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# Synthesis of non-molecular nitrogen phases at Mbar pressures by direct laser-heating

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*Direct* laser heating of molecular N<sub>2</sub> to above 1400 K at 120-130 GPa results in the formation of a reddish amorphous phase and a transparent crystalline solid above 2000 K. Raman and x-ray data confirm that the transparent phase is *cubic-gauche* nitrogen (*cg-N*), while the reddish color of the amorphous phase might indicate the presence of N=N bonds. The quenched amorphous phase is stable down to at least 70GPa, analogous to *cg-N*, and could be a new non-molecular phase or an extension of the already known  $\eta$ -phase. A chemo-physical phase diagram is presented which emphasizes the difference between pressure- and temperature-induced transitions from molecular to non-molecular solids, as found in other low *Z* systems.

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Extended forms of simple low- $Z$  materials are of fundamental importance in developing condensed matter theory [1,2] and novel materials with advanced mechanical, optical, and energetic properties [3-5]. These materials, however, are typically stabilized at formidable pressure-temperature conditions, thus imposing tremendous technical challenges that at present can only be realized in a diamond anvil cell (DAC). At a pressure of 100GPa (or 1 Mbar) and a compression energy ( $P\Delta V$ ) often exceeding one eV, localized electrons have acquired very high kinetic energy and can therefore mix strongly with valence and core electrons of their own or nearby molecules. Such core swelling and/or valence mixing can induce transformations from molecular to non-molecular extended solids such as polymers and metals [6]. A competing pathway is provided by rapid electronic band broadening leading to an insulator-metal transition. Materials at high temperatures, on the other hand, often transform into open structures like bcc because of the large increase in entropy and eventually ionize, dissociate or even decompose. Combining the effects of extreme pressure and temperature (or *Mbar chemistry*) one can probe the balance between pressure-induced electron delocalization ( $P\Delta V$ ) and temperature-induced electron ionization ( $T\Delta S$ ), as it is reflected in crystal structures, phase boundaries and stabilities.

The behavior of nitrogen presents a prime example. It displays a large number of polymorphs, both molecular and non-molecular [7,8], with widely different intermolecular interactions, crystal structures, and chemical bonds. Among those, the prediction and discovery of *cg-N* are the most celebrated recent example [1,9], where molecular nitrogen in the  $\zeta$ -phase transforms to a non-molecular extended solid with the

atoms arranged in a puckered layer structure. Because *cg*-N is built by strong N-N covalent bonds, replacing substantially weaker intermolecular interactions in  $\zeta$ -N<sub>2</sub>, the material strength of *cg*-N is greatly enhanced to support large lattice strains and exhibits a large activation barrier toward the reverse transformation. In fact, *cg*-N is predicted to be meta-stable even at ambient conditions [10]. Furthermore, the theory [1] predicts that *cg*-N contains a high energy density stimulating the experimental efforts to synthesize it by chemical methods [11].

High-pressure synthesis of *cg*-N poses great experimental challenges. While previous theoretical calculations [1] predicted that transformation conditions should be in reach at a pressure of  $50 \pm 15$  GPa at room temperature the first experimental claim reported a pressure of at least 110 GPa and a temperature of 2000 K [9]. In fact, the discovery appeared to require several key modifications to the traditional DAC geometry, among them the deliberate placement of thin sheets of infrared laser (1064 nm) absorbing materials covering the whole sample chamber to generate the necessary temperatures as well as the use of non-metallic c-BN gasket inserts [9]. While apparently necessary in achieving the transformation conditions the introduction of boron, TiN or platinum have nevertheless cast some doubt on the experimental results, especially with regard to the possibility of highly exothermic reactions between the absorber plates and the nitrogen sample itself as observed by others previously [12-14]. For example, the onset of the reaction between boron and nitrogen under a pressure of 10 GPa requires 1800 K, very similar to the temperatures required for the synthesis of polymeric nitrogen [12]. Moreover, the synthesis of other nitrides, such as PtN<sub>2</sub> or IrN<sub>2</sub>, from their elemental constituents also requires threshold pressures and temperatures in excess of about 50 GPa

and 2000 K [13,14]. For PtN<sub>2</sub>, one of the ensuing sharp Raman lines actually is observed in close proximity to the spectral position of the previously reported Raman line of *cg*-nitrogen. The authors of ref. [9] provide angle dispersive X-ray scattering data as additional support for their claim, but even those results have recently been questioned [15] and attempts to laser heat nitrogen in sample configurations similar to those in ref. [9] with absorbers and gasket inserts have failed [15].

We therefore attempted *direct* laser-heating of pure nitrogen in the  $\zeta$ -N<sub>2</sub> phase at 120-130 GPa in a traditional DAC geometry and found that it leads to the formation of two extended forms of nitrogen; reddish amorphous nitrogen and transparent crystalline nitrogen analogous to *cg*-N reported previously, as shown in Figs. 1 and 2. The reddish amorphous phase could be new, different from all other phases of nitrogen reported to date, or it could be an extension of the previously observed  $\eta$ -phase. Its existence is important to understand the subtle difference between the pressure- and temperature-induced changes that lead to different forms of the extended phases observed/predicted to date.

For the experiments we employed membrane-driven DAC's designed and fabricated at LLNL equipped with diamond anvils of 100  $\mu\text{m}$  flats beveled out to a diameter of 300  $\mu\text{m}$  at an angle of 8.5°. Ultra high purity nitrogen gas (99.999%) was condensed into a small sample chamber ( $\sim 50$   $\mu\text{m}$  in diameter and  $\sim 25$   $\mu\text{m}$  thick) in a Re gasket in a cryogenic gas loading vessel. Pressures were measured by ruby luminescence up to 100 GPa, above by the diamond phonon line [16] for Raman studies, or by the tungsten equation of state [17] for x-ray studies. Heating was performed by focusing the 1053 nm radiation of two YLF lasers ( $\sim 60$  W) simultaneously onto the samples without use of any

special laser irradiation absorbing agents. Temperatures were either measured by the spectro-radiometric method or estimated.

Angle-dispersive x-ray diffraction (ADXRD) images were obtained at the micro-diffraction beam-line 16IDB of the High Pressure Collaborative Access Team (HPCAT) at the Advanced Photon Source (APS). The recorded two-dimensional diffraction images were then integrated to produce high quality x-ray diffraction patterns using the FIT2D program and analyzed with the XRDA and GSAS software.

Nitrogen transforms into the  $\zeta$ -phase at 70 GPa and develops a brownish color (Fig. 1a and b) above 125-130 GPa indicating the first changes on the way from the  $\zeta$  - to the  $\eta$ -phase. CARS experiments on the sample ( $\lambda_1 = 532$  nm,  $\lambda_2 = 608$  nm) at 133 GPa indicated that the optical absorption gap had decreased into the visible region to about 2.62 eV ( $\lambda_{AS} = 473$  nm or 2.62 eV) since the Anti-stokes radiation of the CARS experiments was almost completely absorbed (reduction by more than a factor 10 compared to the intensity received at 120 GPa). This moment was therefore chosen to initiate laser heating in the hope that the tail of the optical absorption would extend out to 1053 nm (1.178 eV) and facilitate coupling between sample and laser radiation without an absorber plate. Fig. 1 shows images of the first sample from several stages of the experiment: Panels a) and b) show the gradual darkening, c) the sample after the first heating to 1400 K, d) the formation of transparent and dark-red regions after the 2<sup>nd</sup> heating, and e) the sample after pressure release to 80 GPa shortly before gasket failure. Sample 2 went through the same stages with the same features except that after the 2<sup>nd</sup> heating some molecular N<sub>2</sub> was still observed (Fig. 2a) and that a 3<sup>rd</sup> heating converted the amorphous phase back to molecular N<sub>2</sub>.

Both samples – one at 127 and the other at 133 GPa – were heated first to 1400 K. We found a small pressure decrease ( $\sim 2\text{-}5$  GPa) and a color change to more reddish-yellowish, but the Raman spectrum was still characteristic for the  $\zeta$ -phase (Fig. 1c and Fig. 3, curve a). Further heating of the samples to higher temperatures was challenging and required the full power of the laser heating system (on the order of 60 W), which even then lead to a few bright flashes only. They appeared to correlate with the formation of the transparent regions (see Fig. 1d). We estimated the peak temperature of the flashes to be at least 2000 K or higher. The quenched samples showed that two phases were formed from the  $\zeta$ -phase (Fig. 1d and Fig. 2a): dark reddish amorphous nitrogen with virtually no Raman features (Fig. 3, curve b) and the transparent crystalline phase (*cg-N*) exhibiting a sharp vibron at  $865\text{ cm}^{-1}$  (Fig. 3, curve c). Note that the appearance of the  $865\text{ cm}^{-1}$  band correlates with the disappearance of the  $\text{N}_2$  vibron at  $2390\text{ cm}^{-1}$ , clearly indicating the formation of an extended solid with N-N single bonds. No further change of the transparent *cg-N* phase could be induced in subsequent heating attempts, once it was formed; however, the reddish amorphous phase could be transformed further to either *cg-N* or back to the  $\zeta$ -phase in the 2nd sample (see Fig. 2b). This indicates that the amorphous phase forms at somewhat lower temperatures than *cg-N*, presumably between 1400 and 2000 K.

Our observations during laser-heating are similar to the ones made by Eremets et al. [9] in that a darkening of the sample was observed after heating to 1400 K accompanied by a pressure drop but no significant change in the Raman spectrum of the molecular nitrogen. In ref. [9] further heating to 1700 K produced even further darkening with a significant decrease of the molecular vibron. With heating beyond 2000 K the



authors of ref. [9] observed that the molecular Raman signatures in the lattice and vibron region all but vanished while a ring around the absorber plate appeared, which was attributed to melting and instead of further darkening with even higher heat the sample became transparent (albeit not visible in [9] due to the absorber plate). In our case, the sample coupled to the pump radiation only in some locations - mostly close to the edges of the gasket - and produced flashes that were estimated to be higher in temperature than  $\sim 2000$  K but the resulting dark red phase in the center and the large pockets of a transparent new phase are consistent with the observations in [9].

Both the reddish amorphous phase and the transparent *cg*-N phase were quenchable at least down to 70 GPa where gasket failure occurred. The pressure dependence of the  $865\text{ cm}^{-1}$  band is similar to that of the low-frequency Raman mode as calculated for the  $I2_13$  structure (S.G. 199) and published previously [9,10] (Fig. 3 top panel). The Raman mode remains very sharp, FWHM within  $\sim 6.5\text{ cm}^{-1}$ , over the entire range, so it can be used as an un-calibrated but very precise pressure sensor. On the other hand, the reddish amorphous phase (Fig. 1d and Fig. 2a) showed no Raman features (Fig. 3, curve b), kept its color over the entire pressure range (Fig. 1e), and induced strong photo-luminescence from a 488 nm laser beam. Its distinctive reddish color could characterize it as being different from the amorphous nitrogen in the  $\eta$ -phase [18-20] since we are starting out with a brownish/grayish sample color before heating and obtain a reddish color afterwards while the pressure remains almost unchanged. The distinctive red color of the amorphous phase observed here may represent the conversion of  $\text{N}\equiv\text{N}$  triple bonds to conjugated  $\text{N}=\text{N}$  double bonds. This conjecture could also explain the increase in color intensity with further heating since the color of a system of conjugated double bonds (-

N=N-N=N-) intensifies by increasing the number of double bonds [21]. Another explanation would be that simply more molecular nitrogen became converted to the amorphous phase. The presence of conjugated N=N bonds in the red amorphous phase then lowers the activation barrier for the formation of a singly bonded network structure and, thus is likely a precursor to *cg*-N. The absence of this phase in previous experiments [9] might simply reflect the catalytic nature of the nitrogen conversion to *cg*-N on a surface of amorphous boron or TiN, thus by-passing this precursory state. In fact, we consider that such a strong kinetic effect may even retard, if not preclude, the formation of *cg*-N at ambient temperature even at 240 GPa. Further experiments are planned to determine the exact nature of the reddish amorphous phase. Several of our observations indicate that the reddish amorphous phase and the  $\eta$ -phase are quite similar – on the other hand the change to a red color after heating - with the pressure almost unchanged - points to some differences. The fact that the reddish phase can be converted back to molecular nitrogen eliminates impurities as source of the reddish color.

Our x-ray diffraction data confirm the Raman result that the transparent phase is a cubic form of nitrogen. X-ray diffraction images (insert of Fig. 4) suggest moderate to strong preferred orientation. The pattern at 77 GPa contains additional traces of hcp-Re and the pattern at 123 GPa shows the presence of the pressure marker tungsten. The intensity distribution, however, was found to be different from the previous report [9]: while we were able to extend the pattern to include the (321) peak at  $2\theta=25.83^\circ$ , the (220) peak was either absent or barely visible in the patterns, and the (222) peak was also missing. The (hkl) extinction conditions are clearly matched to six cubic space groups:  $I2_13$ ,  $I23$ ,  $I-43m$ ,  $I432$ ,  $Im-3$  or  $Im-3m$ . Density considerations require eight nitrogen atoms per unit

cell. A calculation of the intensity distribution for the last three does not produce a match. The first three space groups, however, allow the Wyckoff positions (8a or 8c) to vary. In principle one could determine the  $x$ -parameter from the intensity ratio of the (110) and (200) ring pattern despite the limited opening of the diamond anvil cell, which affects the diffraction peak intensities mainly at lower  $d$ -spacing. The texture of the sample, however, renders the results for  $x$  and the bond lengths too speculative. For the 77 GPa pattern the best match occurs again for space group  $I2_13$  with  $x=0.034$  and an increase in  $x$  to 0.067 [9] or 0.085 [1] continuously worsens the reproduction of the intensity ratio of the (110) and (200) rings.

The top insert of Fig. 4 shows the present EOS data together with previously determined atomic volumes [22,23]. Fitting a Birch-Murnaghan equation with  $B'=4$  to the  $cg$ -N data results in a zero pressure atomic volume of  $6.69 \text{ \AA}^3$  and a bulk modulus  $B_0$  of 261 GPa. Mailhiot et al. [1] had predicted  $6.67 \text{ \AA}^3$  and a  $B_0$  of 341 GPa, astonishingly close to the present data.

Based on present and previous [18,19,22-25] results, we propose a conceptual chemophysical phase diagram in Fig. 5 with emphasis on the molecular to non-molecular phase transformation. The boundary (dot-dash line) is constructed based on these facts: (i) all laser-heating experiments show that a transition occurs above 110 GPa, below which nitrogen remains molecular. (ii) The transition pressure rapidly increases at temperatures lower than 500K [18,19]. (iii) Theoretical calculations of the Grüneisen parameter  $\gamma = V(\partial P/\partial E)_V$  based on previous shock-wave data [24,26], give rise to a nearly vertical molecular-to-nonmolecular transformation line at temperatures above 2000 K and even deep into the liquid.

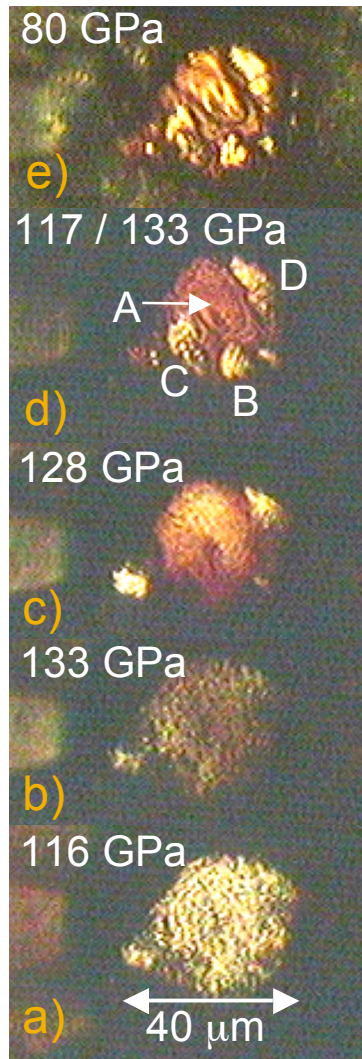
Note the strong curvature in the molecular/non-molecular phase boundary in Fig. 5, which signifies the strong kinetic effects associated with the transition at relatively low temperatures between 400-700K. Therefore, the polymerization to *cg*-N at ambient temperature (blue arrow) is strongly delayed, if not limited, which may in turn provide an alternate route to an insulator-metal transition. The semi-conducting nature of amorphous  $\eta$ -N is perhaps the state arising prior to such a band-gap closure. However, such kinetic issues are less important at high temperatures, as indicated by the nearly vertical transition line. Thus, nitrogen polymerization is relatively more viable at high temperatures (red arrow), as the increase in entropy favors more dissociated states (i.e., less saturated nitrogen bonds). Indeed, the formation of the reddish amorphous phase and then *cg*-N at high temperatures suggests a stepwise opening of the nitrogen-nitrogen triple bonds in  $\zeta$ -N<sub>2</sub> to N=N and then to N-N. This transition model may then be viewed as a concerted *SN*-2 type polymerization [27], with the amorphous phase acting as a “transition” state. While the existence of such an intermediate substantially lowers the transition threshold for the formation of an extended solid, understanding the stability and structure of amorphous nitrogen may be more challenging, both experimentally and theoretically, as it may represent one of many local energy minima existing on a complicated energy landscape [28].

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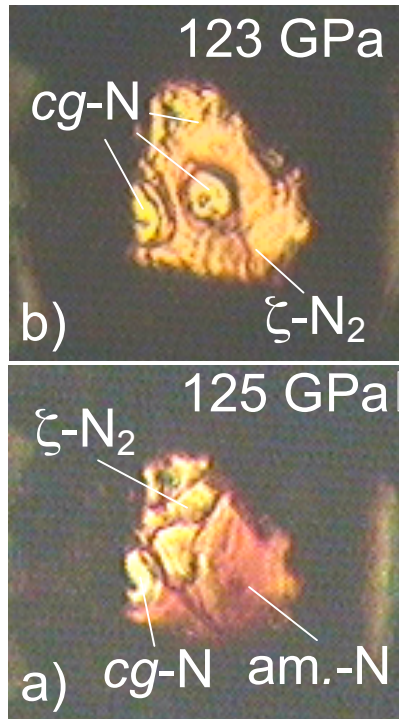
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**FIG. 1** (Color online) Micro-photographic images of nitrogen phases in the first sample. All images were taken at room temperature: a) Sample at 116 GPa – the sample is still transparent. b) At 133 GPa – the sample has begun to darken considerably. c) After the first laser heating to 1400 K. Raman spectroscopy still sees the molecular signature of the  $\zeta$ -phase (see Fig. 3, curve a). d) After the 2<sup>nd</sup> laser heating the sample consists of several phases: Reddish amorphous nitrogen at location A and single-bonded *cg*-N at locations B, C and D. The sample sustains large pressure gradients (117 GPa at A and 133 GPa at B to D). e) The sample after decompression to 80 GPa.

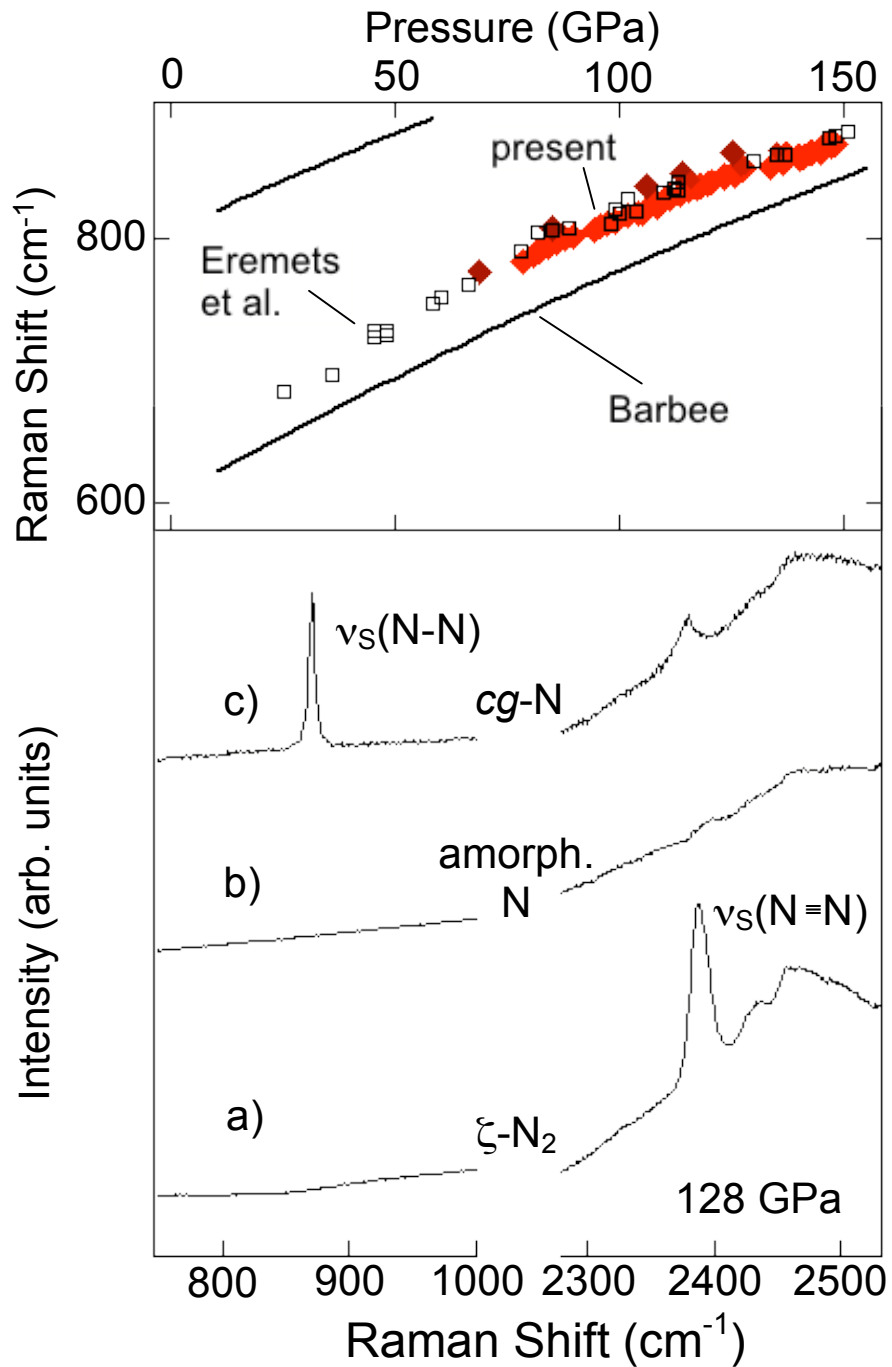


**FIG. 2** (Color online) Micro-photographic images of nitrogen phases in the second sample after the second heating to 2000 K.

a) The sample consists of several phases: Reddish amorphous nitrogen (called am. N), the single-bonded *cg*-N at the left edge, and the remaining  $\zeta$ -N<sub>2</sub>.

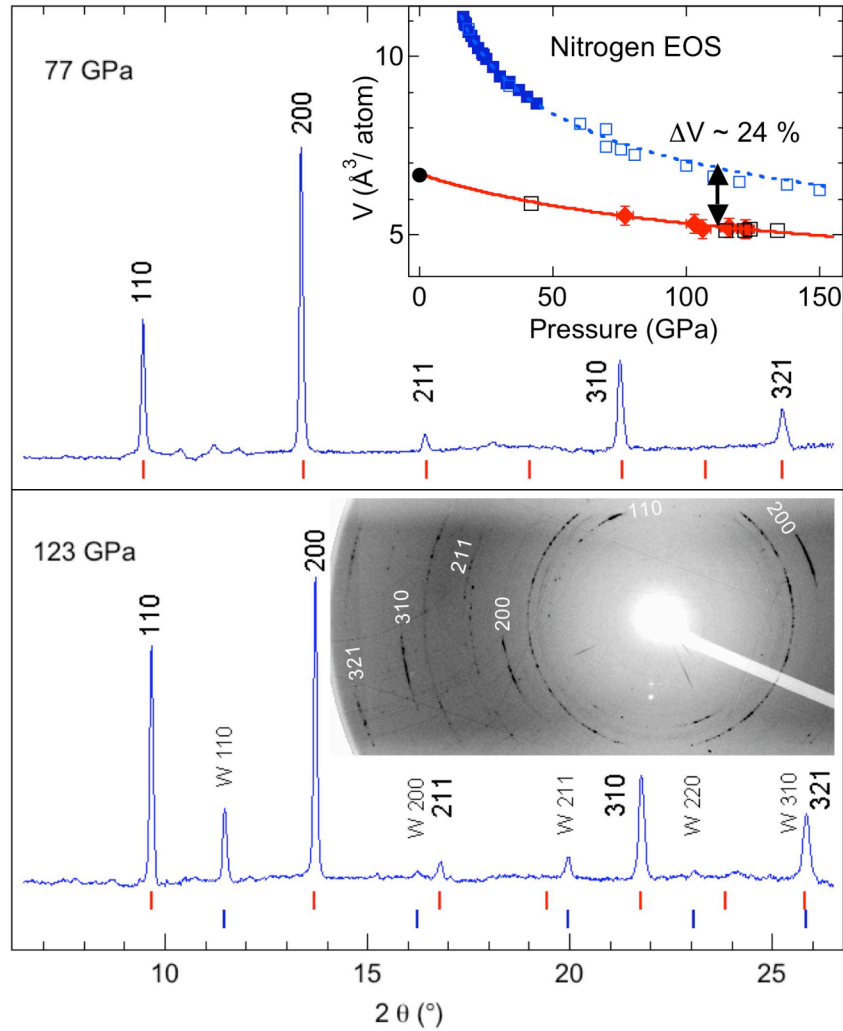
b) A third heating transformed even more of the sample to *cg*-N in the center and at the top while the reddish amorphous phase has reverted back to molecular  $\zeta$ -N<sub>2</sub>. The slightly reddish color indicates that the back-transformation was not complete.



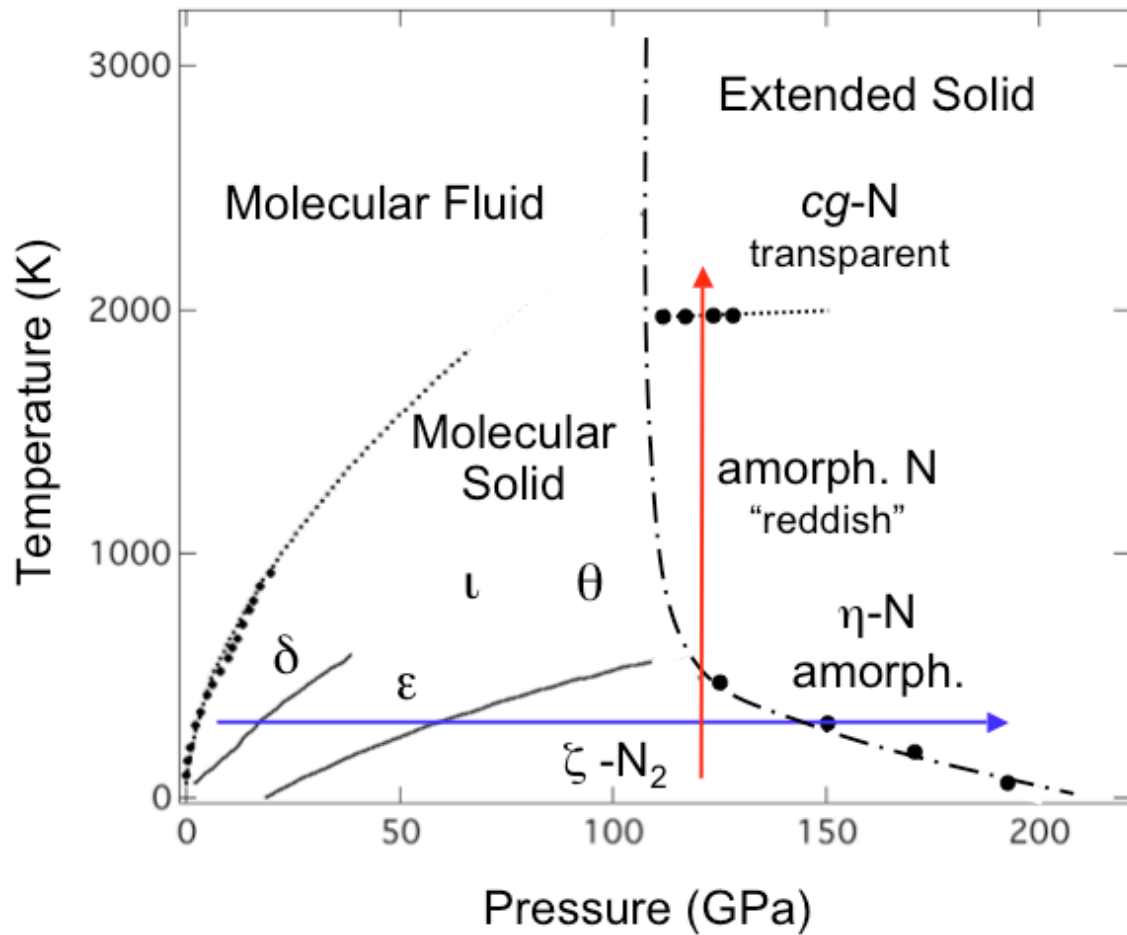


**FIG. 3:** (Color online) Raman spectra taken from quenched nitrogen after laser-heating at 128 GPa. Bottom panel: (a) Un-transformed  $\zeta$ -N<sub>2</sub>. (b) Amorphous red phase as shown in Fig. 1d or 2a. (c) *cg*-N as recorded from the bright locations in Fig. 1d or e) and Fig. 2b.

Top panel: Pressure shift of the Raman peak of the N-N bond: Red symbols represent current data, the black lines calculations [10] and the hollow squares previous measurements [9].



**FIG. 4** (Color online) X-ray diffraction patterns of *cg*-N at 123 GPa and 77 GPa after direct laser-heating. Beam size 6 x 6  $\mu\text{m}$ , wavelength 0.4125 Å. The 123 GPa pattern originates from the center close to the W pressure sensor (Fig. 2b). The 2D-image identifies the diffraction rings of *cg*-N. The 77 GPa pattern shows the diffraction at the center away from the W pressure sensor with small traces of  $\zeta$ -N<sub>2</sub> and the Rhenium gasket. (Top insert) Atomic volume of *cg*-N vs. pressure: Blue filled and hollow squares represent molecular N<sub>2</sub> [22,23], the blue dashed line a Birch-Murnaghan fit. Red diamonds show the EOS data of *cg*-N from the present study, hollow black squares from previous data [23]. The black dot at  $p=0$  signifies the theoretical prediction [1].



**FIG. 5:** (Color online) Conceptual phase/chemical transformation diagram of nitrogen illustrating the molecular to non-molecular transition at high pressures and temperatures. The transition boundary (dot-dash line) is based on present and previous high-pressure data [9,18,19,22-26]. The melt curve (dotted line) represents a Simon-type extrapolation of previous melt data (small black dots) [25]. The molecular  $\alpha$ -,  $\beta$ -, and  $\gamma$ -phases at low pressures are not shown. Note that  $\zeta$ -N<sub>2</sub> transforms into semi-conducting amorphous  $\eta$ -N at low temperatures, yet becomes reddish amorphous nitrogen at medium and transparent *cg*-N at high temperatures. The strong curvature of the phase boundary at lower temperatures signifies the strong kinetic effects associated with the molecular-to-non-molecular transformation. Blue (compression) and red (heating) arrows represent experimental pathways.