

# EXAFS study of local structure and lattice dynamics in copper nitride $\text{Cu}_3\text{N}$

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Structural phase transitions (SPTs) driven by the soft-mode mechanism are common among perovskite  $\text{ABX}_3$  compounds and can be induced by temperature or pressure variation. Upon the soft-mode SPT, the crystal becomes unstable against a particular phonon mode, which can be the transverse-optical mode at the Brillouin zone centre as in ferroelectric compounds ( $\text{BaTiO}_3$ ,  $\text{PbTiO}_3$ ,  $\text{KTaO}_3$ ) or the rotational mode at the Brillouin zone corner as, for example, in  $\text{SrTiO}_3$ ,  $\text{NaNbO}_3$ ,  $\text{NaWO}_3$ , and  $\text{KMnF}_3$ . Other two closely related compounds with the perovskite-like structure  $\text{ReO}_3$  and  $\text{WO}_3$ , having vacant A-site, show a number of pressure-induced SPTs [1], however, only  $\text{WO}_3$  undergoes several temperature-induced SPTs [2]. In contrast to  $\text{ReO}_3$  and  $\text{WO}_3$ , which have been extensively studied in the past both experimentally and theoretically, a little attention has been paid to copper nitride ( $\text{Cu}_3\text{N}$ ), having a cubic anti- $\text{ReO}_3$ -type structure composed of the  $\text{NCu}_6$  octahedra joined by corners [3]. In particular, no x-ray absorption spectroscopy (EXAFS) studies have been performed to our knowledge on  $\text{Cu}_3\text{N}$ . Practical interest in copper nitride has grown recently motivated by its possible applications as a material for write-once read many (WORM) optical storage devices [4] and for a fabrication of low-resistance magnetic tunnel junctions for the use in non-volatile magnetic random access memories [5].

The dynamic properties of  $\text{Cu}_3\text{N}$  lattice are determined by anisotropic thermal vibrations of Cu atoms, whose thermal ellipsoids are flattened perpendicular to the N–Cu–N bonds [6]. The thermal displacement parameters indicate that there could be some degree of positional disorder at the Cu site [6]. Therefore, it is possible that this disorder and the resulting local lattice distortion are a source of the structural instability of  $\text{Cu}_3\text{N}$  under  $\sim 5$  GPa pressure [7]. The precise effect of the copper disorder and thermal displacement on the electronic and optical properties of  $\text{Cu}_3\text{N}$  remains to be determined. The anisotropy of copper atoms thermal vibrations could also lead to the negative thermal expansion of  $\text{Cu}_3\text{N}$  at low temperatures: this problem was never studied until now.

In this study we have performed temperature dependent (from 10 to 300 K) Cu K-edge X-ray absorption spectroscopy investigation of the local atomic structure and lattice dynamics in polycrystalline and thin film copper nitride.

Polycrystalline  $\text{Cu}_3\text{N}$  was commercial powder (99.5% purity, AlfaAesar).  $\text{Cu}_3\text{N}$  thin films were prepared by dc magnetron sputtering in pure  $\text{N}_2$  atmosphere on glass and polyimide substrates, maintained at  $20^\circ\text{C}$  and  $190^\circ\text{C}$  during deposition. All samples were characterized by x-ray powder diffraction (XRD). X-ray absorption measurements at Cu K-edge were performed in transmission mode at the HASYLAB/DESY C1 beamline in the temperature range of 10–300 K. The storage ring DORIS III operated at  $E=4.44$  GeV and  $I_{\text{max}}=140$  mA. The higher order harmonics were effectively eliminated by detuning of the monochromator Si(111) crystals to 60% of the rocking curve maximum, using the beam-stabilization feedback control. The x-ray beam intensity was measured by ionization chambers filled with argon and krypton gases. The Oxford Instruments liquid helium flow cryostat was used to maintain the required sample temperature. The powder sample was deposited on Millipore filter and fixed by Scotch tape.

The EXAFS signals were extracted and analysed using conventional procedure as is implemented in the EDA package [8]. The FEFF8.2 [9] code was used to generate the scattering amplitude and phase shift functions for Cu–N and Cu–Cu atom pairs based on crystallographic data for  $\text{Cu}_3\text{N}$  [3]. EXAFS results suggest that the Cu–N and Cu–Cu interatomic distances are nearly unchanged within the error (0.005 Å) at all studied temperatures. This result is in good agreement with the estimated ( $\sim 0.0037$  Å) thermal bond elongation [10] in the 0–300 K interval. Mean-square

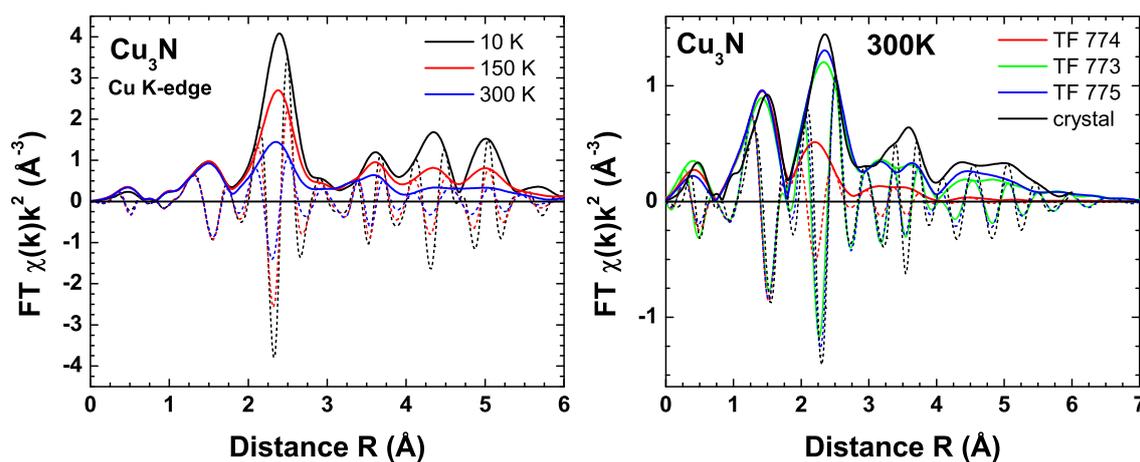


Figure 1: Temperature dependence of the experimental Cu K-edge EXAFS spectra  $\chi(k)k^2$  and their Fourier transforms (FT) for polycrystalline  $\text{Cu}_3\text{N}$  and thin films.

relative displacement  $\text{MSRD}(\text{Cu-N})$  changes weakly with temperature and has relatively small absolute value. This indicates strong Cu–N bonding and is in good agreement with a prediction of significant bond covalency by *ab initio* calculations [11].  $\text{MSRD}(\text{Cu-Cu})$  changes rapidly with temperature, being larger than that observed in metallic copper [12]. This can be explained by strong anisotropy of copper atom vibrations perpendicular to the N–Cu–N chain in agreement with  $\text{MSD}_\perp(\text{Cu})$  values by diffraction [13]. In nanocrystalline thin films, a relaxation of the atomic structure is observed and results in (i) a decrease of the Cu–N and Cu–Cu distances and (ii) an increase of the disorder.

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## References

- [1] J.-E. Jorgensen, J. D. Jorgensen, B. Batlogg, J. Remeika, J. D. Axe, *Phys. Rev. B* **33**, 4793 (1986); J.-E. Jorgensen, J. Staun Olsen, L. Gerward, *J. Appl. Crystallogr.* **33**, 279 (2000).
- [2] E. Salje, *Acta Crystallogr. B* **33**, 547 (1977).
- [3] R. Juza, H. Hahn, *Z. Anorg. Allg. Chem.* **239**, 282 (1938).
- [4] M. Asano, K. Umeda, A. Tasaki, *Jpn. J. Appl. Phys.* **29**, 1985 (1990).
- [5] D.M. Borsa, S. Grachev, C. Presura, D.O. Boerma, *Appl. Phys. Lett.* **80**, 1823 (2002).
- [6] G. Paniconi, Z. Stoeva, H. Doberstein, R.I. Smith, B.L. Gallagher, D.H. Gregory, *Sol. State Sci.* **9**, 907 (2007).
- [7] J.G. Zhao, L.X. Yang, Y. Yu, S.J. You, J. Liu, C.Q. Jin, *Phys. stat. sol. (b)* **243**, 573 (2006).
- [8] A. Kuzmin, *Physica B* **208-209**, 175 (1995).
- [9] J.J. Rehr and R.C. Albers, *Rev. Mod. Phys.* **72**, 621 (2000).
- [10] G. V. Vajenin, C. Hoch, R. E. Dinnebier, A. Senyshyn, R. Niewa, *Z. Anorg. Allg. Chem.* **636**, 94 (2010).
- [11] U. Hahn, W. Weber, *Phys. Rev. B* **53**, 12684 (1996).
- [12] S. a Beccara, G. Dalba, P. Fornasini, R. Grisenti, F. Pederiva, A. Sanson, D. Diop, F. Rocca, *Phys. Rev. B* **68**, 140301(R) (2003).
- [13] U. Zachwiecha, H. Jacobs, *J. Less-Common Met.* **161**, 175 (1990).