Pressure-induced metallization and structural evolution of \( \text{Cu}_3\text{N} \)

J. G. Zhao\(^1\), L. X. Yang\(^1\), Y. Yu\(^1\), S. J. You\(^1\), J. Liu\(^2\), and C. Q. Jin*\(^1\)

\(^1\)Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100080, P.R. China
\(^2\)Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100039, P.R. China

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In situ resistance evolution with pressure of anti-perovskite nitride \( \text{Cu}_3\text{N} \) was measured using the diamond anvil cell (DAC) technique up to 20.0 GPa at room temperature. A sharp drop of resistance from \( 10^5 \) \( \Omega \) at ambient pressure to several \( \Omega \) was observed in the range 3.0–10.0 GPa. This is an indication of the pressure-induced metallization in the \( \text{Cu}_3\text{N} \) semiconductor. Meanwhile we also performed the high-pressure energy dispersive X-ray diffraction experiments on \( \text{Cu}_3\text{N} \) at the pressures up to 39.2 GPa. It was found that a crystal structure phase transition begins to take place at \( \sim 5.0 \) GPa on \( \text{Cu}_3\text{N} \), which is generally consistent with the electronic conductance results.

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1 Introduction

\( \text{Cu}_3\text{N} \) crystallizes into the anti-\( \text{ReO}_3 \) type structure of space group \( \text{Pm}3\text{m} \), with the lattice constant being 0.3817 nm \([1]\). The Cu atom is in the position of \( 3d \) \((0.5, 0, 0)\) and the N atom is in the B-site of the normal \( \text{ABO}_3 \)-type cubic perovskite structure, with the atomic position being: \( 1a \) \((0, 0, 0)\). At very low temperature (about 300–470 °C) \([2–4]\), \( \text{Cu}_3\text{N} \) decomposes into \( \text{Cu} \) and \( \text{N}_2 \) and becomes a conductor from a semiconductor. So it can be used as the write-once optical recording material upon heating \([4–7]\). Since the 1980s, the \( \text{Cu}_3\text{N} \) film has attracted more and more attention due to its possible application prospects as an optical storage compound. Several groups obtained \( \text{Cu}_3\text{N} \) films through different methods, including reactive sputtering \([4]\), radio-frequency (rf) magnetron sputtering \([5, 8–10]\), molecular-beam epitaxy \([11, 12]\), heteroepitaxial growth \([13]\), ion-assisted vapor deposition \([14]\), etc. Since the lattice mismatch as well as the different thermal expansion coefficient between the thin film and the substrate always leads to strain, it is important to learn how pressure will affect the structure and consequently the physical behaviors of this functional material. This can be very well reflected in the strain enhancement on the superconducting transition temperature of high-\( T_c \) cuprates \([15]\). Pressure, temperature and chemical potential are three common thermodynamical parameters to control the matter state. The knowledge about the pressure behavior is very helpful to fully understand the overall properties of materials. At ambient pressure and temperature, \( \text{Cu}_3\text{N} \) is cubic without distortion. Six Cu atoms form an octahedron around one N atom, while two neighboring octahedrons connect each other through their vertex atom of Cu, forming a 3-dimensional crystal lattice. Compared with the normal \( \text{ABO}_3 \)-type perovskite, there is no atom at the A-site in the lattice of \( \text{Cu}_3\text{N} \), which will enable rotations of these \( \text{NCu}_6 \) octahedrons. Also, the low decomposition temperature means weak \( \text{Cu}–\text{N} \) bonding, indicating that it is relatively easy for \( \text{Cu}_3\text{N} \) to be subjected to pressure modification. Moreover, the narrow band gap of about 1 eV observed in

* Corresponding author: e-mail: cqjin@aphy.iphy.ac.cn
Cu$_3$N strongly suggests that pressure-induced metallization could happen since pressure generally increases the conductivity due to band gap narrowing or band overlap effect. So, it is expected that some changes either electronic conductivity or crystal structure, will take place in Cu$_3$N upon compression. Here we report for the first time the joint investigation of the high-pressure properties of Cu$_3$N based on the diamond anvil cell (DAC) technique by using both in situ measurements of resistance versus pressure to study the electronic property, and in situ high-pressure energy dispersive X-ray diffraction experiments with synchrotron radiation to study the structural stability.

2 Experimental

The experiment of the in situ resistance versus pressure was made on an intelligent model ZL5 LCR measuring system. The top size of the culet of the diamond is 500 µm in diameter. Two parallel molybdenum sheets were used as electrodes that are made by photoetching a base substrate composed of phenolic methyl. The electrode thickness is 8–10 µm, while the width of the electrode is 1 mm. The distance between the two electrodes is 60–80 µm. Details of the experimental technique can be found in Ref. [16].

The in situ high-pressure X-ray energy dispersive diffraction experiment on Cu$_3$N was carried out at room temperature at the Beijing Synchrotron Radiation Facilities (BSRF). White radiation was used during the experiment. In our experiment, the culet of diamond is 500 µm in diameter and the hole in a T301 stainless steel gasket is 300 µm in diameter. The powder sample is loaded into the hole in the gasket and the silver powder is covered with the sample as an inner pressure standard. Here we used the equation of state of Ag to calculate the internal pressure [17]. The spot size of the focused X-ray beam was 120 × 120 µm and the storage ring operated at 2.2 GeV and 70–100 mA. In this experiment, the relation of energy of photon and channel was $E = 0.50566 + 0.00839 \times \text{channel}$. The diffraction angle $\theta$ was fixed at 10° in order to avoid the overlap with fluorescent peaks of Cu and Ag in the experimental energy range. From the (111) and (2 00) diffraction peaks of Ag and the formula $E (\text{keV}) \times d (\text{nm}) = 0.619925/\sin \theta$, we obtained the $d$ spacing of the sample at different pressures.

3 Results and discussion

Figure 1 shows the well-reproduced relationships of resistance versus pressure while loading and unloading pressure for Cu$_3$N in three experimental runs with the $y$-axis on a logarithmic scale. In the log $R$-$P$ curve while loading pressure, the initial change at the pressures up to 3.0 GPa is small because a pre-
pressed process up to 2.9 GPa was carried out for Cu$_3$N. It is noted that the resistance of the sample is semiconductor-like with a value of about $10^5$ Ω at ambient pressure. It drops sharply in the pressure range of 3.0–10.0 GPa by about five orders of magnitude and thereafter remains at several ohms while the pressure is above 10.0 GPa, with the value being 3.3 Ω at 20.0 GPa. Clearly this is an indication of the metallization of Cu$_3$N under high pressure. This metallized transition has been confirmed recently by Yang et al. [18] through the in situ high-pressure measurements of resistance versus temperature using the DAC technique, with the metallization pressure being ~5.5 GPa. Since there is a phase transition at several GPa as discussed in the following structure studies, it is thus inferred that the resistance drop was caused by the formation of the new high-pressure phase.

When the pressure is released, the resistance increases very sluggishly. When loading totally returns to ambient pressure, the resistance is only about several Ohms. The electronic property seems to be irreversible after pressure release, but there may be a large deformation in the sample, so the resistance can resume the initial value if the time is enough long after pressure release because the crystal structure phase transition is reversible, as discussed in the following experimental results. Actually, we performed an in situ resistance measurement by pressing the Cu$_3$N up to 5.0 GPa using a conventional cubic-anvil type high-pressure facility. Although the pressure-quenched sample shows the same X-ray diffraction pattern as that of the ambient phase, there was a dramatic drop of the resistance, as we observed in Fig. 1. Tens of days after the pressure release, the Cu$_3$N sample finally recovered to the initial high resistance, which indicates the electronic property can be reversible.

The interesting point is that we observed the pressure-induced metallization of Cu$_3$N at a low pressure of several GPa. This is the pressure range matching the strain force level originated between the thin film and the substrate [19]. This result implies that it is possible to mimic the pressure-induced metallization observed in this experiment merely by tuning the strain effects given a suitable mismatch factor between the substrate and deposited thin film. In that case, this pressure-related property could be considered as a pressure-calibration material.

Figure 2 shows the spectra of X-ray energy dispersive diffraction results of Cu$_3$N at various pressures. The diffraction data are collected in the pressure range of 0–39.2 GPa. There are four peaks of Ag: (111), (200), (220) and (311) and five peaks of the sample, indicated with (a), (b), (c), (d) and (e) in the X-ray diffraction (XRD) patterns. There are also three escaping peaks, indicated with asterisks, that result from the high rank of the peak (111) and (200) of Ag and the peak (b) of sample. All diffraction peaks shift with increasing pressure. The indices of peak (a), (b), (c), (d) and (e) are (110), (111), (200), (210) and (220), for the ambient structure of Cu$_3$N, respectively. The peaks (a), (d) and (e) exist only in

![Fig. 2 Spectra of energy dispersive XRD of Cu$_3$N at room temperature from ambient up to 39.2 GPa. The indices of the peaks at ambient pressure are denoted.](image-url)
the region 0.0–4.8 GPa and vanish at 7.4 GPa, indicating that there may be a crystal structure phase transition at ~5.0 GPa. All the diffraction peaks of Cu$_3$N could return to the original sites when the pressure is released from the maximum to ambient, so the phase transition is reversible.

The relationships of $d$-values of peaks (a), (b), (c), (d) and (e) versus pressure are shown in Fig. 3. The $d$-values of fcc copper at ambient pressure are also included, indicating that Cu$_3$N does not decompose into Cu and N$_2$ in the experimental pressure range. According to the peak intensity evolution and the $d$-value change tendency, Fig. 3 can be viewed as three regions. Region I corresponds to low pressure (0.0–5.0 GPa), where $d_{(a)}$, $d_{(c)}$, $d_{(d)}$ and $d_{(e)}$ are decreasing and $d_{(b)}$ is increasing from 0.9 GPa with increasing pressure. In the region from 5.0 to 12.0 GPa, which is denoted Region II, $d_{(b)}$ is lightly increasing with increasing pressure. When the pressure is higher than 12.0 GPa denoted with Region III, $d_{(b)}$ is decreasing with increasing pressure, implying Cu$_3$N becomes the high-pressure phase completely at about 12.0 GPa. So there are two phases for Cu$_3$N under high pressure up to 39.2 GPa. The ambient phase (α-phase) and the high-pressure phase (β-phase) correspond to Region I and III, respectively, and Region II is the mixture of the two phases. The result is consistent with the aforementioned in situ measurement of resistance versus pressure. The slight increase of $d_{(b)}$ is unusual, but the result is repeatable in the subsequent experiment. The increase of some $d$-values may not necessarily mean that the volume of unit cell must increase. For example, in the case of face-centered cubic nitride TiN, the increase of $d$-spacing of peak (111) in the pressure range of 7.0–11.0 GPa does not result in an increase of volume of the primitive unit cell $V_p$, which corresponds to the volume of one cubic cell of the initial Fm3m phase because the $d$-values of other peaks are decreasing with increasing pressure during the isostructural phase transition. The overall effects lead to the decrease of the unit cell volume upon a phase transition from a cubic to a possible rhombohedral [20]. However, in the current experiments, the synchrotron energy limitation does not allow us to collect more diffraction peaks of the sample. In other words, one should expect that some $d$-values will decrease with applied pressure in the same pressure range.

Here, we provide a brief discussion of the variety of electronic property and the crystal structure phase transition of Cu$_3$N under high pressure. The pressure-induced rotation and distortion of the NCu$_6$ octahedrons can make Cu$_3$N have a modulation cell containing eight primary unit cells of ambient phase. A similar mechanism has been observed in pressure-induced structure transitions in ReO$_3$ [21–23].

![Fig. 3](image)

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**Fig. 3** Pressure dependences of $d$ (with the same assignments as Fig. 2) for Cu$_3$N. The $d$-values of fcc copper at ambient pressure are also included. Lines are guides for the eye. There are three regions up to 39.2 GPa. Region I is for the ambient α-phase, Region III corresponds to the high-pressure β-phase, and Region II is the mixture of the two phases.
Since the crystal structure is so similar between ReO$_3$ and Cu$_3$N, their pressure behavior is also reasonably expected to be comparable. Because the modulated unit cell resembles the primitive cell, only very weak superstructure peaks are supplemented in addition to the XRD pattern of the primitive cell [22]. Therefore, this type of pressure-induced phase transition due to the octahedron tilting is hard to identify merely from X-ray data. Neutron diffraction is more sensitive to light atoms (e.g. N in Cu$_3$N) than X-ray diffraction, so in situ neutron diffraction experiment under high pressure will be easier to detect this slightly distorted structure. Figure 4a shows the schematic view of the distorted structure, indicating the zigzag tilting of the neighboring NCu$_6$ octahedron. Taking into consideration the case of ReO$_3$, the phase transition makes a new structure with a cubic-centered symmetry with space group Im3, which may be assigned as one of the candidates of the $\beta$-phase of Cu$_3$N. We have plotted the simulated XRD pattern of the new structure assuming the lattice parameter as $2a_p$, where $a_p$ indicates the lattice of the primitive ambient unit cell. Figure 4b shows the patterns as well as the ambient phase pattern as a comparison, with the X-ray wavelength being 1.5406 Å. It is clear that the two sets of XRD patterns are quite similar.
in terms of the position and intensity of the main peaks. Additionally, the new phase has a set of superstructure peaks. The pressure-induced band widening and overlapping effects could result in the metallization behavior of this narrow band gap nitride Cu$_3$N. Since the ab initio result suggests that the band gap of Cu$_3$N with space group Im3 is nearly closed at ~6.0–8.0 GPa, the resistance of the ambient phase will become much smaller with the application of pressure, which can account for the dramatic decrease of resistance observed in Fig. 1. The aforementioned structure is just speculation for the β-phase of Cu$_3$N, and the detailed structure will be refined based on the further high-pressure angle-resolved X-ray or neutron experiments.

4 Conclusions

In summary, the relationship of resistance versus pressure for the anti-perovskite nitride Cu$_3$N reveals a metallization-like change of conductivity at several GPa. The low metallization pressure implies that Cu$_3$N might be a possible pressure-induced calibration compound. The structural evolution with pressure of Cu$_3$N has been investigated through in situ high-pressure X-ray energy dispersive diffraction experiments. According to the change of d-values, it is inferred that the crystal structure phase transition from the ambient α-phase to high-pressure β-phase happens at ~5.0 GPa.

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