Communication



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# Single-Crystal X-Ray Diffraction Study of $CuN_2$ at 50 GPa

**Huawei Chen [1,2], Mohammad F. Mahmood [1], Gaston Garbarino [3], Mohamed Mezouar [3] and Alexander F. Goncharov [2,*]**

[1] Department of Mathematics, Howard University, Washington DC 20059 U.S.A
[2] The Earth and Planets Laboratory, Carnegie Science, Washington DC, 20015, U.S.A.
[3] European Synchrotron Radiation Facility, Grenoble Cedex F-38043(France)
* Correspondence: agoncharov@carnegiescience.edu

**Abstract:** We report single-crystal X-ray diffraction data for the $CuN_2$ phase at 50 GPa. $CuN_2$ crystallizes in a hexagonal structure with lattice parameters: a = 2.692(1) Å, and c = 7.199(2) Å, belonging to the space group $P6_3/mmc$, consistent with previous powder diffraction studies. The N-N bond length is determined to be 1.19(1) Å, indicating a double bond between nitrogen atoms under these conditions. Using an empirical equation to estimate the formal charge, we calculate the copper oxidation state to be approximately +1.2. This study highlights the importance of single-crystal X-ray diffraction in precisely determining crystal structures and intermolecular distances under high-pressure conditions.

**Keywords:** copper; nitride; diamond-anvil cell

## 1. Introduction

Transition metal nitrides have attracted significant research attention as potential high-energy density materials (HEDMs).[1–5] Copper nitrides, in particular, have been investigated as HEDMs up to 50 GPa, where the $CuN_2$ phase has been previously observed.[6] However, the limitations of powder X-ray diffraction, such as difficulties in accurately determining oxidation states and N–N bond lengths, have led researchers to rely on density functional theory (DFT) calculations to infer these properties.[6] In contrast, single-crystal X-ray diffraction provides superior precision in resolving crystal structures and atomic positions, especially for compounds synthesized under high-pressure conditions.[7,8] The N-N bond length in polynitrides significantly influences related physical properties such as metallicity and bulk modulus.[2,7] Therefore, single-crystal X-ray diffraction of the $CuN_2$ phase is essential for elucidating its crystal chemistry under high-pressure conditions.

## 2. Results

Using powder diffraction, the crystal structure of $CuN_2$ was indexed to a hexagonal phase with lattice parameters a = 2.70(1) Å and c = 7.21(1) Å at 50 GPa as determined with UNITCELL.[9] These results are based on X-ray diffraction data presented in Figure 1. The starting materials, copper and nitrogen, were also identified in the diffraction patterns.[10] The refined crystal structure of $CuN_2$, resolved using single-crystal X-ray diffraction, is shown in Figure 2. The refined crystallographic data for $CuN_2$ at 50 GPa are presented in Table 1.

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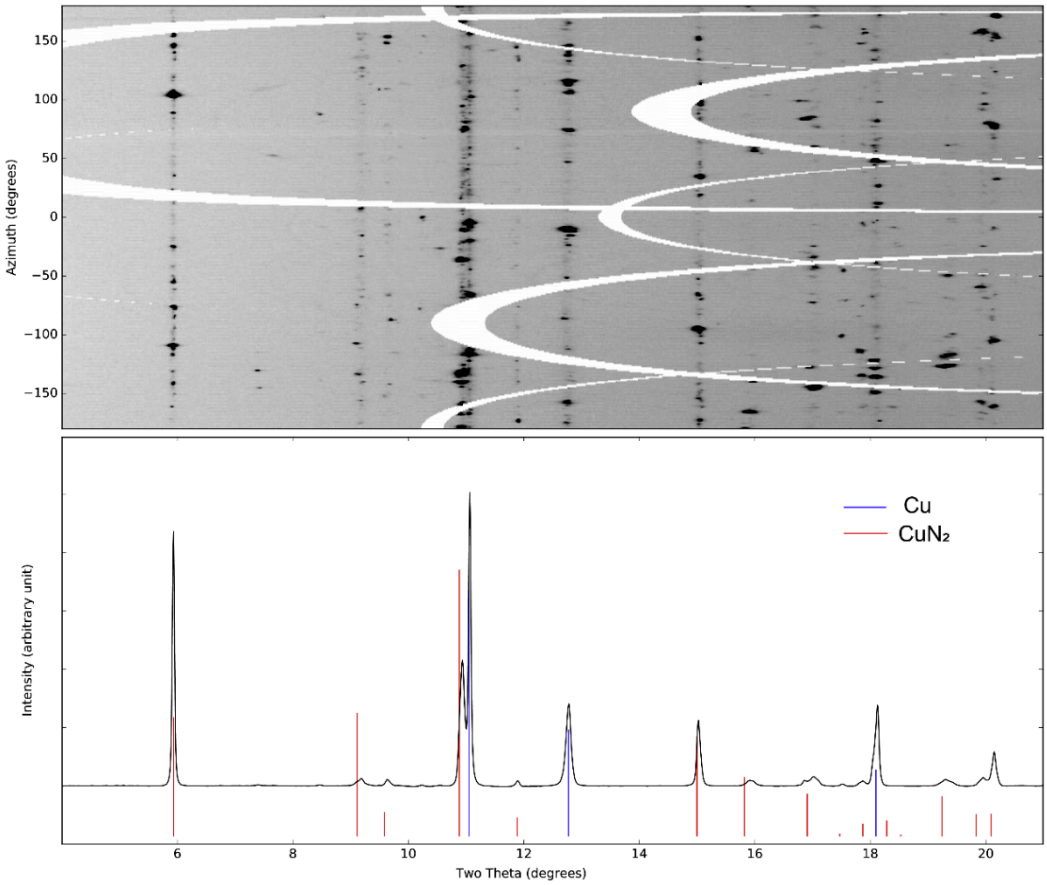


**Figure 1.** X-ray diffraction pattern and corresponding 2D diffraction ("cake") images collected after laser heating. The pattern is indexed to $CuN_2$ (red), ε-nitrogen (minor peaks not indexed in the image), and unreacted copper (blue).

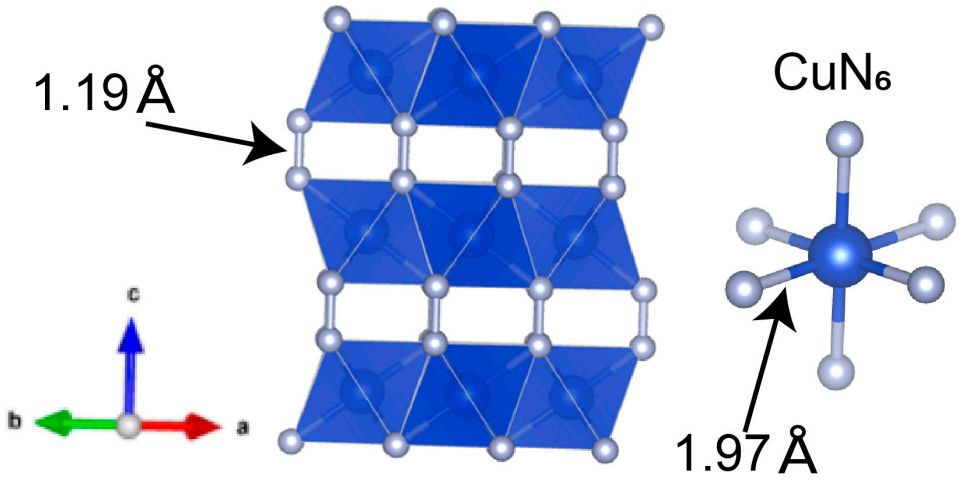


**Figure 2.** Crystal structure of $CuN_2$ at 50 GPa. Blue octahedra represents Cu-N coordination, with each Cu atom surrounded by six nitrogen atoms. The N-N bond is shown in light blue. The Cu-N bond length is 1.97(1) Å.

**Table 1.** Crystal structure parameters and refinement statistics for $CuN_2$ obtained from single-crystal X-ray diffraction at 50 GPa.

| Single crystal report for | $Cu_2N_4$ |
|---|---|
| Formula weight | 183.118 |
| Temperature/K | 300 |

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| | |
|---|---|
| Crystal system | hexagonal |
| Space group | $P6_3/mmc$ |
| a/Å | 2.6921(9) |
| b/Å | 2.6921(9) |
| c/Å | 7.1992(16) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 120 |
| Volume/Å$^3$ | 45.19(2) |
| Z | 1 |
| $\rho_{calc}$g/cm$^3$ | 6.73 |
| μ/mm$^{-1}$ | 3.997 |
| F(000) | 86.3 |
| Radiation | synchrotron ($\lambda$ = 0.37380) |
| 2Θ range for data collection/° | 12.84 to 40.6 |
| Index ranges | $-1 \le h \le 1$, $-4 \le k \le 4$, $-13 \le l \le 12$ |
| Independent reflections | 23 [$R_{int}$ = 0.5167, $R_{sigma}$ = 0.2578] |
| Data/restraints/parameters | 23/0/5 |
| Goodness-of-fit on $F^2$ | 1.408 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0836, $wR_2$ = 0.2064 |
| Final R indexes [all data] | $R_1$ = 0.0895, $wR_2$ = 0.3216 |

Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$)

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| N | 3333 | -3333 | 6676(13) | 8(2) |
| Cu | 0 | 0 | 5000 | 33(3) |

## 3. Discussion

Our single-crystal X-ray diffraction results are generally consistent with previous powder X-ray diffraction studies conducted at similar pressures.[6] We confirmed the crystal structure and atomic bonding in the $CuN_2$ phase. However, unlike powder diffraction, single-crystal X-ray diffraction allows for precise determination of bond distances. The N–N bond length was determined to be 1.19(1) Å, suggesting the presence of a $(N\text{-}N)^{2-}$ unit.[2,7] This value closely matches DFT calculations, which report an N–N bond length of 1.197 Å.[6] Additionally, the Cu–N bond distance was determined to be 1.97(1) Å. No evidence of a Jahn–Teller distortion was observed, indicating that the oxidation state of copper in $CuN_2$ is likely not +2. Given the critical role of N–N bonding in determining the oxidation state of copper and the physical properties of polynitrides—such as metallicity and bulk modulus—we estimated the copper oxidation state using an empirical equation.[2] The equation relates N–N bond length (BL) to the formal charge (FC) of the $N_2^{n-}$ unit: BL = 0.074(1) Å · FC + 1.104 Å. Using the measured N–N bond length of 1.19(1) Å for $CuN_2$ at 50 GPa, we calculate the formal charge of the N–N unit to be approximately –1.2(1). This value is consistent with DFT calculations, which estimate the copper oxidation state to lie between +1 and +2.[6]

## 4. Materials and Methods

Diamond anvil cell experiments: A rhenium (Re) gasket was indented, and a center hole was drilled to form a sample chamber. The indented gasket was placed between two opposing diamond anvils. Copper metal was loaded into the sample chamber, and high-purity nitrogen gas was then introduced using the gas-loading system at the Earth and Planetary Laboratory (EPL), Carnegie Science. The DAC was then compressed to target pressures for subsequent laser heating.

Laser heating experiments were conducted at EPL. In a typical experiment, an infrared laser was directed onto the sample, and X-ray diffraction data were collected after laser heating. The X-ray wavelength used was 0.3738 Å at beamline ID27 of the European Synchrotron Radiation Facility

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(ESRF).[11] Two-dimensional diffraction images were integrated into one-dimensional patterns using Dioptas[12] software. We used 1s exposure time for collecting powder X-ray diffraction patterns. A 1-second exposure time was used for collecting powder X-ray diffraction patterns. The resulting diffraction patterns were plotted using Peakpo.[13]

Single-crystal X-ray diffraction data were acquired from selected spots after laser heating. The diamond anvil cell was rotated up to ±30° to collect single-crystal diffraction data. Orthoenstatite crystals were used to calibrate the single-crystal diffraction setup. The orthoenstatite, with the composition $(Mg_{1.93}Fe_{0.06})(Si_{1.93}Al_{0.06})O_6$ crystallizes in the orthorhombic space group, *Pbca* with lattice parameters a = 8.812(1) Å, b = 5.183(1) Å, and c = 18.239(1) Å. Data integration and reduction were performed using CrysAlisPro.[14,15] The crystal structure was solved using Olex2 with the intrinsic phasing method.[15,16] The atomic position of Cu was resolved, and electron density maps were examined for residual electron density, which was interpreted as potential nitrogen positions. The structure was refined iteratively until the calculated and observed single-crystal X-ray diffraction patterns were in agreement. A typical weighted R-factor (Rwp) of less than 10% was achieved, indicating a reliable structural fit.

**Supplementary Materials:** The following supporting information can be downloaded at the website of this paper posted on Preprints.org.

**Author Contributions:** Conceptualization, HC, AFG and MFM.; methodology, GG and MM.; software, AFG.; validation HC, AFG and MFM.; formal analysis, HC.; investigation, HC.; resources, MFM.; data curation, AFG.; writing—original draft preparation, HC.; writing—review and editing, AFG.; visualization, HC.; supervision, AFG.; project administration, AFG and MFM.; funding acquisition, AFG and MFM. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** Deposition Numbers 2444907 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe.

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**Conflicts of Interest:** The authors declare no conflicts of interest.

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