Only conditional stability. Magic clusters. Similar to atomic nuclei.
Unusual stable compositions are typical.
Explanation of carcinogenicity of oxide dust?

Prediction of Stable Molecules is a Very Different Problem



Stability of molecules does not follow from straight comparison of energies





1. Energy falls almost monotonically with number of atoms.

2. Infinite crystal always wins by energy.

3. Correct comparison of energies – only with neighbor compositions.

4. $\Delta^2 E$ is a proper measure.

$\Delta^2 E > 0$ indicates the most abundant ("magic") molecules



Binding energy grows with the size of cluster. We define stability relative to neighboring compositions. Stability is due to filled shells (electronic, atomic).



Predicting stable Na-CI molecules

(NaCl)_n ridge of stability.

Numerous minor islands of stability.



(result of M. Fedyaeva and S.V. Lepeshkin)



Magic numbers of electrons = 2, 10, 18, 36, 54, 86, 118)



Unusual compositions of transition metal oxide clusters [Yu & Oganov, Phys. Chem. Chem. Phys., 2018]



Do crystals grow from such particles ("inorganic synthons")?

New tool: map of stability of molecules



(result of A. Mikhaylova).

(Sandu et al., PCCP, 2021)

Why is organic chemistry so diverse? (Lepeshkin & Oganov, *J. Phys. Chem. Lett.* 2022)



Figure 3. Structures of magic (poly)unsaturated HCs.

Benzene and its derivatives (#4)	(a)
C ₆ H ₆ C ₇ H ₈ C ₈ H ₁₀ C ₉ H ₁₂ C ₁₀ H ₁₄ C ₉ H	H ₁₀ C ₁₀ H ₁₂
体快快快扶扶	\$
Naphtalene and its derivatives (#5) $C_{10}H_8$ $C_{11}H_{10}$ $C_{12}H_{12}$ $C_{13}H_{14}$ $C_{14}H_{14}$	
Pyrene and its derivatives (#6) $C_{16}H_{10}$ $C_{17}H_{12}$ $C_{18}H_{14}$ $C_{19}H_{16}$ $C_{20}H_{16}$	
Other regular PAHs	
C ₈ H ₆ C ₁₂ H ₈ C ₁₄ H ₈ C ₁₄ H ₁₀ C ₁₈ H ₁₀ C ₂	₀ H ₁₀ C ₂₀ H ₁₂
A the the the the the	3 ###
Radicalic PAHs (#7)	(b)
C ₅ H ₅ C ₉ H ₇ C ₁₃ H ₉ C ₁₅ H ₉ C ₁₇ H ₉ C ₁₇ H	111 C ₁₉ H ₁₁
中安安安安安	à tất
Dehydrogenated PAHs (#8)	(c)
C ₁₅ H ₇ C ₁₆ H ₆ C ₁₆ H ₈ C ₁₇ H ₅ C ₁₈ H	I ₆ C ₁₈ H ₈
\$\$+\$\$\$+\$\$\$+\$\$\$+\$\$	à 444

Figure 4. Structures of magic (poly)aromatic HCs.



Figure 5. Structures of magic saturated HCs.

Which hydrocarbons are stable? (Lepeshkin & Oganov, *J. Phys. Chem. Lett.* 2022)

-Homologous series: alkanes etc. -Huge diversity, explaining the diversity of organic chemistry.



Predicting Optimal Materials

-Superior thermoelectrics: possible! -New superhard materials: WB₅ etc.

Pareto optimization of properties & stability.Mendelevian search for exploring chemical space.

Towards materials design: example of thermoelectrics



http://www.gizmag.com/ge-dual-piezo-cooling-jet/25447/

How to improve efficiency of thermoelectric devices?

"One shouldn't work on semiconductors, that is a filthy mess; who knows whether any semiconductors exist"

-W. Pauli, letter to R. Peierls (1931)



Multiobjective (Pareto) optimization finds a new thermoelectric polymorph of Bi₂Te₃

Computer Physics Communications 222 (2018) 152–157

Efficient technique for computational design of thermoelectric materials

Maribel Núñez-Valdez, Zahed Allahyari, Tao Fan, Artem R. Oganov



Pareto optimization of ZT and stability in the Bi-Te system

Similar conclusions from data mining



Fast and reliable calculations of thermoelectric properties are enabled by AICON program (Fan & Oganov, 2020, 2021).



Tao Fan ^A ⊠, Artem R. Oganov

Computer Physics Communications Volume 251, June 2020, 107074



Computer Physics Communications 266 (2021) 10802

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Computer Physics Communications

www.elsevier.com/locate/cpc

AICON: A program for calculating thermal conductivity quickly and accurately $\Rightarrow, \Rightarrow \Rightarrow$

AICON2: A program for calculating transport properties quickly and accurately $^{\diamond,\,\diamond\,\diamond}$

Tao Fan*, Artem R. Oganov



Predicted material with ZT~3.4. If confirmed, will be transformative.

Coevolution: sampling very large search spaces





Coevolution to enhance sampling of the chemical space: COPEX method (Liu, Niu, Oganov, 2021)



USPEX Can Predict Optimal Material Among All Possible Compounds



Mendeleev number (Pettifor, 1984). Prediction of stability, structure, and properties of materials



Mendeleev numbers of the elements



Figure 5. The heat of solution of B in liquid metal A according to the semi-empirical model of Miedema *et al* (1977). The full-solid lines and the diagonal correspond to the contour $\Delta H_{\rm sol} = 0$. The dotted and full shaded regions correspond to $0 < \Delta H_{\rm sol} < 200$ and $\Delta H_{\rm sol} > 200$ kJ mol⁻¹ respectively. The light full and broken lines correspond to the contours $\Delta H_{\rm sol} = -200$ and $\Delta H_{\rm sol} = -400$ kJ mol⁻¹ respectively.

Enthalpies of formation of compounds

Mendeleev Number – a way to arrange elements and compounds by properties

Mandalaay Atom Mandalaay Atom Mandalaay Atom

[Pettifor, 1984; Allahyari & Oganov, NPJ Comp. Mat., 2020; J. Phys. Chem. C, 2020]

endeleev	Atom	Mendeleev	Atom	Merideleev	Atom		100
Number		Number		Number	-		
1	Fr	32	П	62	Po		90
2	Cs	33	U	63	Fe		80
3	Rb	34	Pa	64	Cu		· · · · · · · · · · · · · · · · · · ·
4	к	35	Zr	65	Co		
0	на	36	Pu	66	AS	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	
7	Ba Sm	37	ND	67	Kr		
8	Gd	39	Ta	69	Mo		· 40-
9	Eu	40	In	70	1		<u></u> 명 30-
10	Sr	41	Pb	71	Pd	$\underbrace{\mathbf{h}_{1} \cdots \mathbf{h}_{k}}_{\mathbf{h}_{1} \cdots \mathbf{h}_{k}} \underbrace{\mathbf{h}_{1} \cdots \mathbf{h}_{k}}_{\mathbf{h}_{k} \cdots \mathbf{h}_{k} \cdots \mathbf{h}_{k} \cdots \mathbf{h}_{k}} \underbrace{\mathbf{h}_{k} \cdots \mathbf{h}_{k}}_{\mathbf{h}_{k} \cdots \mathbf{h}_{k} \cdots \mathbf{h}_{k}} \underbrace{\mathbf{h}_{k} \cdots \mathbf{h}_{k}}_{\mathbf{h}_{k} \cdots \mathbf{h}_{k}} \underbrace{\mathbf{h}_{k} \cdots \mathbf{h}_{k}}_{\mathbf{h}_{k} \cdots \mathbf{h}_{k} \cdots \mathbf{h}_{k}} \underbrace{\mathbf{h}_{k} \cdots \mathbf{h}_{k}}_{\mathbf{h}_{k} \cdots \mathbf{h}_{k}}}_{\mathbf{h}_{k} \cdots \mathbf{h}_{k}} \underbrace{\mathbf{h}_{k} \cdots \mathbf{h}_{k}}_{\mathbf{h}_{k} \cdots \mathbf{h}_{k}}}_{\mathbf{h}_{k} \cdots \mathbf{h}_{k}} \underbrace{\mathbf{h}_{k} \cdots \mathbf{h}_{k}}_{\mathbf{h}_{k} \cdots \mathbf{h}_{k}}}_{\mathbf{h}_{k} \cdots \mathbf{h}_{k}} \underbrace{\mathbf{h}_{k} \cdots \mathbf{h}_{k}}}_{\mathbf{h}_{k} \cdots \mathbf{h}_{k}}}_{\mathbf{h}_{k} \cdots \mathbf{h}_{k}}} \underbrace{\mathbf{h}_{k} \cdots \mathbf{h}_{k}}}_{\mathbf{h}_{k} \cdots \mathbf{h}_{k}}}_{\mathbf{h}_{k} \cdots \mathbf{h}_{k}}}_{\mathbf{h}_{k} \cdots \mathbf{h}_{k}}}$	20
11	Tm	42	Cd	72	Ir	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10
12	Pm	43	Xe	73	Os	Ein 19 The string entropy to be a first string to be a string to b	
13	Ca	44	ті	74	Р	Fig. 1.6 the same change change intercept mis modified periodic table puts all the elements in sequential order, given by the relative ordering number .#. From Petifor (1988).	0 10 20 30 40 50 60 70 80 90 100
14	Na	45	AI	75	Ru	Dattifor's construction	
15	Ac	46	Bi	76	Pt		· Comparison with
16	La	47	Sn	77	At		
17	Yb	48	Hg	78	Rh		Pettifor's numbers
18	Tb	49	Zn	79	w		
19	Y	50	Ga	80	Rn		
20	Dy	51	V	81	Se		
21	Ho	52	Mn	82	В		
22	Ce	53	Sb	83	Au	80	
23	Er	54	Te	84	s		45 70 45
24	Li Th	55	Cr	85	Br	40	40 40
25	10	56	Ro	07		60	60 G
27	Pr	58	Ge	88	C		
28	Nd	59	Be	89	N		
29	Ma	60	Si	90	0	Ē 40 1 25 Ē 40 1 25 Ē 40 1 25 Ē 40 1 25 Ē 40 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	
30	Sc	61	Тс	91	F		
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						Atomic number (AN) Petutor's Mendeleev number (M	Modified Mendeleev number (MNm) Mendeleev number in this work(US)

Grouping of hardness by (a) sequential number, empirical (Pettifor's and Glawe's) and our non-empirical Mendeleev numbers.

Non-empirical Mendeleev numbers work best [Allahyari & Oganov, J.Phys.Chem. C., 2020]

Highly ferromagnetic phases are formed by Fe and Co, some lanthanoids and actinoids



Most exothermic compounds are formed by very different elements:

ThF₄ (-4.11 eV/atom), AcF₃ (-4.09 eV/atom), CaF₂ (-3.92 eV/atom), ZrF₄ (-3.62 eV/atom), Th₄O₇ (-3.61 eV/atom), Y₂O₃ (-3.48 eV/atom), Al₂O₃ (-2.95 eV/atom), CaO (-2.95 eV/atom), SiO₂ (-2.79 eV/atom).



Mendelevian search for the hardest possible material: diamond and lonsdaleite are found!

[Allahyari & Oganov, NPJ Comp. Mat., 2020]



Very recent story of a material harder than diamond

- Fujii (PRL, 2020) claimed "pentadiamond" to have unique elastic moduli.
- Both machine learning and DFT calculations prove this wrong (Brazhkin & Oganov, arxiv.org).





Table 1. Calculated elastic properties of pentadiamond in comparison with Y. Fujii et al. [1].

Desperty	V Entit at al [1]	This work (Quantum	This work (VASD)	This work
Property		ESPRESSO)	This work (VASP)	(machine learning)
a, Å	9.195	9.184	9.191	9.195
E-E(diam), meV/atom	275	263	267	-
C ₁₁ , GPa	1715.3	539	537	409
C ₁₂ , GPa	-283.5	105	106	118
C ₄₄ , GPa	1187.5	141	143	200
B, GPa	381	250	249	215
G, GPa	1113	172	169	176
Y, <u>GPa</u>	1691	420	413	415
σ	-0.241	0.22	0.22	0.18
H _v , GPa	210	20	20	26

Advanced algorithms predict new supermaterials



Machine learning + Structure prediction will shape computational materials science

Challenges:

Very large systems Disordered systems



Prediction of grain boundary structures



Polymers for capacitors Exotic compounds Room-temperature superconductivity Thermoelectrics with ZT~3.4 New molecules and nanoparticles Electrides

Diamond is the hardest material



Protein structure prediction





Artem R. Oganov Professor, head of laboratory



Zahed Allahyari Postdoc



Pavel Bushlanov Postdoc



Sergey Lepeshkin Postdoc



Vladimir Baturin Postdoc



A. Goncharov Experimental confirmation



V. Blatov



I. Troyan Experimental confirmation



Dmitrii Semenok PhD student



Efim Mazhnik PhD student



Tao Fan PhD student



X. Dong



Q. Zhu



X. F. Zhou





A. Kvashnin