Scientists predict new high-energy compounds

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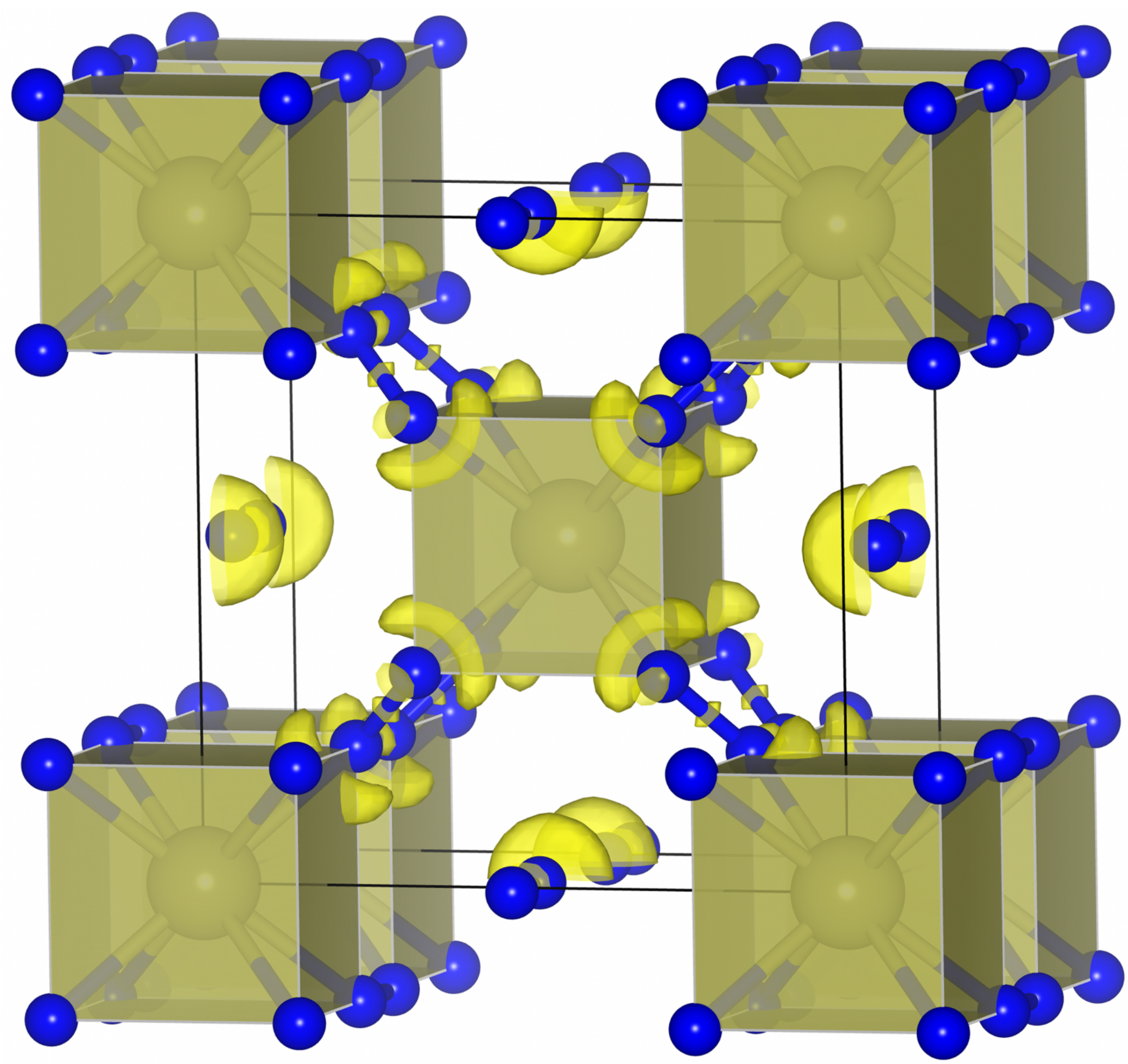

Hafnium nitride (HfN10) structure. Credit: MIPT

Using theoretical methods, an international group of scientists led by Artem R. Oganov, Professor of Skoltech, Stony Brook University and Moscow Institute of Physics and Technology predicted unusual nitrides of hafnium and chromium with the chemical formulae HfN_{10} (and its zirconium analogue ZrN_{10}) and CrN_4. These compounds can be obtained at relatively low pressures and contain high-energy groups of nitrogen atoms. Pure polymeric nitrogen is an ideal high-energy compound that packs so much energy per unit volume or mass that it could be used as a powerful explosive if it were not for the gigantic pressures required for its synthesis. This work shows that nitrogen polymerizes at much lower pressures in the presence of metal ions. The authors also predicted a range of new hafnium nitrides as well as nitrides, carbides and borides of chromium, with an unusual combination of properties (high hardness, electrical conductivity, and toughness).

Superhard materials can be divided into two main classes: compounds of boron, carbon, nitrogen and oxygen, and compounds of transition metals with boron, carbon and nitrogen. The scientists studied four systems in two simultaneously published works: hafnium-nitrogen, chromium-nitrogen, chromium-carbon and chromium-boron. Several new materials that can be formed at relatively low pressure were predicted. Among them there are materials with an unusual combination of very high hardness and electrical conductivity. In particular, newly predicted carbide Cr_2C should even be stable at atmospheric pressure; and researchers were able to resolve for the first time the crystal structure of a known compound Cr_2N. The most interesting finding is the chemical compound with the formula HfN_{10}—here, there are 10 nitrogen atoms per hafnium atom. Its structure is very peculiar from a chemical point of view: The hafnium atoms and N2 molecules are sandwiched between infinite chains of nitrogen atoms. Such a structure is formed under relatively low pressure of 0.23 Mbar. Professor Artem R. Oganov says, "This finding brings us back to one of the Holy Grails in material science, the search for polymeric nitrogen, an ideal high-energy-density material."

The fact of the matter is that all good explosive compounds contain nitrogen—at the moment of explosion, the nitrogen atoms forming the extraordinary stable N2 molecule release a vast amount of energy. The more nitrogen atoms in a compound, and the more unusual their bonding, the more energy will be released as a result of the explosion. Polymeric nitrogen was first predicted by American physicist C. Mailhiot in 1992 and then synthesized in 2004 by Russian physicist Michael Eremets under pressures exceeding 1 million atmospheres. At such pressures, only micron-sized samples can be made, which rules out practical applications.

Professor Oganov says, "Our group works on several projects related to metal polynitrides. This is a promising class of high-energy-density compounds, requiring much lower pressures than pure polymeric nitrogen (e.g., 5 times lower in case of HfN_{10}, or even less for CrN_4, and this is likely not the limit). Chemists have long dreamed about synthesising polymeric nitrogen in large quantities. We have proposed the compound class that can fulfil this dream."

More information: Alexander G. Kvashnin et al, Computational Search for Novel Hard Chromium-Based Materials, *The Journal of Physical Chemistry Letters* (2017). DOI: 10.1021/acs.jpclett.6b02821

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