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FY07 LDRD Final Report Synthesis under High Pressure and Temperature of New Metal Nitrides

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Auspices Statement

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FY07 LDRD Final Report
Synthesis under High Pressure and Temperature of New Metal Nitrides
LDRD Project Tracking Code: 05-ERD-039

Jonathan Crowhurst, Principal Investigator

Abstract

The original aim of this LDRD was to determine with unprecedented precision the melting curve of iron to geophysically relevant pressures. In the course of developing much of the technology and techniques required to obtain this information we have encountered and studied novel chemical reactions some of whose products are stable or metastable under ambient conditions. Specifically we have synthesized nitrides of the platinum group metals including platinum, iridium, and palladium. We have also carried out in depth first principles theoretical investigations into the nature of these materials. We believed that the scientific impact of continuing this work would be greater than that of the original goals of this project. Indeed the work has led to a number of high profile publications with additional publications in preparation.

While nitrides of the transition metals are generally of tremendous technological importance, those of the noble metals in particular have enjoyed much experimental and theoretical attention in the very short time since they were first synthesized. The field was and clearly remains open for further study. While the scientific motivation for this research is different from that originally proposed, many of the associated methods in which we have now gained experience are similar or identical. These include use of the diamond anvil cell combined with technologies to generate high temperatures, the *in-situ* technique of Raman scattering using our purpose-built, state-of-the-art system, analytical techniques for determining the composition of recovered samples such as x-ray photoelectron spectroscopy, and finally synchrotron-based techniques such as x-ray diffraction for structural and equation of state determinations. Close interactions between theorists and experimentalists has and will continue to allow our group to rapidly and reliably interpret complicated results on the structure and dynamics of these compounds and also additional novel materials. Although the purely scientific dividends of this project have been substantial, there remains the possibility of a technological application – now that nitrides with likely desirable properties have been shown to exist, large-scale synthesis techniques can be considered.

Introduction

Traditionally, the transition metal nitrides have been of great technological and fundamental importance because of their strength and durability. More recently, there has been additional interest in these materials because of other properties that include interesting and potentially useful optical, electronic, and magnetic effects[1-5]. Until recently, there had been no synthesis of bulk nitrides of the noble metals despite considerable effort. Such compounds may be expected to have properties that would make them highly desirable for technological applications. An example is

that of gold nitride, which is more durable than pure gold, while apparently still electrically conducting[6]. Another is that of platinum nitride, which has been found to possess a bulk modulus of 370 GPa[1] (comparable to that of cubic boron nitride. Actually distinct from the bulk modulus a theoretical investigation has yielded a hardness comparable to titanium nitride[7] while a very recent theoretical paper reports a hardness comparable to cubic boron nitride[8] – the latter therefore implies that platinum nitride is "superhard"). We have now synthesized under extreme conditions three different platinum-group nitrides (specifically those of Pt, Ir, and very recently Pd) and have and continue to evaluate their physical characteristics. First-principles simulations have been simultaneously carried out to confirm experimental findings and to suggest likely interesting or useful properties that will stimulate further measurements.

Research Activities

The static pressures involved in this work are high. We have found synthesis pressures for IrN_x, PtN_x, and PdN_x to be 48 GPa, 50 GPa and 59 GPa respectively. The only device capable of generating such conditions is the diamond anvil cell (DAC). Furthermore, synthesis temperatures are also high (in the case of PtN_x, for example, this temperature exceeds 2000 K). There are only two ways of generating such temperatures in the DAC: by laser heating or by internal electrical (ohmic) heating. Both methods were essential to the goals of our original proposal to determine the melting curve of iron, and we have now gained much experience with both techniques. Although we have thus far exclusively used laser heating to synthesize the nitride compounds, we will consider in future the use of internal electrical heating, which has some technical advantages. Our primary diagnostic for *in-situ* determination of compound formation has been and will continue to be Raman scattering (Figures 1 and 2). The application of this technique to the diamond cell in this regard has proven very convenient; although the total quantity of material synthesized has been extremely small, each compound has exhibited very intense Raman modes (most likely a consequence of tightly bound pairs of nitrogen atoms). Furthermore, although we have largely relied on thermal emission to determine synthesis temperatures, the ratio of the intensities of the Stokes and anti-Stokes Raman scattering peaks can also be used for this purpose, and is particularly useful in the case in which thermal emission is insufficient (below approximately 1000 K). Although PtN_x and IrN_x form at high temperature, we have used this technique to show that at least one phase of PdN_x forms below 1000 K. Thus far, we have determined synthesis pressures by assuming pressure before and during heating to be the same. This is, of course, an approximation - heating should almost always be expected to contribute an additional pressure, which may be significant depending on temperature and nominal pressure. We have adopted this procedure due to the total lack of an optical pressure gauge that is believable under simultaneous high temperature. This same issue was identified in our original proposal to determine accurate melting pressures for iron. To overcome the need to make this approximation, we have developed a new pressure scale - based on cubic boron nitride - that is good at high temperatures. We will, in future, adopt this scale when necessary.

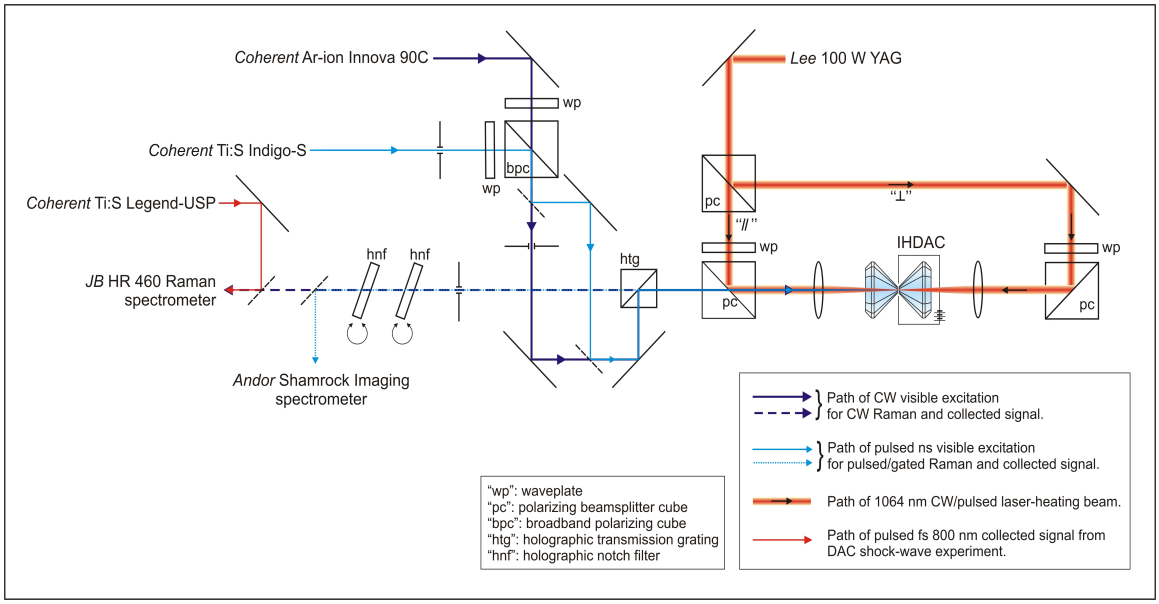


Figure 1. Schematic of the combined pulsed/cw Raman double-sided laser-heating system we have built in B235.

Analysis of synthesized compounds

Raman scattering has provided insight into some of the characteristics of the synthesized compounds. The number of Raman modes permits general conclusions to be made concerning their structure while the intensities can be used to infer if the material is likely to be electrically insulating. We have obtained direct structural information using the technique of synchrotron x-ray diffraction (Fig. 3). By obtaining XRD patterns at different pressures we have also been able to determine the equations-of-state (EOS) of the new compounds. To determine their stoichiometries (in the case of platinum and iridium nitride) we have employed x-ray photoelectron spectroscopy (XPS) to effectively analyze the recovered materials. Scanning electron micrographs (Fig. 4) and energy dispersive x-ray spectroscopy have also proven useful.

Theoretical approach

We have used density functional theory to investigate theoretically the new compounds. Thus far we have considered formation energies of candidate structures in order to determine the most thermodynamically stable (Fig 5). Once a structure has been decided upon, corresponding Raman modes are calculated and comparisons made with Raman, XPS, and XRD results. Pressure-volume calculations performed in both the generalized gradient and local density approximations are compared with the experimental EOS.

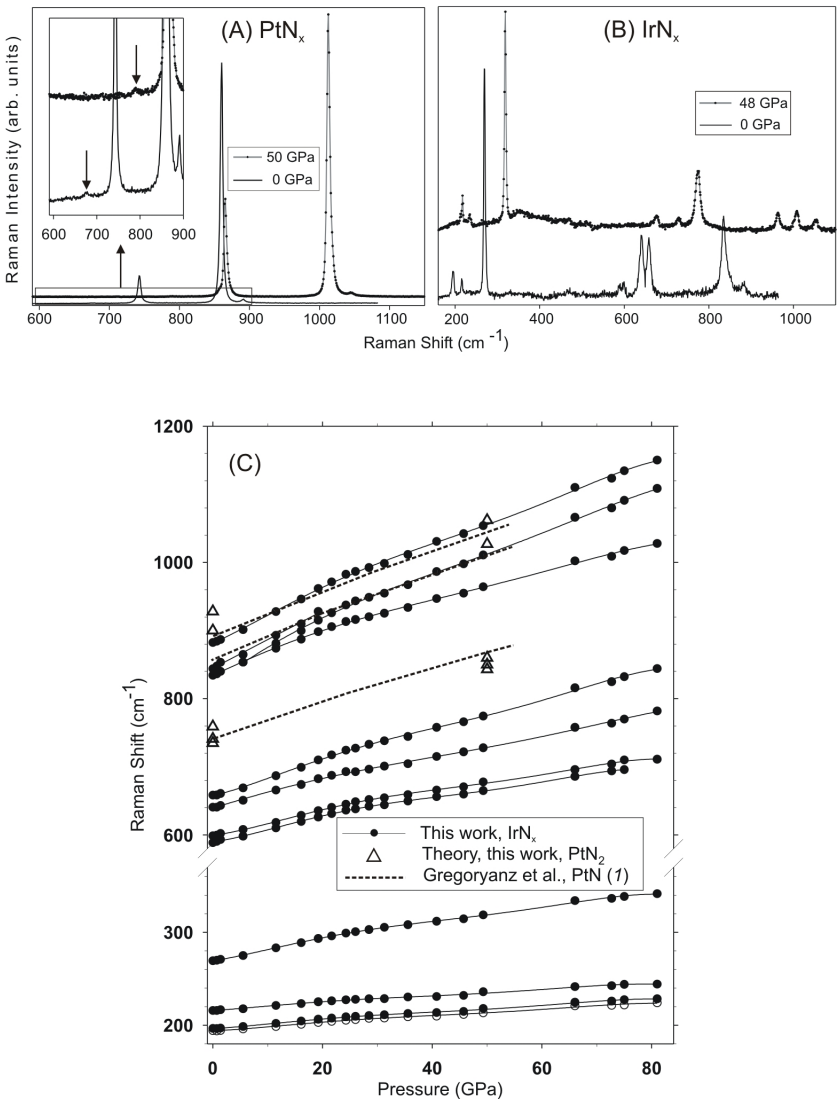


Figure 2**.** (A) Raman spectra of platinum nitride at ambient pressure and at 50 GPa (B) Raman spectrum after heating iridium in the presence of nitrogen at 48 GPa, and of the recovered product at 0 GPa. (C) Dependences of observed Raman modes of iridium nitride on pressure (after Crowhurst et al, 2006).

We have and continue to explore the crystal structures as well as the chemistry of the nitrides formed with the third-row transition metal elements. We now understand the electronic and mechanical properties of these compounds in terms of the fundamental bonding (involving an unexpectedly large hybridization between the nitrogen and the transition metal electronic states) and crystal symmetries in these systems. Usually the elements in the same group of the periodic table are expected to behave in similar ways. Thus, one would expect that the nitrides of Pd, Rh, Ni, and Co should behave similarly to those of Ir and Pt. In light of the recent research done in the field of high-Tc superconducting systems such as YBCO, we have reason to

believe that the 4d states in Pd and Rh should be more localized than their corresponding 5d states in Pt and Ir, and furthermore that the 3d states in Ni and Co might be highly localized, giving rise to strong electronic correlations and non-Fermi liquid behavior, leading to very novel electronic as well as thermodynamic behavior. Different from this but still purely theoretical at this point are our calculations that predict that there are structures of still higher stability than those thus far synthesized for the platinum group nitrides (Figs. 6 and 7). Experimental efforts to find these structures will continue to be made.

Accomplishments to date

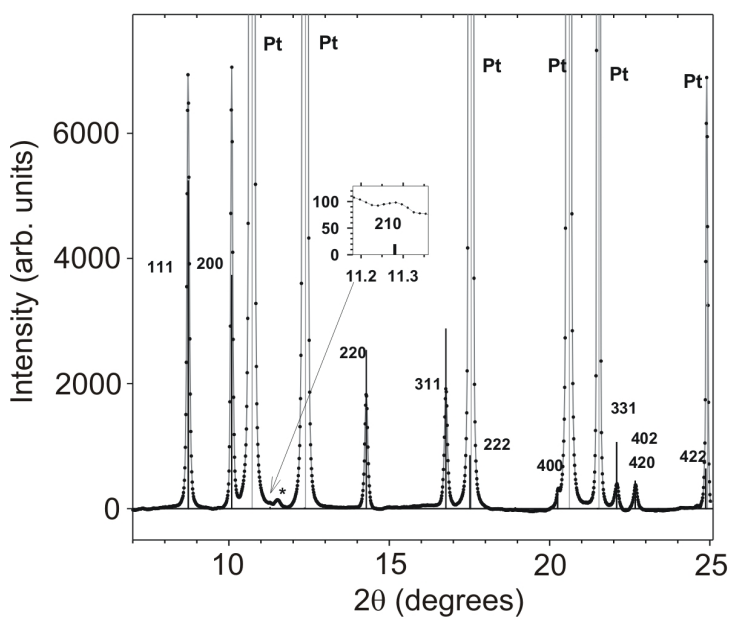


Figure 3. Powder x-ray diffraction pattern of PtN_2 obtained at 0 GPa. The reflections of PtN_2 are indexed assuming the pyrite structure. Black vertical bars show the calculated positions and intensities of the reflections. The gray vertical lines indicate unreacted platinum. The star corresponds to the 101 reflection of rhenium. The inset shows a very weak reflection that is forbidden for the more symmetric fluorite and zinc-blende structures (after Crowhurst et al, 2006).

- We have synthesized the first bulk nitride of iridium[9] and have accurately determined the structure, stoichiometry, and Raman spectrum of platinum nitride. The latter work combines experimental and theoretical results. It resolves a debate in the literature concerning the nature of platinum nitride[10-15]. (See also Refs. 16-20). It has been published in ***Science*** in 2006 (See Figs 2 – 5).

- We have synthesized the first nitride of palladium and determined its structure and EOS at Beamline 12.2.2 of the Advanced Light Source, Lawrence Berkeley National Laboratory, and at Beamline 13-ID of the APS (Argonne National Laboratory). We have published some of these results in an invited paper to the ***Journal of Materials Research*** in 2008. This invitation was a result of our invited presentation at the MRS, Boston 2006 Meeting being named best of session.

- We carried out a theoretical study into the possibility of additional lower energy structures in which the platinum group nitrides may crystallize. We published these results in ***Physical Review Letters*** in 2008 (See Figs. 6 and 7).

- We have performed XRD measurements of cubic boron nitride (cBN) to 70 GPa and 3500 K. This data forms the basis of a synchrotron-based high-temperature pressure scale. We published our results in ***Physical Review B*** in 2007. We have also developed an optical high-temperature pressure scale based on Raman scattering in

cBN and on first-principles calculations that is good to at least 1750 K and 40 GPa. This work was published in ***Physical Review B*** in 2005.

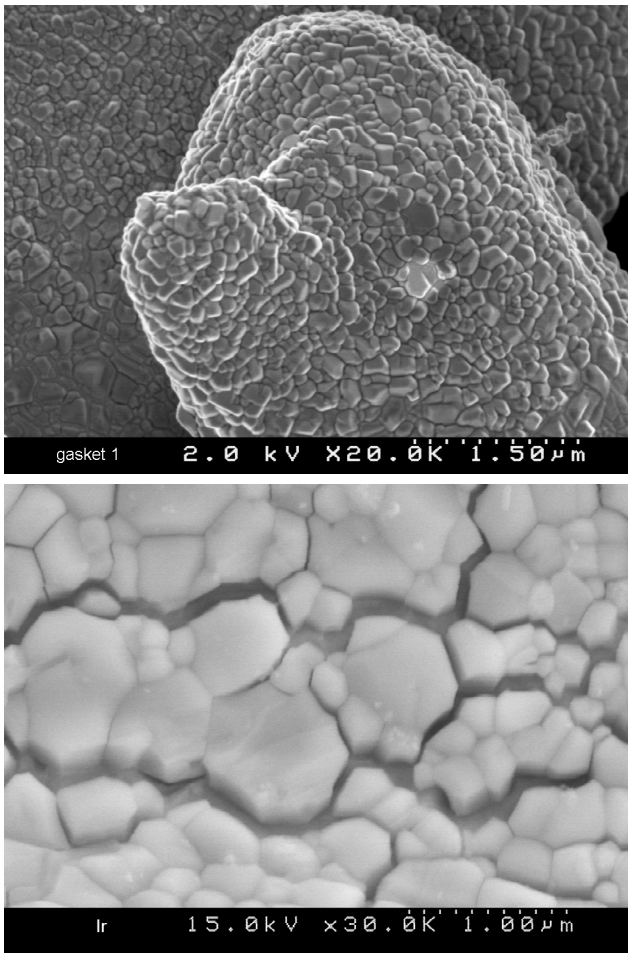


Figure 4. SEM images of recovered material. Upper panel: metal was platinum. Lower panel: metal was iridium. Nitrogen was found in all the regions that exhibited the distinctive surface texture that is apparent in the images (After Crowhurst et al, 2006).

- We have presented some of the results above at various international conferences. Please see below.

Potential scientific and technological impact

The major impact of this work has been the elucidation of new noble metal chemistry, which has resulted in publications in high-profile journals. Our experimental results provide a rigorous test of first-principles theoretical approaches. Once compounds with useful properties have been shown to exist under ambient conditions, large scale synthesis techniques (e.g., nitrogen ion irradiation) can now be considered.

Relevance to LLNL and exit plan.

Apart from the points mentioned above, successful completion of the project necessarily implies wide-ranging experience on the part of the investigating team to pursue further research into chemistry under extreme conditions. One particular example is our enhanced ability to perform Raman spectroscopic measurements on relevant materials in the Chapman-Jouguet state and to identify intermediate and final reaction products. More specifically, our experience has led to additional similar experiments on high nitrogen content materials that may find application as propellants or explosives. This preliminary work has already received funding from the DTRA agency and we expect more funding to follow. We also expect the experimental and theoretical experience we have gained here to be vitally useful to the study of actinide chemistry under high temperatures which form the basis of a proposal currently under review by BES on which a number of us are investigators and similarly a major LDRD SI proposal on nuclear attribution also currently under review.

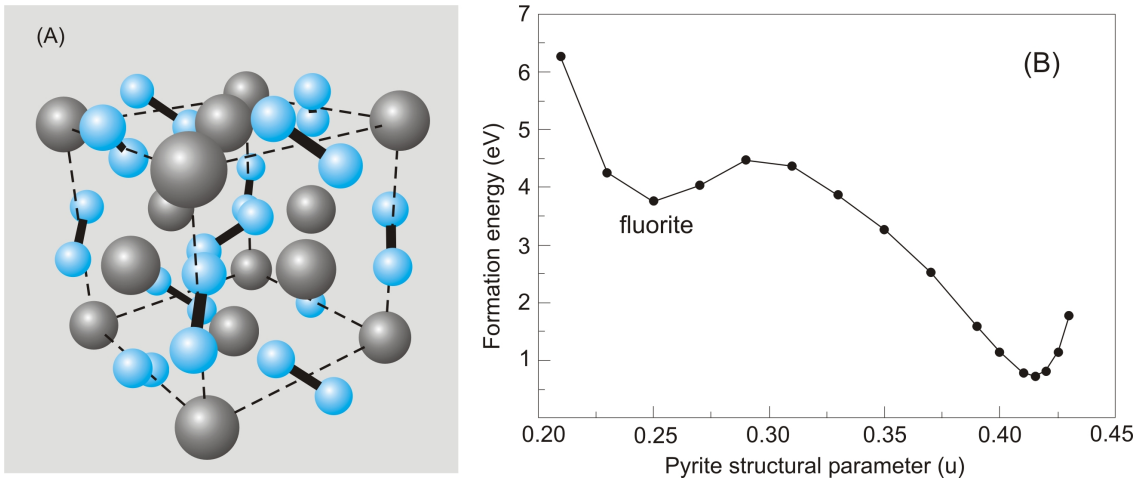


Figure 5. (A) Diagram of the proposed pyrite structure of PtN_2. Grey and blue spheres represent platinum and nitrogen respectively. (B) Energy of formation of the pyrite phase of PtN_2 vs structural parameter *u* (after Crowhurst et al, 2006).

List of papers arising directly from this LDRD:

D. Aberg, B. Sadigh, J. C. Crowhurst, A. F. Goncharov, Thermodynamic ground states of platinum metal nitrides, ***Phys. Rev. Lett***. 100, 095501 (2008).

J. C. Crowhurst, A. F. Goncharov, B. Sadigh, J. M. Zaug, D. Aberg, Y. Meng, V. Prakapenka, Synthesis and characterization of nitrides of iridium and palladium, ***J. Mat. Res***., 23, 1 (2008). Invited contribution.

J. C. Crowhurst, A. F. Goncharov, B. Sadigh, C. L. Evans, P. G. Morrall, J. L. Ferreira, A. J. Nelson, Synthesis and characterization of the nitrides of platinum and iridium, ***Science***, 311, 1277, (2006).

Some other papers closely associated with this LDRD:

A. F. Goncharov , J. C. Crowhurst, J. K. Dewhurst, S. Sharma, C. Sanloup, E. Gregoryanz, N. Guignot, M. Mezour, Thermal equation of state of cubic boron nitride. Implications for a high-temperature pressure scale, 75, 224114 ***Phys. Rev. B***. (2007).

A. F. Goncharov, J. C. Crowhurst, J. K. Dewhurst, S. Sharma, Raman spectroscopy of cubic boron nitride under extreme conditions, ***Phys. Rev. B*** 72, 100104 (2005).

A. F. Goncharov, J. C. Crowhurst, Raman scattering under extreme conditions, ***Low. Temp. Phys***. 139, 727 (2005).

Invited presentations associated with this LDRD:

J. C. Crowhurst, High pressure techniques: laser heating, impulsive stimulated light scattering, combined dynamic and static loading, Presentation to Class of 2008, Course EPS235, University of California Berkeley, 2008.

J. C. Crowhurst, Chemistry and physics under extreme conditions: characterization of known and novel systems, high pressure elasticity, combined dynamic and static loading, Geophysical Laboratory, Carnegie Institution of Washington, 2008.

J. C. Crowhurst, Synthesis under extreme conditions of new transition metal nitrides. Study of Matter under Extreme Conditions, Miami, 2007.

J. C. Crowhurst, High-pressure synthesis and characterization of the nitrides of some of the Group 9 and 10 transition metals. Material Research Society, Boston 2006. Named the outstanding paper of the session.

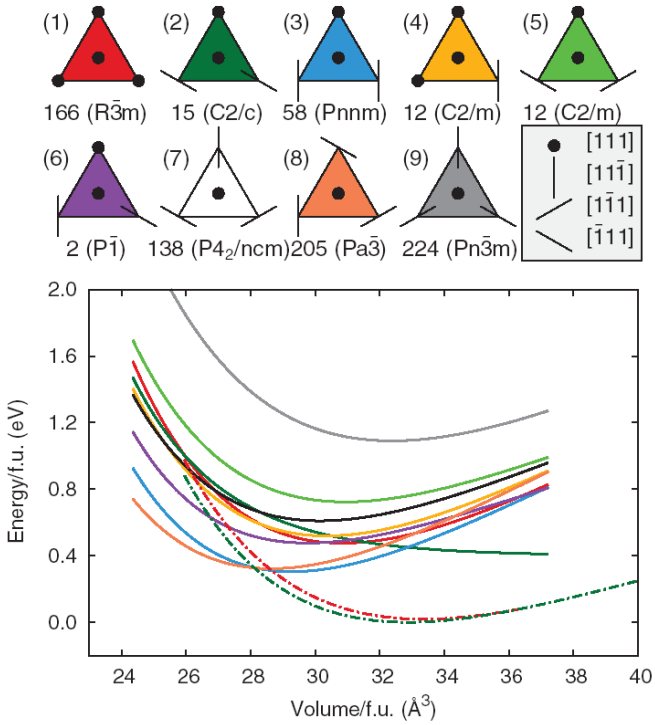


Fig. 6. Top: projections of all possible distinct nitrogen dimer orientations derived from the 12-atom conventional unit cell, along with the space group number and Hermann-Maugin symbol of the corresponding structure. Bottom: energy/f.u. vs volume curves from LDA for the above relaxed structures (solid lines) in the case of PdN_2. Each structure can be identified by matching the line color to the corresponding triangle color. Note that structure 7 corresponds to the black line. The green and red dashed lines correspond to the STAA and STAB structures, respectively (after Aberg et al 2008).

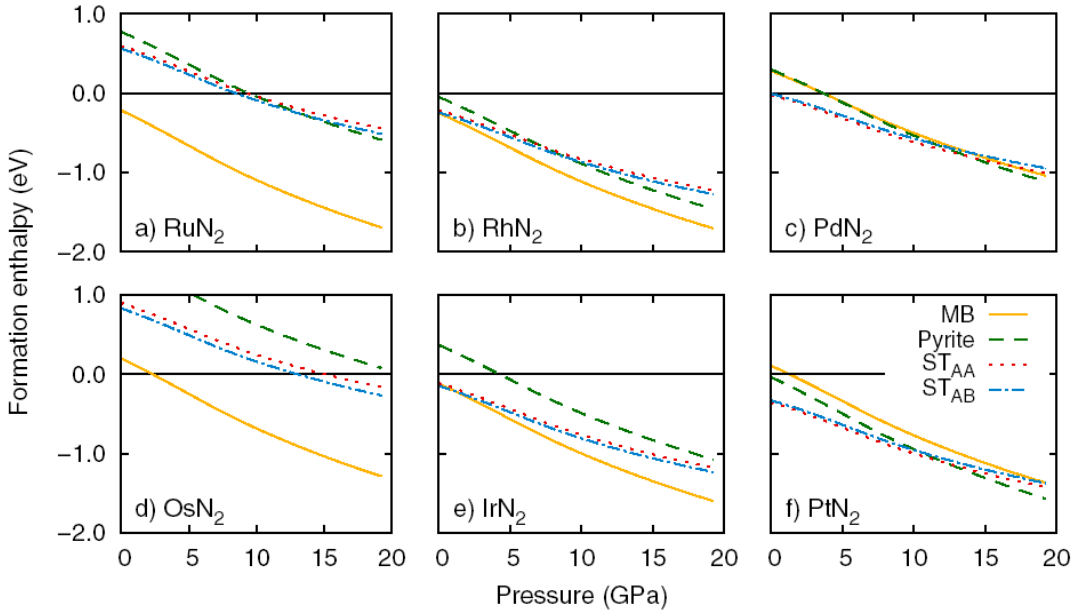
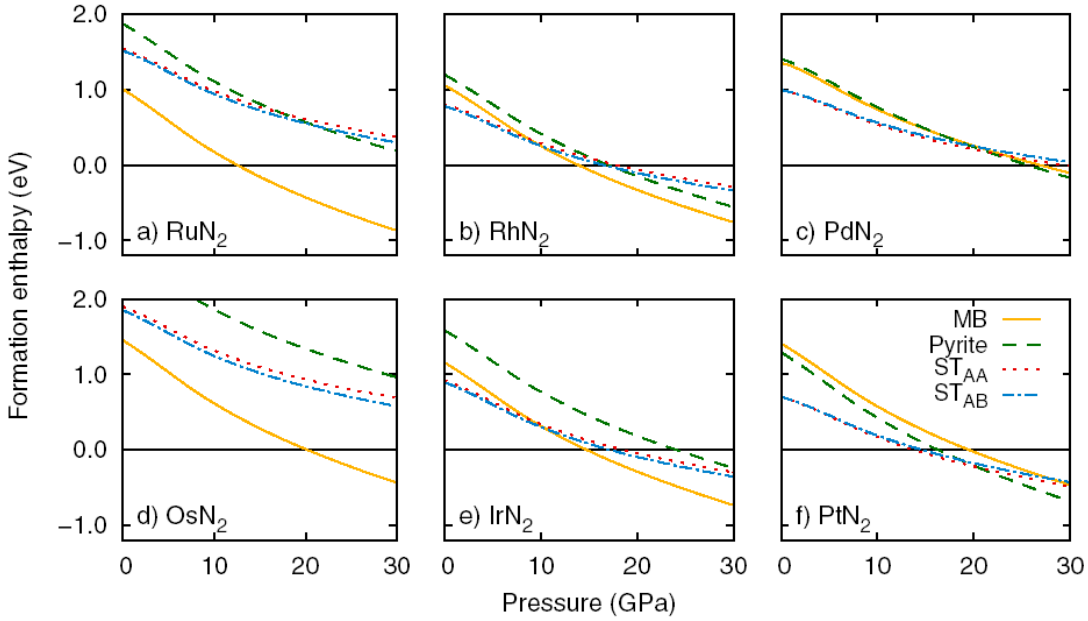


Fig. 7 (A). LDA formation enthalpies per formula unit of (a) RuN_2, (b) RhN_2, (c) PdN_2, (d) OsN_2, (e) IrN_2, and (f) PtN_2 as a function of pressure for marcasite or baddeleyite (MB), pyrite, and the two simple tetragonal structures (after Aberg et al 2008). (B). GGA formation enthalpies per formula unit of (a) RuN_2, (b) RhN_2, (c) PdN_2, (d) OsN_2, (e) IrN_2, and (f) PtN_2 as a function of pressure for marcasite or baddeleyite (MB), pyrite, and the two simple tetragonal structures (after Aberg et al 2008).



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