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Stable All-Nitrogen Metallic Salt at Terapascal Pressures

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The phase diagram and equation of state of dense nitrogen are of interest in understanding the fundamental physics and chemistry under extreme conditions, including planetary processes, and in discovering new materials. We predict several stable phases of nitrogen at multi-TPa pressures, including a P4/nbm structure consisting of partially charged N5+ pairs and N5− tetrahedra, which is stable in the range 2.5–6.8 TPa. This is followed by a modulated layered structure between 6.8 and 12.6 TPa, which also exhibits a significant charge transfer. The P4/nbm metallic nitrogen salt and the modulated structure are stable at high pressures and temperatures, and they exhibit strongly ionic features and charge density distortions, which is unexpected in an element under such extreme conditions and could represent a new class of nitrogen materials. The P–T phase diagram of nitrogen at TPa pressures is investigated using quasiharmonic phonon calculations and ab initio molecular dynamics simulations.

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The polymerization of molecular nitrogen under pressure has been very actively researched over the past two decades and has stimulated many experimental [1–12] and theoretical [13–31] investigations. Density functional theory studies suggested that the dissociation of nitrogen could occur at high pressures which are, nevertheless, attainable in diamond anvil cell experiments. In a ground-breaking paper, Mailhiot et al. [16] predicted the polymerization of nitrogen molecules under pressure, leading to the formation of the “cubic gauche” (cg) framework structure (space group I23). After considerable efforts [1,2], cg nitrogen was finally synthesized by Eremets et al. [5], a decade after its prediction. Novel techniques must be developed if cg-N is to be recovered to ambient pressure [5], which could lead to the synthesis of polymeric nitrogen [5] or high-N content salts [32]. Such materials are expected to be excellent candidates as high-energy-density materials.

The N≡N triple bond is one of the strongest known, and breaking it requires surmounting a substantial energetic barrier. However, at high temperatures the triple bond breaks at pressures above about 110 GPa [5], a much lower pressure than predicted for the single bond in H2 [33] and the double bond in O2, which is predicted to survive up to about 1.9 TPa [34,35]. Once the N≡N triple bond is broken, a wide variety of structures can be adopted, similar to phosphorus and arsenic.

After extensive searches for high-pressure nitrogen structures, the sequence of low-temperature phase transitions cg → Pb2a2 → P232121 appeared to be accepted [28,29]. That view was challenged recently, when a cagelike diamondoid “N10” structure (space group I43m) was found to be more stable than any other candidate above 263 GPa [31]. Recently, the melting behavior of nitrogen and phases beyond cg-N have also been investigated [10–12,30].

Recently, dynamical shock wave [36–38] and ramped compression experiments [39–41] have increasingly been used to investigate materials at TPa pressures. Even more extreme conditions are attainable today in laser ignition experiments [42] and laser-induced microexplosions [43]. Experimental determinations of structures at TPa pressures will soon be possible [41], and experiments aimed at compressing nitrogen to TPa pressures are ongoing [44]. However, there is very little knowledge of the structures and properties of nitrogen under these conditions, and therefore theoretical predictions are particularly important [34,45–48]. Understanding the energetics of elements is crucial before one can understand the energetics of the compounds they might form.

Although an increase in coordination number with pressure seems physically reasonable, it is by no means universal. Aluminum, for example, is expected to adopt more open structures at TPa pressures as the valence electrons move away from the ions in the formation of “electride structures” [47]. Well-packed structures are strongly disfavored in oxygen up to at least 25 TPa [34], which is well beyond dissociation. The coordination number of nitrogen has not been determined beyond 800 GPa, at which pressure the insulating N10 (I43m) phase is stable.

We have used ab initio random structure searching (AIRSS) [49,50] and density functional theory methods to find candidate structures of nitrogen up to multi-TPa pressures. Details of the searches are provided in the Supplemental Material [51]. These searches have enabled
FIG. 1 (color online). Crystal structures of the newly predicted nitrogen phases. (a) $P4_{2}1/nbm$, (b) $P2_{1}1$, (c) A supercell of $P2_{1}$ viewed along the a axis. The colored spheres in (a) and (b) represent atoms with different charge environments, as described in the text. Atoms in different layers in (c) have been shown with different colors.

The unique structure of the $P4_{2}1/nbm$ phase led us to perform a Bader charge transfer analysis [52]. As summarized in Table I, we found that the $N_{3}$ tetrahedra are negatively charged ($-0.37|e|$) and serve as anions, while the positively charged $N_{2}$ dimers ($+0.37|e|$) act as cations. The charge transfers depends on the precise definition of the atomic charges, but the computed charges are substantial, and the overall picture is independent of their definition. We therefore suggest that the $P4_{2}1/nbm$ structure resembles an all-nitrogen salt.

Our best candidate structure beyond 6.8 TPa, of symmetry $P2_{1}$ with 10 atoms in the unit cell, also shows a very strong charge transfer. The computed Bader charges range between $-0.20$ and $+0.35|e|$. This structure can be viewed as two distorted and buckled square layers, rotated with respect to one another by about arctan $\frac{1}{3}$. Similar energetically competitive structures, such as the $Fdd2$ structure, can be formed with different rotation angles. It is likely that the most stable structure at these pressures is an incommensurate charge density wave (CDW) phase. Nevertheless, even after additional directed searches as described in the Supplemental Material [51], the 10-atom $P2_{1}$ phase remains the best candidate. The appearance of strong charge transfer effects in an element at such high pressures is most unexpected, as the resulting Coulomb energy is substantial.

At lower pressures, we found a $Cmca$ structure similar to “black phosphorus” to be stable within a narrow pressure range. As depicted in the Supplemental Material [51], the $Cmca$ structure consists of threefold-coordinated nitrogen atoms and has zigzag layers, with a shortest N-N distance of about 1.15 Å at 2.5 TPa, which is much shorter than the N-N separation between the layers of about 1.56 Å. Layered structures also appear in the high-pressure phases of other small molecules of first row atoms, e.g., CO [53] and $CO_{2}$ [54].

As can be seen in the enthalpy-pressure relations of Fig. 2, solid nitrogen undergoes a series of structural phase transitions beyond the previously known polymeric

| Structures   | $P$ (TPa) | Lattice parameters (Å) | Atomic positions | $Q_b$ (|e|) |
|--------------|-----------|------------------------|------------------|---------|
| $Cmca$       | 2.5       | $a = 2.090, b = 3.041, c = 2.617$ | 8f $(0.0, 0.3966, 0.8157)$ | 0       |
| $P4_{2}1/nbm$| 2.5       | $a = 3.424, c = 2.466$ | 2d $(0.0, 0.5, 0.5)$ | $-0.07$ |
|              |           |                        | 4g $(0.0, 0.0, 0.7376)$ | 0.18    |
|              |           |                        | 8m $(0.1808, 0.6808, 0.7879)$ | $-0.07$ |
| $P2_{1}$     | 8.0       | $a = 2.579, b = 2.396, c = 2.390$ | 2a $(0.7889, 0.9079, 0.0325)$ | 0.03    |
|              |           | $\beta = 62.903^\circ$ | 2a $(0.2912, 0.2331, 0.5345)$ | 0.01    |
|              |           |                        | 2a $(0.1858, 0.6314, 0.3824)$ | $-0.20$ |
|              |           |                        | 2a $(0.2487, 0.8206, 0.7525)$ | 0.35    |
|              |           |                        | 2a $(0.6866, 0.5078, 0.8789)$ | $-0.19$ |
| $R\bar{3}m$  | 12        | $a = 1.613, c = 1.468$ | 3b $(0.0, 0.0, 0.5)$ | 0       |
| $I4_{1}/amd$ | 30        | $a = 0.890, c = 3.452$ | 4a $(0.0, 0.25, 0.875)$ | 0       |
Although the $Z$ is the most favorable phase in the range 6.8–12.6 TPa, whereupon it transforms into a sixfold-coordinated hexagonal. The partially ionic $P4/nbm$ phase is stable over a wide pressure range, but compression to about 6.8 TPa leads to the layered $P2_1$ structure. The $P2_1$ structure is the most favorable phase in the range 6.8–12.6 TPa, whereupon it transforms into a sixfold-coordinated hexagonal $R3m$ phase. As shown within the inset to Fig. 2, nitrogen forms a $I4_1/amd$ structure similar to Cs-IV [55] at about 30 TPa.

We have established the dynamical stability of the proposed structures by computing their phonon spectra over a wide range of pressures. A selection of phonon spectra is shown in the Supplemental Material [51]. The phonon dispersion relation of $P4/nbm$ shows steep acoustic branches together with fairly flat optical modes. This supports the view that $P4/nbm$ is formed of “units;” the N-N vibrations as well as the breathing mode of the tetrahedra are essentially dispersionless, and are well screened by the electronic cloud. One might expect $P2_1$ to show two relatively soft modes corresponding to a shearing of layers but, in fact, while one of them drops to a very low frequency of 187 cm$^{-1}$ at $\Gamma$, the other has a much higher frequency of about 1210 cm$^{-1}$. This difference in frequency arises from the alignment of shear directions with respect to the ripples in the layers.

We have extended our calculations to include nuclear motion effects so that we can investigate their key role in high-temperature dynamical compression experiments. At low pressures, it is not a straightforward scheme, and provides an estimated upper bound for the melting temperature, $T_m$. Our calculated melting temperature could be compared with an experimental Hugoniot. Our results suggest a noticeable increase in $T_m$ with pressure, perhaps monotonic. The melting temperature is about 4700 K for N10 ($I\bar{4}m$) at 400 GPa, and is as high as 8700 K at 8 TPa for $P2_1$, which is comparable to carbon under similar conditions [57]. The phase diagram of Fig. 3 is generated from a synthesis of our melting data and QHA vibrational results.
structures and projected density of states of the relevant structures are shown in the Supplemental Material [51].

The formation of $N_2$ pairs and $N_4$ tetrahedra in $P4/nbm$ is confirmed by the charge density plot in Fig. 4(b), where the atoms between the tetrahedron center and corners, and between the two atoms within the dimers, form strong covalent bonds. The electron localization function shown in the Supplemental Material [51] provides additional evidence for the formation of tetrahedra and dimers in $P4/nbm$.

The emergence of charged units from an elemental compound has also been observed in $\gamma$ boron [58]. The pressures of interest in the present study are, however, much larger than those at which $\gamma$ boron has been observed and, besides, $P4/nbm$ nitrogen is a very different system. The charge transfer in boron satisfies its tendency to form electron deficient icosahedra. Based on the structural richness of phosphorus and arsenic, one might assume that nitrogen could form similarly rich bonding patterns once the triple bond is broken. At 2 TPa, however, packing efficiency is crucial and one would expect structures with high coordination numbers to be formed. In this metallic phase the variation in coordination (or the inhomogeneity of the density of ions) leads to charge transfer from the highly coordinated atoms (“$N_2$ pairs”) to the lower coordinated ones (“tetrahedra” corners). This charge transfer allows the $P4/nbm$ structure to form a unique metallic all-nitrogen salt. Each atom in the 1D chains perpendicular to the layers of tetrahedra has four long bonds to the corners of the tetrahedra; thus, only one electron is left. The 1D chain with uniform N-N distances is unstable and undergoes a Peierls distortion, similar to that in lithium [59], and $N_2$ pairs are formed.

Although $P2_1$ also shows a clear charge transfer, the atomic arrangement is completely different from that in $P4/nbm$. This phase is formed by distorted, buckled, and rotated square layers, resembling a CDW. CDWs have been observed previously in chalcogenides under pressure [60]. We believe that nitrogen may actually adopt an incommensurate structure between 6 and 12 TPa. In light of the charge transfer, the buckling of layers could be viewed not only as a symmetry breaking, but also as allowing the positive and negative ions to approach one another and reduce the energy. In addition, while carbon expels charge from the $2s$ levels above 3 TPa [48], eventually forming an electride, the bottom of the valence band of $P2_1$ still has a large $2s$ population. Charge depletion from the $2s$ levels only arises with the transition to the $R\bar{3}m$ phase, at almost 12 TPa. Electride structures are found, for example, in carbon [48] and aluminum [47] at very high pressures, but they do not appear in nitrogen up to at least 100 TPa. While intuition suggests that close-packed structures should be favored under extreme pressures, this is not the case for nitrogen even at 100 TPa where, for example, the face-centered-cubic structure is almost 2 eV per atom higher in enthalpy than $I4_1/amd$.

In conclusion, we have presented a $P$-$T$ phase diagram for nitrogen using results from first-principles methods. We have used the ab initio random structure searching method to investigate N at TPa pressures. We do not find stable close-packed phases below 100 TPa. We have proposed five additional pressure driven phase transitions and two novel phases with unusual behavior. The $P4/nbm$ structure can be seen as a $(N_4^{\delta+}N_4^{\delta-})_2$ metallic salt, formed from dimers and tetrahedra. The layered $P2_1$ structure also shows strong charge transfer and an undulation resembling a CDW. Our ab initio molecular dynamics and Z-method calculations provide a first estimate of the melting curve of nitrogen at TPa pressures.

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