Metallization of Cu$_3$N Semiconductor under High Pressure

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Using the four-probe method, we investigate the electrical conductivity of Cu$_3$N under high pressure with the diamond anvil cell. Cu$_3$N is a semiconductor at ambient pressure showing a band gap about 1 eV. With the application of quasi-hydrostatic pressures, its resistance decreases dramatically over five orders of magnitude from ambient to 9 GPa. The compound became a metal at pressure about 5.5 GPa, which is in well agreement with the recent first principle calculation.

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Cooper nitride (Cu$_3$N, a = 0.3817 nm) has the cubic anti-ReO$_3$ structure. Pure Cu$_3$N is a semiconductor and it has been estimated that the value of the energy band gap is less than 1 eV through the LAPW calculation. Due to the low decomposing temperature Cu$_3$N can easily become copper metal and nitrogen upon laser heating. This makes it a potential material for optical data storage. Since volume will decrease and their band gap will gradually close with increasing pressure, so a lot of materials will undergo a semiconductor-to-metal or even metal-to-superconductor transition under enough high pressure. This was very well established in the recent remarkable works such as on oxygen, sulfur, and iodine. The semiconductor-to-metal transition of Cu$_3$N has recently been recalculated by Yu et al. to occur at about 6 GPa based on the phonon spectrum soft model. In this Letter, we report the experimental observation of the metallization behaviour of bulk Cu$_3$N induced by pressure using diamond anvil cell (DAC) as a function of temperature.

The high quality Cu$_3$N powder was pressed into a slice and then we cut and selected a small piece about 100 $\mu$m×50 $\mu$m×50 $\mu$m. We performed the measurements of electrical conductivity of Cu$_3$N bulk under variant pressures using the four-probe method. The high-pressure experiment was carried out with a diamond anvil cell instrument. The culet of the diamond is 800 $\mu$m in diameter. The gasket material is T301 stainless steel. The gasket pre indented up to 10 GPa was drilled with a small hole of 300 $\mu$m in diameter, which serves as the sample chamber. In order to obtain a good hydrostatic pressure environment we chose MgO fine powders (1 $\mu$m in diameter) as the pressure medium. A Au wire of 12 $\mu$m in diameter was adopted as the electrical probe. To prevent the short circuit of electrical probes, the gasket was covered with a thin layer of Al$_2$O$_3$ fine powders. The pressure inside the chamber was calibrated by measuring the fluorescence peak shift of the ruby chips, which were mounted together with the specimen to determine in situ the sample pressure.

Figure 1 shows the x-ray diffraction pattern of Cu$_3$N powder as well as the crystal structure (inset). Figure 2 shows the temperature dependence of the electrical resistance for the Cu$_3$N sample under different applied pressure. It is clear that the Cu$_3$N shows a semiconductive-like behaviour at ambient pressure, characterized by resistance increase with decreasing temperature. With pressure increasing, the absolute value of resistance decreased rapidly with more than 5 order of magnitude changes from ambient to 9 GPa. In particular, the semiconductive behaviour was effectively suppressed at high pressure, as indicated by the slope change of $R - T$ curve at different pressures. It is noted that the $R - T$ curve becomes almost flat at 5.5 GPa. Figure 3 shows the pressure dependence of the resistance of Cu$_3$N at several selected temperatures (140 K, 170 K, 240 K). The resistance of the sample decreases with the increasing pressure, whereas the decrease rates for different temperatures are different. The lower the temperature is, the quicker the resistance decreases, so that the $R$-$P$ curves for the different temperatures intersect at about 5.5 GPa, which is an indication of the semiconductor-to-metal transition. Eventually, the resistance shows a positive $dR/dT$ at 5.5 GPa, implying that Cu$_3$N becomes a metal. Yu et al. calculated the pressure-induced metallization in Cu$_3$N. They show that the lowest energy point of conduction bands is located at the $M$ point and the highest energy point of valence bands is located at the $R$ point and following the decrease of volume a conduction band crosses the Fermi level at the $M$ point, which eventually leads to the over-

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lap of the indirect band gap at the $R$ and $M$ points at about 6 GPa.\textsuperscript{[8]} We have experimentally demonstrated the semiconductor-to-metal transition of Cu$_3$N at the almost the same pressure. It is noted that the critical pressure in the experiment for the metallization is in good agreement with the Yu first-principle calculation. The results indicate that the transition metal nitride has significant difference in terms of chemical bonding character, which gives rise to a more extended electronic structure rather than the narrow band feature of the transition metal oxides. This trait promised transition metal nitrides relatively low resistance, which makes them easier to be metallized under high pressure.

![X-ray diffraction (XRD) pattern of Cu$_3$N. Inset: the crystal structure, showing an anti-ReO$_3$ framework.](image1)

**Fig. 1.** X-ray diffraction (XRD) pattern of Cu$_3$N. Inset: the crystal structure, showing an anti-ReO$_3$ framework.

![The resistance of Cu$_3$N as a function of temperature at variant of pressure up to 9 GPa, indicating a dramatic decrease of magnitude companying a metallization transition about 5.5 GPa.](image2)

**Fig. 2.** The resistance of Cu$_3$N as a function of temperature at variant of pressure up to 9 GPa, indicating a dramatic decrease of magnitude companying a metallization transition about 5.5 GPa.

![The $R$–$P$ relationship of Cu$_3$N under different temperatures (140 K, 170 K, 240 K), showing a metallization at about 5.5 GPa.](image3)

**Fig. 3.** The $R$–$P$ relationship of Cu$_3$N under different temperatures (140 K, 170 K, 240 K), showing a metallization at about 5.5 GPa.

In conclusion, by using high pressure we have observed the gradual metallization of Cu$_3$N semiconductors. Cu$_3$N is successfully metallized at 5.5 GPa. The metallization pressure is in good agreement with the first principle calculation. This is most possibly resulted from the energy gap merging up under pressure.

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