Pressure-Driven Energy Band Gap Narrowing of λ-N_2

Yue Li(李月)[1], Jingyi Liu(刘静仪)[1], Binbin Wu(吴彬彬)[1], Yu Tao(陶雨)[1], Yanlei Geng(耿延雷)[2], Xiaoli Wang(王晓丽)[2*], and Li Lei(雷力) [1*]

[1]*Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China*
[2]*School of Physics and Electronic Information, Yantai University, Yantai 264005, China*

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Probing the energy band gap of solid nitrogen at high pressures is of importance for understanding pressure-driven changes in electronic structures and insulator-to-metal transitions under high pressure. The λ-N_2 formed by cold compression is known to be the most stable one in all solid nitrogen phases observed so far. By optimizing the optical system, we successfully measured the high-pressure absorption spectra of λ-N_2 covering the polymeric-nitrogen synthetic pressures (124 GPa–165 GPa). The measured optical band gap decreases with increasing pressure, from 2.23 eV at 124 GPa to 1.55 eV at 165 GPa, with a negative pressure coefficient of −18.4 meV/GPa, which is consistent with the result from our *ab initio* total-energy calculations (−22.6 meV/GPa). The extrapolative metallization pressure for the λ-N_2 is around 288(18) GPa, which is close to the metallization pressure (280 GPa) for the η-N_2 expected by previous absorption edge and direct electrical measurements. Our results provide a direct spectroscopic evidence for the pressure-driven band gap narrowing of solid nitrogen.

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There is a great interest in investigating the insulator-to-metal transitions in classical simple diatomic molecules (such as H_2, O_2, and N_2) at controlled pressures.[1–3] The high-pressure dissociation process generally involves intermolecular and intramolecular transitions, which may lead to reduction of atomic spacing and enhancement of interaction between close neighboring molecules and affect the symmetry, bonding, electronic structures, etc.[4–8] The band overlap caused by the compression is an important factor in promoting the transformation of molecules into atomic and even metallic states.[4] It is believed that the transformation of hydrogen into a solid metallic state at ultrahigh pressures could be experimentally evidenced by high-pressure absorption and reflection spectroscopy.[9–12] Significant increases in conductivity have been observed at high pressure in the dense hydrogen,[10] and the visible absorption spectroscopy of hydrogen has also been successfully measured up to 310 GPa, with the relationship between the band gap and the pressure obtained.[7]

Similarly, it was also expected that solid nitrogen would undergo a transition to a metallic state at high pressure with progressive depletion of the energy band gap.[8,13–16] Under high pressure, solid nitrogen experiences significant changes in optical transmittance, from transparent to opaque,[14] which reflects the possible pressure-driven energy band gap closure. The dimming of nitrogen means that it enters the visible light range (1.6 eV–3.1 eV) from the ultraviolet region (> 3.1 eV). The optically opaque solid nitrogen may be still a semiconductor non-diatomic phase at 240 GPa, and it has the characteristics of a narrow band gap, the disappearance of Raman and infrared vibrations, and the disordered structure.[15,16] Observing the optical and transmittance change of compressed nitrogen is a direct and simple method to obtain rough relationship between optical band gap and pressure. High-pressure absorption spectroscopy is an important and reliable experimental method to measure optical band gap as a function of pressure. It could provide useful quantitative information on the energy band gap for the dimming nitrogen at megabar pressures.

In 2000, Goncharov *et al.*[14] measured the optical absorption spectroscopy of η-N_2 when it turned yellow and completely opaque, and by analyzing its absorption edge. The light absorption gap is determined to be 0.6 eV–0.7 eV at 151 GPa–160 GPa, showing a negative growth. Eremets *et al.*[15] then combined optical and electrical measurements to study the η-N_2 at different temperatures and pressures, identifying a band gap of 0.4 eV at 240 GPa (300 K). Gregoryanz *et al.*[8] also showed the absorption edge properties of η-N_2 up to 268 GPa by visible transmission spectra, and the extrapolation showed that the metallization of nitrogen would occur around 280 GPa.[8]

Nitrogen is a heavily studied template system, which reveals a highly complex phase diagram, presenting a benchmark for calibrating theoretical simulation methods. Studies have been focused on the molecular-to-polymeric transition in nitrogen due to its potential application as a high-energy-density material (HEDM).[17–26] Under high-pressure and high-temperature conditions (typically > 110 GPa, > 2000 K), the solid molecular nitrogen phase will dissociate, and the intermolecular triple bonds of N≡N will be ruptured, forming different single-bond polymeric phases such as cg-N,[18–21] LP-N,[22,23] PLP-N,[24] HLP-N,[23] and BP-N.[25,26] The polymeric-nitrogen synthetic pressure covers a wide regime, from 110 GPa to 244 GPa.[17] It is noted that the dense nitrogen is typi-

*Corresponding authors. Email: lei@scu.edu.cn; xlwang@ytu.edu.cn
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cally optical opaque at so high pressures, which reflects the narrow energy band gap in the solid nitrogen. This feature is suitable to be laser-heated by a near-infrared ($\sim$1064 nm) ytterbium fiber laser (YFL) to overcome the energy barrier[17,21,24] from molecular to polymeric form.

The λ-N_2, originally discovered in 2016 by Frost,[27] is known to be the most stable solid molecular phase.[28] Recently, an isostructural phase transition in λ-N_2 caused by slight redirection of nitrogen molecules has been observed at approximately 50 GPa at room temperature by our research group.[28] The λ-N_2 exhibits an exceptionally wide range of pressure–temperature (P–T) stability.[28] However, it also gradually moves from transparent towards the opaque direction with the continuous increase of pressure up to 120 GPa,[27–30] which corresponds to a decrease of the optical band gap. Notably, quantitative characterization of piezochromic processes is still lacking. Probing the energy band of solid nitrogen at high pressures is helpful in revealing the pressure-induced electronic structural properties, and may provide useful information on the pressure-induced dissociation and metallization transformation of the diatomic molecular systems.

In this Letter, we systematically investigate properties of dense nitrogen by combining experimental and theoretical methods, optimize the high-pressure absorption spectroscopy system, and successfully obtain the optical band gap of λ-N_2 at pressures from 124 GPa to 165 GPa by analyzing its absorption edge. First-principle calculations are also performed to analyze the band gap and structural properties. The spectroscopic results are also compared with the previous data of η-N_2 and solid hydrogen, providing valuable information to deepen the understanding of its structure-property relationship.

In our high-pressure experiments, a 100 μm culet diamond anvil cell (DAC) was used, and we pre-compressed a high purity rhenium sheet with thickness from 250 μm to 4 μm as the gasket material. A circular sample chamber with a diameter of about 30 μm was cut with a laser. The λ-N_2 was formed by direct compression of purity liquid nitrogen ($>$99.9%) at low temperature (77 K) from ambient pressure. After the DAC was warmed to room temperature, it was continuously compressed from 109 GPa up to 165 GPa (at room temperature) for the Raman and absorption spectroscopy measurements. The pressure was calibrated by the high-frequency edge of the diamond phonon.[31] High-pressure Raman experiments were performed on a custom-built confocal Raman spectroscopy system with an EMCCD (Andor DU970P-BVF) as the detector and excited by employing a wavelength of 532 nm (RGB Nova Pro, 300 mW) with power of 50 mW, in collection with a Mitutoyo objective (M Plan Apo SL 20×, W.D. = 34 mm, N.A. = 0.28).[28,29] The high-pressure absorption spectroscopy measurement system uses a stable light source as the incident laser directly coupled with the sample [Fig. 1(a)], which provides a fairly wide spectral range from ultraviolet to near-infrared, approximately from 215 nm–2500 nm. A color-temperature-balancing color glass filter was employed to make the deuterium lamp output a uniform spectrum.

For simple diatomic molecular systems, a UV-vis absorption spectroscope is used to measure the absorption cutoff edge of light to determine the band gap width. The effect of high pressure on the absorbance of substances is usually indirect, due to the enhancement of intermolecular interaction of ultra-high-pressure strong solid nitrogen, the frequency of intermolecular collisions increases, which causes changes in the band structure. It is important to note that when molecular nitrogen becomes optically opaque in UV-vis absorption experiments, it does not mean that metallization has occurred.[16] During the measurement process, there is a great loss due to the scattering of light and refraction of the objective lens. Conventional absorption spectroscopy is not suitable for measuring solid nitrogen at megabar pressures because it is difficult to achieve double-point confocal in a small sample cavity ($\sim$20 μm). With the coaxial transmit-receive system using two symmetrical objectives, the light source is illuminated to the sample chamber through the DAC, ensuring that the transmitter and the receiver are focused at the same spatial point.

Limited by objectives and instruments, in this work we mainly studied the band 380–800 nm in the high-pressure absorption experiment. The incident spot was approximately 25 μm, which is 5 μm smaller than the sample chamber. This was one of the indispensable conditions for the successful measurement of absorption spectroscopy for samples with pressures above 100 GPa. The optical band gap above 5 eV is difficult to be measured directly due to the diamond self-absorption feature from the DAC.

We performed structural optimization using a methodology based on *ab initio* total-energy calculations within the framework of density functional theory.[32] Geometrical optimization and electronic properties calculations were executed using the Vienna *ab initio* simulation package (VASP).[33] The exchange–correlation functional within the generalized gradient approximation Perdew–Burke–Ernzerhof,[34,35] the B3LYP hybrid functional,[36] the HSE06 hybrid functional,[37,38] and the metaGGA-SCAN hybrid function were successively employed for single-point energy calculations.[39] The projector-augmented-wave method was employed with nitrogen potentials,[39] taking N $2s^2 2p^3$ as valence electrons adopted from the VASP potential library. The Van der Waals density functional, namely optB86b-vdW, was adopted to treat dispersion forces. The cutoff energy (900 eV) for the expansion of the wave function into plane waves and Monkhorst–Pack k-meshes (k-points density 0.02 Å^{-1}) are chosen to ensure that all the enthalpy calculations are well converged to be better than 1 meV/atom.[40] Our work demonstrated an optimized monoclinic structure (λ-N_2 with space group $P2_1/c$; a = 2.918 Å, b = 2.893 Å, c = 5.550 Å, and β = 132.517 Å for lattice parameters; x = 0.069, y = 0.375, and z = 0.454 for N fractional atomic coordinates at 40 GPa. ζ-N_2 with space group $P222_1$; a = 4.159 (2) Å, b = 2.765 (2) Å, and c = 5.039 Å for lattice parameters; x_1 = 0.3975, y_1 = 0.8666, z_1 = 0.1989, x_2 = −0.0799, y_2 = 0.6409, and z_2 = 0.0592 for N fractional atomic coordinates at 80 GPa). Additionally, we investigated the variation of the band gap in the pressure range of 50 GPa–200 GPa

and compared it with the experimental results.

The λ-N_2 obtained at low temperature and high pressure exhibits a very wide range of stability intervals, 5 GPa–110 GPa at 77 K and 30 GPa–176 GPa at 300 K, which was found to be the most stable solid molecular nitrogen known so far.[28] Figure 2(b) shows our experimental path in the P–T phase diagram of λ-N_2. With the pressure increasing, the λ-N_2 changes from transparent to opaque [Fig. 1(c)]. When the pressure reaches 130 GPa, a dark red shadow appears in the middle of the sample chamber, and the light transmittance of the sample begins to decrease. Subsequently, when the pressure reaches up to 165 GPa, the nitrogen sample is completely blackened, accompanied by the gradual weakening of the high-frequency vibrons and low-frequency lattice modes, also the broadening of the Raman signal [Fig. 1(d)]. Philip *et al.* reported that this change of the Raman signal may be related to the pressure-driven optical energy band gap closure associated with the enhancement of intermolecular interactions.[41] This is also consistent with the results of previous generations,[27–29] with optical transparency and obvious λ-N_2 properties. For comparison, the ζ-N_2 phase begins to show brown at 70 GPa, and conventional solid molecular nitrogen will begin to dim above 120 GPa at room temperature, corresponding to the η phase.

High-pressure visible absorption spectra of λ-N_2 in the pressure range from 124 GPa to 165 GPa are shown in Fig. 2(a). The detection of photons must pass through a pair of diamond anvils, so we first need to measure the absorbance of the diamond anvil cell without loading any sample as the relative incident light intensity I_0. By collecting transmitted light intensity I, and incident light intensity I_0, we are able to measure the optical band gap of the high-pressure sample. A distinct absorption peak appears at about 480 nm, and as the pressure increases, the absorption peak shifts and widens to a longer wavelength direction, in which the absorbance of solid nitrogen gradually increases. Electronic band structure of λ-N_2 at 100 GPa [Fig. 2(c)] with calculations, showing a direct band gap characteristics. This compression-induced discoloration can also be fitted to its corresponding optical band gap by the *Tauc* formula as follows:[42–44]

$$(\alpha h\nu)^2 = A(h\nu - E_g), \tag{1}$$

where α is the absorption coefficient, h is the Planck constant, ν is the frequency, A is a constant, and E_g is the semiconductor energy gap. The optical band gap can be determined to be 2.23 eV at 124 GPa of λ-N_2 [Fig. 2(b)]. The direct band gap of λ-N_2 exhibits negative pressure dependence. As the pressure increases, the corresponding optical band gap decreases. When solid nitrogen becomes completely opaque, the optical band gap is about 1.55 eV at 165 GPa. As depicted in Fig. 2, a dramatic surge in absorbance is observed when λ-N_2 abruptly turns darker at around 140 GPa, with a distinct jump occurring between pressure points of 136 GPa and 140 GPa. The opacity at 140 GPa is quite pronounced due to the internal stress concentration of the solid molecular nitrogen, and the absorbance also changes significantly under a small pressure gradient. We believe that it is still a semiconductor state at this pressure. The slope fitted in the range of 124 GPa–165 GPa is around −18.4 meV/GPa. Our calculation also shows that the atomic volume parameter of λ-N_2 is lower than that of ζ-N_2 at the same pressures [Fig. 2(e)].

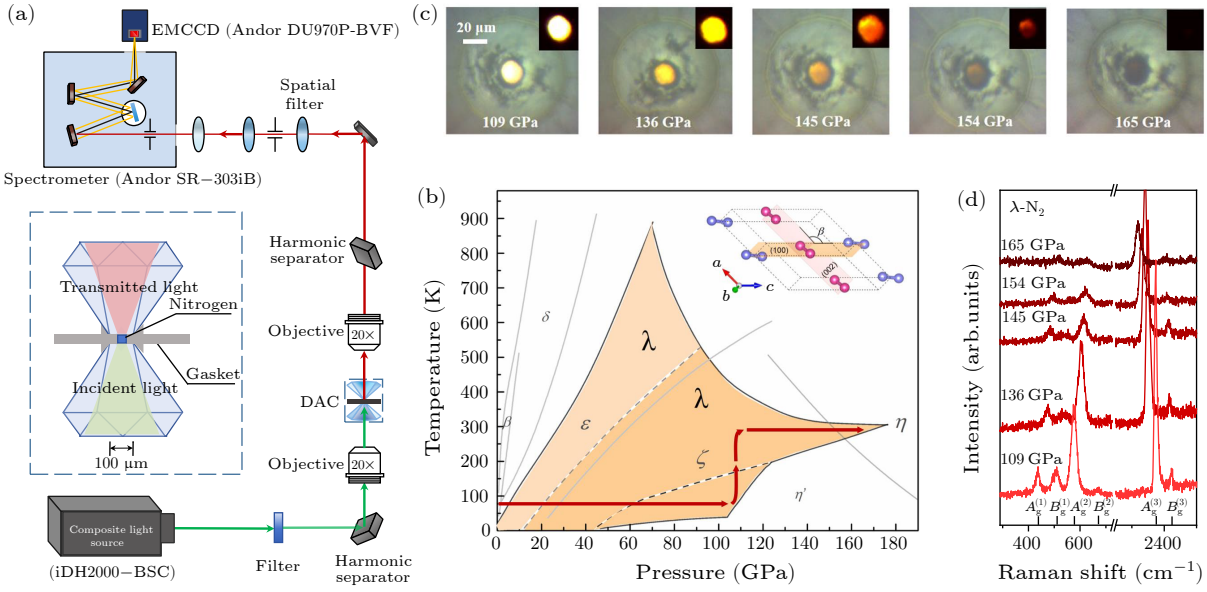

Fig. 1. (a) Schematic diagram of the high-pressure absorption spectroscopy system. (b) The experimental path on the P–T phase diagram of nitrogen. The orange section is the stable region of the λ-N_2, inset is the crystal structure of λ-N_2. (c) The photomicrograph of the sample cavities at different pressures, showing the transmission visual observation of the sample with or without projected light (right-top). (d) The high-pressure Raman spectra of the λ-N_2 at the measurement points for absorption spectroscopy.

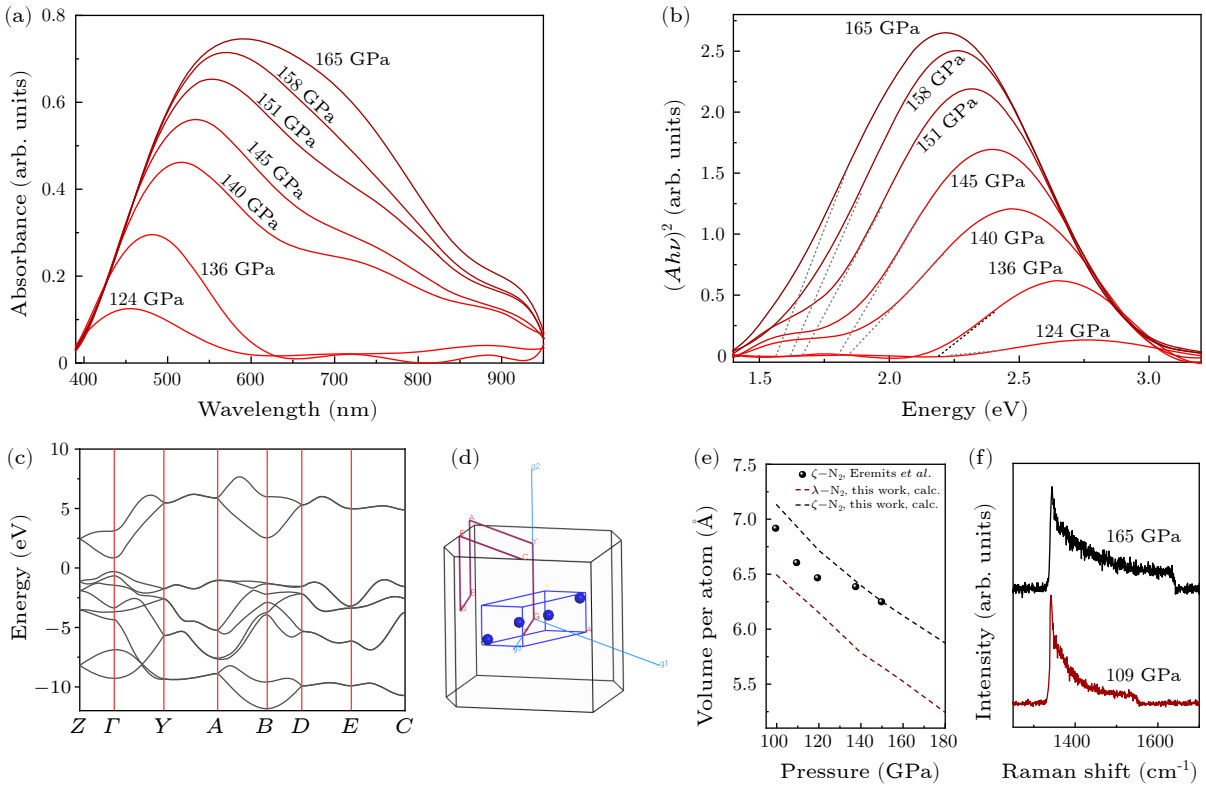

Fig. 2. Typical high-pressure absorption spectra of λ-N_2. (a) The optical absorption spectra collected at different pressures; (b) the optical band gap extracted from the absorption spectra in (a) by fitting the curve with the *Tauc* relation. Calculated (c) band structure for structure nitrogen at 100 GPa at 0 K. (d) Brillouin zone of λ-N_2. (e) P–V compression curves for ζ-N_2 and λ-N_2. Solid black shapes represent the available experimental data for ζ-N_2.[45] The red dashed lines represent our calculation data for λ-N_2, and the black dashed line for ζ-N_2. (f) The diamond Raman spectra at 109 GPa and 165 GPa.

Optical observations suggest that at sufficiently high pressure, the molecular solid becomes opaque and its optical band gap decreases accordingly.[7,8,14,15] Figure 3 shows the correlation between the measured and calculated energy band-gap values as a function of the applied pressure for the solid nitrogen and hydrogen. Since the tangent points taken are slightly different during data processing, and the intersection points determined by the same pressure are different, we show the existence of this deviation with an error bar. The optical band gap of λ-N_2 is relatively higher than that of the amorphous η-N_2, and the E_g for all solid molecular phases in response to an external pressure P is a negative correlation. The relationship can be expressed as

$$\frac{dE_g}{dP} = a. \tag{2}$$

The proportionality constant a is called the band-gap pressure coefficient, which is related to the relative volume under high pressure. The decrease of a indicates the increase of ionicity in semiconductors of groups Ⅳ, Ⅲ–Ⅴ, and Ⅱ–Ⅵ.[46] In molecular solids, the symmetry changes caused in the ordering of molecular orientations and the enhancement of intermolecular interaction are reflected by the changes of the energy bands. The value of a derived from our experiments (−18.4 meV/GPa) is in rough agreement with our theoretical calculated value (−22.6 meV/GPa), suggesting the E_g narrowing of λ-N_2. Theoretical calculation of the band gap shows the results lower than the experimental data, which is also related to low temperature in calculation. Through linear extrapolations, the metallization pressure for λ-N_2 could be about 288(18) GPa, which is very close to the extrapolative metallization pressure for the η phase, 280(12) GPa.

We find that the high-density solid molecular phase possesses higher band-gap pressure coefficients. The λ-N_2 formed by cold compression is found to have a higher density as compared to other normal solid phases.[28] Due to the η-N_2 being an amorphous phase, the P–V curve cannot be calculated accordingly, here we suppose that the density of η-N_2 is consistent with its former amorphous η-N_2 phase in terms of the P–V relation. The high-density λ-N_2 has higher E_g and an absolute value of a as compared to other solid molecular phases [Fig. 3(a)]. Similarly, the solid hydrogen enters the Ⅲ phase at 190 GPa and the Ⅳ phase above 220 GPa upon room-temperature compression,[7] the absolute value of a increases from 4.7 meV/GPa (Ⅲ phase) to 12.0 meV/GPa (Ⅳ phase) as shown in Fig. 3. Interestingly, the variation of nitrogen η phase is similar to that of the hydrogen Ⅲ phases, and the slope of λ phase is closed to that of hydrogen Ⅳ phase. Solid nitrogen synthesized by different P–T paths has different chemical bond properties in which atomic distance and energy are different,[24,47] and high-energy nitrogen molecules have greater mobility, which is also the reason for increasing light absorption and stabilizing λ-N_2 band gap. This may also be related to lattices-induced dipole moments or molecular binding. The molecular phase λ-N_2, which is evenly more stable than ζ-N_2, would dissociate

under high pressure and turn into amorphous polymeric phase η-N_2. This transition from the semiconducting to the metallic phase happens at precisely the same conditions as observed through spectroscopy and direct electrical measurements. It is worth noting that the "chemical pressure" is stronger than the "physical ones" and that the strong intramolecular bonding can be broken by pressure.[48] The intra-molecular triple bonding appears to independent of the crystal structure and turns into the single bonded state under pressure. With the pressure increases, both the lattice constant and intramolecular bond index decrease. High-pressure phases at room temperature exhibit increasing bond strength, resulting in the electron localization and faster band closure.

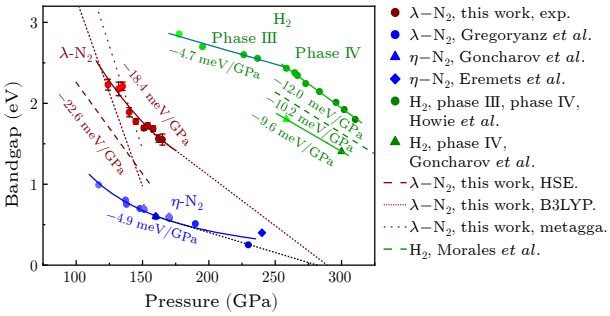

Fig. 3. Energy band gap as a function of pressure for solid molecular nitrogen and solid molecular hydrogen. The red gradient solid circle is the band gap of λ-N_2 obtained with absorption spectroscopy in this work, and the red dashed line is our calculated value. The data presented correspond to the following works: Gregoryanz *et al.*[8] and Goncharov *et al.*[14] measured the band gap of η-N_2 with pressure by absorption spectroscopy, including decompression date for the pressure below 150 GPa. The electronic measurement results of Eremets *et al.*[15] are represented by solid blue. Here we also list the band gap of hydrogen using green solid: Howie *et al.*[7] and Goncharov *et al.*[49] The green dashed line shows the nonlocal vdW-DF2 exchange-correlation functions by Morales *et al.*[50]

In summary, we have measured high-pressure absorption spectra of λ-N_2 at pressures from 124 GPa (2.23 eV) to 165 GPa (1.55 eV), and found that the optical band gap is negatively correlated with the pressure (-18.4 meV/GPa). It is deduced that the band gap of λ-N_2 would be closed at the pressure of 288(18) GPa. Our results provide valuable information on the energy band gap of solid nitrogen at high pressures.

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